COPPER SMELTING IN THE EARLY BRONZE AGE SOUTHERN AEGEAN: A TECHNOLOGICAL AND CONTEXTUAL ANALYSIS

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To my family

Στην οικογένειά μου

ABSTRACT

This thesis is a study of copper-smelting technology in the southern Aegean during the Early Bronze Age. The aim is to develop a framework and methodology that can help promote the integration of archaeological and archaeometallurgical research in this area. To investigate the social dynamics of early metal technology, a three-fold approach is employed. Firstly, an analytical methodology for the reconstruction of prehistoric smelting processes is developed and used for the study of metallurgical remains from the Early Bronze Age site of Chrysokamino in northeastern Crete. Secondly, a comparative analysis of copper-smelting techniques in the Early Bronze Age southern Aegean is undertaken, shedding light to the range of alternative technical strategies employed in the various tasks of the production sequence. Finally, a contextual analysis of copper-smelting activities, their spatial organisation and contextual associations, helps to reveal some of the social and political underpinnings of technological choices in early copper production in the Aegean.

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LIST OF ABBREVIATIONS

EBA	Early Bronze Age
EB	Early Bronze
EH, MH, LH	Early Helladic, Middle Helladic, Late Helladic.
EC, MC, LC	Early Cycladic, Middle Cycladic, Late Cycladic.
EM, MM, LM	Early Minoan, Middle Minoan, Late Minoan.

CHAPTER ONE

INTRODUCTION

Aims, Scope and Structure of Thesis

1.1 The problem

The important role of metal in the articulation of power relations in the southern Aegean during the Early Bronze Age (EBA) has long been appreciated by archaeologists working in this area (Day *et al* 1998; Day and Wilson 2002; Broodbank 1993; Nakou 1995; Renfrew 1972: 480-5). According to current models, metal production during this period was controlled by emerging social groups monopolising the technological knowledge necessary for the execution of critical tasks of the metallurgical process (Nakou 1995). How much do we actually know, however, about early metal technologies in the EBA southern Aegean? And what can we make of the particular techniques employed in the production of metal and the manufacture of metal artefacts? These are questions that previous research in the field has not investigated in any detail.

First of all, the analytical priorities of archeaometallurgical research in this area have significantly constrained our understanding of metal technology. Not only has the question of provenance dominated the field in the past 25 years (e.g. Begemann *et al* 1992; Gale and StosGale1981; Pernicka *et al* 1990; Stos-Gale 1993); technological studies have also, as a rule, been limited to the investigation of the chemical composition of finished artefacts (e.g. Craddock 1976; Kayafa *et al* 1997; Mangou and Ioannou 1997; Stos-Gale *et al* 1996). As a consequence, we currently know very little about the range of techniques employed in the Aegean in the various tasks in the metallurgical sequence, from the mining of the ore and the extraction of metal to its shaping into finished artefacts.

Equally detrimental has been the lack of a conceptual framework that would enable the integration of scientific information on early metal technologies with current archaeological models for the EBA Aegean. At the heart of this problem lies a problematic definition of technology, which is viewed as an objective set of relations between things that can be explained by reference to natural laws of energy and matter. As a result, although the empowering potential of technological knowledge associated with skilled craftsmanship is a common theme in the archaeological literature, the social, political and symbolic underpinnings of technological choices have been given little attention.

1.2 Aims and objectives of thesis

The aim of this thesis is to offer an alternative framework for the study of metallurgical technology in the EBA southern Aegean. Focusing on the process of copper smelting, this study wishes to demonstrate how the detailed empirical description of metal techniques, using scientific analysis, can enhance our understanding of the role of metal in early Aegean societies. The specific objectives of this thesis are the following:

1) To introduce an analytical methodology for the reconstruction of early copper smelting processes, benefiting from more recent developments in archaeometallurgy.

2) To demonstrate the potential of this methodology, using as a case study the copper-smelting site of Chrysokamino in northeastern Crete.

3) To offer a synthesis of existing evidence for copper smelting techniques in the EBA southern Aegean.

4) To propose a framework for the incorporation of analytical results in archaeological models of that period.

1.3 Geographical and chronological scope of thesis

The geographical scope of the thesis is the southern Aegean; the area, that is, comprising the eastern coast of the south Mainland, the Cycladic islands and Crete (**Map 1.1**). The chronological period covered by this study is the Early Bronze Age, which roughly corresponds to the 3^{rd} millennium BC (**Table 1.1**).

1.4 Structure of thesis

The role of archaeometallurgical research in the development of archaeological narratives of early Aegean metallurgy is examined in **Chapter Two**. It is shown that technology-oriented research became marginalised when archaeological interest shifted from questions of origins and diffusion to issues of social organisation. In the light of new archaeological approaches, however, which emphasise the relationship between technological knowledge and power in the EBA Aegean, the importance of technological studies of metal production needs to be reconsidered. A methodology for a new archaeometallurgical program is proposed, which includes (i) a detailed empirical description of techniques, (ii) a comparative technological analysis and (iii) a contextual analysis.

Chapter Three outlines the principles of early copper smelting technology. The role and behaviour of slag and the importance of the furnace temperature and redox conditions in the smelting process are discussed using information from previous archaeometallurgical studies and modern metallurgical thermodynamics. Early copper smelting processes are then classified on the basis of the raw materials used and the redox conditions created in the furnace. The material correlates of each process as imprinted on its products and by-products are also discussed.

Chapter Four is a technological study of metallurgical remains from the EBA copper-smelting site of Chrysokamino in northeastern Crete. Ore and slag samples from the site are analysed using a range of scientific techniques, shedding light to major aspects of the smelting process, including the nature of the raw materials, the smelting conditions, the efficiency of the slag/metal separation and the chemical composition of the copper produced. Combining these pieces of information, a reconstruction of the smelting process is formulated.

Chapter Five draws together archaeological and analytical evidence for copper smelting from the EBA southern Aegean, offering a picture of the range of smelting techniques employed during that time. Technological choices made during each task in the process, from the selection and preparation of raw materials to the post-smelting treatment of the slag, are investigated and comparisons are made between different smelting sites.

Chapter Six investigates the political underpinnings of a technological choice evidenced in a small number of sites in the EBA southern Aegean, namely the use of arsenic-rich raw materials in the copper-smelting process. For this purpose, a contextual analysis of copper-smelting activities featuring this technological choice is undertaken, focusing particularly on their spatial relation to other tasks in the copper-production sequence and other areas of human activity.

Chapter Seven summarises the conclusions reached in this thesis and outlines questions that need to be addressed by future research in this field.

CHAPTER TWO

ARCHAEOLOGICAL SCIENCE
and the Study of Early Bronze Age Aegean Metallurgy

2.1 Introduction

Archaeometallurgical research has a long history in the archaeology of the EBA Aegean, from the sporadic chemical analyses of metal artefacts found in pioneering excavation reports of the early 20th century (e.g. Papavasileiou 1910; Tsountas 1898) to the systematic analyses of numerous metal and metallurgical assemblages undertaken today (e.g. Gale and Stos-Gale 1981; Gale *et al* 1985; Mangou and Ioannou 1999; Pernicka *et al* 1990). This long period of time has witnessed the emergence of an important imbalance in the field, which has now reached its pinnacle. There is indeed a marked contrast between *technology-oriented* studies, which have had little impact outside a relatively small circle of specialists, and *provenance-oriented* studies, which have become popular among archaeologists studying the Aegean Early Bronze Age.

This chapter has two objectives. The first is to investigate the reasons for this imbalance by looking at the role of scientific analysis, throughout this period, in the development of archaeological narratives of early metallurgy in the Aegean. The second objective is to argue that current archaeological perspectives call for a new archaeometallurgical programme investigating the active role of technology in the articulation of power relations during the Early Bronze Age.

2.2 The technological development of early Aegean metallurgy

There exists a substantial archaeological literature tracing the development of metallurgy in the Aegean, from the first appearance of metal artefacts during the Neolithic to the fluorescence of the Late Bronze Age palatial metal industries (Branigan 1968, 1974; Craddock 1976; Mangou and Ioannou 1997, 1998, 1999; McGeehan-Liritzis 1996; Muhly 1985, 1988, 1999; Tripathi 1988). Scientific analysis has held a central place in this archaeological programme. It was only with the advent of spectroscopic techniques and the analysis of numerous artefacts (e.g. Junghans *et al* 1968) that technical aspects of metal production and metalworking could be studied in a detailed and systematic manner. Distinctions between native and smelted copper (e.g. Rapp 1982), native silver and silver produced from argentiferous lead ores by cupellation (Gale and Stos-Gale 1981), and the various alloys of copper (e.g. Mangou and Ioannou 1997, 1998, 1999; Kayafa *et al* 1997) were only possible through the chemical analysis of metal artefacts. Scientific analysis, with its ability for material characterisation, was therefore essential for the identification of "technological stages" (Wertime 1964) in metal assemblages.

An invaluable contribution of such studies was that they offered a systematic description of the archaeological material (from both a typological and an analytical perspective) in a firm chronological framework. They made, therefore, a first step towards (i) pinpointing the time and place where major technological developments occurred, and (ii) defining the spatio-temporal boundaries of early Aegean metallurgical traditions. We have thus learnt that metal appeared in Greece already from the Middle Neolithic in the sites of Dikili Tash and Sitagroi, and that such innovations should be associated, directly or indirectly, with the flourishing metallurgy of the southern Balkan cultures (Muhly 1985; McGeehan-Liritzis 1983). The earliest evidence for copper smelting comes from the site of Promahonas on the Greek-Bulgarian borders (Koukouli-Chrysanthaki and Bassiakos 2002) whereas silver was extracted at the site of Upper Lamptrai in Attica in as early as the FN-EB 1 period (Douni and Kakavogianni 2002). It has also been established that the technology of copper alloying in the Aegean followed the well-known sequence from the use of unalloyed copper to the alloying with arsenic and, in the later EBA, with tin probably arriving from Anatolia (Charles 1967; Mangou and Ioannou 1997, 1998, 1999; Muhly 1985; Pernicka *et al* 1990; Stos-Gale *et al* 1984). Such developments did not occur simultaneously in all areas of the Aegean. Branigan (1974: 110-3) was able to identify two leading metallurgical centres in the EBA, Troad and Crete, although more recent studies have established the key role of Cyclades in the development of Minoan metallurgy (e.g. Stos-Gale 1993). Moreover, regionalism, both in metal types and range of materials, has long been noted and allowed the identification of regional and local traditions throughout the Aegean (Branigan 1974: 123-7; McGeehan-Liritzis 1996: 200).

Although of strong descriptive potential, research on the development of early Aegean metallurgy was less successful in articulating a satisfactory interpretative framework. Technological development was viewed as "a unilinear progression over time" (Pfaffenberger 1992: 494), a progress that awaited dormant only to be realised in any region once the necessary knowledge was either discovered or passed over from more developed areas. What had thus to be established was not why specific techniques were adopted in a given spatio-temporal context, for they were bound to be adopted, but rather whether they were locally invented or borrowed from neighbouring areas where the new technology was already available (see, for example, the debate between Renfrew 1967 and Muhly 1988). From this perspective, areas showing evidence of "slow progress" were described as "backward" or "conservative" whereas those that quickly adopted new inventions were seen as "leading" and "technologically competent" (e.g. Kayafa *et al* 1997; McGeehan-Liritzis 1996: 17).

A more serious drawback of this approach, however, was that discussions remained largely restricted within the realm of technology and its independent, "hard" laws of evolution. Making little or no reference to its social and cultural context, metallurgical technology was presented as something that can be studied in isolation and, by extension, as something that actually operated separately from human societies. That the study of metallurgical technology eventually became itself isolated from archaeology, as shown in the following section, was thus of its own making.

2.3 Metallurgy and craft specialisation

Fundamental changes in archaeological perceptions of early Aegean metallurgy came about in the late sixties with the work of Colin Renfrew (1967, 1972). Renfrew's interest was not so much in locating the ancestry of Aegean metallurgy in areas like southern Europe, Anatolia or the Near East. Instead, he sought to understand the changes that this new technology brought about in the communities of the Aegean and its role in the processes underlying the emergence of the palatial societies of the Middle and Late Bronze Age. In his own words, "the invention of metallurgy was one of those decisive steps which led directly towards the emergence of civilization in the Aegean" (Renfrew 1972: 309).

Three major elements can be identified in Renfrew's writings on EBA Aegean metallurgy. Firstly, this new technology transformed the idea of wealth. Either as artefacts of use value (weapons and tools) that could be hoarded (Renfrew 1967, 1972: 320-5), or as prestige items that could be conspicuously displayed and consumed (Renfrew 1986: 162), metal objects were potential vehicles for the emergence and reproduction of social ranking. Secondly, as a response to the increased demand for metal artefacts and due to its inherent technical complexity, metallurgy soon became specialised (Renfrew 1972: 340-1). Society had passed beyond a subsistence economy, he argued, as the high desirability of metal motivated agricultural intensification for the production of surplus. Finally, social stratification, as witnessed in the "pronounced hierarchy of wealth...in the graves" (Renfrew 1972: 484), emerged -at least partly- through the control of specialised production (for similar models see Brumfiel and Earle 1987; Earle 1999; Kristiansen 1987).

The concept of craft specialisation and its association with complex societies has been ever since a common theme in archaeological literature of the EBA in southern Aegean (Cherry 1983; Day and Wilson 2002; Konsola 1986; Perlès and Vitelli 1999; Pullen 1985; Whitelaw *et al* 1997). Studies seeking evidence for specialisation in various crafts became common (e.g. on millstones: Runnels 1981; on obsidian: Torrence 1986; on pottery: Whitelaw *et al* 1997). In the case of metallurgy, commonly cited evidence in support of specialisation have been the massive slag heap at Skouries on Kythnos dating to the EC II period (Stos-Gale 1989), the workshops at Kastri on Syros, where remains of crucibles together with a group of chisels were found in a room with a hearth (Tsountas 1899), Raphina in Attica where two pits containing slag, tuyères and furnace remains have been interpreted as smelters (Theocharis 1951, 1952), and, more recently, Poros Katsambas on Crete where evidence for large-scale copper-working activities has been unearthed (Day and Wilson 2002; Dimopoulou 1997). Adding to this evidence the inherent technical complexity of extracting metal from its ores and shaping it into artefacts (Kayafa *et al* 1997; Stos-Gale 1993; see also Kristiansen 1987; Ottaway 2001), little doubt remained about the specialist character of early Aegean metallurgy.

The impact of this new archaeological programme on the way metals and metallurgical production were to be studied was immense. Unlike earlier approaches, which emphasised metallurgical *technology* as an index of progress within a techno-evolutionary paradigm, it was metallurgy as an *economic process* that was important in the study of the emergence of complex societies. And since "political economy...is not technology" (Marx 1974 [1856]: 126), metallurgical production was from now on to be looked at from an *organisational* rather than a *technical* perspective. In this context, archaeometallurgy or, to be more specific, the branch concerned with the reconstruction of metallurgical techniques, now appeared out of place. This is not to say that technological studies were abandoned. On the contrary, there followed a very productive period with the investigation of prehistoric mines (Wagner and Weisgerber 1985; Spitaels 1984) and metallurgical sites (e.g. Coleman 1977; Hadjianastasiou and McGillivray 1988; Gale *et al* 1985) as well as the chemical analysis of numerous metal artefacts (e.g. Craddock 1976; Kayafa *et al* 1997; Mangou and Ioannou 1997, 1998, 1999; Pernicka *et al* 1990). This body of data, however, never really found a place in the dominant archaeological discourse but rather remained wedded to -by now unpopular- discussions of technological progress, origins and diffusion (cf. Muhly 1988: 2). If archaeometallurgy was to find a place back in Aegean archaeology, it had to do more than that; it had to contribute to the study of the organisation of production in a way that was not possible by other archaeological means. And so it did, in the most emphatic way, with the introduction of lead isotope analysis.

2.4 Metals and long distance trade

The evidence for interregional exchange in the Aegean during the third millennium BC has been known for a long time. Once again, it was Renfrew who drew attention to the correlation between the sudden development of metallurgy in the EB 2 period and the sharp increase in interregional contacts, an "international spirit" which transformed the previously unconnected cultural regions of the Aegean into a "larger cultural organism" (Renfrew 1967; 1972: 451). Widely distributed materials in this period included marble (figurines and vessels), pottery (especially the sauceboat), obsidian and metal (Broodbank 2000: 305-9), but it was the latter, a universally desirable material, Renfrew argued, that provided the impetus for extensive contacts and trade. How widely metal was exchanged, however, and whether this exchange was in raw materials or finished products, were questions that archaeology could not answer. Although it was acknowledged that mineral resources in the Aegean were probably localised (Renfrew 1972: 465), there was a strong regionalism both in the metal repertory and the types of metals and alloys used in different areas of the Aegean (Branigan 1974: 123-30). This pattern seemed to reflect the operation, in each area, of autonomous metal industries which, at least in the case of copper, were probably based on the exploitation of local ore sources (Branigan 1974: 62-3; Renfrew 1972: 337).

This picture was challenged by lead isotope analysis, a revolutionary technique introduced to Aegean archaeology in the late seventies for the provenancing of metal artefacts. A series of articles published by the Oxford (e.g. Gale and Stos-Gale 1981, Stos-Gale 1989, 1993) and the Heidelberg/Mainz groups (Begemann *et al* 1992, 1995; Pernicka *et al* 1990) argued, based on isotopic data, that the metal used in most artefacts in the EBA Aegean had been produced using ores from a *limited number of deposits* (**Map 2.1**). For silver and lead, the major sources were the argentiferous lead deposits of Siphnos and the polymetallic deposit at Laurion, both of which had yielded direct evidence for mining activities dating to the EBA (Spitaels 1984; Wagner and Weisgerber 1985). Turning to copper, the main sources in the Aegean were the island of Kythnos, where a massive slag heap dating to the Early Cycladic II period had been discovered (Hadjianastasiou and McGillivray 1988; Gale *et al* 1985; Stos-Gale 1989), and Laurion (Stos-Gale 1993, 1998; Stos-Gale and

Macdonald 1991). As for tin bronzes, which, as already mentioned, made their appearance in the Aegean in the later stages of the EBA, their non-Aegean, probably Anatolian, origin was firmly established (Pernicka *et al* 1990; Stos-Gale *et al* 1984).

An unexpected picture of metal circulation in the Aegean during the EBA was, therefore, drawn by lead isotope analysis. What was witnessed in the archaeological record, it was argued, was not simply the exchange of finished artefacts between independent metal producing regions. On the contrary, it was through the movement of raw materials from the metalliferous areas of the Laurion and Western Cyclades to the metalworking areas of Crete, the Mainland and the eastern Cyclades, that the manufacture of metal objects was enabled in the first place. And in the insular Aegean context, such movement of materials was bound to long-range maritime voyaging.

The character of maritime activity in the early Cyclades during the EB 2 period (the *Keros-Syros* culture) was the subject of a detailed analysis by Cyprian Broodbank (1989, 1993, 2000). His point of departure was the presence of certain exceptional Cycladic sites, which "are not only relatively large in size, but also unusually rich in marble, pottery and/or metal finds, and possess a quasi-monopoly in the uncommon Keros-Syros painted wares as well as in rare pieces of extra-Cycladic material" (Broodbank 1993: 318). What differentiated these larger and richer communities was, according to Broodbank, their ability to control long distance maritime trade. An ability, which stemmed from the fact that it was only these *larger* island communities, which he termed "trade centres", that could afford the reallocation of manpower from subsistence activities to the labour-demanding operation of longboats (Broodbank 1989: 330-1).

It was in this context that the surprising absence of evidence for direct control over ore deposits (and, for that matter, the obsidian quarries on Melos; Torrence 1986: 169-71) was to be understood. For, as Broodbank (1993: 323-4) argued, despite the lack of direct control of these resources by "the inhabitants of Siphnos and Kythnos", it was only the trade centres, from among the Cycladic communities, that could reach them and acquire the metal that the locals produced. "[T]he value of metal for most people in the early Cyclades lay not just in its properties but also in its exotic and invisible origins" (Broodbank 1993: 323) and power lay with those who acted as a bridge between the spatially isolated producers and consumers (Broodbank 2000: 296).

The "international spirit" of the EB 2 period in the Aegean, which saw the flow of Cycladic materials to the entire Aegean, reflected the trading activity of these communities beyond the confines of the Cyclades. For them, the incentive was to "incorporate external innovations in ways that allowed them to maintain their pre-eminence inside the worlds of the islands" (Broodbank 2000: 318) whereas for the outside communities, it was the acquisition of prestigeous *exotic* materials and technologies, among which, metal was the most important (Carter 1998; Day *et al* 1998; Day and Wilson 2002). Similar mechanisms underpinned the emergence of new nodal sites in the later EBA, including Troy, Poliochni, and Thermi in northeastern Aegean and Lefkandi and Manika in the Euboean gulf, as they controlled the inflow of Anatolian *materials*, such as the tin bronzes, and *habits*, including the new modes of consumption reflected on the pottery set of the Kastri group (Broodbank 2000: 318; Nakou 1997).

Bringing to the fore the level and complexity of metal circulation during the EBA, lead isotope analysis thus instigated a new generation of approaches to early Aegean metallurgy; approaches instilled with notions of *distance* and *mobility*. Broodbank went so far as to displace entirely the locus of power from the field of production to that of long-distance voyaging and trade. But even when focus was placed on production, as shown in the following section, archaeological analysis was bound to follow similar paths.

2.5 Technological knowledge and "exclusion by production"

A novel interpretation of the "metallurgical explosion" (Renfrew 1972: 338), the sudden increase in the amount and range of metal artefacts in the archaeological record of the EB 2 period in the Aegean, was offered by Georgia Nakou (1995). What the *Metallschock* represented, according to Nakou (1995:2), was "a *change in depositional behaviour* and thus a deliberate redirection of symbolic expression" (original emphasis). In the Neolithic context, the circulation of highly distinctive artefacts, including those of metal, was a mechanism of integration for the widely dispersed settlements of that period. Being objects of supra-individual significance, metal artefacts circulated over long distances and were only deposited after long periods of curation thus having a reduced visibility in the archaeological record of this period. Starting in the EB 1, there was a "deliberate departure from the Aegean Neolithic use of metal: metal was appropriated from the communal domain of inter-group integration rituals and was channelled into symbolic usage associated with circumscribed groups in society culminating in mortuary display" (Nakou 1995: 13). Metals, in a limited number of symbolically potent types (such as the dagger), identified those who "were engaged in a package of restricted activities" (Nakou 1995: 18). Their life cycles were tied to that of their possessors; they were made for them and buried with them. It is such strategies, the regular deposition that they ensured and the resulting cumulative effect in the archaeological record that we now identify as the *Metallschock* of the EB 2 period.

In considering how metal acquisition was controlled by those emergent corporate groups during the EBA, it was in the patterns of ore exploitation and processing (as reconstructed by lead isotope analysis) that Nakou sought the mechanism of exclusion, accepting Broodbank's (1993) suggestion that the answer lay in the spatial separation of metal production areas from the broader population:

> "We have then a situation whereby the initial acquisition and transformation of metals is spatially separated from the consuming population, and the metals are only brought to the settlement (and probably not all settlements) in their processed or partially processed form" (Nakou 1995: 18).

Unlike Broodbank, however, who essentially regarded this isolation as a "favourable coincidence" to be exploited by emergent trade centres, Nakou (1995) suggested that it reflected particular strategies concerning the spatial allocation of metallurgical activities in relation to the bulk of the population. Conducting metallurgical activities in deliberately distanced locations, Nakou argued, not only enabled the safeguarding of the associated technological know-how (and thus the control of metal production); the adoption of "esoteric" practices was "an integral part of the group's selfdefinition in relation to non members" (Nakou 1995: 18). Being separated from the broader population, metallurgical activities became mystified, the role of specific groups in their execution was emphasised and their solidarity was reinforced. Such strategies of exclusion concentrated on the initial stages of the production process, namely the collection and processing of ore for the production of metal (Nakou 1995). Metallurgical production should be therefore divided into "critical" stages that constituted restricted, exclusive activities, and "non-critical" stages (namely metalworking) that were more widespread and, consequently, of lower symbolic potential.

Power, in Aegean societies during the EBA, lay in the participation in restricted networks and activities (a symbolism of exclusion; Manning 1994) and, in this context, long-distance voyaging and several kinds of technical know-how were drawn into the definition of emergent corporate groups of exclusive membership (Nakou 1995). The particular characteristics of metal, namely the localised nature of its sources and the inherent technical complexity of its processing, made it an ideal vehicle for such strategies. These strategies, although originally developed in the insular Cycladic landscape, were rapidly emulated throughout the southern Aegean (especially on Crete) as reflected in the adoption of new depositional practices, such as the formal burial with metal and other rare goods (Nakou 1995: 23; see also Broodbank 2000: 318; Day *et al* 1998).

2.6 From provenance to technology: towards a new analytical programme for the study of EBA Aegean metallurgy

Having followed the developments of archaeological and archaeometallurgical research on EBA Aegean metallurgy during the last decades, we can now return to the question posed at the beginning of this chapter. Why have technological studies remained peripheral, to say the least, to current archaeological discussions of that period when provenance-oriented research has gained such popularity?

Some of the reasons for this imbalance have been already touched upon earlier in this chapter. First of all, provenance studies, with their ability to reconstruct trade/exchange networks by distinguishing local from imported artefacts/materials in archaeological sites, could be directly incorporated in studies of social and economic ogranisation of the EBA Aegean. It is in fact for the same reason that questions of provenance have also dominated analytical studies of other archaeological materials in this area, ceramics being the most obvious example (e.g. Attas *et al* 1987; Betancourt and Myers 2000; Day *et al* 1998; Whitelaw *et al* 1997). Moreover, a provenance-oriented approach has been regarded as best suited to explore the complex circulation of metal from the ore deposits to smelting and metalworking sites evidenced in the archaeological record of this period (Stos-Gale 1998: 721). We could finally add a historical reason here: the Aegean Bronze Age was, after all, among those case studies with which, two decades ago, lead isotope analysis was established in archaeology as a strong tool for the provenancing of metal artefacts (Gale and Stos-Gale 1981; Gale *et al* 1985; Stos-Gale *et al* 1984).

Why technological studies have been divorced from the current archaeological discourse is more difficult to understand, especially when recent studies have taken so much care in establishing the relationship between technological knowledge and power in the EBA Aegean (e.g. Broodbank 1993; Day *et al* 1998; Day and Wilson 2002; Nakou 1995). It could be argued that at the root of this paradox lies a problematic definition of technology. To be more specific, implicit in these studies has been an artificial separation of prehistoric technology from the social relations of production through which it was enacted (Dobres and Hoffman 1994: 227; Ingold 1999: ix). *Technology*, as "an objective system of relations among things" (Ingold 2000: 313), could be explained in neutral terms by reference to the natural laws of matter and energy. *Production*, on the other hand, being a system of relations among people, was a more appropriate object of sociological analysis. Therefore, although technology or, more accurately, *technological knowledge* eventually became viewed as integral to the organisation of metallurgical production in the EBA Aegean, archaeological focus was not on what this knowledge exactly consisted of (i.e. the particular techniques used) but rather on its differential distribution among social units (such as individuals, households or settlements). Archaeologists, in other words, were concerned with identifying the social groups that were exclusively involved in metallurgical activities by monopolising the necessary technological knowledge. The actual techniques that these groups employed in the course of metal production were not seen as relevant to this archaeological agenda.

This "objectified" view of technology is hardly justifiable considering the important premise that *similar material ends can be reached from different technical paths* (Lemmonier 1992, 1993; Mahias 1993; van der Leeuw 1993). In other words, while prehistoric metallurgy took place within broad chemical, physical and mechanical constraints imposed by the nature of the materials in hand, artisans were still able to employ different technical strategies to produce metals and alloys and shape them into artefacts (Lechtman 1994; Ottaway 2001). Laws of matter and energy should be therefore viewed as a *background structure* within which, culturally reasoned *technological choices* were made and *technical variants* developed (Dobres and Hoffman 1994). In their capacity as choices within a spectrum of possibilities, techniques thus expressed and mediated social values and attitudes about the right and wrong ways of doing things (Lemonnier 1992: 81). What is important here is that such social values and attitudes were neither static nor necessarily shared by those engaged in material production. Rather, they were subject to multiple interpretations that were expressed, contrasted and evaluated in the unfolding of technological activities (Dobres 2000: 104). This is exactly what previous studies of early Aegean metallurgy have failed to appreciate. It is hardly sufficient to view power in terms of restricted access to knowledge, though this provided an important index for social differentiation. Rather, analysis should be also concerned with attempts to establish *particular forms* of knowledge (and, of course, the artisans associated with them) as dominant: as the way things *should* be done (see Edmonds 1990; Pfaffenberger 1992: 506).

This view of technology as a social arena in which potentially conflicting interests were defined, expressed and negotiated, brings technological studies of metal production to the centre of discussions of power relations in the EBA Aegean. At the same time, however, it calls for a reconsideration of the subject and methodology of technology-oriented archaeometallurgical research in this area.

The first necessary task is the *identification* and detailed *empirical description* of the range of techniques at work during this period. The concept of the *chaîne opératoire* is of great value here because it allows a view of production as "a temporally extended series of interrelated operational choices rather than an instantaneous act of creation" (Dietler and Herbich 1998: 238). A *chaîne opératoire* research compels us to delineate manufacturing processes from beginning to end (Dobres 2000: 169). This, in the case of metallurgical production, translates to a study of the entire sequence of technical tasks from the original discovery and mining of ore deposits to the extraction of metal and its shaping into objects (Ottaway 2001).

In analytical terms, this means to break from the dominant tradition in Aegean archaeometallurgy of focusing almost exclusively on the chemical composition of finished artefacts (e.g. Craddock 1976; Kayafa *et al* 1997; Mangou and Ioannou 1997, 1998, 1999; Pernicka *et al* 1990; Stos-Gale *et al* 1996). This approach has offered a view of metallurgical technology that has been both *biased*, as it has focused on the final stages of the production sequence, and *restrictive*, as it has reduced fabrication techniques to the selection of different metals and alloys in the manufacture of objects. It is necessary instead to adopt a broader methodology that (i) investigates the material remains of *every stage* of the metallurgical sequence, and (ii) combines different analytical techniques and types of evidence in order to shed light to various technical aspects of these processes. The potential of a broad methodology in the study of prehistoric metal technologies has long been demonstrated by numerous studies throughout the Old World (e.g. Bachmann 1982; Budd 1991; Hauptmann *et al* 1988; Merkel *et al* 1994; Northover 1989; Tite *et al* 1990) and it is high time it was also introduced in the Aegean.

The next task is a *comparative analysis* in order to investigate the degree of technological variability; the existence, in other words, of alternative technical strategies for the performance of similar tasks. Once again, a *chaîne opératoire* research proves useful as it enables us to identify normative or diverse technical behaviour in each stage of the metallurgical sequence. This direct evaluation of the actual performances and limitations characterising each task (Gosselain 1998) offers a "window" into the social rules of technological conduct that existed, and their rigidity or flexibility (Dobres 1995: 40-1). Moreover, it allows a distinction between "common" and "unusual" techniques as well as a study of their geographical distribution and its correlation with the cultural units in this area.

The third and most challenging task is a *contextual analysis* of metallurgical techniques in the EBA Aegean. Since our analysis is concerned with the contestation of potentially conflicting forms of knowledge in the unfolding of technological activities, a microscale orientation seems more appropriate:

> A microscale orientation can be used to account for archaeological variability (1) to model the dynamic social processes involed in ongoing, day-to-day technological endeavors, and (2) to consider the differential participation of the actors and groups involved (Dobres and Hoffman 1994: 213).

What is proposed here is a focus on the *localised social and material circumstances,* in which metallurgical activities were undertaken, technological choices made and given cultural significance and tensions within collectivities of technicians created and resolved (Dobres 1995). It is in such contexts of *face-to-face interactions* among different craftsmen and/or outsiders that alternative statements could be made about the right or better way to do things, technical variants be contrasted and different levels of competence be displayed. Moreover, a micro-scalar approach enables a study of the contextual associations of metallurgical activities and hence of the cultural resources that were drawn upon to establish authoritative forms of technological knowledge and practice.

To summarise, the new approach to early Aegean metallurgy proposed here focuses on the ways in which artisans, in the course of daily routines of production, expressed, reaffirmed and contested authoritative forms of knowledge about how things should be done and by whom. It has been argued that this view of production can take further the relationship between technological knowledge and social power as this has been emphasised in recent archaeological discussions of that period. At a methodological level, three analytical components have been proposed: (i) empirical description of techniques; (ii) comparative technological analysis; and (iii) contextual analysis.

It is, of course, beyond the scope of a single piece of work to undertake this new archaeometallurgical programme in its entirety. The aim of this thesis is instead to address certain issues on EBA Aegean metallurgy using the methodology outlined above in order to illustrate its interpretative potential. Thus, this work focuses exclusively on *copper metallurgy* and more specifically on the process of *smelting* while its geographical scope is limited to the southern Aegean region, where most known prehistoric copper-smelting sites are located (**Map 2.2**).

Following the methodological principles outlined above, this thesis has three main objectives. The first objective is to introduce to Aegean archaeometallurgy an analytical methodology for the detailed reconstruction of copper-smelting techniques. For this purpose, the principles of prehistoric copper-smelting technology are outlined and an analytical methodology is developed which is then employed for the study of copper smelting remains from the Early Minoan site of Chrysokamino in northeastern Crete. The second objective is to conduct the first comparative analysis of copper smelting techniques in the EBA southern Aegean, drawing upon archaeological and analytical evidence from various smelting sites in this region. Finally, using the introduction of an arsenical ingredient in the copper-smelting process as an example, an attempt is made to investigate the ways in which technological choices were pressed into the negotiation of privileged roles among those engaged in metallurgical activities.

CHAPTER THREE

PRINCIPLES OF EARLY COPPER SMELTING TECHNOLOGY

3.1 Introduction

This chapter provides an overview of pyrometallurgical processes employed in prehistory for the extraction of copper from its ores, with a special focus on the process of smelting. The thermodynamic profile of each process is discussed, drawing upon archaeological evidence, information from experimental work and modern metallurgical theory. In addition, the important role of the slag and the furnace conditions is considered.

3.2 Raw materials and beneficiation

Copper is found in nature mostly in the form of *sulphidic* and *oxidised minerals* (Newton and Wilson 1942: 6). The first mineralogical category includes *pure sulphides* and *sulphide mixtures* whereas the second includes *carbonates*, *oxides*, *silicates* and *sulphates*. Complex localised geological processes have effected the concentration of copper minerals in exploitable deposits, which are called *ore bodies*. Most sulphidic deposits were formed by processes of precipitation and deposition from metalliferous solutions filling cavities in the Earth's crust (such as geological faults/contacts, rock fissures or pores) whereas oxidised ores were formed by the leaching of sulphides at the upper parts of sulphidic deposits by percolating surface waters (see Evans 1993 for an comprehensive review of ore formation processes).

In the ore body, copper minerals (called the *ore minerals*) occur in conjunction with other materials including (Biswas and Davenport 1976: 30):

1. *Metallic minerals*: These are minerals of other metals deposited together with copper from the mineralising solutions; minerals of iron are the commonest but elements like zinc, lead, arsenic, silver and gold are also present especially in polymetallic ores.

2. *Rock minerals*. These may be minerals deposited from the mineralising solutions (e.g. quartz) and/or material deriving from the rocks hosting the mineralisation (e.g. limestone). The unwanted copper-free minerals in the ore (both metallic and rock) are collectively described by the term *gangue*.

All three classes of material are present (to a greater or lesser extent) in the ore collected from the deposit during mining. To extract the copper, the mined ore needs to be subjected to a sequence of processes each removing some part of the unwanted materials (Doonan 1994: 84). In considering the techniques employed in prehistory for the extraction of copper from its ores, the metallurgical sequence can be divided into two major stages: *beneficiation* and *pyrometallurgical treatment*.

The aim of beneficiation was to remove a significant part of the gangue material by simple physical processes. Firstly, the ore was crushed to a small size, using stone hammers and often mortar stones, in order to separate, as much as possible, the grains of metalliferous minerals from the grains of gangue materials (Craddock 1995: 157-161; O'Brien 1994:173; Tylecote 1987: 56-59). This was followed by a *sorting* process, which effected the separation of copper-rich grains from the rest of the materials by exploiting differences in a specific property (Tylecote 1987: 53-64). The simplest method was hand-sorting, whereby the richer grains, identified by their colour, lustre, smell and density were collected by hand (e.g. Schmidt 1997: 57). Differences in density also formed the basis of more sophisticated beneficiation techniques, such as washing or jigging, employed in prehistoric and historic periods (see Craddock 1995: 156-167 for the most recent summary of early beneficiation techniques). Although a lengthy and difficult manual task, beneficiation effected a dramatic increase in the grade of the ore: according to archaeological and experimental evidence, the copper content in the concentrate could reach up to 20-50% (Doonan 1994: 87; Merkel 1990: Table 4; O'Brien 1994: Table 12). However, beneficiation could only go so far as to increase the proportion of copper-minerals in the ore by removing as much gangue as possible. Within the ore-minerals, copper was *chemically bound* with other elements (the most important being oxygen, sulphur and iron) so further separation could only be achieved by pyrometallurgical (i.e. high-temperature) operations, the most important of which was *smelting.*

3.3 Smelting and the formation of slag

The term smelting, when used in the context of early copper production, describes a wide range of metallurgical processes that shared the following characteristics (e.g. Bachmann 1980; Hauptmann *et al* 2003; Doonan 1999; Eibner 1982; Merkel *et al* 1994; Shugar 2003; Zwicker *et al* 1985):

1. the process took place at high temperatures, usually above 1100°C ensuring that many (often most) components of the ore were molten.

2. the gangue minerals, often aided by the addition of a *flux*, fused (partially or fully) into an oxide phase called *slag.*

3. most copper present in the ore concentrated in a metallic phase, which, depending on the mineralogy of the charge and the smelting conditions, was metallic copper and/or a copper-iron sulphide mixture called *matte.*

A distinct metallurgical process, which does not comply with this description, is that of *slagless smelting.* The idea of a slagless smelting process has been raised by various scholars as an explanation for the lack of smelting slags in Bronze Age Britain (e.g. Budd *et al* 1992). It is based on the fact that by smelting copper ores containing little or no gangue material, it would have been possible for early smelters to produce copper at low temperatures without the formation of any significant amount of slag (Craddock 1999). In fact, experimental work has raised the possibility that such processes often took place at the solid-state (Pollard *et al* 1991).

Such low-temperature processes, however, could not have been used for the majority of copper ores which, even after beneficiation, contained considerable amounts of gangue material. To be more specific, although particles of metallic copper would be formed, due to the presence of an unmelted gangue matrix they would not coalesce into larger nodules remaining instead as a largely irretrievable fine dispersion within the semi-fused gangue (Tylecote 1987: 107; see also Peters 1907: 9). Remains of such processes have been reported from various Chalcolithic copper-smelting sites, usually consisting of heterogeneous conglomerates with only partial formation of slag, containing partly decomposed ores, lumps of charcoal and abundant copper droplets raising the copper content up to 50% (e.g. Bachmann 1982: 21; Golden *et al* 2001; Hauptmann *et al* 1996; Merkel and Rothenberg 1999; Rovira 2001; Shugar 2003).

For gangue-bearing copper ores to be efficiently smelted it was necessary to fuse the gangue materials into a sufficiently fluid slag which, having a lower density than liquid copper/matte, could allow metallic droplets to sink and coalesce into retrievable nodules or, even better, into an ingot at the bottom of the smelting vessel. The formation of a fluid slag, however, presented early smelters with a difficult challenge due to the high melting point of gangue minerals typically found in copper ores (for example, iron-oxide melts at 1369°C, silica at 1723°C and lime at 2570°C). It was only when such oxides were present in *specific proportions* that a liquid slag could be formed at temperatures attainable in prehistoric smelting furnaces (usually no more than 1300°C; e.g. Tite *et al* 1990: Table 4). The gangue minerals in some ores were in exactly the right proportions (*self-fluxing ores*) and could be smelted directly (Tylecote 1987: 108). When this was not the case, however, a *flux* needed to be added to the smelting charge in order to produce an oxide mixture with a sufficiently low liquidus temperature. Archaeometallurgical studies of copper slags from various areas in the Old World have shown that siliceous gangue materials (typically associated with oxidised copper ores: Craddock 1999: 182; Tylecote 1987: 108) were usually fluxed with iron- or manganese-oxides (e.g. Bachmann 1980; Hauptmann *et al* 1988; Merkel *et al* 1994) whereas ferrous gangue minerals (typically associated with copper sulphides due to the predominance of iron in sulphidic deposits: Biswas and Davenport 1976: 30; Netwon and Wilson 1942: 10) were usually fluxed with silica (e.g. Bachmann 1982: 22; Craddock 1999: 182; Moesta 1986). Indeed, most archaeological slags consist predominantly of iron-silicates or iron-manganese-silicates and their composition often approximates the compounds fayalite $2FeO.SiO_2$, knebelite $2(Fe,Mn)O.SiO_2$ and tephroid $2MnO.SiO_2$, which have low liquidus temperatures (Bachmann 1982: 14). In addition, prehistoric slags usually contain smaller amounts of lime, phosphorus, alkalis (mainly potassium) and alumina deriving from the furnace/crucible walls and the fuel ash (Bachmann 1980; Hauptmann *et al* 1988; Koucky and Steinberg 1982; Merkel 1990; Merkel and Rothenberg 1999; Shugar 2003).

As Bachmann (1980) rightly argues, the separation of metal from the molten slag was controlled to a great extent by the viscosity of the slag. The formation of a viscous slag resulted in high copper losses as many metallic particles remained mechanically entrained in the slag, while a fluid ("free running") slag allowed such particles to settle forming a separate layer underneath it. The viscosity of a slag was, in turn, mainly determined by its chemical composition and the smelting temperature. As a rule, acidic oxides (mainly SiO_2 but usually also Al_2O_3 and P_2O_5) tend to polymerise to large anionic units thus increasing the viscosity of the slag whereas basic oxides (like FeO, MnO, CaO, MgO, K_2O, Na_2O) have the opposite effect as they promote the dissociation of the anionic complexes thus lowering the viscosity of the slag (Bottinga and Weil 1972). This correlation between the basicity of a slag and its viscosity is reflected in Bachmann's (1982: 19) definition of the *viscosity index* (Kv):

$$K_V = \frac{\textbf{Basic oxides}}{\textbf{Acidic oxides}} = \frac{\textbf{CaO + MgO + FeO + MnO + alkalis (wt-\%)}}{\textbf{SiO}_2\textbf{ + Al2O}_3\textbf{ (wt-\%)}} \quad \textbf{(Eq. 3.1)}$$

The values of K_V usually range from 0.5 to 1; the higher the viscosity index the lower the viscosity of the slag. Viscosity, however, decreases rapidly when temperature rises well above the liquidus temperature of the slag (Turkdogan 1983:

11) so, as Gilchrist (1989: 204) argues, a fluid slag can be achieved over quite a range of compositions if the temperature is raised enough. Therefore, unless highly siliceous, slags with low liquidus temperatures are usually characterised by relatively low viscosities at normal smelting temperatures (Peters 1907: 376). For example, according to Hauptmann's calculations (1985: fig.51), the viscosity of Bronze Age copper slags from Maysar in Oman was below 7.5 poise, i.e. not much higher that the viscosity of modern slags, which is generally up to 5 poise (Gilchrist 1989: 204).

3.4 The furnace atmosphere during smelting

So far, discussion has concentrated on the formation and behaviour of the slag because, as Peters (1907: 7) emphasises, 'it is the *slag* and not the *metal* which is always the first object of the smelter's concern when it comes to the treatment of the ore' (emphasis in the original). Nonetheless, the useful product of smelting was the metallic phase and (as discussed in detail in the following sections) the nature of this metallic phase depended heavily on the smelting conditions. The most influential factor was the *furnace atmosphere*.

The furnace atmosphere consists of gases produced from interactions between the air supplied in the furnace (e.g. by the bellows), the fuel (usually charcoal) and the liquid phases. Nitrogen, which is the main component in the atmospheric air, is inert so it has no participation in the reactions taking place during smelting. Reactions between the oxygen and the fuel are the complete and incomplete combustion of carbon:

$$\mathbf{C + O_2 = CO_2} \qquad \textbf{(Eq. 3.2a)}$$

$$\mathbf{C + \frac{1}{2} O_2 = CO} \qquad \textbf{(Eq. 3.2b)}$$

The complete combustion of carbon (**Eq. 3.2a**) requires more oxygen (i.e. sufficient supply of air) and releases more heat (thus resulting in higher temperatures) than the incomplete combustion (**Eq. 3.2b**) (Avery *et al* 1988). However, in the presence of abundant charcoal and at the high temperatures created by the combustion reactions,

CO_2 readily reacts with solid carbon generating CO according to the endothermic *Boudouard reaction* (Gilchrist 1989: 223):

$$\mathbf{2\,C + CO_2 = 2\,CO} \qquad \textbf{(Eq. 3.3)}$$

The three gases, O_2, CO and CO_2 reach (or constantly move towards) an equilibrium which is governed by the following overall reaction:

$$\mathbf{CO + \tfrac{1}{2}\,O_2 = CO_2} \qquad \textbf{(Eq. 3.4)}$$

The equilibrium is given by the following expression:

$$K_1 = \frac{pCO_2}{pCO \cdot pO_2^{1/2}} \Rightarrow \frac{pCO_2}{pCO} = K_1 \cdot pO_2^{1/2} \quad \textbf{(Eq. 3.5)}$$

where K_1 is the equilibrium constant of reaction **3.4** (it is a function of temperature), and pCO, pCO_2 and pO_2 the partial pressures of CO, CO_2 and O_2 respectively. The quantities (pCO_2/pCO) and pO_2 are equivalent expressions of the *redox conditions* in the smelting furnace. High values of (pCO_2/pCO) and pO_2 indicate *oxidising conditions* in the furnace whereas low values indicate *reducing conditions.*

Both the temperature and the gas composition in the furnace (and therefore its reducing or oxidising capacity) depend on many parameters including the fuel:(ore+flux) ratio in the smelting charge, the rate and mechanism of oxygen supply and the overall furnace design (Avery *et al* 1988; Bamberger and Wincierz 1990). In addition, the temperature and redox conditions can vary significantly throughout the furnace (Avery *et al* 1988). Allowing for possible oversimplifications, some general rules can be argued to apply:

- Higher fuel:(ore+flux) ratios in the charge result in more reducing conditions during smelting (Rostoker and Sadowski 1980).

- Open-shaped smelting vessels (e.g. like the smelting hearths in Kölschbach *et al* 2000: fig.2) allow more oxygen to enter creating more oxidising conditions. In contrast, closed-shaped smelting vessels with controlled air supply (e.g. shaft furnaces) are associated with more reducing conditions.

- The area in front of the tuyères is the most oxidising and features the highest temperature in the furnace. In the areas around this *combustion zone*, the temperature drops and the atmosphere becomes more reducing (i.e. richer in CO) due to the Boudouard reaction. Evidently, in the case of open-shaped or small-sized furnaces, a large combustion zone (deep penetration of air) may be created which can cover the entire space in the furnace.

- The area below the tuyères is generally reducing especially when layers of chaff or charcoal are laid at the bottom of the furnace before the smelting operation (Schmidt 1997: fig. 5.7).

The reason that redox conditions are an important parameter in copper smelting is that they influence the equilibria between metals, oxides and sulphides and, therefore, determine the nature of both the slag and the metallic phase formed during the process. From this point of departure, Yazawa (1980) classified modern copper smelting processes according to the prevailing redox conditions in each of them; an approach which has been adopted by Moesta *et al.* (1989) in the study of early copper production. It is from a similar *thermodynamic* perspective, that the following sections provide an overview of major early copper smelting processes.

3.5 Smelting of oxidised copper ores

The smelting of oxidised copper ores is a single-step process aiming to convert copper oxides to metallic copper by creating a *reducing atmosphere* in the furnace (Newton and Wilson 1942: 151). The basic reaction is:

$$\mathbf{Cu_2O + CO = 2\,Cu + CO_2} \qquad \textbf{(Eq. 3.5)}$$

Copper is a fairly noble metal so its oxides can be reduced at moderate reducing conditions, e.g. $pO_2 < 10^{-5} - 10^{-4}$ atm at 1200-1300°C (Gilchrist 1989: fig.48). Such moderate redox conditions have indeed been suggested for many early smelting practices (Golden *et al* 2001; Hauptmann 1989, 2003; Merkel and Rothernberg 1999). Moreover, copper-oxide has a limited solubility in silicate slags as its activity has a strong positive deviation from the ideal law (Ruddle *et al* 1966: 10). This means that as long as the furnace atmosphere does not become too oxidising, copper losses in the slag due to dissolution of cuprous oxide remain low (Richardson and Billington 1956; Ruddle *et al* 1966; Taylor and Jeffes 1975). To be more specific, the dissolution of cuprous oxide in the slag is governed by the following reaction (expressing copper oxide as $CuO_{0.5}$ because copper in slag is believed to exist as this mononucleus cuprous species: Altman and Kellogg 1972: 163; Turkgodan 1983: 309):

$$\mathbf{CuO_{0.5} = Cu + 1/4\ O_2} \qquad \textbf{(Eq. 3.6)}$$

whose equilibrium is:

$$\mathbf{K_2 = \frac{pO_2^{1/4}}{a_{CuO0.5}} \Rightarrow a_{CuO0.5} = K_2^{-1} \cdot pO_2^{1/4}} \qquad \textbf{(Eq. 3.7)}$$

This relation between copper solubility and pO_2 for various types of slag at 1300°C is given in **Figure 3.1.** It can be seen that unless the atmosphere becomes too oxidising ($pO_2 > 10^{-6}$-10^{-5}atm), copper losses from dissolution do not exceed the 2-3%.

The redox conditions, however, affect also the behaviour of ferrous slags, which are very common in prehistoric copper production (e.g. Hauptmann *et al* 2003). The reason is that the oxidation state of iron in the slag is very sensitive to changes in the furnace atmosphere. For optimal slag behaviour, iron must be in its ferrous state (Fe^{2+}), which is necessary for the formation of silicates. With increasingly oxidising conditions, however, ferrous cations are oxidised to ferric cations and this can ultimately result in the precipitation of solid magnetite:

$$3FeO_{(slag)} + 1/2\ O_2 = Fe_3O_{4\ (solid)} \qquad \text{(Eq. 3.8)}$$

In iron-silicates (silica saturated) the precipitation of solid magnetite takes place when $pO_2 > 10^{-6}$atm at 1300°C but at lower temperatures it can take place at much more reducing conditions (e.g. $pO_2 > 10^{-9}$atm at 1140°C) (Verein Deutscher Eisenhüttenleute 1981: fig.106). The formation of solid magnetite has detrimental effects on the efficiency of the smelting process because it raises the viscosity of the slag (Biswas and Davenport 1976: 95) thus impeding the slag/metal separation. To keep magnetite in solution in the liquid slag, the temperature needs to be significantly raised; this means that *the liquidus temperature of ferrous slags is affected by the redox conditions* (see Kongoli and Yazawa 2001).

Smelting oxidised copper ores under strongly reducing conditions can also be problematic when using ferrous slags because iron can be dissolved in the metallic copper (Newton and Wilson 1942: 154). The dissolution takes place according to the reaction:

$$FeO_{(slag)} = Fe_{(copper)} + 1/2\ O2 \qquad \text{(Eq. 3.9)}$$

whose equilibrium is:

$$K_3 = \frac{a_{Fe} \cdot pO_2^{1/4}}{a_{FeO}} \Rightarrow a_{Fe} = K_3 \cdot a_{FeO} \cdot pO_2^{-1/4} \qquad \text{(Eq. 3.10)}$$

The correlation between the amount of iron dissolved in copper and the redox conditions during smelting, to which Craddock (e.g. 1995: 137ff, 1999) has repeatedly drawn attention, is illustrated in **Figure 3.2**. High smelting temperatures also increase the solubility of iron in copper and hence promote further dissolution.

Excessive dissolution of iron in copper has two negative effects on the smelting process: (i) it removes iron from the slag, which therefore becomes more siliceous and thus more viscous (Peters 1907: 142), (ii) it results in a very contaminated copper product that would then require excessive purification by refining (in

Merkel's smelting experiments, copper ingots contained as much as 20% iron; Merkel 1990). It follows that in early copper-smelting processes using a ferrous slag, a compromise needed to be made: the atmosphere had to be sufficiently reducing to minimise copper losses (both by dissolution of cuprous oxide in the slag and by the precipitation of solid magnetite) but not very reducing to prevent the dissolution of iron in the metallic copper. In other words, ferrous slags operated well only within a range of redox conditions, a problem that was not shared by the manganese-based slags and this may explain their selection in some areas like Oman and Cyprus (Hauptmann 1989: 130).

The product of the smelting of oxidised copper ores under a reducing atmosphere, called *black copper,* was generally subjected to *refining* in order to remove iron and other impurities. The refining process involved remelting copper in a crucible under moderate to oxidising conditions. Metallic iron rose to the surface of liquid copper, where it became oxidised and was slagged by silica and alkalis from the crucible walls (Tylecote 1987: 193). The efficiency of refining in removing iron from smelted copper has been established experimentally by Tylecote *et al.* (1977) and more recently by Merkel (1990). Merkel's experiments have shown that simple remelting removes about 90% of the iron whereas after careful refining, the levels of iron drop below the 0.1% (Merkel 1990: Table 13).

3.6 Smelting of sulphidic copper ores

The processing of sulphidic copper ores differs from that of oxidised ores in one major aspect: carbon cannot reduce metal sulphides because the carbon sulphide C_2S is itself very unstable (Gilchrist 1989: 151). The extraction of copper from its sulphides requires, instead, the *burning-off* of sulphur with the use of oxygen before, during or after the smelting process. These alternatives are explored below.

3.6.1 Dead roasting and reduction smelting

Roasting is a solid-state operation taking place prior to smelting. Sulphidic ores are heated at temperatures around 600-900°C usually piled in heaps to allow easy contact with the air (Tylecote 1987: 111). This effects the oxidation of sulphides according to reactions such as the following (Bachmann 1982: 22; Craddock 1995: 149):

$$\mathbf{4\ FeS_2 + 11\ O_2 = 2\ Fe_2O_3 + 8\ SO_2}$$

$$\mathbf{4\ CuFeS_2 + 7\ O_2 = 2\ Fe_2O_3 + 4\ CuS + 4\ SO_2} \quad \text{(Eq. 3.11a, b, c)}$$

$$\mathbf{CuFeS_2 + 3\ O_2 = FeO + CuO + 2SO_2}$$

(Note that the first reaction involves pyrite which is usually the predominant component of sulphidic deposits).

Dead-roasting (**Eq. 3.11c**) represents the extreme case of roasting, whereby prolonged processing and higher temperatures result in the complete oxidation of copper and iron sulphides (Gilchrist 1989: 264). The product of dead-roasting contains mainly oxides of iron and copper and is therefore identical to oxidised ores (Tylecote 1987: 130). Consequently, dead-roasted sulphidic ores can undergo smelting at a reducing atmosphere for the production of black copper (i.e. in the way described in Section 3.5) as experimental work by Rostoker and Sadowski (1980) and Tylecote *et al* (1977) has established.

3.6.2 Partial roasting and matte smelting

Although one would expect dead roasting to have been a universally employed method, as it reverts sulphidic ores into the easily reducible oxides, this has hardly been the case. As Peters (1907: 40-1) notes, although the greater portion of the sulphur is easily and quickly burned off during roasting, as its percentage in the ore diminishes, its removal becomes extremely difficult and requires heavy firing, prolonged roasting time and continuous stirring of the heap. An alternative process, which is known to have been employed in prehistory (e.g.Cyprus.: Bachmann 1982: 25-6; Austria: Doonan 1996 and Eibner 1982) involved the *partial roasting* of the ore aiming to burn some of the sulphur and (more importantly) to oxidise some of the iron so as to ensure the formation of slag during smelting. Due to the predominance of pyrite in sulphidic copper deposits, iron-oxide was abundant in the roasted ore so fluxing with quartz was usually necessary (Craddock 1995: 150).

The ore was smelted in a reducing atmosphere ($pO_2=10^{-7}$-10^{-6}atm) aiming to collect most copper in a liquid iron-copper sulphide called *matte* (Craddock 1995: 142). Copper-iron mattes have a narrow compositional range: any sulphur in excess of the Cu_2S-FeS pseudo-binary vaporises whereas as matte becomes sulphur deficient, a second phase precipitates (**Figure 3.3**). For practical purposes, however, mattes can be considered to belong to the Cu_2S - FeS system.

The copper grade in mattes produced during smelting can range from 20 to 80% (Newton and Wilson 1942: 115) and is largely determined by the redox conditions in the furnace (Sridhar *et al* 1997; Yazawa 1980). The reason is that pyrite (FeS) can be partially oxidised to FeO in which case it is removed from the matte entering the slag:

$$\mathbf{FeS_{(matte)} + 3/2\ O_2 = FeO_{(slag)} + SO_2 \qquad (Eq.\ 3.12)}$$

while if any copper oxides are formed (or if any copper oxides were originally present in the charge), they are sulphurised by FeS according to the reaction (Biswas and Davenport 1976: 180):

$$\mathbf{Cu_2O_{(slag)} + FeS_{(matte)} = FeO_{(slag)} + Cu_2S_{(matte)} \qquad (Eq.\ 3.13)}$$

which has a very high equilibrium constant:

$$\mathbf{K_4 = \frac{a_{FeO} \cdot a_{Cu_2S}}{a_{FeS} \cdot a_{Cu_2O}} = 10^4 \qquad (Eq.\ 3.14)}$$

suggesting that the sulphurisation is almost complete. It follows that the more oxidising the smelting conditions are, the higher the copper-grade of the matte will be (**Figure 3.4**).

High-grade mattes were (and still are in modern practice) generally avoided during smelting because they result in higher copper losses in the slag (**Figure 3.5**). Firstly, high-grade mattes occur in more oxidising conditions which, as already described in Section 3.5, increase both the solubility of copper in the slag and the possibility of precipitation of solid magnetite. Moreover, as matte particles inevitably remain entrained in the slag during smelting, their higher copper grade increases the level of copper losses (Biswas and Davenport 1976: 207). It is no surprise, therefore, that in Bronze Age slags from site S1 in the Ramsau valley, the copper grade of matte ranged from 40 to 60% maintaining copper losses in the slag to less than 1% (Doonan 1996: fig. 3.19 and Tables 3.2a-c).

Since the product of smelting was matte, further processing was necessary to produce metallic copper. Two alternative processes are believed to have been employed in prehistory for this purpose. The first process involved the *dead roasting* of the matte in order to convert iron and copper sulphides to oxides (Bachmann 1982: 22):

$$\begin{aligned} \mathbf{Cu_2S + 3/2\ O_2 = Cu_2O + SO_2} \\ \mathbf{FeS + 3/2\ O_2 = FeO + SO_2} \end{aligned} \qquad \textbf{(Eq. 3.15a, b)}$$

The dead-roasted matte could then be smelted in a reducing atmosphere, fluxed with quartz, in the way described in Section 3.5 (Bachmann 1982: 22; Craddock 1995: 150; Eibner 1982; Tylecote 1976: 29-30).

The second process was *matte-converting* which involved the melting of copper matte under strongly oxidising conditions aiming to oxidise the iron and then the sulphur thus producing metallic copper (Rosenqvist 1983: 328). Two phases can be distinguished in the converter process. Firstly FeS was oxidised and slagged by fluxing with silica. Any copper oxides formed in the process were re-sulphurised by FeS according to the reaction **3.9**. When all pyrite had been consumed, the remaining *white metal* (i.e. Cu_2S) became increasingly sulphur deficient (path a→b in **Figure 3.6**) until a second phase, consisting of copper with 1.2% sulphur (called *blister copper*), appeared (point b) according to the so-called "roast-reaction" (Newton and Wilson 1942: 163, 171):

$Cu_2S + 3/2\ O_2 = Cu_2O + SO_2$ (oxidation of white metal) (Eq. 3.16a)

$Cu_2S + 2\ Cu_2O = 6Cu + SO_2$ (roast-reaction) (Eq. 3.16b)

Further removal of sulphur, according to these reactions, consumed the white metal, producing more blister copper (path b→c), until the entire sulphidic phase disappeared (point c). Continuation of the oxidising process purified blister copper by burning off the remaining sulphur but caution had to be taken to prevent oxidation of copper.

Matte converting is an oxidising process ($pO_2 = 10^{-6}$-10^{-5}atm) so it is inevitably associated with significant copper losses (Newton and Wilson 1942: 175), both due to the dissolution of cuprous oxide in the slag and due to mechanical entrainment of metallic particles (not least because of the massive magnetite precipitation). Although FeS can act as a reducing agent lessening these effects, it is consumed at the end of the first converting stage (Biswas and Davenport 1976: 185). In modern processes, the slag is removed once FeS is consumed, to prevent losses from excessive dissolution of cuprous oxide and it is not impossible that a similar practice existed in earlier traditions.

The practice of matte-converting in prehistory has been suggested by Zwicker and Goudarzloo (1979) and Doonan (1999) in the context of LBA copper-production in Eastern Alps. Their hypothesis is based on analysed slag samples containing blister copper and matte, which were magnetite saturated, indicating oxidising conditions similar to those prevailing during the converter process.

3.6.3 Direct smelting to blister copper

As already described in the previous section, typical matte-smelting processes usually take place under reducing conditions, the pO_2 rarely exceeding the 10^{-8}-10^{-7}atm. If more oxidising conditions do prevail then the matte composition moves towards that of white metal (Cu_2S) and, in accordance to the principles of matte converting, blister copper eventually forms. The process can be described by the overall reaction (Biswas and Davenport 1976: 221):

$$4\,CuFeS_2 + 10.5\,O_2 = 4\,Cu + FeO_{(slag)} + Fe_3O_4 + 8\,SO_2 \qquad \text{(Eq. 3.17)}$$

As seen in this reaction, roasting is not necessary because iron is oxidised *during smelting*. Moreover, being an oxidising process, direct smelting can result in high copper losses in the slag both by dissolution of cuprous oxide and by mechanical entrainment of metallic particles (magnetite increasing the viscosity of the slag).

Certain peculiar Bronze Age furnaces lacking front walls (i.e. exposing the charge to the air), which have been identified in Austria, are though to be associated with such oxidising smelting processes (Moesta and Schlick 1989). A similar process has also been proposed for the much earlier slags from Maysar in Oman which feature copper prills surrounded by Cu_2S and Cu_2O in eutectic intergrowth, corresponding to the *roast-reaction* outlined in the previous section (Hauptmann *et al* 1989: fig. 36).

3.7 Co-smelting of oxidised and sulphidic copper ores

The co-smelting of sulphidic and oxidised copper ores was introduced in archeometallurgical literature by Heskel (1982: 99-119) but it was Rostoker *et al* (1989) who established it both thermodynamically and experimentally. The principle of this technique is similar to that of direct smelting, in that oxygen is supplied in the smelting process to drive off sulphur producing blister copper, although in co-smelting, oxygen is not present as a gas but rather within the oxidised ores. A charge of such 'mixed' sulphide-oxide composition could derive from various sources including (a) the oxidation zone of copper deposits if residual hypogene sulphides had survived the weathering process; (b) the partial roasting of sulphidic ores; and (c) the mixing of dead-roasted and unroasted sulphidic copper ores (Craddock 1995: 137; Craddock 1999; Rostoker *et al* 1989: 85).

According to Rostoker *et al* (1989: Table 1) the production of metallic copper in co-smelting is effected by the interaction between copper-oxides and the sulphides of both copper *and* iron. Their experiments, however, showed that "...[T]he iron sulfide portion of the mineral reacts selectively in the reduction of the oxide to metal" (Rostoker *et al* 1989: 75). An alternative interpretation, which complies with the principles of matte converting and direct smelting, is that during co-smelting, FeS does not reduce but rather sulphurises copper oxides to Cu_2S, which then reacts with copper oxide according to the roast-reaction (**3.16b**) to produce blister copper. This model is represented in **Figure 3.7** in which, for the sake of simplicity, it is assumed that the ore contains Cu_2O, FeS and Cu_2S.

(Path 1) $Cu_2O + FeS = Cu_2S + FeO$: This is the sulphurisation reaction (**3.13**), which can be assumed to proceed for almost as long as the two reactants are available (high equilibrium constant). It increases the copper grade of the matte as indicated by the experimental results of Rostoker *et al* (1989).

(Path 2) $Cu_2S + 2Cu_2O = 6\ Cu + SO_2$: This is the roast-reaction (**3.16b**) and is the one that produces blister copper. It is very likely that it does not come into action until most of the FeS has been consumed (see Biswas and Davenport 1976: 222). In other words, it can be assumed that the two reactions take place more or less *in sequence*.

This, however, is not the whole story, since the discussion so far has not considered the furnace atmosphere which has an active role in controlling both the Cu_2O/Cu equilibrium (see Section 3.5) and the composition of the matte (see Section 3.6). In this context, the rate of reactions becomes a key factor in determining the end products of the process. Although modelling such a complex process is impossible without systematic experimental work (e.g. Bourgarit *et al* 2002), it can be argued that:

- Co-smelting in a *reducing atmosphere* produces blister copper but much of the sulphidic component remains in the matte (e.g. experiments 5A-B, 6 in Rostoker *et al* 1989).

- Co-smelting in an *oxidising atmosphere* produces blister copper and minimises the amount of residual matte (Bourgarit 2002); however, copper losses are increased by the dissolution of cuprous oxide in the slag.

- When the oxide component in the charge is low, the smelting conditions must be more oxidising to minimise the amount of residual matte and increase the amount of blister copper (Bourgarit *et al* 2002). The process then approximates that of *direct smelting* (see Section 3.6.3).

- When the oxide component in the charge is high, the smelting conditions must be more reducing to minimise copper losses in the slag. The process then approximates that of *reduction smelting* (Section 3.5)

Archaeological evidence reflecting co-smelting practices have been discovered in the Chalcolithic sites of Shahr-i-Sokhta in Iran (Hauptmann *et al* 2003), Abu Matar in Palestine (Shugar 2003) and Al Claus in southern France (Bourgarit *et al* 2002).

3.8 Conclusions

The aim of this chapter was to outline the principles underpinning early copper smelting processes. It was argued that their efficiency depended on two major conditions: (i) the formation of a fluid slag, which was achieved by adding (when necessary) appropriate fluxes in the charge and by reaching and maintaining a sufficiently high temperature in the furnace; and (ii) the manipulation of the atmosphere in the furnace by controlling the amount of fuel added in the charge and the amount of air (and the way in which it was) supplied in the furnace. Moreover, various process models that have been proposed in the past for the production of copper in prehistory were discussed. Such models serve to demonstrate the multiple ways in which metallic copper could be extracted from its ores, and to highlight distinctive characteristics that can be identified in smelting remains using appropriate analytical techniques. From this starting point, the next chapter investigates the technology employed at the Early Minoan site of Chrysokamino on eastern Crete for the smelting of copper ores.

CHAPTER FOUR

TECHNOLOGICAL ANALYSIS OF COPPER SMELTING REMAINS
from Chrysokamino in Northeastern Crete

4.1 Introduction

The association of Chrysokamino (*Greek*: “Golden furnace”), a small peninsula in the eastern fringe of the gulf of Mirabello in northeastern Crete (**Map 4.1**), with metallurgical activities has been known for over a century (Boyd 1901). However, the site was only recently excavated unearthing remains of copper smelting activities dating to the 3rd millennium BC (Betancourt *et al* 1999). In 2000, Dr Yannis Bassiakos (Laboratory of Archaeometry, N.C.S.R. Demokritos, Athens) and the director of the excavation Prof. Philip Betancourt selected a number of copper-ore and slag samples for the purposes of an analytical study aiming to shed light to major technological aspects of the smelting process evidened at the site. This assemblage was kindly offered to the author in June 2002 to provide the basis of this doctoral dissertation. The background and the results of the technological study are presented in this chapter.

4.2 Geological and geomorphological context

Crete is situated at the centre of the *Hellenic Arc*, a convergent zone extending from Peloponnese through Crete to the Taurus Mountains of south western Turkey, associated with the subduction of the African lithosphere under the Aegean (Papanikolaou 1985: fig. 1). Increased geotectonic activity deriving from the position of Crete on the arc, has given to the island a form of “a series of upfaulted horstblocks of pre-Neogene rocks separated by grabens filled by Neogene and Recent sedimentary rocks (Hall *et al* 1984: 501).

The complex history of evolution of Crete is reflected in the geological and topographical diversity of the Kavousi area at the northeastern part of the island, where the site of Chrysokamino is located (**Maps 4.2-3**). There are three major topographical units. The Kavousi plain is a north-south orientated basin (an extension of the Isthmus of Ierapetra) with fluvials, colluvials and alluvials reaching the sea, on its north end, at the bay of Tholos. The plain is bordered from the east by Permian-Triassic uplands, the division being an abrupt rise in elevation formed by a steep fault front along the west face of mounts Kapsas and Papoura (Haggis 1992: 74). This eastern mountain-front is an outcrop of Permian crystalline bluish limestone except for the areas on the east and south of the modern village of Kavousi where Permian-Triassic phyllites and Triassic black dolomites overly the limestone (Papastamatiou 1959). To the west of the Kampos plain lies a series of low coastal hills (100-200m altitude) which are continuations of the Permian-Triassic uplands: Schoinias, Chomatas and Chalepa. Triassic dolomite, Permian-Triassic phyllite and Permian crystalline limestone in alternating bands form the bedrock of these hills (Papastamatiou 1959). Their eastern slopes are gradual inclines, the steepest being less than 30 degrees whereas the west side of the front, facing the sea, consists of very steep slopes and vertical cliff faces (Haggis 1992: 72).

The metallurgical site is located on a small promontory at the coastal front of Chomatas, one of the hills bordering the Kavousi plain from the west (**Plate 4.1**). Betancourt *et al* (1999: 351) describe the promontory as "an isolated point of land perched about 38m above the sea with no immediately adjacent boat landing available and backed by a sharp but walkable ridge rising another 80m without significant levels areas" (**Plate 4.2**). Only the upper parts of the hillsides are extensively terraced while descent to the coastline is through steep or very steep ravines making access to the metallurgical site quite difficult (Betancourt *et al* 1999: 350). Most material is located in a narrow trough, formed between the headland of the promontory and the hillside (**Plate 4.3**), in which the frequent north winds are channelled creating very strong draughts (Betancourt in press). The site is located on phyllitic bedrock exposed to *in situ* weathering which has produced a very powdery white residue. Occasional outcrops of the phyllitic bedrock are visible, bearing a system of quasi-parallel fine veins of white calcite. The underlying 'Plattenkalk' carbonate formation consists of solid and relatively thinly bedded or slabby, grey to bluish semi-metamorphic limestone (Papastamatiou 1959). A contact between the phyllitic and carbonate units is visible some 100m from the site.

An interesting geological feature of the area is a weathering-resistant carbonate ledge traversing the local phyllites (Betancourt *et al* 1999: 352). The selective weathering of the phyllites has often resulted in the exposure of the ledge forming localised protuberances; in those cases, iron hydroxides are visible on the lower contact between the carbonate ledge and the phyllites (**Plate 4.4**). Similar iron hydroxide crusts can be frequently seen on rock fragments within the tumble covering the slope on the east of the promontory. Those thin crusts develop locally into a weak iron mineralisation hosted in the Plattenkalk/phyllite contact near the site (**Plate 4.5**). Similar iron occurrences are present throughout the Kavousi area. The possible role of this mineralisation in the smelting process is discussed later in the chapter.

In contrast, no copper deposits have been identified in the broader Kavousi area (Betancourt *et al* 1999; Branigan 1968: 50-52 and fig. 118; Stos-Gale 1993). The original interpretation of the nearby cave of Kolonospilia as a copper mine (Mosso 1910: 219) has been rejected by Diallinas (Branigan 1968: 50) who examined the cave but found no evidence of a mineralisation. It seems, therefore, that copper ores were transported from elsewhere to be smelted at Chrysokamino (Betancourt *et al* 1999: 352).

4.3 Archaeological research at Chrysokamino

The first references to the presence of metallurgical remains of a possible Minoan date at Chrysokamino date back to the beginnings of the century (Boyd 1901; Mosso 1910). The remains were believed to be associated with copper production while the nearby Kolonospilia cave was regarded, at least by Mosso (1910: 289-292), to be the mine where the ore was collected. Although diagnostic pottery was absent from the metallurgical site itself, the smelting activities were thought to be roughly contemporary with the neighbouring Minoan sites of Pseira and Gournia (Hall 1910 as cited in Betancourt *et al* 1999: 345), a view strengthened by the material from Kolonospilia, which suggested that the cave was used from the Final Neolithic onwards (see Haggis 1992: 260).

Chrysokamino was not discussed again until the late 1960s when both Faure (1966) and Branigan (1968) raised strong doubts about its suggested Minoan date. Faure argued for a "recent" date on the basis of the highly vitrified state of the slag fragments, the absence of soil accumulation and an unsupported belief that the copper ore processed was chalcopyrite (Faure 1966). Similarly, Branigan (1968: 50-1) argued that the material should probably be associated with the activities of a group of itinerant smiths called "Chalkiades" (*Greek*: copper-smiths), which operated on Crete during the 14th century AD. That the operations were conducted by itinerant craftsmen was, according to Branigan (1968), indicated by the small amount of debris present at Chrysokamino and the absence of a nearby copper deposit (the cave had by then been examined by Diallinas who had dismissed its interpretation as a mine). As for the late date of the metallurgical operations, this was based on the results of an unpublished preliminary study of slag sample(s) by Sargent, using Electron Probe Microanalysis, which showed that:

> "...a reasonably high temperature had been achieved in smelting in the region of 1150°F (*sic*) [1150°C is probably meant] or more. The recovery rate was very high indeed, and there was also some evidence to suggest that calcium, probably in the form of limestone, had been deliberately added during the smelting operations. All of these features suggest a relatively modern date for the slag which Sargent suggests is not earlier than about the 12th century AD" (Branigan 1968: 50).

So certain was Branigan that the smelting activities at Chrysokamino were not prehistoric, that he made no reference to the site in his later detailed study of Aegean metallurgy in the Early and Middle Bronze Age (see esp. Branigan 1974: 62-3).

In the 1990s, Chrysokamino re-appeared in the literature in two articles by the Oxford group (Stos-Gale 1993, 1998) who visited the site and collected slag samples for preliminary laboratory analyses. Their results suggested that the slag was "primitive" and the entrapped copper prills contained "up to several percent arsenic", a composition that was consistent with the arsenical copper used in the Aegean during the Early Bronze Age (Stos-Gale 1993: 124). No pieces of charcoal were found to allow ^{14}C dating but two early dates (2420±345 BC and 2710±365 BC) obtained by thermoluminescence dating of the coarse ceramic fragments, placed the metallurgical activities firmly in the 3rd millennium BC (Stos-Gale 1998: Table 2). Stos-Gale (1998: 725 and Table 3) also reported the results of lead isotope analysis of four slag samples from the site, according to which "some samples" were consistent with the isotopic composition of ores from Laurion while "other samples" had isotopic ratios similar to Cycladic copper ores. That the ores smelted at Chrysokamino derived from multiple copper sources has been confirmed by a more recent lead isotope study including a larger number of slag samples (Stos-Gale and Gale in press).

A breakthrough in the study of Chrysokamino came about with the excavation of the site by the American School of Classical Studies in Athens under the direction of Professor Phillip Betancourt in the period from 1995 to 1999. The excavations yielded a wide range of metallurgical and non-metallurgical evidence including slag, ores, refractories, pottery and architectural remains, all of which are currently studied in various interdisciplinary projects. At present, excavation results have been presented in preliminary reports (Betancourt in press; Betancourt *et al* 1999). The information provided below derives from these reports, communication with Prof. P. Betancourt and the co-director of the excavation Prof. J. Muhly, and personal observations made during visits to the site.

4.4 Presentation of archaeological material from Chrysokamino

4.4.1 Slag

The predominant material excavated at Chrysokamino was black-coloured slag, which formed a 700-800 kg deposit scattered over an area of *ca.* 10 x 40 m^2 (Betancourt in press). Due to the partial erosion of the deposit into the sea, it is difficult to estimate its original size. Its limited spatial extent, however, suggests that it hardly exceeded the 1-1.5ton. The deposit did not exhibit visible layering so it was excavated using a system of arbitrary 10cm deep spits (Betancourt in press).

The slag is found in a heavily fragmented state. Not a single intact slag cake has been recovered from the site. Instead, most pieces are under 2-3cm in size while much slag is completely pulverised (**Plate 4.6**). This suggests that slag was crushed (and often ground) after the completion of the smelt in order to retrieve entrapped globules of metal, a practice that was common in prehistory (e.g. Rothenberg 1990: figs. 13 and 62; Koucky and Steinberg 1982; Levy *et al* 2002) and is also attested in other EB copper smelting sites in southern Aegean (see Section 5.6.3).

In terms of texture, the slag from Chrysokamino is fairly homogeneous. Slag fragments are generally glassy although differences in the degree of vitrification can be noted both among and within individual fragments. The only inclusions visible macroscopically are minute copper prills (<1 mm) and rare small fragments of quartz (<2 mm), probably reflecting unfused pieces of gangue material or flux. In addition, the porosity of the slag is very limited and of small size (<1 mm). These features suggest that the gangue minerals (possibly with the addition of a flux) were successfully fused into a fluid slag during smelting, enabling a good level of slag/metal separation.

The fragmented state of the slag and the presence of epigenetic material deriving from the calcareous environment do not allow a detailed study of morphological features that could provide information about the shape, size and texture of the original slag cakes. In addition, it is difficult to investigate whether different types of slag (e.g. furnace slag and tapped slag) are present at the site. On some of the larger slag fragments, however, which maintain a sufficient part of their original surface, there are obvious flow features that could probably be associated with the tapping of liquid slag outside the furnace, a fact further supported by the presence of small pieces of rock entrapped on their lower surface (**Plate 4.7**). Some slag fragments, in particular, could in fact be interpreted as 'runners'; i.e. the part of the slag that was just outside the tap-hole on the furnace when solidified (**Plate 4.8**). The possibility that slag was tapped from the furnace during the smelting process is discussed in more detail later in the chapter.

4.4.2 Furnace fragments

Mixed with the slag pieces at the site were thousands of fragments of coarse, low-fired ceramics with abundant organic matter (Betancourt *et al* 1999). The fragments of the ceramic shafts found at Chrysokamino bear numerous perforations (**Figure 4.1**), a feature that has been noted in other copper smelting sites in southern Aegean from the Final Neolithic onwards, namely Raphina in Attica, Kephala on Keos and the Kythnian sites of Sideri and Aspra Spitia (see Section 5.5.1).

According to the excavators (Betancourt *et al* 1999), the fragments derived from the walls and bases of tapering cylindrical objects, with a diameter ranging from 20-25cm at the top to 40-45cm at the base (the height could not be estimated), with open tops and flat bases. The interior of fragments from the lower parts of the cylinders had vitreous coatings so the latter were interpreted as shaft furnaces (Betancourt *et al* 1999: 354) (**Figure 4.2**).

This reconstruction appears accurate in all respects apart from the suggestion that the furnaces had closed bottoms (Betancourt *et al* 1999). During smelting, the furnace must be strong enough to hold the liquid charge at temperatures above 1000°C. More importantly, the liquid slag can chemically attack and dissolve a substantial part of the refractory material, especially from the lower parts of the furnace (e.g. Rothenberg 1985: 128). Merkel's experiments showed that an average of 3kg of the firebricks used for the construction of the furnace, were dissolved in the slag during *each* smelting operation (Merkel 1990: 98). Similarly, in her study of two copper smelting sites in Thailand dating to the 2nd millennium BC, Bennett (1989: 343-4) observed that the thickness of a base fragment from a ceramic smelting vessel was reduced due to chemical attack by the slag from 3.6 to 1.6cm.

Considering the above, it is difficult to accept that the hot liquid charge (slag and copper) could be contained in a closed-bottom shaft with a wall (and bottom) thickness of 1-2cm (**Figure 4.1: 1, 2**). It seems more reasonable to suggest that the shaft was open at the bottom and stood on top of a clay-lined depression in the ground (Stos-Gale 1998: 721) (**Figure 4.3**). In this way, the shaft would be neither subjected to a heavy load nor significantly attacked by the slag because the latter would have been accumulated inside the depression where it would not be in contact with the ceramic material. A yet unpublished piece of clay-lining, about 4-5cm in thickness with signs of burning on its upper surface, adds further support to the suggestion for the presence of a lined furnace-bottom underneath the ceramic shaft.

4.4.3 Pot-bellows

Another type of metallurgical evidence recovered during excavation are fragments of a minimum of ten pot-bellows. They were drum-shaped cylinders (diameters varying from 28 to 48cm) with closed flat tops bearing one or more large rectilinear holes (**Figure 4.4a**). The lower, open part of the bellows, which was facing down during use, has been difficult to reconstruct due to bad preservation but some straight rims that have been found may be from this part (Betancourt *et al* 1999: 358). The bellows are made of coarse "Mirabello fabric", a fabric that was commonly used during the EM period for the production of cooking vessels and has been geographically associated with the granodioritic intrusions on the coastal area west from Pacheia Ammos and Gournia (Betancourt *et al* 1999: 359; Whitelaw *et al* 1997).

According to the reconstruction proposed by Harriet Blitzer, a leather bag with silts and flaps was attached to the "open" top while the "rim" was facing the ground, sealed with mud (as suggested by examples with fused mud on their exterior) to prevent air losses. The user (**Figure 4.4b**) forced air through the nozzle by working the leather bag and this was channelled into the furnace with the aid of pipes and tuyères (Betancourt *et al* 1999: 359). A tuyère fragment has indeed been discovered at the site but no information has yet been reported on its shape and size (Betancourt *et al* 1999: 354).

Direct calculation of the total volume and the effective volume of the bellows is difficult due to their unknown height. However, the surviving parts are very similar in size to the bellows used by Merkel (1990: fig. 121) in his smelting experiments. The *effective volume* of Merkel's bellows was about 6lt so a similar value can be assumed for those found at Chrysokamino. In the same experiments it was shown that the air supply rate for each bellows was about 200-300lt/min using a moderate operating pace (Merkel 1990: 109). As pot bellows are operated in pairs (**Figure 4.4b**; see also Merkel 1990: fig. 122; Schmidt 1997: fig. 4.17), it follows that each user could provide a total of up to 600lt/min of air during smelting. To ensure sufficient air flow (1000-2000lt/min) and penetration, at least two pairs of bellows positioned in opposite sides of the 40cm wide furnace would have been probably required (see Bamberger and Wincierz 1990; Doonan 1996: 134-5; Merkel 1990). Although evidence from the lower parts of the furnaces at Chrysokamino are fragmentary, the lack of large holes (necessary for the positioning of the tuyères) on the ceramic fragments suggests that the tuyères were positioned *underneath* the shaft, probably along small channels opened on the ground (see **Figure 4.3**), at an angle of about 30^{0} pointing to the centre of the hearth (see Bamberger and Wincierz 1990).

4.4.4 Copper ores

A small number of pieces of oxidised copper ores (less than 3cm in size) have been reported from the site. No tailings were found during the excavation suggesting that the ore was already beneficiated when it was brought to Chrysokamino (Betancourt *et al* 1999). Twenty-seven ore pieces were examined by Dr Bassiakos and the author and were found to consist of green oxidised copper minerals (probably malachite) in a predominantly siliceous matrix with some iron hydroxides. These finds provide useful information on the character of the smelting processes taking place at Chrysokamino. Firstly, they suggest that the process was probably the ***reduction*** of copper oxides to metallic copper in a reducing atmosphere, a process whose principles have been described in Section 3.5. Secondly, the predominance of quartz in the gangue (typical in oxidised ores) raises the possibility that iron- or manganese-oxide was used in the smelting process as flux. These possibilities are examined analytically later in the chapter.

4.4.5 Stone tools

A maximum of 22 possible stone tools have been identified, most made of various kinds of limestone and/or dolomite (probably from adjacent areas), but only a few can be attributed with certainty to the classes of pounders, grinders and working surfaces (Betancourt *et al* 1999). In the absence of evidence for *in situ* ore beneficiation, the main function of the stone tools probably was to crush and grind the slag after smelting in order to retrieve any entrapped metal. Indeed, wear traces on many tools seem to suggest that they were used for the working of a hard material such as slag (Betancourt *et al* 1999: 366).

4.4.6 Other archaeological material

A later addition to the metallurgical site was an apsidal hut built on top of a 45cm-thick deposit of slag and furnace fragments (Betancourt *et al* 1999: 360). Three superimposed floors were identified at the interior yielding evidence for a hearth, sherds of cups, cooking dishes, jars and basins, and pieces of pot-bellows (Betancourt *et al* 1999). All the pottery dates to the EM III period. The discovery of cooking vessels at the site, some from within the hut itself, may suggest that the hearth was used for the preparation of food. However, since pieces of pot-bellows were also found in the hut, a metallurgical use (e.g. refining of smelted copper) should not be excluded.

Very limited information on the ceramic assemblage from the site has been published so far (Betancourt *et al* 1999: 356-8). A few hundred sherds have been recovered and most belong to the EM III period. No pottery of later date has been found but there are a few sherds dating to the Final Neolithic, one to the EM I-IIa and one to the EM IIb (Betancourt *et al* 1999). All pottery is considered to be of local origin: the fine pottery has the White-on-Dark decoration, which is typical of the region, while the coarse pottery has been made using the local Mirabello fabric (Betancourt *et al* 1999).

4.4.7 Dating the smelting activities at Chrysokamino

Although most of the pottery from Chrysokamino dates to the EM III period (2200-2000 BC; Manning 1995: fig.2), the excavators place the beginnings of the smelting activities at the site in the Final Neolithic. Their argument is based on the presence of FN pottery at the site and the fact that the apsidal hut, containing EM III pottery, was built over 45cm of accumulation of slag reflecting a previous long period of use (Betancourt *et al* 1999: 363). Although no conclusive arguments can be offered before the full publication of the excavation, there are strong indications suggesting that the period of metallurgical activities at the site was not as long as proposed. Firstly, it is very possible that the Final Neolithic and EM I-II sherds discovered at Chrysokamino were part of the "background" of the location, predating, in other words, the metallurgical activities (Day pers.comm.). This suggestion is supported by the ceramic evidence for continuous human activities from the Neolithic onwards from the adjacent Kolonospilia cave and other areas near the site (see Haggis 1992: 260). The presence of only two sherds dating to the "intermediate" EM I-II periods among the metallurgical debris makes the suggestion of a tight EM III date for Chrysokamino even stronger. Similar conclusions can be reached from a consideration of the amount of slag present at Chrysokamino. As already noted, the original size of the slag deposit was probably less than 1-1.5t, which roughly corresponds to anything between 25 and 75 smelting operations, assuming that 20-40kg of slag were produced in each smelting operation (a reasonable estimation given the large base diameter of the furnaces). Although the rate of production at the site cannot at present be inferred, it seems difficult to imagine that this small number of smelting operations reflects activities spanning from the Final Neolithic to the end of the Early Bronze Age, a period, that is, of more than 1000 years. Based on the above, it is suggested that the site of Chrysokamino hosted a limited number of copper smelting operations during the EM III period.

4.5 Questions on the technology of copper smelting at Chrysokamino

The aim of this analytical study is to understand the copper smelting technology employed at Chrysokamino towards the end of the Early Bronze Age. Important information on various aspects of the process was obtained from the macroscopic examination of the excavated material (see previous section). However, as shown in Chapter 3, the description of early smelting technologies requires a deeper understanding of a wide range of parameters relating to the nature of the raw materials, the operation of the furnace, the behaviour of the slag and the nature of the metallic product. For example, what temperatures and redox conditions were achieved in the furnace? How effective was the slag/metal separation? Was the slag tapped or did it solidify inside the furnace?

Further questions, relating more specifically to the smelting technology at Chrysokamino, have been raised by the results of the preliminary analyses by Sargent and Stos-Gale (Section 4.3). Firstly, Sargent has argued that calcium (i.e. lime) was used as a flux in the smelting process at Chrysokamino (Branigan 1968: 50). Lime-fluxing is generally associated with the smelting of iron in blast furnaces in medieval periods (Tylecote 1976: 81ff) so its use in a prehistoric context is an intriguing possibility that needs to be investigated. In addition, Stos-Gale (1993) has noted the presence of arsenic in the copper prills embedded in slag from Chrysokamino. A number of theoretical models exist for the early production of arsenical copper in smelting, either by (consciously or "unintentionally") using arsenic-bearing copper ores or by adding arsenical substances to the smelting charge (e.g. Lechtmann and Klein 1999; Merkel and Shimada 1988; Merkel *et al* 1994; Pollard *et al* 1991; Rostoker and Dvorak 1991; Rovira 1999; Shugar 2003). Understanding the way in which arsenical copper was produced at Chrysokamino is not only important for the reconstruction of the smelting technology at this site; it could also contribute to our grasping of the arsenical copper "phenomenon" (O'Brien 1999: 33) characterising the EBA period in the Aegean and other areas in the Old World.

Based on the above, the questions this analytical study sets out to investigate are summarised below:

Raw materials:

- What type(s) of copper ore was smelted at Chrysokamino and what were the associated gangue minerals?
- Is there evidence for the use of fluxes in the process?
- Was arsenic present in the copper ores or in other ingredients added to the charge?

Smelting conditions:

- What was the maximum temperature reached in the furnace?
- What were the redox conditions in the furnace?

Slag/metal separation:

- Was the slag tapped or did it solidify inside the furnace?
- What were the copper losses in the slag?
- What was the nature of copper losses in the slag (dissolution of cuprous oxide or entrapment of metallic particles)?

Product:

- Was arsenical copper produced at Chrysokamino?
- What other elements were present in the metallic product?

4.6 Samples included in the analysis

4.6.1 Slag samples

Forty-eight slag samples were collected by Betancourt and Bassiakos in 2000 for the purposes of laboratory analysis. Forty-five of them derived from passes 3 and 4 (30 and 40cm below surface) in the main excavation trench (trench X-N-20), opened at the thickest part of the deposit along the narrow trough. The remaining three slag fragments were surface finds (**Table 4.1**). The stratified samples were selected randomly whereas two of the surface finds were 'uncommon' pieces. One of them turned out upon examination in the laboratory to be a piece of rock from the local geology and was therefore excluded; the other was found to be a piece of *iron-ore*. This was a very important find because it could reflect the use of a ferrous flux in the smelting process, especially since all copper ores found at the site are associated with siliceous gangue minerals. Unfortunately, without systematic re-examination of the excavated material, it is not possible to establish whether more such pieces are present in the deposit. They may have been misclassified as slags or pieces of rock from the local geology (Betancourt pers.comm.).

4.6.2 Copper-ore samples

Three small pieces of copper ore, collected from the surface of the site by Dr Bassiakos after the completion of the excavation, are included in the analytical study (**Plate 4.9**). They are similar to other pieces found at the site; they consist, that is, of green copper minerals (probably malachite) in a siliceous matrix with small presence of iron hydroxides (see Section 4.4.4) (**Table 4.1**).

4.7 Methodology for the analysis of slag

It has long been appreciated that the chemical and mineralogical characterisation of archaeological slag samples is an invaluable tool for the reconstruction of early copper-smelting technologies (Bachmann 1980, 1982; Hauptmann 1989; Doonan 1996: 47). Not only does slag offer the best record of the chemo-physical phenomena that took place during smelting; it is usually the predominant (if not the sole) type of surviving evidence in early copper-smelting sites. It is therefore no surprise that archaeometallurgical studies have placed great emphasis in developing a strong analytical methodology for its investigation. Although a standardised methodology has not yet been established, most modern studies of archaeological slags have been based on a combination of *microscopic analysis*, *chemical analysis* and *phase* *microanalysis* (e.g. Bachmann 1980; Doonan 1996; Hauptmann 1985, 1989; Hauptmann *et al* 2003; Moesta *et al* 1989; Rovira 2001; Shugar 2003; Zwicker *et al* 1985). A similar multi-analytical approach has been employed in this study.

4.7.1 Optical microscopy

The study of polished slag specimens under the polarising optical microscope is one of the most important analytical tools for the archaeometallurgist. Optical microscopy is a low-cost technique, which allows the study of the major mineralogical phases present in the slag, their texture and intergrowth.

The micro-texture of slag provides useful information on the liquefaction and solidification of the slag during and after smelting. The level of homogeneity of slag and the presence or absence of unfused pieces of raw materials offer a measure of how efficiently the gangue minerals (often with the aid of a flux) were fused into a fluid slag (Golden *et al* 2001; Hauptmann 1989; Merkel and Rothenberg 1999). Information on whether the slag solidified inside the furnace or was tapped during smelting can be deduced from its vitrification and the texture of the silicate crystals. Slow solidification (i.e. inside the furnace) allows the crystallisation of the silicate melt and the formation of euhedral crystals often exhibiting characteristic zoning (Bennett 1989: 339; Doonan 1996: fig. 3.16; Hauptmann 1985). In contrast, rapid solidification (i.e. in contact with the air) promotes the formation of glass and fine silicate crystalline formations, such as laths and dendrites (Bachmann 1982: 15; Dimou *et al* 2001).

Examination of polished slag specimens under the optical microscope also allows the identification of the predominant metallic phase present in the slag. As described in Chapter 3, copper-smelting processes, depending on the mineralogy of the raw materials and the furnace conditions, can produce metallic copper and/or matte at varying proportions. In the absence of direct evidence, such as copper or matte nodules or 'ingots', it is from the nature and relative proportions of various metallic inclusions entrapped in the slag that one may obtain information on the nature of the product of the smelting process, and optical microscopy is an ideal analytical tool for this work (Bachmann 1982; Doonan 1996: 56-7; Hauptmann *et al* 2003; Shugar 2003).

Microscopic examination of slag samples from Chrysokamino was conducted using a Nikon Optiphot polarising microscope. The specimens were examined using reflected light at a range of magnifications from x25 to x1000 using plane-polarised light (PPL), cross-polarised light (XPL) and dark field view (DF). To prepare the polished sections, one or more pieces were taken from each ore and slag sample using a Buehler low-speed cutting-wheel. The pieces were mounted in Buehler Epoxy resin, ground using a sequence of grits (240, 400, 800, 1200, 2500) and finally polished using 6, 3 and 1 μm diamond pastes.

4.7.2 Chemical analysis

Measuring the chemical composition of slag has probably been the most commonly employed approach in the study of early copper-smelting processes. Being the collector of most unwanted materials in the charge, slag offers an accurate record of the raw materials used in the process and the level of control exerted by the smelters over the composition of the smelting charge (Bachmann 1982; Manasse and Mellini 2002; Rovira 1999). In addition, when fragments of copper ore are also recovered from a smelting site, comparison of the major oxides in the slag with the composition of the gangue minerals of the ore can reveal the use of fluxes in the smelting process (Hauptmann *et al* 1988, 2003; Wagner 1986).

The chemical composition of slag is also important for the calculation of its liquidus temperature and viscosity. Although direct measurements of these properties have appeared in rare occasions in archaeometallurgical literature (e.g. Hauptmann *et al* 1988), it is much more common to calculate them indirectly by inputting the chemical composition of the slag in appropriate phase diagrams and/or chemo-physical models. For the estimation of the liquidus temperature of copper-smelting slags, ternary phase diagrams corresponding to subsystems of the general quaternary system CaO-FeO-SiO_2-Al_2O_3 are commonly used (Bachmann 1980: 120). As for models for the calculation of slag viscosity, these are based on the behaviour of various oxides as network formers and network modifiers (Bachmann 1980; Bottinga and Weil 1972; Shaw 1972).

Finally, the copper content of slags offers a measure of the copper losses and hence of the efficiency of the slag/metal separation during the smelting process (Doonan 1996: 49-50; Hauptmann *et al* 1988, 2003).

Various techniques have been employed in the past for the chemical analysis of archaeological slag samples including Inductively Coupled Plasma Spectroscopy (Golden et al 2001; Shugar 2003), Atomic Absorption Spectroscopy (Doonan 1996: 57ff), X-Ray Fluorescence Spectroscopy (Manasse and Mellini 2002; Hauptmann et al 2003) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (Hauptmann *et al* 1996; Okafor 1993; Rovira 1999). The latter technique was employed in this study and the instrument used was a Philips 500 Electron Microscope coupled with a Link EDS spectrometer.

In Scanning Electron Microscopy (SEM) a beam of electrons is focused onto a specimen and scanned across it in a 'raster' of fine lines, causing the emission of X-ray radiation due to the relaxation of excited atoms of the elements present in the specimen (Goodhew et al 2001: 34). An Energy Dispersive Spectroscopy (EDS) detector converts the radiation into a spectrum corresponding to the K and L emission lines of all the elements of interest (Pollard and Heron 1996: 45). A special software quantifies the analytical results making the necessary matrix corrections to account for atomic number (Z), absorption (A) and fluorescence (F) effects on the emission of X-rays by the specimen.

In this study, the SEM-EDS analysis was conducted on pelletised slag specimens. A sample of approximately 2g was cut from clean areas on each slag fragment. This was pulverised using an agate ball mill to a grain size of less than 63μm. About 0.4g of this powder were then formed into flat pellets by dry pressing, impregnated in Buehler Epothin resin in a vacuum oven and ground using a 2500grit grinding paper. Four areas, each about 1.5mm^2, were analysed on each pellet and the results were used to calculate the average elemental composition. In the case of seven slag fragments it was not possible to prepare pellets, either because the fragments were very small or because they were also sampled for Mössbauer analysis. Analysis of these samples was conducted by scanning a large area, free of pores and cracks, on the polished sections prepared for the microscopic analysis.

The settings of the SEM-EDS instrument were: acceleration voltage 20KeV; beam size 0.125μm; tilt angle 20° and measurement time 100sec. The instrument was calibrated between specimens using a cobalt standard. The suite of analysed elements originally included Si, Fe, Ca, Al, Mg, Na, K, Cu, S, Cl and As. The elements Ni, Mn and Ti were added to the list of analysed elements at a later point. Oxygen was calculated stoicheiometrically.

Detection limits values for the SEM-EDS technique given in the literature are at the levels of 0.1 wt-% (Goldstein *et al* 1992: 501). The accuracy and precision of the particular instrument used in this study were evaluated by conducting repeated analyses on (i) test-samples of known composition and (ii) the pelletised slag specimens (see Appendix, Sections A1.1-2). The analytical error was found to be given by the formula:

$$\mathbf{2s = 0.2083 \cdot C^{0.3057} \quad (Eq.\ 4.1)}$$

where s is the standard deviation of repeated analyses and C is the wt-% of the analysed oxide.

According to this formula, the analytical error for measured concentrations above 10 wt-% is less than ±1 wt-% while for concentrations below 0.5 wt-%, the error is in the order of ±0.2 wt-%. Such error levels are satisfactory for the purposes of this study. As for the comparability of the analytical results produced by the two methods (analysis of pelletised specimens and polished sections), this was confirmed by running comparative analyses on 12 slag samples (see Appendix, Section A1.3).

4.7.3 Phase microanalysis

The use of microanalytical techniques, such as SEM-EDS and Electron Probe Microanalysis, in the study of archaeological slags allows the measurement of the chemical composition of individual phases, the most important being residual raw materials, silicate and oxide phases, and metallic inclusions.

The analysis of unfused pieces of copper ore or flux present in the slag enables the characterisation of the raw materials used in the smelting process (Rovira 1999; Shugar 2003). This approach becomes especially important when certain classes of raw materials do not appear in the smelting debris.

The analysis of silicate and oxide phases, such as silicate crystals, glass and spinels is not very common in the study of archaeological slags. However, these phases are the major products of the solidification of the liquid slag and the partitioning of elements between them offers invaluable insights to this process (Hauptmann 1985; Kresten *et al* 1998; Manasse and Mellini 2002). Armed with this knowledge, it is then possible to select the most appropriate phase diagram to describe the slag and make more accurate estimations of its liquidus temperature and its viscosity.

Perhaps the most important use of microanalysis in the study of archaeological slags, however, is the analysis of the metallic inclusions suspended in them. As already mentioned, such inclusions are often the sole evidence available on the product of the smelting process. The chemical analysis of metallic inclusions enables not only the chemical characterisation of the smelting product (e.g. Rovira 1999; Shugar 2003; Zwicker *et al* 1972; 1985) but also the estimation of the thermodynamic profile of the smelting process based on the partitioning of iron between the slag and the metallic phase be that matte, metallic copper or both. The latter approach is based on the premise outlined in Section 3.5, namely that the levels of iron in metallic phases (both matte and metallic copper) increase as the furnace atmosphere becomes increasingly reducing.

In this study, phase microanalysis was conducted on carbon-coated polished slag specimens using the SEM-EDS instrument and the settings described in the previous section. Since most solid phases in the slag exhibit chemical heterogeneity caused by precipitations during and after solidification, the analysis of each phase was conducted on a large area thus obtaining an average composition.

4.7.4 Mössbauer Spectroscopy

As shown in the previous chapter, one of the most important parameters in copper smelting is the furnace atmosphere because its reducing or oxidising capacity determines the nature of the metallic phase. As the oxidation state of iron is very sensitive to changes in the partial pressure of oxygen (pO_2) during copper smelting, it is possible to use the Fe^{2+}/Fe^{3+} ratio for the estimation of the redox conditions in the furnace. This ratio cannot be determined using standard chemical techniques, like Atomic Absorption Spectroscopy or SEM-EDS, because they cannot distinguish the different oxidation states of iron. Among the techniques available for this purpose, wet chemistry (Bachmann 1982: 8; Hauptmann *et al* 2003) and Mössbauer Spectroscopy (Doonan 1996: 58; Moesta *et al* 1989) are the two alternatives commonly used in archaeometallurgical studies. The latter technique was used in this study for the determination of the Fe^{2+}/Fe^{3+} ratio in five slag samples. The analysis was conducted by Dr. Andreas Simopoulos from the Institute of Materials Science of the National Centre of Scientific Analysis 'Demokritos' in Athens.

4.8 Methodology for the analysis of ores

Pieces of unused raw materials are not very commonly discovered at prehistoric copper-smelting sites. When such finds are available, however, their analysis can offer important insights into the smelting process under investigation. Apart from their significance for provenancing purposes, the mineralogical and chemical characterisation of raw materials offers a background against which the technical parameters of the process can be understood and assessed. To be more specific, through the study of ore samples it is possible to examine whether the ore (i) was sulphidic and/or oxidised; (ii) was self-fluxing or required the addition of a flux; and (iii) contained other metals, such as nickel, bismuth, arsenic or antimony (Golden *et al* 2001; Hauptmann 1989, 1996, 2003; Rovira and Gómez Ramos 1998; Shugar 2003; Wagner 1986; Zwicker *et al* 1985).

* Most samples showed few signs of corrosion. When present, corrosion was usually limited to the outer parts of the slag fragments (up to a depth of 1mm) or to areas surrounding major cracks. Among the analysed samples, only sample A16 showed evidence for significant corrosion (see Section 4.11.2).

4.8.1 Optical microscopy and phase microanalysis

Examination of ore samples under the polarising optical microscope allows the identification of translucent and opaque minerals present in an ore sample, based on their optical properties, and also the description of their texture and intergrowth (Picot and Johan 1982). This technique can be supplemented by SEM-EDS microanalysis, which, by determining the chemical composition of individual minerals, can allow their identification whenever this is not possible by optical microscopy alone. Polished sections of the three ore samples were prepared, following the same procedure as in the case of slag (see above), and were examined under the optical microscope and SEM-EDS instrument described in the previous sections.

4.8.2 Chemical analysis

Due to the small size of the ore pieces, it was not possible to prepare pelletised specimens. Instead, the chemical composition of each ore sample was obtained from the average of multiple analyses on areas of the polished section using the SEM-EDS instrument described above. The suit of determined elements was the same as in the case of slag (see previous section).

4.9 Optical microscopy of slag from Chrysokamino

Examination of 46 polished slag specimens from Chrysokamino revealed a range of mineralogical phases, textures and intergrowths. The major phases in most samples were silicate laths and free iron-oxides embedded in a glassy matrix; copper prills and matte inclusions were also frequent while unfused pieces of raw materials were generally rare.* Based on microstructural differences, slag samples can be divided into four groups (MG1-4), two of which (MG-1 and MG-2) comprise 87% of the studied material (**Table 4.2**). The classification of slag samples into groups does not imply the existence of distinct classes of material, as the boundaries between them are anything but clear. Nonetheless, this approach allows a more accurate description of the microstructural diversity witnessed in the material therefore facilitating its study and interpretation.

4.9.1 Group MG-1 (27 samples, 59%)

The microstructure of the largest group in the assemblage is characterised by the presence of abundant wustite and/or magnetite crystals embedded in a siliceous matrix ranging from fully vitrified to extensively crystallised. The predominant metallic phase is copper.

- *Matrix*: The siliceous matrix ranges from fully vitrified to extensively crystallised (**Table 4.3**). When present, silicate crystals usually have a fine dendritic/lathy texture indicative of rapid precipitation from a liquid solution (**Plate 4.10**). Vitrified areas often show red striations probably resulting from fine dispersions of cuprite and metallic copper (Hauptmann *et al* 2003; Shugar 2003).

- *Iron-oxides*: Wustite (FeO) and magnetite (Fe_3O_4) crystals are abundant in all samples, the latter usually being the dominant free oxide (**Table 4.3**). Wustite is always present in dendritic form whereas magnetite crystals are generally present as large skeletons near the centre of the slag fragments changing to numerous aligned dendrites with excessive growth along a single direction near the surface (**Plate 4.11**). This difference is clearly associated with differences in the cooling rate of various areas in the slag cake: closer to the surface, the drop in temperature is steeper and the rapid crystal growth produce fine-armed dendrites whose shape and size is primarily determined by kinetic factors. A notable feature of many slag samples is the presence of thin bands of magnetite present at the interior of the fragment (**Plate 4.12**). In many cases these bands run uninterrupted through the sample but they are more commonly discontinuous. In either case, the microstructure of the slag is different on the two sides of the band.

- *Copper prills*: Copper prills are common in most slag samples in this group. Their diameter ranges from a few microns to 1 mm in some rare cases. Many copper prills contain a second grey phase that, according to SEM-EDS analysis, is the arsenic-rich compound Cu_3As (**Plate 4.13**). Moreover, small matte particles are often embedded in copper prills although this phase is more often present as 'rims' surrounding the metallic prills (**Plate 4.14**).

- *Matte inclusions*: Although common in most slag samples in this group, matte inclusions are significantly fewer than copper prills with which they are often associated (see above). Most matte inclusions have characteristic Widmastätten structure resulting from solid-state precipitations from the sulphide-solution (Doonan 1996: 57; Fulton and Goodner 1909) (**Plate 4.15**). Other precipitates in the matte include metallic copper ('moss copper': Fulton and Goodner 1909) and the grey arsenic-rich phase (compare with Lechtman and Klein 1999: fig.14).

- *Cuprite*: Cuprite (Cu_2O) inclusions are rare in slag samples in this group. When present, cuprite is usually found in clearly corroded areas of the samples suggesting that it is a secondary corrosion product rather than a primary phase formed during the solidification of the slag.

- *Delafossite*: Delafossite ($Cu_2O.Fe_2O_3$), a mineral that is generally associated with moderately reducing conditions in the smelting furnace is rare in this group. It is present in only five samples (A03, A15, A16, A18, A23) in needle-like form (compare with Shugar 2003: fig. 3 and Golden *et al* 2001: fig. 6) (**Plate 4.16**).

- *Unfused materials*: There are very few inclusions in the slag representing raw materials that were not dissolved in the slag during smelting. Small silica grains (<1mm) with signs of severe fragmentation are present but very rare. Only in sample A16 does a small cluster of such grains exist; one of them shows signs of on-going dissolution while another shows fine dispersions of red copper-minerals probably reflecting residual copper-ore (cuprite?). More common, but still rare, are remains of iron-ore present either as minute heavily altered ore-fragments (**Plate 4.17**) or, more often, as agglomerations of iron-oxides that have clearly resulted from the decomposition of larger inclusions (**Plate 4.18**; compare with Hauptmann *et al* 2003: fig.6).

- *Furnace material*: Small fragments of ceramic material are present in four slag samples (A05, A20, A23, B15) probably reflecting the dissolution of refractory materials in the slag (**Plate 4.19**).

4.9.2 Group MG-2 (13 samples, 28%)

This is the second largest group identified in the slag assemblage. The microstructure is characterised by extensive vitrification of the siliceous matrix, limited presence of iron-oxide crystals and common presence of silica grains. The predominant metallic phase is copper.

- *Matrix*: The siliceous matrix is predominantly glassy, with ruby-red striations, although some devitrification, in the form of long chains of 'star-shaped' silicate crystals, can be seen in some of the samples (**Plate 4.20**; compare with Dimou *et al* 2001: fig.6).

- *Silica grains*: Silica grains, up to 2mm in size, are common in many samples in this group (**Table 4.4; Plate 4.21**). They show signs of extensive fragmentation but their boundaries are non-reactive, i.e. there is no indication for on-going dissolution.

- *Iron-oxides*: Free-iron oxides are absent from samples A10, A11, A12, A14, A26 and B11. In the remaining samples, wustite and mainly magnetite are present as concentrations of very fine dendrites and skeletons in various areas within each sample (**Table 4.4**). The overall microstructure of these areas approximates that of the glassy examples of group MG-1 (**Plate 4.22**).

- *Metallic inclusions*: Same as those in group MG-1.

- *Cuprite*: Fine dispersions of cuprite, together with metallic copper, are probably responsible for the ruby-red striations present inside the glassy matrix (Hauptmann *et al* 2003; Shugar 2003).

4.9.3 Group MG-3 (3 samples, 6.5%)

This small group is similar to MG-2 except for the fact that it contains large areas with lath-like silicate crystals **(Plate 4.23)**.

- *Matrix*: Long silicate laths of random orientation are embedded in a vitreous matrix that is identical to that of group MG-2.

- *Iron-oxides*: Very fine iron-oxide crystals are found concentrated in small areas in each sample.

- *Metallic inclusions*: Same as those in group MG-1 except for the fact that they are generally rarer.

- *Cuprite*: Fine dispersions of cuprite, together with metallic copper, are probably responsible for the ruby-red striations present inside the glassy matrix.

4.9.4 Group MG-4 (3 samples, 6.5%)

The microstructure of this small group is characterised by extensive crystallisation of the siliceous matrix and the presence of very fine iron-oxide crystals filling the interstices between the silicates **(Plate 4.24)**. The predominant metallic phase is copper though metal prills are rare. Unfused raw materials are absent.

- *Matrix*: The siliceous matrix is fully crystallised. Silicate crystals have a lath-like texture.

- *Iron-oxides*: Very fine iron-oxide crystals occupy the interstices between the silicate laths. Due to the minute size of the crystals, distinction between wustite and magnetite is not possible. Both dendrites and skeletons are present.

- *Metallic inclusions*: Same as those in group MG-1 except for the fact that they are generally rarer.

4.10 Chemical analysis of slag from Chrysokamino

The bulk chemical composition of slag samples from Chrysokamino, as determined by SEM-EDS analysis, is given in **Tables 4.5-6**. According to the analytical results, the samples belong to the system Al_2O_3-CaO-FeO_x-SiO_2 (alumina - lime - iron-oxide - silica), most forming a relatively tight cluster on the pseudo-ternary diagram (SiO_2 + Al_2O_3)-CaO-FeO (**Figure 4.5**). Four samples (from group MG-2) containing frequent unfused quartz grains are characterised by higher levels of SiO_2. All slag samples contain small quantities of MgO, MnO, alkalis and low levels of copper (1.1% CuO or 0.9% Cu on average).

In comparison to most early slags in the Aegean (see Section 5.3.2) and other areas in the Old World, slag samples from Chrysokamino show significantly higher levels of lime. To be more specific, the levels of lime in prehistoric copper smelting slags are typically below 10-12% (e.g. Bachmann 1982; Doonan 1996: Table 3.2; Hauptmann *et al* 1988; Merkel and Rothenberg 1999). In the case of Chrysokamino, however, the levels of lime are much higher; the average lime content *in the main cluster* of samples is 18%. Although care was taken to ensure that the analysed specimens were collected from clean areas of each slag fragment, there is a question of whether the high levels of lime reflect contamination by the calcareous epigenetic material which, as described above, has penetrated the fragments through open pores and cracks.

*Due to the same limitation, it was also not possible to conduct *multiple* microanalyses on all analysed samples. It should be noted, however, that whenever multiple analyses were conducted on a single sample, phases of the same type showed little variability in their composition (the sole exception being the arsenic content of metallic phases; see below).

There are two arguments suggesting that the high lime levels have not resulted from post-depositional contamination of the samples. Firstly, similar levels of lime were obtained from the SEM-EDS analysis of polished sections of slag samples (Section A1.3). In these analyses, however, there is no question of contamination because the scanned areas were carefully selected so as to be free of pores and cracks where the epigenetic material could have penetrated. Secondly, phase microanalysis showed that all siliceous phases in the slag samples are rich in lime (see below) as would be expected from the solidification of a lime-rich slag. It follows that the chemical composition of the slag samples, as determined by SEM-EDS analysis, has not been affected (or, at least, not significantly affected) by contamination from epigenetic calcareous materials. The high levels of lime present in the slag from Chrysokamino are, therefore, an indication of an uncommon technological choice made in the smelting process that needs to be investigated.

4.11 Phase microanalysis of slag

Based on optical microscopy, the slag samples from Chrysokamino were divided into four groups characterised by different mineralogical and general microstructural characteristics (Section 4.9). Groups MG-3 and MG-4, each comprising less than 7% of the assemblage, contain the same types of metallic inclusions as those found in the two major groups (MG-1 and 2) differing only in the abundance and texture of the oxide and siliceous phases formed during solidification. In other words, the two groups form a small minority in the assemblage and do not demonstrate any feature that could suggest that they represent a distinct metallurgical process (see Section 4.14 for a more detailed discussion). Therefore, as there was a limitation to the number of microanalyses and Mössbauer analyses that could be conducted in this study, it was decided to concentrate on the two major groups, which were more representative of the material from Chrysokamino.*The chemical composition of silicate crystals, glass phases, copper prills and matte inclusions in slag samples from groups MG-1 and MG-2 was measured by SEM-EDS. The results are presented in **Tables 4.7-12.**

4.11.1 Silicate crystals and glass

The chemical composition of silicate crystals in the analysed slag samples (**Table 4.7**) corresponds to the groups of pyroxenes and olivines, most samples approximating the composition of the compounds hedenbergite and $CaO.FeO.SiO_2$ olivine. As shown in **Figure 4.6**, the chemical composition of the crystals deviates from those predicted by the system $CaO\text{-}FeO\text{-}SiO_2$. There are two reasons for this deviation. Firstly, this phase diagram does not take into consideration the presence of alumina, which can enter the silicate crystals in considerable amounts, especially in the case of pyroxenes (see Hauptmann 1985: Table 8). Secondly, the overall texture of the silicate crystals suggests that they were formed rapidly (see previous section) so deviations from equilibrium compositions should be expected.

A similar picture is drawn by the chemical analysis of the glassy areas in slag samples from Chrysokamino (**Table 4.8**; **Figure 4.6**). The composition of most glass phases forms, as expected, a tight cluster at the centre of the $CaO\text{-}FeO\text{-}SiO_2$ diagram between the crystallisation lines of the pyroxenes and olivines. That the composition of the silicate crystals shows displacement from the crystallisation lines towards the composition of the glass is indicative of rapid solidification of the liquid slag, which did not allow the partitioning of the various oxides into phases as dictated by the equilibrium, resulting instead to the formation of phases with 'intermediate' non-equilibrium compositions.

4.11.2 Copper prills

Copper prills embedded in slag samples from Chrysokamino belong to the quaternary alloy-system Cu-Fe-As-Ni (copper-iron-arsenic-nickel) (**Tables 4.9-10; Figure 4.7**). Sulphur is present at very low levels. Elements like cobalt, antimony and bismuth were not detected by the SEM-EDS instrument.

- *Iron*: The iron content in the prills ranges from 1 to 3.6% (**Table 4.10**). These levels are too low to result in massive precipitation of γ-iron in the prills (Roeder *et al* 1984) and, indeed, no such feature was observed under the optical and the electron microscope. The only exception is a large prill (d=*ca* 1mm) present in sample A18 containing massive α-iron dendrites and sulphidic inclusions embedded in a copper matrix. The composition of this prill was found by EDS analysis to be 69.7% Fe, 23.7% Cu, 3.9% As and 0.8% S (not included in **Table 4.9**).

- *Arsenic*: The prills in all analysed samples contain arsenic thus confirming the preliminary analyses reported by the Oxford group (Stos-Gale 1993). Exceptions are the analysed prills from sample A16, which appear to be arsenic-free. These results, however, are misleading because in the same sample, there are large corroded prills (on which no quantitative analysis was conducted due to their corrosion), showing massive precipitation of the grey arsenic-rich phase (Cu_3As) indicative of high levels of arsenic. As the results from the analysis of this sample may have been influenced by weathering/corrosion processes, they have been excluded from subsequent discussions. In the remaining slag samples, the level of arsenic in the prills ranges from 1.5 to more than 20% in rare cases (**Table 4.10**). The limit of solid solubility of arsenic in copper (which is ca. 8%; Northover 1989) was, therefore, often exceeded resulting in the precipitation of the grey arsenic-rich phase (Cu_3As) commonly observed in prills under the optical microscope (see above).

- *Nickel*: The prills in all analysed samples (except for sample A16) contain nickel usually at levels below 2% (**Table 4.10**).

4.11.3 Matte inclusions

Matte inclusions in the analysed slag samples show very high copper grades, approximating the composition of 'white metal' Cu_2S (**Tables 4.11-12**). The iron content rarely exceeds the 6-7% (on average) whereas nickel and arsenic are present at very low levels (<2%). Closer examination of the analytical results shows that the measured copper contents of the matte inclusions are slightly higher than those predicted by the phase diagram of the ternary system Cu-Fe-S (**Figure 4.8**).

There are two reasons for this deviation. Firstly the phase diagram in **Figure 4.8** does not include nickel and arsenic which are present in the analysed matte inclusions. A more important reason, however, is that matte compositions were measured using area-scan analysis (instead of point analysis). Consequently, precipitated and mechanically entrapped copper-rich phases, which are common in the matte inclusions (see Section 4.9.1), were often incorporated in the analysis thus increasing the measured copper content. It should be noted, however that regardless of their exact source, deviations from the theoretical values are small and can, therefore, be excluded from consideration during the interpretation of the analytical results.

4.12 Mössbauer spectroscopy of slag

The results of the Mössbauer analysis are given in **Table 4.13**. Four iron-bearing phases were identified in the samples:

- Silicate crystals of the **pyroxene** series. This phase contains only ferrous cations.
- A **ferrous phase** whose mineralogy was not determined.
- An **intermediate phase** whose mineralogy was not determined. This phase contains ferrous and ferric cations in a 1:1 ratio.
- The iron-oxide **magnetite** which contains ferrous and ferric cations in a 1:2 ratio.

The Fe^{2+}/Fe^{3+} ratio was calculated from the relative proportions of these phases in the analysed samples (**Table 4.13**). As shown in the table, iron is present in the slag samples mainly in its ferrous (divalent) state, the Fe^{2+}/Fe^{3+} ranging from 5 to 19.

4.13 Microscopic and chemical analysis of ores

4.13.1 Copper ores

Three fragments of copper-ore were available for laboratory analysis. Macroscopic examination showed that they consisted of oxidised minerals of copper and iron adhering to siliceous rocks. Examination of polished specimens under the polarising microscope and the SEM allowed the identification of the following mineralogical phases:

- *ORE-1* (**Plate 4.25**): The predominant copper mineral is malachite with a small amount of azurite. The gangue consists mainly of quartz and other siliceous minerals. Iron-hydroxides are also present but at much lower levels. Inside the oxidised matrix there are small inclusions of sulphidic minerals which were identified with the aid of SEM-EDS microanalysis. Pyrite (FeS_2) is the predominant sulphide, occasionally containing small quantities of barium (baryte?). Covellite (CuS), chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) are also present. The mineralogy and texture of those inclusions is characteristic of residual hypogene sulphides that survived the weathering process in the oxidation zone of a copper deposit.

- *ORE-2* (**Plate 4.26**): This sample is similar, both mineralogically and texturally, to ORE-1. However, it does not contain residual sulphidic inclusions.

- *ORE-3* (**Plate 4.27**): This sample consists of a flake of malachite, with some orange-brown iron 'staining', adhering to a piece of quartz. No other minerals are visible under the microscope.

The chemical composition of the three samples was measured by SEM-EDS analysis (**Tables 4.14-15**). In the case of sample ORE-3, which consisted of a very fine flake of malachite adhering to a quartz fragment, two separate analyses were conducted, one for the copper-mineral and one for the gangue. The generally low levels of sulphur in all three samples reflect the predominance of oxidised minerals. In the case of ORE-1, however, the small presence of residual sulphides raises the sulphur content to 1.5%. Quartz is by far the predominant oxide in the gangue followed by iron oxides and alumina while the levels of lime are extremely low. Due to the limitations of SEM-EDS, no attempt was made to measure all minor and trace elements present in the copper ores. However, nickel and arsenic were measured because they were also present in copper prills embedded in the slag samples (see Section 4.9); both were below 0.2% in all three ore-samples.

4.13.2 Iron ore

Among the various 'uncommon slag samples' collected for laboratory analysis was a piece of *iron-ore*. The piece was about 3 to 4cm in size and consisted of yellow-orange iron hydroxides (**Plate 4.28**). Microscopic examination showed that the dominant iron mineral in the ore is goethite, demonstrating characteristic botryoidal texture in cross-polarised light, locally altered to limonite (**Plate 4.29**). An interesting feature is the presence of numerous small rhomboid crystals of calcite (ca. 100-300 μm in size) dispersed throughout the iron matrix. The bulk chemical composition of the iron-ore was obtained by SEM-EDS analysis (**Tables 4.14-15**). The presence of the calcite crystals raises the CaO level to *ca.* 23%; in contrast, the ore contains only 5% SiO_2. Copper, arsenic and nickel are present at very low levels.

4.14 The significance of the classification of slag samples

Examination of the chemical composition of the four slag-groups, as defined by optical microscopy, shows a very strong correlation between chemical composition and microstructure. To be more specific, most samples of group MG-1 form the main cluster on the pseudo-ternary diagram (SiO_2 + Al_2O_3)-CaO-FeO, those of groups MG-3 and MG-4 form a distinct cluster characterised by lower levels of FeO whereas samples of group MG-2 form a more dispersed cluster partly overlapping with the clusters of the other three groups (**Figure 4.9**). How should this pattern be interpreted?

To answer this question it is necessary to consider the criteria according to which slag samples were divided into these four groups. In the absence of any variability in the nature of metallic phases (i.e. copper and matte inclusions) in the samples, classification was based on the major phases present in the slag, namely *silicate crystals*, *glass* and *free iron-oxides*. These phases are the main products from the solidification of the silicate melt (i.e. the liquid slag) and their relative proportions are largely determined by its chemical composition (i.e. the major oxides). That the four groups have distinct chemical compositions is a reflection of this generic relation. To be more specific:

- The higher levels of FeO in the samples of group MG-1 have led to the formation of frequent free iron-oxide inclusions. Such inclusions are rare to absent in other groups due to their low FeO content. In contrast, due to their low FeO contents and their compositional 'proximity' to the pyroxene crystallisation line, samples in groups MG-3 and MG-4 are mainly composed by wollastonite crystals ($CaO.SiO_2$). Moreover, group MG-3 is richer in silica than MG-4 and, therefore, shows a higher degree of vitrification.

- Turning to group MG-2, four samples contain frequent unfused silica grains so their composition is characterised by very high levels of SiO_2 (see **Figure 4.5**).

As shown in **Figure 4.10**, the composition of the remaining samples in group MG-2 fall very close to the composition of the glassy areas of group MG-1. It follows that the samples in group MG-2 are simply larger examples of the glassy areas also present in the samples from the predominant group MG-1. As for their formation, this should be probably attributed to the rapid solidification of the slag resulting in heterogeneous microstructures within the cake.

The evidence argues against the presence of different types of slag associated with different metallurgical processes, such as smelting and refining/casting, taking place at Chrysokamino. If the four groups did represent distinct processes, then they should also contain different types of metallic inclusions but this is clearly not the case. What we witness instead is a chemical and microstructural variability that probably reflects the different microenvironments existing (i) in the furnace during smelting and (ii) within the slag during solidification, be that inside or outside the furnace (Schmidt 1997: 131-4). Depending on its exact position in the furnace, a slag 'pocket' interacted differently with the furnace material, the tuyères, the fuel, the metal ingot and the furnace gases. And since the smelting process ran in non-equilibrium conditions, such differences could not be leveled-out entirely. Instead they remained localised, becoming imprinted on an inhomogeneous slag cake.

Group MG-1 comprises no less than 59% of the slag assemblage so its chemical composition and microstructure describe the largest part of the slag cake. As for the samples of the second largest group (MG-2), these reflect large areas in the slag cake, which became highly vitrified. Turning to the samples in the much smaller groups MG-3 and MG-4, these are richer in lime and poorer in iron-oxide and should probably be interpreted either as those parts of the slag cake which were in close contact with the furnace material or, more probably, as the slagged furnace material itself. Indeed, samples with similar compositions have often been encountered in archaeological smelting sites, always representing a small part of the assemblage (e.g. Bachmann 1980; Merkel 1990: note 15; Rothenberg 1990).

To conclude, the chemical and mineralogical variability of the slag assemblage from Chrysokamino should not be overemphasised. There can be little doubt that there was a single process at work at the site and most samples suggest that the slag was fairly homogeneous. Groups MG-1 and MG-2 should be regarded as typical for the site whereas groups MG-3 and MG-4 are very small and probably reflect a *localised* material input from the furnace material to the peripheral parts of the slag cake.

4.15 Investigation of the raw materials used in the smelting process

Investigating the mass balance of a smelting process is a powerful means to visualise the nature and relative quantities of materials going in and out of the furnace. The approach followed here, is based on the simple premise that all elements present at the output (i.e. in the slag and metallic phases) of the process must be accounted for by materials present at the input (raw materials). Through the comparison of copper-ores, slag and metallic inclusions, it is therefore possible either to confirm their chemical similarity or to postulate the existence of additional raw materials that for some reason do not appear in the archaeological record.

4.15.1 Comparison between copper-ores and slag

As shown in Section 4.13.1, the gangue minerals of the three copper-ore samples included in this study are predominantly siliceous. Although not subjected to laboratory analyses, most of the 27 pieces of copper-ore from the site were found in macroscopic examination to comply with this mineralogical pattern (Section 4.4.4). Copper ores with highly siliceous gangue minerals were rarely smelted in antiquity without the use of an appropriate flux, which was usually an iron or manganese ore (Craddock 1999; Tylecote 1987: 108).

Indeed, in comparison to the copper-ores, slag samples from Chrysokamino contain significantly higher levels of iron and (interestingly) lime, falling into the area of low liquidus temperatures in the SiO_2-CaO-FeO system (**Figure 4.11**). This compositional displacement towards lower liquidus temperatures is by itself a very strong indication for the use of a flux in the process. Does this mean, however, that the increased levels of both FeO *and* CaO in the slag should be attributed to an additional raw material (i.e. a flux) used in the smelting process?

As far as FeO is concerned, this is almost certainly the case because there are no alternative sources that could have introduced this oxide into the slag. In the case of lime, however, things are more complex. To be more specific, analytical and experimental studies of early copper smelting have shown that substantial amounts of lime can be introduced to the slag from fuel ash and eroded furnace material (Merkel 1990; Merkel and Rothenberg 1999; Shugar 2003; Tylecote *et al* 1977). Merkel and Rothenberg (1999: 163), in particular, emphasise the possibility that high calcium levels in prehistoric slag may represent the use of too much fuel (resulting in excess fuel ash) by "less experienced workers" in their attempt to smelt copper. These questions are particularly relevant to the case of Chrysokamino. Although the contribution of fuel ash cannot be estimated, there is direct evidence for the contribution to the composition of the slag by eroded furnace material. Not only have pieces of refractory material been identified microscopically in some slag samples (Section 4.9.1), the presence of *ca.* 7% alumina in the slag samples from this site also suggests that slag has dissolved an appreciable amount of furnace wall or lining (Section 4.10).

However, although these two sources have certainly influenced the chemical composition of the slag, they do not themselves suffice to account for its high lime levels. To be more specific, it is generally accepted that fuel ash and eroded furnace material could have contributed no more than 6-8% of CaO in the bulk composition (Merkel 1990; Merkel and Rothenberg 1999; Shugar 2003; Tylecote *et al* 1977). This is not to suggest that some parts of the slag cake, especially those located near the slag/furnace interface, could not have taken up higher amounts of lime. After all, in the previous section it was proposed that the lime-rich slag groups MG-3 and MG-4 may reflect this exact phenomenon. What is argued here, however, is that the fuel ash and the furnace erosion cannot by themselves account for more than 6-8% of lime in the *bulk composition* of the *main body* of the slag cake, and this is substantially lower than the mean lime content in the major slag group MG-1, which is 18%. In other words, not only iron-oxide but also lime appear to have been introduced in the slag by an additional raw material(s) that was used to flux the highly siliceous copper-ores smelted at Chrysokamino.

This does not mean that Sargent (in Branigan 1968: 50) was right to suggest that limestone fluxing was employed at Chrysokamino. As already mentioned, this practice has been associated with the introduction of the blast furnace (i.e. very high furnace temperatures) in iron-smelting during Medieval times but has never been suggested for a prehistoric process, let alone one that dates to the 3rd millennium BC! More importantly, however, Sargent's hypothesis cannot account for the increase in *both* the FeO and CaO levels in the slag.

A more plausible interpretation may be offered by the piece of iron-ore found at the site. As described in Section 4.13.2, the predominant minerals in the ore are the iron hydroxides goethite and limonite but the ore also contains small crystals of calcite raising its CaO content to 23%. Mineralogically, therefore, the iron ore is different from the copper ores found at the site. Considering also that it contains no traces of copper, it follows that the iron-ore fragment does not represent a gangue mineral discarded during some process of *in situ* beneficiation but rather a material that was *separately* introduced to the metallurgical assemblage. There is, therefore, a strong possibility that the iron ore was used as a flux in the smelting process.

Indeed, the use of this material as a fluxing agent could explain the uncommon chemical composition of the slag from Chrysokamino. **Figure 4.12** shows the position of the copper ores, the iron ore and the slag samples on the SiO_2-CaO-FeO ternary diagram while the theoretical 'mixing line' represents the slag compositions deriving from the use of the iron-ore as flux in the smelting process. As seen in the diagram, due to the substantial amount of calcite in the iron-ore, its use as a flux would have resulted in the formation of a slag with uncommonly high levels of lime. So, if the contribution of lime by the fuel ash and the furnace material (6-8%) is also taken into account, the amount of lime in the slag samples from Chrysokamino can be accounted for by the raw materials used in the process.

As also discussed in the following chapter (Section 5.3.2), Chrysokamino is the only known case in southern Aegean where such a calc-ferrous flux was used in copper smelting, a fact indicated by the much lower levels of lime in slag samples from other sites in this region. Was there any particular reason for the smelters at Chrysokamino to use this uncommon fluxing material? The answer may be provided by the weak iron mineralisation associated with calcite that has been discovered near the metallurgical remains and similar iron occurrences, which are present throughout this area, hosted in the Plattenkalk/phyllite contacts (Section 4.2). Although no detailed geological and mineralogical study of these iron occurrences has yet been conducted, examination of two representative geological samples (one from the vicinity of Chrysokamino and another from the nearby island of Pseira) under the polarising microscope has revealed a notable mineralogical similarity to the iron-ore fragment found at the smelting site **(Plate 4.30)**. If these iron occurrences are indeed the source of the calc-ferrous flux, the distinctive chemical composition of the slag from Chrysokamino reflects the use of local materials in the smelting process.

*(i.e. maximum possible levels of arsenic and nickel in the smelted copper if losses due to volatilisation or dissolution into the slag are disregarded).

4.15.2 Comparison between copper-ores and metallic inclusions

In the previous section, focus was on the major oxides in the slag, such as lime, silica, iron-oxide and alumina, which have derived from the gangue minerals of the ore, the fluxes, the refractories and the fuel. This section focuses, instead, on elements that entered the metallic phases during smelting, namely arsenic, nickel and iron (see Sections 4.11.2-3). The presence of iron in copper is to be expected when a ferrous slag is used and its levels are determined by the temperature and, more importantly, the redox conditions in the furnace (Craddock and Meeks 1987; Craddock 1999; Merkel 1990; Merkel and Rothenberg 1999; Shugar 2003). The source of arsenic and nickel, however, must be established and the first place to look at is the copper ore itself.

It is thus interesting to note that these elements are present at very low levels in the three analysed copper-ore samples. **Figure 4.13** compares the levels of arsenic and nickel in the copper prills suspended in the slag with those that would have derived if all arsenic, nickel and copper present in the three copper-ore samples were reduced to metal.* It is clear from this diagram that the levels of arsenic in the prills, in particular, are higher by one to two orders of magnitude. Evidently, more conclusive results will derive from the analysis of more copper-ore fragments from Chrysokamino using more sensitive techniques than the SEM-EDS available for this study. On present evidence, however, it is argued that arsenic and probably nickel have not derived from the copper ores smelted at Chrysokamino but from another material that was *added* to the smelting charge in order to produce arsenical copper.

The use of an additional ingredient in the smelting process is also supported by the results of lead isotope analysis of slag samples from the site which, as already mentioned, suggest that ores from various copper deposits were smelted at Chrysokamino (Stos-Gale 1998; Stos-Gale and Gale in press). It follows that, unless all these deposits were characterised by very similar arsenic/copper and nickel/copper ratios, the two elements were introduced to the smelting furnace separately from the copper ores.

It is not possible at present to identify the arsenic-bearing mineral that might have been used at Chrysokamino. Experimental studies have shown that various minerals (e.g. arsenides, arsenates or sulpharsenides) can be co-smelted with copper ores to produce copper-arsenic alloys (Lechtman and Klein 1999; Merkel *et al* 1994; Rostoker and Dvorak 1991). That such minerals were recognised and used by early Aegean metallurgists has been recently established by Doonan *et al* (in press) who have made a convincing case for the addition of roasted iron-arsenides in melted copper at the EM I-II site of Poros Katsambas near Knossos (see Section 5.4). Therefore, as nickel is common in arsenides and sulpharsenides, the use of such a mineral in the smelting process at Chrysokamino could be envisaged. This is particularly so, in the light of the evidence from the Middle Bronze Age levels of the site Nichoria in Messenia, which suggest the addition of an iron-nickel arsenide to melted copper to produce arsenical copper (Cooke and Nielson 1978).

4.15.3 Conclusions

Based on comparisons between the copper ores, the slag and the metallic inclusions from Chrysokamino, the following conclusions were reached regarding the raw materials used in the smelting process:

1. To flux the highly siliceous copper ores, a (probably local) iron ore with appreciable amounts of calcite was added to the smelting charge.

2. Some lime was also introduced into the slag by the fuel ash and eroded furnace material. The latter is probably the source of the *ca.* 7% alumina that is also present in the slag.

3. An arsenical mineral, probably containing some nickel, was used to promote the production of arsenical copper. The mineral cannot yet be identified but, based on the evidence from other sites in the Aegean, it may have been a nickeliferous arsenide or a sulpharsenide.

4.16 Estimation of the furnace temperature during smelting

The standard method for the estimation of the operating temperature of ancient smelting furnaces involves the calculation of the liquidus temperature of the slag from the corresponding phase diagram. For this purpose, Bachmann (1980) has proposed a procedure that allows the selection of the most appropriate sub-system in the Al_2O_3-CaO-FeO-SiO_2 system based on the relative abundances of the various oxides present in the slag.

Although this is a useful approach, it should not be employed uncritically in the study of early copper-smelting processes. First of all, as Bachmann himself argues (1980: 110), it is necessary to examine whether unfused materials (very common in prehistoric slags) are present in the slag samples because their inclusion in the calculation of the liquidus temperature will result in overestimated smelting temperatures. Secondly, in the moderately reducing conditions characterising early copper-smelting practices, the first phase to precipitate from the liquid slag (thus determining the liquidus temperature) is very often *magnetite*. This compound, however, is not always included in the ternary diagrams employed in archaeometallurgical studies (Hauptmann *et al* 1989). This is because modern phase diagrams usually describe slag systems at iron saturation and therefore under strongly reducing conditions ($pO_2 = 10^{-11}$-10^{-12} atm). Under such conditions, however, iron is present in the slag in its ferrous state and no magnetite is precipitated. Moreover, a recent study of the liquidus temperature of Al_2O_3-MgO-CaO-FeO-Fe_2O_3-SiO_2 slags by Kongoli and Yazawa (2001) has shown that the effects of common oxides (e.g. Al_2O_3, MgO or CaO) on the liquidus temperature of the slag may be different under reducing and oxidising conditions.

The use of phase diagrams for the determination of the liquidus temperature is applicable in the case of the slag from Chrysokamino because unfused materials are very rare suggesting that the slag was fully liquefied during smelting (Section 4.6.3). Only four samples, all belonging to group MG-2, contain frequent pieces of free silica and these were not included in this procedure.

The phase diagram selected for the estimation of the liquidus temperature, contains the major oxides present in the slag from Chrysokamino, namely CaO, FeO and SiO_2, as well as 7% wt Al_2O_3, which is in agreement with the mean concentration of this oxide in the analysed samples (Section 4.10). Moreover, the phase diagram corresponds to moderate reducing conditions ($pO_2 = 10^{-8}$ atm) therefore taking into consideration the precipitation of magnetite, which is a common phase in most examined slag samples. In fact, most solid phases predicted by this diagram are in agreement with the mineralogy of the slag samples, as derived from the microscopic analysis, therefore confirming this selection.

As seen in **Figure 4.14**, all samples fall in the areas of magnetite and pyroxene (wollastonite) saturation. The liquidus temperature of most samples ranges from 1150 to 1230°C. The small cluster, which falls well inside the pyroxene (wollastonite) saturation area and corresponds to higher liquidus temperatures, should probably be disregarded. Most samples in this cluster belong to the groups MG-3 and MG-4, which, as noted in Section 4.14, may correspond to slagged furnace lining thus giving misleadingly high results.

The calculated liquidus temperature (1150 to 1230°C) reflects the *minimum* temperature necessary to fully liquefy the slag. However, the evidence suggests that the furnaces at Chrysokamino operated at higher temperatures. Firstly, the texture of the slag samples (rarity of unfused materials, fair homogeneity) indicate that the slag was perfectly liquefied during smelting. Secondly, the low levels of copper (*ca.* 1%) in them indicate that the viscosity of the slag was sufficiently low to allow a very good slag/metal separation (see also Section 4.19). It follows that the maximum furnace temperature, in the combustion zone at the level of the tuyères, was at least 50-100°C above the liquidus temperature, in other words, about 1300°C.

4.17 Estimation of the redox conditions in the furnace

The study of the redox conditions (i.e. the oxygen potential pO_2) during smelting is usually based on the investigation of elements exhibiting multiple valency states in typical copper-smelting conditions, the most important being copper and iron

(Craddock 1999; Hauptmann *et al* 1989; Shugar 2003). Copper phases associated with moderately reducing conditions ($pO_2 = ca.\ 10^{-5}$ atm at 1300°C), such as cuprite ($Cu^{2+}{}_2O$) and delafossite ($Cu^{2+}{}_2O.Fe^{3+}{}_2O_3$), are rare in slags from Chrysokamino (see Section 4.9) suggesting that the furnace conditions were more reducing. At more reducing conditions, estimations of the partial pressure of oxygen at a given temperature can be deduced from the relative abundance of ferrous and ferric cations in the slag taking into consideration the effects on their activities by other oxide components (Turkdogan 1983: 237). Of particular importance in the slag from Chrysokamino are the oxides SiO_2 and CaO because the former tends to stabilise the divalent iron while the latter tends to stabilise the trivalent (Timucin and Morris 1970). The quantification of these effects in the calculation of the pO_2 from the Fe^{2+}/Fe^{3+} ratio is a very complex procedure that can be conducted using either thermodynamic software packages (e.g. Doonan 1996: 60) or appropriate phase diagrams (e.g. Moesta *et al* 1989). In this study, the estimation of the redox conditions was based on phase diagrams available in the literature.

The relative abundance of ferrous to ferric cations in five slag samples was measured using Mössbauer spectrocopy (Section 4.12). By plotting the data on a phase diagram (with pO_2-isobars) from the work of Timucin and Morris (1970: fig.5), a range of $\log pO_2$ (atm) values from -8.2 to -10.7 is obtained (**Table 4.16**; **Figure 4.15**). This phase diagram, however, corresponds to a silica content of 30% and a temperature of 1450°C. The derived pO_2 values have, therefore, to be corrected in order to correspond to the true silica contents of the slag samples and to the estimated furnace temperature of 1300°C.

The effect of the silica content was estimated by extrapolation from data from the same work (Timucin and Morris 1970: fig.12) and the following correction was employed: each calculated $\log pO_2$ (atm) value was raised by 1.5 unit for every 10% silica above the level of 30%. Unfortunately, there was not sufficient data in the literature to estimate the effects of temperature on the Fe^{2+}/Fe^{3+} in the CaO-FeO-Fe_2O_3-SiO_2 slag system at a given pO_2 so corrections were based on data from the work of Altman and Kellog (1972) on the slag system FeO-Fe_2O_3-SiO_2. Based on this data, the $\log pO_2$ (atm) values calcuated for T=1450°C were lowered by 1.7 units to correspond to a temperature of 1300°C. The corrected values suggest a pO_2 range from *ca.* $10^{-7.8}$ to $10^{-9.8}$atm at 1300°C (**Table 4.16**) although, given the errors introduced during the various corrections, this may actually be anything between 10^{-7} to 10^{-10} atm.

Similar pO_2 values can be deduced from a consideration of the copper-content in the matte which, excluding the precipitated phases (see section on matte analysis), ranges from 70-75 to almost 80% (Section 4.11.4) (Sridhar *et al* 1997: fig.5; Yazawa 1980: fig.2). Finally, the iron content in copper prills, with an average value of 2.2% (Section 4.11.2), is also compatible with such intermediate redox conditions (e.g. compare with Merkel 1990 and Shugar 2003).

It should be emphasised that the calculated pO_2 values correspond to the area at the bottom of the furnace where the liquid slag was collected. Further up the furnace, the combined action of the pot-bellows and the strong winds, penetrating through the numerous perforations on the ceramic shaft, would have created extremely complex and variable conditions during the smelting process. Although the complete pO_2/temperature profile in the perforated furnaces at Chrysokamino can only be investigated through experimental work, it is safe to assume that in contrast to a typical shaft furnace, the presence of perforations subjected the descending charge to more oxidising conditions (**Figure 4.16**). Closer to the bottom of the furnace, the atmosphere was more reducing (except, of course, for the area just in front of the tuyères) promoting the formation of metallic copper and a slag with the high Fe^{2+}/Fe^{3+} ratios measured by the Mössbauer analysis.

4.18 Thermodynamic profile of the smelting process

Having estimated the temperature and oxygen potential in the furnace, it is now possible to investigate the thermodynamic profile of the smelting process. To deal with the complexity of the $pO2$/temperature conditions in the perforated furnaces used at Chrysokamino, however, a simplification is deemed necessary. Following the approach used for the study of modern shaft furnaces (e.g. Peacey and Davenport 1979: 76ff), the perforated furnace is divided here into two parts (see **Figure 4.16**). These include the *upper* segment, characterised by low temperatures and fairly oxidising conditions, and the *lower* segment (near the level of the tuyères), characterised by high temperatures and more reducing conditions. Although the boundaries of the two segments are anything but clear, this conceptual division allows the visualisation of the chemical and physical transformations that the raw materials underwent as they descended inside the shaft.

According to the analysis presented above (Section 4.15), the raw materials used in the smelting process included copper hydroxy-carbonates (with a small amount of residual sulphides), siliceous gangue minerals, a lime-rich ferrous flux and a nickeliferous arsenical mineral. Moreover, although no direct evidence has been found at the site, charcoal was probably mixed with the charge to act as fuel. The amount of sulphur in the charge is also uncertain. If this element was mainly introduced in the charge by the residual sulphides present in the copper-ores then (according to the analysis of the three ore samples) its amount would have been minimal. If, however, the arsenical mineral added to the charge was a sulpharsenide or a sulpharsenate then more sulphur would have been introduced to the process although, in any case, the oxidised components in the charge would have been predominant.

4.18.1 Reactions in the low-T / high-pO_2 zone of the furnace

The conditions in these parts of the furnace would have had no significant effect on the copper carbonates or the iron hydroxides (apart from their calcination due to the increasing temperature; Bachmann 1982: 21) but would have burnt-off much of the sulphur present in the charge and removed much of the arsenic as As_2O_3 (cf. Lechtman and Klein 1999: 510). This is a very important point not only because As_2O_3 is a poisonous gas making its emission dangerous for the smelters (Lechtman and Klein 1999) but also because the uncontrollable volatilisation allowed them limited control over the amount of arsenic actually entering the copper as indicated by the fluctuating arsenic content in the copper prills (Section 4.11.2).

4.18.2 Reactions in the high-T / low-pO_2 zone of the furnace

Closer to the combustion zone in the furnace, the temperature was sufficiently high to ensure fusion of the gangue minerals with the flux forming a fluid slag as indicated by the homogeneity of all slag samples and the rarity of unfused or semi-fused raw materials in them. The temperature necessary to liquefy most slag samples from Chrysokamino was calculated to 1150-1230°C (Section 4.16) but a temperature of about 1300°C would have been necessary to produce a sufficiently fluid slag.

The atmosphere at the lower parts of the furnace was also more reducing (except, of course, for the area just in front of the tuyères) promoting the reduction of copper-oxides to metallic copper. Indeed, both the mineralogy of the slag (rarity of cuprite and delafossite, common presence of wustite) and the high Fe^{2+}/Fe^{3+} ratios measured by Mössbauer spectroscopy point to fairly reducing conditions, the partial pressure of oxygen (pO_2) ranging from $10^{-7.8}$ to $10^{-9.8}$atm (Section 4.17). The reducing atmosphere and the presence of a cover of slag then allowed the remaining arsenic to be collected, together with most nickel and some iron, into the formed copper. As for any sulphides that had survived the oxidising conditions at the upper parts of the furnace, they formed a matte phase that progressively became copper-rich due to the tendency of iron-sulphides to react with copper oxides (see Section 3.7; *contra* Craddock *et al* 2003; *contra* Hauptmann *et al* 1988). Such copper-rich matte inclusions are common in slags from Chrysokamino.

To conclude, the mineralogy of the slag and the chemical composition of the copper prills only reflect the conditions at the lower parts of the furnace. The thermodynamic profile of the process was, however, more complex since the raw materials passed from a slightly oxidising to a moderately reducing zone in the shaft. Although the pO_2/T conditions in the upper parts of the furnace did not significantly affect the copper/slag equilibrium, they caused the removal of sulphur and, more importantly, arsenic from the charge thus affecting the chemical composition of the copper and the amount of matte formed. Overall, the metallurgical process can be described as the *smelting of oxidised ores at a reducing atmosphere* although, as described in this section, more complex chemical reactions were involved.

4.19 Slag tapping

The possibility that slag was tapped during the copper-smelting process at Chrysokamino was raised at the beginning of this chapter based on the macro-morphology of some of the larger slag fragments, characterised by clear flow-features and presence of small pieces of rocks entrapped on their lower surface (Section 4.4.1).

The scientific analysis of slag from Chrysokamino adds further support to this argument since the micro-texture of the analysed samples is indicative of very rapid cooling of the slag in contact with the air. The predominance of glassy phases in most slag samples (Section 4.9) is a well-known feature of rapidly solidified (i.e. tapped) smelting slags (Bachmann 1982: 15). The same is suggested by the fine, lathy or "dendritic" texture and non-equilibrium chemical composition of the silicate crystals embedded in the slag (Sections 4.9 and 4.11). Finally, a very important piece of evidence is provided by the thin bands of magnetite present in many slag samples from the site (Section 4.9). A similar textural feature has been identified by Okafor (1993: 446; see also Hauptmann *et al* 2003: fig. 2) in early iron smelting slags from Nigeria and has been shown to reflect successive tap-cycles. Whether the presence of these bands indicates a similar process at Chrysokamino is questionable as the thickness of individual 'slag-layers' rarely exceeds the 2-3mm. However, as they are a strong indication of solidification in contact with the air, it seems very plausible to argue that they were formed during the 'folding' of a rapidly solidifying slag as it ran outside the furnace.

In conclusion, the macro- and micro-texture of the slag samples from Chrysokamino suggests that slag was tapped during the smelting operations at the site. The tapping process would have involved the opening of a hole, probably just below the level of the furnace pit, allowing the fluid slag to flow out of the furnace. Unfortunately, evidence from the lower parts of the furnaces is still scant and ambiguous and it is impossible to describe the procedure accurately.

It should also be noted that although much of the liquefied slag was tapped during the smelting process, a large part remained inside the furnace (up to 50% of the total amount: Merkel 1990). This 'furnace slag' would have probably consisted of (i) a slag layer that was left above the copper ingot to prevent it from oxidising and (ii) those areas of the slag bath that had been in contact with the furnace lining and had, therefore, become probably more viscous (cf. Merkel 1990).

4.20 Investigation of the nature of copper losses in the slag

The study of the copper losses in the slag from Chrysokamino is very important for our understanding of the copper smelting technology at work at this site. As described in the previous chapter, copper losses are of two major types: (i) dissolution of cuprous oxide and (ii) mechanical entrainment of metallic particles (Jalkanen *et al* 2003; Sridhar *et al* 1997). Of course, the two phenomena are not entirely independent since both are controlled -to a greater or lesser extent- by the chemical composition of the slag, the furnace temperature and the redox conditions. However, the former is more sensitive to the redox conditions in the furnace whereas the latter depends more on the viscosity of the slag. Therefore, since the two types of copper losses are related to different practical aspects of the smelting process, it is useful to investigate how each was dealt with by the smelters at Chrysokamino.

Central to this investigation is the distinction between the two types of copper losses. In other words, how much of the copper found in the slag is to be attributed to the dissolution of cuprous oxide and how much represents the entrapment of metallic particles? The distinction is particularly complicated since during the solidification of the slag, some of the dissolved copper precipitates in the form of round metallic inclusions, which are difficult to distinguish, either chemically or optically, from those that were entrapped in the slag during smelting (Jalkanen *et al* 2003; Ruddle 1968).

In this study, a new approach is proposed for the distinction between the two types of copper losses in the slag. Firstly, the theoretical solubility of copper in CaO-FeO-SiO_2 slags at redox conditions corresponding to the calculated pO_2 values is estimated. It is then assumed that copper losses in excess to the copper solubility should be attributed to the mechanical entrapment of metal particles. To test this hypothesis, the copper content in the slag samples is then plotted against their viscosity, calculated using two different methods, to examine whether higher copper losses are related to more viscous slag samples.

Figure 4.17 shows the five slag samples analysed by Mössbauer spectroscopy plotted on the diagram of the solubility of copper in CaO-FeO-SiO_2 slags at various redox conditions. As seen in the diagram, the theoretical copper solubility in these slags, at oxygen partial pressures from *ca.* $10^{-7.8}$ to $10^{-9.8}$ (i.e. the range estimated in Section 4.17), is at the order of *ca.* 0.3-0.9 wt-%. It could, therefore, be argued that any amount of copper *above* this range should be attributed to the mechanical entrainment of metallic particles in the slag.

The next step is to examine the effects of slag viscosity on copper losses. The most commonly employed method for the estimation of the viscosity of archaeological slags is the use of Bachmann's (1980) empirical formula, which correlates viscosity to the viscosity index of the slag (see Section 3.3) and the furnace temperature (e.g. Bennett 1989). This method can offer a rough estimate of slag viscosity at temperatures well above its liquidus temperature (Kresten 1986; see also Freestone 1988). A similar empirical model, developed by Shaw (1972) for the calculation of the viscosity of magmatic silicate liquids, has been built into the CHEMCAST 2.0 software by Ford (1992). Shaw's (1972) model differs from that of Bachmann in that in takes into consideration (i) more oxides, (ii) the partial pressure of oxygen and (iii) the dual role of alumina as a network former and a network modifier. It is, however, developed for magmatic melts, which generally have much lower iron levels than those present in metallurgical slags (see Freestone 1988).

Using these two models, the viscosity of slag samples from groups MG-1 and MG-2 (except for those with frequent unfused silica grains) from Chrysokamino was estimated for a furnace temperature of 1300°C (i.e. well above their liquidus temperatures). Samples from groups MG-3 and MG-4 were not included in these estimations because they may represent pieces of slagged furnace material (Section 4.14). The results produced by the two methods differ significantly **(Table 4.17,**

Figure 4.18). To be more specific, Bachmann's model produces viscosity values that are lower by a factor of 10 to 100 compared to the values produced by CHEMCAST. A similar pattern has been noted by Hauptmann (1985: fig. 51) in his study of prehistoric copper-smelting slags from Oman. Unfortunately, since each method for viscosity estimations has, as already mentioned, its own advantages and disadvantages, it is not possible, at present, to say which of the two has provided more accurate results.

The differences in their results, however, should not be overestimated. Both methods suggest that the slag from Chrysokamino was very fluid at 1300°C, its viscosity being (in most cases) less than 10 poise. More importantly, the results of the two methods show a very strong positive correlation (see **Figure 4.18**), resulting in a very similar ordering of the slag samples on a scale of increasing viscosity. In other words, although there is still uncertainty about the *absolute* viscosity values for the slag from Chrysokamino, it has been possible to firmly establish the *relative* viscosity of each slag sample in comparison to others.

Figure 4.19 shows the viscosity of slag samples from Chrysokamino plotted against their copper content. Despite the considerable dispersion of the points, an expected pattern emerges in both diagrams, namely that copper losses in the slag increase with increasing viscosity. Most slag samples have low viscosities and their copper contents fall between 0.3 and 0.9%, but this reaches the 2-3% in more viscous samples.

What conclusions can be drawn from the above discussion? First, it appears that the copper content in most samples is within the range of copper solubility in CaO-FeO-SiO_2 slags at the calculated partial pressures of oxygen (indicated on **Figure 4.19** by the shaded bands) suggesting that copper losses in the slag from Chrysokamino were mainly controlled by the redox conditions in the furnace. Only in a small number of samples does viscosity influence the amount of copper lost in the slag. In other words, the separation between the *formed copper particles* and the slag was very efficient because the latter was very fluid as a result of the use of the calc-ferrous flux and the attainment of high temperatures inside the furnace.

Moreover, the dissolution of cuprous oxide in the slag, which was the predominant type of copper loss, was kept fairly low (i.e. 0.3-0.9%) by creating sufficiently reducing conditions inside the furnace. Undoubtedly, the amount of dissolved $CuO_{0.5}$ could have been further lowered by creating an even stronger reducing atmosphere during smelting. Given the ferrous nature of the slag, however, this practice would have introduced serious problems to the process. To be more specific, the excessive dissolution of iron in the copper, caused by such a strongly reducing atmosphere, would have had detrimental effects on the viscosity of the slag and the purity of the smelted copper (see Section 3.5). Opting for moderate redox conditions, smelters at Chrysokamino could therefore produce a fairly pure copper (1.0-3.6% Fe; Section 4.11.2) with very low copper losses in the slag.

It is probably in this context that the role of the perforations in the furnace design should be examined. Due to the presence of perforations on the shaft, which allowed the penetration of the wind, the charcoal was ignited higher up the stack than it would have been in a closed shaft, resulting in an increase in temperature. The charge was thus preheated to a higher temperature before reaching the level of the tuyères and the fusion of the gangue minerals and the flux became more effective resulting in a more fluid slag and a better slag/metal separation. Of course, the introduction of more air in the system compromised the reducing atmosphere in the furnace. However, as shown in this section, copper is a fairly noble metal so even moderate reducing conditions can keep the dissolution of cuprous oxide at very low levels, enabling at the same time the production of a purer metal. The common assumption that stronger redox conditions in copper-smelting are indicative of a more advanced metallurgical technology (e.g. Craddock 1995: 137ff) should be, therefore, reconsidered.

To argue, however, that the recovery of copper was very high during smelting raises an important question. If the slag/metal separation was so efficient, why did smelters at Chrysokamino have to crush the slag after the end of the smelting process to retrieve entrapped nodules of metal? Indeed, the crushing of slag after the end of the smelting process certainly argues against the collection of *all* copper at the bottom of the furnace forming an ingot. However, it should also be noted that most slag fragments at Chrysokamino range from 1 to 2cm so the entrapped metal nodules were probably of the same size. In other words, although some copper *did* remain entrapped, the low viscosity of the slag allowed minute prills to coalesce into larger nodules that could be easily collected by hand.

It should be noted, though, that in addition to the small slag fragments, the excavation at Chrysokamino has revealed substantial quantities of pulverised slag. The amount of powder is too large to have been produced during the crushing of the slag into small pieces. It is, therefore, possible that the smelters needed occasionally to grind the slag presumably to expose minute copper inclusions. Interestingly, the wear pattern of some of the stone tools found at the site has been associated with a grinding function (Betancourt *et al* 1999: 366). Such minute metallic particles would have been impossible to collect by hand so a sorting process (washing?) must have been employed to separate them from the pulverised slag. It is not possible, at present, to explain the different degrees of comminution of the slag. Perhaps the laborious grinding/washing process was used for the more viscous(?) furnace slag or after less successful smelts.

4.21 Characterisation of the product of the smelting process

The main product of the smelting process consisted of a copper-arsenic alloy with lower levels of iron and nickel. In addition to this, a copper-rich matte was produced, which entered the metal ingot/nodules forming small inclusions in them (see Craddock *et al* 2003; Roman 1990). Some separate matte nodules might have also been formed during the process, if sufficient sulphur was available, but no such finds have yet been reported from the site.

The levels of arsenic in the copper were highly variable (ranging from 1.5 to more than 20% in the copper prills suspended in slag samples) due to the uncontrollable formation of the volatile As_2O_3 (Section 4.18). In contrast, the nickel content was relatively constant (*ca.* 0.5-2%) because this element is generally concentrated in the metallic phase. As for iron, it probably showed minor fluctuations due to the variable redox conditions but was generally between 0.5 and 4%.

The levels of iron present in the smelted copper would have rendered the metal very brittle (Papadimitriou 2001) so an additional refining stage would have been necessary to remove it before shaping it into useful objects. The process would have certainly removed some arsenic although, if a slightly reducing atmosphere was retained, losses would have been relatively small (McKerrell and Tylecote 1972). Nickel, on the other hand, would have remained largely unaffected. A rough estimation of the chemical composition of the refined copper is: 2-10% arsenic, 0.5-2% nickel and less than 0.5% iron.

4.22 Reconstruction of the smelting process at Chrysokamino

Having examined the various aspects of the smelting technology at work at Chrysokamino, it is now possible to offer a general reconstruction of the process.

The raw materials, including the copper-ores, the calc-ferrous flux, the arsenic-nickel mineral and the fuel were crushed to a small size (no more than a centimetre) to facilitate the various reactions during smelting, and then charged to the probably preheated furnace (**Figure 4.20**).

The air necessary to burn the charcoal was provided by one or two pairs of pot-bellows and the wind penetrating through the perforations. The maximum temperature, at the level of the tuyères, was about 1300°C and the partial pressure of oxygen was *ca.* 10^{-8} to 10^{-10}atm, enabling the formation of a fluid slag and the reduction of copper oxides to metallic copper. As the smelting operation proceeded, raw materials were periodically charged from the top of the shaft and liquid slag accumulated in the furnace pit while prills of metallic copper sunk through it forming an ingot at the bottom (**Figure 4.21**). When the liquid slag reached the level of the tuyères, the smelters tapped some of it out of the furnace to enable the continuation of the process.

Once the raw materials were used up, the process was terminated and the contents of the furnace were left to cool down. The shaft was then broken into small pieces probably to release any materials fused onto its lower parts. Although some slag had been tapped during the smelting process, a large part remained inside the furnace covering the copper ingot formed below. The ingot contained small inclusions of high-grade matte, which was also produced during the smelting process. Some metal, however, did not separate but rather remained entrapped in the slag, which then needed to be crushed and/or pulverised to enable further separation.

A simple remelting in a relatively reducing atmosphere would have been necessary to remove the iron present in the smelted copper without causing significant arsenic-losses. However, no evidence of this process has been found at the site.

4.23 Conclusions

Although commonly treated as a single stage in the metallurgical sequence, copper-smelting involved in reality a complex series of operations and a considerable number of decisions, ranging from the selection and preparation of the raw materials and the construction of the furnace to the conduct of the smelt and the subsequent processing of the slag. It follows that an accurate reconstruction of prehistoric smelting technologies requires the investigation of all these different aspects of the process, a task that can only be carried out by using a wide range of analytical techniques. In this chapter, such a multi-analytical approach was employed in the study of copper-smelting remains from the Early Minoan site of Chrysokamino enabling the reconstruction of the most important aspects of the metallurgical process (**Figure 4.22**). In the following chapter, the scope of this study is broadened and the copper smelting technology at work at Chrysokamino is examined in relation to other metallurgical traditions witnessed in the southern Aegean during the Early Bronze Age.

CHAPTER FIVE

COMPARATIVE ANALYSIS OF COPPER SMELTING TECHNIQUES in the Southern Aegean During the Early Bronze Age

5.1 Introduction

The purpose of this chapter is to assemble all the evidence for copper-smelting activities from the southern Aegean in order to provide a picture of the range of smelting techniques at work during the EBA. Available analytical and archaeological information is examined, evaluated and often re-interpreted, shedding light to important aspects of the smelting processes conducted in various sites in this area. Following the same principles underpinning the analysis of the metallurgical remains from Chrysokamino, various technical aspects of the smelting process are discussed, including the nature of the *raw materials*, the design of the *furnace*, the *smelting conditions* and the techniques for the *separation* of copper from the slag. The comparative analysis reveals a complex picture of technical differences and similarities among the various smelting sites, a picture that has long remained hidden due to the restrictive analytical approaches the study of early Aegean metallurgical technology.

5.2 EBA copper-smelting sites in the southern Aegean

One of the most important problems in the study of early Aegean metallurgy is the dearth of accurately dated and properly characterised archaeometallurgical material, a problem that stems from the paucity of excavations and technological studies of metallurgical sites. In this study, all known evidence (or possible evidence) for

FN/EBA copper-smelting activities in the southern Aegean, coming from 21 sites, is collected and evaluated (**Table 5.1**, **Map 5.1**).

There are fifteen known sites in this area, which have yielded typical evidence for early copper-smelting activities. The predominant type of evidence is slag, its amount ranging from some tens of kilograms in the smaller slag scatters, to thousands of tons in the massive slag heaps, though pieces of ore and metallurgical refractories are also common (**Table 5.2**). That copper was the metal produced at these sites has been established by macroscopic examination and scientific analysis of the evidence (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998). Only in the case of the slag scatter at Konakia on Keros are there still doubts about its association with copper rather than iron smelting, because copper prills are not visible in the slag under the optical microscope (Bassiakos 1988; Bassiakos and Doumas 1998). Moreover, the predominance of wustite indicates very strong reducing conditions, compatible with the bloomery (iron) smelting process (*contra* Bassiakos and Doumas 1998). Nonetheless, given the presence of 0.4-07% of copper in the slag, which is too high for iron-smelting slags (Tylecote 1987: 1), and the proximity of the metallurgical remains to a weak iron-copper mineralisation, Bassiakos and Doumas (1998) are probably right to suggest that the metal produced at Konakia was copper rather than iron.

Establishing the date of the copper-smelting remains at these sites is a much more difficult task. Slag scatters and heaps are usually found in isolated areas near ore deposits. Diagnostic pottery is generally absent and the lack of systematic excavations allows in most cases only rough estimations to be made, based on surface finds alone (e.g. Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998; Philaniotou-Hadjianastasiou 2000). Although scientific dating techniques have offered valuable alternatives, they have their own limitations: the applicability of ^{14}C dating (e.g. Stos-Gale 1989) is restricted by the general absence of charcoal from southern Aegean copper-smelting sites, while TL dating (e.g. Stos-Gale 1998; Zacharias *et al* 2002) offers very limited chronological resolution. The dating evidence from slag scatters and heaps in the southern Aegean is summarised in **Table 5.3**. As shown in this table, two copper-smelting sites (Skouries and Chrysokamino) can be assigned to a particular sub-period of the EBA, nine can be placed, with varying degrees of certainty, to the third millennium BC, while the remaining three sites (Aghios Symeon, Avessalos and Aerata) cannot be dated.

In addition to slag scatters and heaps, small groups of ambiguous vitrified material and installations of uncertain function, found inside or near prehistoric settlements, have often been associated in the past with copper smelting. In the absence of massive accumulations of slag, which is the most reliable indication of smelting activity, the accurate interpretation of such evidence requires detailed macroscopic and laboratory analysis. Indeed, similar remains, commonly found in domestic contexts, can result from metalworking activities (e.g. crucible slag formed during the melting of copper; see Cooke and Nielson 1978) or processes entirely unrelated to metallurgy (e.g. burnt ceramics or mud bricks; Bachmann 1982: 20). Evidence of this type has been reported from six sites in the southern Aegean (**Table 5.4**) and their suggested association with copper-smelting activities is evaluated below.

Manika (Euboea)

Sampson (1988: 18) has reported small fragments of "slag" found in deposits with Early Helladic pottery and obsidian in this settlement. Chemical analysis of one sample, using Atomic Absorption Spectroscopy, has been thought to prove the association of these finds with smelting of either copper or argentiferous ores (Sampson 1988: 17). The published analytical data (Ni: 3350ppm, Co: 450ppm, Cu: 760ppm, Zn: 560ppm and Mn: 285ppm), however, is hardly convincing. Not only are the levels of copper too low for copper-smelting slag, there is also no information on the major oxides present in the samples (e.g. SiO_2, FeO, CaO, Al_2O_3, alkalis) to allow their association with specific (if any) metallurgical activities.

Raphina (Attica)

Two large ovoid pits, *ca.* 3.2m x 4.2m wide and about 1m deep, containing metallurgical debris were discovered at this settlement, one with remains of a stone structure at its bottom (Theocharis 1951, 1952). Material from the pits included "abundant copper slag", four clay-tips (probably placed at the end of blowing pipes), which Theocharis incorrectly interpreted as feeders for bivalve moulds (Muhly 1985), and ceramic fragments, some of which were perforated, with copper traces on them. Given that slag is produced in large quantities only during smelting (crucible slag usually coming in very small quantities), the material should be probably associated with this process. Moreover, perforated ceramics are known from other EBA smelting sites from SE Aegean (see below) so their presence at Raphina adds further support to the suggestion that copper-smelting activities took place there.

Kolonna (Aigina)

A peculiar installation built during the fourth phase of the settlement has been interpreted by the excavators as a "metallurgical furnace" (Walter and Felten 1981: 23ff). The proposed reconstruction (**Figure 5.1**), however, is problematic as it assumes that liquid copper from the furnace chamber ('Ofenaufbau') flowed through a *ca.* 1.8m long channel ('Schmelzrinne') down to the ingot-mould ('Barrenform'). The problem is that molten copper would have rapidly solidified once it entered the channel where, despite the refractory properties of the building material, temperatures would have been much lower than those inside the melting chamber (*contra* Walter and Felten 1981: 24-5). However, as the 'channel' has indeed been exposed to high temperatures and analysis of the 'slagged' interior has revealed the presence of considerable amounts of copper (Walter and Felten 1981: Tables 5,6 and 6b), the installation must have been somehow related to metallurgy. In this case, its overall shape and size seem much more relevant to smelting operations than to any metalworking (e.g. copper-melting) process.

Kephala (Keos)

Eight pieces of slag and a small number of perforated metallurgical ceramics have been reported from the Final Neolithic settlement and the adjacent cemetery. Slag samples were subjected to scientific analysis separately by Conophagos and Tylecote & Cooke (both in Coleman 1977: 113-4) and were found to have derived from copper smelting. Cooke's (in Coleman 1977: 114) doubts concerning the FN dating of the smelting activities (which he considers to reflect an advanced technology that is not compatible with this period) should be disregarded because there are *stratified* FN finds of perforated ceramic fragments with adhering *smelting slag* from the site (Coleman 1977: 113).

Avyssos (Paros)

Five surface fragments of "slag" have been reported by Tsountas (1898: 175-6) from this EC I settlement but they have not been subjected to scientific analysis. This interpretation clearly awaits analytical confirmation since another find from Kastri on Syros also described by Tsountas (1899: 124) as "slag", was later found by scientific analysis to be a corroded lump of arsenical-copper (Stos-Gale et al 1984).

Kavos North (Keros)

Broodbank (2000: 231) has reported the presence of metallurgical debris from the site Daskaleio on Keros. The scattered material, which comprised several pieces of slag containing copper prills, occurred in greater density at an adjacent location (exposed to strong wind) called Kavos North. While Broodbank's (2000: 295) description of the metallurgical process reflected in this material as "secondary smelting" is rather confusing, more recent analysis of the metallurgical remains (Georgakopoulou 2004) has served to clarify matters, demonstrating the association of the slag with copper-smelting processes.

To summarise, the metallurgical remains from Raphina in Attica, Kolonna on Aigina, Kephala on Keos and Kavos North on Keros, dating to the FN and EBA periods (**Table 5.5**), can be associated, on present evidence, with copper-smelting activities. Adding the slag scatters and heaps described above, a total of nineteen sites with copper smelting remains dating to the 3rd millennium BC are included in the following comparative technological analysis.

This large collection of material presents several problems. Firstly, many sites in the list either are undated (3 sites) or can only be broadly dated with varying degrees of certainty to the Early Bronze Age (9 sites). Inevitably, the chronological resolution of the comparative analysis is limited. In addition, there is considerable variation in the amount and quality of analytical work conducted at each site. The analysis of the material from Chrysokamino, presented in the previous chapter, currently stands out as the most detailed technological study of an EBA copper-smelting process in the Aegean. Elsewhere, analytical work has been restricted to lead isotope, chemical and some microscopic analysis of small numbers of slag samples (e.g. Bassiakos and Doumas 1998; Gale *et al* 1985; Papastamataki 1998). More recent analytical projects (Kythnos: Bassiakos and Philaniotou-Hadjianastasiou in press; Keros: Georgakopoulou 2004) have employed a broader analytical methodology but their results have so far been presented only in preliminary reports. Consequently, the comparative analysis is more detailed in the case of those aspects of the smelting process for which archaeological or analytical evidence is available.

5.3 Copper ores and fluxes

The analysis of metallurgical material from Chrysokamino, presented in the previous chapter, showed that the copper ores used in the smelting process were oxidised with a small amount of residual sulphides. In addition, a lime-rich iron ore was used to flux the highly siliceous gangue minerals of the ore. This section considers the evidence from other copper-smelting sites in the southern Aegean to examine whether similar or different raw materials were used there for the production of copper.

5.3.1 Copper ores

According to currently available evidence, early copper production in the southern Aegean was based on the mining and smelting of ores from the oxidation zone of copper deposits. Firstly, loose pieces of ore, found mixed with the metallurgical debris at six smelting sites in this area (**Table 5.6**) were in all cases *oxidised*, malachite being the predominant copper mineral, associated with quartz and/or iron (hydr)oxides.

Secondly, both the high copper to sulphur ratios (**Table 5.7**) and the predominance of copper over matte inclusions in analysed slag samples from various sites suggest that copper, rather than matte, was the main product of the copper-smelting process (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998). The possibility of direct smelting of sulphidic ores to blister copper can be excluded because this process would have also resulted in very high copper losses in the slag (*ca.* 10 wt-%) and low iron levels in the copper produced (<0.5 wt-%). Instead, copper losses in slag from various smelting-sites in this area are well below 10 wt-% on average (**Table 5.7**), and the copper prills suspended in the slag contain in all cases more than 1 wt-% iron (**Table 5.8**). In other words, the chemistry and mineralogy of the slag suggest that the smelted ores were predominantly oxidised, containing only a small amount of residual sulphides (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998).

Thirdly, the limited evidence for prehistoric copper mining from the southern Aegean shows that ore procurement was concentrated on the upper parts (i.e. the oxidation zone) of copper deposits. There are three known prehistoric copper mines in the southern Aegean, all from the island of Kythnos. At the locations Petra and Aspra Kellia on northwestern Kythnos, Bassiakos and Philaniotou-Hadjianastasiou (in press) discovered debris from the opencast mining of the exposed part of quartzite lenses, bearing malachite and azurite, which traversed the local schists. Although there is no datable evidence, an early date has been suggested for these two sites based on the mining techniques, the presence of obsidian and the proximity of the mines to the Early Cycladic copper-smelting sites of Sideri and Aspra Spitia (Bassiakos and Philaniotou-Hadjianastasiou in press). Similarly, at the location Cape Tzoulis, a few kilometres to the south of the massive EC II slag heap at Skouries, lies a small trench mine following an oxidised cupriferous vein of iron ore traversing the local marbles (Philaniotou-Hadjianastasiou 2000; Hadjianastasiou and McGillivray 1988; Stos-Gale 1989). Ceramic sherds found at the entrance of the mine place the mining activities to the Early Cycladic period (*ibid.*). As for the underground galleries reported by Gale *et al* (1985) and Stos-Gale (1989) from the same island, they date to the Roman period and the mined metal was iron, not copper (Bassiakos pers. comm.). The evidence from both copper-mining and copper-smelting sites, therefore, suggests that early copper production in the Aegean was based on the exploitation of ores from the upper parts of ore deposits, where oxidised copper minerals predominated.

This picture should not be attributed to a lack of technical knowledge for the mining of the deeper sulphidic parts of copper orebodies. Archaeometallurgical survey on the island of Siphnos (Wagner *et al* 1980; Wagner and Weisgerber 1985) has revealed the presence of complex networks of underground galleries exploiting rich argentiferous lead ores which, at least at the location Aghios Sostis, have been securely dated to the EC I period. Similar evidence, though of a much smaller scale, has been reported from Thorikos in Laurion (Spitaels 1984) where an outcrop of argentiferous galena or cerussite was mined during the EH III period first by opencast mining and then by opening a horizontal gallery following the mineralisation for about 5-10 meters inside the hill front. In other words, although there is evidence for EBA underground mining in the archaeological record of the southern Aegean, it is always associated with lead/silver rather than copper extraction.

So why was early copper production in the southern Aegean restricted to the exploitation of oxidised ores? An obvious explanation could be that the technical knowledge necessary for the smelting of sulphidic ores was not available in this area. However, it is also possible to associate this technological choice with the particular geological context of the southern Aegean. To be more specific, although hypogene (i.e. sulphidic) copper ore bodies are not uncommon in this area (though much less common than they are in northern Greece), they are generally characterised by very low copper grades (Bassiakos pers.comm.). The copper grade in the large mixed-sulphide deposit at Ermioni in Argolid, for example, is a meagre 2.5% (Robertson *et al* 1987). The extraction of copper from such pyritic ores would have been impossible in prehistory because it would have required beneficiation techniques that have been only recently introduced into metallurgical practice. In the oxidation zone of such deposits, however, the differential leaching of iron and copper by percolating surface waters would have resulted in the concentration of the formed copper carbonates (Evans 1993). In addition, the sharp colour contrast between the green/blue copper hydro-carbonates and the red/orange iron hydroxides would have allowed the collection of the richest ore pieces for further processing. Therefore, although the low copper grade of mixed sulphide deposits in the southern Aegean prevented their exploitation in prehistory, their oxidation zone offered suitable raw materials for the production of copper.

5.3.2 Fluxing

The majority of copper deposits in the southern Aegean consist of iron-copper mineralisations associated with quartz/quartzite intrusions filling faults and fissures in metamorphic rocks such as schists and marbles (Conophagos 1980: 161; Gale *et al* 1985; McGeehan-Liritzis 1983; Skarpelis *et al* 1992). The gangue material of copper ores collected from such deposits could, therefore, range from highly siliceous to highly ferrous, so the careful preparation of the raw materials would have been an essential prerequisite for the formation of a fluid slag during smelting. The analysis of material from Chrysokamino has revealed the use of a local iron ore to flux the siliceous copper ores smelted at this site (see Section 4.15.1). The evidence presented below suggests that similar ore preparation techniques were probably employed at other EBA copper-smelting sites in the southern Aegean.

The chemical composition of the slag testifies to the particular care taken by the smelters in the preparation of the raw materials allowing an assessment of the consistency of (and hence the level of control exerted over) the smelting charge. This is well illustrated in **Figure 5.2**, which shows the position of copper ores and slag fragments from the island of Kythnos on the pseudo-ternary CaO-FeO-(SiO_2+Al_2O_3) diagram. As seen on the diagram, copper ores demonstrate great variability, some being siliceous and others ferrous, while significant levels of lime, probably reflecting the schist/marble host rocks of the local mineralisations, are common (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985). In contrast to this variability, most slag samples from the island form a relatively tight cluster on the diagram in a compositional area of the slag system that is characterised by low liquidus temperatures. Due to the limited number of chemical analyses of ore samples from the southern Aegean, such comparisons are not possible for other copper-smelting sites. However, analysed slag samples from various sites are generally consistent in terms of chemical composition and, what is equally important, fall in the area of the phase diagram corresponding to slags with low liquidus-temperatures (**Figure 5.3**). This picture suggests that craftsmen in the EBA southern Aegean were able to control the composition of the charge in order to promote the formation of a liquid slag during smelting. What specific techniques, however, were they using to achieve the desired composition?

Due to their particular nature (see above), copper deposits in this area usually contained the necessary earthly components for the formation of a fluid slag, namely *quartz*, *iron oxide* and some *lime* from the host rocks. The relative proportions of these oxides, however, were highly variable both within the same and among different deposits (see, for example, **Figure 5.3**). In this context, fluxing the siliceous copper ores with iron ore and the ferrous copper ores with quartz were the two extremes in a continuum of possibilities that were available for the preparation of an easily smelted charge. These could have ranged from the careful selection of ore pieces with appropriate quartz to iron ratio (i.e. self-fluxing ores) or the removal of any excess quartz or iron oxide, to the mixing of iron-rich with silica-rich pieces of copper ore from the same or different deposit(s) (cf. Bassiakos and Philaniotou-Hadjianastasiou in press; Stos-Gale 1989). Although such techniques could have left no obvious traces in the archaeological record, some insight is offered by pieces of unused raw materials found mixed with the metallurgical debris at various EBA copper-smelting sites in the southern Aegean (see **Table 5.6**). These include pieces of possible fluxing materials, which are in all cases of either iron-ore or quartz, but also pieces of copper ore that appear to have been discarded in a final stage of "beneficiation" probably due to their low copper-grade.

To conclude, the marked consistency in the composition of the smelting charge, as revealed by the chemical analysis of slag fragments from the southern Aegean, was probably achieved through a combination of ore-preparation techniques employed at various points from the initial collection of the ore to the charging of the furnace. The particular techniques may have varied among sites but there is a common overall pattern of use of iron-ore and quartz as the main "earthly" components of the charge. Nonetheless, within this dominant tradition there was still room for choice, as suggested by the use of an unusual lime-rich iron ore as flux at Chrysokamino (see Section 4.15.1). Further research, focusing on evidence for ore preparation techniques, both at the mining and the smelting sites is required in order to better understand the range of technical variants at work during this period.

5.4 The production of arsenical copper

A central place in Aegean archaeometallurgy holds the question on the "mode of production of arsenical copper" (Kayafa *et al* 1997: 42) during the EBA. To be more specific, it has long been unclear whether early arsenical coppers represent a deliberate alloying practice (the addition, in other words, of an arsenical substance to copper at some stage of the metallurgical sequence) or whether they reflect the deliberate or unconscious exploitation of arsenic-bearing copper ores (Charles 1967; Craddock 1976; Gale and Stos-Gale 1989; Mangou and Ioannou 1997; Kayafa *et al* 1997; Stos-Gale *et al* 1996). At the heart of this debate has been the issue of *intentionality*. Was this alloy the product of a conscious technological choice or was it simply the product of chance, and should not be used to define technological traditions (cf. Northover 1989; O'Brien 1999)?

Central to this question is the chemical composition of copper produced during smelting, which, in turn, relates to the nature of the raw materials used in the process. If the proponents of the "inadvertent production" model are right, the arsenic levels in the copper prills embedded in slag from copper-smelting sites should be highly variable reflecting the occasional, accidental introduction of arsenic-rich ores into the smelting process. In contrast, the validity of the "intentional production" model depends on the ability to show either that the smelted copper is arsenic-free or that, if arsenic is present, it should be attributed to the conscious use of arsenic-bearing raw materials. What does the evidence from smelting sites in the southern Aegean suggest?

According to available data from the analysis of copper-prills suspended in slag fragments (**Table 5.8**), the great majority of smelting sites (7 out of 10 sites for which analytical data is available) produced copper with low levels of arsenic, not exceeding the 0.6%. Two conclusions can be directly drawn from this. Firstly, copper ores in the southern Aegean generally contained too little arsenic to yield arsenic-rich copper during smelting. Secondly, the addition of arsenical substances to the smelting charge in order to enable the production of this alloy, was not a common practice. Therefore, to account for the predominance of arsenical copper in metal assemblages from this period, it should probably be assumed that arsenic was introduced into copper at a subsequent stage of the metallurgical sequence, most likely when the metal was melted to be cast into moulds. Indeed, analytical work on material from two metalworking sites in this area has provided evidence for such alloying techniques. In their study of metalworking debris from Poros Katsambas near Knossos, Doonan *et al* (in press) found evidence for the alloying of copper by adding roasted löllingite (an iron arsenide) to the melted metal. Similar, though more ambiguous, evidence comes from the Middle Bronze Age levels of the Nichoria settlement in Messenia. There, microscopic analysis of crucible slag samples by Cooke and Nielson (1978) revealed the presence of iron-nickel arsenide inclusions that may suggest the use of such a mineral for the alloying of copper.

This is not, however, the full story. As seen in **Table 5.8**, the copper produced at the copper-smelting sites of Chrysokamino on Crete, Kavos North on Keros and Skouries on Kythnos often contained high levels of arsenic. At Chrysokamino, as already argued, an arsenic-bearing mineral was *intentionally added* to the smelting charge in order to produce arsenical copper (Section 4.15.2). However, do the evidence from the other two sites suggest a similar practice? In other words, was arsenical-copper produced at Kavos North and Skouries "accidentally" through the unintentional smelting of arsenic-bearing copper-ores (as the variable arsenic-levels in the slag could be taken to suggest) or did its production involve the conscious use of arsenic-rich raw materials?

Preliminary results from the analysis of the copper-smelting assemblage from Kavos North on Keros have produced a very interesting picture:

> "Two different types of slag were identified and it is argued that these correspond to two separate smelting processes, involving the use of different types of ore and resulting in two distinct products, pure and arsenical copper. The latter is accompanied by a number of other base metal impurities" (Georgakopoulou 2004).

Unfortunately, it is not clear in the text whether arsenical copper was produced by smelting arsenic-bearing copper ores or by adding an arsenical substance in the charge as was the practice at Chrysokamino. Nonetheless, Georgakopoulou argues that arsenical copper and pure copper were produced by two *distinct* smelting processes. In other words, regardless of the particular nature of the ores used for the smelting of arsenical copper at Kavos North, the evidence shows the that there existed a *conceptual distinction* between arsenic-rich and arsenic-free raw materials and each type was used *separately* (and therefore *consciously*) for the production of a different type of copper.

Turning to the large copper-smelting site of Skouries on Kythnos, archaeometallurgical research has produced more controversial results concerning the production of arsenical copper. The material was originally studied by the Oxford group (Gale *et al* 1985; Gale and Stos-Gale 1989) who argued that copper prills in 10 analysed slag fragments contained highly variable levels of arsenic ranging from 0.1 to 6.6% (Gale and Stos-Gale 1989: Table 5). A similar variation in arsenic levels was noted in copper-ore fragments found among the smelting debris and also in copper ores from various mineralisations on Kythnos (Gale and Stos-Gale 1989). Based on the above, Gale and Stos-Gale (1989: 34) argued that "arsenical copper was sometimes accidentally produced in Early Cycladic times in the copper smelting practiced on Kythnos".

This argument has been challenged by a more recent archaeometallurgical project on Kythnos by Bassiakos and Philaniotou-Hadjianstasiou (in press). To be more specific, a large number of copper-prills were analysed in 23 slag samples from Skouries and 70 slag samples from other locations on the island but none contained more than 0.6% arsenic (see above). It follows that arsenic-rich slag fragments are present only at Skouries and constitute a much smaller part of the slag heap than Gale and Stos-Gale had assumed.

Moreover, a closer look at the analyses of copper prills reported by Gale and Stos-Gale (1989) shows that the levels of arsenic have a bimodal distribution with prills in 6 samples containing less than 0.7% arsenic on average (i.e. similar to the levels reported by Bassiakos and Philaniotou-Hadjianastasiou) and those in 4 samples containing more than 2.5%. This pattern could not have resulted from the smelting of copper ores with variable levels of arsenic as Gale and Stos-Gale (1989) have suggested. In fact, even the analyses of copper ores from Kythnos reported by Gale *et al* (1985: Table 4) may need to be reconsidered as, according to the arsenic to copper ratios, *all* ore samples would have theoretically yielded arsenical copper (4-60% arsenic) during smelting. What we could argue, instead is that the picture at Skouries seems to parallel the situation at Kavos North where two *distinct* smelting processes were at work, one producing arsenical copper and the other arsenic-free copper. It could thus be argued that, in a probably small number of smelting operations at Skouries, smelters used *different raw materials* with unusually high arsenic contents. Whether arsenic was present in the copper ores or was added as a separate mineral cannot be answered without further analysis. Whatever the case, however, the use of arsenic-rich raw materials for the smelting of arsenical copper at Skouries appears to have been a *conscious* choice.

To conclude, the evidence from copper-smelting and copper-working sites from the southern Aegean suggests that the production of arsenical copper in the Early Bronze Age was a *conscious* technological choice. At least two major techniques were at work for the production of this alloy, one involving the smelting of arsenic-rich raw materials and the other the addition of an arsenical substance into liquid copper prior to its shaping into objects.

5.5 Furnace design

It has already been argued in Chapter 3 (see Section 3.4) that the furnace design is among the most important factors in copper smelting, having a considerable influence over the temperature and redox conditions attained during the process. The evidence from the EBA southern Aegean suggests that copper-smelting furnaces were usually clay-built but varied considerably in shape, size and overall design (**Table 5.9**). Variability is also noted in the mechanisms for the supply of air in the furnace, ranging from the use of natural draught to the employment of pot-bellows.

5.5.1 Perforated furnaces

An interesting feature of the smelting furnaces used at Chrysokamino was the presence of numerous perforations on the ceramic shaft (Section 4.4.2). As shown below, this particular feature of the furnace design appears to have had a wide distribution in the southern Aegean throughout the 3rd millennium BC. Interestingly, perforated copper-smelting furnaces are unknown in other areas in the Old World, the closest "parallel" coming from 1st millennium AD contexts in Thailand (Bennett 1989). They therefore constitute a local innovation that was never adopted outside this area.

The perforated metallurgical ceramics from Kephala on Keos (**Figure 5.4**) are the earliest known examples of this furnace type in the southern Aegean, dating to the Final Neolithic period. Although the finds have been interpreted by Coleman (1977: 4) as fragments of either *clay-lining* or *crucibles*, they are probably remains of small shaft furnaces. Indeed, given the presence of perforations, their interpretation as remains of clay furnace-lining is hardly convincing. Moreover, the fragment which was supposedly the rim of a crucible (see **Figure 5.4**; no. 148) is not only flattened but also much thicker than the rest of the perforated sherds, so it is more likely the base of an open-bottomed vessel, namely a small shaft. A precise reconstruction of the shaft is not possible on present evidence but it appears to have been slightly curved (beehive shaped?) and probably smaller than those from Chrysokamino (compare to **Figure 4.1**).

Later examples of perforated metallurgical ceramics, dating to the EH II period, come from the site of Raphina on the eastern shore of Attica. Unfortunately, there are no drawings or photographs of the finds while the sole description given by the excavator is that they bear visible signs of burning and traces of copper (Theocharis 1951). Without further examination of the metallurgical assemblage, it is thus impossible to offer a reconstruction of the furnaces used at this site.

The most recently discovered examples of perforated furnaces come from northwestern Kythnos. There, at the two neighbouring copper-smelting sites of Sideri and Aspra Spitia, Bassiakos and Philaniotou-Hadjianastasiou (in press) discovered hundreds of perforated ceramic fragments which, according to their reconstruction, belonged to free-standing beehive-shaped shaft furnaces with an internal diameter of *ca.* 50cm at the base and *ca.* 45cm at the top rim. The furnace walls are much thicker than those from Chrysokamino, ranging from *ca.* 6.5-8cm at the base to *ca.* 2-3cm at the upper rim. No datable pottery has been found on the surface of the site but TL dates from the burnt fragments (2350±640 BC; Zacharias et al 2002) place the perforated furnaces from this site firmly in the EBA.

According to present evidence, therefore, the use of perforated ceramics in copper-smelting is witnessed throughout the southern Aegean, from the Mainland to the eastern end of Crete, spanning from the FN to the end of the EBA, a period of some 1,000 years. Should this common feature be taken to reflect a shared technology for the smelting of copper ores? To answer this question, it is first necessary to consider the role of the perforations in the copper-smelting process.

There is little doubt that the presence of perforations on the shaft was associated with the supply of air in the furnace. However, this does not mean that perforated furnaces in the southern Aegean relied on natural draught. Indeed, fragments of pot bellows have been found at Chrysokamino (see Section 4.4.3) and clay-tips, indicating the use of blow-pipes, are known from Raphina (Theocharis 1951) and Aspra Spitia (Bassiakos and Philaniotou-Hadjianastasiou in press). Moreover, given the overall similarity of the smelting remains at Aspra Spitia and Sideri, it is very likely that future excavations at the latter site will yield evidence for the use of blow-pipes and clay-tips. In other words, most sites with perforated metallurgical ceramics have evidence for the "manual" supply of air in the furnace. What was then the function of the perforations?

In the previous chapter (see Section 4.20) it was argued that the role of perforations on the furnace shafts at Chrysokamino was probably to raise the temperature in the upper parts of the stack enabling the preheating of the ore thus improving the fusion of the gangue and the flux into a fluid slag. In order for the perforations to fulfil this function efficiently, however, the furnace at this site was situated at a location exposed to very strong winds. In contrast, the smelting locations at Sideri and Aspra Spitia on Kythnos are not characterised by particularly strong winds (Bassiakos pers. comm.). As for the furnaces at Raphina, these were placed adjacent to the walls of 1m deep pits, hindering the penetration of the wind through the perforations. Even the shape of the perforations on the furnace-wall fragments from Sideri and Aspra Spitia, being at a downward angle of 25 to 60 degrees (Bassiakos and Philaniotou-Hadjianastasiou in press), does not seem particularly suited for allowing the unobstructed flow of air inside the furnace.

In their study of the material from the sites of Sideri and Aspra Spitia, Bassiakos and Philaniotou-Hadjianstasiou (in press) offered an alternative interpretation, arguing that the perforations on the shafts might have enabled the users of the blow-pipes to accurately direct the air blast to different parts of the furnace during the smelting process. There is certainly some validity in this suggestion since the size of the clay-tip found at Aspra Spitia fits well inside the 1.5-2cm wide perforations, and the downward slope of the perforations seems well suited to this function. Nonetheless, as it would have been very difficult to attain the necessary temperatures in such large furnaces using only blow-pipes (see Rehder 1994), some air supply by natural draught (i.e. penetration of wind through the perforations) in addition to the air blasts from the blow-pipes was probably also necessary. A similar mechanism could also be proposed for the perforated metallurgical ceramics at Raphina, where clay-tips have also been discovered, although further information on the material from this site is necessary for this hypothesis to be tested.

It is impossible, on present evidence, to offer a more accurate reconstruction of the operation of the perforated furnaces in the EBA southern Aegean. Further work, including replication smelting experiments, is necessary to shed more light on their behaviour during the process. What the evidence suggests, however, is that perforated smelting vessels were used in different ways at various sites in this area for the smelting of copper. In other words, rather that viewing the wide distribution of perforated furnaces as a reflection of a *common smelting technology*, it is important to emphasise that this technical element was often incorporated in *diverse smelting technologies* possibly serving a different function in each case.

5.5.2 Ceramic shaft furnaces

Abundant clay fragments (without perforations) have been found mixed with the slag in four smelting sites in the southern Aegean, namely Skouries and Pounda on Kythnos, and Kephala and Avessalos on Seriphos (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985).

Some of these fragments are probably remains of clay-lining. Indeed, excavation of one of the circular structures present at Skouries revealed the presence of a pit (40cm in diameter and of about the same depth) lined with small stones and, above them, a layer of clay (Hadjianastasiou and McGillivray 1988). According to Stos-Gale (1989) this pit probably represents the bottom of one of the furnaces used at Skouries for copper smelting as its diameter coincides well with the diameter of intact slag cakes and large clay fragments from the site.

Gale *et al* (1985) have raised the possibility, however, that some of the clay fragments found at Skouries, having an average thickness of *ca.* 3cm, are pieces of the walls of small shaft furnaces. Similarly Bassiakos and Philaniotou-Hadjianastasiou (in press) have interpreted the clay fragments they found at the site Pounta on the same island as pieces of a “clay furnace”.

Although the distinction between the remains from clay-lining and small ceramic shaft-furnaces can often be problematic (Craddock 1995: 171), there is indirect evidence to suggest that the latter were employed in the southern Aegean. To be more specific, the four sites with abundant clay fragments have also yielded numerous pieces of large slag cakes that often bore clear evidence for tapping (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985). The high smelting temperatures and slag tapping processes reflected on these finds, are not compatible with the use of simple clay-lined bowl-furnaces so it is probably valid to assume that a shaft was placed on top of the smelting pits. It should be noted, however, that without a systematic study of the clay fragments from these sites, this argument remains speculative.

5.5.3 Other furnace designs

In addition to the two major furnace types described above, some less common furnaces were also in use in the southern Aegean during the EBA. The peculiar installation at Kolonna on Aigina (see Section 5.2) is one such case. Another example comes from the island of Seriphos where two smelting hearths (yet unpublished) were recently discovered (Bassiakos pers. comm.). According to the evidence, copper ores were smelted in two shallow depressions at the foot of a steep hill front without any built superstructure. The location of the hill front, facing into the prevailing wind, ensured the supply of the necessary air by natural draught (compare to hearths at Feinan: Craddock 1995: fig. 4.3). The material has not yet been studied and there is, at present, no dating evidence from the site. However, the smelting technology could suggest a prehistoric (and relatively early) date.

5.5.4 Conclusions

The previous discussion of the evidence revealed a considerable variability in the types of furnace used in the southern Aegean during the EBA for the smelting of copper ores. These ranged from shallow hearths using natural draught to shaft furnaces, with or without perforations, operated with blow-pipes or pot-bellows. As seen on **Map 5.2**, there is no clear pattern in the distribution of the various the furnace types. Moreover, different types appear to have co-existed in areas with many copper-smelting sites like the islands of Kythnos and Seriphos.

5.6 The conduct of the smelt

Having considered the raw materials and furnace types used in the southern Aegean during the Early Bronze Age for copper smelting, it is now useful to investigate the chemistry and thermodynamics of the smelting processes themselves. Although the study of such aspects requires detailed analytical data that is not available for most smelting sites in this region, some interesting conclusions can still be drawn.

5.6.1 Furnace temperature

Most slag samples from the southern Aegean are fairly homogeneous, unfused raw materials being generally rare (Bassiakos and Philaniotou-Hadjianastasiou in press; Bassiakos and Doumas 1998; Gale *et al* 1985; Papastamataki 1998). Semi-fused "furnace conglomerates" like, for example, those from Chalcolithic contexts in Palestine (Bachmann 1982; Merkel and Rothenberg 1999), Jordan (Hauptmann 1985) and southeastern Spain (Rovira 1999) have not yet been found in this region. In fact, evidence from smelting sites in the area (including Skouries, Sideri and Aspra Spitia on Kythnos, Kephala and Avessalos on Seriphos and Chrysokamino on Crete) suggest that, in some processes, the slag was not only fully liquefied but also fluid enough to be tapped outside the furnace (Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985).

The production of a fluid slag by prehistoric smelters in the southern Aegean should be attributed to their skill not only to *control the charge composition*, using various techniques of ore preparation (Section 5.3.2), but also to *attain sufficiently high temperatures* inside the furnace. An approximation of the temperatures at which prehistoric Aegean copper-smelting furnaces operated can be inferred from the liquidus temperature of the slag. Based on the chemical composition of slag samples from various smelting sites and using an appropriate phase diagram (**Figure 5.5**), liquidus temperatures in the range between *ca.* 1150 and 1350°C are estimated (compare with Gale *et al* 1985; Papastamataki 1998). Assuming that the furnaces operated at least at some 50°C above the liquidus temperature of the slag to prevent "choking" (Freestone 1988), minimum temperatures of *ca.* 1200-1400°C can be inferred for most smelting processes in this area.

5.6.2 Redox conditions

The study of the furnace atmosphere during a copper-smelting process requires detailed information on the mineralogy of the slag and the chemical composition of the various phases present in it. In the analysis of the metallurgical material from Chrysokamino, for example, the estimation of the partial pressure of oxygen ($pO_2 = 10^{-7.5}$-$10^{-9.5}$atm) was based on the measurement of the Fe^{2+}/Fe^{3+} ratio in the slag, using Mössbauer spectroscopy, and was confirmed by reference to the levels of iron in the copper and matte phases (see Section 4.17). In the absence of quantitative data for the Fe^{2+}/Fe^{3+} ratios in slag samples from copper-smelting sites in the southeastern Aegean, rough estimations of the redox conditions can be proposed on the basis of available information on the relative proportions of magnetite ($Fe^{2+}O.Fe^{3+}{}_2O_3$) and wustite ($Fe^{2+}O$) in the slag and, more importantly, the amount of iron dissolved in the suspended copper prills (see **Table 5.8**).

The general picture drawn by the evidence suggests that early Aegean copper-smelting processes were conducted in moderately reducing conditions. That the conditions were not strongly reducing (i.e. $pO_2 <$ *ca.* 10^{-10}atm) is indicated not only by the common presence of magnetite (often predominating over wustite) in most analysed slag samples but also by the generally low levels of iron (<8.5% on average per site) present in the suspended copper prills (see Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; compare to smelting experiments by Merkel 1990). On the other hand, the absence of minerals like delafossite ($Cu_2O.Fe_2O_3$) or primary cuprite (Cu_2O), and the presence of more than 1% iron in the prills from most sites suggest that smelting conditions were not too oxidising (i.e. $pO_2 >$ *ca.* 10^{-6}atm) either. Based on the above, it is argued that the partial pressure of oxygen in prehistoric copper-smelting processes in the southern Aegean ranged approximately between 10^{-6} and 10^{-10}atm (assuming smelting temperatures of *ca.* 1300°C). The smelting processes conducted at Skouries and Pounda on Kythnos and Konakia on Keros were the most reducing. This is indicated by the predominance of wustite over magnetite and/or the high levels of iron in the copper prills (see **Table 5.8**). In contrast, the least reducing smelting processes were those taking place at Aghios Symeon on Keos, where copper prills suspended in the slag are virtually free of iron (Papastamataki 1998), and at Sideri and Aspra Spitia on Kythnos, where the average iron content in the copper prills is only 1.2%.

It is interesting to note here the correlation between the furnace design and the redox conditions created during the smelting process. According to available analytical data, smelting processes conducted in perforated furnaces (i.e. at Chrysokamino, Sideri and Aspra Spitia) were less reducing than those conducted in closed shaft-furnaces (i.e. at Pounta and Skouries). This is suggested by the much lower levels of iron in the smelted copper from the former sites, which range from 1.2 to 2.2%, compared to those found at the latter sites, which range from 5.3 to 8.3%. This picture is not surprising: the presence of perforations on the smelting furnace allowed the penetration of the wind thus introducing more oxygen to the process. Further analytical work, including, for example, the study of slag from the open hearths from Seriphos (see above), will shed more light on the correlation between furnace design and redox conditions.

5.6.3 Copper losses in slag

Due to the complete liquefaction of the slag during smelting and the creation of a fairly reducing furnace atmosphere (see above), copper-smelting processes in the southern Aegean were characterised by low copper losses in the slag. The average copper contents in slag samples from various sites in this area is usually below 5% (**Figure 5.6**). Nonetheless, differences between sites are notable, the slag samples from Chrysokamino having the lowest levels of copper and those from Kephala the highest. How should these differences be interpreted? In other words, do differences in efficiency in slag/metal separation witnessed in the various sites reflect differences in the reducing capacity of the furnace atmosphere or differences in the viscosity of the slag?

Figure 5.7 shows the relationship between the amount of copper present in slag from Chrysokamino (multiple samples) and various smelting sites on Kythnos (average values), and the amount of iron dissolved in the suspended copper prills, the latter being a fairly accurate reflection of the redox conditions in the furnace during smelting. Two patterns are immediately visible on the diagram. On the one hand, there are small differences in the copper losses between the four Kythnian sites (Pounta, Lefkes, Sideri/Aspra Kellia and Skouries) despite the notable differences in the reducing capacity of the furnace atmosphere reflected in the different levels of iron in the prills. At these sites, therefore, copper losses appear to have been determined not so much by the redox conditions but rather by the mechanical suspension of copper prills due to the high viscosity of the slag. Similarly, the considerably higher efficiency (i.e. lower copper losses) of the smelting process at Chrysokamino is not related to the redox conditions. Indeed, the levels of iron in the copper prills in slag from Chrysokamino are similar to those suspended in the slag from the various Kythnian sites. What differentiates the smelting process at this site is, therefore, a better separation of the formed metal particles from the slag; a minimisation, that is, of the losses due to the *mechanical entrapment* of copper in the slag. How was this better separation achieved at this site?

Two mechanisms can be proposed. Firstly, the slag from Chrysokamino was probably less viscous allowing the easier sinking and coalescence of metal prills. This is well illustrated in **Plate 5.1**, which shows the abundance of small copper prills suspended in a slag sample from Sideri on Kythnos contrasting the rarity of such inclusions in a typical sample from Chrysokamino. The lower viscosity of the slag from Chrysokamino was probably achieved by conducting the smelt at temperatures well above its liquidus temperature. Secondly, after the completion of the smelting processes at Chrysokamino, the slag was finely crushed and often ground to retrieve any entrapped metallic particles. Although the crushing of slag is also evidenced in other smelting sites of the southern Aegean (Bassiakos and Philaniotou-Hadjianstasiou in press; Gale *et al* 1986; Stos-Gale 1989), nowhere was this process conducted with such thoroughness as it was at Chrysokamino (**Table**

5.10). At Skouries, Sideri and Aspra Spitia on Kythnos as well as in Avessalos and Kephala on Seriphos, for example, intact or semi-intact slag cakes are common.

5.6.4 Conclusions

In very general terms, EBA copper-smelting processes were conducted at *ca.* 1200-1400°C in a furnace atmosphere of pO_2 = *ca.* 10^{-6} to 10^{-10}atm. The slag was in all cases fully liquefied and copper-losses were maintained below 5%. Differences, however, did exist, resulting in variable levels of smelting efficiency. According to the evidence, higher levels of efficiency were achieved (i) by conducting the smelt at higher temperatures and (ii) by crushing the slag to retrieve entrapped metal inclusions after the completion of the smelt.

5.7 Addressing technological variability in copper-smelting practices in the EBA southern Aegean

The foregoing analysis of copper-smelting techniques in the EBA southern Aegean has brought forward a complex picture of differences and similarities. Although the appreciation of the full implications of this variability must await further analysis, which has not been possible here, some observations may still be discussed.

First of all, the evidence argues against a uniform southern Aegean "technological package" practised ubiquitously around this region. Despite the paucity of archaeological and analytical evidence, it has been possible to demonstrate that a range of alternative techniques was employed in each stage of the smelting process, from the selection of the raw materials to the post-smelting treatment of the slag (**Figure 5.8**). In fact, one of the most striking conclusions of the comparative analysis was that despite the sharing of some technical features, *there are no two known sites in the southern Aegean with identical copper-smelting technologies*, with the possible exception of the neighbouring sites of Sideri and Aspra Spitia on Kythnos. Undoubtedly, the limited chronological resolution of this analysis may have masked possible diachronic changes in copper-smelting technology. We should note, however, that technological variability is also pronounced among sites which are known to have been roughly contemporary, namely Raphina in Attica (EH II), Skouries on Kythnos and Kavos North on Keros (EC II), Kolonna on Aigina (EH III), and Chrysokamino in east Crete (EM III).

On the other hand, if these diverse sequences are broken down into their components, we can immediately notice that individual techniques, such as the use of iron-silicate slag, the addition of arsenical ingredients in the smelting charge or the use of perforated shaft furnaces are shared by geographically dispersed sites. That this may be taken to imply *direct exchange of information* among people engaged in copper-smelting activities is a valid assumption. First of all, none of the aforementioned techniques *could have been copied from the intermediate products or the finished artefacts* being instead only known to those physically present during the execution of the smelting operations (compare to Nakou 1995). Moreover, the inherent *mobility* of early Aegean copper metallurgy, involving the movement of people and materials from the metalliferous sources to the smelting and metalworking sites (Stos-Gale 1998) facilitated such contacts, which may have ranged from simple encounters to even occasional co-operations between diverse social groups in the course of metal procurement expeditions.

To this we will return in the next chapter. What needs to be emphasised here is that such conditions allowed at least some awareness on the part of those participating in smelting activities, of the technical variants at work during that time. The suite of techniques that each one of them actually employed in the course of his/her work were therefore *choices* in the true sense of the word. That is, they were selected from a range of (at least partly) known alternatives, which could be evaluated and then adopted, modified or totally rejected (see Lemonnier 1993: 9). This has important implications on our interpretation of technological variability in early copper-smelting practices in the southern Aegean. Although technical differences and similarities among different sites may partly reflect complex processes of transfer of technological knowledge, they should also be associated with *conscious* attempts by artisans to emphasise similarity (i.e. conformity) or difference (i.e. divergence) through the adoption, modification or rejection of available techniques. In other words, in their capacity as choices expressing personal/collective views about how things should be done, smelting techniques were actively involved in the construction of personal/collective identities of artisans involved in such productive activities.

5.8 Conclusions

An axiomatic statement was put forward at the beginning of this thesis, namely that *similar material ends can be generally reached from different technological paths.* This statement has been supported by the evidence presented in this chapter, which revealed a range of techniques employed in copper-smelting activities in the southern Aegean during the EBA. Indeed, although the local geology directed prehistoric exploitation in all areas to the oxidation zone of copper deposits, raw materials were processed in a variety of ways using different kinds of procedures and equipment. Undoubtedly, there remain many gaps in our understanding of this variability due mainly to the paucity of excavations and detailed analytical studies of copper-smelting sites, which leaves us with limited information on the smelting techniques at work during that time, in a largely unsettled chronological framework. Despite these limitations, however, it has been possible to argue not only that technological choices *were* available but also that they enabled early Aegean smelters to situate themselves in a broader framework of reference.

CHAPTER SIX

CONTEXTUALISING A TECHNOLOGICAL CHOICE:
Arsenical Copper Smelting in the Southern Aegean During the Early Bronze Age

6.1 Introduction

The aim of this thesis, as stated in Chapter 2, has been to show how *particular forms of technological knowledge* were *established* or *challenged* by early Aegean metallurgists, in the course of daily routines of production. The previous chapter made the first necessary step towards this end, by demonstrating the existence of alternative techniques in the execution of the various tasks of copper smelting, from the preparation of the ore to the post-smelting treatment of products and by-products. This chapter takes the argument further by investigating one case where alternative technical solutions were available for the achievement of the same material end, namely the *production of arsenical copper* in the southern Aegean during the EBA. It will be argued that the introduction of an arsenical mineral in the copper-smelting process, an ambiguous and potentially dangerous technological choice evidenced in a small number of sites in this area, was an attempt by certain artisans to appropriate an important material transformation thus claiming a privileged role for themselves among their peers.

6.2 The two techniques for the production of arsenical copper

As shown in the previous chapter (Section 5.4), arsenical copper was produced in the southern Aegean during the EBA in at least two different ways. The most common technique was to add an arsenical substance to melted copper before shaping it into artefacts. In three sites, namely Chrysokamino in east Crete, Kavos North on Keros and Skouries on Kythnos, however, arsenical copper was produced in smelting and, at least in the case of Chrysokamino, scientific analysis has shown that this probably involved the addition of an arsenical mineral in the charge.

What is important to emphasise, in the light of the above, is that the wide distribution of arsenical copper throughout the southern Aegean during the EBA does not reflect a uniform technology as previous studies (e.g. Mangou and Ioannou 1999; Muhly 1985) have assumed. The two techniques employed in this area for the production of this alloy had important technical differences. Firstly, being by nature a much less controlled process, the smelting of arsenical copper would have resulted not only in a more variable product but also in increased emission of highly toxic arsenical gases (Lechtman and Klein 1999; Tylecote *et al* 1977). This technical difficulty was probably even greater in the case of Chrysokamino, where the use of perforated furnaces created more oxidising conditions in the upper parts of the shaft (Section 4.17). Secondly, the production of arsenical copper during smelting reduced the level of flexibility in the subsequent metalworking stages, denying the option of preparing an alloy according to the particular requirements of the artefact in preparation. From a strictly technical point of view, it could, therefore, be argued that this technique imposed important technical limitations compared to the addition of an arsenical substance into melted copper.

However, to consider the smelting of arsenical copper along these lines may be misleading as it implies that techniques should be evaluated in terms of their supposed contribution to an agreed-upon end, which remained constant throughout the metallurgical sequence. In other words, we risk mistaking here the inevitable inter-dependence of consecutive technical actions for a harmonious co-operation to fulfill a shared objective, ultimately materialised in the finished artefact.

Functionalist interpretations of this kind, stemming from the study of decision-making processes from the end result backwards (see van der Leeuw 1989) are particularly problematic in the context of early copper metallurgy. The multiplicity and complexity of tasks involved - from the original discovery of an ore deposit to the last stroke of the hammer on the finished artefact - not only raised exceptional demands in reserves of labour and a wide range of skills, but also created the possibility for different people to participate in *different ways* and at *different points* during the process. There were inherent tensions in such a situation, emerging not the least from attempts to emphasise particular kinds of knowledge, and the authority that they sustained, potentially at the expense of others. In this ongoing process of redefinition of roles and statuses, technological choices (not only about *how* but also about *where, when, by whom* and *with whom* a particular task was to be carried out) were caught up in the negotiation of potentially conflicting interests among those involved in the productive process (Dobres 2000: 121-3).

It is important in this respect to note that arsenical copper had certain qualities that probably made it a particularly valued material in the EBA southern Aegean. Not only did this alloy have superior casting and mechanical properties compared to pure copper (e.g. Budd and Ottaway 1991; Charles 1967; Northover 1989; O'Brien 1999); it also acquired a distinctive silvery surface during casting through the inverse segregation phenomenon (Gillis 1999; Hosler 1988; La Niece and Carradice 1989; McKerrell and Tylecote 1972; Nakou 1997). Considering also that smelters and smiths in this area made conscious efforts to transform pure copper to arsenical copper, it is probably valid to argue that this alloy had a special place in the value system of southern Aegean societies. If this is accepted then it could be further argued that prestige lay with those possessing the knowledge and skill necessary for this material transformation. And given that arsenic could be introduced into copper in at least two stages in the metallurgical sequence (i.e. during smelting and metalworking), there could be multiple claims to the right to perform this status-enhancing activity.

From this perspective, it is argued here that particular groups engaged in copper-smelting activities in the southern Aegean during the EBA, introduced an arsenical ingredient in the smelting process in order to appropriate this important material transformation. What is more important, this strategy only became meaningful and efficient within broader spatial rearrangements of copper production activities in this area. To be more specific, the smelting of arsenical copper is only evidenced in particular spatial configurations, which not only established smelting as a *separate* and *vital stage* in the metallurgical sequence but also rendered technological choices and technical competence in the execution of smelting operations, *highly visible*. These spatial arrangements are discussed in detail in the following sections.

6.3 Current models on the spatial organisation of early Aegean copper production

The spatial distribution of the various stages of the metallurgical sequence in the EBA southern Aegean was first addressed by Broodbank (1989) and Nakou (1995) in the context of interpretive models for the emergence of social stratification during this period. The aim of both scholars was to identify the mechanism whereby metal production was controlled by emerging elites; a mechanism, which they believed was reflected in the spatial arrangement of production sites. From this point of departure, though from slightly different perspectives (Sections 2.4-5), both Broodbank (1993) and Nakou (1995) emphasised the spatial separation of Early Bronze Age metal production sites (i.e. mining and smelting sites) from contemporary settlements. According to Broodbank (1993, 2000: 294-6), this spatial separation of producers and consumers allowed large trading settlements, monopolizing long-distance maritime activity, to regulate the flow of metal from the production areas to settlements. Nakou (1995), on the other hand, interpreted the isolation of copper smelting sites as a strategy by particular groups of people to safeguard, and thus to monopolise, the necessary technical knowledge for the extraction of metal from its ores.

Despite their differences, the two models were based on the common premise that there existed a *single mechanism of control* of metal production, which must be reflected in a similarly *common underlying pattern* in its spatial organisation. As a consequence of this assumption (and due to the limited number of smelting sites known at the time), their spatial analysis sought to stress conformity and reduce variability. The evidence presented below, however, suggests that copper-smelting activities in the EBA southern Aegean were taking place in a variety of contexts, each of which emphasised particular technical roles and actions and created different conditions for the communication of these actions between the participants and the broader population. This should not come as a surprise because, if we have been right to argue that there existed potentially conflicting interests within the heterogeneous groups of people involved in copper production, we should expect multiple and often contradicting strategies to have been employed in the negotiation of power and authority among them.

6.4 The procurement of copper ores

Before investigating the particular contexts of copper-smelting activities, it is necessary to take a step backwards to examine the geological background of southeastern Aegean and the ways in which copper-ore procurement was organised during the EBA.

Massive copper deposits are unknown in the southern Aegean (Marinos 1982; Stos-Gale 1998). The procurement of copper ores during the EBA was based instead on the exploitation of small-to-medium outcrops of oxidised minerals, similar to those reported from the Kythnian mining sites of Cape Tzoulis, Petra and Aspra Kellia on Kythnos (Bassiakos and Hadjianastasiou-Philaniotou in press; Stos-Gale 1998). Such copper occurrences were probably found in greater abundance in specific areas, like the island of Kythnos or the Lauriotic peninsula (Stos-Gale and McDonald 1991), but were also present throughout the southern Aegean. Indeed, recent fieldwork and isotopic studies have revealed possible evidence for the prehistoric exploitation of many copper mineralisations on the Aegean islands (e.g. Bassiakos and Doumas 1998; Papadopoulos 2002; Philaniotou-Hadjianastasiou 2000; Stos-Gale 1998), the Greek Mainland (McGeehan-Liritzis 1988; Maxwell *et al* 2002; Risberg *et al* 2002) and Crete (Stos-Gale 1993, 1998) (**Map 6.1**). Even in the richer source-areas, however, surface copper occurrences were probably scattered rather than concentrated into large ore-bodies (Kayafa *et al* 1997: 43; Stos-Gale 1989; 1993).

Against this geological background, it seems rather unlikely that the acquisition of copper ores relied on the long-term exploitation of single ore-bodies. Given also the apparent lack of permanent settlements in the vicinity of copper deposits (Broodbank 1993; Nakou 1995), we could argue that ore-procurement involved extensive expeditions to source-areas for the discovery of new copper occurrences followed by short episodes of intensive mining activity for their exploitation (cf. Broodbank 2000: 294; Stos-Gale 1998; see also Buleli 1993; Terry Childs 1998). What this picture suggests is that the procurement of copper ores - the first task in the copper production sequence - was an activity characterised by increased mobility or better, a *lack of permanence and spatial specificity.*

6.5 "Exceptional" contexts of copper-smelting activities

Copper-smelting activities in the EBA southern Aegean were often caught up in this continuous movement from one location to another imposed by the local ore geology. Indeed, small slag concentrations found in the vicinity of surface copper occurrences in this area seem to represent a practice whereby each newly discovered deposit was mined and the ores smelted at once at a suitable nearby location. Such sites include the smaller slag scatters on *Kythnos*, the slag deposit at *Aghios Symeon on Keos* (located near a sulphidic Fe-Cu deposit with surface oxidised outcrops), as well as *Konakia on Keros* and *Petalloura on eastern Siphnos*, both found near weak secondary iron-copper mineralisations (Bassiakos and Doumas 1998; Bassiakos and Philaniotou-Hadjianastasiou in press; Philaniotou-Hadjianastasiou 2000; Papastamataki 1998: 765). The same appears also to be the case for the larger slag concentrations at *Sideri and Aspra Spitia on Kythnos* since the amount of slag found there can be accounted for by the comparatively large nearby mineralisations at Petra and Aspra Kellia (see Bassiakos and Philaniotou-Hadjianastasiou in press).

Carrying out smelting operations at transient locations was thus a common practice in the southern Aegean, as indicated by the large number of small slag scatters inside the mineralised regions. Yet, it was certainly not the only one. As shown in this section, there is an increasing amount of evidence suggesting that certain smelting activities were spatially detached from the mining of ore deposits, taking place instead in permanent locations and in the presence of outsiders. These "exceptional" cases fall into two categories. The first includes smelting sites located near or inside habitation areas. The second is best represented by the site of Skouries on Kythnos (but possibly also includes the large slag heaps at Avessalos and Kephala on

Seriphos), where it appears that diverse social groups gathered for the execution of smelting operations.

6.5.1 Copper-smelting near habitation areas

Contrary to what Broodbank (1993) and Nakou (1995) have argued in the past, there is strong evidence from at least four sites in the EBA southern Aegean for the smelting of copper-ores near habitation areas (**Map 6.2**). At *Kolonna*, the smelting installation is located inside the settlement (Walter and Felten 1981: 23). At *Raphina*, the metallurgical pits are about 100-150m from the excavated part of the settlement (Theocharis 1952: fig.1). The slag scatter at *Kavos North* is found at about 50 meters from the site of Daskaleio (Broodbank 2000: fig. 67). Finally, the smelting site of *Chrysokamino* on eastern Crete is located on the fringes of the most fertile soils of the entire Kavousi plain, where archaeological survey has identified notable EBA sherd concentrations (Betancourt *et al* 1999: fig.4; Haggis 2002: fig.7.1) (**Map 6.3**).

An important observation is that direct or indirect involvement of "outsiders" is implied by the inclusion within these "smelting events" of other activities, such as the preparation and consumption of food and drink, or their association with exceptional places or landmarks. Cooking vessels and decorated tableware are reported at Chrysokamino (Betancourt *et al* 1999: 356). The same is true for Raphina where large quantities of pottery, much of it decorated, were recovered from the fill of one of the two smelting pits (mixed with the smelting debris) and from a small building found next to it (Theocharis 1951: 79-80, 1952: fig.2). Turning to Kolonna, the smelting installation was constructed during the fourth phase of the settlement on the ruins of the earlier Corridor House (Walter and Felten 1981: 23), thus making a direct reference to the history of this exceptional building. As for Kavos North, smelting activities were performed near the site of Daskaleio-Kavos which, either as a pan-Cycladic sanctuary (Renfrew 1984) or as a central settlement of southeastern Cyclades (Broodbank 2000: 225-36), hosted unique ritual activities inferred from the rich and diverse material of the "special deposit" (including a unique concentration of marble figurine fragments and vessels).

To summarise, the evidence from these four sites, two of which have yielded evidence for the smelting of arsenical copper, reflect a different spatial configuration of copper production. Ores, probably collected during procurement expeditions to mineralised regions, were smelted in the vicinity of habitation areas and, although critical aspects of the process were probably kept hidden from sight, the evidence suggests that these events attracted and took place in the presence of a broader audience.

6.5.2 Copper-smelting at Skouries on Kythnos

Even a cursory glance at known EBA smelting sites reveals the marked differences in size between the numerous small slag scatters of some hundreds of kilograms and the much rarer massive heaps weighing thousands of tons. Using a range of 20 to 40kg of slag per smelt (which is a reasonable guess given the large size of preserved smelting furnaces from this period; see Section 5.5), the number of smelting operations represented in each slag deposit can be estimated (**Table 6.1**). Despite the obvious uncertainty in the calculations, it is still possible to distinguish between large heaps produced by hundreds of thousands (or even millions in the case of Avessalos) of smelts, and smaller scatters that represent some tens or hundreds of smelting operations.

Such differences of scale have not gone unnoticed by students of early copper metallurgy in the southern Aegean. The EC II site of Skouries on Kythnos, as the only dated and better studied example of massive slag heap in this area, has been the focus of particular attention. The amount of slag from this site, exceeding the size of small individual copper occurrences on the island of Kythnos, did not simply indicate the large scale of production. It also suggested that ores from many sources were carried there to be processed. Lead isotope analysis on slag samples has indeed produced dispersed measurements that could be associated with multiple ore deposits, some perhaps outside the island of Kythnos (Stos-Gale 1993, 1998). Adding to this the fact that most copper-based artefacts in the southern Aegean seemed to be isotopically consistent with the copper produced at this site (Stos-Gale 1993, 1998), it is hardly surprising that the site at Skouries has often been interpreted as a “large-scale enterprise” that played a central role in early Aegean copper metallurgy (Stos-Gale 1998: 724).

The view of Skouries as a *large production unit* can be, however, challenged by a careful examination of the archaeological evidence from this site. Important, in this respect, are the approximately twenty circular structures present there. They are built from schist slabs with a maximum diameter of 4m and a wall thickness of approximately 0.5m (Hadjianastasiou and McGillivray 1988; Stos-Gale 1989) (**Plate 6.1**). Although the role of these structures remains at present unresolved, their unique architecture and the absence of any typical domestic evidence from their interior do seem to indicate a special function associated with the metallurgical activities on the site (Hadjianastasiou and McGillivray 1988). Along these lines, their interpretation has varied from shelters for furnaces (in the presence of a small bowl-furnace on the floor of the single excavated structure) to shelters for the crushing of ores or slag (Kayafa *et al* 1997). While it was the obvious problems of operating a smelting furnace in a closed space which probably led into questioning the contemporaneity of the excavated structure and the bowl-furnace (Stos-Gale 1989), a different interpretation, which would allow for the operation of smelting furnaces at their interior, is that they were stone ‘fences’ similar to those discovered at Site 30 in Timna (Rothenberg 1990: fig.18) (**Plate 6.2**).

In either case, it is the presence on the same site of multiple structures serving the same function that is the most intriguing. Although it cannot at present be established that they were all contemporary, the investment in their construction indicating a long period of use, the fact that Skouries was a single-period site, and the horizontal expansion of the structure-complex seem to suggest that some of them did co-exist. If this is correct, then we may envisage the execution of similar metallurgical tasks by different groups of people in separate structures at the site.

Rather than offhandedly interpreting this as yet another reflection of the scale of production at Skouries, it is important to emphasise the contrast between the large number of circular structures, on the one hand, and their small size on the other. Indeed, the floor area of the largest examples is *ca.* 7m^2, a value comparable to the floor areas of *individual rooms* in EBA domestic contexts (e.g. Room 89 at Myrtos

Fournou Korifi: Warren 1972: fig. 28; Room A at Raphina: Theocharis 1952: fig. 5; Thermi I: Lamb 1936, Plan 1). Considering that the structures were not metallurgical installations *per se* but rather constituted a special type of architecture that hosted specific metallurgical activities, their dimensions and relative location should therefore inform us on how those activities were spatially arranged (cf. Doonan 1999). From this perspective, one could regard the circular structures as *demarcating* separate working areas effecting the *fragmentation* of the apparently large labour-force into distinct workgroups (cf. Edmonds 1993). A contrasting picture thus emerges with small groups, on the one hand, of about 3 to 5 persons, working in those narrow spaces in close co-operation, and an assemblage of many such groups, on the other, performing similar tasks in small distance *but also in restricted view* from one another. Moreover, the differences in size (Hadjianastasiou and McGillivray 1988) and the spatial dispersion of the circular structures (Stos-Gale 1998) probably indicate a process of gradual agglomeration rather than a single building episode. These observations seem to question the 'industry-model', indicating instead that Skouries was a place that attracted *different groups of people*, possibly from diverse geographical backgrounds, for the performance of smelting activities (cf. Broodbank 2000: 294). Considering also the number of smelting operations represented in the accumulated debris (*ca.* 125,000-250,000), we could also argue that such events took place at Skouries over a long period of time. Whether such groups originated from within Cyclades, as the surface finds from the site seem to suggest, or people from other parts of the southern Aegean also participated in these events, remains to be shown by future excavations at the site.

Although various environmental advantages have been emphasised (e.g. exposure to strong winds, flux resources: Stos-Gale 1993) those were available in numerous locations on Kythnos, so there is no reason to suggest that it was the *particular features* of the area at Skouries that attracted smelting expeditions there. Unlike the two obsidian outcrops at Melos where the concentration of natural resources invited repeated episodes of quarrying activity (Torrence 1986), Skouries should probably be viewed as a nodal point *created* through the realignment of the routes of copper-production expeditions. To seek for a single motivation behind this process would be to ignore the complex dynamics of development of a site with a long history of use. What we *could* argue, however, is that the coming together of various groups at the site was a central part of its history and probably one that would have attracted more people to participate.

Though the lack of systematic excavations at the site obviously constrains interpretation, the few glimpses that we can catch suggest that those encounters were formalised events. The considerable labour-investment necessary for the construction of each circular structure shows not only pronounced commitment to that place but also an effort to order movement and action in the site. A preliminary survey has indeed indicated that different tasks of the smelting process (beneficiation, smelting and slag crushing) were carried out in different areas of the site (Stos-Gale 1998), thus suggesting the operation of specific spatial rules. The range of other activities, that those events entailed remains largely elusive but we could speculate that a variety of social transactions may have taken place among the gathered groups. Social ties could have been established and reworked through the exchange of information and gifts, perhaps also the reciprocal exchange of skilled labour and raw materials for the execution of the metallurgical tasks.

While it was the presence of the circular structures that permitted the view of Skouries as a locus of encounters between diverse social groups engaged in copper smelting activities, we could probably envisage similar events taking place at other smelting sites during that time, the strongest candidates being the large slag heaps at Kephala and Avessalos on Seriphos. This model has intriguing implications. Firstly, such events may have been partly responsible for the direct exchange of technical information, which is reflected in the sharing of "invisible" technical elements between spatially dispersed copper-smelting sites (see Section 5.7). Moreover, if these large copper-smelting sites prove in the future to be roughly contemporary, they could reveal the presence of multiple, and possibly competing, allegiances formed between the various groups in the southern Aegean engaged in the production of copper. Unfortunately, such arguments cannot be further developed before future excavations provide the necessary material evidence. Nonetheless, working with such questions in mind, may channel the study of the large smelting sites in the southern Aegean along more fruitful paths.

6.5.3 A note on chronology

As both the settlements with smelting evidence and the site of Skouries date to the second half of the EBA (i.e. EB 2-3 periods), one could be tempted to suggest that it was during that time that smelting activities became spatially separated from ore procurement. Two points argue against this suggestion. Firstly, all small scatters discovered near ore deposits remain poorly dated so it is possible that some of them also date to the late EBA. More importantly, though, copper smelting remains have also been found inside the FN settlement of Kephala on Keos so this practice is evidenced already from the beginnings of the 3rd millennium BC. Whether a chronological pattern actually exists is, therefore, a question that can only be resolved with future fieldwork, excavation and scientific dating of more prehistoric copper-smelting sites in this area.

6.6 Conspicuous production and the smelting of arsenical copper

The previous section established the contextual "exceptionality" of certain copper-smelting activities. What makes this important for this discussion is that among these exceptional sites were those with evidence for the smelting of arsenical copper. Rather than viewing this as a mere coincidence, we should investigate the particular conditions created by the conduct of smelting operations in such contexts and how these conditions promoted the development of this uncommon smelting technique.

In this vein, we should note, first of all, that the spatial separation of the tasks involved in copper production, namely the procurement of ore and its smelting to produce metal, stressed the distribution of roles among those engaged in such activities. It may be true that due to the complexity of the various technical tasks, it was probably always the case that "some people...[were] better at finding the right mineral, others at preparing the smelting charges and/or extracting and melting together the metal prills" (Stos-Gale 1998: 723). This inherent division of tasks, however, was not given equal weight in all cases. When smelting activities were conducted near the areas of ore procurement (i.e. the mined copper deposits), for instance, all members of the workgroup operated in total isolation from outsiders. In this context, any distribution of roles among individuals could have been known only to the workgroup itself. Moreover, working in close proximity to one another may have promoted a more flexible organisation of production, in which those specialised in one particular activity could also participate in the execution of other tasks in the production sequence. Evidence for this practice may be found at the site of Sideri, where pieces of slag were used as tools, most likely to crush the ore in preparation for the smelting process (Bassiakos pers.com.). This use of by-products of one activity (smelting) as tools for another (ore preparation) could indeed be taken to reflect a close cooperation between "specialists" in the workgroup. In contrast, the spatial separation of copper smelting from ore procurement, as reflected in the "exceptional" smelting sites, brought this inherent division of labour into sharp relief, especially since smelting activities were conducted in the presence of others. In this context, those engaged in copper-smelting activities could be distinguished from those involved in the procurement of ore, each being associated with the particular task that he or she undertook in the production sequence.

The two spatial configurations of copper production could be therefore taken to reflect different strategies of manipulation of the inherent diversity of tasks involved in copper production in order to promote specific categorisations of human activity and -by extension- specific personal and group identities. To be more specific, whereas the conduct of ore procurement and smelting activities in close proximity to one another emphasised the unity of copper-production and hence more the idea of participation than the specific role of each individual in the process, the allocation of particular places for the execution of copper smelting had the opposite effect.

It is, in fact, very tempting to read in the spatial separation of copper smelting activities an underlying effort by early Aegean smelters to "exalt" their craft, making it both visible and distinguishable from other technical tasks involved in copper production (compare to Reid and McLean 1995). This is further supported by the contextual evidence from these "exceptional" smelting sites, which reflects a special concern with elaborating the entire event. We could thus recall the evidence for the preparation and consumption of food at Chrysokamino and Raphina, the association of smelting activities with important landmarks, such as the ruins of the Corridor House at Kolonna or the special deposit at Daskaleio-Kavos, and the general picture of formality evidenced at Skouries (Sections 6.5.1-2). A similar effect, namely the elaboration and privileging of the smelting process, may have also been effected by the very act of assigning *permanent* locations for the conduct of such activities. This contrasted with the inherent lack of spatial specificity of ore procurement expeditions (Section 6.4), allowing smelting loci to emerge as *points of reference*; places, that is, which drew together spatially dispersed activities at particular moments. In conclusion, it could be argued that the conduct of smelting operations at these "exceptional" sites was underpinned by strategies to elevate the role of particular individuals and/or groups in the production of copper.

Such strategies were further promoted by the fact that the actions of smelting groups in such contexts were highly visible. The scale and composition of the audience was, of course, different in each occasion. At smelting sites near habitation areas it may have consisted of people from the broader population, whereas at the site of Skouries (and other large smelting sites) of the diverse groups that worked there side-by-side. In both cases, however, smelting activities were made into "arenas" in which technical competence was highly conspicuous, and the success or failure in the performance of roles had direct repercussions on the status of craftsmen to the eyes of the participants (see Dobres 1995; Ingold 1993). The entire event could thus easily revert to (or always was) a competition among participating craftsmen to negotiate their authority, consolidating or upgrading their role in the process (see Schmidt 1997: 87-90). Competitive performance could have operated either within a group cooperating for the execution of a smelting process or among different groups undertaking the same task. The latter was certainly the case at the site of Skouries where diverse groups gathered for the conduct of smelting activities. Similarly, the presence of two metallurgical pits at Raphina at a distance of *ca.* 15m from one another (Theocharis 1952: 134), if proven contemporary, may suggest that competing groups may have existed even within the same village community.

It was in such occasions, where authority and reputation were negotiated through direct comparisons between technical actors, and competitive performance was at the core of the event, that the uncommon practice of introducing an arsenical ingredient in the smelting process emerged. As already argued in Section 6.2, the production of arsenical copper was an important material transformation, which could bestow reputation and prestige to artisans displaying competence in its performance. From this perspective, the incorporation of this transformation in the copper-smelting process in such a *conspicuous way* could be interpreted as an attempt on the part of particular individuals and/or groups of individuals engaged in copper-smelting activities to earn reputation and status among their peers and the broader community. It was not important, in this context, whether the smelting of arsenical copper had technical limitations compared to other alloying techniques (see Section 6.2) because the entire event was structured so as to draw attention to the process of smelting downplaying the tasks that preceded or succeeded it in the metallurgical sequence. After all, this technological choice was not so much about optimising the smelting process or, for that matter, the entire sequence of tasks leading to the manufacture of copper-based artefacts. Rather, it was about redefining the social relations of copper production, challenging existing norms about how arsenical copper should be produced and by whom. And as such, it should be viewed as part of broader strategies that aimed to elevate the place and status of copper-smelting activities (and those artisans associated with them) in the metallurgical sequence.

6.7 Metallurgical technology and power in the EBA southern Aegean

The foregoing analysis has serious implications for models that have attempted to address the place of metal production in the articulation of power relations in the EBA southern Aegean. These models have, as a rule, sought to identify a single mechanism whereby particular groups of people controlled the production of metal artefacts appropriating their empowering potential (e.g. Day and Wilson 2002; Broodbank 1993; Manning 1994; Nakou 1995). Technological knowledge, in this context, was viewed as a resource that could be monopolised, facilitating the control of metal production (Nakou 1995; see also Carter 1998; Day *et al* 1998).

This thesis took a rather different stance. Although accepting that differential access to technological knowledge acted as an index for social differentiation, it was further argued that social rules about *how* things should be made and *by whom* could be challenged in the unfolding of the metallurgical sequence. Metal production was a multifarious project demanding various forms of co-operation, on the one hand, and a distribution of roles on the other. This differential participation in the process offered possibilities for various kinds of personal and group identities to be defined and expressed. In this respect, Broodbank (2000: 299) has been right to argue that the status of artisans probably varied with the precise stage of the metallurgical process in which they were involved. As demonstrated in this chapter, however, such reputation and status were not fixed or uncontested. Rather, various strategies were employed in order to elevate particular tasks in the metallurgical sequence potentially at the expense of others. Such strategies are reflected, for example, in the various spatial configurations of copper production activities in the EBA southern Aegean. Moreover, the example of arsenical-copper smelting has shown that technological choices were also implicated in the negotiation of reputation and authority of those engaged in metallurgical activities.

Georgia Nakou (1995) has proposed the division of the metallurgical sequence into "critical" stages, including the procurement of ores and their smelting for the production of metal, and "non-critical" stages, including the various tasks for the shaping of metal into artefacts. According to this model, it was by controlling the "critical" stages of the process that social groups attained exceptional power in the southern Aegean during the Early Bronze Age. Following from the foregoing discussion, it could be argued, instead, that the relative importance of a stage in the sequence was not pre-given but defined and negotiated in practice.

CHAPTER SEVEN

CONCLUSIONS AND FURTHER WORK

7.1 Introduction

The purpose of this thesis has been to present an alternative framework and methodology for the study of metallurgical technology in the EBA southern Aegean. Throughout the preceding chapters it was argued that prehistoric technologies were social arenas in which conflicting interests could be defined, expressed and negotiated. The adoption of particular techniques and the rejection of others, the display of technical competence or the inability to successfully carry out a particular task, all could promote or undermine the reputation and authority of those engaged in metallurgical production. To investigate these dimensions of early Aegean metallurgy a three-fold methodology was proposed, including (i) a detailed description of techniques; (ii) a comparative technological study; and (iii) a contextual analysis of metallurgical activities. These three tasks were carried out in Chapters 4, 5 and 6. This chapter summarises the conclusions and outlines questions for future research in this field.

7.2 Reconstruction of the copper-smelting process at Chrysokamino

Chapter 4 demonstrated the potential of a methodology integrating archaeological evidence with analytical information, in the reconstruction of early copper-smelting processes. The EM site of Chrysokamino in northeastern Crete, being the only copper-smelting site in the EBA southern Aegean to have been systematically excavated, offered an ideal case study for this purpose. Appreciating the multi-faceted character of copper smelting technology, a multi-analytical methodology was employed, which integrated macroscopic, microscopic, chemical, and electronic information from the analysis of ore and slag samples from the site. The following conclusions, concerning the smelting technology evidenced at this site, were reached:

1. Siliceous oxidised ores, fluxed with a lime-rich iron ore (possibly of local origin), were the main raw materials. An arsenical ingredient, containing some nickel, was probably also added to the smelting charge to promote the production of arsenical copper.
2. High temperatures (at least 1300°C) were attained in the combustion zone of the furnace and the atmosphere was fairly reducing, the pO_2 ranging between 10^{-10} and 10^{-7}atm. The introduction of perforations on the furnace shaft raised the temperature higher up the stack, allowing the raw materials to be preheated before reaching the combustion zone, resulting in a better fusion and the formation of a fluid slag. The introduction of more oxygen in the system did not affect significantly the reduction of copper oxides but probably caused some arsenic to be lost due to volatilisation.
3. Copper losses in the slag were generally low, not exceeding the 1 wt-%. This was achieved (i) by forming a fluid slag allowing copper to coalesce into sizeable nodules, some forming an ingot at the bottom of the furnace, and (ii) by thoroughly crushing the slag after the completion of the smelt in order to retrieve any entrapped metal.
4. The product of the smelting process was metallic copper containing arsenic, iron, nickel and a small amount of high-grade matte inclusions. A refining process was, therefore, necessary in order to purify the metal before shaping it into useful objects.

Although this thesis has hopefully offered many insights into the smelting process at Chrysokamino, there are certain issues that need to be further investigated. Firstly, the use of an arsenical ingredient in the smelting process is a hypothesis which has been based on the low levels of arsenic and nickel in the smelted copper ores. However, only three ore samples from Chrysokamino could be analysed in this thesis, using a technique (i.e. SEM-EDS) with limitations in the measurement of elements at low concentrations. To confirm this hypothesis, a larger number of ore samples needs to be analysed using a more appropriate analytical technique, such as Neutron Activation Analysis (NAA) or Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

The behaviour of the perforated furnaces at Chrysokamino during smelting also needs to be further investigated. In this thesis, it was argued that the presence of perforations in the shaft raised the temperature in the upper parts of the furnace creating also more oxidising conditions. Given, however, the complexity of the phenomenon, air being jointly supplied by the wind penetrating from the perforations and the bellows at the bottom of the shaft, it is impossible to offer a more accurate reconstruction of the T/pO_2 profile of the furnace. This can only be achieved by conducting smelting experiments designed in such a way as to replicate the conditions at Chrysokamino. In other words, it is necessary (i) to prepare pot-bellows similar to those evidenced at Chrysokamino, and (ii) to simulate the strong winds prevailing at this site, either by conducting the smelt in a location exposed to wind or by using a motor-fan. The temperature at various positions on the shaft can be directly measured using thermocouples while the redox conditions can be estimated from the analysis of the products and by-products of the process.

Finally, the study of the metallurgical remains from Chrysokamino raises important questions concerning the use of lead isotope analysis for the provenancing of early Aegean metal artefacts. To be more specific, the ferrous flux and the arsenical ingredient used in the smelting process probably had some contribution to the isotopic composition of the smelted copper and the slag. Consequently, any attempt to associate the slag from Chrysokamino or any artefacts made of copper produced at this site with specific copper deposits based on lead isotopes alone, may produce misleading results. The site of Chrysokamino, which has yielded pieces of copper ore, flux and slag, offers an ideal case study for an analytical project investigating possible changes in the isotopic composition of copper during smelting caused by the use of multiple raw materials.

7.3 Comparative analysis of copper-smelting techniques in the EBA southern Aegean

Chapter 5 offered the first comparative study of early copper-smelting techniques in the southern Aegean. Available archaeological and analytical evidence were examined and major technical aspects of the smelting process were investigated, revealing a complex picture of technical differences and similarities between various smelting sites:

1. Copper production in the southern Aegean during the EBA was based on the smelting of ores from the oxidation zone of copper deposits. In contrast, the low copper grade of local sulphidic deposits did not allow their exploitation in prehistory.
2. Various techniques were probably employed for the preparation of the charge, ensuring the formation of liquid slag during smelting. These may have ranged from the careful selection of ore pieces with appropriate quartz to iron ratio or the removal of any excess quartz or iron oxide, to the mixing of iron-rich with silica-rich pieces of copper ore from the same or different deposits or the use of siliceous or ferrous fluxes.
3. Currently available evidence suggests that arsenical copper was intentionally produced in the southern Aegean during the EBA. Two different alloying techniques were identified. The first (and more common) technique was the addition of an arsenical mineral to melted copper while the second technique, evidenced in three sites, involved the *conscious* use of arsenic-rich raw materials in the smelting process.
4. Various types of smelting furnaces are evidenced in this area. Perforated shaft furnaces, which are unknown outside the southern Aegean, were used over a long period of time spanning from the FN to the end of the EBA. Non-perforated shaft furnaces are known from Kythnos and Seriphos. Finally, a peculiar installation, probably associated with copper smelting, has been reported from Kolonna on Aigina, and two open hearths, of unknown but probably early date, have been found on the island of Seriphos.
5. Most smelting processes in this area took place at high temperatures (>1100-1200°C) and in moderate redox conditions ($pO_2 = 10^{-10}$-10^{-6}atm). Although

copper losses were low in most cases, differences in the levels of efficiency were notable. According to the evidence, higher levels of efficiency were achieved (i) by conducting the smelt at higher temperatures and (ii) by crushing the slag to retrieve entrapped metal inclusions after the completion of the smelt.

There remain, of course, many gaps in our understanding of technological variability in early Aegean copper-smelting practices, which need to be addressed by future research in this area. Of utmost importance is the systematic excavation of metallurgical sites, not only to recover a more complete record of prehistoric smelting technologies but also to allow the construction of a firm chronological framework for comparative analysis. Equally important, however, is the development of a standardised analytical methodology for the reconstruction of smelting techniques in this area. The clear definition and separate investigation of the most important aspects of the process (i.e. mass balance, smelting conditions and slag/metal separation), proposed in this study, may be a first step in this direction, articulating a firm set of questions that need to be addressed in all analytical studies of early smelting technologies.

7.4 Arsenical copper smelting in context

Chapter 6 demonstrated the potential of contextual analysis in the study of the social dynamics of prehistoric technologies. Analysis concentrated on an ambiguous and potentially dangerous technological practice, namely the use of arsenic-rich raw materials in the copper smelting process, evidenced in a small number of sites in the EBA southern Aegean. The contextual analysis showed that this technique seems to have been practiced in exceptional occasions, in which smelting emerged as a separate and vital stage in the metallurgical sequence, and the actions of smelting groups were highly visible. In such events, where direct comparisons could be made between different technical actors and people "jockeyed" for social position and recognition, the appropriation of an important material transformation (i.e. the transformation of pure copper to arsenical copper) was a very efficient strategy. This technological choice should be thus viewed as part of broader strategies that aimed to elevate the place and status of particular people engaged in copper-smelting activities.

This approach to the analysis of prehistoric technology could enhance future research on early Aegean metallurgy if also applied to the study of other technical tasks in the metallurgical sequence. In this endeavour, the detailed reconstruction of technological choices is, undoubtedly, of great importance. Equally necessary, however, is the broadening of the scope of analysis, encompassing not only the material remains of metallurgical activities but also the social contexts in which such activities were carried out. This is certainly a challenging task but one that can promote a more human-centred understanding of technology therefore bridging the gap between archaeometallurgy and archaeology in this area.

7.5 Concluding comments

As Patrick McGovern (1995) has rightly argued, it is for archaeologists to decide whether any form of science, which has found its way into archaeology, produces worthwhile results. Unfortunately, analytical studies of metallurgical technology in the Early Bronze Age Aegean have failed to respond to the new demands of archaeological research in this area and have thus become marginalised. It is, therefore, essential that we redefine our discipline, setting a new agenda that is (or can prove to be) relevant to the current archaeological discourse. Hopefully, this thesis has made a small step in this direction.

APPENDIX

STATISTICAL EVALUATION OF ANALYTICAL RESULTS

of Scanning Electron Microscopy – Energy Dispersive Spectroscopy

A.1 Estimation of accuracy and precision of the SEM-EDS analysis using test-samples

For a first evaluation of the results obtained by the SEM-EDS instrument, replicate analyses were conducted using test-samples of known composition. The standard deviation and mean relative error of each determined oxide were calculated and used for the expression of the precision and the accuracy of the analysis.

Precision is the degree of agreement between replicate measurements of the same quantity (Christian 1994: 22). In this study, precision is expressed by *two times the estimated standard deviation* (2s) and by *two times the relative standard deviation* (2RSD) of the replicate measurements. The estimated standard deviation (s) of a finite set of experimental data (<30) is given by the following expression:

$$\mathbf{s = \sqrt{\Sigma\, (x_i - x_m)^2 \,/\, (N-1)}}$$

where x_i is the ith measurement, x_m is the mean value of the measurements and N is the number of measurements. The relative standard deviation (RSD) is the standard deviation expressed as a percentage of the mean:

$$\mathbf{RSD = 100 \cdot s / x_m\ (\%)}$$

where s is the estimated standard deviation and x_m is the mean value of the measurements.

Accuracy is the degree of agreement between a measured value and the accepted true value (Christian 1994: 22). In this study, accuracy is expressed by the *mean error* (ME) and the *mean relative error* (MRE). The mean error (ME) of a finite set of experimental data is the difference between the accepted true value and the mean value of the experimental measurements:

$$\mathbf{ME = x_m - x_o}$$

where x_m is the mean of the experimental data and x_o is the accepted true value. The relative mean error (RME) is the mean error expressed as a percentage of the accepted true value:

$$\mathbf{RME = ME / x_o\ (\%)}$$

where ME is the mean error and x_o is the accepted true value.

A.1.1 Analysis of test-sample SRM 2711

The material used in the first test-sample was the soil standard SRM 2711 of the National Institute of Standards & Technology, Department of Commerce, USA (**Table A.1**). Thirteen (13) replicate analyses were conducted and the concentration of eight major and minor oxides was determined. As seen in **Figure A.1**, there is a strong correlation between the precision of the analysis and the concentration of the determined oxide. The only oxide not conforming to this pattern is that of sodium (Na_2O), which shows poorer precision due to its volatilisation during EDS analysis. If this oxide is not taken into consideration, however, the estimated precision of the analysis is very satisfactory. To be more specific, according to the results of regression analysis, $2RSD = 21.506\ x_m^{-0.4858}$.

Therefore:

- For **major oxides** (> 1%) the 2RSD is less than 7% (relative value).

- For **minor oxides** with concentrations ≥0.2% the 2RSD is less than 50% (relative value) reaching the 21% at concentrations near 1%.

Indicative values of 2s and 2RSD for various concentrations are given below in tabular form:

x_m (%)	2s	2RSD
0.2	± 0.09	± 47.00%
0.5	± 0.15	± 30.12%
1	± 0.22	± 21.51%
2	± 0.31	± 15.36%
5	± 0.49	± 9.84%
10	± 0.70	± 7.03%
20	± 1.00	± 5.02%
50	± 1.60	± 3.22%

The mean error and the relative mean error of the measurements of the various oxides, as calculated from the certified concentrations in the standard, are given in **Table A.1**; the mean error is plotted in **Figure A.2.** For most oxides, the difference between the mean measured value and the certified value is less than 0.7s, suggesting that systematic errors, if any, are not significant in comparison to the precision of the analysis. However, there are two exceptions in this pattern: magnesia (MgO) and iron oxide (FeO) which show negative errors in the order of 1.4s and 1.6s respectively, i.e. significant in comparison to the precision of the analysis. Errors in the determination of magnesia are not important for the purposes of this study because this oxide, although commonly found in early copper slags, is a minor component and has no interpretative value. This is not the case, however, for iron, which is an important component of the slag and all the metallic phases suspended in it. Any significant bias in the determination of iron can therefore influence the reconstruction of the smelting process.

A.1.2 Analysis of test-sample TS2

Careful microscopic examination of test-sample SRM 2711 revealed that iron is mainly found in rare iron-oxide particles embedded in the soil matrix. It may, therefore, be the case that these rare particles have often been 'missed' during analysis thus introducing a systematic negative error in the measurement of iron. To test this hypothesis, a second test-sample (TS2) was prepared from weighed quantities of (99.99% purity) silica, alumina, calcium carbonate and iron oxide (**Table A.2**). To avoid problems of inhomogeneity, the pelletised sample was this time placed on a platinum foil and heated to a temperature of *ca.* 1300°C to ensure fusion of the oxides.

Ten (10) replicate analyses were conducted determining the concentration of the four oxides (**Table A.2**). As expected, the homogenisation of the sample improved dramatically the precision of the analysis (**Figure A.3**). However, the mean error and the relative mean error of the measured concentrations of CaO and SiO_2 (**Figure A.4**) are very high reflecting a clear case of systematic error. That the systematic error is not related to the instrument but rather to the preparation of the sample, is strongly suggested by the fact that the errors have opposite signs compared to the errors of the analysis of test-sample SRM2711 (see Table A.1). In retrospect, two sources of error can be identified in the sample preparation procedure:

1. The materials used for the preparation of the sample had not been dried before weighing. If any of the two major components (silica and/or lime) contained substantial amounts of absorbed water, a significant error would have been introduced.

2. The pellet was heated in a furnace to ensure partial fusion of the mixed oxide powders. However, the selected temperature was much closer to the liquidus temperature of the mixture than anticipated effecting the perfect fusion of the

powdered compounds and the collapse of the pellet. In this process, it is very likely that fractional vaporisation occurred affecting the composition of the liquefied oxide mixture.

Due to these errors in the experimental procedure, the true composition of sample TS2 is effectively unknown so the calculated mean error and relative mean error of the iron-oxide measurements are meaningless. As it has not been possible to prepare another test sample, an indirect approach is employed for the evaluation of the measured iron-oxide concentration using alumina as an internal standard. Alumina is selected for this purpose for three reasons:

1. The analysis of sample SRM 2711 showed no significant systematic errors in the determination of alumina (ME=0.42s).

2. The concentration of alumina is similar (*ca.* 13.5%) in both test-samples improving the comparability of the results.

3. The other two oxides in sample TS2 (lime and silica) show significant errors.

As shown in **Table A.3**, the relative mean error in the measured FeO/Al_2O_3 ratio in sample SRM 2711 is -6.61% reflecting the high systematic negative error of FeO (which is -7.8%). In contrast the relative mean error in the measured FeO/Al_2O_3 ratio in sample TS2 is +0.49% reflecting much more accurate measurements of the FeO concentration. In fact, the high accuracy of the measurements is indicated by the fact that their mean error corresponds to only 0.21s *despite the much higher precision in the analysis of this sample*. Based on the above, it is possible to argue that there is no significant systematic negative error in the determination of iron oxide introduced by the instrument used in the analysis.

A.1.3 Conclusions

The aim of these preliminary analyses was to make a first evaluation of the results obtained by the SEM-EDS instrument. The accuracy and precision of the analysis were calculated for major and minor oxides. The mean error in the determination of each oxide is generally very small compared to the standard deviation of replicate analysis. This is true also for iron-oxide as confirmed in Section A1.1.2; magnesia, however, may be an exception. Based on the evaluation of the analytical data it is concluded that *the main source of uncertainty in the determination of all oxides is the precision of the analysis*, which is satisfactory for the purposes of this study.

The statistical analysis of the experimental data from the analysis of the test-samples also determined the way in which the analytical results should be presented. In reporting the data of an analytical measurement, it is important that the number of digits used to express the results are consistent with the measured precision (Christian 1994: 15). To be more specific, the reported result should contain all of the digits that are known plus the first uncertain one; these are called the *significant figures*. Having calculated the precision of the SEM-EDS analysis of the two-test samples the following norm has been adopted:

1. Concentrations above 10% are reported with two significant figures; e.g. 42%.
2. Concentrations between 1 and 10% are reported with two significant figures; e.g. 5.4%.
3. Concentrations below 1% are reported with one significant figure; e.g. 0.3%.

A.2 Evaluation of results of the SEM-EDS analysis of pelletised slag samples

A first estimation of the precision of the SEM-EDS analysis was enabled by the analysis of the two test-samples (see previous section). However, the test-samples contained only a small number of oxides, most being present at concentrations above 1%. In contrast, the analysis of pelletised slag samples involved the determination of 17 oxides whose concentrations ranged from <0.5 to >50%. Since four area-scans have been conducted on each slag pellet (**Table A.4**), it has been possible to estimate the precision of the instrument for the complete suit of measured oxides and the entire range of concentrations.

The estimated standard deviation and the relative standard deviation were calculated for each of the 17 oxides measured in the 39 pellets (see Table A.4) and plotted against the mean measured value (**Figure A.5**). The values for Na_2O were plotted separately due to the problems in the analysis of this element (see previous section). As seen in the plots, the precision of the SEM-EDS analysis of pelletised slag samples (excluding Na_2O) is very similar to that calculated from the analysis of test-sample SRM 2711 (which was prepared in exactly the same way) suggesting that the conclusions reached in the previous section, regarding the precision of the analysis, apply to all 17 measured oxides and for the entire range of concentrations from <0.5 to>50%.

A.3 Test of the comparability of results of the SEM-EDS analysis of pelletised and polished slag samples

Although the chemical composition of most slag samples was measured by SEM-EDS analysis of pelletised specimens, in the case of 7 slag samples it was measured using the same technique on polished specimens. To check the comparability of the results, 12 slag samples were analysed using both methods. Only 6 major and minor oxides were determined. The results are presented in **Table A.6** and plotted in **Figure A.6**. As seen in the two plots, differences in the results of the two methods of analysis are within or close to their combined uncertainty (2s) confirming that the two methods produce comparable results.

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FIGURES

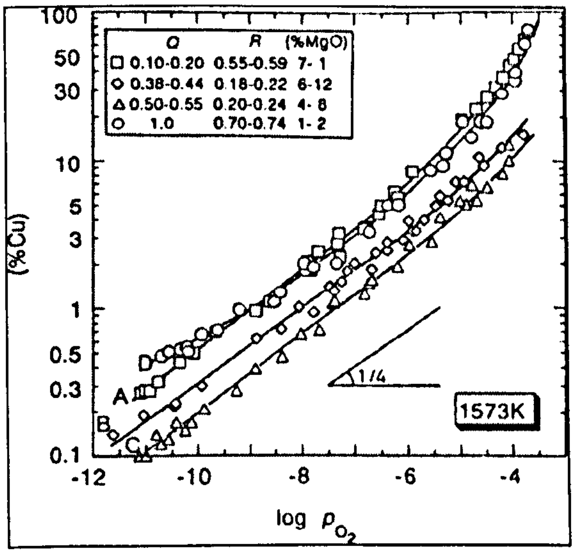


Figure 3.1 Solubility of copper (as cuprous oxide) in CaO-FeO$_x$-SiO$_2$ slags as a function of the partial pressure of oxygen (after Vartiainen and Kytö 2002: fig.3).

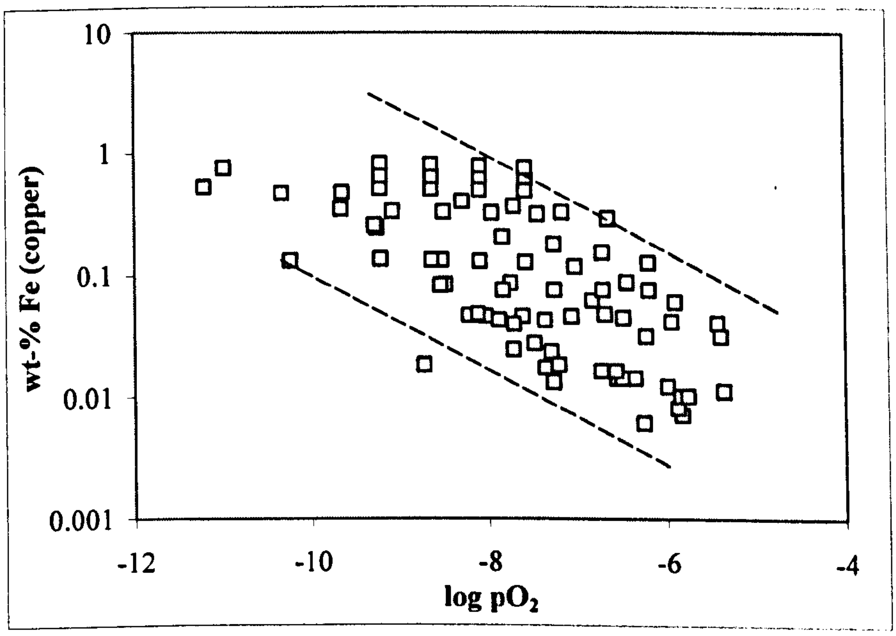


Figure 3.2 Wt-% iron in copper equilibrated with iron-silicate slags at various temperatures as a function of the partial pressure of oxygen (data from Altman and Kellogg 1972; Ruddle *et al* 1966).

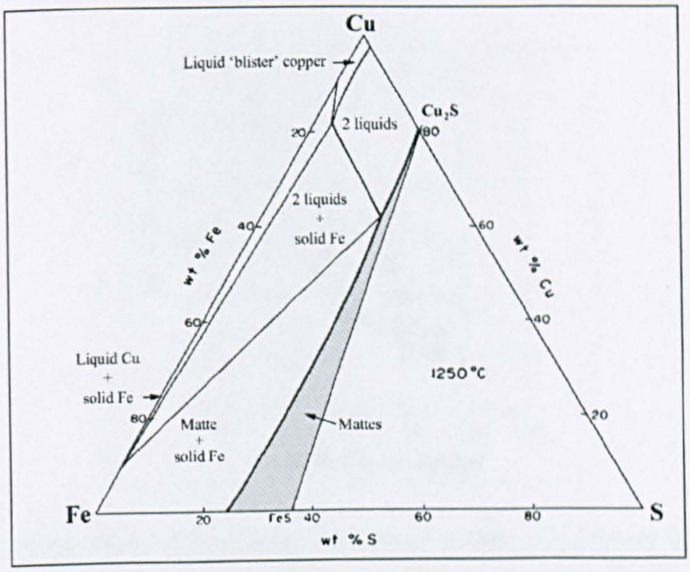


Figure 3.3 Compositional range of copper-smelting mattes at 1250°C on the system copper-iron-sulphur (after Biswas and Davenport 1976: fig.4.2; *modified*).

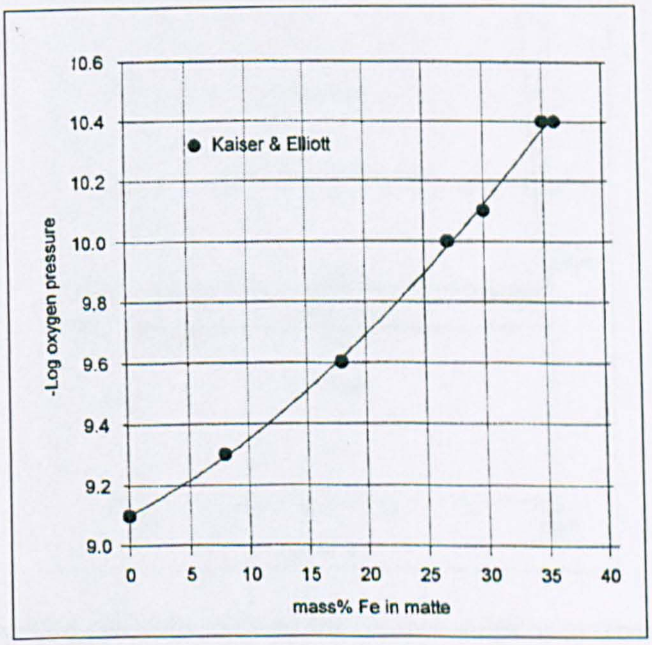


Figure 3.4 Relationship between partial pressure of oxygen and iron content of matte in copper smelting (after Sridhar *et al* 1997: fig.5).

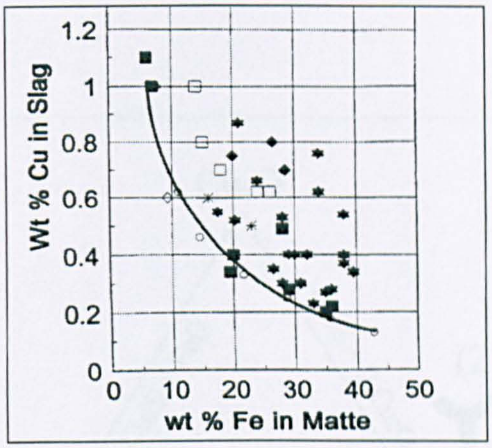


Figure 3.5 Relationship between iron content in matte and copper losses in slag from various modern metallurgical plants (after Sridhar *et al* 1997: fig.8).

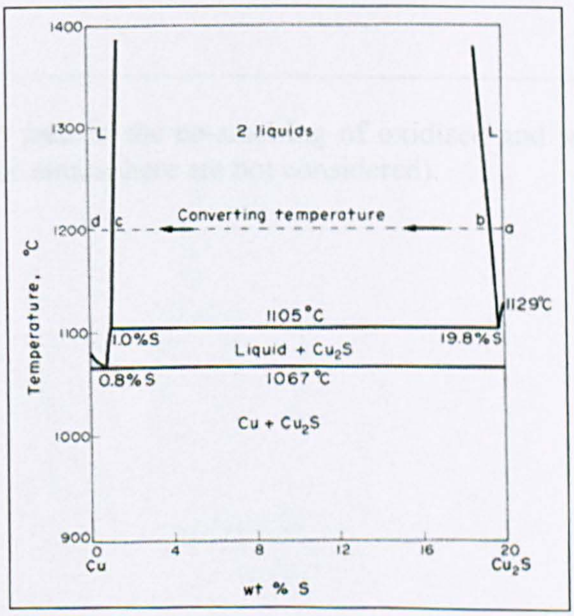


Figure 3.6 Converting reaction path on the copper-sulphur system (after Biswas and Davenport 1976: fig. 9.2).

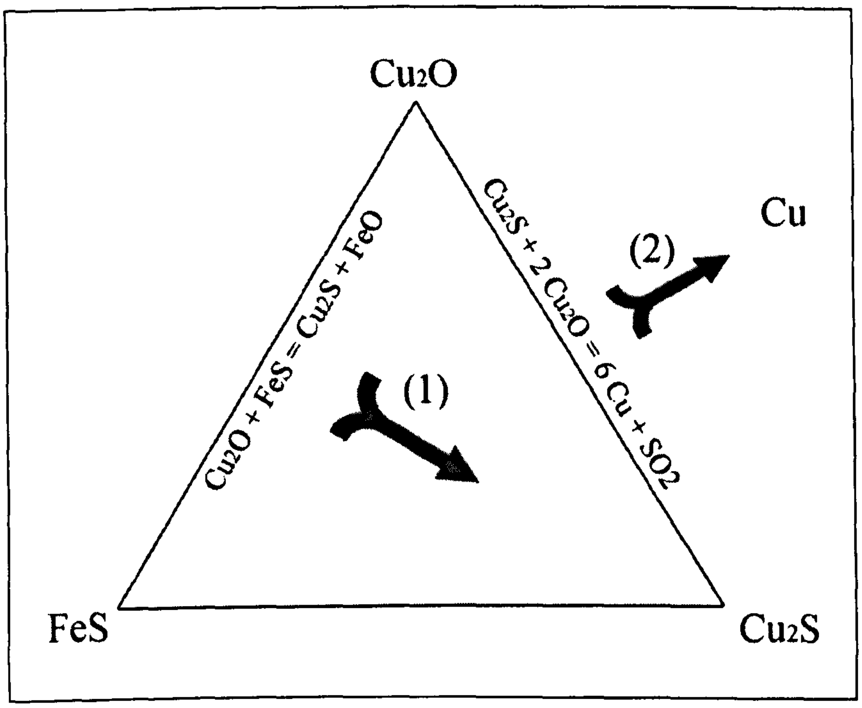


Figure 3.7 Reaction path in the co-smelting of oxidised and sulphidic copper ores (the effects of furnace atmosphere are not considered).

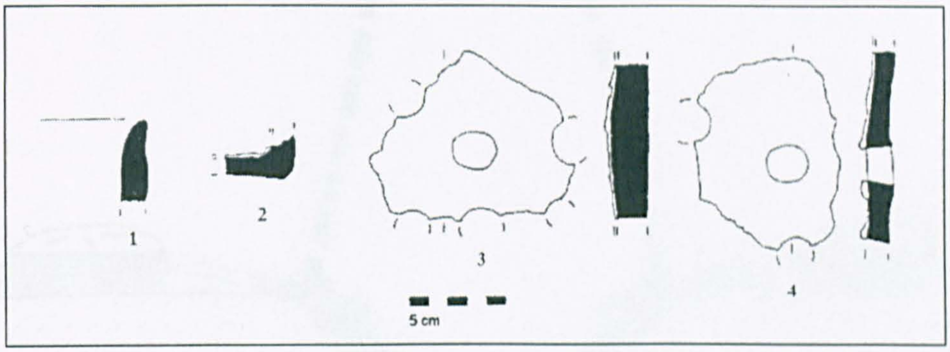


Figure 4.1 Furnace fragments from Chrysokamino (after Betancourt *et al* 1999: fig. 6).

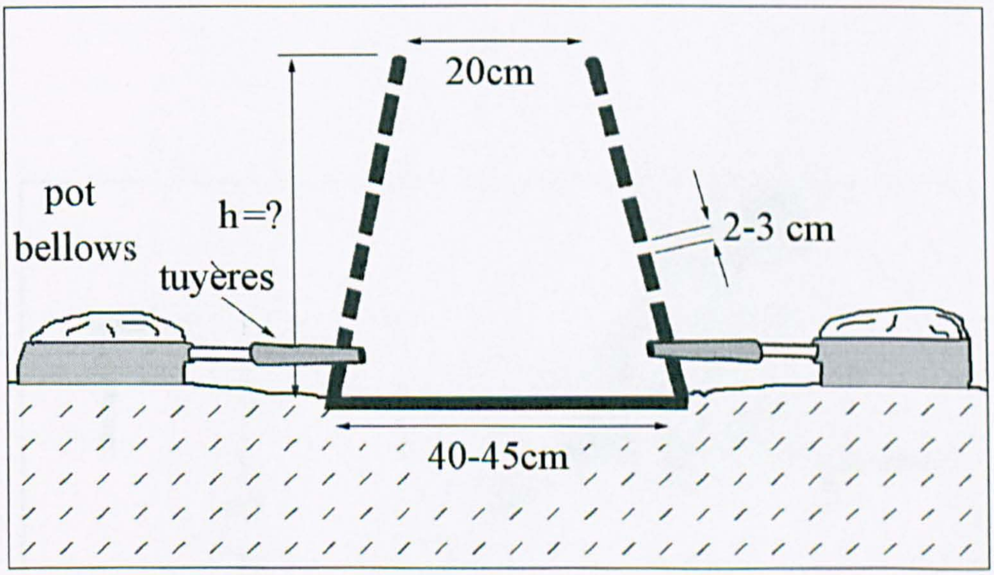


Figure 4.2 The excavators' reconstruction of the ceramic furnaces at Chrysokamino (based on information in Betancourt *et al* 1999).

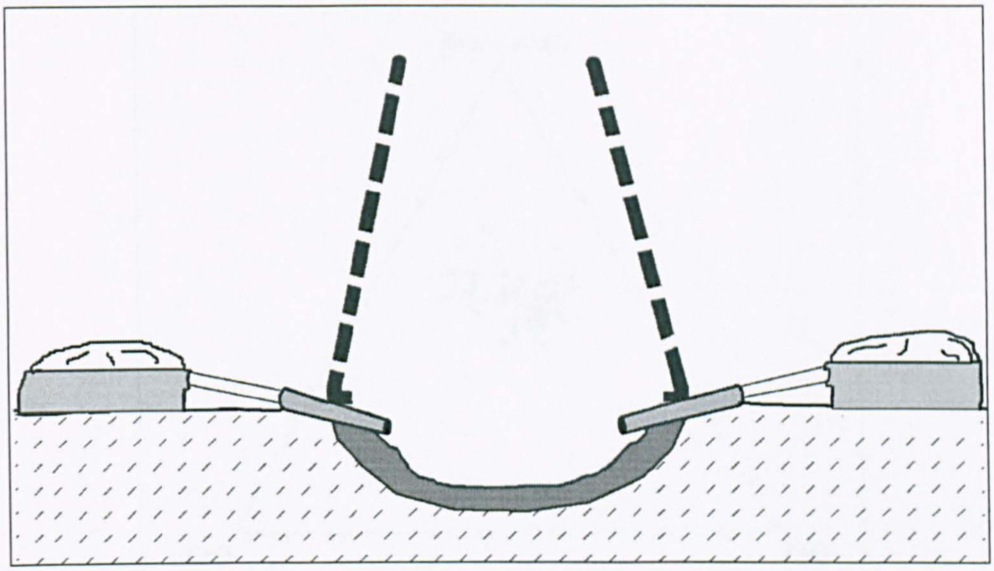
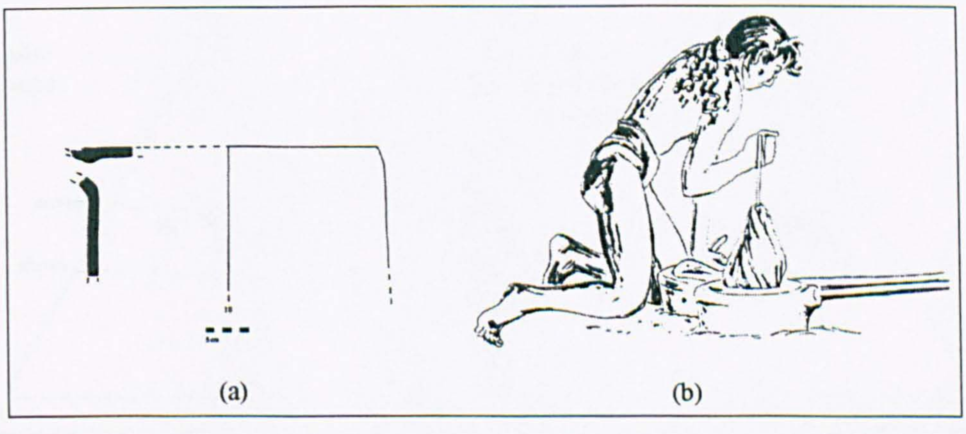


Figure 4.3 Proposed reconstruction of the ceramic furnaces at Chrysokamino (dimensions as in **Fig. 4.2**).



(a) (b)

Figure 4.4 Pot-bellows from Chrysokamino: (a) best preserved example; (b) suggested reconstruction (after Betancourt *et al* 1999: fig. 7, 9).

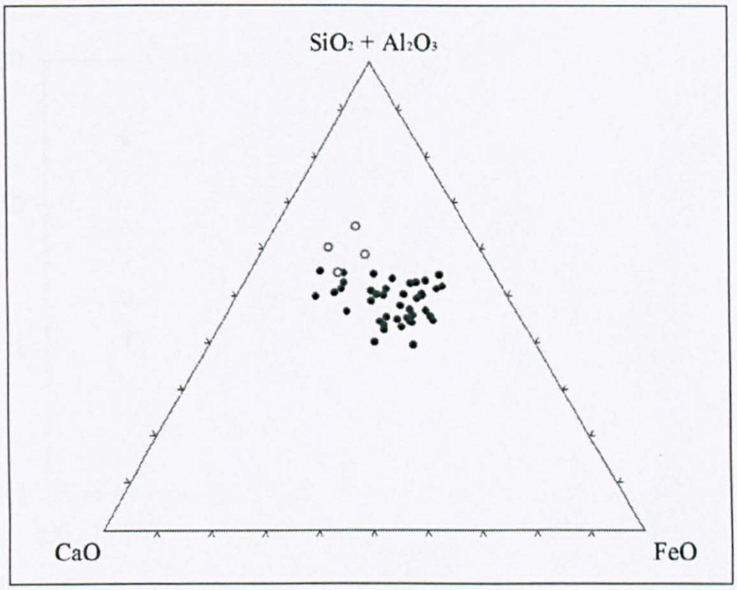


Figure 4.5 Reduced chemical composition of slag samples from Chrysokamino plotted on the system (SiO_2 + Al_2O_3)-CaO-FeO. Open circles indicate samples with frequent unfused silica grains.

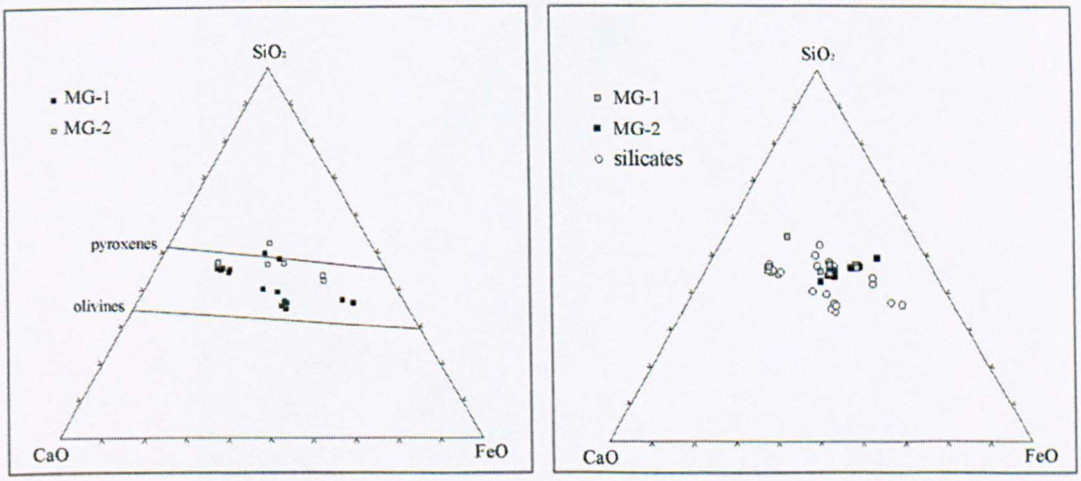


Figure 4.6 Reduced chemical composition of silicates (*left*) and glass (right) in slag from Chrysokamino plotted on the system CaO-FeO- SiO_2.

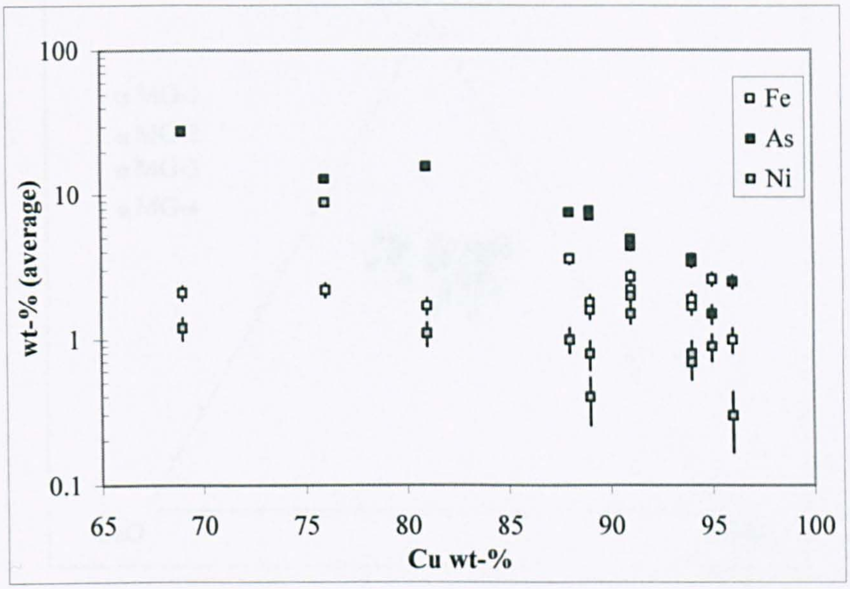


Figure 4.7 Iron, arsenic and nickel levels in analysed copper prills (average values per slag sample). Error bars = 2s.

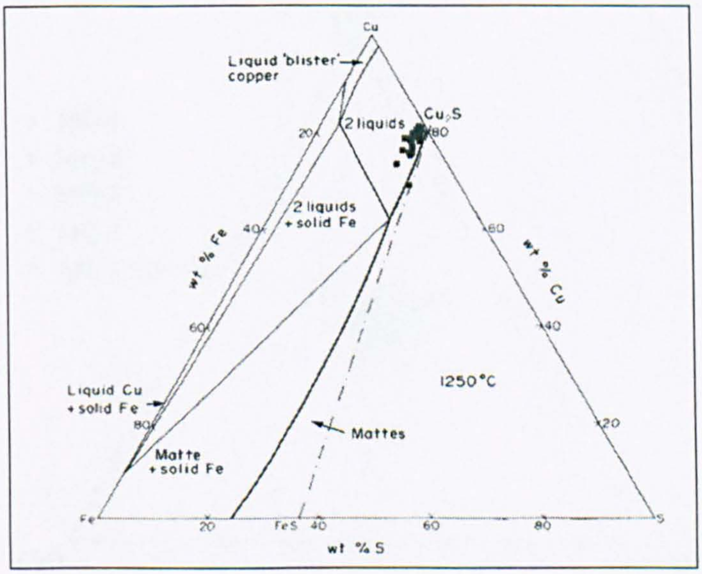


Figure 4.8 Reduced chemical composition of matte inclusions embedded in slag from Chrysokamino plotted on the system copper-iron-sulphur (diagram after Biswas and Davenport 1976: fig. 4.2).

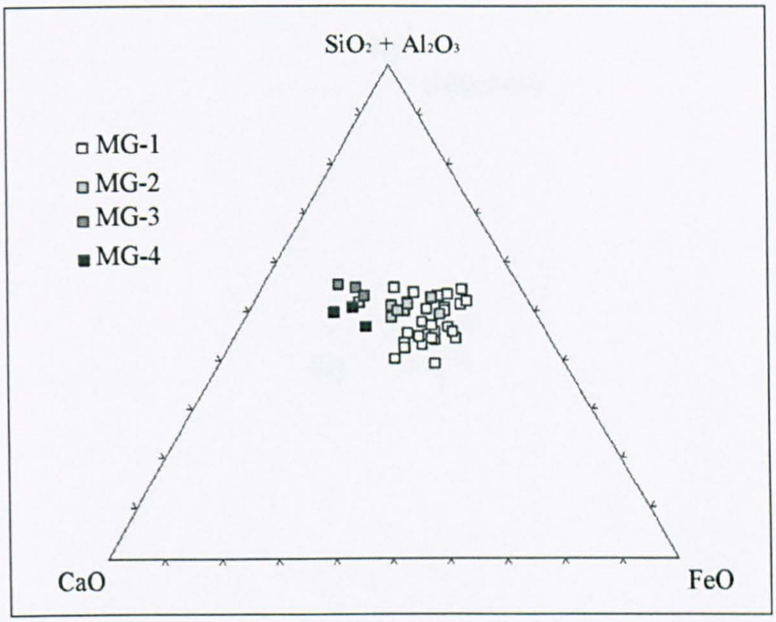


Figure 4.9 Reduced chemical composition of samples from the four slag groups from Chrysokamino plotted on the system (SiO_2 + Al_2O_3) -CaO-FeO. Samples from group MG-2 with frequent unfused quartz grains have been excluded.

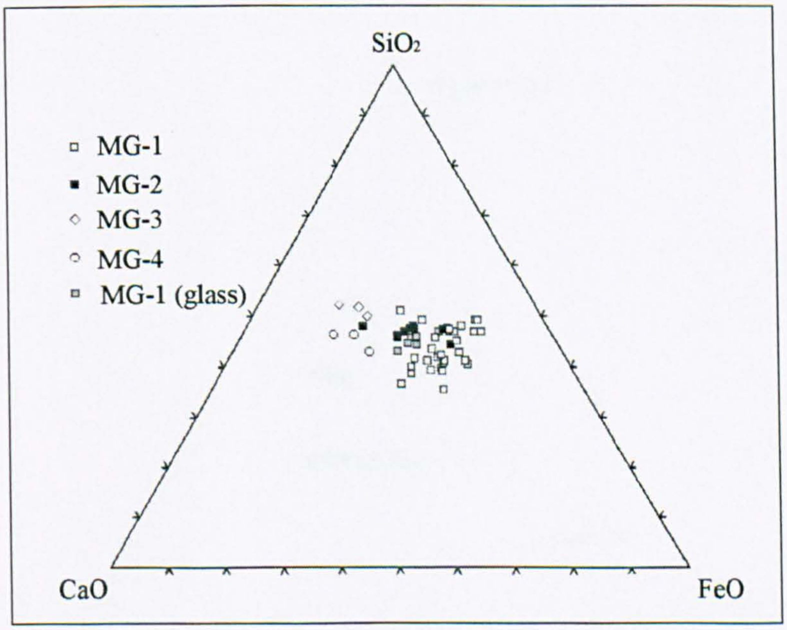


Figure 4.10 Reduced chemical composition of slag samples from Chrysokamino and the glass phase in samples of group MG-1 plotted on the system SiO_2-CaO-FeO. Samples from group MG-2 with frequent unfused quartz grains have been excluded.

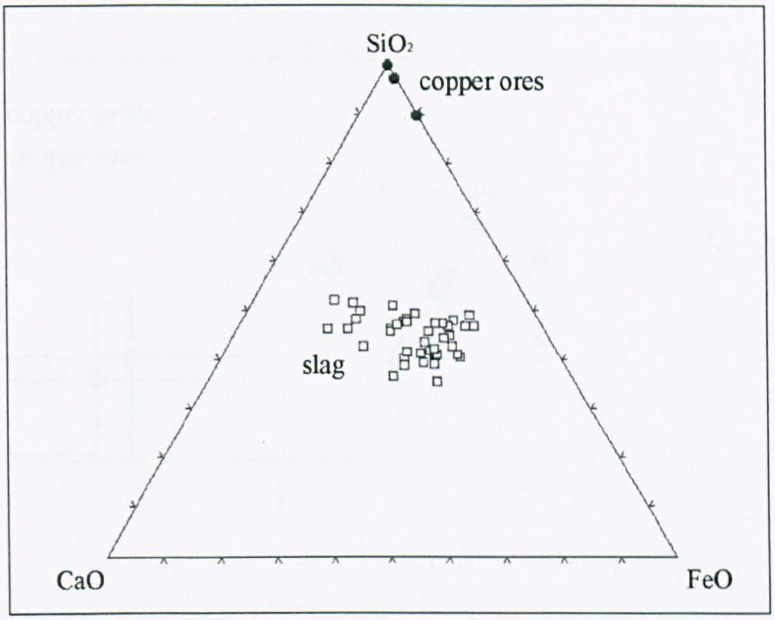


Figure 4.11 Reduced chemical composition of copper-ore and slag samples from Chrysokamino plotted on the system SiO_2-CaO-FeO. Samples from group MG-2 with frequent unfused quartz grains have been excluded.

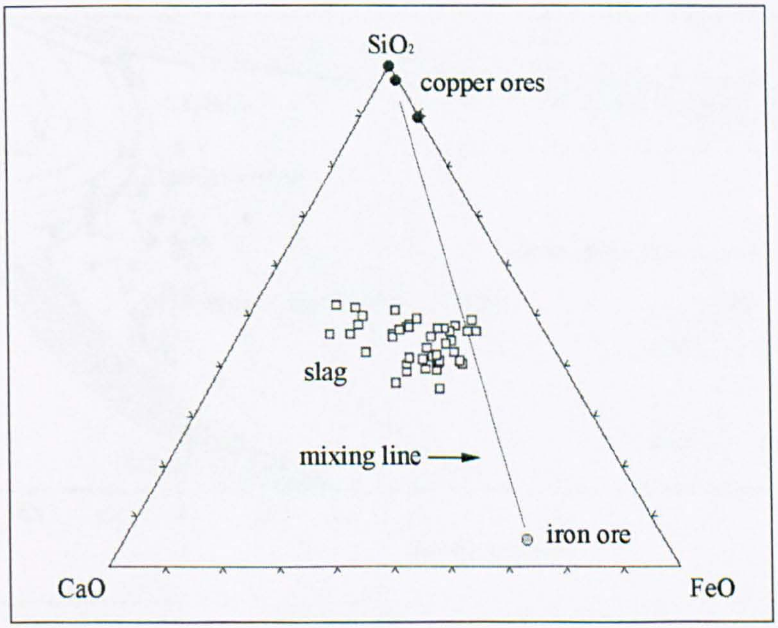


Figure 4.12 Reduced chemical composition of ore and slag samples from Chrysokamino plotted on the system SiO_2-CaO-FeO. Samples from group MG-2 with frequent unfused quartz grains have been excluded.

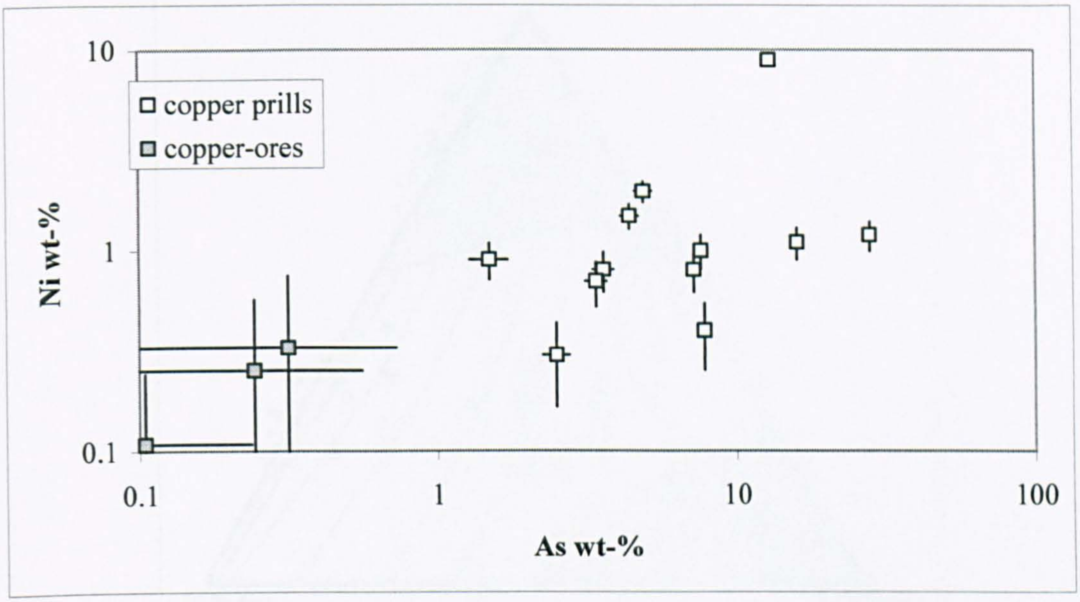


Figure 4.13 Arsenic and nickel levels in copper prills suspended in the slag, and in copper ores from Chrysokamino. Error bars = 2s.

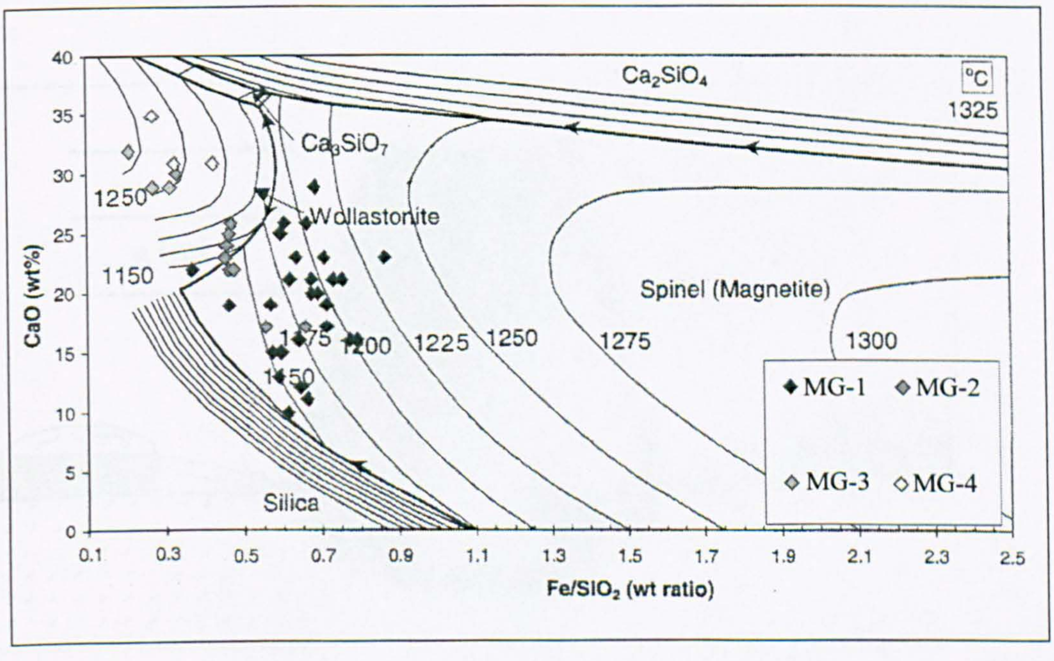


Figure 4.14 Reduced chemical composition of slag samples from Chrysokamino plotted on the Fe/SiO$_2$ – CaO phase diagram. Samples from group MG-2 with frequent unfused quartz grains have been excluded. (diagram after Kongoli and Yazawa 2001: fig. 11, modified).

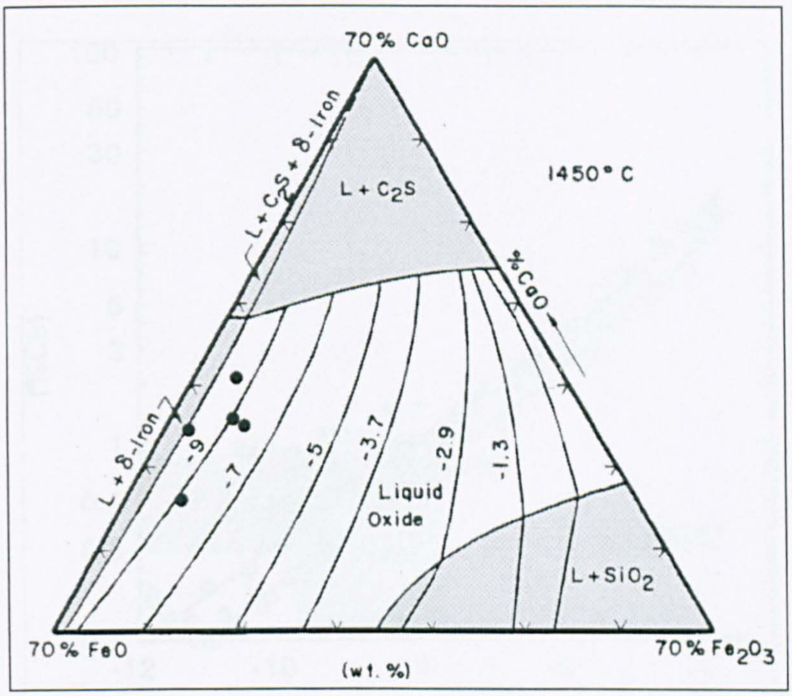


Figure 4.15 Reduced analyses of slag samples plotted on the CaO-FeO-Fe_2O_3 (+30% SiO_2) pseudo-ternary diagram. Lines correspond to oxygen isobars. Crystallisation areas are shaded (diagram from Timucin and Morris 1970: fig.5).

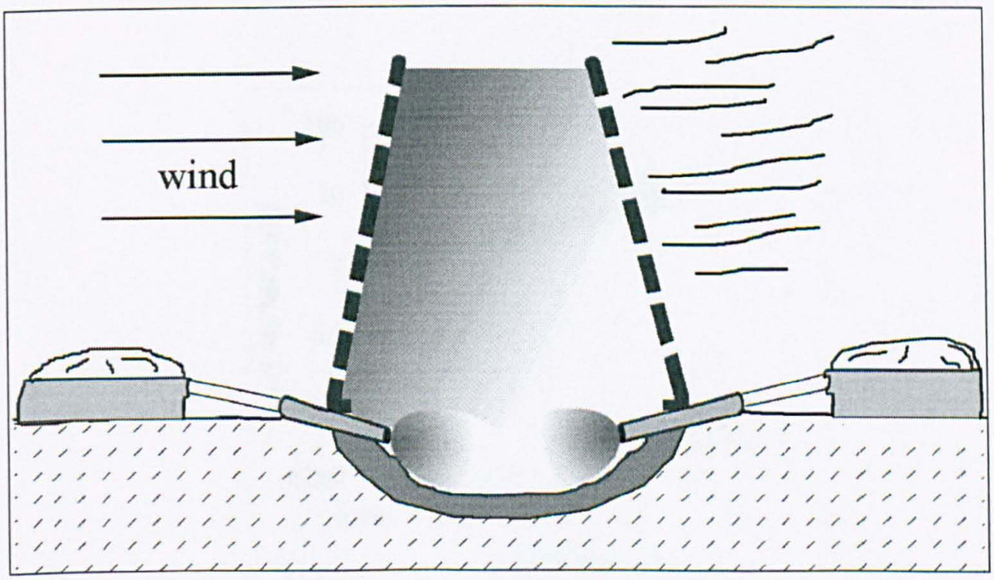


Figure 4.16 Simplified schematic representation of the redox conditions inside the perforated furnace during smelting. Darker areas correspond to more oxidising conditions.

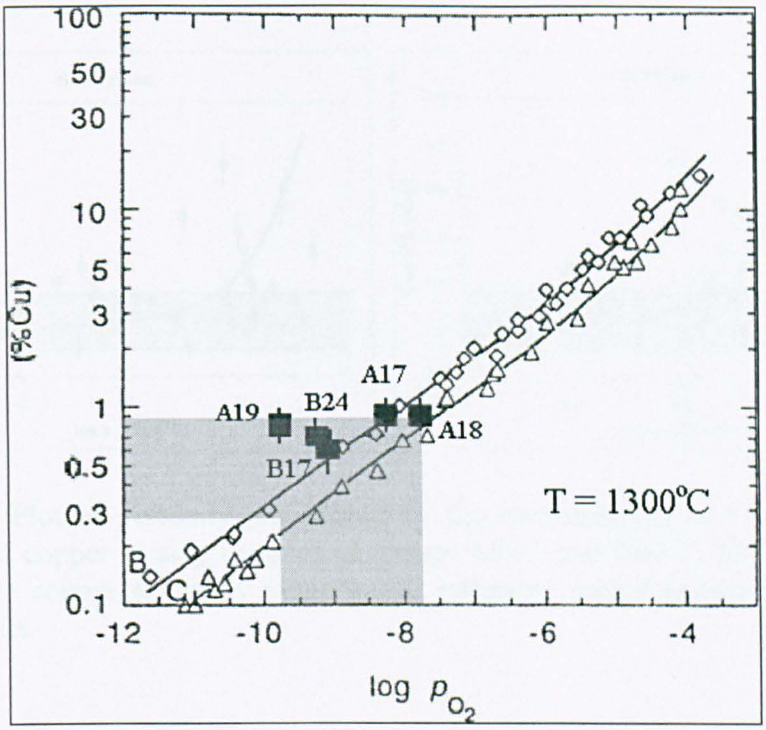


Figure 4.17 Slag samples plotted on the diagram of copper solubility in CaO-FeO-SiO_2 slags against the partial pressure of oxygen (diagram adapted from Vartiainen and Kytö 2002: fig. 3). Error bars = 2s.

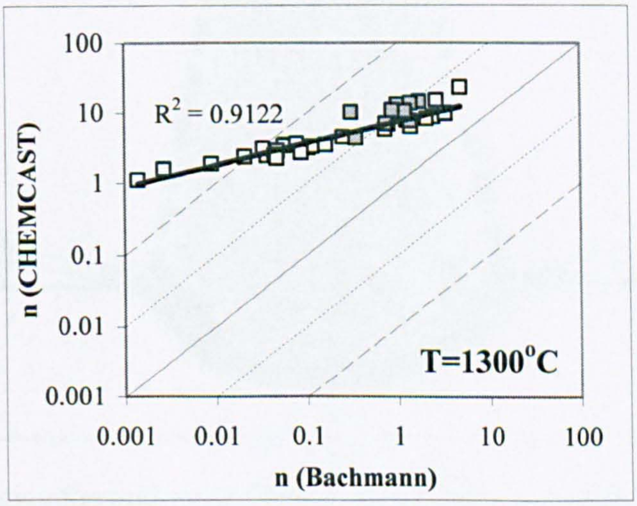


Figure 4.18 Comparison of viscosity values calculated using Bachmann's (1980) empirical formula and the CHEMCAST software for slag samples MG-1 and MG-2.

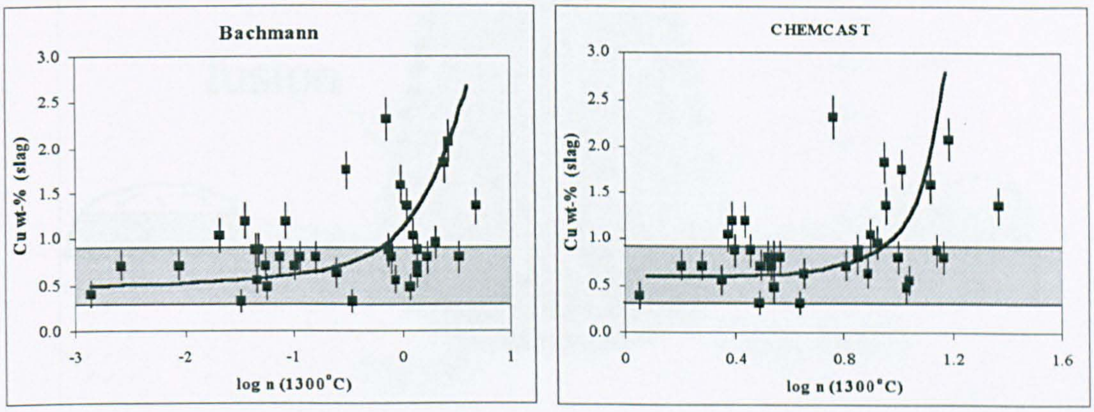


Figure 4.19 Plot of viscosity (calculated by the two methods at 1300°C) against percentage of copper in slag samples of groups MG-1 and MG-2. The shaded band represents the copper solubility range at the estimated partial pressures of oxygen. Error bars = 2s.

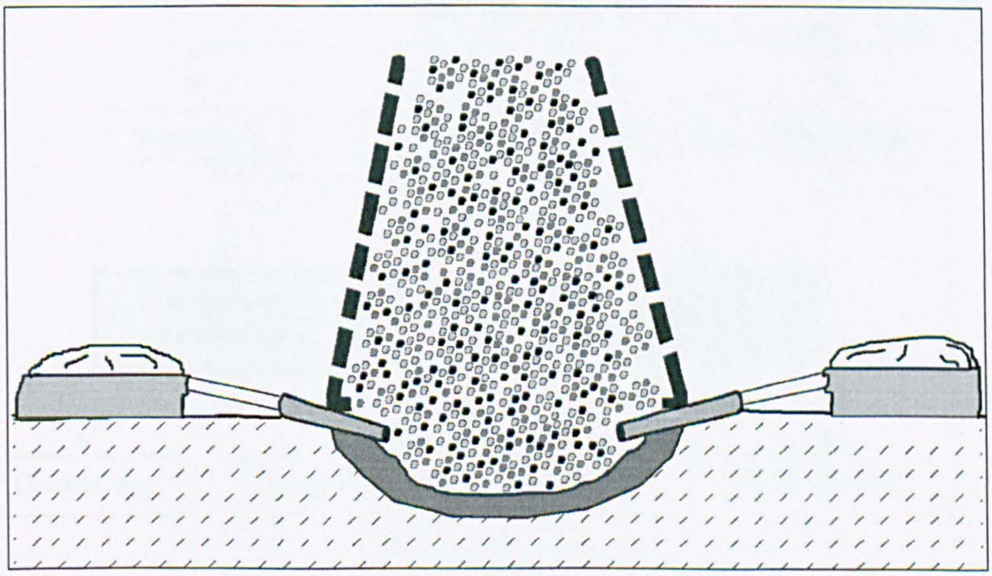


Figure 4.20 Charging the preheated furnace (dimensions as in **Fig. 4.2**).

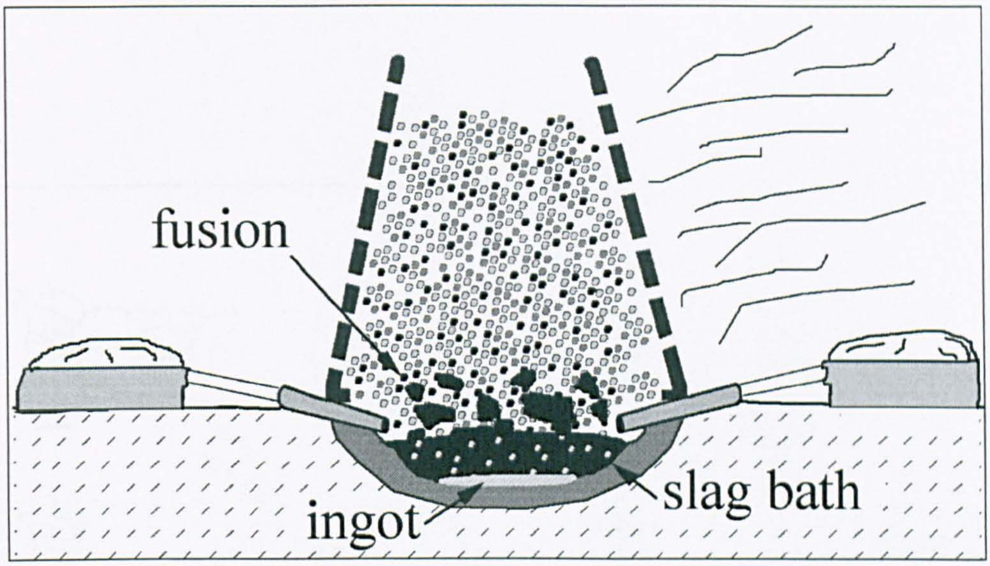


Figure 4.21 Smelting in progress (dimensions as in **Fig. 4.2**).

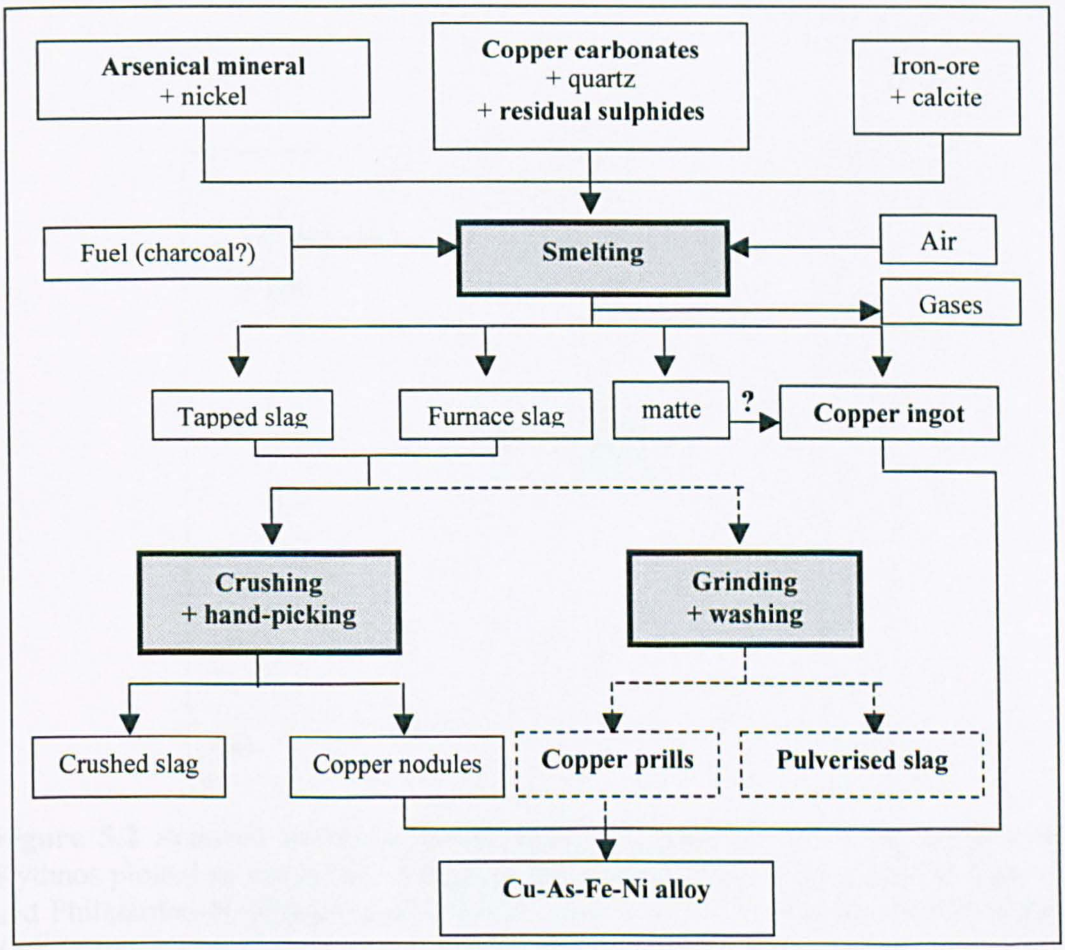


Figure 4.22 Schematic representation of the proposed reconstruction of the copper-smelting process at Chrysokamino.

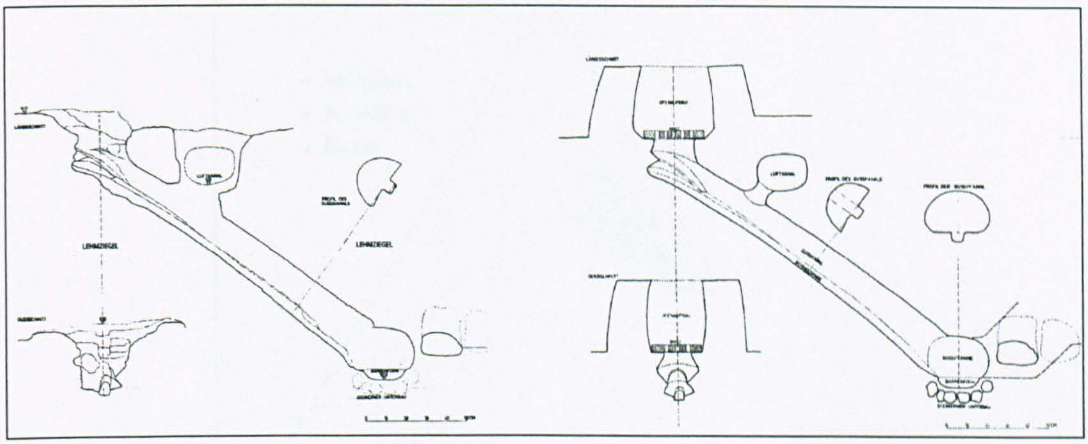


Figure 5.1 Remains (*left*) and reconstruction (*right*) of the peculiar installation at Kolonna on Aigina (after Walter and Felten 1981: figs. 17 and 19).

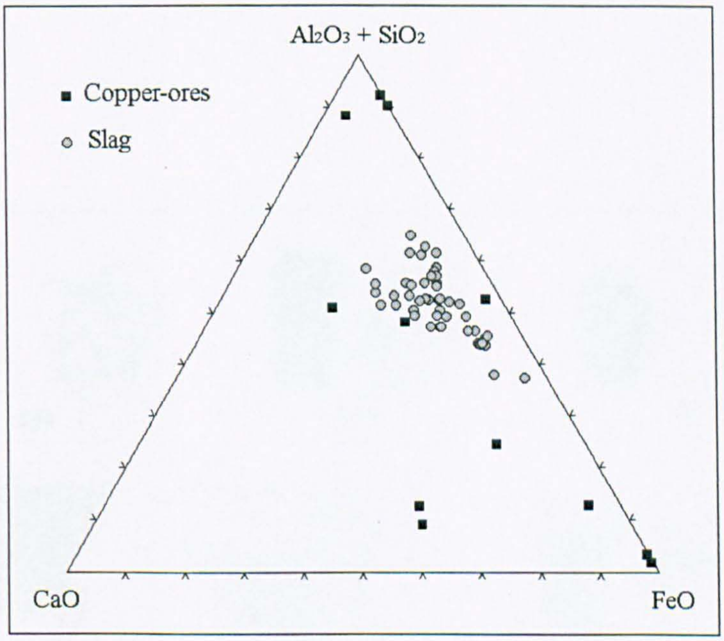


Figure 5.2 Reduced chemical composition of copper-ore and slag samples from Kythnos plotted on the system (SiO_2+Al_2O_3)-CaO-FeO (data for ores from Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; data for slag from **Table 5.7**).

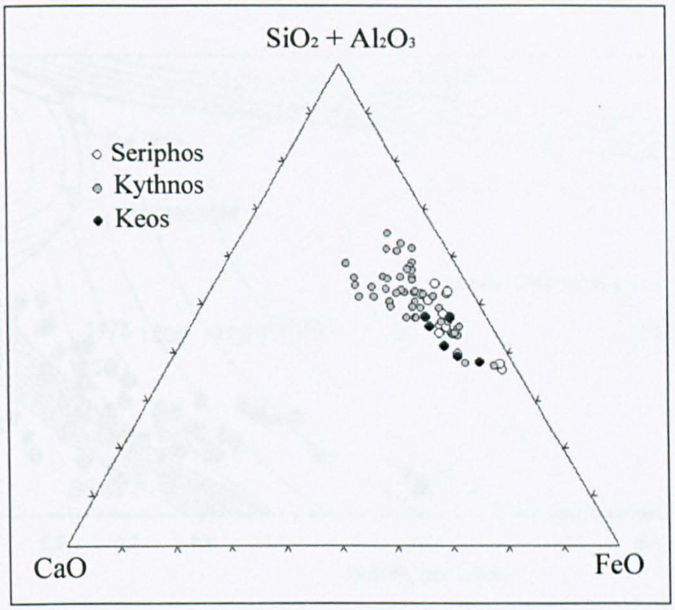


Figure 5.3 Reduced chemical analysis of slag samples from the southern Aegean on the system (SiO_2+Al_2O_3)-CaO-FeO (data from **Table 5.7**).

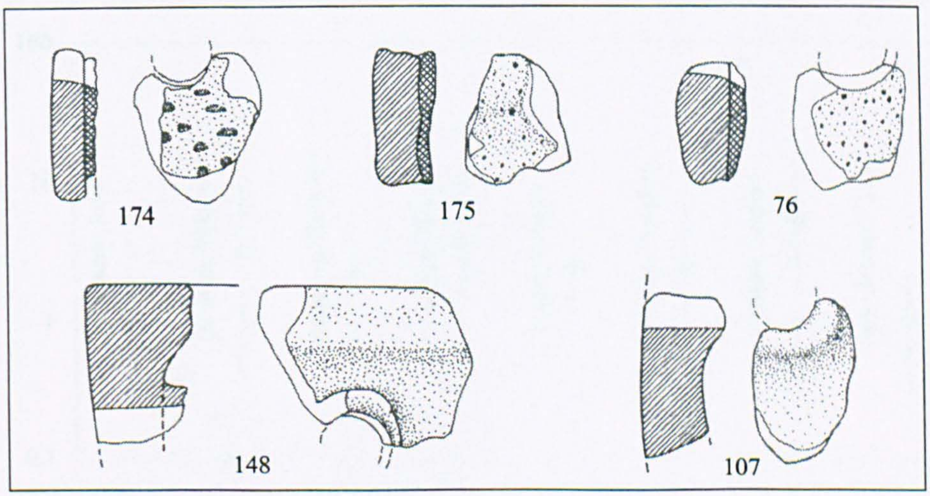


Figure 5.4 Perforated metallurgical ceramics from the FN settlement of Kephala on Keos (after Coleman 1977: pl. 22).

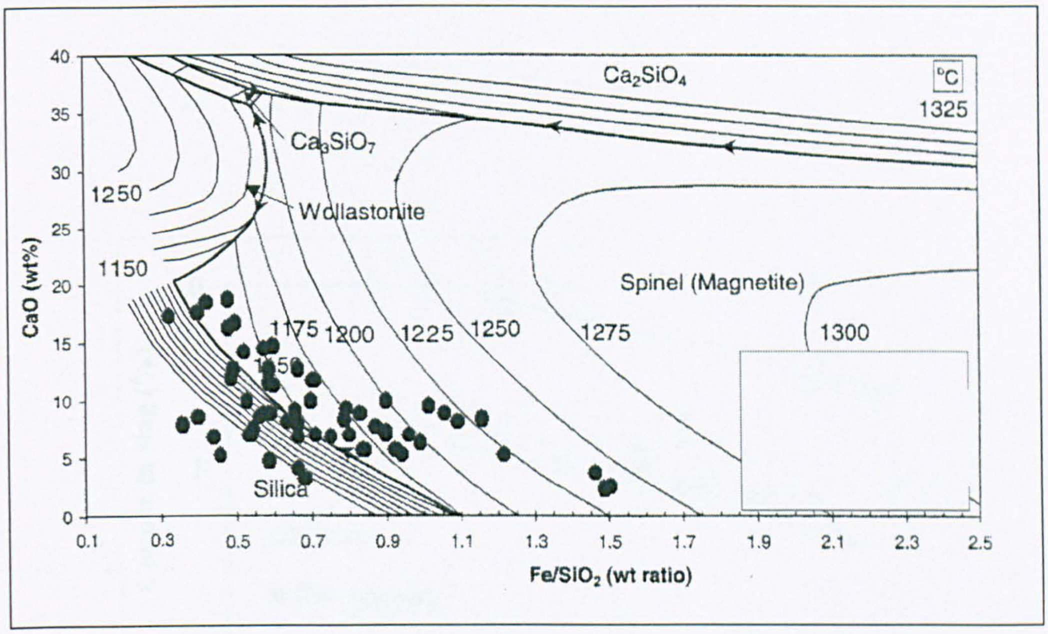


Figure 5.5 Reduced chemical composition of slag samples from the southern Aegean plotted on the Fe/SiO$_2$–CaO phase diagram (data from **Table 5.7**; diagram after Kongoli and Yazawa 2001: fig.11, modified).

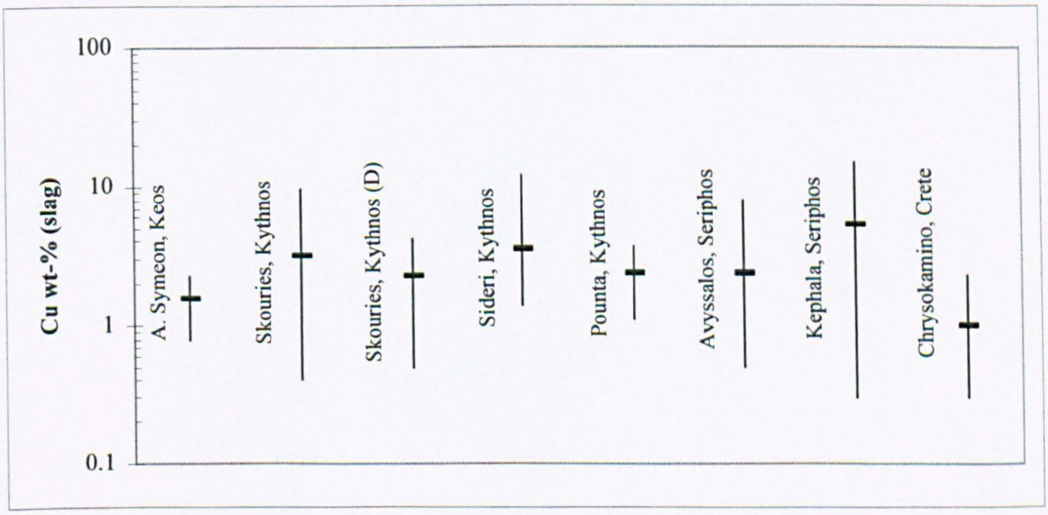


Figure 5.6 Copper losses in slag from copper-smelting sites in the southern Aegean (data from **Table 5.7**; data from Chrysokamino refers to the major slag group MG-1).

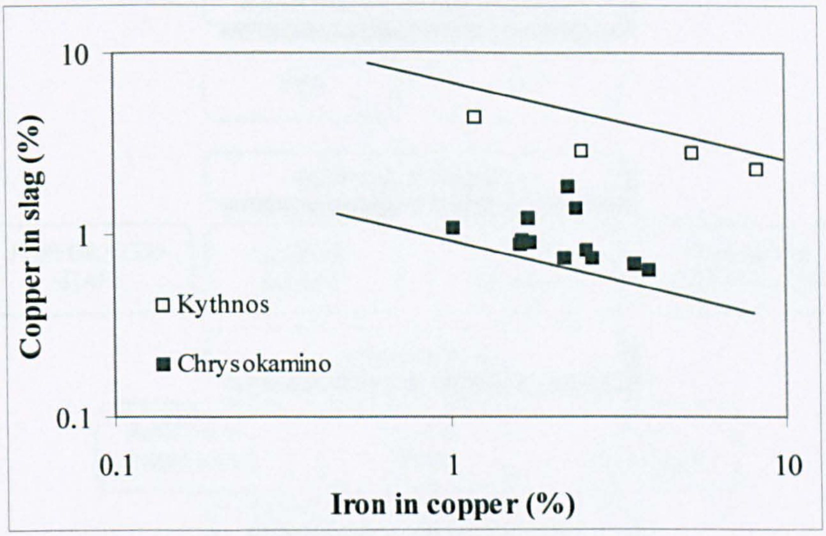


Figure 5.7 Copper losses in slag against iron levels in copper prills in slag samples from Kythnos (various sites) and Chrysokamino (data for Kythnos from Bassiakos and Philaniotou-Hadjianastasiou in press).

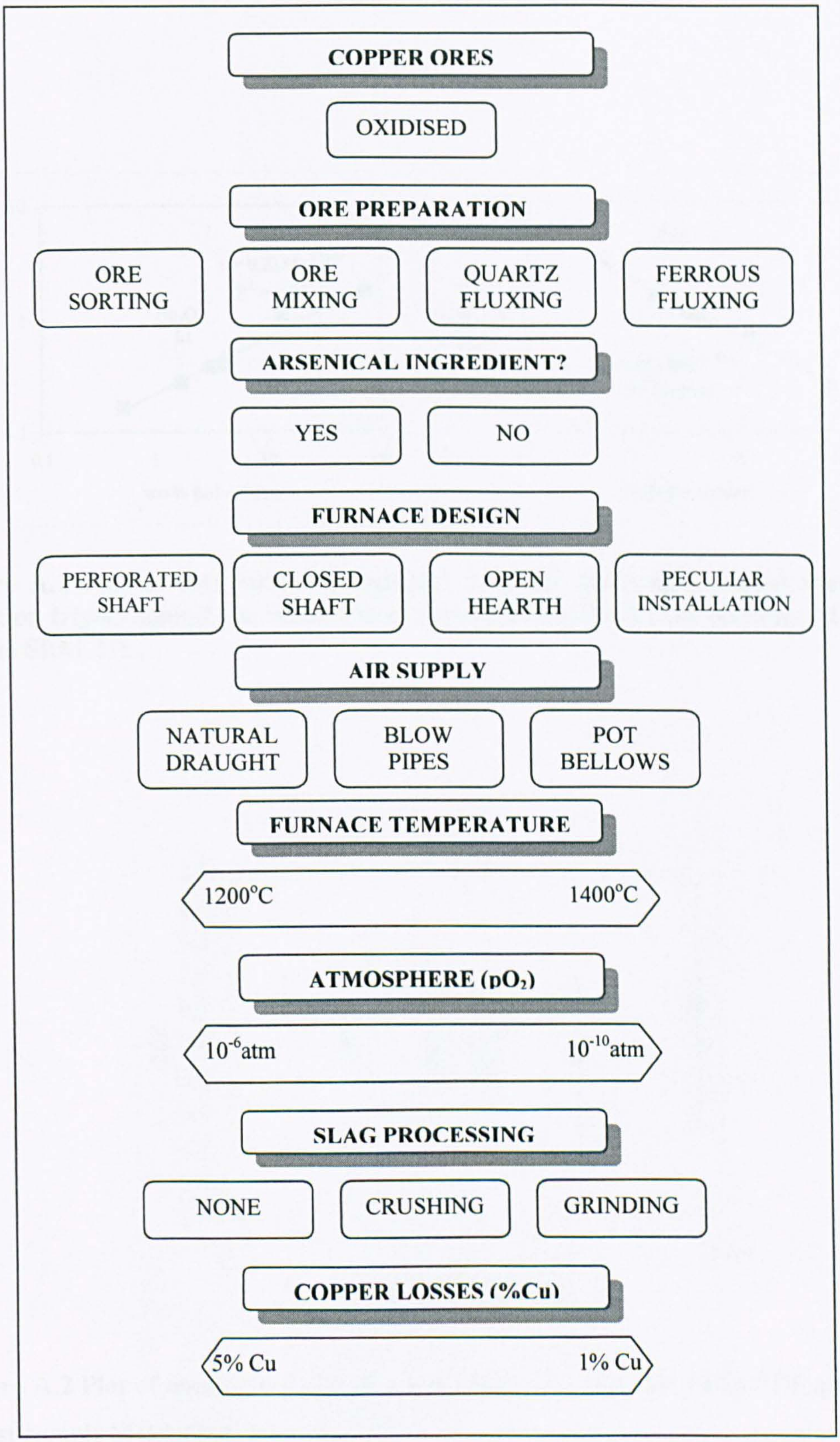


Figure 5.8 Technological choices in the main aspects of the copper-smelting process in the EBA shouthern Aegean.

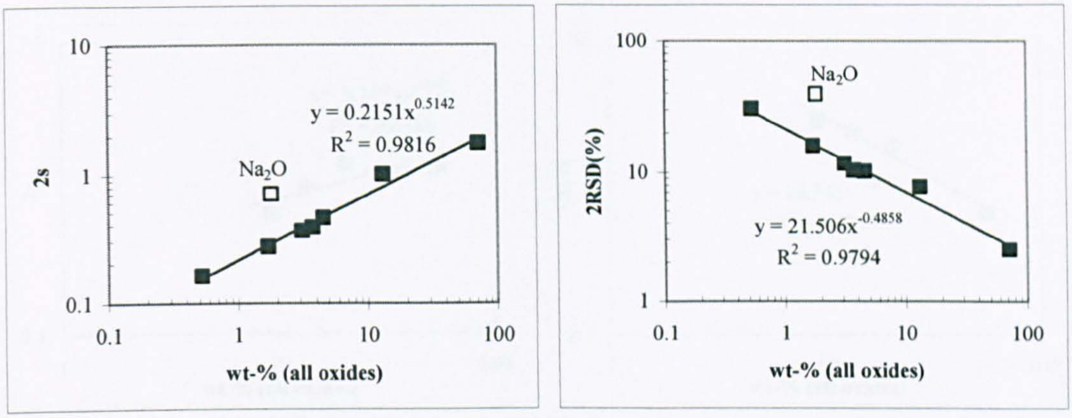


Figure A.1 Plot of two times the standard deviation (left) and relative standard deviation (*right*) against the mean value from replicate SEM-EDS analyses of test-sample SRM 2711.

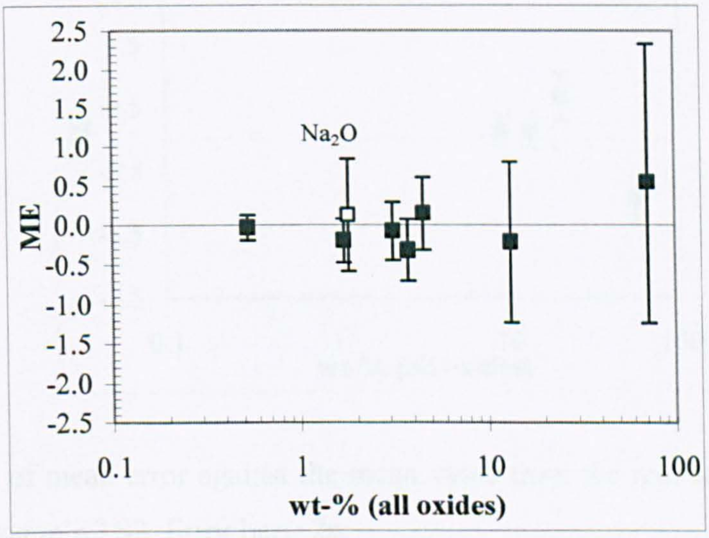


Figure A.2 Plot of mean error against mean value from replicate SEM-EDS analyses of test-sample SRM 2711. Error bars: 2s.

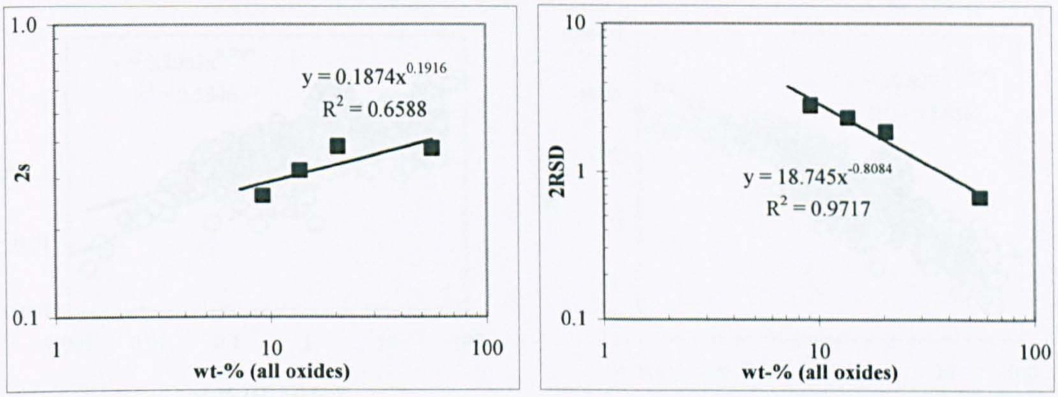


Figure A.3 Plot of two times the standard deviation (*left*) and relative standard deviation (*right*) against the mean value from replicate SEM-EDS analyses of test-sample TS2.

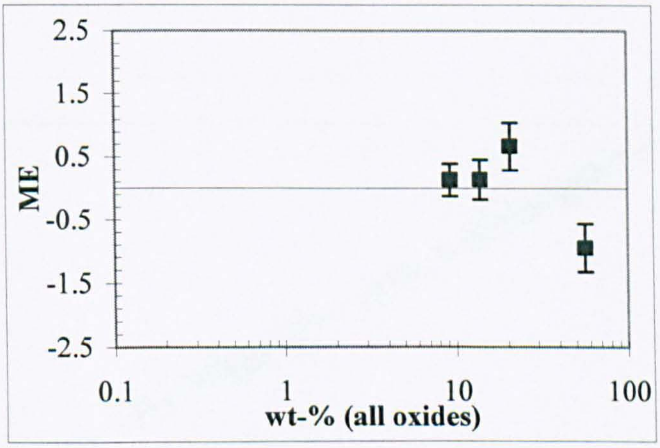


Figure A.4 Plot of mean error against the mean value from the replicate SEM-EDS analyses of test-sample TS2. Error bars: 2s.

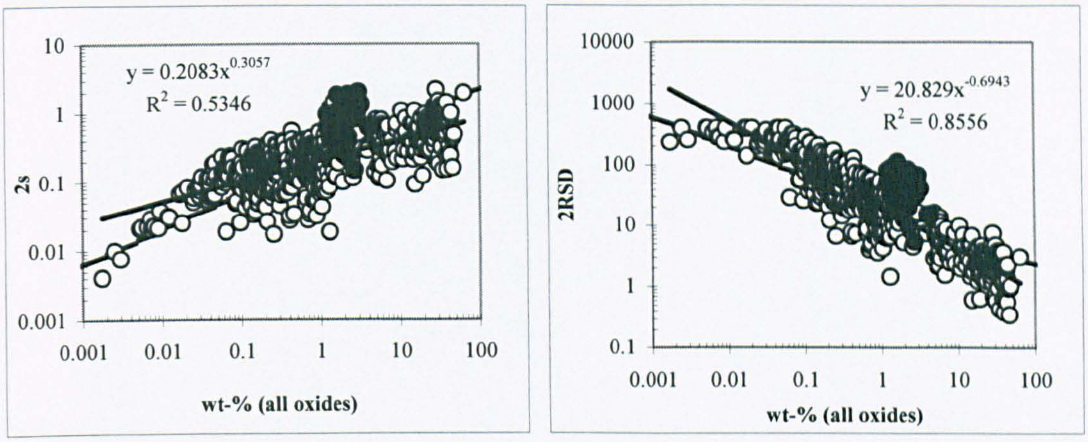


Figure A.5 Plot of two times the estimated standard deviation (*left*) and relative standard deviation (*right*) versus the mean value from replicate SEM-EDS analyses of pelletised slag samples. Filled circles represent data for Na_2O. The dashed line represents the 2s curve as calculated from the analysis of test-sample SRM 2711.

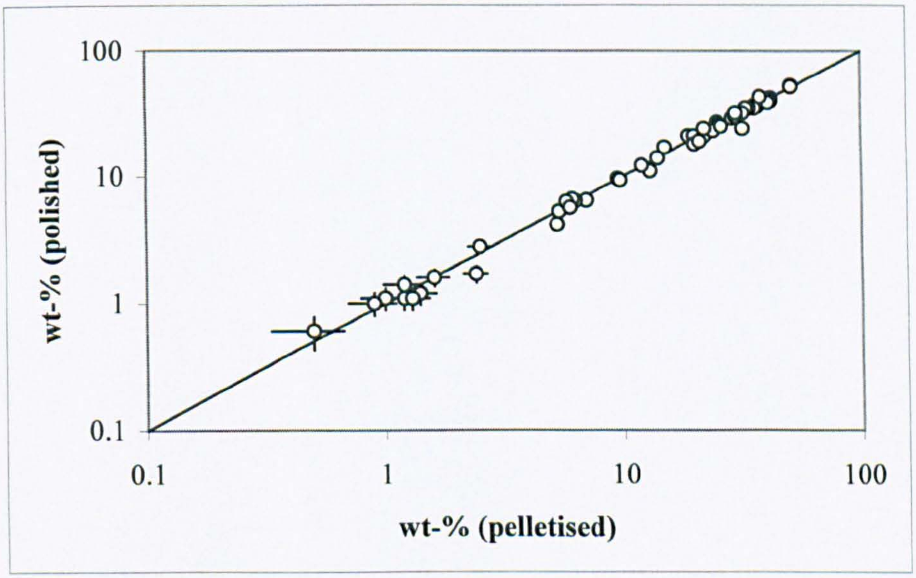


Figure A.6 Results of comparative SEM-EDS analyses of pelletised and polished slag samples. Error bars: 2s.

PLATES

Plate 4.1 The location of Chrysokamino on the coastal front of Chomatas hill (view from south).

Plate 4.2 The promontory at Crysokamino (view from northeast).

Plate 4.3 Accumulation of metallurgical debris in the narrow trough at Chrysokamino.

Plate 4.4 Carbonate ledge in the vicinity of the metallurgical site bearing a thin crust of iron hydroxides.

Plate 4.5 Outcrop of weak iron mineralisation in the vicinity of the metallurgical site.

Plate 4.6 Slag fragments from Chrysokamino.

Plate 4.7 Fragments of tap slag from Chrysokamino with pieces of rock adhering on their lower surface.

Plate 4.8 Fragment of tap slag from Chrysokamino probably corresponding to a “runner”.

Plate 4.9 Loose pieces of copper-ore found among the metallurgical debris at Chrysokamino.

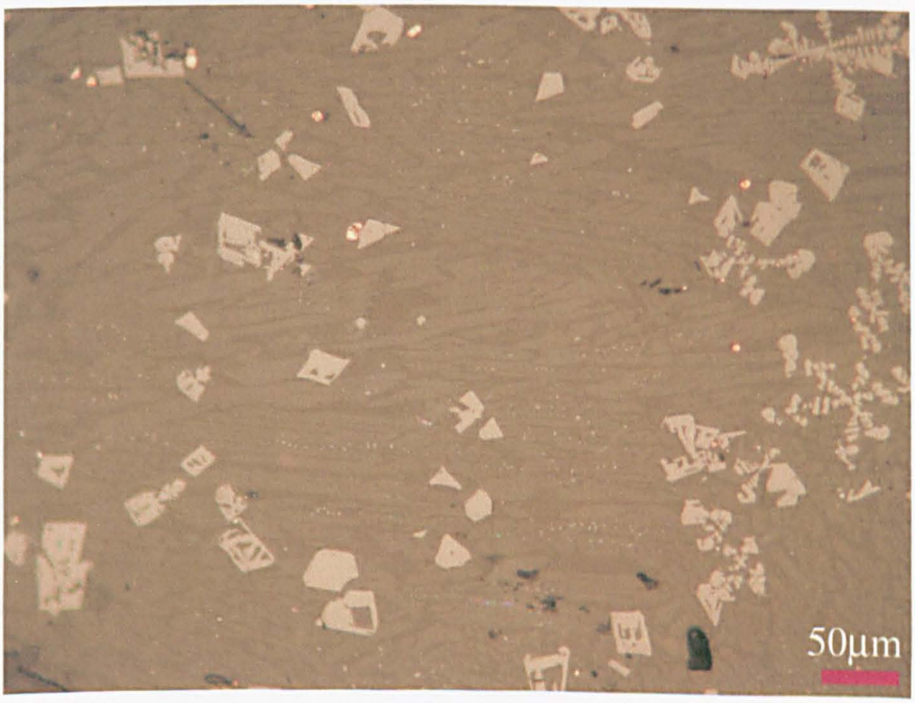


Plate 4.10 Silicate laths in slag from group MG-1 (Sample A05, Optical microscope, PPL).

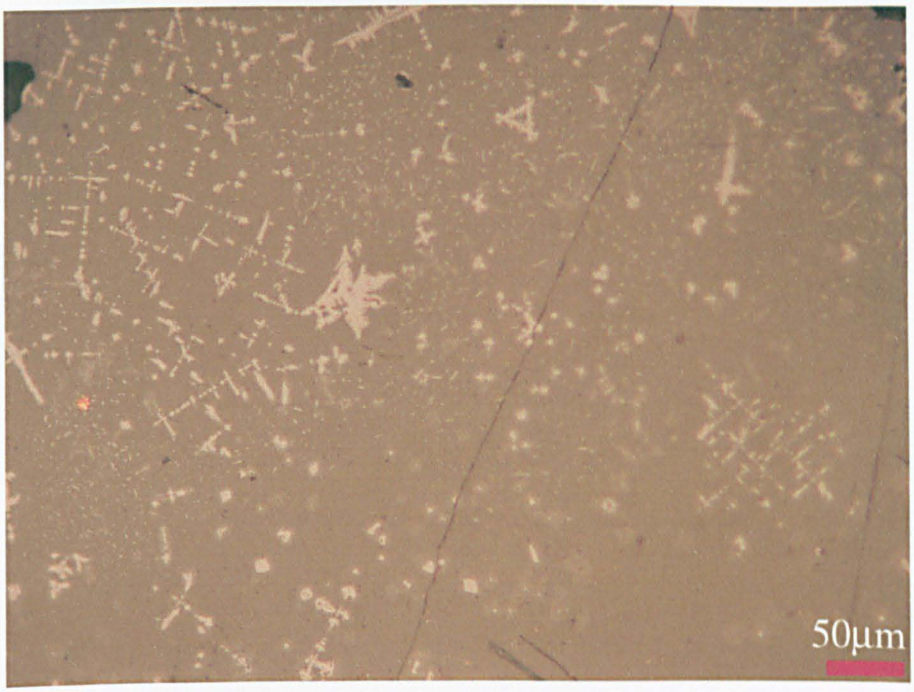


Plate 4.11 Magnetite skeletons and dendrites in slag from group MG-1 (Sample A29, Optical microscope, PPL).

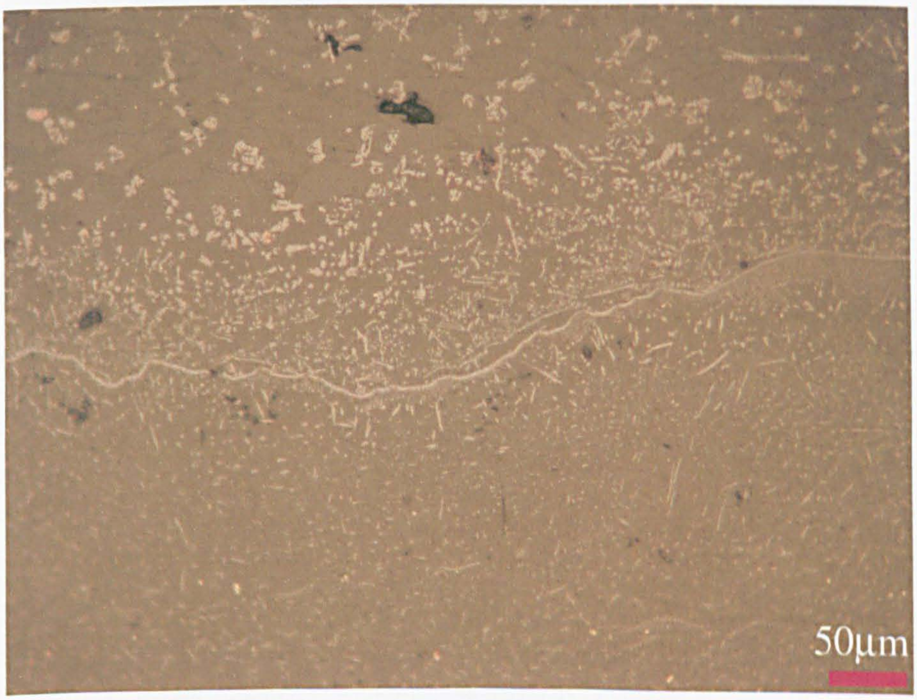


Plate 4.12 Magnetite bands in slag from group MG-1 (Sample A04, Optical microscope, PPL).

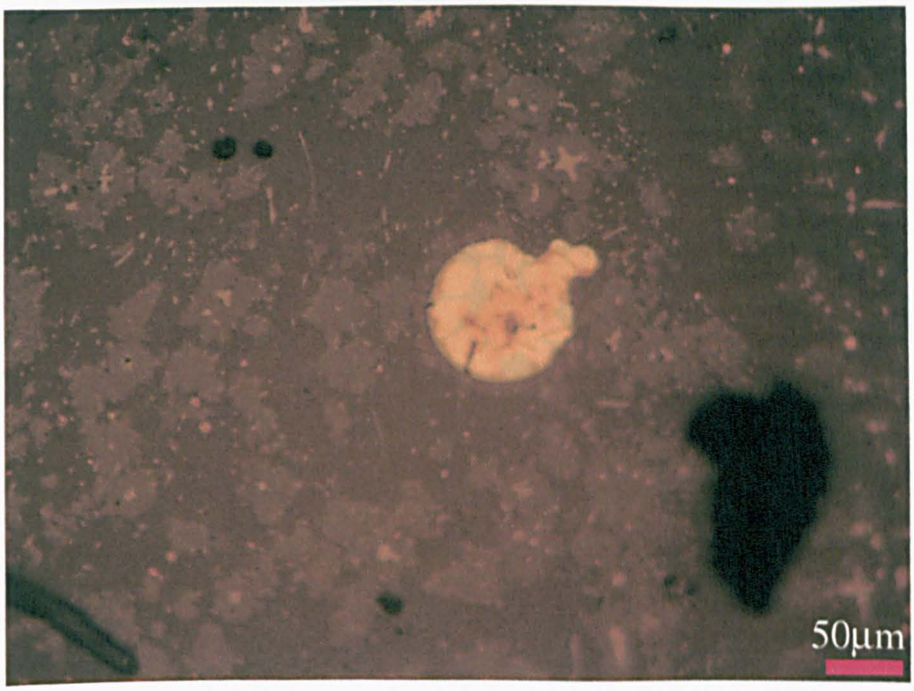


Plate 4.13 Copper prill containing the arsenic-rich phase Cu_3As in slag from group MG-1 (Sample B18, Optical microscope, PPL).

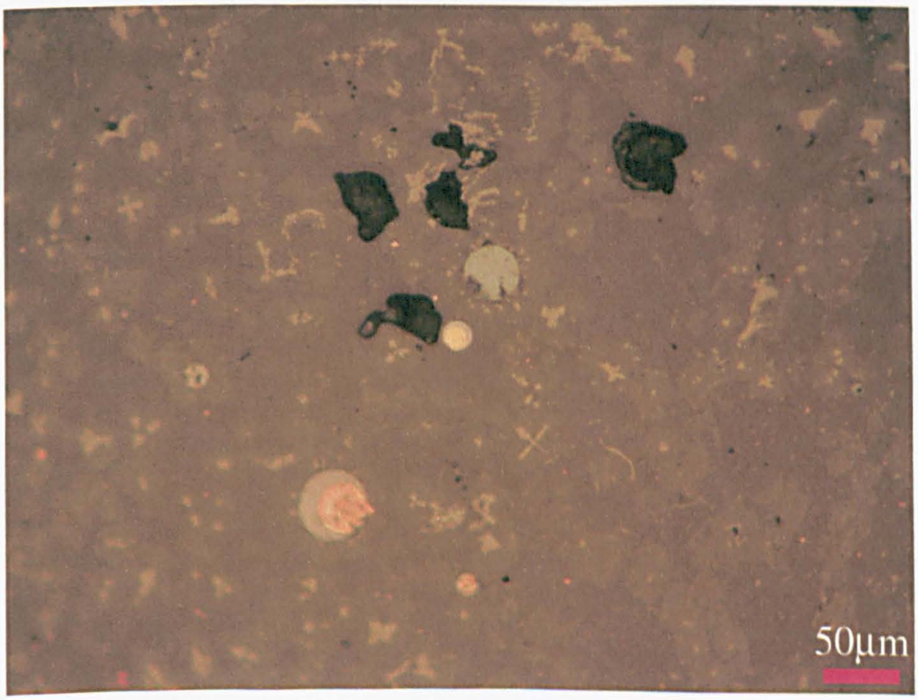


Plate 4.14 Matte rim surrounding copper prills in slag from group MG-1 (Sample B18, Optical microscope, PPL).

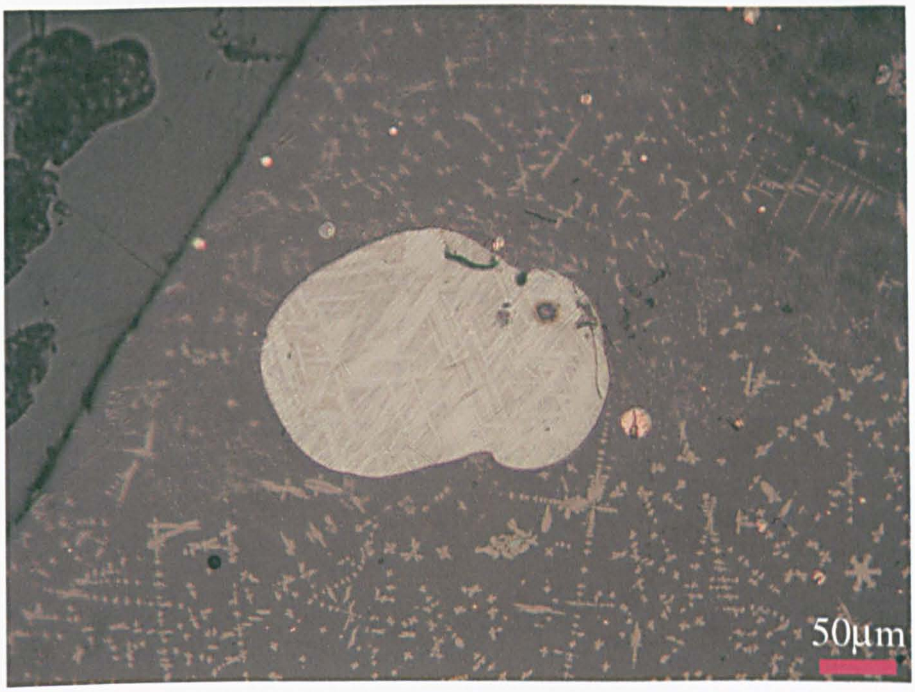


Plate 4.15 Widmastätten structure of matte inclusions in slag from group MG-1 (Sample A17, Optical microscope, PPL).

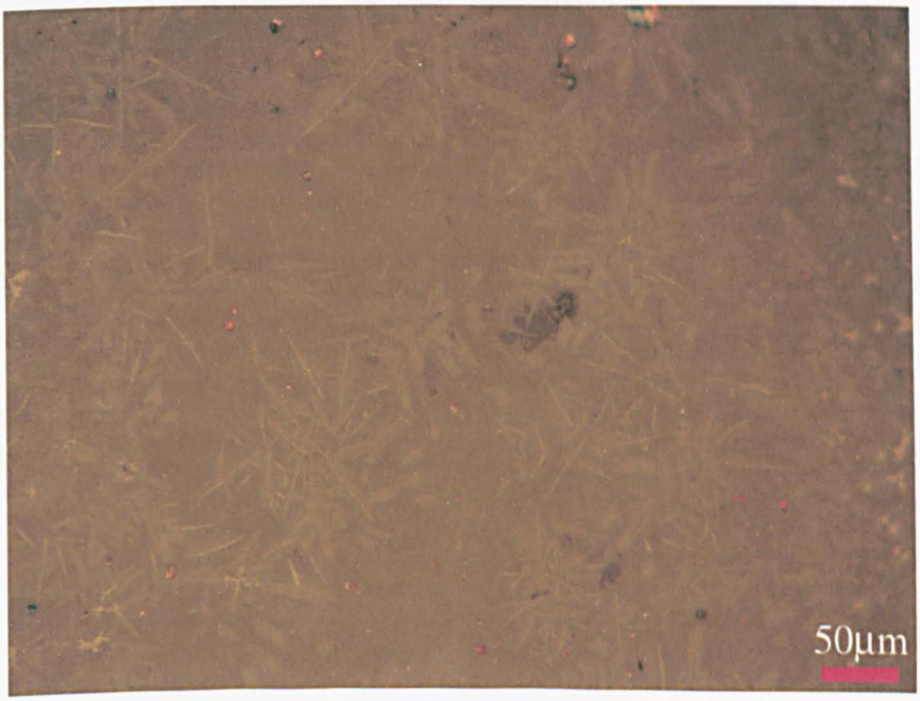


Plate 4.16 Delafossite (light gray, needle-like) laths in slag from group MG-1 (Sample A03, Optical microscope, PPL).

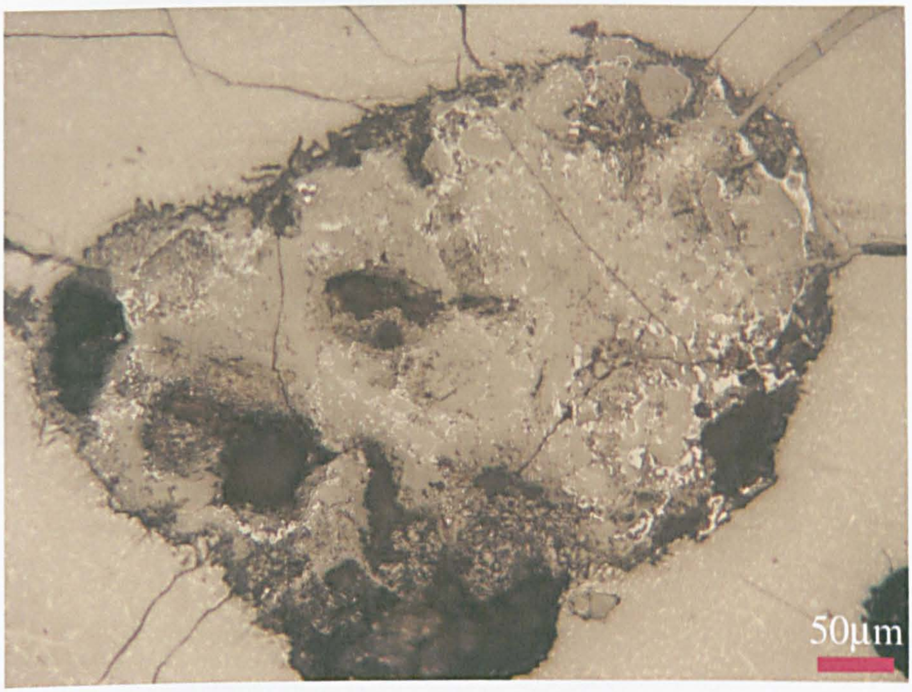


Plate 4.17 Unreacted fragment of iron ore in slag from group MG-1 (Sample B01, Optical microscope, PPL).

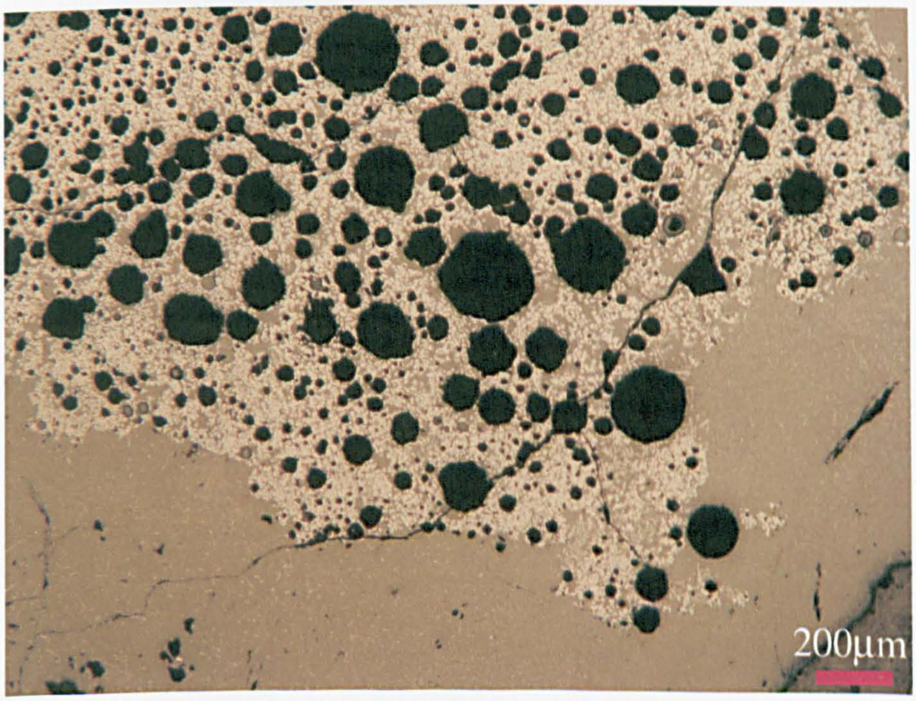


Plate 4.18 Agglomerations of iron oxides in slag from group MG-1 resulting from the decomposition of pieces of iron ore (Sample A04, Optical microscope, PPL).

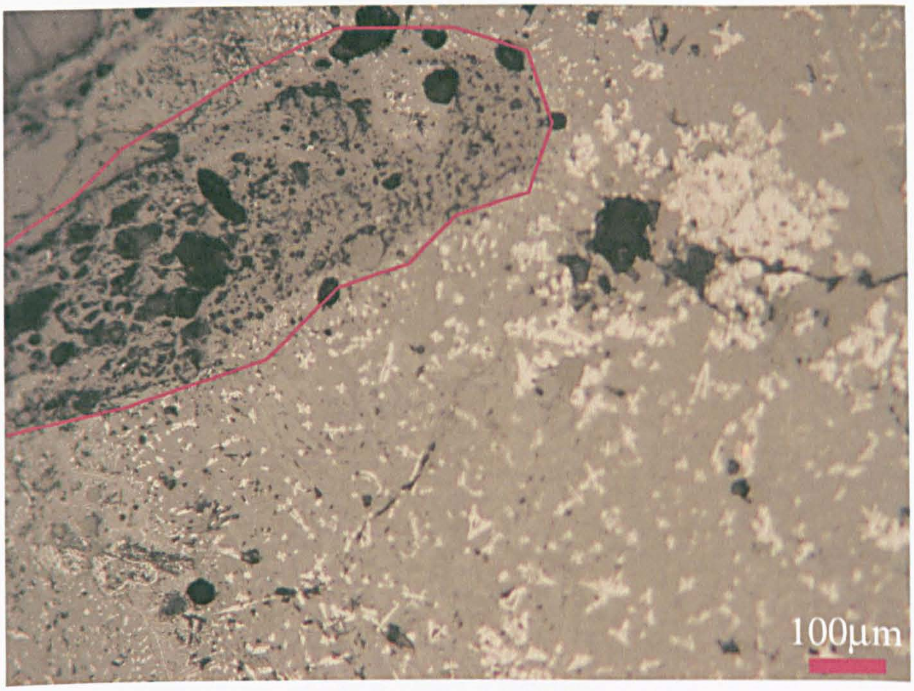


Plate 4.19 Piece of eroded refractory material (marked with red line) in slag from group MG-1 (Sample A05, Optical microscope, PPL).

Plate 4.20 Devitrification inside glass phase in slag from group MG-2 (Sample A19, Optical microscope, PPL).

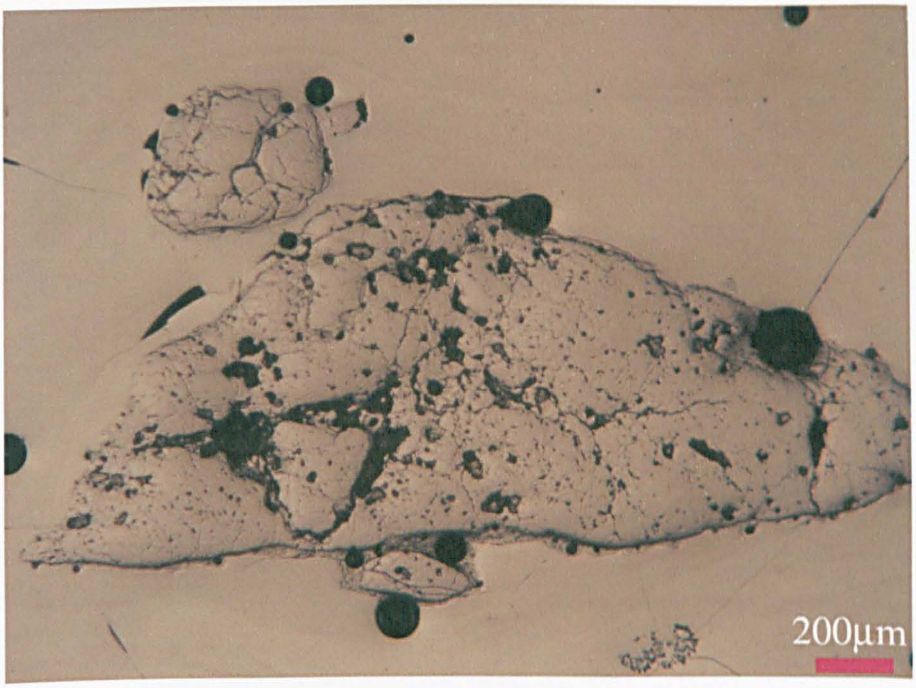


Plate 4.21 Unreacted silica grains in slag from group MG-2 (Sample A10, Optical microscope, PPL).

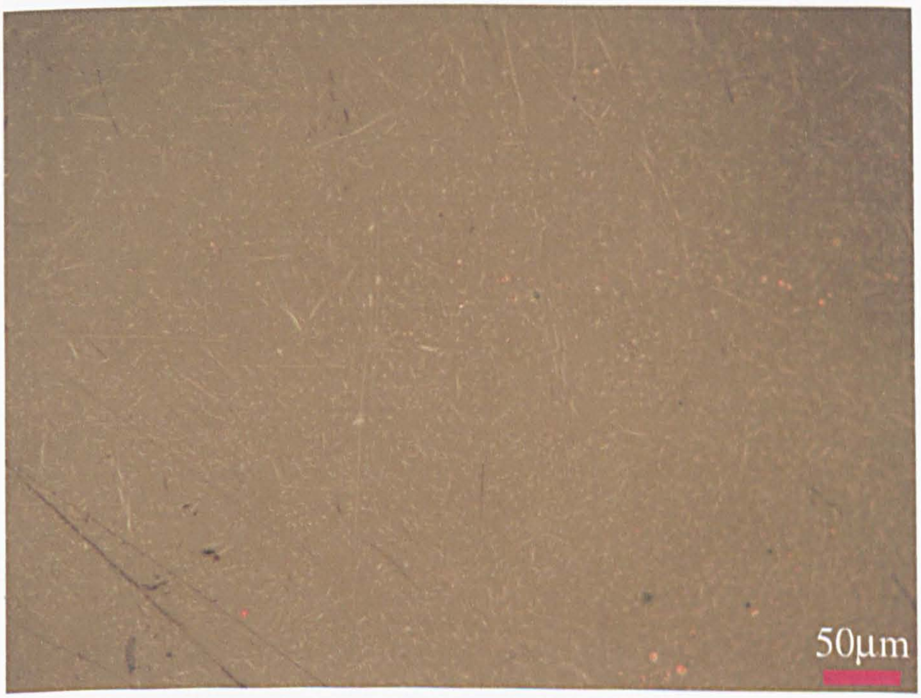


Plate 4.22 Areas with free iron oxides in slag from group MG-2 (Sample B23, Optical microscope, PPL).

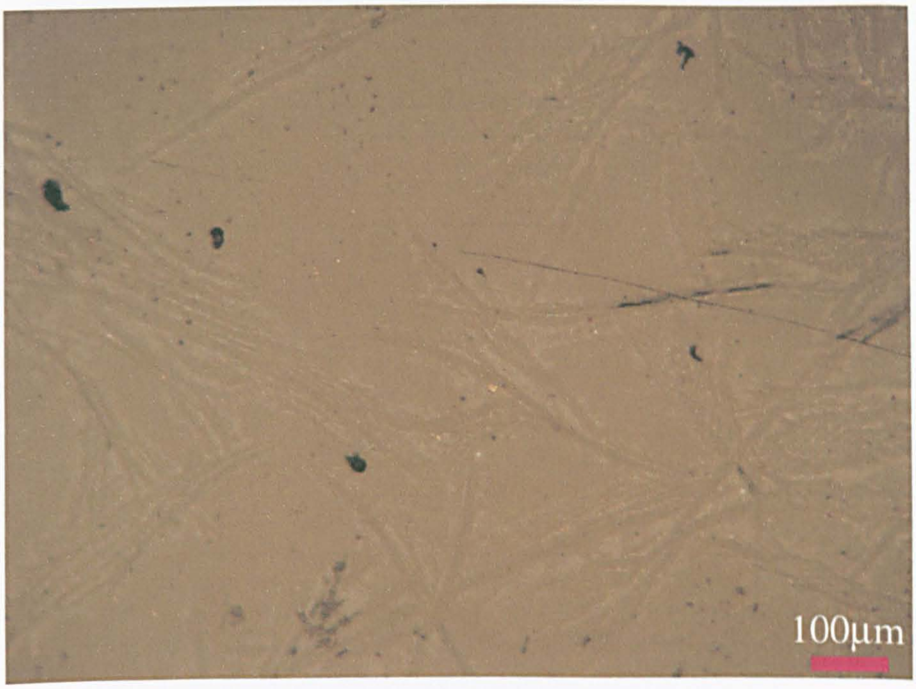


Plate 4.23 Typical microstructure of slag from group MG-3 (Sample B22, Optical microscope, PPL).

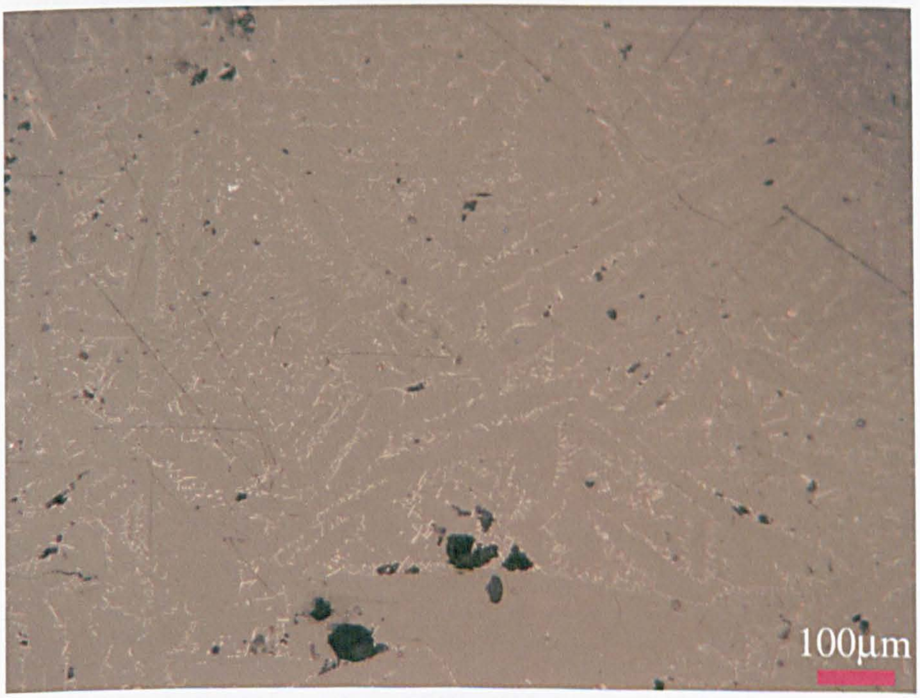


Plate 4.24 Typical microstructure of slag from group MG-4 (Sample A06, Optical microscope, PPL).

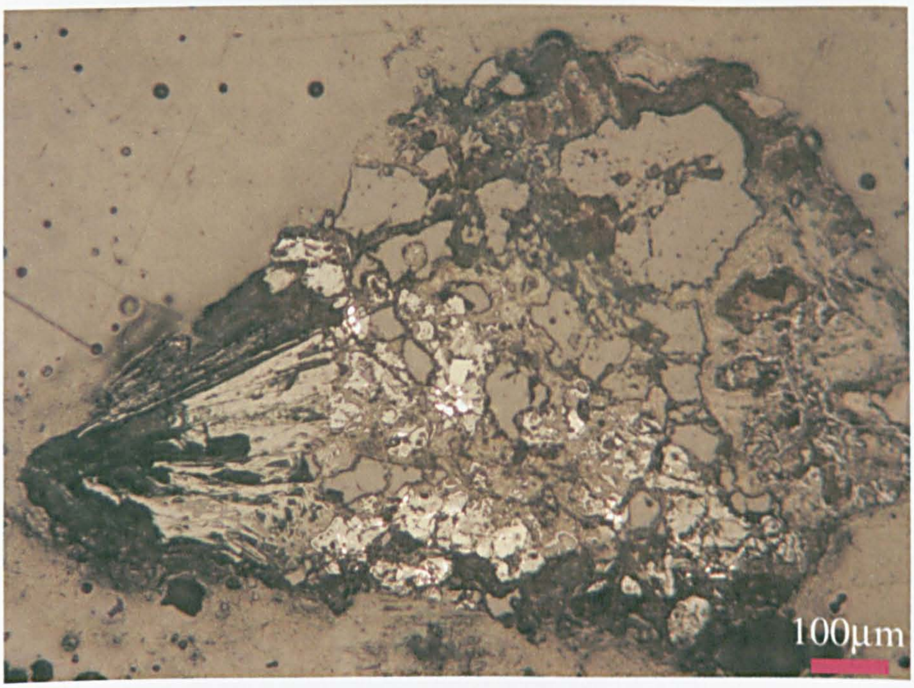


Plate 4.25 Copper-ore sample ORE-1 (Optical microscope, PPL).

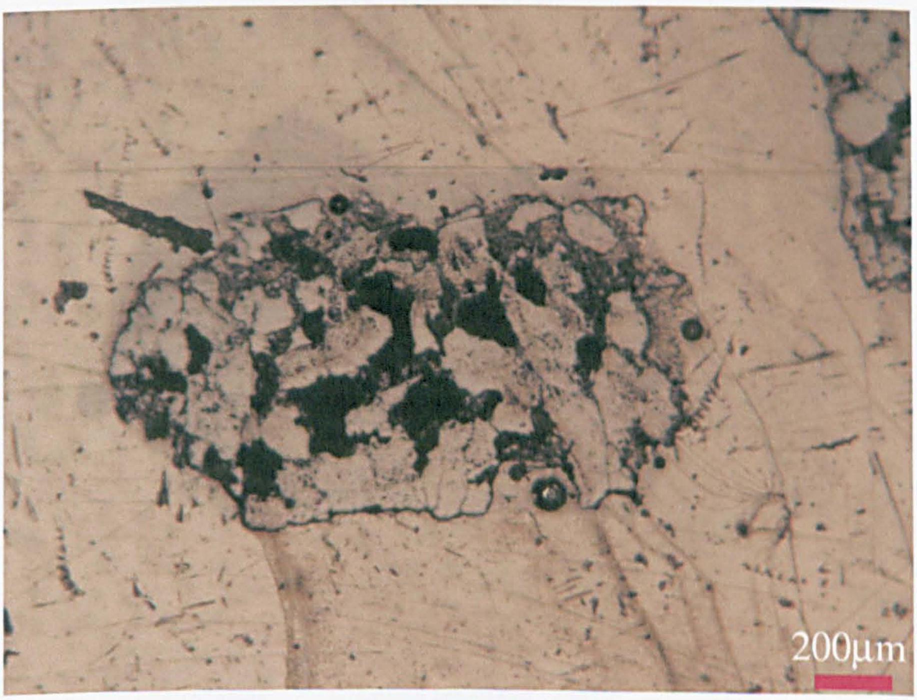


Plate 4.26 Copper-ore sample ORE-2 (Optical microscope, PPL).

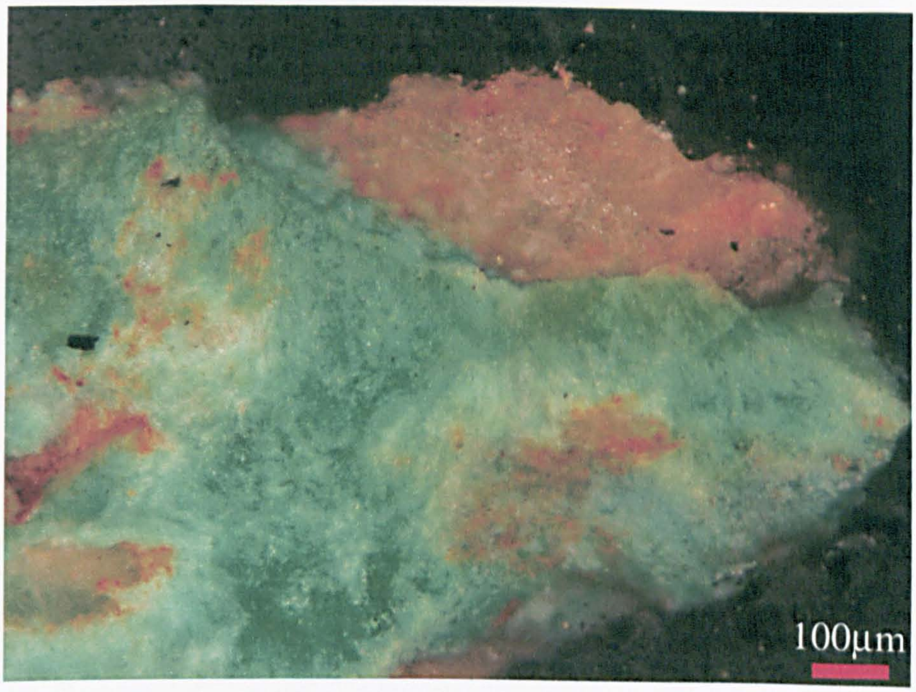


Plate 4.27 Copper-ore sample ORE-3 (Optical microscope, XPL).

Plate 4.28 Iron-ore fragment from Chrysokamino.

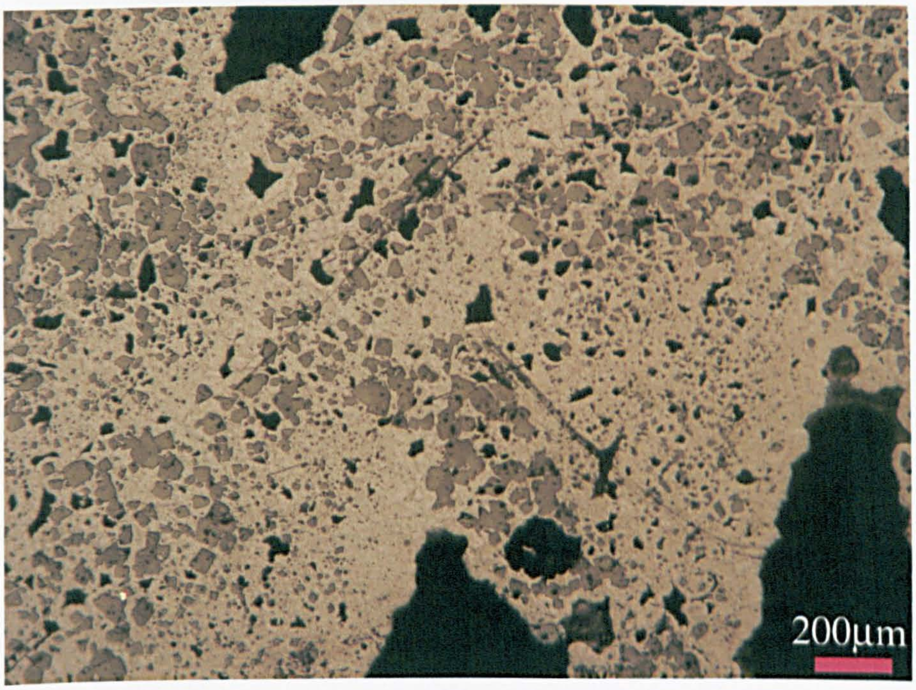


Plate 4.29 Iron-ore sample (Optical microscope, PPL).

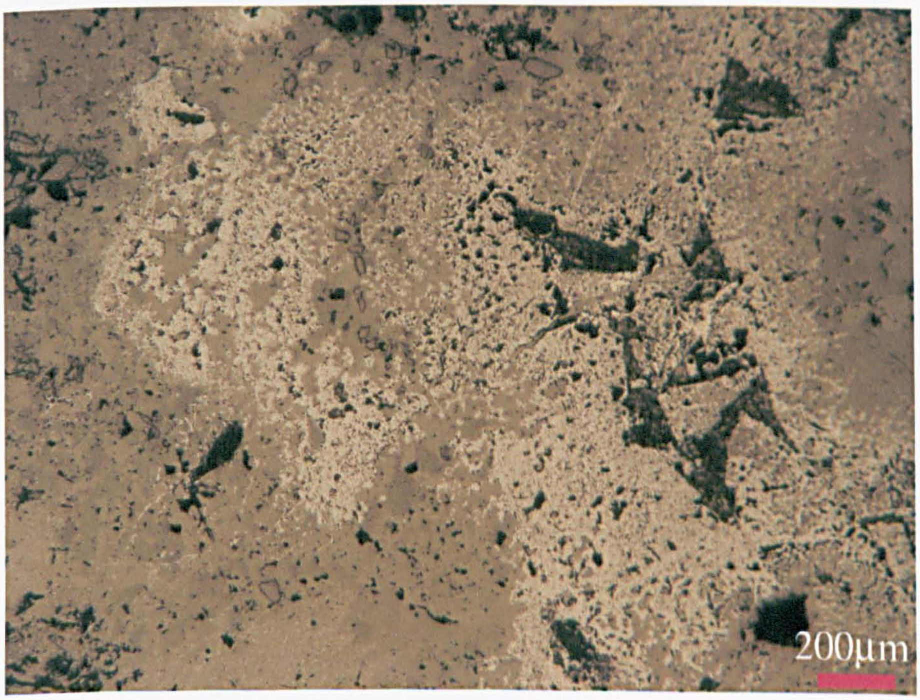


Plate 4.30 Sample from local iron mineralisation (Optical microscope, PPL).

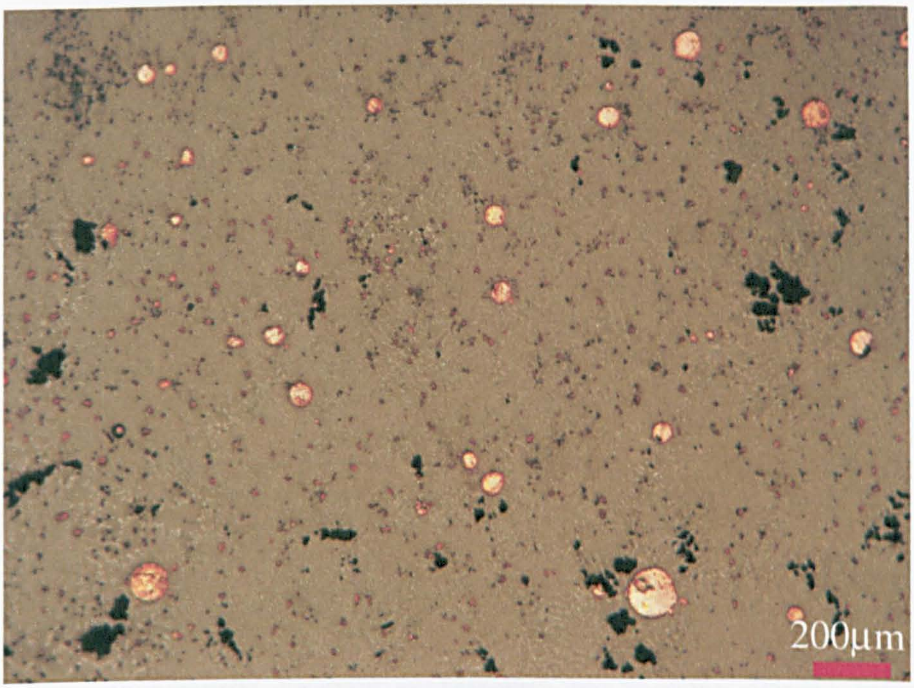


Plate 5.1 Abundant prills suspended in a slag sample from the copper-smelting site of Sideri on Kythnos (Optical microscope, PPL).

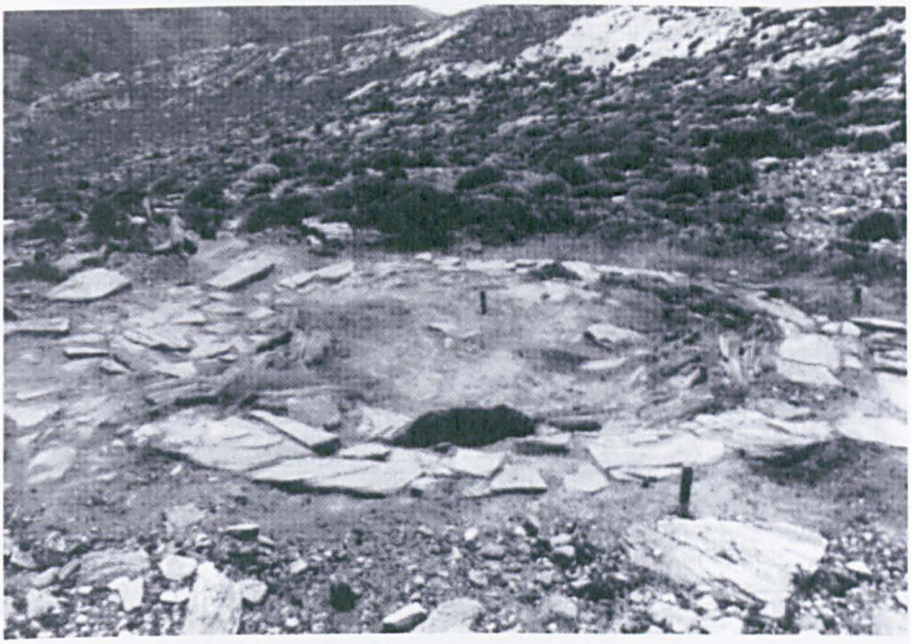
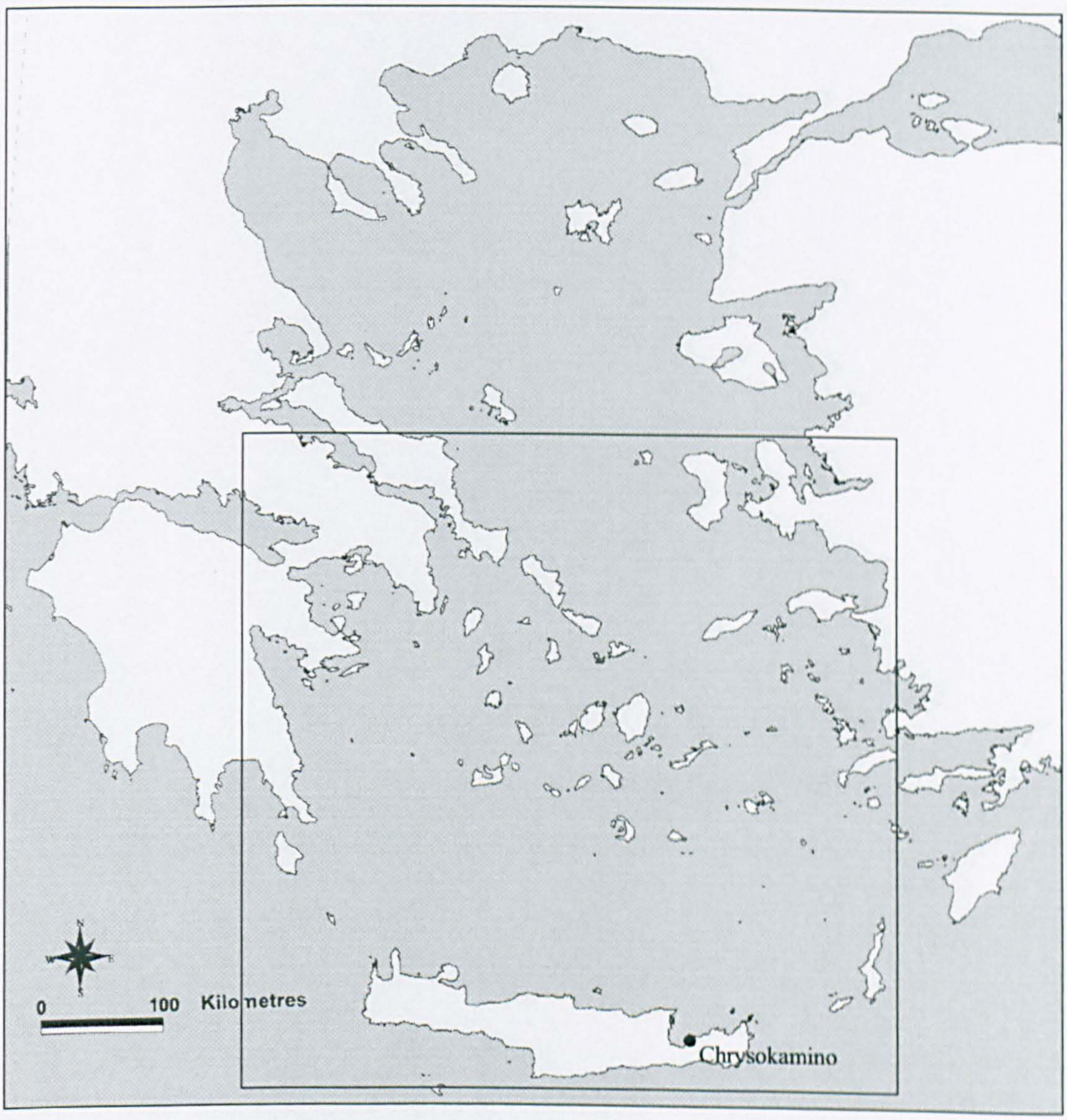


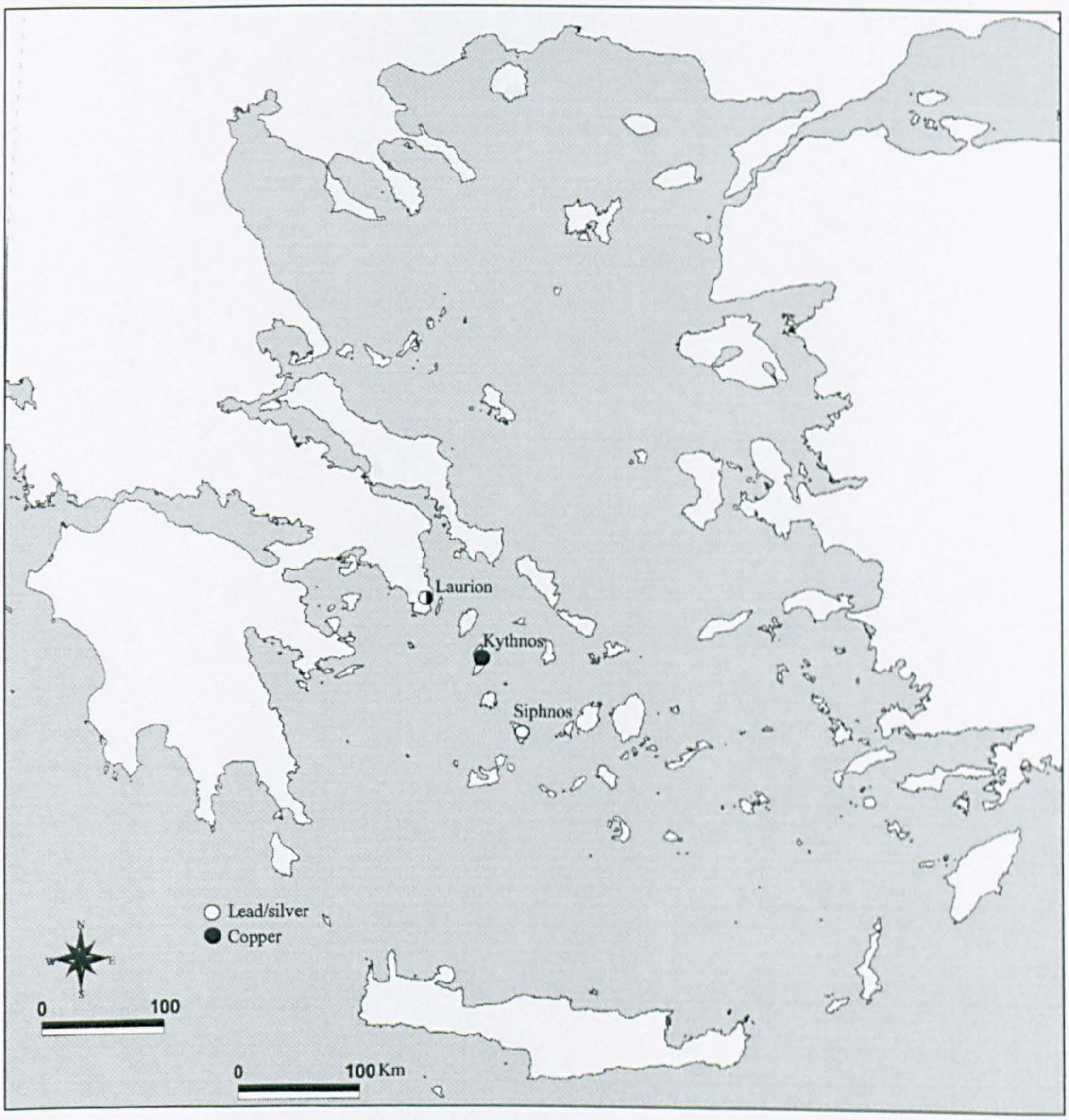
Plate 6.1 Circular structure at Skouries on Kythnos cleared from vegetation (after Stos-Gale 1989: fig. 31.13).

Plate 6.2 'Fenced-in' smelting furnaces from Site 30 in Timna (after Rothenberg 1990: fig.18).

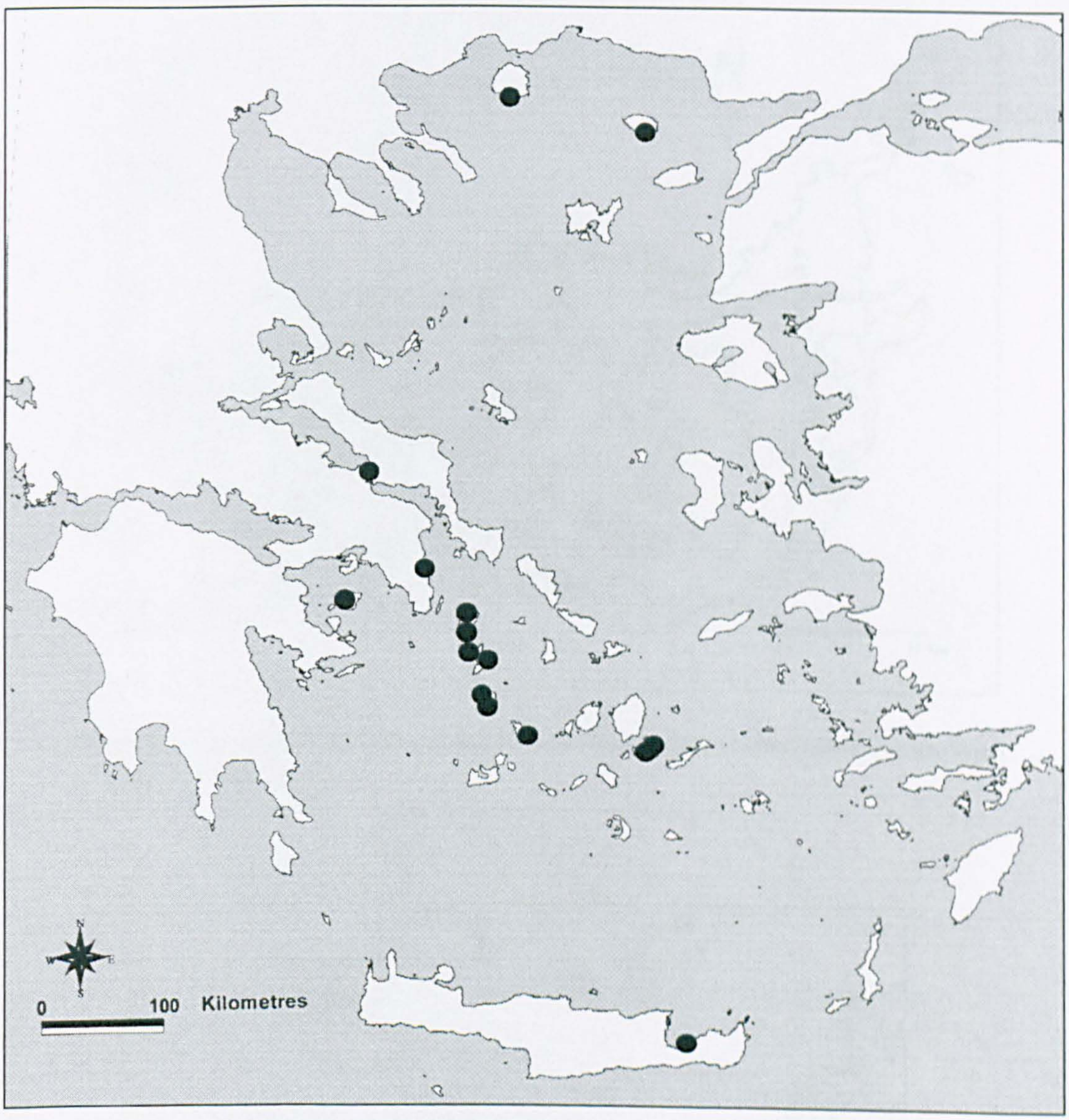
MAPS



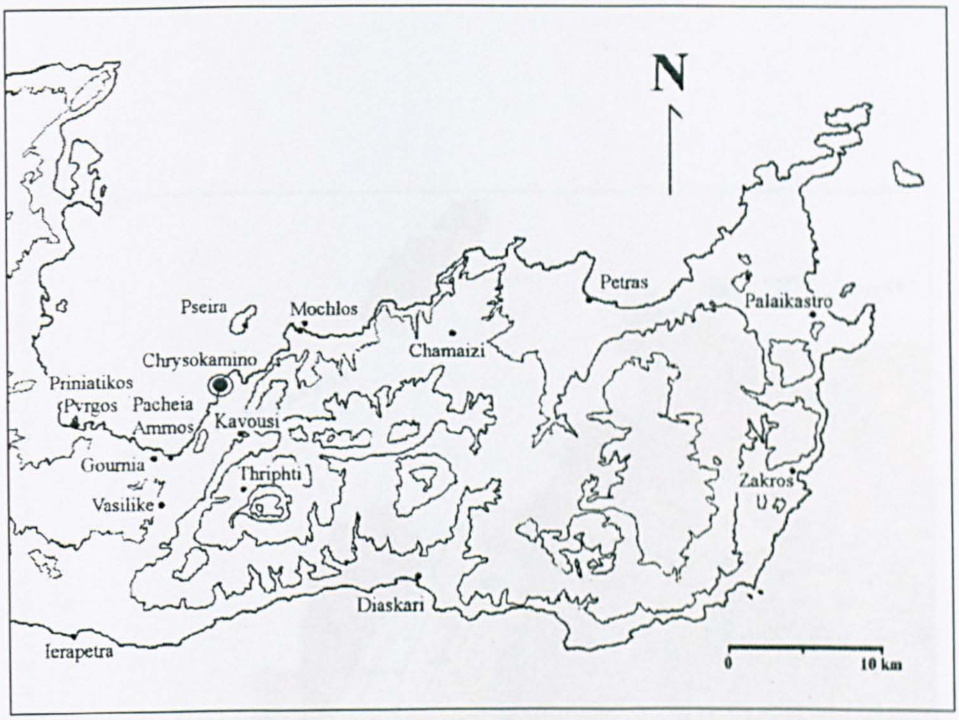
Map 1.1 Geographical scope of study and the location of Chrysokamino.



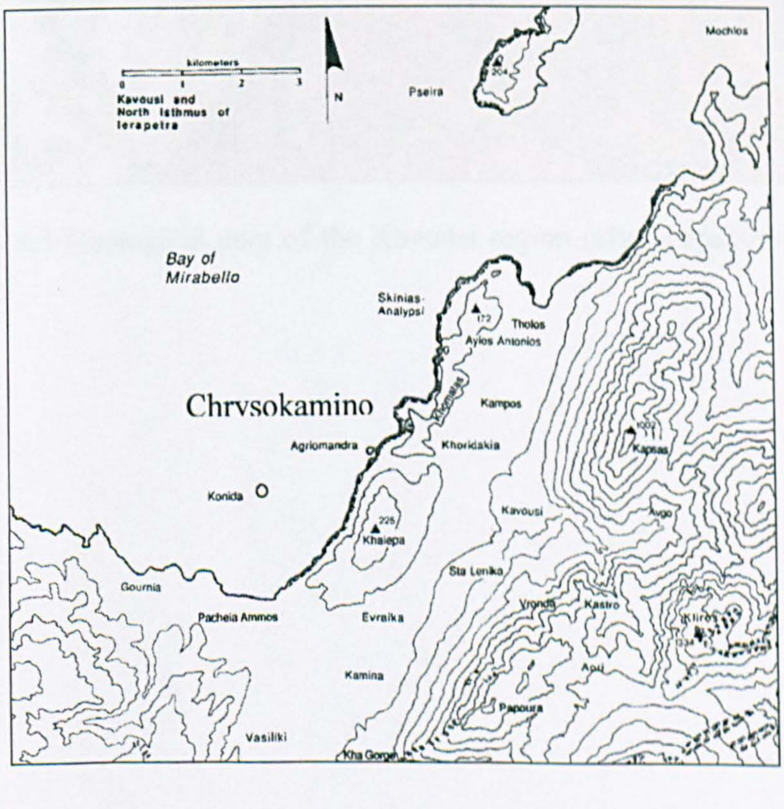
Map 2.1 Major sources of lead/silver and copper ores in the EBA Aegean according to the results of lead isotope analysis.



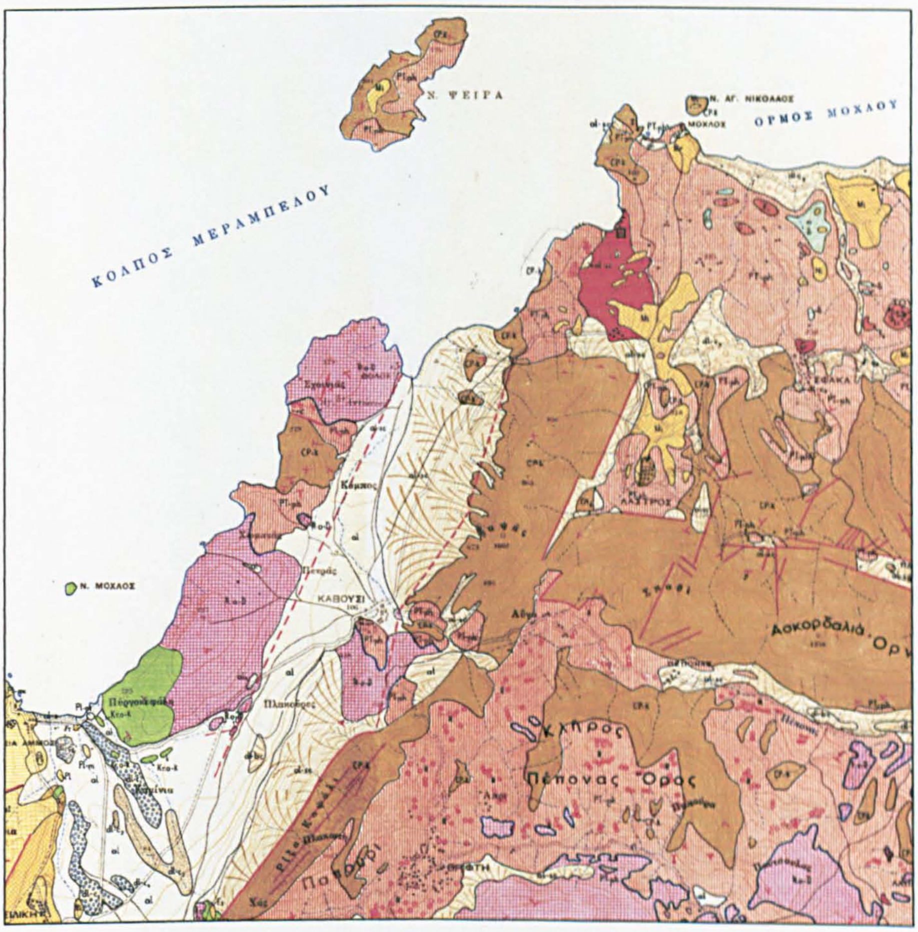
Map 2.2 Distribution of Aegean sites with possible evidence for early copper-smelting activities.



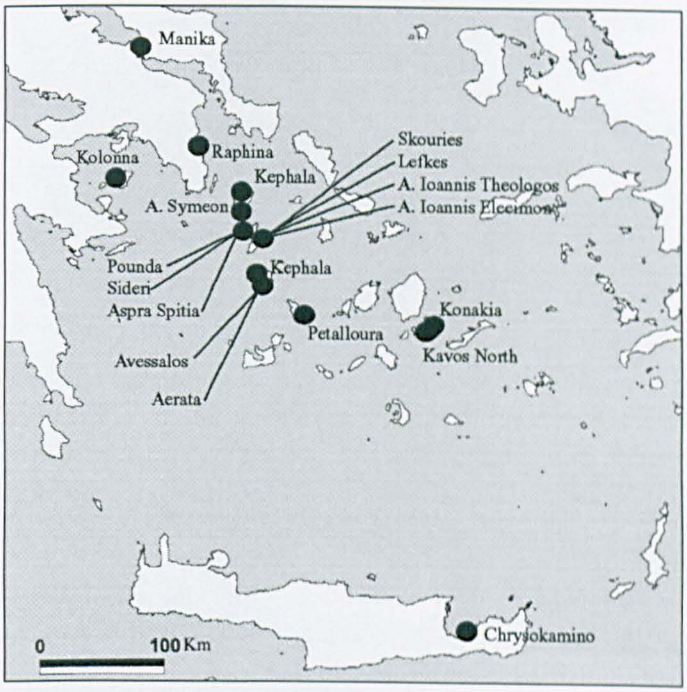
Map 4.1 The site of Chrysokamino in northeastern Crete (after Betancourt *et al* 1999: fig. 1).



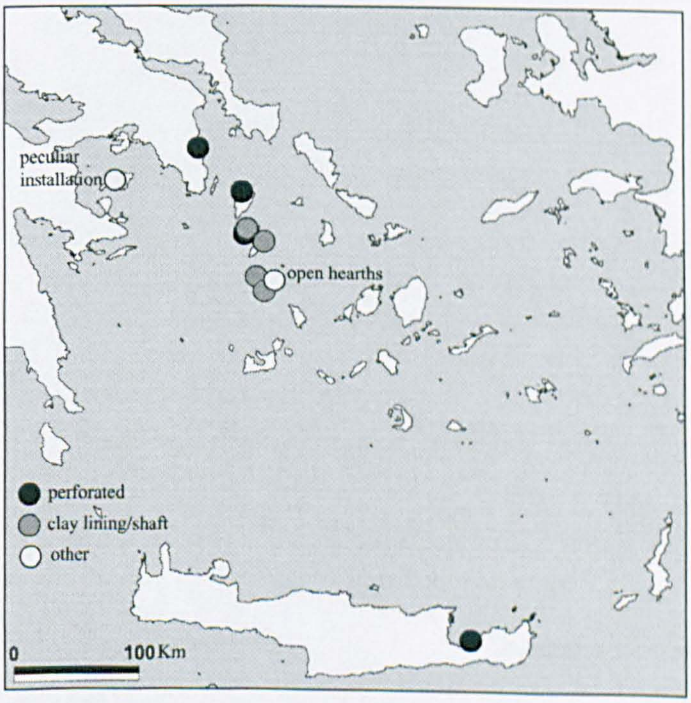
Map 4.2 Topographic map of the Kavousi region (after Haggis 1996: fig.1).



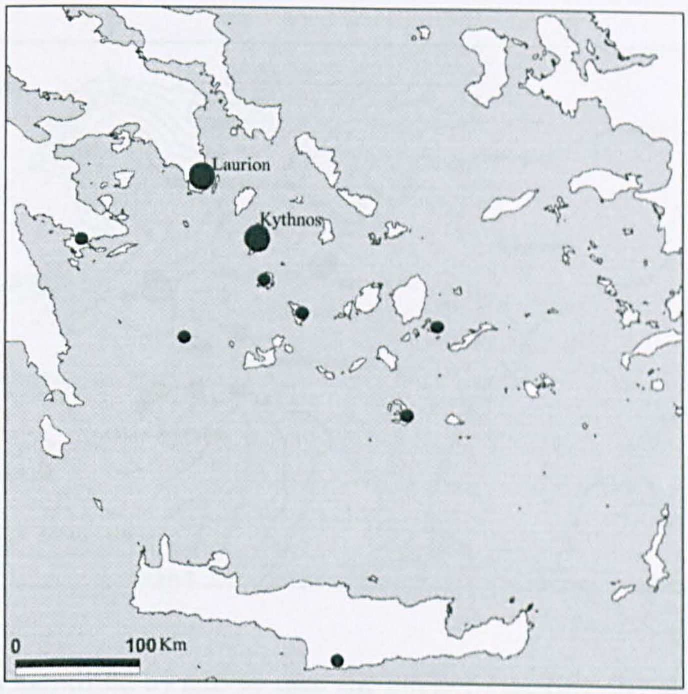
Map 4.3 Geological map of the Kavousi region (after Papastamatiou 1959).



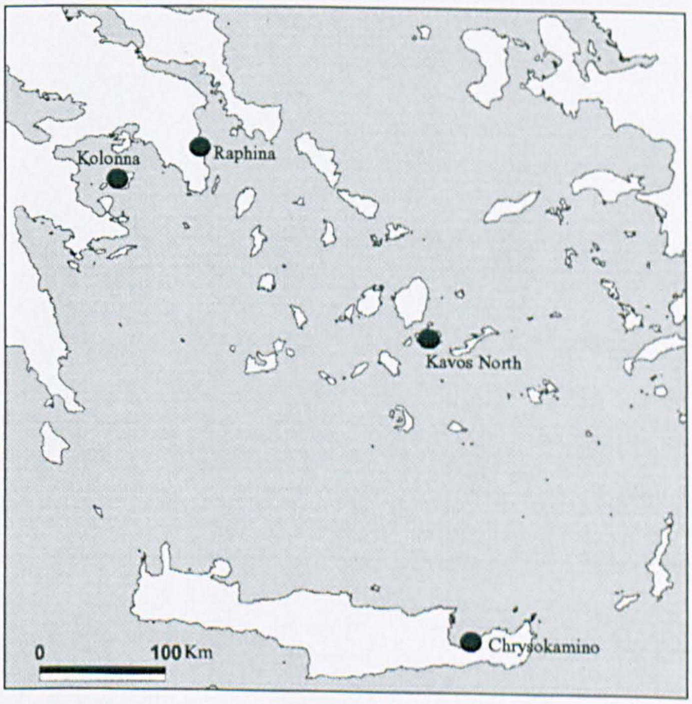
Map 5.1 Southern Aegean sites with possible evidence for early copper-smelting activities.



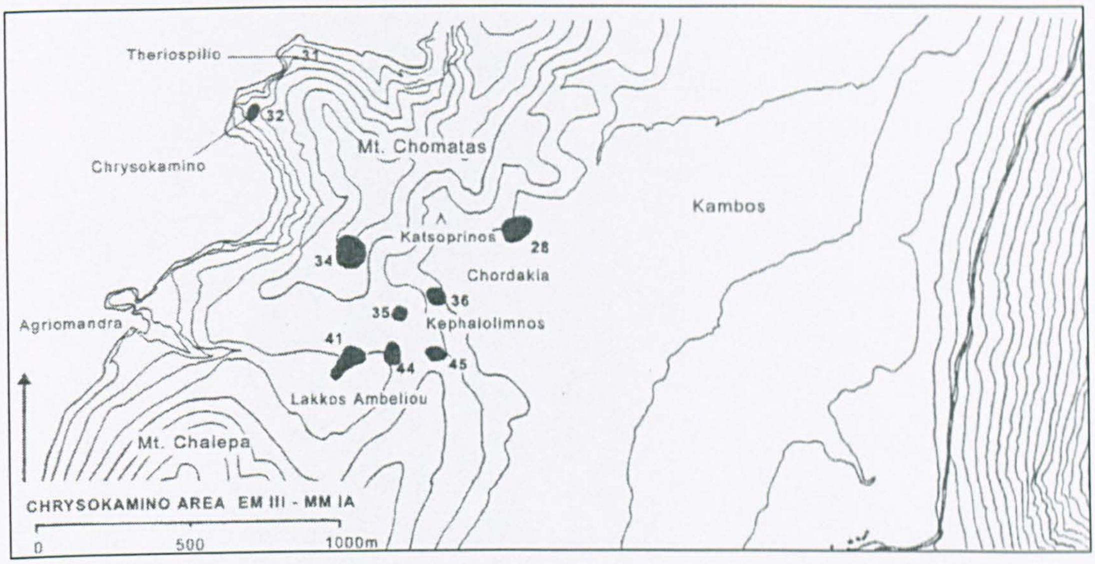
Map 5.2 Distribution of various furnace types used in copper smelting in the FN/EBA southern Aegean.



Map 6.1 Known occurrences of copper minerals in the southern Aegean with possible evidence for prehistoric exploitation.



Map 6.2 EBA copper-smelting sites near/inside habitation areas in the southern Aegean.



Map 6.3 Sites identified by survey near the copper-smelting site at Chrysokamino.

TABLES

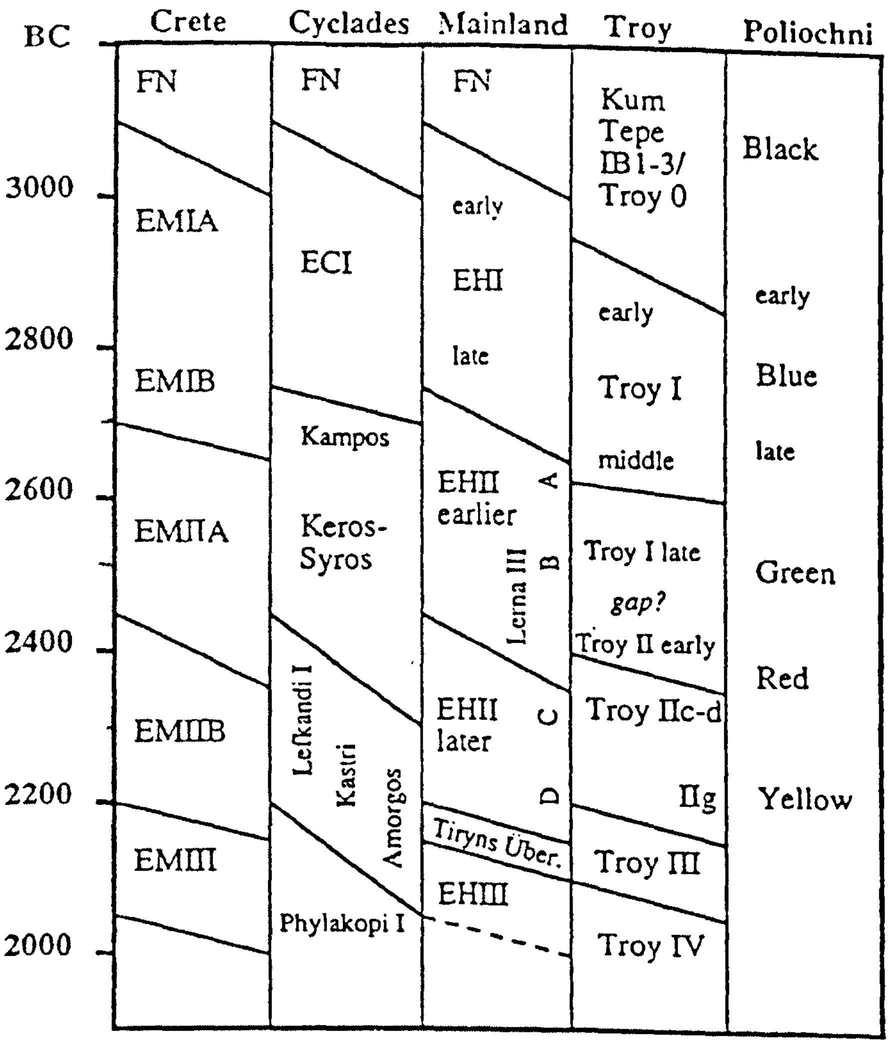


Table 1.1 Early Bronze Age Aegean chronology (after Manning 1995: fig. 2).

Trench	Pass	Slag samples	Copper-ore samples	Iron-ore samples	Other
X-N-20	4 (-0.40m)	Series A 26 samples	-	-	-
	3 (-0.30m)	Series B 19 samples	-	-	-
Surface	-	Series C 1 sample	Series ORE 3 samples	Series IRON ORE 1 sample	Rock fragment (excluded) 1 sample

Table 4.1 Context of ore and slag samples from Chrysokamino included in analytical study.

Microscopic group	Number of samples	Samples
MG-1	27	A03, A04, A05, A07, A08, A09, A15, A16, A17, A18, A20, A21, A23, A25, A29, B01, B05, B06, B07, B12, B13, B14, B15, B18, B20, B24, C01
MG-2	13	A10, A11, A12, A13, A14, A19, A26, A28, B02, B11, B17, B23, B26
MG-3	3	A02, B03, B22
MG-4	3	A01, A06, B09

Table 4.2 Classification of slag samples from Chrysokamino into ‘microscopic’ groups.

Matrix \ Fe-oxides	Wustite	Wustite + Magnetite	Magnetite + Wustite	Magnetite
Extensive crystallisation	A04, A21, B01, B13	B24	A20, A25, B12, B18	A03, A05, A15, A16, A18
Limited crystallisation		B06, B20	A29, B07, B14	A23, B05, C01
Complete vitrification		A07	A09, A17, A08	B15

Table 4.3 Sub-division of microscopic group MG-1 according to the degree of crystallisation of the siliceous matrix and the nature of the free iron oxides.

Silica grains/Fe-oxides	Absent	Rare	Frequent
Absent	B11, A14, A26	A19, B26, A28	B02
Rare			B23
Frequent	A10, A11, A12	A13	

Table 4.4 Sub-division of microscopic group MG-2 according to the presence of free iron oxides and unfused silica grains.

Sample	**SiO_2**	**FeO**	**CaO**	**Al_2O_3**	**MgO**	**MnO**	**Na_2O**	**K_2O**	**CuO**	**SO_3**	**Cl_2O**	**As_2O_3**	**NiO**	**TiO_2**	**P_2O_5**	**BaO**	**ZnO**
A01	36	20	28	5.9	1.6	0.3	1.7	0.8	0.4	0.4	0.2	0.2	nd	0.3	1.0	2.0	0.1
A02	45	12	29	5.5	1.8	0.3	1.8	0.7	0.8	0.2	0.1	0.2	nd	0.1	1.0	1.3	0.1
A03	39	33	11	7.6	1.5	0.7	2.7	0.8	1.3	0.2	0.3	0.1	nd	0.4	0.6	0.3	0.1
A04	31	35	21	5.4	1.6	0.3	2.3	1.1	0.5	0.5	0.1	nd	nd	0.2	0.6	0.4	0.1
A05	34	32	19	6.6	1.7	0.1	2.1	1.2	1.5	0.2	0.2	0.2	0.1	0.2	0.8	1.1	0.1
A06	38	16	28	7.0	3.4	0.9	2.7	1.0	0.7	0.3	0.1	0.1	nd	0.2	0.8	0.9	nd
A07	36	31	19	5.3	1.2	0.2	2.9	0.8	0.6	0.2	0.1	0.1	nd	0.3	0.8	1.3	0.2
A08	36	33	19	5.3	1.5	0.2	1.2	1.0	0.9	0.2	0.1	0.1	nd	0.2	0.8	0.6	nd
A09	34	31	21	5.5	1.5	0.2	2.2	1.0	1.3	0.3	0.2	0.2	0.1	0.2	0.7	0.7	0.1
A10	43	16	25	6.8	1.5	0.3	2.6	1.1	0.6	0.2	0.1	0.2	nd	0.5	0.9	0.6	nd
A11	46	13	18	11	1.6	0.2	4.4	1.1	1.2	0.1	0.2	0.1	nd	0.4	0.5	3.0	0.1
A12	47	11	25	7.2	2.4	0.4	2.0	1.1	1.0	0.2	0.2	0.4	nd	0.4	1.1	0.5	nd
A13	48	18	20	5.9	1.0	0.4	2.2	0.7	1.1	0.2	0.2	0.2	nd	0.3	1.0	0.9	0.2
A14*	38	22	22	7.7	2.4	0.4	2.4	1.0	1.1	nd	0.1	nd	0.1	0.2	0.5	1.2	nd
A15	39	30	12	8.8	1.6	0.3	3.3	0.7	2.3	0.2	0.3	0.1	0.1	0.4	0.8	0.2	nd

Table 4.5 SEM-EDS analysis of slag pellets of series A. Analyses marked with an asterisk have been obtained by multiple area-scans on polished sections (nd: not determined; <0.1 wt-%).

Sample	**SiO_2**	**FeO**	**CaO**	**Al_2O_3**	**MgO**	**MnO**	**Na_2O**	**K_2O**	**CuO**	**SO_3**	**Cl_2O**	**As_2O_3**	**NiO**	**TiO_2**	**P_2O_5**	**BaO**	**ZnO**
A16*	40	31	14	5.9	1.4	0.2	2.5	0.6	1.7	0.2	0.1	0.7	nd	0.2	0.9	0.1	0.5
A17*	35	32	18	7.4	1.8	0.3	1.8	0.9	0.9	0.3	nd	0.1	0.1	0.1	0.5	0.8	nd
A18*	39	34	9.9	8.6	1.8	0.3	3.7	0.9	0.9	nd	0.1	0.1	nd	0.5	0.4	nd	nd
A19*	39	28	15	8.6	2.3	1.2	2.7	1.2	0.8	0.1	0.1	nd	0.1	0.4	0.7	0.3	nd
A20	40	24	17	7.2	1.5	0.4	2.0	0.7	2.6	0.1	0.2	0.6	nd	0.3	0.8	1.5	0.4
A21	32	28	27	4.8	1.3	0.2	2.1	0.7	0.9	0.2	0.1	0.2	nd	0.2	0.6	1.0	0.1
A23	40	32	9.3	9.2	1.9	0.5	2.9	1.3	1.0	0.3	0.1	nd	nd	0.5	0.7	0.1	0.1
A25	43	21	20	6.4	1.4	0.1	2.0	0.9	1.7	0.1	0.2	0.2	nd	0.3	1.0	0.9	0.3
A26	42	25	21	3.9	1.2	0.2	1.8	0.6	2.0	0.1	0.2	0.1	0.1	0.2	0.8	0.5	0.2
A28	42	25	20	5.7	1.3	0.2	1.6	0.7	1.0	0.2	0.2	nd	nd	0.3	0.7	0.9	0.2
A29	37	29	19	7.0	1.6	0.3	2.8	0.9	0.8	0.2	0.1	0.1	nd	0.3	0.7	0.5	nd

Table 4.5 (*cont.*) SEM-EDS analysis of slag pellets of series A. Analyses marked with an asterisk have been obtained by multiple area-scans on polished sections (nd: not determined; <0.1 wt-%).

Sample	SiO_2	FeO	CaO	Al_2O_3	MgO	MnO	Na_2O	K_2O	CuO	SO_3	Cl_2O	As_2O_3	NiO	TiO_2	P_2O_5	BaO	ZnO
B01	35	28	24	5.1	1.5	0.2	1.4	1.1	0.4	0.3	0.1	0.1	nd	0.2	0.9	0.6	0.1
B02	39	23	23	4.9	1.3	0.2	1.2	0.6	2.2	0.1	0.1	0.4	nd	nd	0.8	3.8	0.2
B03	44	15	26	5.5	1.5	0.3	2.0	0.8	1.6	nd	0.1	0.3	nd	0.2	1.0	1.7	0.1
B05	35	27	22	5.7	2.7	0.3	2.6	0.8	1.1	0.1	0.2	0.4	0.1	0.2	0.9	0.9	0.1
B06	36	33	15	6.3	2.1	0.2	3.0	1.1	1.0	0.4	0.2	nd	nd	0.3	0.6	0.7	0.1
B07	35	36	15	6.1	1.6	0.2	2.9	0.9	1.1	0.3	0.2	nd	0.1	0.2	0.7	0.5	nd
B09	38	13	31	5.7	5.9	0.3	1.6	0.8	0.7	0.2	0.1	0.2	nd	0.4	0.8	0.5	0.1
B11	41	17	27	5.7	1.5	0.2	2.3	0.7	1.1	0.1	0.2	0.3	0.1	0.2	0.8	1.0	0.1
B12	39	29	14	9.2	2.5	0.4	1.9	1.0	1.2	0.2	0.2	nd	nd	0.4	0.7	0.5	nd
B13	36	30	21	5.5	1.6	0.1	1.5	0.9	1.0	0.2	0.1	0.1	nd	0.2	1.0	0.5	nd
B14	35	35	15	7.0	1.6	0.3	3.0	0.8	1.5	0.3	0.1	nd	nd	0.3	0.6	0.1	nd
B15	37	31	14	8.0	1.6	0.5	2.7	0.6	2.9	0.2	0.2	0.2	nd	0.2	0.6	0.3	nd
B17*	41	25	20	6.4	1.3	0.5	2.8	0.8	0.6	0.3	nd	0.2	0.1	0.3	0.7	0.7	nd
B18	38	28	17	7.5	1.6	0.4	2.2	1.0	1.0	0.3	0.2	0.2	nd	0.4	0.9	0.7	0.1
B20	33	28	24	5.6	1.8	0.3	2.9	0.9	0.9	0.2	0.1	nd	nd	0.2	0.8	1.3	nd
B22	43	17	26	5.1	1.1	0.2	2.3	0.6	1.3	0.1	0.1	0.5	nd	0.3	0.8	1.4	0.1
B23	36	30	15	8.0	1.9	1.4	3.3	1.0	0.4	0.5	0.2	0.1	nd	0.3	0.7	0.1	nd
B24*	33	32	19	7.8	1.4	0.6	2.0	1.0	0.7	0.4	nd	0.2	nd	0.2	0.3	0.5	0.1
B26	41	24	22	5.2	1.4	0.1	1.9	1.1	0.7	0.3	0.1	nd	0.1	0.2	1.0	0.7	0.2
C01	36	31	18	7.3	1.5	0.3	3.1	0.8	1.0	0.1	nd	nd	0.1	0.4	0.5	0.3	0.1

Table 4.6 SEM-EDS analysis of slag pellets of series B and C. Analyses marked with an asterisk have been obtained by multiple area-scans on polished sections (nd: not determined; <0.1 wt-%).

Group	Sample	SiO_2	FeO	CaO	Al_2O_3	MgO	MnO	Na_2O	K_2O	CuO	SO_3	Cl_2O	As_2O_3	NiO	TiO_2
MG-1	A04	34	35	28	1.0	2.0	NA	0.2	0.4	nd	0.1	nd	nd	NA	NA
	A04	36	29	26	5.7	1.3	NA	0.8	1.1	0.1	NA	0.1	nd	NA	NA
	A05	34	33	28	0.5	2.8	NA	0.6	0.2	0.1	0.1	nd	nd	nd	NA
	A05	42	20	22	8.9	1.0	NA	2.3	2.9	0.3	nd	0.1	0.1	nd	NA
	A15	43	25	21	7.8	2.1	NA	0.6	nd	0.1	0.2	nd	nd	nd	NA
	A18	33	46	11	7.3	1.1	NA	0.4	0.8	0.2	0.4	0.1	nd	nd	NA
	B01	34	32	26	3.1	1.9	0.2	1.2	0.7	0.2	0.3	0.1	0.1	0.1	NA
	B01	34	32	26	2.9	1.9	0.3	1.2	0.7	0.4	0.4	nd	nd	nd	NA
	B01	34	33	26	2.3	2.6	0.3	1.0	0.6	nd	0.2	nd	nd	nd	NA
	B01	41	14	35	4.4	3.5	nd	1.9	0.4	nd	nd	nd	0.4	nd	NA
	B01	41	14	34	4.9	2.8	0.2	2.2	0.7	nd	nd	nd	0.2	nd	NA
	B01	41	13	35	4.2	4.2	0.1	2.1	0.4	0.1	nd	0.1	0.1	0.1	NA
	B12	31	40	12	11	3.8	0.4	0.5	0.1	nd	nd	0.1	nd	nd	0.9
	B13	41	16	34	4.3	2.5	0.1	2.0	0.4	nd	nd	nd	nd	nd	0.1
	B13	41	16	33	4.3	2.4	0.1	2.1	0.6	nd	nd	nd	0.3	nd	0.2
	B20	36	25	28	5.7	1.4	NA	1.4	0.9	0.2	0.2	0.1	0.1	nd	NA
MG-2	A13	47	21	21	5.3	2.4	0.2	0.4	0.6	0.7	nd	nd	0.5	nd	0.4
	A14	41	12	33	6.6	3.1	0.3	3.9	0.3	nd	nd	nd	nd	nd	NA
	A14	40	12	33	6.6	3.8	0.3	3.4	0.3	0.1	nd	nd	nd	0.2	NA
	A14	41	12	33	7.1	3.1	0.1	3.1	0.2	0.1	0.1	nd	nd	nd	NA
	A14	40	22	23	8.0	2.6	0.6	1.5	1.2	0.6	nd	nd	0.1	0.1	NA
	A19	37	36	14	9.0	2.9	NA	1.0	0.9	0.1	nd	nd	nd	0.2	NA
	A19	37	34	13	8.6	3.4	0.8	1.2	1.0	nd	0.2	0.1	0.1	0.1	0.5
	B17	43	27	21	6.3	0.9	NA	1.0	0.6	0.5	0.1	nd	0.1	nd	NA

Table 4.7 SEM-EDS analysis of silicate crystals in slag samples from Chrysokamino (NA: not analysed; nd: not determined; <0.1 wt-%). Samples divided into microscopic groups.

Group	Sample	SiO_2	FeO	CaO	Al_2O_3	MgO	MnO	Na_2O	K_2O	CuO	SO_3	Cl_2O	As_2O_3	NiO	TiO_2
MG-1	A05	40	28	22	6.3	1.8	NA	0.9	nd	0.2	0.1	nd	nd	nd	NA
	A17	39	25	21	7.3	1.9	0.7	3.4	1.2	0.1	0.1	nd	nd	nd	0.1
	A18	42	33	10	8.7	1.6	NA	3.1	1.1	0.2	0.2	nd	nd	nd	NA
	B05	38	25	25	6.7	2.2	NA	2.1	0.7	nd	0.1	0.1	nd	NA	NA
	B12	39	28	16	9.0	1.5	0.4	4.2	1.7	nd	0.2	nd	nd	nd	0.8
	B13	41	30	15	6.7	0.9	0.6	1.5	2.3	nd	0.3	0.1	nd	nd	1.3
	B13	41	31	15	7.8	0.6	0.5	0.6	1.6	0.1	0.1	0.1	nd	nd	1.3
	B24	38	25	22	7.9	1.9	0.6	3.3	1.0	nd	0.3	nd	nd	nd	nd
MG-2	A13	49	13	27	6.0	1.1	0.3	1.4	0.6	0.4	0.1	0.1	nd	nd	0.5
	A14	40	26	22	8.3	2.6	0.4	0.3	0.1	0.2	nd	0.1	nd	nd	NA
	A14	42	25	21	8.3	2.1	0.6	0.7	0.3	nd	nd	nd	0.2	0.1	NA
	A14	40	12	33	7.2	2.8	0.2	3.0	0.3	0.1	nd	0.1	nd	0.1	NA
	A14	39	23	23	7.7	2.4	0.6	2.2	1.1	0.3	0.1	0.1	0.1	0.1	NA
	A19	40	29	15	8.8	2.0	NA	3.1	1.4	0.1	0.1	0.1	0.3	0.1	NA
	A19	39	29	15	8.2	2.6	1.1	2.8	1.4	0.1	0.2	nd	nd	nd	0.4
	B17	41	27	21	5.9	1.5	NA	2.3	1.2	0.2	0.2	0.1	0.1	nd	NA

Table 4.8 SEM-EDS analysis of vitrified areas in slag samples from Chrysokamino (NA: not analysed; nd: not determined; <0.1 wt-%). Samples divided into microscopic groups.

Group	Sample	Cu	Fe	As	Ni	S
MG-1	A05	94	2.8	2.7	0.9	nd
	A05	90	1.3	7.0	1.3	0.1
	A05	95	2.3	2.6	0.3	nd
	A05	95	1.4	2.8	0.7	0.2
	A05	96	0.7	2.9	0.7	nd
	A09	97	2.0	0.8	0.4	0.2
	A09	96	1.0	2.5	0.3	0.2
	A09	95	0.6	4.0	0.1	0.2
	A09	96	0.4	2.8	0.2	0.2
	A15	98	2.3	nd	nd	0.2
	A15	97	2.3	0.1	nd	0.3
	A15	96	2.5	0.9	0.4	0.2
	A15	95	3.3	0.4	0.9	0.1
	A15	90	1.2	8.4	0.8	nd
	A15	89	0.3	9.8	1.0	0.1
	A15	93	1.2	3.6	1.7	0.1
	A15	91	1.8	4.0	0.5	2.9
MG-1	A16	96	3.5	0.2	nd	nd
	A16	97	3.0	nd	nd	nd
	A16	98	1.7	0.1	nd	nd
	A16	99	1.3	nd	0.1	nd
	A17	91	2.2	4.9	2.0	0.2
	A18	90	2.5	5.2	2.0	0.1
	A18	92	3.1	3.2	1.2	0.1
	A18	91	2.5	4.9	1.3	0.2
	B05	89	2.3	7.8	0.9	0.1
	B05	87	1.9	10	0.8	0.1
	B05	72	1.8	23	2.8	0.1
	B05	91	1.2	6.8	0.5	0.1
	B05	67	1.3	31	0.4	0.2
	B20	89	2.8	7.5	1.1	nd
	B20	89	3.6	6.6	0.9	nd
	B20	86	4.9	8.2	0.9	0.1
	B20	88	2.9	8.1	1.0	0.1
MG-1	C01	96	2.1	1.0	1.0	0.1
	C01	95	3.1	1.2	1.0	0.1
	C01	95	2.7	0.9	1.1	0.1
	C01	94	3.4	1.6	0.8	0.1
	C01	94	3.3	1.9	0.5	0.4
	C01	95	2.4	1.4	0.7	0.1
	C01	93	4.7	1.1	0.9	0.1
	C01	96	1.8	1.4	0.9	0.2
	C01	95	2.1	2.1	0.8	0.2
	C01	95	2.3	1.4	0.9	0.2
	C01	95	3.4	0.5	1.1	0.1
	C01	96	0.3	2.2	1.3	0.2
	C01	95	2.8	1.6	0.7	0.1
	C01	94	1.5	3.3	1.0	0.2
MG-2	A11	89	1.6	7.8	0.4	0.9
	A14	88	2.2	6.6	0.8	2.5
	A14	90	1.3	7.8	0.8	nd
	A19	62	0.5	23	15	nd
	B17	65	1.8	33	0.7	0.1
	B17	74	0.7	25	0.3	0.1
	B17	67	3.8	26	2.7	0.1

Table 4.9 SEM-EDS analysis of copper prills embedded in slag samples from Chrysokamino. Samples divided into microscopic group (nd: not determined; <0.1 wt-%).

Group	Sample	No of analyses	Cu	Fe	As	Ni	S
MG-1	A05	5	94	1.7	3.6	0.8	0.1
	A09	4	96	1.0	2.5	0.3	0.2
	A15	7	94	1.9	3.4	0.7	0.5
	A16	4	98	2.4	0.1	nd	nd
	A17	1	91	2.2	4.9	2.0	0.2
	A18	3	91	2.7	4.4	1.5	0.1
	B05	5	81	1.7	16	1.1	0.1
	B20	4	88	3.6	7.6	1.0	0.1
	C01	14	95	2.6	1.5	0.9	0.2
MG-2	A11	1	89	1.6	7.8	0.4	0.9
	A14	2	89	1.8	7.2	0.8	1.3
	A19	1	76	2.2	13	8.9	0.4
	B17	3	69	2.1	28	1.2	0.1

Table 4.10 Mean composition of copper prills in slag samples from Chrysokamino. Samples divided into microscopic group (nd: not determined; <0.1 wt-%).

Group	Sample	Cu	Fe	As	Ni	S
MG-1	A04	77	2.7	0.6	NA	19
	A05	79	1.8	0.3	0.2	19
	A05	79	2.2	0.4	0.2	19
	A05	79	2.6	0.2	nd	18
	A09	79	2.5	0.2	nd	18
	A17	72	6.3	0.4	0.3	21
	A18	74	6.0	0.3	0.2	19
	A18	69	9.4	0.1	0.1	22
	A18	75	5.4	0.1	nd	19
	B01	76	4.6	1.0	0.1	19
	B01	80	1.5	1.0	0.2	18
	B01	79	1.3	2.1	0.3	18
	B05	77	4.3	1.6	NA	17
	B05	78	3.1	0.9	NA	18
	B05	77	3.1	2.2	NA	18
	B05	77	4.3	1.3	NA	18
	B05	79	2.1	1.3	NA	18
	B12	80	0.9	0.1	nd	19
	B13	76	4.5	0.1	nd	20
	B20	79	3.2	0.2	0.1	18
	B20	76	6.8	nd	nd	17
	B20	72	9.2	0.8	0.1	18
	B20	75	5.9	0.3	0.1	19
	B24	69	9.2	0.3	0.5	21
	B24	72	6.6	0.7	0.7	20
	B24	73	6.4	0.4	0.5	19
MG-2	A19	79	1.7	0.7	0.5	18
	A19	80	1.4	0.3	0.3	18
	A19	78	1.0	1.7	1.2	18
	A19	78	5.2	0.3	0.3	16
	B17	75	1.9	4.4	0.2	18
	B17	78	2.4	1.3	0.4	18
	B17	80	1.5	0.6	0.5	18
	B17	75	4.8	0.9	0.2	19

Table 4.11 SEM-EDS analysis of matte inclusions in slag samples from Chrysokamino (NA: not analysed; nd: not determined; <0.1 wt-%). Samples divided into microscopic group.

Group	Sample	No of analyses	Cu	Fe	As	Ni	S
MG-1	A04	1	77	2.7	0.6	NA	19
	A05	3	79	2.2	0.3	0.1	19
	A09	1	79	2.5	0.2	nd	18
	A17	1	72	6.3	0.4	0.3	21
	A18	3	73	6.9	0.2	0.1	20
	B01	3	78	2.5	1.4	0.2	18
	B05	5	78	3.4	1.5	NA	18
	B12	1	80	0.9	0.1	nd	19
	B13	1	76	4.5	0.1	nd	20
	B20	4	76	6.3	0.3	0.1	18
	B24	3	71	7.4	0.5	0.6	20
MG-2	A19	4	79	2.3	0.8	0.6	18
	B17	4	77	2.7	1.8	0.3	18

Table 4.12 Mean composition of matte inclusions in slag samples from Chrysokamino. Samples divided into microscopic group (NA: not analysed; nd: not determined; <0.1 wt-%).

Group	Sample	Pyroxene	Ferrous	Intermediate	Magnetite	Fe^{+2} (%)	Fe^{+3} (%)
MG-1	A17	40	35	0	25	83.3	16.7
	A18	80	0	20	0	90.0	10.0
	B24	40	40	0	20	86.7	13.3
MG-2	A19	40	50	10	0	95.0	5.0
	B17	80	0	20	0	90	10

Table 4.13 Mössbauer analysis of slag samples from Chrysokamino and calculated Fe^{2+}/Fe^{3+} percentages.

Sample	**SiO_2**	**FeO**	**CaO**	**Al_2O_3**	**MgO**	**MnO**	**Na_2O**	**K_2O**	**CuO**	**SO_3**	**Cl_2O**	**As_2O_3**	**NiO**	**TiO_2**	**P_2O_5**	**BaO**	**ZnO**
ORE 1/1	42.478	11.507	0.101	2.438	1.684	0.032	0.737	0.038	37.128	2.812	0.195	0.164	0.066	0.088	0.317	0.197	0.023
ORE 1/2	66.658	5.384	0.232	1.803	0.389	0.000	1.550	0.000	22.203	0.741	0.087	0.000	0.057	0.047	0.502	0.000	0.348
ORE 1/3	63.674	2.713	0.083	0.294	0.696	0.000	0.000	0.000	30.444	1.016	0.157	0.000	0.129	0.000	0.560	0.238	0.000
ORE 2/1	2.018	0.236	0.257	1.282	0.399	0.505	0.000	0.000	94.554	0.332	0.194	0.000	0.000	0.000	0.000	0.000	0.221
ORE 2/2	1.503	0.133	0.390	0.408	1.362	0.421	0.000	0.000	95.172	0.000	0.276	0.261	0.000	0.027	0.046	0.000	0.000
ORE 2/3	3.271	0.083	0.494	1.789	2.791	0.470	0.000	0.113	89.242	0.379	0.289	0.000	0.000	0.439	0.562	0.000	0.066
ORE 2/4	3.196	0.198	0.362	0.278	0.353	0.413	0.000	0.040	94.063	0.345	0.152	0.290	0.000	0.000	0.197	0.000	0.111
ORE 2/5	3.477	0.000	0.363	1.482	0.000	0.620	0.000	0.040	92.814	0.634	0.226	0.006	0.059	0.110	0.108	0.056	0.000
ORE 2/6	91.137	2.704	0.152	0.724	0.432	1.860	0.503	0.048	0.638	0.000	0.205	0.193	0.000	0.000	1.205	0.057	0.142
ORE 2/7	89.548	1.189	0.076	3.811	0.198	2.079	1.099	0.210	0.652	0.043	0.058	0.000	0.012	0.124	0.791	0.111	0.000
ORE 2/8	90.414	2.312	0.194	2.556	0.182	1.086	1.186	0.190	0.539	0.073	0.128	0.000	0.000	0.111	1.013	0.016	0.000
ORE 2/9	95.931	0.409	0.036	1.579	0.064	0.348	0.497	0.100	0.019	0.001	0.113	0.000	0.000	0.000	0.787	0.117	0.000
ORE 2/10	95.523	0.176	0.010	1.507	0.089	0.373	0.876	0.140	0.169	0.000	0.197	0.124	0.004	0.199	0.589	0.000	0.025
ORE 2/11	90.161	3.395	0.384	1.176	0.154	0.967	1.232	0.136	0.709	0.202	0.232	0.000	0.018	0.283	0.868	0.000	0.081
ORE 2/12	83.532	6.083	0.269	1.700	0.245	3.981	1.097	0.166	1.445	0.015	0.130	0.140	0.037	0.131	0.927	0.085	0.017
ORE 3/1	1.533	0.286	0.146	0.924	1.273	0.077	3.370	0.000	91.307	0.026	0.673	0.000	0.100	0.017	0.185	0.072	0.000
ORE 3/2 1	96.715	0.081	0.000	0.759	0.311	0.000	0.917	0.089	0.039	0.000	0.009	0.000	0.000	0.052	1.027	0.000	0.000
ORE 3/2 2	97.698	0.093	0.000	0.180	0.257	0.000	0.396	0.054	0.032	0.000	0.068	0.000	0.000	0.018	1.163	0.000	0.040
IRON ORE 1	5.122	65.388	24.657	0.552	1.171	0.075	1.908	0.108	0.013	0.052	0.212	0.000	0.313	0.000	0.101	0.170	0.158
IRON ORE 2	4.595	69.336	21.833	0.380	1.402	0.315	0.730	0.128	0.067	0.132	0.243	0.111	0.000	0.000	0.471	0.242	0.000

Table 4.14 SEM-EDS analysis (areas scanning) of copper- and iron-ore samples from Chrysokamino. Raw data, not rounded.

Sample	SiO_2	FeO	CaO	Al_2O_3	MgO	MnO	Na_2O	K_2O	CuO	SO_3	Cl_2O	As_2O_3	NiO	TiO_2	P_2O_5	BaO	ZnO
ORE 1	58	6.5	0.1	1.5	0.9	nd	0.8	nd	30	1.5	0.1	0.1	0.1	nd	0.5	0.1	0.1
ORE 2	54	1.4	0.2	1.5	0.5	1.1	0.5	0.1	39	0.2	0.2	0.1	nd	0.1	0.6	nd	0.1
ORE 3 / ore	1.5	0.3	0.1	0.9	1.3	0.1	3.4	nd	91	nd	0.7	nd	0.1	nd	0.2	0.1	nd
ORE 3 / gangue	97	0.1	nd	0.5	0.3	nd	0.7	0.1	nd	nd	nd	nd	nd	nd	1.1	nd	nd
IRON ORE	4.9	67	23	0.5	1.3	0.2	1.3	0.1	nd	0.1	0.2	0.1	0.2	nd	0.3	0.2	0.1

Table 4.15 Mean chemical composition of copper- and iron-ore samples from Chrysokamino (rounded data; nd: not determined; <0.1 wt-%).

Group	Sample	$-\log pO_2$ (initial)	$-\log pO_2$ (corrected for SiO_2)	$-\log pO_2$ (corrected for T)
MG-1	A17	8.2	6.6	8.3
	A18	8.6	6.1	7.8
	B24	10.7	8.1	9.8
MG-2	A19	10.0	7.4	9.1
	B17	8.9	7.5	9.2

Table 4.16 Calculated partial pressures of oxygen based on the results of Mössbauer spectroscopy.

Group	Sample	n (Poise)	
		Bachmann	*Chemcast*
MG-1	A03	1.3	7.9
	A04	<0.1	1.1
	A05	<0.1	2.5
	A07	0.1	3.5
	A08	0.1	3.4
	A09	<0.1	2.4
	A15	2.4	9.0
	A16	1.1	9.1
	A17	0.1	3.2
	A18	1.4	6.5
	A20	2.7	15.5
	A21	<0.1	1.6
	A23	3.3	10.0
	A25	4.8	23.6
	A29	0.3	4.5
	B01	<0.1	3.1
	B05	0.1	2.9
	B06	0.1	3.4
	B07	<0.1	2.5
	B12	2.1	8.4
	B13	0.1	3.7
	B14	0.1	2.8
	B15	0.7	5.9
	B18	0.8	7.1
	B20	<0.1	1.9
	B24	0.1	2.3
	C01	0.2	3.5
MG-2	A14	0.7	7.2
	A19	1.4	7.8
	A26	1.0	13.3
	A28	1.7	14.7
	B02	0.3	10.4
	B11	1.4	14.0
	B17	1.2	10.8
	B23	0.4	4.4
	B26	0.9	11.0

Table 4.17 Calculated viscosities for slag samples in groups MG-1 and MG-2 (samples with frequent silica grains are not included).

Site	**Region**	**References**
Manika	Euboea	Sampson 1988: 18
Raphina	Attica	Theocharis 1951, 1952
Kolonna	Aigina	Walter and Felten 1981: 23
Kephala	Keos	Colemann 1977: 108
A. Symeon	"	Papastamataki 1998
Pounta	Kythnos	Bassiakos and Philaniotou-Hadjianastasiou in press
Sideri	"	Bassiakos and Philaniotou-Hadjianastasiou in press Zacharias *et al* 2002
Aspra Spitia	"	Bassiakos and Philaniotou-Hadjianastasiou in press Zacharias *et al* 2002
Skouries	"	Bassiakos and Philaniotou-Hadjianastasiou in press Gale *et al* 1985 Gale and Stos-Gale 1989 Hadjianastasiou and McGillivray 1988
Lefkes	"	Bassiakos and Philaniotou-Hadjianastasiou in press
A. Ioannis Eleimon	"	Bassiakos and Philaniotou-Hadjianastasiou in press
A. Ioannis Theologos	"	Bassiakos and Philaniotou-Hadjianastasiou in press
Parapola	Parapola	Bassiakos and Athanasas in prep.
Kephala	Seriphos	Gale *et al* 1985 Philaniotou-Hadjianastasiou 2000
Avessalos	"	Gale *et al* 1985
Aerata	"	Papadimitriou and Fragiskos 2003
Petalloura	Siphnos	Philaniotou-Hadjianastasiou 2000
Avyssos	Paros	Tsountas 1898: 175-6
Konakia	Keros	Bassiakos and Doumas 1998
Kavos North	"	Broodbank 2000: 231 Georgakopoulou 2004
Chrysokamino	Crete	Betancourt *et al* 1999

Table 5.1 Sites in the southern Aegean with possible evidence for EBA copper-smelting activities.

Site	Region	Smelting vessel	Ore	Other
A. Symeon	“	-	-	-
Pounta	Kythnos	y		-
Sideri	“	y	y	-
Aspra Spitia	“	y	y	clay-tip
Skouries	“	y	y	-
Lefkes	“	-	-	-
A. Ioannis Eleimon	“	-	-	-
A. Ioannis Theologos	“	-	-	-
Kephala	Seriphos	y	y	-
Avessalos	“	y	y	-
Aerata	“	-	-	-
Petalloura	Siphnos	-	-	-
Konakia	Keros	-	-	-
Chrysokamino	Crete	y	y	pot-bellows

Table 5.2 Possible copper-smelting evidence from slag scatters and slag heaps in the southern Aegean (references as in Table 5.1).

Site	Region	Date	Dating evidence/indications
A. Symeon	“	?	Mixed pottery (surface)
Pounta	Kythnos	EC?	Pottery fabric (surface)
Sideri	“	EBA	TL dating
Aspra Spitia	“	EBA	TL dating
Skouries	“	EC II	Pottery (surface); ^{14}C dating
Lefkes	“	EC	Pottery (surface)
A. Ioannis Eleimon	“	EC	“
A. Ioannis Theologos	“	EC	“
Parapola	Parapola	EH	“
Kephala	Seriphos	EBA?	Furnaces like Skouries; obsidian
Avessalos	“	?	obsidian
Aerata	“	?	-
Petalloura	Siphnos	EC?	Mixed pottery (surface)
Konakia	Keros	EC?	No later occupation(?) on Keros
Chrysokamino	Crete	EM III	Pottery (excavation); TL dating

Table 5.3 Dating of prehistoric copper-slag scatters and heaps in the southern Aegean (references as in Table 5.1).

Site	Region	Slag	Smelting vessel	Ore	Other
Manika	Euboea	small number	-	-	-
Raphina	Attica	numerous finds	y	-	clay-tips
Kolonna	Aigina	small number	y?	-	-
Kephala	Keos	“	y	-	-
Avyssos	Paros	“	-	-	-
Kavos North	“	“	-	y	Cu-prills

Table 5.4 Possible copper-smelting evidence from small assemblages near/inside settlements in the southern Aegean (references as in Table 5.1).

Site	Region	Date	Dating evidence
Raphina	Attica	EH II	Pottery (stratified)
Kolonna	Aigina	EH II	“
Kephala	Keos	FN	“
Kavos North	Keros	EC II	Pottery (surface), adjacent settlement

Table 5.5 Dating of small copper-smelting assemblages near/inside settlements in the southern Aegean (references as in Table 5.1).

Site	Region	Copper ore	Flux
Sideri	Kythnos	malachite and hematite in quartz	-
Skouries	“	malachite in iron-ore	quartz
Avessalos	Seriphos	“oxidised copper-ore”	-
Kavos North	Keros	-	iron-ore
Chrysokamino	Crete	malachite in quartz	lime-rich iron-ore

Table 5.6 Reported pieces of copper ore and flux at early copper-smelting sites in the southern Aegean (references as in Table 5.1).

Site	Region	Sample	Al_2O_3	SiO_2	CaO	FeO	MnO	MgO	Cu	S	Cu/S
A. Symeon	Keos	K1	2.1	31.4	5.2	49.5	0.1	0.7	2.3	0.0	57.5
		K2	4.2	32.9	9.5	43.1	1.2	0.9	1.0	0.0	33.3
		K3	4.0	31.5	8.8	34.0	1.1	0.8	1.3	0.1	26.0
		2	2.5	32.5	8.2	45.9	0.1	0.6	0.8	0.0	20.0
		3	5.9	34.5	9.2	35.5	0.1	1.0	1.9	0.1	38.0
		4	4.2	36.2	5.6	39.2	0.4	2.4	1.9	0.0	63.3
		6	4.2	36.0	5.6	39.2	0.4	2.4	1.8	0.1	36.0
Skouries	Kythnos	1	4.4	32.6	5.3	40.0	0.4	3.3	5.9	0.4	16.4
		2	3.9	43.2	16.7	28.0	0.4	1.2	1.2	0.0	30.0
		3	6.9	50.4	7.9	23.3	0.4	1.1	3.8	0.1	47.5
		4	2.0	38.5	9.0	32.9	1.0	0.8	9.0	0.2	56.3
		5	7.0	44.2	8.5	32.3	0.4	2.1	0.5	0.1	8.3
		6	3.1	40.5	8.7	31.0	0.4	3.3	0.4	0.5	0.9
		7	4.8	33.0	7.0	41.0	0.4	3.0	1.3	0.1	21.7
		8	6.7	43.9	8.7	32.7	0.4	2.6	0.6	0.1	5.5

Table 5.7 Chemical composition (main components) of slag samples from early copper-smelting sites in the southern Aegean (data from Bassiakos pers.com., Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998).

Site	Region	Sample	Al_2O_3	SiO_2	CaO	FeO	MnO	MgO	Cu	S	Cu/S
Skouries	Kythnos	9	6.1	42.9	8.6	22.2	0.3	1.2	9.6	0.9	11.2
		12	9.2	45.0	6.6	25.8	0.3	1.8	3.4	0.2	17.9
		13	6.7	39.5	11.9	24.9	0.6	2.4	7.0	0.1	87.5
		14	3.6	41.4	8.8	31.9	0.5	1.3	0.4	0.8	0.5
		15	6.2	44.2	12.6	28.2	0.4	1.0	1.1	0.3	3.9
		16	5.5	29.7	3.5	56.0	0.2	0.5	1.0	0.4	2.7
		17	4.5	34.4	6.3	44.0	0.3	0.8	2.6	0.4	7.4
		18	9.9	43.4	7.0	30.6	0.2	0.4	2.6	0.4	6.7
		D-1	5.7	45.6	17.4	19.2	0.7	0.4	0.5	0.2	3.2
		D-2	4.6	38.5	5.6	46.3	0.4	0.9	0.5	0.1	3.9
		D-3	4.5	41.4	14.4	30.8	0.7	0.9	3.4	0.1	41.6
		D-4	4.3	40.4	14.6	31.3	0.6	0.9	3.9	0.1	47.7
		D-5	6.4	41.4	11.2	32.2	0.6	0.9	1.1	0.1	13.4
		D-6	6.5	42.0	11.6	32.0	0.6	0.9	1.0	0.1	12.2
		D-7	3.7	42.8	6.7	36.9	0.4	4.4	2.3	0.1	31.6
		D-8	3.4	39.3	11.6	36.0	1.0	0.2	4.2	0.1	66.0
		D-9	3.5	39.7	11.7	36.5	1.0	0.4	3.7	0.1	67.8

Table 5.7 (*cont.*) Chemical composition of slag samples from early copper-smelting sites in the southern Aegean (data from Bassiakos pers.com., Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998).

Site	Region	Sample	Al_2O_3	SiO_2	CaO	FeO	MnO	MgO	Cu	S	Cu/S
Sideri	Kythnos	3	6.5	42.4	9.9	29.2	0.2	4.6	3.9	0.1	71.5
		4	6.0	43.1	5.1	25.7	0.3	2.5	12.4	0.0	682.0
		5	7.5	39.1	6.9	27.1	0.2	4.4	9.4	0.0	344.7
		6	6.6	39.5	18.7	24.8	1.0	0.6	1.5	0.0	165.0
		7	6.2	42.3	18.4	23.2	0.8	0.7	1.5	0.0	41.3
		8	6.4	43.1	17.6	22.3	0.7	0.7	1.5	0.0	33.0
		9	5.8	43.6	14.1	29.5	0.2	2.8	1.4	0.1	12.8
		10	6.1	42.6	16.2	26.5	0.5	1.7	1.5	0.1	20.6
		11	2.2	38.4	7.3	44.8	2.3	0.1	2.4	0.0	52.8
		12	2.2	43.4	7.0	40.2	2.2	0.2	2.4	0.0	66.0
		13	1.7	40.7	6.9	42.3	2.0	0.3	3.1	0.1	42.6
		14	2.1	38.6	7.0	45.0	2.3	0.1	1.9	0.1	26.1
Pounta	Kythnos	1	2.4	38.7	12.6	33.3	0.3	7.6	3.2	0.0	88.0
		2	7.3	41.8	7.3	29.7	0.4	3.3	3.7	0.1	27.1

Table 5.7 (*cont.*) Chemical composition of slag samples from early copper-smelting sites in the southern Aegean (data from Bassiakos pers.com., Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998).

Site	Region	Sample	Al_2O_3	SiO_2	CaO	FeO	MnO	MgO	Cu	S	Cu/S
Pounta	Kythnos	3	7.3	37.4	10.0	33.9	0.1	5.8	2.8	0.1	38.5
		4	10.3	42.2	8.6	30.8	0.4	3.2	1.4	0.1	14.0
		5	2.0	34.2	8.3	51.1	0.2	1.6	1.1	0.1	20.2
		6	7.0	40.3	12.5	30.8	0.5	2.7	2.2	0.1	22.0
Avessalos	Seriphos	1	6.0	37.4	7.8	32.2	0.7	6.2	5.6	0.2	37.3
		2	1.6	39.9	8.4	40.9	0.2	5.1	1.1	0.2	6.5
		3	1.7	42.8	4.8	32.8	0.2	5.8	7.8	0.1	60.0
		4	2.3	41.2	6.9	40.3	0.3	5.1	1.4	0.1	17.5
		5	3.7	37.0	7.6	41.8	0.3	5.6	1.3	0.3	3.8
		6	4.6	29.0	2.5	56.2	1.8	2.1	1.2	0.2	8.0
		7	1.7	45.0	8.0	37.2	0.2	5.2	0.5	0.2	3.1
		8	2.3	36.5	8.8	50.0	0.5	2.4	0.5	0.4	1.3
Kephala	Seriphos	1	1.9	42.9	4.0	37.0	0.3	4.1	5.0	0.2	29.4
		2	5.8	28.9	2.3	55.3	0.2	2.0	0.8	0.6	1.3
		3	2.9	35.3	3.2	31.3	0.2	2.9	15.0	0.3	57.7
		4	4.5	38.0	9.8	44.3	0.3	4.6	0.3	0.5	0.6

Table 5.7 (*cont.*) Chemical composition of slag samples from early copper-smelting sites in the southern Aegean (data from Bassiakos pers.com., Bassiakos and Philaniotou-Hadjianastasiou in press; Gale *et al* 1985; Papastamataki 1998).

Site	Region	Fe (wt-%)	As (wt-%)
A. Symeon	Keos	"pure copper"	"pure copper"
Sideri	Kythnos	1.2	0.1
Aspra Spitia	"	1.2	0.1
Pounta	"	5.3	0.2
Lefkes	"	2.5	0.4
Skouries	"	8.3	0.1 - 6.6
Aerata	Seriphos	-	"traces"
Kavos North	Keros	-	"pure" and "arsenical copper"
Chrysokamino	"	2.1	8.3

Table 5.8 Reported iron and arsenic levels in copper prills suspended in slag from early copper-smelting sites in the southern Aegean (references as in Table 5.1).

Site	Region	Smelting vessel	Air-supply
Raphina	Attica	perforated ceramics	clay-tips
Kolonna	Aigina	peculiar installation	-
Kephala	Keos	perforated shaft	-
Pounta	Kythnos	clay-lining/shaft	-
Sideri	"	perforated shaft	-
Aspra Spitia	"	"	clay-tip
Skouries	"	clay-lined pit; clay-lining/shaft	-
Avessalos	Seriphos	clay-lining/shaft	-
Chrysokamino	Crete	perforated shaft	pot-bellows

Table 5.9 Reported furnace designs and air-supply equipment from early copper-smelting sites in the southern Aegean (references as in Table 5.1).

Site	Region	Morphology/size of Slag
Kephala	Keos	small fragments
Pounta	Kythnos	small to medium (500-600g) fragments
Sideri	"	fragments and complete cakes
Aspra Spitia	"	"
Skouries	"	"
Lefkes	"	small to medium (400g) fragments
Kephala	Seriphos	fragments and complete cakes
Avessalos	"	"
Konakia	Keros	small to medium (200g) fragments
Chrysokamino	Crete	small fragments

Table 5.10 Reported morphology and size of slag fragments from early copper-smelting sites in the southern Aegean (references as in Table 5.1).

Site	**Region**	**Date**	**Slag (tons)** (estimated)	**Estimated number of smelting operations**		
				20kg per smelt	30kg per smelt	40kg per smelt
Avessalos	Seriphos	?	100,000	5,000,000	3,500,000	2,500,000
Skouries	Kythnos	EC II	(?) 5,000	250,000	150,000	125,000
Kephala	Seriphos	EBA?	3,000	150,000	100,000	75,000
Sideri	Kythnos	EBA	5-10	250-500	150-350	125-250
Aspra Spitia	Kythnos	EBA	2-3	100-150	70-100	50-75
Pounta	Kythnos	EC?	<<1	<<50	<<35	<<25
Lefkes	Kythnos	EC	<<1	<<50	<<35	<<25
A. Ioannis Theologos	Kythnos	EC	<<1	<<50	<<35	<<25
A. Ioannis Eleimon	Kythnos	EC	<<1	<<50	<<35	<<25
Petalloura	Siphnos	EC?	<<1	<<50	<<35	<<25
Konakia	Keros	EC?	<<1	<<50	<<35	<<25

Table 6.1 Estimated amount of slag and corresponding number of smelting operations in early copper-smelting sites on metalliferous Cycladic islands (references as in Table 5.1).

Analysis	Al_2O_3	CaO	FeO	MgO	K_2O	SiO_2	TiO_2	Na_2O
certified	13.418	4.384	4.053	1.895	3.196	70.824	0.556	1.673
1	13.756	4.924	3.710	1.831	2.909	69.861	0.652	2.356
2	14.235	4.415	3.488	1.608	3.400	70.802	0.518	1.535
3	12.956	4.502	3.922	1.705	2.968	71.103	0.536	2.307
4	13.008	4.746	3.738	1.614	2.891	71.726	0.541	1.735
5	12.615	4.575	3.544	1.929	3.197	72.378	0.342	1.421
6	12.659	4.276	3.580	1.640	2.967	72.215	0.430	2.233
7	13.263	4.166	3.837	1.413	3.105	72.485	0.568	1.164
8	12.727	4.667	3.523	1.602	2.959	72.517	0.555	1.451
9	13.897	4.733	3.621	1.773	3.319	70.266	0.627	1.765
10	13.477	4.806	4.173	1.872	3.036	70.256	0.459	1.921
11	12.835	4.344	3.883	1.760	3.277	71.446	0.568	1.887
12	12.959	4.307	3.835	1.646	3.389	71.490	0.526	1.848
13	13.283	4.472	3.726	1.741	3.161	71.297	0.512	1.807
Mean	13.205	4.533	3.737	1.703	3.121	71.372	0.526	1.802
2s	1.016	0.461	0.387	0.273	0.365	1.786	0.162	0.713
2RSD	7.697	10.178	10.355	16.052	11.688	2.503	30.789	39.543
ME	-0.213	0.149	-0.316	-0.192	-0.075	0.548	-0.030	0.129
RME	-1.585	3.406	-7.799	-10.152	-2.335	0.774	-5.451	7.729
Abs(ME/s)	0.419	0.648	0.412	0.614	0.371	0.362	1.633	1.407

Table A.1 Certified oxide concentrations and results of replicate SEM-EDS analyses of test-sample SRM 2711 (normalised data).

Analysis	Al_2O_3	FeO	SiO_2	CaO
calculated	13.640	9.091	57.286	19.983
1	13.799	9.044	56.518	20.638
2	13.828	9.095	56.295	20.782
3	13.752	9.174	56.530	20.544
4	13.919	9.165	56.359	20.556
5	13.652	9.200	56.336	20.881
6	13.644	9.328	56.657	20.371
7	14.002	9.209	56.271	20.517
8	13.592	9.433	56.066	20.909
9	13.607	9.428	56.077	20.888
10	14.017	9.206	56.279	20.497
Mean	13.781	9.228	56.339	20.658
2s	0.319	0.260	0.379	0.385
2RSD	2.312	2.817	0.673	1.862
ME	0.141	0.137	-0.947	0.675
RME	1.035	1.509	-1.653	3.379
Abs(ME/s)	0.886	1.055	4.997	3.511

Table A.2 Calculated oxide concentrations and results of replicate SEM-EDS analyses of test-sample TS2 (normalised data).

Sample SRM 2711

Analysis	FeO/Al_2O_3 (%)
certified	30.21
1	26.97
2	24.50
3	30.27
4	28.74
5	28.09
6	28.28
7	28.93
8	27.68
9	26.06
10	30.96
11	30.25
12	29.59
13	28.05
Mean	28.34
s	1.80
ME	-1.87
RME	-6.61
Abs(ME/s)	1.04

Sample TS2

TS2	FeO/Al_2O_3 (%)
calculated	66.65
1	65.54
2	65.77
3	66.71
4	65.85
5	67.39
6	68.37
7	65.77
8	69.40
9	69.29
10	65.68
Mean	66.98
s	1.54
ME	0.33
RME	0.49
Abs(ME/s)	0.21

Table A.3 Certified/calculated FeO/Al_2O_3 wt-% ratios in test-samples SRM 2711 and TS2 and results of replicate SEM-EDS analyses (normalised data).

Sample	**A01**				**A02**				**A03**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	36.779	36.312	36.061	36.191	45.420	45.093	44.927	45.033	39.519	39.340	39.484	39.445
FeO	20.461	20.331	20.739	20.424	12.392	12.068	11.946	11.734	32.848	33.185	32.952	33.173
CaO	28.872	28.133	28.344	28.498	28.760	28.796	29.289	29.084	11.149	10.995	10.913	10.925
Al_2O_3	5.910	6.007	5.821	5.995	5.599	5.472	5.210	5.527	7.679	7.405	7.580	7.741
MgO	1.543	1.590	1.671	1.538	1.908	1.833	1.901	1.599	1.633	1.638	1.491	1.374
MnO	0.199	0.320	0.298	0.252	0.412	0.275	0.228	0.390	0.526	0.766	0.701	0.629
Na_2O	1.080	2.126	2.186	1.517	1.502	1.952	2.115	1.490	2.682	2.832	2.689	2.674
K_2O	0.772	0.757	0.840	0.857	0.704	0.648	0.807	0.776	0.676	0.796	0.746	0.814
CuO	0.407	0.422	0.411	0.384	0.626	0.682	0.790	1.034	1.188	1.220	1.432	1.338
SO_3	0.339	0.437	0.306	0.444	0.160	0.094	0.189	0.286	0.286	0.311	0.133	0.128
Cl_2O	0.162	0.141	0.148	0.195	0.004	0.173	0.090	0.111	0.265	0.303	0.336	0.263
As_2O_3	0.341	0.041	0.000	0.234	0.263	0.461	0.000	0.241	0.000	0.045	0.000	0.237
NiO	0.015	0.000	0.000	0.021	0.047	0.045	0.060	0.000	0.023	0.017	0.060	0.000
TiO_2	0.372	0.285	0.237	0.221	0.001	0.046	0.320	0.119	0.286	0.420	0.476	0.265
P_2O_5	0.778	1.024	0.814	1.202	0.878	1.003	0.805	1.178	0.684	0.550	0.831	0.527
BaO	1.855	1.877	2.130	1.965	1.268	1.297	1.255	1.351	0.333	0.184	0.184	0.473
ZnO	0.120	0.202	0.000	0.067	0.062	0.068	0.075	0.053	0.231	0.000	0.000	0.000

Table A.4 Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A04**				**A05**				**A06**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	30.998	31.431	31.640	31.088	33.339	33.873	33.528	34.366	37.634	38.083	38.067	37.786
FeO	34.650	34.484	34.632	34.559	31.669	31.579	31.971	30.997	16.159	16.148	15.891	15.919
CaO	20.723	21.021	20.874	20.432	18.508	19.245	18.260	18.555	27.981	28.034	28.338	27.581
Al_2O_3	5.403	5.407	5.526	5.461	6.697	6.453	6.422	6.647	6.762	7.221	6.832	7.253
MgO	1.340	1.759	1.869	1.462	1.647	1.593	1.750	1.800	3.600	3.333	3.251	3.338
MnO	0.147	0.343	0.323	0.397	0.071	0.181	0.042	0.090	0.803	0.856	0.949	0.842
Na_2O	3.116	1.783	1.622	2.860	2.702	1.228	2.550	2.079	3.043	1.856	2.511	3.226
K_2O	1.107	1.052	1.115	1.136	1.200	1.242	1.188	1.152	0.980	0.976	0.989	0.887
CuO	0.525	0.599	0.540	0.400	1.483	1.674	1.391	1.479	0.681	0.766	0.545	0.705
SO_3	0.534	0.568	0.427	0.440	0.104	0.369	0.192	0.129	0.343	0.406	0.294	0.158
Cl_2O	0.111	0.085	0.087	0.103	0.183	0.221	0.172	0.209	0.121	0.160	0.151	0.142
As_2O_3	0.000	0.000	0.000	0.181	0.000	0.326	0.205	0.189	0.000	0.000	0.086	0.232
NiO	0.000	0.000	0.000	0.000	0.155	0.000	0.026	0.075	0.000	0.073	0.000	0.000
TiO_2	0.324	0.133	0.099	0.288	0.349	0.142	0.383	0.000	0.336	0.283	0.212	0.066
P_2O_5	0.513	0.763	0.647	0.566	0.839	0.677	0.937	0.749	0.740	0.866	0.922	0.820
BaO	0.428	0.504	0.406	0.439	1.059	1.054	0.988	1.378	0.823	0.945	0.969	0.967
ZnO	0.084	0.071	0.196	0.193	0.000	0.147	0.000	0.110	0.000	0.000	0.000	0.084

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A07**				**A08**				**A09**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	35.712	36.053	36.455	35.791	35.223	35.794	35.491	35.624	34.975	34.679	33.931	33.955
FeO	30.453	31.123	30.940	30.612	32.579	32.550	33.330	33.403	31.087	30.833	31.055	31.068
CaO	19.180	19.686	19.418	19.282	19.268	19.362	19.384	19.412	20.825	20.567	20.615	19.999
Al_2O_3	5.121	5.197	5.351	5.511	5.406	5.356	5.353	5.207	5.624	5.417	5.385	5.681
MgO	1.100	1.365	1.091	1.076	1.682	1.902	1.374	1.202	1.399	1.797	1.179	1.711
MnO	0.352	0.146	0.163	0.150	0.261	0.116	0.157	0.299	0.134	0.119	0.318	0.152
Na_2O	3.504	2.532	2.547	3.014	1.679	1.114	1.064	0.972	1.501	2.111	3.066	1.941
K_2O	0.798	0.690	0.778	0.840	0.960	1.008	1.053	0.911	1.038	1.009	1.034	1.062
CuO	0.807	0.508	0.586	0.313	0.853	0.794	0.821	1.193	0.879	1.173	1.115	2.224
SO_3	0.211	0.103	0.156	0.224	0.237	0.160	0.149	0.233	0.155	0.327	0.178	0.341
Cl_2O	0.085	0.116	0.179	0.120	0.103	0.102	0.153	0.057	0.264	0.214	0.215	0.179
As_2O_3	0.027	0.044	0.094	0.196	0.030	0.166	0.011	0.057	0.352	0.040	0.166	0.225
NiO	0.000	0.000	0.001	0.000	0.000	0.050	0.052	0.000	0.048	0.067	0.000	0.111
TiO_2	0.287	0.285	0.149	0.417	0.299	0.049	0.170	0.255	0.202	0.366	0.241	0.146
P_2O_5	0.964	0.690	0.668	0.915	0.872	0.766	0.774	0.588	0.673	0.587	0.727	0.627
BaO	1.344	1.226	1.284	1.233	0.554	0.715	0.669	0.521	0.848	0.525	0.688	0.582
ZnO	0.058	0.241	0.146	0.310	0.000	0.000	0.000	0.067	0.000	0.175	0.091	0.000

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A10**				**A11**				**A12**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	43.007	43.914	42.840	43.373	45.837	45.781	45.898	45.707	46.926	46.572	46.991	46.573
FeO	16.257	16.360	16.955	16.405	12.711	12.852	12.559	12.561	11.103	11.395	11.430	11.330
CaO	24.761	24.693	25.209	24.640	18.054	18.048	18.032	17.622	25.231	24.557	25.402	25.269
Al_2O_3	6.796	6.765	6.741	6.863	10.835	10.723	11.029	10.461	7.429	7.588	7.076	6.871
MgO	1.371	1.774	1.372	1.532	1.542	1.418	1.458	1.925	2.683	2.478	2.412	2.143
MnO	0.205	0.229	0.419	0.244	0.149	0.341	0.117	0.201	0.413	0.415	0.406	0.385
Na_2O	3.109	1.798	2.455	3.086	4.695	3.959	4.333	4.668	1.564	2.248	1.758	2.395
K_2O	1.037	1.173	1.237	1.058	1.078	1.182	1.085	1.056	1.060	1.131	1.162	1.103
CuO	0.921	0.618	0.524	0.452	0.944	1.380	1.049	1.244	0.982	1.093	0.907	0.954
SO_3	0.183	0.300	0.223	0.151	0.158	0.162	0.084	0.066	0.179	0.173	0.128	0.177
Cl_2O	0.099	0.128	0.110	0.161	0.110	0.208	0.155	0.212	0.198	0.233	0.195	0.184
As_2O_3	0.346	0.173	0.099	0.037	0.199	0.238	0.090	0.000	0.418	0.165	0.389	0.520
NiO	0.000	0.000	0.098	0.029	0.000	0.000	0.000	0.010	0.000	0.022	0.000	0.000
TiO_2	0.490	0.300	0.659	0.388	0.464	0.444	0.410	0.325	0.416	0.362	0.341	0.401
P_2O_5	0.826	1.044	0.788	0.920	0.468	0.424	0.543	0.577	0.992	1.076	0.981	1.151
BaO	0.598	0.708	0.277	0.649	2.716	2.850	3.073	3.291	0.397	0.499	0.425	0.518
ZnO	0.000	0.032	0.000	0.017	0.050	0.000	0.095	0.082	0.015	0.000	0.000	0.033

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A13**				**A15**				**A20**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	47.812	47.800	48.259	47.696	38.802	39.702	39.278	39.741	39.897	40.357	40.486	40.699
FeO	18.137	18.139	18.358	18.303	28.814	29.953	29.671	29.639	23.798	24.153	23.855	24.326
CaO	19.846	19.425	19.799	19.756	11.565	12.147	11.878	12.087	17.129	17.314	17.577	17.498
Al_2O_3	6.115	5.781	5.862	6.035	9.013	8.882	8.685	8.803	7.472	6.977	7.185	7.236
MgO	1.113	1.031	0.853	0.815	1.833	1.319	1.607	1.580	1.744	1.574	1.458	1.303
MnO	0.410	0.403	0.216	0.373	0.241	0.442	0.207	0.472	0.334	0.428	0.488	0.312
Na_2O	2.330	2.251	2.087	2.315	3.997	2.859	3.660	2.506	2.377	2.241	1.671	1.577
K_2O	0.688	0.716	0.691	0.686	0.749	0.744	0.716	0.719	0.676	0.625	0.675	0.758
CuO	1.016	1.487	1.009	1.034	2.871	1.980	2.273	2.094	2.562	2.621	2.493	2.607
SO_3	0.116	0.204	0.154	0.224	0.243	0.151	0.237	0.170	0.148	0.107	0.125	0.157
Cl_2O	0.119	0.152	0.165	0.197	0.280	0.295	0.350	0.338	0.135	0.202	0.232	0.140
As_2O_3	0.077	0.302	0.237	0.079	0.000	0.176	0.000	0.108	0.646	0.509	0.810	0.539
NiO	0.037	0.020	0.100	0.000	0.023	0.102	0.167	0.075	0.000	0.075	0.049	0.000
TiO_2	0.307	0.089	0.355	0.257	0.415	0.358	0.465	0.395	0.345	0.256	0.408	0.149
P_2O_5	0.906	1.215	0.871	1.046	0.895	0.700	0.618	0.971	0.813	0.885	0.766	0.753
BaO	0.809	0.987	0.761	0.897	0.268	0.183	0.114	0.246	1.494	1.450	1.309	1.562
ZnO	0.169	0.007	0.232	0.294	0.000	0.015	0.083	0.064	0.436	0.235	0.420	0.391

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A21**				**A23**				**A25**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	32.354	32.838	32.417	32.209	40.229	40.014	39.737	40.507	43.154	42.991	42.891	42.898
FeO	27.724	27.411	27.908	27.658	32.711	32.217	31.446	31.717	20.606	20.945	20.854	21.555
CaO	27.250	27.388	27.381	27.646	9.388	9.287	9.139	9.188	20.383	20.113	20.184	20.737
Al_2O_3	4.894	4.913	4.759	4.821	8.844	9.546	9.184	9.094	6.154	6.728	6.454	6.261
MgO	1.356	0.994	1.498	1.398	1.970	1.918	1.948	1.853	1.420	1.263	1.557	1.464
MnO	0.184	0.253	0.254	0.261	0.586	0.457	0.521	0.527	0.146	0.193	0.067	0.179
Na_2O	2.222	2.118	1.668	2.289	2.405	2.269	3.738	3.059	1.611	2.152	2.408	1.801
K_2O	0.698	0.727	0.621	0.598	1.292	1.303	1.284	1.283	0.891	0.949	0.908	0.892
CuO	0.850	0.858	1.016	0.849	1.048	0.972	0.827	1.018	2.036	1.580	1.799	1.567
SO_3	0.173	0.303	0.301	0.096	0.129	0.427	0.389	0.263	0.027	0.230	0.189	0.103
Cl_2O	0.103	0.115	0.094	0.143	0.030	0.155	0.100	0.225	0.256	0.295	0.180	0.214
As_2O_3	0.293	0.397	0.051	0.226	0.003	0.000	0.004	0.000	0.457	0.170	0.150	0.068
NiO	0.073	0.000	0.063	0.050	0.003	0.123	0.000	0.027	0.000	0.000	0.024	0.008
TiO_2	0.142	0.240	0.130	0.127	0.470	0.466	0.434	0.467	0.199	0.234	0.290	0.366
P_2O_5	0.593	0.577	0.690	0.493	0.589	0.780	0.854	0.595	1.140	0.812	0.941	1.000
BaO	1.094	0.837	1.044	1.076	0.226	0.075	0.104	0.000	1.067	0.946	0.992	0.723
ZnO	0.000	0.034	0.110	0.062	0.085	0.000	0.300	0.186	0.461	0.406	0.119	0.170

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**A26**				**A28**				**A29**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	42.319	42.368	41.623	42.473	41.783	42.069	41.902	42.027	36.800	36.496	36.801	37.420
FeO	25.066	24.348	24.448	24.641	25.097	25.345	25.067	25.739	29.243	29.005	29.102	29.079
CaO	21.415	21.524	21.212	21.502	19.634	19.846	19.961	19.614	18.704	18.699	18.969	18.953
Al_2O_3	3.931	3.704	3.915	4.055	5.763	5.594	5.419	6.003	6.894	6.830	7.162	7.066
MgO	1.144	1.269	1.306	1.200	1.199	1.562	1.563	1.003	1.458	1.747	1.565	1.618
MnO	0.036	0.231	0.112	0.274	0.137	0.175	0.137	0.158	0.240	0.409	0.213	0.300
Na_2O	1.988	1.549	2.413	1.138	2.651	1.151	2.152	0.628	3.480	3.316	2.493	1.744
K_2O	0.626	0.678	0.649	0.626	0.627	0.692	0.647	0.677	0.805	0.842	0.873	0.899
CuO	1.858	1.895	2.137	2.170	0.800	0.858	0.885	1.374	0.562	0.674	0.814	0.951
SO_3	0.170	0.116	0.048	0.086	0.062	0.230	0.202	0.271	0.239	0.285	0.194	0.161
Cl_2O	0.141	0.218	0.215	0.206	0.228	0.248	0.171	0.227	0.074	0.046	0.163	0.060
As_2O_3	0.163	0.135	0.000	0.000	0.191	0.000	0.000	0.000	0.249	0.000	0.049	0.000
NiO	0.000	0.104	0.000	0.144	0.000	0.000	0.000	0.021	0.000	0.000	0.000	0.000
TiO_2	0.138	0.238	0.209	0.268	0.243	0.260	0.262	0.253	0.289	0.340	0.286	0.369
P_2O_5	0.498	0.898	0.990	0.684	0.593	0.908	0.645	0.707	0.445	0.629	0.689	0.852
BaO	0.410	0.536	0.542	0.404	0.955	0.884	0.919	1.006	0.451	0.633	0.633	0.473
ZnO	0.104	0.195	0.187	0.135	0.045	0.185	0.074	0.299	0.072	0.052	0.000	0.062

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B01**				**B02**				**B03**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	35.175	35.872	35.500	34.674	38.837	38.490	38.245	38.711	44.615	43.746	43.440	43.729
FeO	28.501	28.275	28.134	28.790	22.489	23.253	22.240	22.535	15.321	15.111	15.155	14.992
CaO	24.297	23.670	23.789	24.425	22.443	22.922	22.412	22.685	26.166	25.926	25.687	25.753
Al_2O_3	5.007	5.350	4.954	5.049	5.034	4.810	5.342	4.484	5.628	5.450	5.471	5.573
MgO	1.465	1.151	1.805	1.546	1.602	1.211	1.154	1.400	1.149	1.466	1.580	1.641
MnO	0.157	0.123	0.305	0.348	0.301	0.296	0.066	0.129	0.219	0.349	0.411	0.253
Na_2O	1.330	1.280	1.726	1.451	1.086	0.631	1.340	1.797	1.549	1.901	2.107	2.291
K_2O	1.076	1.185	1.134	1.029	0.600	0.631	0.670	0.667	0.883	0.789	0.781	0.760
CuO	0.611	0.521	0.508	0.135	2.154	2.298	2.556	1.929	1.536	1.736	1.608	1.455
SO_3	0.199	0.327	0.329	0.346	0.086	0.133	0.198	0.172	0.000	0.014	0.023	0.080
Cl_2O	0.116	0.120	0.036	0.120	0.170	0.114	0.128	0.079	0.090	0.158	0.102	0.166
As_2O_3	0.302	0.170	0.011	0.000	0.073	0.393	0.588	0.709	0.309	0.267	0.627	0.170
NiO	0.016	0.114	0.000	0.027	0.000	0.000	0.038	0.000	0.000	0.000	0.000	0.003
TiO_2	0.454	0.153	0.000	0.364	0.000	0.029	0.000	0.000	0.199	0.147	0.180	0.136
P_2O_5	0.805	0.950	0.939	0.974	0.926	0.827	0.828	0.781	0.731	0.957	0.959	1.211
BaO	0.493	0.657	0.802	0.629	3.987	3.656	3.931	3.802	1.533	1.931	1.758	1.706
ZnO	0.000	0.088	0.035	0.102	0.219	0.311	0.268	0.129	0.078	0.060	0.118	0.090

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B05**				**B06**				**B07**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	34.425	34.902	35.057	34.225	35.171	35.638	36.166	36.080	34.673	35.208	34.896	34.676
FeO	27.333	27.155	27.049	26.873	32.768	33.342	32.256	33.707	35.864	36.360	35.982	35.175
CaO	22.412	22.243	22.387	22.098	14.896	14.995	16.066	15.413	14.416	14.664	14.614	14.546
Al_2O_3	5.727	5.824	5.745	5.550	6.759	6.128	6.066	6.211	6.350	6.133	5.889	6.139
MgO	2.747	2.591	2.738	2.728	1.829	2.034	2.161	2.208	1.598	1.478	1.607	1.560
MnO	0.312	0.364	0.331	0.288	0.217	0.155	0.157	0.095	0.212	0.110	0.155	0.198
Na_2O	2.900	2.474	1.681	3.270	4.311	3.159	2.850	1.824	3.101	2.186	3.041	3.382
K_2O	0.857	0.828	0.825	0.747	1.013	1.099	1.009	1.125	0.847	0.889	0.821	0.847
CuO	0.999	0.996	1.272	1.078	0.904	1.045	1.012	0.934	0.914	1.182	0.976	1.166
SO_3	0.066	0.134	0.173	0.189	0.340	0.538	0.383	0.291	0.409	0.177	0.332	0.441
Cl_2O	0.203	0.182	0.087	0.213	0.078	0.258	0.166	0.151	0.272	0.142	0.251	0.288
As_2O_3	0.276	0.636	0.199	0.319	0.000	0.005	0.030	0.085	0.000	0.086	0.029	0.000
NiO	0.072	0.000	0.138	0.068	0.081	0.000	0.025	0.000	0.112	0.011	0.079	0.136
TiO_2	0.121	0.156	0.228	0.284	0.273	0.259	0.263	0.330	0.066	0.206	0.152	0.210
P_2O_5	0.775	0.753	1.079	0.892	0.676	0.773	0.615	0.534	0.520	0.754	0.696	0.765
BaO	0.728	0.767	0.990	0.946	0.690	0.575	0.705	0.808	0.558	0.419	0.455	0.476
ZnO	0.052	0.000	0.026	0.237	0.000	0.000	0.074	0.210	0.094	0.000	0.030	0.000

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B08**				**B09**				**B10**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	34.412	34.669	35.310	34.578	38.393	38.341	38.450	38.163	64.426	64.753	62.814	63.007
FeO	27.089	27.546	27.316	26.676	13.218	13.478	12.998	13.311	4.601	4.707	5.328	5.375
CaO	23.213	24.164	23.510	23.555	30.640	30.805	32.165	30.595	11.659	11.629	11.661	12.490
Al_2O_3	6.090	6.083	5.416	6.133	5.920	5.719	5.397	5.893	10.180	10.265	11.344	10.497
MgO	1.814	2.083	1.781	1.789	5.617	6.151	5.427	6.251	2.284	2.336	2.247	1.771
MnO	0.136	0.203	0.197	0.270	0.368	0.282	0.277	0.221	0.051	0.109	0.093	0.103
Na_2O	3.108	1.552	2.319	2.500	2.088	1.296	1.541	1.496	4.340	3.597	4.014	4.135
K_2O	0.989	0.980	1.055	1.004	0.854	0.803	0.797	0.800	0.807	0.748	0.769	0.863
CuO	0.355	0.475	0.523	0.783	0.563	0.710	0.656	0.742	0.103	0.275	0.144	0.036
SO_3	0.286	0.272	0.342	0.511	0.104	0.307	0.196	0.166	0.000	0.000	0.000	0.000
Cl_2O	0.330	0.129	0.213	0.228	0.080	0.183	0.136	0.154	0.115	0.210	0.183	0.203
As_2O_3	0.000	0.000	0.000	0.000	0.083	0.141	0.206	0.399	0.000	0.053	0.036	0.063
NiO	0.075	0.003	0.028	0.015	0.074	0.000	0.037	0.047	0.086	0.000	0.031	0.000
TiO_2	0.165	0.283	0.202	0.147	0.348	0.330	0.336	0.405	0.578	0.613	0.531	0.498
P_2O_5	0.966	0.939	0.923	0.718	1.009	0.783	0.775	0.745	0.771	0.633	0.710	0.746
BaO	0.860	0.622	0.801	1.029	0.559	0.643	0.516	0.447	0.000	0.028	0.019	0.025
ZnO	0.118	0.000	0.066	0.069	0.087	0.034	0.097	0.170	0.000	0.048	0.081	0.191

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B11**				**B12**				**B13**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	41.530	41.481	41.440	41.157	38.924	38.855	37.659	39.318	35.754	36.169	35.045	36.463
FeO	17.451	17.732	17.517	16.971	28.221	28.139	30.383	28.258	30.429	29.902	31.246	30.368
CaO	27.158	27.513	26.089	26.720	14.379	14.157	14.222	14.586	20.189	20.579	21.354	20.735
Al_2O_3	5.292	5.646	6.168	5.678	9.314	9.403	8.684	9.445	5.576	5.738	4.997	5.655
MgO	1.362	1.236	1.623	1.700	2.490	2.332	2.573	2.488	1.501	1.697	1.643	1.715
MnO	0.335	0.184	0.243	0.221	0.421	0.269	0.387	0.461	0.211	0.000	0.130	0.166
Na_2O	1.662	2.094	2.381	3.028	2.006	1.971	1.867	1.696	1.942	1.965	1.403	0.890
K_2O	0.725	0.734	0.726	0.766	1.110	1.029	0.941	0.995	0.885	0.864	0.890	0.902
CuO	1.198	1.252	1.090	0.909	1.086	1.361	1.232	1.111	1.072	0.873	0.992	0.938
SO_3	0.221	0.000	0.076	0.000	0.218	0.321	0.207	0.106	0.342	0.126	0.240	0.241
Cl_2O	0.229	0.111	0.177	0.163	0.197	0.226	0.216	0.203	0.097	0.168	0.121	0.131
As_2O_3	0.482	0.216	0.334	0.354	0.000	0.122	0.043	0.000	0.232	0.000	0.081	0.000
NiO	0.151	0.000	0.077	0.053	0.000	0.000	0.008	0.022	0.073	0.017	0.030	0.000
TiO_2	0.136	0.090	0.186	0.348	0.402	0.377	0.393	0.472	0.201	0.272	0.244	0.278
P_2O_5	0.987	0.792	0.800	0.729	0.786	0.772	0.682	0.468	1.086	0.969	1.036	0.988
BaO	0.944	0.874	0.953	1.036	0.386	0.610	0.468	0.379	0.414	0.667	0.546	0.512
ZnO	0.142	0.052	0.124	0.172	0.067	0.066	0.040	0.000	0.000	0.000	0.007	0.024

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B14**				**B15**				**B18**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
SiO_2	35.138	34.289	34.303	35.193	36.961	35.790	36.888	37.258	38.353	38.570	37.955	38.573
FeO	34.546	34.032	34.170	35.383	30.997	31.163	31.075	31.201	28.357	28.430	27.223	28.049
CaO	15.116	14.541	14.801	15.409	13.801	13.593	14.407	14.111	17.648	17.451	16.945	17.333
Al_2O_3	6.949	7.161	6.864	7.121	8.104	8.059	8.053	7.881	7.307	7.533	7.555	7.409
MgO	1.617	1.889	1.712	1.252	1.667	1.638	1.377	1.747	1.539	1.467	1.717	1.597
MnO	0.229	0.192	0.325	0.369	0.623	0.553	0.366	0.522	0.379	0.404	0.300	0.397
Na_2O	3.421	3.638	3.166	1.756	2.473	4.061	2.570	1.792	1.727	1.388	3.529	2.353
K_2O	0.833	0.886	0.735	0.861	0.559	0.581	0.673	0.728	0.932	0.923	0.993	0.994
CuO	0.880	1.662	2.476	1.004	2.785	2.617	3.132	2.884	0.949	1.255	1.028	0.824
SO_3	0.232	0.228	0.366	0.363	0.196	0.362	0.064	0.148	0.312	0.335	0.285	0.292
Cl_2O	0.136	0.156	0.088	0.141	0.337	0.209	0.230	0.211	0.206	0.155	0.225	0.153
As_2O_3	0.008	0.121	0.000	0.000	0.316	0.072	0.093	0.205	0.292	0.075	0.229	0.123
NiO	0.000	0.004	0.000	0.008	0.089	0.011	0.014	0.048	0.000	0.072	0.091	0.000
TiO_2	0.081	0.299	0.234	0.505	0.235	0.240	0.281	0.209	0.462	0.362	0.221	0.357
P_2O_5	0.649	0.481	0.666	0.616	0.551	0.711	0.643	0.607	0.954	0.944	0.763	0.853
BaO	0.169	0.285	0.100	0.000	0.313	0.246	0.142	0.435	0.590	0.590	0.791	0.677
ZnO	0.000	0.161	0.000	0.023	0.000	0.100	0.000	0.020	0.000	0.052	0.158	0.023

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	B20				B22				B23			
	1	2	3	4	1	2	3	4	1	2	3	4
SiO_2	33.605	33.303	33.589	33.338	43.277	43.861	43.295	43.280	36.483	35.542	37.081	36.145
FeO	27.928	27.106	27.658	27.534	16.761	16.404	16.849	16.624	30.727	30.309	30.381	30.116
CaO	24.140	23.855	24.051	23.833	25.826	26.401	25.831	25.866	15.393	15.385	15.290	15.353
Al_2O_3	5.569	5.711	5.600	5.660	5.116	4.924	5.278	4.906	7.969	7.733	8.090	8.219
MgO	1.547	1.910	2.281	1.526	1.082	1.383	0.825	1.261	1.914	2.336	1.783	1.371
MnO	0.312	0.262	0.233	0.220	0.195	0.174	0.301	0.183	1.393	1.465	1.258	1.435
Na_2O	2.089	3.392	2.389	3.672	2.064	2.118	2.467	2.503	2.855	3.772	2.531	3.846
K_2O	0.972	0.894	0.834	0.909	0.641	0.504	0.658	0.529	1.005	1.058	1.032	1.095
CuO	1.043	0.884	0.813	0.668	1.667	1.105	1.226	1.254	0.457	0.354	0.477	0.478
SO_3	0.236	0.212	0.225	0.319	0.136	0.036	0.135	0.069	0.499	0.452	0.407	0.631
Cl_2O	0.179	0.104	0.147	0.114	0.070	0.153	0.173	0.168	0.154	0.147	0.087	0.249
As_2O_3	0.107	0.000	0.000	0.077	0.371	0.418	0.357	0.726	0.000	0.012	0.323	0.086
NiO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.114	0.009	0.020
TiO_2	0.208	0.303	0.063	0.162	0.301	0.269	0.176	0.318	0.361	0.404	0.188	0.271
P_2O_5	0.770	0.844	0.713	0.699	0.904	0.758	0.892	0.770	0.778	0.716	0.770	0.589
BaO	1.300	1.083	1.380	1.247	1.422	1.412	1.544	1.381	0.006	0.209	0.277	0.102
ZnO	0.000	0.142	0.027	0.027	0.174	0.086	0.000	0.170	0.003	0.000	0.023	0.000

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**B26**			
	1	**2**	**3**	**4**
SiO_2	40.739	41.101	40.450	41.292
FeO	23.593	24.105	23.524	24.264
CaO	22.042	22.537	22.217	22.731
Al_2O_3	5.263	5.543	5.154	5.014
MgO	1.255	1.078	1.783	1.329
MnO	0.235	0.147	0.141	0.034
Na_2O	2.452	0.885	2.283	1.834
K_2O	0.989	1.136	1.114	1.003
CuO	0.764	0.792	0.868	0.397
SO_3	0.362	0.266	0.154	0.270
Cl_2O	0.189	0.179	0.119	0.059
As_2O_3	0.000	0.179	0.000	0.000
NiO	0.000	0.177	0.060	0.009
TiO_2	0.068	0.185	0.282	0.067
P_2O_5	1.130	0.924	0.942	0.909
BaO	0.709	0.638	0.562	0.704
ZnO	0.215	0.134	0.352	0.089

Table A.4 (cont.) Quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	SiO_2		FeO		CaO		Al_2O_3		MgO		MnO		Na_2O		K_2O	
	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s
A01	36.336	0.626	20.489	0.351	28.462	0.623	5.933	0.173	1.586	0.123	0.267	0.107	1.727	1.054	0.807	0.099
A02	45.118	0.425	12.035	0.550	28.982	0.501	5.452	0.339	1.810	0.290	0.326	0.178	1.765	0.635	0.734	0.143
A03	39.447	0.155	33.040	0.333	10.996	0.217	7.601	0.293	1.534	0.253	0.656	0.206	2.719	0.151	0.758	0.124
A04	31.289	0.598	34.581	0.152	20.763	0.503	5.449	0.115	1.608	0.495	0.303	0.217	2.345	1.505	1.103	0.072
A05	33.777	0.902	31.554	0.815	18.642	0.845	6.555	0.275	1.698	0.189	0.096	0.120	2.140	1.326	1.196	0.074
A06	37.893	0.440	16.029	0.288	27.984	0.622	7.017	0.512	3.381	0.303	0.863	0.124	2.659	1.231	0.958	0.095
A07	36.003	0.670	30.782	0.609	19.392	0.438	5.295	0.346	1.158	0.277	0.203	0.200	2.899	0.922	0.777	0.126
A08	35.533	0.482	32.966	0.928	19.357	0.125	5.331	0.172	1.540	0.625	0.208	0.172	1.207	0.640	0.983	0.122
A09	34.385	1.049	31.011	0.238	20.502	0.706	5.527	0.295	1.522	0.571	0.181	0.185	2.155	1.319	1.036	0.043
A10	43.284	0.951	16.494	0.627	24.826	0.521	6.791	0.106	1.512	0.380	0.274	0.196	2.612	1.243	1.126	0.190
A11	45.806	0.163	12.671	0.280	17.939	0.423	10.762	0.474	1.586	0.464	0.202	0.198	4.414	0.690	1.100	0.112
A12	46.766	0.449	11.315	0.294	25.115	0.758	7.241	0.653	2.429	0.446	0.405	0.027	1.991	0.788	1.114	0.087
A13	47.892	0.501	18.234	0.227	19.707	0.382	5.948	0.307	0.953	0.285	0.351	0.182	2.246	0.222	0.695	0.028
A15	39.381	0.878	29.519	0.982	11.919	0.526	8.846	0.276	1.585	0.421	0.341	0.272	3.256	1.382	0.732	0.034
A20	40.360	0.678	24.033	0.500	17.380	0.400	7.218	0.407	1.520	0.372	0.391	0.164	1.967	0.802	0.684	0.110
A21	32.455	0.540	27.675	0.411	27.416	0.332	4.847	0.141	1.312	0.440	0.238	0.072	2.074	0.560	0.661	0.123
A23	40.122	0.653	32.023	1.118	9.251	0.221	9.167	0.581	1.922	0.102	0.523	0.105	2.868	1.350	1.291	0.019
A25	42.984	0.245	20.990	0.806	20.354	0.559	6.399	0.504	1.426	0.246	0.146	0.113	1.993	0.712	0.910	0.054
A26	42.196	0.774	24.626	0.635	21.413	0.284	3.901	0.291	1.230	0.144	0.163	0.218	1.772	1.101	0.645	0.049
A28	41.945	0.259	25.312	0.621	19.764	0.337	5.695	0.498	1.332	0.556	0.152	0.037	1.646	1.843	0.661	0.059
A29	36.879	0.776	29.107	0.199	18.831	0.300	6.988	0.306	1.597	0.240	0.291	0.174	2.758	1.605	0.855	0.081

Table A.5 Mean value and standard deviation of quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**CuO**		**SO_3**		**Cl_2O**		As_2O_3		**NiO**		**TiO_2**		**P_2O_5**		**BaO**		**ZnO**	
	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s
A01	0.406	0.032	0.382	0.139	0.162	0.048	0.154	0.322	0.009	0.021	0.279	0.136	0.955	0.395	1.957	0.250	0.097	0.171
A02	0.783	0.361	0.182	0.160	0.095	0.140	0.241	0.378	0.038	0.052	0.122	0.282	0.966	0.327	1.293	0.085	0.065	0.019
A03	1.295	0.224	0.215	0.195	0.292	0.070	0.071	0.226	0.025	0.051	0.362	0.205	0.648	0.281	0.294	0.278	0.058	0.231
A04	0.516	0.167	0.492	0.139	0.097	0.025	0.045	0.181	0.000	0.000	0.211	0.223	0.622	0.218	0.444	0.084	0.136	0.136
A05	1.507	0.239	0.199	0.239	0.196	0.045	0.180	0.269	0.064	0.136	0.219	0.361	0.801	0.225	1.120	0.350	0.064	0.151
A06	0.674	0.187	0.300	0.211	0.144	0.033	0.080	0.219	0.018	0.073	0.224	0.234	0.837	0.154	0.926	0.139	0.021	0.084
A07	0.554	0.409	0.174	0.111	0.125	0.079	0.090	0.152	0.000	0.001	0.285	0.219	0.809	0.304	1.272	0.109	0.189	0.220
A08	0.915	0.373	0.195	0.093	0.104	0.078	0.066	0.139	0.026	0.059	0.193	0.220	0.750	0.237	0.615	0.184	0.017	0.067
A09	1.348	1.196	0.250	0.195	0.218	0.070	0.196	0.259	0.057	0.092	0.239	0.187	0.654	0.121	0.661	0.284	0.067	0.168
A10	0.629	0.413	0.214	0.129	0.125	0.054	0.164	0.267	0.032	0.092	0.459	0.308	0.895	0.228	0.558	0.385	0.012	0.031
A11	1.154	0.390	0.118	0.099	0.171	0.097	0.132	0.216	0.003	0.010	0.411	0.123	0.503	0.139	2.983	0.506	0.057	0.085
A12	0.984	0.158	0.164	0.049	0.203	0.042	0.373	0.299	0.006	0.022	0.380	0.069	1.050	0.159	0.460	0.116	0.012	0.031
A13	1.137	0.468	0.175	0.098	0.158	0.065	0.174	0.227	0.039	0.086	0.252	0.232	1.010	0.313	0.864	0.200	0.176	0.247
A15	2.305	0.793	0.200	0.093	0.316	0.067	0.071	0.173	0.092	0.120	0.408	0.089	0.796	0.329	0.203	0.139	0.041	0.079
A20	2.571	0.115	0.134	0.045	0.177	0.095	0.626	0.272	0.031	0.075	0.290	0.225	0.804	0.119	1.454	0.214	0.371	0.184
A21	0.893	0.164	0.218	0.203	0.114	0.043	0.242	0.291	0.047	0.065	0.160	0.108	0.588	0.162	1.013	0.238	0.052	0.093
A23	0.966	0.196	0.302	0.270	0.128	0.165	0.002	0.004	0.038	0.116	0.459	0.034	0.705	0.267	0.101	0.188	0.143	0.259
A25	1.746	0.442	0.137	0.181	0.236	0.100	0.211	0.339	0.008	0.023	0.272	0.146	0.973	0.272	0.932	0.296	0.289	0.339
A26	2.015	0.322	0.105	0.103	0.195	0.073	0.075	0.174	0.062	0.147	0.213	0.111	0.768	0.441	0.473	0.153	0.155	0.087
A28	0.979	0.531	0.191	0.181	0.219	0.066	0.048	0.191	0.005	0.021	0.255	0.017	0.713	0.276	0.941	0.104	0.151	0.232
A29	0.750	0.338	0.220	0.108	0.086	0.106	0.075	0.237	0.000	0.000	0.321	0.081	0.654	0.336	0.548	0.198	0.047	0.064

Table A.5 (cont.) Mean value and standard deviation of quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**SiO_2**		**FeO**		**CaO**		**Al_2O_3**		**MgO**		**MnO**		**Na_2O**		**K_2O**	
	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s
B01	35.305	1.016	28.425	0.573	24.045	0.743	5.090	0.355	1.492	0.539	0.233	0.220	1.447	0.399	1.106	0.136
B02	38.571	0.521	22.629	0.871	22.616	0.476	4.918	0.724	1.342	0.406	0.198	0.238	1.214	0.974	0.642	0.066
B03	43.883	1.016	15.145	0.272	25.883	0.428	5.531	0.169	1.459	0.438	0.308	0.176	1.962	0.636	0.803	0.109
B05	34.652	0.783	27.103	0.385	22.285	0.290	5.712	0.231	2.701	0.147	0.324	0.064	2.581	1.365	0.814	0.094
B06	35.764	0.916	33.018	1.277	15.343	1.064	6.291	0.635	2.058	0.339	0.156	0.100	3.036	2.048	1.061	0.119
B07	34.863	0.505	35.845	0.989	14.560	0.215	6.128	0.377	1.561	0.118	0.169	0.092	2.928	1.032	0.851	0.056
B08	34.742	0.786	27.157	0.742	23.610	0.798	5.930	0.688	1.867	0.290	0.201	0.110	2.370	1.282	1.007	0.067
B09	38.337	0.248	13.251	0.400	31.051	1.496	5.732	0.481	5.861	0.804	0.287	0.121	1.605	0.678	0.814	0.054
B10	63.750	1.963	5.003	0.811	11.860	0.841	10.572	1.065	2.159	0.523	0.089	0.052	4.021	0.627	0.797	0.101
B11	41.402	0.335	17.418	0.642	26.870	1.227	5.696	0.720	1.480	0.435	0.246	0.129	2.291	1.146	0.738	0.039
B12	38.689	1.433	28.750	2.179	14.336	0.382	9.211	0.712	2.471	0.201	0.384	0.165	1.885	0.278	1.019	0.142
B13	35.858	1.230	30.486	1.117	20.714	0.969	5.492	0.672	1.639	0.194	0.127	0.182	1.550	1.022	0.885	0.032
B14	34.731	1.005	34.533	1.214	14.967	0.754	7.024	0.281	1.618	0.537	0.279	0.164	2.995	1.697	0.829	0.132
B15	36.724	1.286	31.109	0.183	13.978	0.713	8.024	0.196	1.607	0.321	0.516	0.217	2.724	1.912	0.635	0.158
B18	38.363	0.581	28.015	1.106	17.344	0.592	7.451	0.231	1.580	0.211	0.370	0.096	2.249	1.884	0.961	0.077
B20	33.459	0.321	27.557	0.685	23.970	0.300	5.635	0.126	1.816	0.713	0.257	0.082	2.886	1.530	0.902	0.113
B22	43.428	0.577	16.660	0.388	25.981	0.561	5.056	0.352	1.138	0.485	0.213	0.118	2.288	0.458	0.583	0.156
B23	36.313	1.287	30.383	0.510	15.355	0.094	8.003	0.414	1.851	0.795	1.388	0.183	3.251	1.317	1.048	0.077
B26	40.896	0.750	23.872	0.737	22.382	0.620	5.244	0.448	1.361	0.600	0.139	0.165	1.864	1.405	1.061	0.150

Table A.5 (cont.) Mean value and standard deviation of quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**CuO**		**SO_3**		**Cl_2O**		**As_2O_3**		**NiO**		**TiO_2**		**P_2O_5**		**BaO**		**ZnO**	
	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s	mean	2s
B01	0.444	0.422	0.300	0.136	0.098	0.083	0.121	0.287	0.039	0.102	0.243	0.410	0.917	0.152	0.645	0.253	0.056	0.095
B02	2.234	0.526	0.147	0.098	0.123	0.075	0.441	0.555	0.010	0.038	0.007	0.029	0.841	0.122	3.844	0.295	0.232	0.156
B03	1.584	0.238	0.029	0.070	0.129	0.077	0.343	0.396	0.001	0.003	0.166	0.058	0.965	0.392	1.732	0.328	0.087	0.049
B05	1.086	0.259	0.141	0.110	0.171	0.115	0.358	0.384	0.070	0.113	0.197	0.146	0.875	0.298	0.858	0.259	0.079	0.215
B06	0.974	0.131	0.388	0.214	0.163	0.148	0.030	0.078	0.026	0.076	0.281	0.066	0.649	0.202	0.695	0.191	0.071	0.198
B07	1.059	0.270	0.340	0.236	0.238	0.132	0.029	0.081	0.084	0.109	0.158	0.134	0.684	0.227	0.477	0.118	0.031	0.089
B08	0.534	0.361	0.353	0.219	0.225	0.165	0.000	0.000	0.030	0.063	0.199	0.121	0.887	0.227	0.828	0.336	0.063	0.097
B09	0.668	0.157	0.193	0.170	0.138	0.087	0.207	0.275	0.039	0.061	0.355	0.069	0.828	0.243	0.541	0.164	0.097	0.112
B10	0.140	0.201	0.000	0.000	0.178	0.087	0.038	0.055	0.029	0.081	0.555	0.102	0.715	0.120	0.018	0.025	0.080	0.162
B11	1.112	0.303	0.074	0.208	0.170	0.097	0.346	0.218	0.070	0.125	0.190	0.225	0.827	0.223	0.952	0.133	0.122	0.102
B12	1.198	0.253	0.213	0.176	0.211	0.026	0.041	0.115	0.007	0.021	0.411	0.084	0.677	0.294	0.461	0.215	0.043	0.063
B13	0.969	0.169	0.237	0.177	0.129	0.059	0.078	0.219	0.030	0.062	0.249	0.070	1.020	0.105	0.535	0.209	0.008	0.023
B14	1.506	1.465	0.297	0.155	0.130	0.059	0.032	0.119	0.003	0.008	0.280	0.352	0.603	0.168	0.139	0.240	0.046	0.155
B15	2.855	0.431	0.193	0.251	0.247	0.122	0.172	0.225	0.041	0.073	0.241	0.060	0.628	0.134	0.284	0.246	0.030	0.095
B18	1.014	0.363	0.306	0.045	0.185	0.073	0.180	0.197	0.041	0.095	0.351	0.198	0.879	0.179	0.662	0.191	0.058	0.140
B20	0.852	0.312	0.248	0.097	0.136	0.068	0.046	0.109	0.000	0.000	0.184	0.200	0.757	0.132	1.253	0.251	0.049	0.127
B22	1.313	0.489	0.094	0.100	0.141	0.096	0.468	0.348	0.000	0.000	0.266	0.127	0.831	0.155	1.440	0.143	0.108	0.165
B23	0.442	0.118	0.497	0.194	0.159	0.134	0.105	0.300	0.038	0.102	0.306	0.192	0.713	0.175	0.149	0.238	0.007	0.022
B26	0.705	0.420	0.263	0.170	0.137	0.120	0.045	0.179	0.062	0.163	0.151	0.207	0.976	0.207	0.653	0.138	0.198	0.231

Table A.5 (cont.) Mean value and standard deviation of quadruplicate SEM-EDS analyses on pelletised slag samples (normalised data).

Sample	**SiO_2**		**FeO**		**CaO**		**Al_2O_3**		**MgO**		**CuO**	
	pellet	polished	pellet	polished	pellet	polished	pellet	polished	pellet	polished	pellet	polished
A05	36	35	34	35	20	21	7.0	6.5	1.8	0.9	1.6	1.6
A09	36	37	33	35	22	21	5.9	6.0	1.6	0.9	1.4	1.2
A11	51	53	14	14	20	18	12	12	1.8	1.4	1.3	1.1
A13	51	52	19	21	21	19	6.3	6.4	1.0	1.1	1.2	1.1
A15	42	42	32	32	13	11	9.5	9.6	1.7	1.5	2.5	2.8
B01	37	36	30	30	25	26	5.4	5.3	1.6	2.0	0.5	0.6
B02	42	40	25	27	25	25	5.3	4.2	1.5	1.6	2.4	1.7
B05	37	38	29	29	24	23	6.1	6.6	2.9	3.0	1.2	1.4
B12	41	39	30	30	15	17	9.7	9.3	2.6	2.7	1.3	1.1
B13	38	43	32	24	22	24	5.8	6.3	1.7	1.7	1.0	1.1
B20	36	35	30	32	26	25	6.0	5.7	2.0	1.9	0.9	1.0

Table A.6 Comparative SEM-EDS analyses of pelletised and polished slag samples (normalised data).