Forging a new Age: the technological origins of iron metallurgy in the Late Bronze Age Near East.



Volume I: Text

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Abstract

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A gradually expanding body of evidence for the production and use of iron prior to the 1st millennium BC has contributed towards a realisation that the chronology of iron metallurgy extends farther back into the history of metal-using cultures than previously anticipated. This has brought into question whether iron metallurgy sprang from the technological developments in copper production achieved by the Late Bronze Age in the Near East. More recently, the close integration of finds analysis with the primary contexts of metal production assemblages has provided an opportunity to define the relationship of copper producers with iron during the second millennium BC and earlier. Evidence from a number of sites across the Near East demonstrates that iron in the form of oxides and sulphides would have constituted a significant proportion of the minerals exploited by Middle to Late Bronze Age copper producers. The large scale reduction of these mixed ores that took place across the period may have resulted in the earliest instances of the production of metallic iron as a by-product from which later iron extraction technologies precipitated. Mixed charges of iron and copper oxides and copper-iron sulphides were smelted in both a crucible and reconstructed prehistoric furnace in varying ratios in a series of experiments. Metallographic analysis of the resulting assemblages revealed that metallic iron was produced in substantial quantities as prills both dissolved and as phases in the copper when reducing the copper and iron oxide charges. Significant quantities of iron were also shown to remain in the intermediary products of copper-iron sulphide smelting. Separation of the metallic iron and copper was attempted by means of a crucible and the feasibility of producing workable metallic

iron through a co-smelt with copper was assessed. Though diminutive, the quantities of iron that could have been produced by Late Bronze Age metallurgists could have been sufficient to supply the elite demand for a decorative and exclusive material, a role which iron has often been speculated to have fulfilled in its earliest incarnations. Perhaps more crucially, the presence of iron across the breadth of metallurgical practices utilized by Late Bronze Age metal producers would have engendered an experience and understanding which later developed into the full scale ferrous industries that have since granted iron hegemony over the metals in human manufacture.

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Completion of this degree has been met with unprecedented challenges from personal loss, health concerns and not least a worldwide pandemic. At nearly every turn a new hurdle has been raised to be overcome yet at each such instance people both familiar and less so have stepped in to offer unconditional support. I will be forever grateful for their kindness and generosity.

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I dedicate this thesis to my grandmother Norah Downes.

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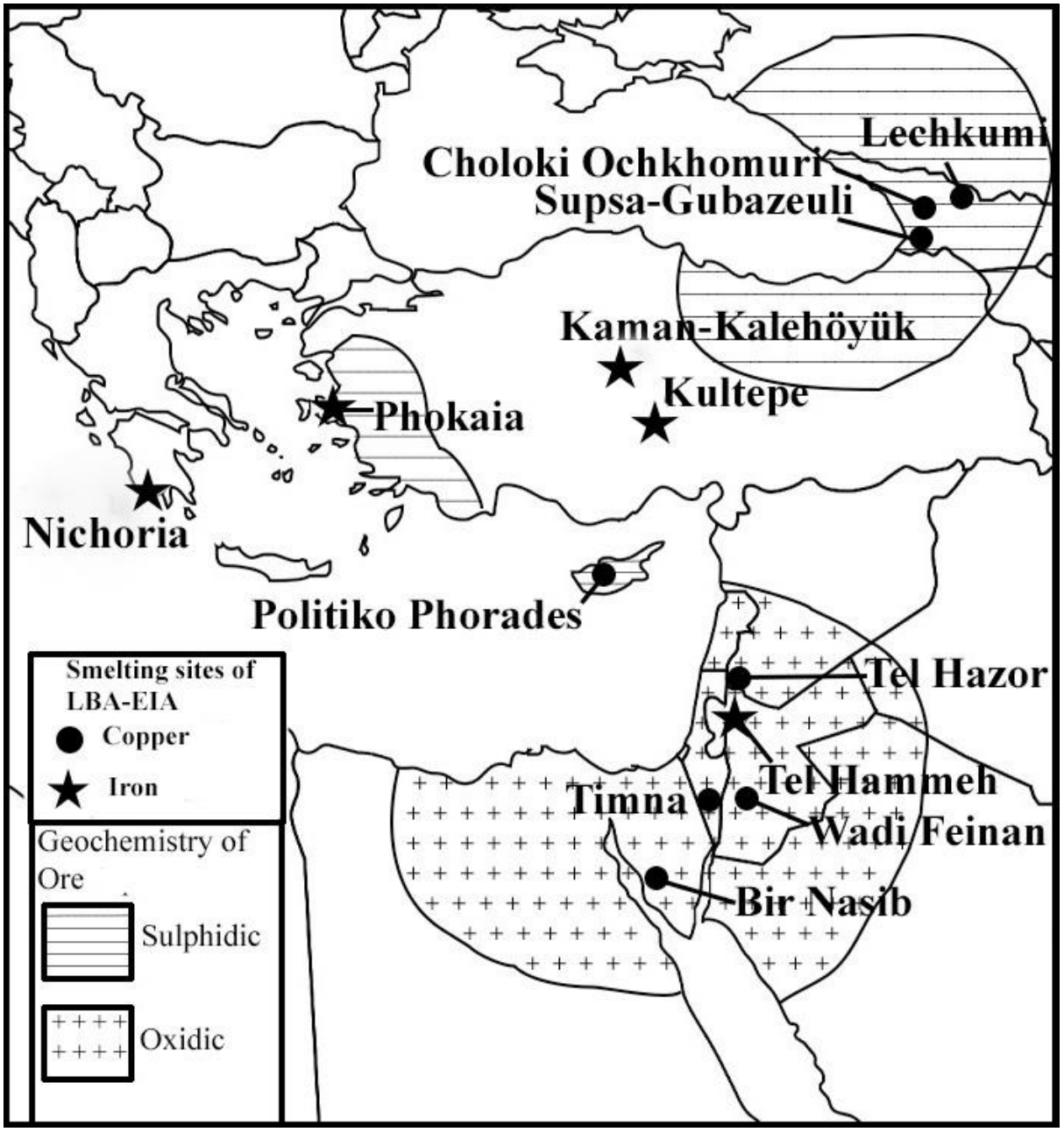
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Map of major smelting sites in the Near East from the second to early first millennium BC with reference to the geochemistry of the primarily exploited ore deposits by greater proportion of sulphides or oxides. Adapted from Eppelbaum and Khesin 2012; Erb-Satullo, Khakhutaishvili and Gilmour 2014, 2017; Hauptmann 2007, 2020.

Dates BCE	Anatolia	Caucasus	Cyprus	Levant	Egypt (dynasties)	Greece
2000						
	OAC	MB II	EC IIIB-MC I	MB I	11th-early 12th	MH
1900						
			MC II		Mid-late 12th	
1800						
			MC III	MB II	13th	
1700						
1600	OHK	MB III	LC I	MB III/LB	15th	
				LB IA	18th (Tuthmosis III to New Kingdom and Amarna period).	
1500						
1400	MHK	LB I		LB IB		LH I
			LC IIA	LB IIA		LH II
1300						
1200	HEP	LB II	LC IIB	LB IIB	19th	LH IIIA
		LB III	LC IIC	LB III/I IA		LH IIIB
1100						
	EIA I		LC IIIA	I IB	20th	LH IIIC
1000		I IA	LC IIIB/ CG IA		21st	SMyc
900				I IIA	22nd	EPG
800			CG IB/ CG II			MPG
700	EIA II	I IB	CG III	I IIB		LPG
					23rd	EG
		I IIA		I IIIA	24th	MG

Table I: Second to first millennium BC chronologies of five major regions of the Near East.

Abbreviations

OAC Old Assyrian Colony
OHK Old Hittite Kingdom
MHK Middle Hittite Kingdom
HEP Hittite Empire Period
EIA Early Iron Age
EH Early Helladic
MH Middle Helladic
LH Late Helladic
MB Middle Bronze
LB Late Bronze
I Iron
SMyc Sub-Mycenaean
EPG Early Proto-Geometric
MPG Middle Proto-Geometric
LPG Late Proto-Geometric
EG Early Geometric
EC Early Cypriot
MC Middle Cypriot
LC Late Cypriot
CG Cypro-Geometric
MG Middle Geometric

Table I

Light grey Evidence for smelted iron.

Dark grey Evidence for iron smelting.

Chronologies adapted from:

Erb-Satullo 2019, et al. 2014; Dickinson 2006; Iacovou 2007; Manning et al. 2018; Mazar et al. 2005; Toffolo et al. 2014; Yalçın 1999; Höflmayer 2017; Workman et al. 2021; Catling et al. 1983.

Chapter One: Introduction

1.1: *Introduction*

There have been major developments in our understanding of iron metallurgy prior to the 1st millennium BC over recent decades. An expanding body of evidence for metal production during the 2nd millennium BC in the Near East from new and revisited sites- many of which lie in long neglected regions such as the south Caucasus (Gilmour et al. 2020), Iran and Jordan (Ben-Yosef et al. 2010; Danti 2013) has contributed towards the gradual realisation that the chronology of iron production and use extends farther back into the history of metal using cultures than was previously anticipated (Haarer 2001). Recognition of a longer chronology brought several implications with it regarding technological change through the processes of invention, innovation and adoption of iron metallurgy. The discovery of the earliest Near Eastern examples of smelted iron in the regions of Anatolia (Akanuma 2008; Yalçın 1999), the Levant (Veldhuijzen and Rehren 2007) and on Cyprus (Kassianidou 1994) which saw some of the most intensive copper production in the Near East during the 2nd millennium BC would appear to reaffirm the technologically deterministic model that iron metallurgy in the Near East sprang from developments within preceding copper related practices (Waldbaum 1999; Wertime and Muhly 1980:5). This is a situation at odds with Sub-Saharan Africa which hosted minimal copper production prior to its Iron Age or indeed China where bloomery iron was likely introduced from the bordering western steppe around 500BC (Bandama 2020:3; Bronson 1999:177-182; Killick 2009; Wagner 2021:406). The question of whether the technological developments achieved by the 1st Millennium BC in the Near East facilitated the rapid transmission and spread of iron from a single point of origins (Bebermeier et al. 2016; Muhly et al. 1985; Waldbaum 1999) or whether it was an independent and localized invention representing the sum of long practice and experience with iron among copper producers (Gale et al. 1990) is therefore unclear. Closer scrutiny of both early iron artefacts and experimentally reproduced smelted iron has given rise

to an appreciation that the earliest forms of iron available to Bronze Age peoples was certainly not a superior material to bronze as its scarcity and particular properties rendered it often less suitable for both expressive and utility purposes than the long–worked copper alloys which persisted well into the 1st millennium BC (McConchie 2004:20; Workman et al. 2021). The use of iron was therefore socially, not technologically, determined for much of this early period across which iron metallurgy was beginning to be established in the Near East; at a time when most cultures were wholly ignorant of the eutectic properties of iron when mixed with carbon in the alloy steel (Buchwald 2005:7-8; McConchie 2004:94). Social rather than technological factors, such as the assertion of geo-political control over the economy through the monopolization or patronage of newly established metal industries and trade networks by elites may have facilitated the early circulation of iron prior to the 1st millennium BC (Bebermeier et al. 2019:154-258; Mirau 1997:105; Yahalom-Mack et al. 2017). Another little explored ramification of an extended chronology for ironworking is that iron either must have been produced alongside copper as a by-product of copper smelting (Craddock and Meeks 1987; Pleiner 2000:212; Tholander 1982) or was deliberately extracted by a few contemporary specialists (Muhly et al. 1985), though archaeological evidence for either of these hypotheses is extremely limited. If indeed the smelting of iron in the Near East arose from copper related metallurgical practices it will prove crucial to any study into the origins of iron metallurgy to identify the elements of Late Bronze to Early Iron Age copper production that permitted this innovation. The growing sophistication of methods for the analysis of metallurgical debris has allowed archaeometallurgists to reconstruct metallurgical practices and associated formation processes to produce assemblages that more accurately reflect the archaeological record. The trend towards the close involvement of archaeological scientists with the primary contexts of metallurgical assemblages allows for the integration of structural and spatial data (site layout, furnace type/dimensions, slag deposition patterns) with chemical data from materials analysis. Resulting studies, though in their infancy, have shown great promise (Eliyahu-Behar et al. 2012, Erb-Satullo and Walton 2017, Ilani et

al. 2020). These studies provide a strong basis for the reconstruction and re-enactment of the metallurgical operations taking place in the Late Bronze Age. By reconstructing these processes it may be possible to estimate the scale and efficiency at which these operations could reduce ferrous minerals into metallic iron in comparison to the later practices employed during the Iron Age across the Near East. As iron implements gradually succeeded copper alloys by proportion of metal assemblages dating from the early to middle 1st Millennium BC, it is only through comparison of Iron Age production sites to those of the Late Bronze Age that we can reveal the context for this innovation in light of the physical and chemical boundaries (temperature, reduction-oxidation atmosphere, reaction volumes etc.) that had to be overcome through technological means in order to produce these substantial quantities of malleable wrought iron at a competitive scale (Erb-Satullo 2019:557-579; Maddin et al. 1977:122-124; Veldhuijzen et al. 2012:237-239). From these developments we can begin to reveal how Late Bronze Age Near Eastern cultures first experienced iron and how this early interaction set the stage for the widespread adoption of iron across the region in the age to come.

1.2: *Research Aims*

Establishing the technological precedents under which cultures of the Near East first began to encounter and engage with metallic iron is crucial in explaining the later patterns of innovation that led to the widespread adoption of iron metallurgy in the first millennium BC. Yet despite this, the pyrometallurgical processes employed by Late Bronze Age copper producers in the region have arguably received less attention from the scholarship (Gottlieb 2010; Morris 1989; Waldbaum 1978; Wertime and Muhly 1980). As early as the seventies the prominent archaeometallurgist Theodore Wertime had recognised the need for a closer scrutiny of Bronze Age technologies in studies into the

beginnings of iron metallurgy in his titular statement: “Arguments over diffusion and independent invention ignore the complex metallurgic crafts leading to iron” (1973:875). More detrimental still has been the paucity of research into the frequent occurrence of iron in ancient copper alloys. Craddock and Meeks recognised this deficit in the opening passage of a rare article discussing the topic: “Ancient Bronze is rarely pure, and of all the ancillary metals found therein, iron is one of the most interesting yet sadly the most neglected” (1987:187). Without a fundamental understanding of the metallurgical technologies and products associated with contemporary cultures it is perhaps unsurprising that the origins of iron in the Near East remains obscure. Often reliant upon textual evidence, leading theories have scarcely progressed beyond the classical historical interpretations of the 19th century beyond a discussion of the mechanisms for the diffusion of iron across the region (Erb-Satullo 2019:558; Veldjhuijzen and Rehren 2007;189-191; Wertime and Muhly 1980:4). Clearly it appears that the old question of the origins of iron metallurgy could benefit greatly from a novel approach placing antecedent metallurgical practices at the forefront of the discussion. By advancing understandings of the relation of iron to the complex metallurgical operations employed by metal producers during this period it may allow for the re-assessment of the available evidence for the earliest appearances of smelted iron in the Near East. Eschewing the traditionally pursued themes of where iron metallurgy first began and at what time this research instead considers how iron could have been produced and under which circumstances, within the contexts of metal production in the Near East during the 2nd millennium BC. From this basis three core questions can be identified that this thesis will aim to address:

- **Were the chemical and physical requirements for the extraction of metallic iron achieved during Late Bronze Age smelting practises in the Near East?**

  The production of metallic iron could not have been the objective of metal producers prior to the adoption and use of the metal- how then did iron enter into the chemical component of primarily non-ferrous smelting operations? Iron required a more strongly reducing environment to be extracted from its ores compared to copper; were the pyrometallurgical traditions employed for copper smelting sufficient also to extract metallic iron? If so, what technological developments facilitated it?

- **Can metallic iron be produced as a by-product of copper smelting operations?**

  If metallic iron can be produced during copper smelting, to what extent does this occur and how does this affect the process? Which conditions were most favourable for the extraction of metallic iron and in what form could metallic iron be recovered from each operation? Secondary production through melting and casting of ingots was regularly practised; did iron in smelted copper become involved in this process?

- **What are the technological implications for the production of metallic iron during copper smelting operations of the Late Bronze Age in the Near East?**

  In what quantities was iron produced and was it suitable for secondary production? How did the co-production of iron contribute towards technological change in the region? What innovations were required to establish an extractive metallurgy of iron? Why did the use of iron not emerge earlier and was the appearance of iron reflected in changing production strategies employed across the region and over time?

1.3: *Research Objectives*

The extraction of metallic iron through direct reduction of a ferrous mineral requires certain conditions to be met which were not necessarily achieved during the smelting of copper and other non-ferrous metals in the Near East from the mid to late 2nd millennium BC. It is therefore necessary to define these processes in terms of physical and chemical events to assess whether the required conditions for the extraction of iron were present (Hauptmann 2020:178-191). The most significant of these factors in the study of extractive metallurgy can be summarised as follows:

- **Charge Composition**

  The charge represents the chemical compounds, other than the fuel, that are placed into the furnace to undergo a chemical reaction and produce the desired metal contained therein. The composition of the charge largely determines the chemical processes that occur during smelting.

- **Redox Conditions**

  Redox, or reduction-oxidation reactions, refers to a chemical reaction during which the oxidation state of one atom changes due to the gain (reduction) or loss (oxidation) of an electron to another atom. In the contexts of prehistoric smelting, the redox conditions are controlled by the combustion of a carbon fuel in the furnace (usually charcoal) and release of carbon monoxide and dioxide gases, the supply of oxygen from the atmosphere through artificial and natural draught and the chemical composition of the charge. It is through the manipulation of these conditions that the desired metal can be extracted from an ore.

- **Temperature**

  Temperature is a determining factor in the rate of reaction and the state of the chemicals contained within the furnace. Certain reactions are only favoured at specific temperatures and so it is only through achieving these temperatures within the furnace that the desired metal can be produced. Maintenance of sufficient temperatures to render the furnace contents partially or fully liquid increases the mobility of the material allowing for greater density segregation and assisting in the recovery of the desired metal. Temperature in a prehistoric furnace was controlled through the combustion of a carbon fuel (such as charcoal) with oxygen in an exothermic reaction. The rate of combustion could be increased by increasing the partial pressure of oxygen in the furnace through forced or natural draught, achieving higher temperatures.

This thesis will begin by attempting to define each of these factors within the contexts of primarily non-ferrous smelting practices in the Near East during the 2nd millennium BC. To this end a re-appraisal of the evidence from the academic literature and archaeological record has been undertaken. Based on this research the potential for the extraction of metallic iron to occur during these processes is assessed. The conclusions derived from this study were used to instruct an experimental methodology and were applied to the reconstruction of furnaces and experimental design. From this the Author hopes to provide a comprehensive basis for a theoretical discussion regarding the co-smelting of iron alongside copper and other metals in a prehistoric context. As the subject has rarely been approached from the perspective of the metallurgy of iron this may prove of value to wide-ranging research into the smelting practises of the Late Bronze Age.

The smelting of metals is highly variable and takes place within a dynamic system. Determining factors such as pyro-technology, technical operation, ore composition and systemic limitations directly affected the outcome of prehistoric smelting. Quantifying these processes based purely on the limited evidence available from the archaeological record is immensely challenging however reconstructions can provide much data for archaeometallurgists to draw upon. In order to address the possibility that metallic iron may have been produced during copper smelting, the Author has embraced an experimental and reconstructive methodology informed by the conclusions derived from the discussion at the beginning of the thesis. This methodology consists of reconstructions of Late Bronze Age furnaces based on extant remains from sites across the Near East which were used in a series of experimental smelts. The objective of the experiments was to reproduce the formation processes and end-products of a copper smelt from the period with the proportion of iron in the charge acting as the primary controlled variable. The experiments aimed to simulate the affects of varying iron contents in the charge introduced by the different production strategies employed by copper smelters of the Late Bronze Age Near East. Samples of copper collected from these experiments were then subjected to re-melting and casting to imitate the secondary production of copper metal into ingots which formed a major component of copper production in the region. The results of the experiments were determined through metallographic examination and chemical analysis to produce a dataset suitable for comparative study. This data was used in concert with published data produced from the chemical analysis of Late Bronze Age copper alloys to contribute towards a hypothesis regarding the extraction of iron during copper production across the Near East.

1.4: *Burning Questions: an experimental approach*

Since the development of Archaeology as a methodology for revealing the human past, a key objective of the discipline has been to relate material culture to the human behaviours of which it is a product. With the growing sophistication of archaeological methods among academics in Europe and their widespread application across global empires over the first half of the 20th century, this challenge was initially viewed with confidence (Wylie 1993:20). Hawkes (1954) even specified the degree of confidence that could be taken in relating technologies to human behaviours in a formal 'ladder of inference' which contested that revealing the processes of manufacture behind artefacts was the least difficult undertaking in archaeological endeavour (Renfew 1990:124). For the first time, broad comparative treatment of the archaeological record based on chronologies informed by stratigraphic and typological analysis was possible, forming the basis for the grand synthetic arguments constructed by Childe (Trigger 1986:4-8; Tringham 1983:86-87). Synthetic approaches to the history of technology among past cultures had been prevalent since the encyclopaedic works of the previous century and continued to be promoted, with technologically deterministic narratives remaining dominant in the literature (Pollard and Gosden 2023:19-29). Technological development was widely construed as a consequence of social and cultural evolution driven by external factors such as urbanization, migration and diffusion (Pollard and Gosden 2023:30-32; Trigger 1986:10-12). Under this culture-historical auspice the cognitive aspects of technology, as they relate to the technical practices and learning processes of past humans, were neglected. This position would be revised following the revolution in carbon dating; the inadequacies of these synthetic explanations fell into sharp relief when the chronological frameworks for the conjectured diffusion of innovation from the Near East to western Europe were dismantled (Kern 2020: 208-209; Tringham 1983:87). Cultural and technological development could no longer be seen necessarily as a consequence of these external factors. In response Binford argued that technological development among past cultures was the result of cultural adaptation to environmental and social conditions in what would become the new

archaeology or processualism movement (1962:219; Shanks and Hodder 2013:3). As past environments were quantifiable, this provided a conceptual basis to apply scientific methodologies to the question of technological change, permitting the relationship between human cognitive and physical behaviour and material culture to be brought to the fore (Shanks and Hodder 2013:1-2). Here Binford challenged the earlier assertions of Hawkes that the techniques and methods of manufacture behind material culture were the most easily understood in the hierarchy of inference, stating that these processes were no more divorced from environmental or social circumstances than any other form of cultural activity (1968:21; Renfrew 1990:124). An alternative was offered where material culture was categorised into groups dependent on whether it represented an adaptation to environmental, social or cognitive pressures; termed technomic, socio-centric and ideocentric respectively (Binford 1962:219). Of these, Binford recognised that technomic artefacts correlated directly to the environment, therefore the associated formation processes (technical, technological) could be extrapolated from the archaeological record through scientific methodology (1962:219; Shanks and Hodder 2013:2). The new approach was exemplified in the development of middle-range theory, which sought to establish an epistemological basis for explaining the archaeological record without drawing upon theories regarding the past behaviours underlying its formation (Bell 2014:44; Binford 1983:213; Yu et al. 2015:4). This opened the way for two sources of analogy available in the modern day: ethnography and experiment (Bell 2014:44). Both methods allowed for the observation of behavioural, technological and physical phenomena in a dynamic context which could be defined as the environment in ethnography or the experimental conditions in experimental archaeology (Bell 2014:44; Yu et al. 2015:4). Resulting observations could then be applied to the 'static' archaeological record to make inferences about the dynamic processes of formation that led to its deposition (Bell 2014:44-45; Schiffer 1995:70; Yu et al. 2015:4-6). No less crucial for the development of the experimental field in archaeology was the optimism of processual thought based on logical positivism, without which the discipline undoubtedly would have failed to commit to the arduous task

of reconstructing experimental conditions to test hypotheses (Bell 1994:14; Shanks and Hodder 2013:2). These concepts would later come to be attacked regarding the objectivity of interpretations based on science and on perceived social patterns in what would become Post-processualism (Bell 2014:45; Shanks and Hodder 2013:3). The criticism of middle-range theories presented by post-processualists would have a number of implications for experimental archaeology. Firstly is the degree to which observations can remain objective when they remain embedded in social, cultural and theoretical perspectives (Hodder 1995). Even if these observations are made on an empirical basis they are still part of a value-driven process in which the archaeologist has identified a specific feature of the archaeological record to the exclusion of features deemed irrelevant to the theory of interest (Shanks and Hodder 2013:3). Secondly is the use of present day correlates to test theories, such as ethnography and experiment, which are selected and applied to past cultures on a subjective basis that cannot be independent of theory (Shanks and Hodder 2013:3-6). Bell describes this issue in experiment as a "philosophical conundrum" as the "...Gathering of data is not independent of the theory to be tested." (2014:43). The selection of phenomena to evaluate through experiment, the building of a hypothesis and the variables considered in the experimental methodology are all subject to an assessment of their value relative to a preconceived theoretical basis. The running debates between the two positions over the following decades were characterized by polarization between objectivism and relativism, leading to marginalisation of experimental approaches as a consequence of this conceptual ambiguity (Bell 2014:42; Shanks and Hodder 2013:3). In recent years the two sides have come closer to reconciliation as the greater significance of factors such as agency, cognition and the socially embedded nature of archaeological knowledge has come to be recognised (Bell et al. 2009; Renfrew 1994, 2006; Shanks and Hodder 2013:3-4,10-30). Theories utilizing data derived from a diverse array of approaches in archaeological interpretation have since been considered more favourably (Bell 2014:42). The substantial contribution experimental archaeology can make towards these and other areas of interest has subsequently led to a gradual resurgence of its application and a

shift in the debate over objectivity to questions of control versus actualism, experientialism and incorporating theory in experimentation (Deady et al. 2013; Foulds 2013; Schenck 2011). While the debate over the validity of experimental approaches may be far from reaching academic consensus, it is the hypothetical nature of experiment that makes it ideally suited to contribute towards the open-ended dialogues that persist in archaeological thinking. It provides a productive framework for cross-disciplinary engagement by raising specific questions through a well-defined methodology which can then be directly evaluated, re-affirmed or revised by others adopting the same or alternate methodologies.

Experiment is a core element of the scientific method that represents a series of steps to be applied to test an initial position based upon observations of physical phenomena or theory (Bell 2014:43; Outram 2008:1). These steps can be defined as:

- Observation- A specific physical phenomena or theory is identified and recorded. This process must remain objective by adhering to principles of empiricism.
- Formation of a hypothesis- A hypothesis is an assertion which aims to explain these observations on a theoretical basis.
- Experimental methodology- A means of testing the hypothesis is constructed, aiming to be replicable so that the results can be demonstrated repeatedly.
- Conclusion- Through analysis of the resulting data it is determined whether the hypothesis was proven false or if it remains the best explanation of the observed phenomena.

As the first step, the objective of the observation phase can be summarised as deciding what dilemma or phenomena the hypothesis seeks to address/explain. This informs the entire experimental process requiring accurate identification of the subject in question while aiming to be objective (Bell 2014:45). Given the temporal disconnect between archaeologists and past phenomena, with many interceding variables from erosion to depositional bias, this is no easy feat. This process is often reliant upon analogy with observable phenomena derived from ethnographic, experimental or environmental contexts (Bell 2014:43; Ferguson 2010:1-2). Analogies can broadly be consigned to two categories: formal or comparative analogies and relational or causal analogies (Bell 2014:43). The use of analogy requires critical evaluation to ensure a correlation between the phenomena being observed and that which has been inferred from the archaeological record (Wylie 2002:136-137). For instance, experimental archaeology is best placed to draw upon relational analogy in experimental design as this is concerned with causal relationships; such as copper becoming molten when its temperature exceeds its melting point (Bell 2014:43). An equally important aspect is to relate experiment explicitly to a theoretical context (Ferguson 2010:2). Three types of experiment can be highlighted through their relation to theory: crucial experiments aim to support an established theory against competing explanations, corroborative experiments aim to provide evidence for a single theory and new phenomena experiments produce data that is not explained by current theory and may generate new theories (Ferguson 2010:3). To test the validity of a theory, the concepts and logic of that theory have to be accurately and explicitly understood so as not to introduce unrelated variables around which an inappropriate hypothesis may be built. Observations may be based directly upon the material evidence from the archaeological record, for which Ascher describes a scheme for placing artefacts into a hypothetico-deductive context (1961:795). In the scheme of inference devised by Thompson (1958) the deductive process would begin with an *indicative* assignment i.e. a bowl. Then an indicated conclusion regarding its function could be made, such as being used to hold food. The form of the artefact could then be related to this function and other analogues, i.e. the bowl is small

and open similar to food bowls used in other cultures. From this *probative* data the most probable explanation could be made that the bowl was for holding food. A hypothesis could then be made to test the probative data through experiment; this bowl was made to hold food, can it hold food when placed inside? (Ascher 1961:795; Reynolds 1999:387-388). From the results the probable conclusion regarding its function could be discarded or remain sufficient as an explanation. Once the phenomena in question has been defined through interpretation of the archaeological record, analogy or in terms of a pre-existing theory; the next step is to formulate a hypothesis to account for it. A hypothesis represents a clear empirical prediction of the outcome of the experiment drawn from the observational stage and will therefore determine the variables used in the experiment (Bell 2014:43; Eren et al. 2016:108). Prior to testing or consideration of variables the initial prediction may be termed a 'working hypothesis' which is derived from interpretation of the observed phenomena (Ascher 1961:795). As more data becomes available from testing or the setting up of experimental conditions the working hypothesis may be revised in which case the experiment has to be concluded before re-formulating a better hypothesis (Reynolds 1999:388). Alternatively, an experiment may be framed *inductively*; recreating experimental conditions to inform the conclusion (Schenck 2011:90). Both methods do not exclude the postulating of multiple hypotheses based on the data from a single experiment if they share variables and the methodology remains appropriate (Reynolds 1999:388). An experiment may prove more valuable if the hypothesis is framed within a pre-existing theoretical context, deriving from a question already posited in previous studies or based upon a speculative theory, allowing for comparison of the methodology with previous research and application of the results to a wider theoretical dialogue rather than in isolation (Ferguson 2010:3; Outram 2008:4).

An experimental methodology is designed primarily to test the validity of the hypothesis by producing results that directly correlate to it, achieved through consideration and control of variables, which themselves determine the conditions of the experiment (Bell 2014:43; Reynolds 1998:388). A major caveat of experimental design is that it should be replicable and capable of being repeated (Bell 2014:43; Coles 1973:158; Reynolds 1998:388). In an archaeological context exact replication is rarely achievable due to chance factors which may affect variables, such as a local sand used in a temper being more refractory than that used in the original experiment and thus producing different results despite following the same methodology (Bell 2014:44). A strictly non-replicable experiment is not necessarily invalidated; comparison with close approximates, provided the difference between variables is understood, can be conclusive and is especially valuable for cross-disciplinary engagement and comparison (Bell 2014:44-45). As a central component of experimental design, the control of variables has been a matter of debate between adherents to strict control according to a scientific methodology and proponents of actualism in experimentation (Ferguson 2010:4; Schenck 2011). In the former camp tight control of variables is seen as essential to the scientific process for producing valid data on which to base conclusions (Schenck 2011:88). Experiments cleaving to these principles have often been described as 'laboratory' and examples range from the testing of clay cooking pots at varying temperatures by Schiffer et al. (1994) to the study of cut marks on bone from steel or stone tools produced by Mathieu (2002). This approach has been criticised for removing the actualistic component from experiment, namely the real conditions and materials present in the past (Schenck 2011:88). Often termed 'field' experiments, actualistic experimentation has typically been employed for more complex technologies such as metallurgy where the greater number of variables limits the control that can be exerted over them e.g. the serial reconstructions of furnaces and smelting of bog ores at Snowdonia National Park by Peter Crew (2013). Such experiments can be particularly beneficial for the formulation of superior hypotheses by granting an insight into limitations or unanticipated events relating to past technologies when all the expected variables are present

(Schenck 2011:90-91). This can be instrumental in inductive methodologies which are investigating processes of formation inferred from the archaeological record (Schenck 2011:88). By exercising less control over variables however less data can be procured and communicated within a scientific context raising doubts over the value of such experiments (Ferguson 2010:4; Schenck 2011:88). Another challenge for actualist approaches is the extent to which past environments and circumstances are truly replicable. Poor replication in such experiments may risk the introduction of false variables that were not present in the past resulting in misleading data (Schenck 2011:88). Ultimately this debate may have served to obfuscate the real issue which Schenck highlights in the following: "The question of what the controlled variables are really meant to accomplish in terms of knowledge is rarely addressed..." (2011:89). Experiments that address this question can be expected to produce data that directly correlates with the hypothesis even if the differential control of variables affects the results. One means of achieving this is to incorporate both 'laboratory' and 'field' experiments in experimental research to allow for comparison of the results to determine how less control over more variables in the field affects the major variable being tested (Ferguson 2010:4; Schenck 2011:91-92). Of paramount importance in experimental design is the clarity of the methodology which is crucial for the application of the data to a wider experimental discourse (Bell 2014:44; Ferguson 2010:2). The advantages of a clear and well presented methodology are threefold:

- The methodology can be related explicitly to the hypothesis which aids in constructing and communicating lines of reasoning applied to the data.
- The methodology will be more amenable to replication and the results more likely to be reproduced accurately by third parties.
- Criticism will be more effective if the process is properly understood by third parties.

In the conclusive stage of an experiment the results derived from the experimental methodology are compared to the predicted parameters stated in the hypothesis. If there is shown to be no correlation between the hypothesis and results then it is rejected as false and discarded (Bell 2014:43; Reynolds 1999:388). In the event of a positive correlation, the hypothesis stands as the best pendent explanation and can be accepted. This process is above all reflective both in calculating the degree of correlation with the results and by critically evaluating the suitability of the methodology for exploring the variables defined by the hypothesis. From these assessments the need for further experimentation and potential revision of the hypothesis or methodology can be determined.

The application of experimental methods in archaeology developed from an epistemological demand to test theories regarding the past independently of the archaeological record. Despite facing challenges over the objectivity of experimental approaches, the data that they can contribute is no longer considered dispensable for constructing archaeological theory (Bell 2014:42). Best practice in experimental archaeology can be defined as having a strong empirical basis in observation of the archaeological record and appropriate use of analogy. A hypothesis will directly address the question raised during observation and may be adopted from pre-existing theory or alternatively may remain unspecified as part of inductive reasoning during the experiment. Experimental methodology should be clearly expressed and closely replicable, ideally incorporating both highly controlled and actualistic elements which can be corroborated to determine the truest outcome of variable control. Conclusions will demonstrate a negative or positive correlation of the results to the hypothesis and will be reflective of the suitability of the methodology chosen. It is these principles that the experiment presented in this thesis, described in Chapter 4, will attempt to adhere to as an example of a valuable approach to archaeological research.

1.5: *The Sky's the limit: the early appearance of iron in the Bronze age.*

During the first half of the 20th century, a small number of iron artefacts were discovered that appeared to pre-date any evidence of iron extraction technology and many fell into the Early and Middle Bronze Ages; a period thought to significantly precede the deliberate extraction of iron. With the development of bulk analytical techniques such as X-ray fluorescence spectroscopy; chemical analysis of these artefacts revealed their high nickel content, which varied between 3-16 wt. % (Buchwald 2005:22-25; Coghlan 1956; Photos 1989:404; Rickard 1941). The chemistry of meteorites whose composition of low nickel ferrites (Fe,Ni) kamacite containing 5-12 wt. % Ni and austenite, along with taenite (30-50 wt. % Ni) results in an iron with up to 5-25 wt. % Ni in total, was seen to correlate to the unusually high nickel content of these early iron artefacts. These nickel-iron alloys were thus revealed as meteoric in origin which explained both their antiquity and their diminutive occurrences within the archaeological record for iron artefacts. This provenance was further corroborated with textual sources from New Kingdom Egypt which described the use of 'thunderbolt' iron (represented prior to the 13th century BC with the hieroglyph ***bi3*** and later developing into ***bi3 n pt*** with the suffix 'in the sky') and Hittite Anatolia where texts described 'iron from heaven' which has been accredited to the Sumerian word **AN.BAR GE** borrowed by the Hittites (Johnson et al. 2013:48; Photos 1989:403; Wainwright 1932:8-12; Yalçın 1999:182-184). The analysis and discovery of high nickel contents from notable finds such as the iron dagger discovered in the tomb of Tutankhamun (1323BC, 10.8 wt % Ni, see figure 1.1 below) appeared conclusive in explaining such an early provenance for iron artefacts in these regions (Buchwald 2005:24; Comelli et al. 2016:1301; Yalçın 1999:180-181). Despite the prevalence of this theory of meteoritic origins for early iron, support for it has begun to be eroded by more recent studies which have challenged the accuracy of those scientific methods employed and the legitimacy of the interpretations given. Further analysis of these early artefacts has demonstrated that many only contain less than 5 wt. % nickel of their total mass which many in the field of archaeometallurgy consider too low to confirm the iron as meteoritic in origins (Comelli et al

2016:1306; Yalçın 1999:180). Calls from the literature to re-evaluate the technological significance of meteoric iron artefacts with regards to the working of iron and associated practices point out that it was probably a major factor in the rise in favour for the use of iron in Bronze Age cultures (Comelli et al 2016:1307; Rehren et al 2013: 4791).



Fig.1.1: Meteoritic iron dagger from the tomb of Tutankhamun (1332-1323BC). Taken from Comelli et al. (2016:3).

The presence of high nickel content in other iron-bearing geological deposits such as pyrrhotites (FeS), pentlandites ($(Fe,Ni)_9S_8$) peridotites ($(Mg,Fe)_2SiO_4$ with Ca, Cr, Al, Na), laterites (metalliferous soils) and riverine magnetites (Fe_3O_4) which could have been exploited during the Bronze Age suggests these may have been the source of iron for many artefacts that have been assigned a meteoric provenance (Jambon 2017:50-53: Piaskowski 1988; Photos 1989:403-406). While experimental data into the smelting of these minerals to produce iron using prehistoric methods remains very limited they are a potential source of iron in the Bronze Age though there is little corresponding archaeological evidence that these ores were ever exploited. The pyro-metallurgical processes required to extract iron from these ores must be taken into account as segregation of the nickel from the iron could have occurred especially during more intensive and selective operations such as matte

smelting, a phenomenon recognised in modern processes today (Gilchrist 1980:378; Norgate and Jahanshahi 2010:69-70). As such sulphidic ores which would have necessitated removal of the sulphur through a matte process are not favourable candidates; excluding pyrrhotites and pentlandites from the debate. Evidence for the smelting of laterites (highly variable secondary deposits formed of iron oxides and minerals such as sodium and magnesium leached from basic igneous rocks in wet temperate zones) is also limited however their wide geological distribution and visual relation to iron (reddish brown to dark red) has continued to attract attention from the literature (Gordon and Killick 1993:69; Photos 1989:405; Pryce and Natapintu 2009; Jambon 2017). Laboratory experiments have shown that a 92.5% Fe to 7.5% Ni alloy can be produced by reducing even low grade laterites (see figures 1.2 and 1.3) with carbon monoxide at temperatures not exceeding 1200^{o}C (Li et al. 2018) In a series of experimental smelts conducted by E. Photos using laterite containing 0.5 to 1.3 wt. % NiO it was noted that the nickel content of the iron blooms fluctuated greatly across samples and that the iron bearing the highest concentrations of nickel (15-20 wt. % Ni) were the first to be expelled from the bloom upon working or became entrained in the slag (1989:417). Recent research into the reduction of Central Anatolian laterite containing limonite produced a ferronickel alloy that separated cleanly from the slag in a crucible at temperatures of 1480-1490^{o}C resulting in an alloy with a Nickel-Cobalt content ranging from 12-18 wt.% (Pournaderi et al. 2017). The addition of coal (carbon) proved to be a determining factor in the proportion of iron in the final alloy, with an increase in carbon corresponding to the reduction of more iron but greater chemical and physical losses of Nickel in the slag. The application of these controlled procedures to prehistoric processes is limited but demonstrates the potential for prehistoric cultures to reduce ores that would have been widely accessible. The findings of Pournaderi et al. confirmed those of E. Photos (1989) as further hot forging to consolidate the blooms into billets decreased the total nickel content to around 0.5-3 wt. % however samples taken from grain and weld boundaries had significantly higher nickel contents which were consistent across the boundary. The enrichment of smelted iron with nickel during the direct reduction

of nickel rich iron ores and laterites is plausible though it is unlikely that this iron would, when forged into an artefact, retain a nickel content that could be ascribed to a meteoritic origins. Difficulties inherent to the process of smelting such ores, which are typically poor with low iron contents and many contaminants, cast major doubts over the possibility of metal industries operating during the Early to Middle Bronze Ages successfully producing iron in this manner (Jambon 2017:52; Pryce and Natapintu 2009: 256-258). As it represents a more complicated procedure it is unlikely that the smelting of nickel rich iron ores would precede the much less arduous and technically demanding reduction of iron from pure oxides such as haematite.

Table I. Chemical Composition of the Laterite Ore

Component	Total Fe	Ni	Co	MgO	SiO_2	Al_2O_3	CaO
Content (Weight Percent)	9.67	0.82	0.03	31.49	37.37	1.89	0.03

Fig 1.2: Chemical composition of the laterite ore reduced with carbon monoxide in an experiment by Li et al. (2018:3068). An iron content of 9.67 wt. % is low in comparison to oxide ores from zones of secondary enrichment likely to be exploited in the Bronze Age.

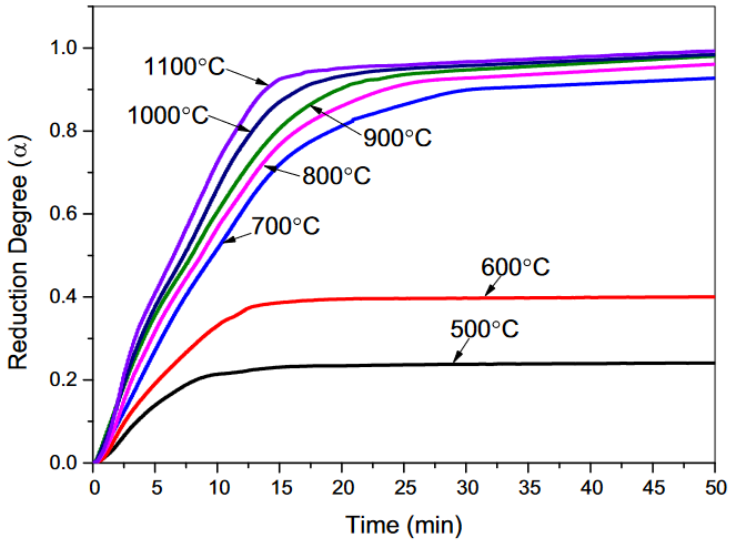


Fig1.3: Changes of reduction degree (iron oxide in laterite converted into iron metal) with time at different tempuratures during isothermal reduction of nickel laterite ore. Almost total reduction is reached at 1100°C, achievable in a Late Bronze Age furnace. Taken from Li et al. (2018:3070).

In recent years, many new analyses of early iron artefacts have shifted the focus from the comparison of nickel content to more definitive methods that utilise metallography, the composition ratios of related minerals and strategic sampling to eliminate many of the shortfalls identified in earlier studies (Buchwald 2005; Coghlan 1956; Rickard 1941). Such methods include the metallographic study of the artefacts to reveal the Widmanstätten crystal structure long recognised in meteorites, consisting of interwoven bands of kamacite and taenite (nickel iron) along boundaries of plessite (Phelan and Dippenaar 2004). While this structure is so distinct as to be easily recognisable it is limited to determining the origins of unworked iron artefacts only as hot forging of the iron at 1000°C deforms

the structure with the formation of martensite (Tylecote 1987:103). Analysis of the ratio of iron to nickel and cobalt has also been proposed as a means to determine meteoritic origins (Jambon 2017:47). Given that the surface oxidation or weathering of meteoritic iron can deplete the surface nickel content, measurements of the Fe/Ni ratios taken from the surface (the majority of studies into these rare artefacts are restricted to non-destructive surface measurements) are insufficient and often fall within the expected range of results taken from weathered meteorites. Through comparison to the effect of weathering on the cobalt to Ni/Fe ratios of iron meteorites it is possible to determine a terrestrial origin for the artefacts if these ratios do not match those observed in meteorites. Jambon concludes that the vast majority of iron artefacts that displayed notable nickel contents from the Early to Late Bronze Age were in fact meteoritic (2017:48-51). With the development of new tomographic techniques to map the internal structures of artefacts unambiguous identification of even the most corroded artefacts can be achieved (Johnson et al. 2013:997). In an analysis of a heavily oxidized iron bead from the Gerzeh cemetery in Egypt (c.3400-3100BC), computerized imagery of the internal structure was used to identify a Widmanstätten structure and confirm the iron as being meteoritic (Johnson et al 2013:1004). Whilst this technique would be limited to identifying cold worked meteoritic iron only, the potential of this non-destructive method to analyze corroded and heavily oxidized artefacts cannot be understated. The debate over the terrestrial versus meteoric origins of early iron in the Bronze Age remains ongoing and despite the development of ever more sophisticated techniques to control sample bias it is likely to remain unresolved until more experimental data for the smelting of nickel rich iron-bearing minerals is produced. Only through comparison of iron smelted from these ores to those artefacts for which we can identify a meteoritic origins will the ability to distinguish the two in the archaeological record become apparent. Without this comparative data archaeometallurgists must rely on discretion, which given the absence of sites for the primary production of iron for much of the Early to Middle Bronze Ages leaves the theory of meteoritic origins as the most favourable. This does not exclude this period as being critical for the development of iron

technology in the Late Bronze to Early Iron age however, as the advancements in furnace and draught technologies as well as the first use of extraneous minerals to improve the efficiency of the reductive processes were achieved over the course of the Bronze Age (Comelli et al. 2016; Craddock 1995:130-152). The working of meteoritic iron also represents the earliest engagement of humans with iron and the first experience of its properties which would have been distinct from the existing copper alloys of the time. The working of iron must be distinguished from the smelting of iron however, which required pyro-technical skill an order of magnitude greater than that required for smithing and which bore little technological relation to the open hearth that might have been used (Pleiner 2000:12). Meteoric iron can therefore be dismissed as a direct technological precedent to extractive iron metallurgy in the Near East. For the purposes of this thesis the author will largely dismiss the majority of iron artefacts from the Early to Middle Bronze Ages and focus on the technological precedents that had been established in extractive metallurgical technologies practiced in the Late Bronze Age Near East even though these doubtlessly had their roots in the metallurgical practices of earlier cultures, among whom the incidental extraction of iron could well have occurred if only in extremely limited quantities.

1.6: *Iron in Africa: a case against deterministic approaches*

With the onset of studies into the indigenous metalworking practices of sub-Saharan Africa in the latter half of the 19th century it became apparent that the production of copper was limited to a few specialists confined to distinct regions. Remnants of copper production have been recovered from sites in the historically attested Egyptian satellite state of Nubia during the Old Kingdom through to the new Kingdom periods (2686-1633 BC), Ethiopia by 500 BC and southern Mauritania from as early as 900-300BC (Badama 2020:1-5; Bisson et al. 2000:89; Childs and Killick 1993:320). Yet despite this diminutive presence and wide geographical dispersal of isolated copper smelting practices, the production of iron had flourished across sub-Saharan Africa by the third century AD (Alpern 2005:61-64; Childs and Killick 1993:320-321; Schmidt and Avery 1983:433-434). In contrast to the Near East, where a period of unprecedented intensity in copper smelting and production had preceded the coming of iron, smelting technology in sub-Saharan Africa appears to have represented a novel phenomena which rapidly spread to its southern limit in South Africa across a vast geographical distribution and between such disparate populations as would belie conventional models of transmission and adoption (Holl et al. 2009:59-61; Killick 2009:412; Wertime and Muhly 1980:21-25). This presents a major challenge to the determinist view that the technological demands of the direct reduction of iron from an oxide could only be fulfilled by specialists coming from a long tradition of pyro-metallurgical practice. If the invention of iron had been achieved in Africa independently of any prior metallurgical traditions; could it also have been developed outside of Near Eastern traditions before seeing widespread adoption by copper producers? If the beginnings of iron metallurgy in Africa fell within the middle to late 2nd millennium BC the possibility of the diffusion of the technology north into Eurasia with the displacement of local copper metallurgy presents an intriguing premise which underscores the importance of securing the chronology and technological contexts for early iron production across both continents. At the center stage of investigations into iron metallurgy in sub-Saharan Africa a debate has raged regarding the indigenous origins for iron

production versus the transmission of the technology from North African or Horn of Africa cultures (Alpern 2005: 41-44; Childs and Killick 1993:319-322; Diop 1968; Holl et al. 2009:59-60; Killick 2009:405-407). The outcome of this debate has significant ramifications for studies into Eurasia as an indigenous origins for iron metallurgy in sub-Saharan Africa puts into dispute theories that claim that preexisting metallurgical practices were necessary prerequisites for the adoption of iron. The basis for the arguments in favour for an independent invention of iron cite both the early dates potentially ascribed to a number of sub-Saharan iron smelting sites in Africa (Badama 2020:3-5; Zangato and Holl 2010) as well as the diversity of iron smelting practices found there-many of which were significantly divergent from those seen north of the Sahara (Killick 2015; Schmidt 1978; Schmidt and Childs 1985). Starting in the 1970s, early sites began to be carbon dated most notably in the western regions of the sub-continent including Niger, Cameroon and Mauritania and also Central Africa, particularly those surrounding the Great Lakes in the East Africa Rift Valley (Alpern 2005:72-75; Holl et al. 2009: 59; Killick 2009:404). Early first millennium BC dates produced for sites at Termit and Taruga in southern Niger through carbon dating were seen by many to substantiate existing theories of an independent invention of iron in the region (Alpern 2005:70-76; Holl 2009:59-60). When further sites were dated in the Great Lakes region at Rwanda and Burundi to the first half of the 1st millennium BC this appeared to confirm theories for an independent invention of iron metallurgy (Clist 1989; 81-86; Killick 2009:407). Initially encouraging, the pedigree of these dates proved to be short lived as they came under increasing scientific scrutiny. Dating of these sites has proven particularly contentious and extremely limited in scope in comparison to North Africa and Eurasia. In a recent example, Zangato and Holl presented evidence from sites in north-central Africa including Djohong in the Cameroons and the Ndio area to form a hypothesis that iron production in the region may have began as early as the third millennium BC (2010:7-8). These results were viewed with skepticism largely on the basis of the limitations of carbon dating for this period in Africa (Chirikure 2010: 25; MacEastern 2010). These limitations have manifested as three central issues;

firstly, the 'flattening' of the calibration curve during the mid-first millennium BC allowed for no greater resolution than between the years 800-400BC with the years 2500-2000BC being subject to fluctuation (Holl et al. 2009:60). Zangato and Holl (2010:19-21) disputed the relevancy of this criticism by claiming that their 3rd millennium BC dates fell outside of the 'flattening' of the calibration curve and so could be considered accurate (Chirikure 2010:25; Holl et al. 2010:60). Critics have also pointed out that the wide range of calibrated dates generated for much of the studied material, many of which fall within a margin of no less than 400 years, are insufficient to demonstrate that iron metallurgy in Africa pre-dated those cultures identified as possible sources of transmission later in the 1st millennium BC (Alpern 2005:73-75; Killick 2009:406). Furthermore these dates cannot be compared to the archaeological record due to a paucity of data relating to chronological sequences such as pottery typologies or linguistic developments (Alpern 2005: 76). The second issue, referred to as the 'Old Wood' conundrum, posits that older burnt brush and dried wood from Savannah environments would have been preferentially exploited over livewood and might give a much earlier date than when it was finally combusted. This has cast doubt over the legitimacy of many early dates for African iron smelting (Childs and Killick 1993:321; Holl et al. 2010:59-60). The third obstacle to reliable dating can be consigned to sample bias, which can arise from unexpected intrusion of older or newer sources of carbon into archaeological sites. MacEastern points to one example of an iron-smelting installation excavated along the Chad-Cameroon pipeline from which a dated sample gave a date within the 2nd millennium BC (2010:40). After these dates were shown not to correlate with other sites situated along the pipeline two further samples were taken from the same furnace and these gave a date for the turn of the 2nd millennium AD. In this instance, older charcoal may have fallen into the excavated furnace and been confused with the contemporary material (MacEastern 2010:40). On a similar basis Clist (2013) and Chirikure (2010) point out that at a site in Oboui, which Zangato and Holl (2010) date to the 3rd millennium BC, the samples may have been taken from disturbed ground which could have affected the results of dating.

Until more reliable dates can be produced for those iron smelting sites in sub-Saharan Africa speculated to fall within the 1st Millennium BC, a more convincing argument for an indigenous origins may be the apparent diversity and divergence of African furnaces from their North-African and Eurasian counterparts (Killick 2015; Schmidt 2018). Semi-complete furnaces excavated at early Iron Age sites at Taruga in Niger and Buhaya, Rwanda and Burundi in the Great Lakes region display considerable variance from those at Meroe dating to the latter half of the 1st Millennium BC (Killick 2009:406; Schmidt and Avery 1983:429). It is not certain whether these furnaces represent a later divergence from an imported technology however they are much more closely interrelated than to the furnaces employed north of the Sahara (Killick 2009:406; Schmidt and Avery 1983:429). Estimation of the efficiency of the furnaces studied at these sites based upon the findings of large slag blocks also reveals a level of technical sophistication which was absent in most contemporary cultures north of the Sahara, lending little credence to diffusionist theories of the origination of the technology from there (Killick 2009:406; Schmidt and Avery 1983:429). Diversity in sub-Saharan metallurgical practices has also been documented in the modern period, many of which were unique south of the Sahara (Killick 2016:70). These techniques likely developed as a response to local geological, ecological or geographical circumstances and include innovations such as the pre-heating of the airflow to raise temperatures within the furnace or improving fuel efficiency through furnace structure in resource scarce mountainous regions (Killick 2016:70; Schmidt and Avery 1983:423-425). In an unprecedented study, Schmidt (1978) embarked on a combined ethnographic and experimental investigation into the iron smelting practices of the Haya people in north-western Tanzania. Observation of local smelting practices revealed that through a system of preheating the airflow through the *tuyeres* the furnace operated more efficiently and used less fuel resources (Schmidt and Childs 2018:55-56). The furnaces, slags and particularly the heavily slagged *tuyeres* were compared with the assemblages discovered at two nearby smelting sites north of Lake Victoria named KM2 and KM3, dating from the second century BC and first century AD respectively (Schmidt and Childs

2018:67,71). Many features were shared between the modern smelters and the historical assemblages such as roasting pits and remarkably the slagged *tuyeres* which indicated that a form of pre-heating was practiced at these sites almost two millennia before similar processes were exploited in Europe (Schmidt and Childs 2018:55). While theories in favour of an indigenous origins of iron-smelting in sub-Saharan Africa clearly suffer from ambiguity in dating and identification, close examination of the technological and cultural contexts of these sites have started to reveal complex innovations which continue to challenge previous assertions regarding technological change (Killick 2015; Schmidt 2018). Accepting an indigenous origins does not exclude the application of technologically determinist theories as it may be an underestimation to assume that there was no pyrotechnological basis existent in sub-Saharan populations prior to the arrival of iron metallurgy. Controlled use of fire and the earliest production of ceramics well predate the 1st millennium BC with later innovations in pyrotechnology attesting to an intimacy with these practices among host populations (Killick 2016:67-68). How these underlying processes could have become sophisticated enough to allow for the direct reduction of iron prior to any metallurgical engagement is a matter of intense speculation which, despite lying at the heart of the debate, has been almost totally neglected (Okafor 2014). Barring a resolution to the numerous discrepancies between interpretations of the evidence for iron metallurgy in sub-Saharan Africa any attempt to make a comparison to Eurasia is problematic. The Near East in particular was subject to such a specific set of technological and social circumstances during the 2nd millennium BC that technological syntheses rarely transcend the regional level. Incoherences with an 'Iron from Africa' narrative range from the slow uptake of iron metallurgy in nearby dynastic Upper Egypt during the 1st millennium BC (Killick 2009:405) in contrast to far-off Anatolia and the Levant to differences in pyrotechnology and minimal evidence for interaction between populations in West Africa, from which the earliest dates for African iron smelting occur, and the Near East (Badama 2020). Nevertheless, extractive metallurgy reached southern Africa across a great and diverse expanse where almost no parallel technology could be expected to exist (Alpern

2005:83). By extension, iron metallurgy may have developed independently or even in spite of earlier copper smelting practices in the Near East. This has serious implications for studies into the transmission and adoption of iron metallurgy and may be cause for a reevaluation of the capability of non-metal using cultures to adopt metallurgy and employ pyrotechnology more proficiently than previously thought.

1.7: *Achieving wrought iron production in the Late Bronze Age.*

The discovery of unprecedented quantities of iron from sites across the Near East dating to the second millennium BC onwards would suggest that the direct reduction of iron from ores had become achievable by the Late Bronze Age (Haarer 2001). A number of syntheses have attempted to list all the known occurrences of iron artefacts dating to Late Bronze Age contexts in the Near East with total figures estimated around the tens of kilograms (Pleiner and Bjorkman 1978:283-285; Moorey 1999:278; Waldbaum 1978). While these quantities may appear insubstantial, these studies have heavily relied upon textual sources of the Hittite and Mesopotamian dynasties which relate that considerably greater quantities of iron were in circulation though highly prized by the late second millennium BC (Pleiner and Bjorkman 1978:284-285; Van Der Brugge 2013:89-96; Waldbaum 1980:30-32; Yalçın 1999:181-182). The corrosion of iron deposits has been estimated in recent studies at an average rate of a 4µm retreat of the surface per year which in 2000 years would total 8mm of penetration and loss of the surface (Neff et al. 2005). This would outside of anoxic conditions completely destroy the majority of small to medium sized iron artefacts dating to the 2nd millennium BC with the loss of 16mm of material. In contrast copper is predicted to corrode at a rate of 0.45mm of surficial retreat in 2000 years, just under 1mm for artefacts deposited in the 2nd millennium BC (Tylecote 1979:367). This may also explain the infrequency of iron finds in LBA contexts in comparison to the accounts from historic sources with the only remnants of these artefacts being undetectable traces of iron enriched soils or corrosion residues. The lesser 'lifespan' of small decorative iron goods, as a result of rusting, could have also limited their entry into grave assemblages as they may no longer have been desirable possessions at the time of the individual's death. This transience of iron compared to copper may have deemed it unsuitable for mortuary rites by the host culture until larger and more diverse iron objects could be produced to fulfil the display purposes of copper. The greater proportion of iron artefacts dating prior to the 1st millennium BC in the Near East have been recovered from sites on Cyprus, in the Levant and most abundantly in Anatolia (Erb-

Satullo 2019:562-565; Waldbaum 1999; Yahalom-Mack and Eliyahu-Behar 2015). Boasting perhaps the most comprehensive record for smelted iron artefacts in the eastern Mediterranean dating from the late 2nd to early 1st millennium BC, Cyprus has long been recognised as an early iron producer which specialised in the crafting of small bronze-riveted iron daggers starting in the Late Cypriot period around 1200BC (Kassianidou 1994; Sherratt 1994:60-62). Cypriot production and trade in copper across the eastern Mediterranean beginning from the 2nd millennium BC was intensive. Findings of 'oxhide' copper ingots at sites across the Mediterranean basin were shown through chemical analysis to have originated on the island and a lively overseas trade is attested to by the unparalleled Uluburun and Cape Gelidonya wreck discoveries (Kassianidou 1994:73-75; Pulak 2010; Stos-Gale 1997). The long cultivation of metallurgical practices on Cyprus, which began to intensify during the Middle Cypriot (19th century BC) period attested to by metallurgical remains found in association with a mine at Ambelikou, emerged in response to the local geology which sported a duality of rich copper deposits thoroughly married to mass sulphides which defied the direct-to-copper methods employed in the reduction of oxides (Kassianidou 2013:38-39; Van Brempt and Kassianidou 2016). Though no evidence for the production of iron on the island exists prior to 700BC, the abundance of iron rich minerals within genetic copper deposits has led some to speculate that iron was produced, incidentally or deliberately, as a by-product of the copper matte extraction process (Craddock 1995:255; Kassianidou 1994; Maddin 1982:311; Pleiner 2000:13; Steinberg and Koucky 1974:158). For the Levant, the archaeological record supports the appearance of smelted iron from 1200BC with some dispute regarding the dates of a number of earlier outliers (Yahalom-Mack and Eliyahu-Behar 2015:286). The discovery of exceptionally well preserved smelting remains within urban contexts has generated a wealth of data regarding the co-existence of both copper and iron related practices during the early 1st millennium BC (Yahalom-Mack and Eliyahu-Behar 2015; Veldhuijzen and Rehren 2007). Though the arrival of iron in the region pre-dated the earliest of these sites local production accompanied a 'utilitarian' phase of iron use for tools in contrast to earlier

imported iron constituting purely decorative items such as bracelets, chains and rings (Yahalom-Mack and Eliyahu-Behar 2015:287-290). As the premier region for early iron finds, the Late Bronze Age cultures of Anatolia have long garnered attention as the forerunners of iron extraction in the Near East (Muhly et al. 1985:69; Yalçın 1999:178-179). Detailed and explicit records of trade between the Hittite and Assyrian dynasties survive from the latter half of the second millennium BC and have occupied much of the debate regarding the origins of iron metallurgy in the Near East (Erb-Satullo 2019:564; Yalçin 1999:177-178). The growing frequency with which iron artefacts show up in grave and settlement contexts across Anatolia from the late 3rd to 1st millennium BC appears to corroborate the textual sources (Akanuma 2008; Yalçın 1999:180). Assertions that iron extraction could have been achieved in Anatolia by the end of the 3rd Millennium BC, initially based on a number of miscellaneous iron objects such as a 'mace-head' from the CGII-CAI period at Troy, have been a constant refrain (Muhly et al. 1985:70; Nakai et al. 2008:323; Yalçin 1999:177-178). Most recently the recovery of heavily corroded iron fragments in close proximity to hematite at Kaman-Kalehöyük from strata dating from the 22nd century BC has compounded this view (Akanuma et al. 2007:137-138; Akanuma et al.2008:319-320). Chemical analysis of an ornate iron dagger from Alacahöyük (2400-2300BC) revealed a markedly high nickel content indicating that it was meteoritic in origin which calls such an early occurrence of iron extraction into question (Nakai et al. 2008:323). Though proponents point to contemporary evidence such as the fragments of raw iron excavated at Kaman-Kalehöyük, the presence of copper in some of the samples which derived from the iron itself, means that they may been a by-product of copper smelting processes (Akanuma et al. 2007:137-138; Akanuma et al.2008:319-320). Less ambiguous examples of smelted iron in the form of two fragments from Kültepe in Central Anatolia dating from 1900-1800BC do support the development of iron extraction in the region in the early second millennium if no earlier (Akanuma 2003:147-149). The close economic association of these regions situated around the east Mediterranean littoral has led to the prevailing view that iron extraction developed in Anatolia in the early to mid 2nd millennium

BC and had diffused into neighbouring regions by the late 2nd to early 1st millennium BC where it had already begun to take on a utilitarian purpose among those cultures (Muhly et al. 1985:83; Erb-Satullo 2019:565). A later penetration of the technology further inland into Western Iran and up into the Caucasus has been envisaged with the increasing numbers of iron grave goods dating to the first half of the 1st millennium BC found in those regions (Erb-Satullo et al. 2020:1-3; Pigott 2004:350-353). While such a pattern is discernible, the infrequency of iron finds and wide chronology over which they occur in Middle to Late Bronze Age contexts presents only a rudimentary picture which cannot at present be collaborated with evidence from contemporary metal production sites.

Despite the presence of smelted iron dated to this period and its relation to contemporary textual sources no remains attesting to the deliberate extraction of iron in the early to mid second millennium BC have yet been recovered (Erb-Satullo 2019:565; Veldhuijzen and Rehren 2007:189-191). Though an incontrovertible example of iron smelting in the Late Bronze Age has remained elusive; archaeological sites across several regions have been identified for the close association of iron and copper production debris. In the Levant, the discovery of fragments of iron at a 13th century BC workshop at Kamid-el-Loz in modern-day Lebanon led to claims by the excavators of an early attempt to reduce hematite ores found in close proximity (Veldhuijzen and Rehren 2007:190). The presence of small 'greenish' copper-rich slags and the interpretation of the site as one of secondary production does not correlate with this hypothesis and the assemblage could have been the waste product of any number of unrelated processes employed at the site (Veldhuijzen and Rehren 2007:190). Similarly, a claim for early iron ore processing and smelting was made for the site of Tel Yinam in Israel where iron slags and ochres were found in situ with low bowl-like structures identified as furnaces (Liebowitz and Folk 1984: 277–279; Veldhuijzen and Rehren 2007:189-190). Reappraisals have since identified the site as one of ochre production ruling out iron smelting due to the low iron content

of associated slags and unsuitability of the low furnace structures to reduce iron (Pigott 2003). Beginning in the 1970s, survey of prehistoric sites related to metallurgy in the southern Caucasus revealed that an extensive sequence of metallurgical activities took place across the region from the Late Bronze Age through to the classical period (1500BC-500BC) (Erb-Satullo, Gilmour and Khakhutaishvili 2014:5-7; Gilmour et al. 2020). Preliminary reports speculated that a specialised local industry exploited magnetite sands from the eastern Black Sea littoral to produce smelted iron in the Mid to Late Bronze Age (Khakhutaishvili 2009:107-110, 121). Upon revisitation of these sites beginning in 2009, the identification of the majority of the sites dating to before 500BC was revised as many were reclassified as sites of copper production that exploited the mixed sulphide ores of the region (Erb-Satullo, Gilmour and Khakhutaishvili 2014, 2015, 2017). Exercising caution with positive identification using absolute dating and materials analysis has served to eliminate many prospective examples of iron smelting from the question of origins. However over-reliance upon these methods without an appreciation of how the earliest forms of iron metallurgy might appear or enter into the archaeological record could have led to much of the evidence being overlooked. The wide array of metallurgical practices in operation across the Near East during the 2nd millennium BC defies easy recognition with waste products from the extractive metallurgy of copper and iron such as slag often being chemically indistinguishable by bulk analysis (see figure 1.4) and requiring the identification of copper metal or matte (sulphide) prills to make a distinction (Hauptmann 2020:248; Pleiner 2000:254; Thornton et al. 2008:309-310). Clearly a spatial association of ores, slags and metals is no longer a sufficient basis to confirm evidence for one metallurgical operation over another without a fundamental understanding of all the possible formation processes that could have produced the assemblage. Identification of early sites has also been held back by a paucity of data on the chemistry of furnace linings, furnace typologies, structure and function as a result of a lack of archaeological research, experimental reconstruction, inter-disciplinary communication and general neglect of the topic. At present, the scope of investigations into primary iron extraction during the 2nd

millennium BC is limited to an appreciation that iron-bearing ores were beneficiated and utilized in a number of metallurgical operations employed in the Near East and that there was no visible separation or specialisation of iron metallurgy from copper production across this period (Erb-Satullo 2019; Hauptmann 2020:310, 457,424).

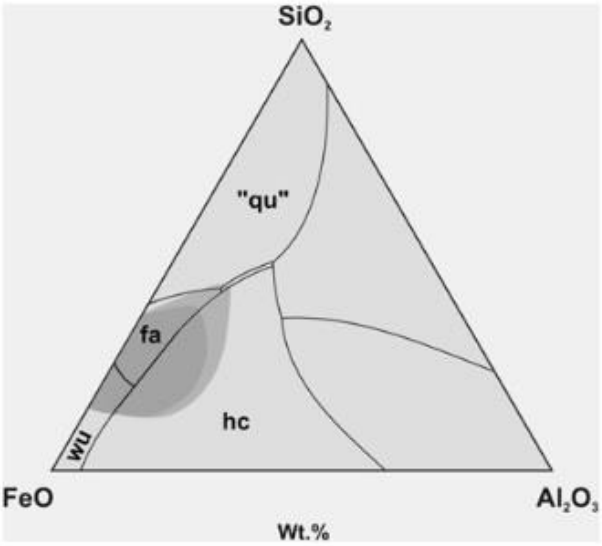


Fig.1.4: Average bulk chemical compositions of ancient slags from various supra-regional iron (dark grey) and copper (lighter grey) smelting sites shown in ternary FeO-SiO_2-Al_2O_3 system. Both slags share close compositions of wüstite (**wu**), fayalite (**fa**), quartz (**qu**) and hercynite (**hc**). Taken from Hauptmann (2020:187).

Given the challenges of identifying primary production of iron during the Bronze Age, the observer might ask why the focus hasn't shifted towards evidence for secondary production, which for iron remains archaeologically distinct from copper-related activities. Various processes constituting the secondary production of iron such as forging and smithing leave behind residual evidence in the form of hammerscale, small flaky or spheroidal oxides that are sundered from the iron by percussive forces during these operations (Hauptmann 2020:243,360). Though there are no reports of hammerscale in the Near East prior to the end of the 2nd millennium BC it begins to appear as early as 900BC at Tel

Beth Shemesh in Israel and by the 7th century BC at a similar time as other Tel sites in Syria and Jordan (Veldhuijzen and Rehren 2007:191). This roughly coincides with the adoption of iron for utilitarian use in the Levant and represents an expansion of iron use and therefore secondary production methods in the manufacture of a greater diversity of implements or decorative items (Yahalom-Mack and Eliyahu-Behar 2015:285-286). The deposition of increasing quantities of hammerscale would be expected as a result of the intensification of forging and smithing activities; a useful correlation for determining the development of iron metallurgy following its adoption but from which almost no information regarding the earlier invention of iron can be derived. That evidence for the secondary production of iron prior to the 1st millennium BC remains undetected might be caused by numerous factors. The small decorative objects of smelted iron that circulated the Near East during the Late Bronze Age did not necessitate the later scale of operations to create. As the mass of iron being worked by the smith would typically be well under a kilogram the act of forging would be brief and unprolific in terms of material evidence produced as waste. The apparent lack of organisation of the secondary production of iron into smithies or workshops during this period also characterizes such activities as being dispersed, transient and infrequent possibly occupying only a small proportion of the total time invested by metal producers in comparison to smelting and casting copper. In the absence of pre-first millennium BC smithing sites it is clear that studies into early iron metallurgy must instead rely on materials analysis of iron artefacts and the evidence from primarily copper-related production sites; highlighting the need for a comprehensive understanding of the metallurgical practices employed by the Late Bronze Age.

The analysis of bronze artefacts from the Near East dating from the second millennium BC has revealed that many contained inclusions of iron from the presence of various iron oxides and ‘prills’ of metallic iron (Craddock and Meeks 1987:189; Hauptmann 2020:406). Copper slags, glassy

silicates that form from gangue and other metallic oxides in the furnace, also display a general increase in iron content in the form of oxides and metallic prills by comparison to the Early and Middle Bronze Ages (Cooke and Aschenbrenner 1975:25-252; Craddock and Meeks 1987:187-188; Erb-Satullo, Gilmour and Khakhutiashvili 2014:157; Wertime and Muhly 1980:28). Iron content of raw copper ingots appears to have gradually increased from the Early to Middle Bronze Ages and risen dramatically during the late/transitional phase in the Near East (Craddock and Meeks 1987:190). This phenomenon has long been associated with the technological developments in copper metallurgy during the Late Bronze Age and has been understood in the contexts of both physical and chemical processes. The driving forces behind these developments have remained a source of inveterate debate within the discipline. Adaptation to ore geology (Powell et al. 2017; Thornton 2009), scale and efficiency of economy (Knapp and Kassianidou 2001), collapse of exchange networks (Shennan 1993), technical innovation (Craddock 2000) and even social organisation (Orfanou et al. 2023; Erb-Satullo et al. 2018) have all featured as explanations for the evolution of metallurgical practices employed across the Bronze Age. In relation to Iron, three factors in particular have been associated with the increase in iron content of ancient copper assemblages across the Bronze Age: ore geology in determining the content of iron in the furnace charge (Cooke and Aschenbrenner 1975), deliberate addition of iron-bearing ores into the charge (Hauptmann 2007:157) and the achieving of higher temperatures and reducing conditions with the introduction and upscaling of the furnace (Craddock and Meeks 1987). The introduction of substantial amounts of iron into smelting operations via the exploitation of mixed sulphide ores such as chalcopyrite could well explain the trend towards higher iron contents in some copper artefacts and slags by the Late Bronze Age (Shell 1997). This alone cannot account for the phenomenon entirely; high iron content of artefacts and slags is reported less frequently in the Middle and Early Bronze Ages in spite of evidence for exploitation of mixed sulphides across those periods (Bourgarit 2007). Therefore the contribution of mixed sulphides to

rising iron contents must be assessed in light of concurrent technological developments and production strategies.

The deliberate addition of ores other than the primary metal-bearing ore to the charge is a practice termed ‘slagging’ by archaeometallurgists and has been recognised in historical analogues since the early 20th century (Bourgarit et al. 2007:3-5; Hauptmann 2007:157-158). This method utilises the properties of a secondary mineral to control the physical and chemical conditions within the furnace or crucible and maintain desirable parameters for the reduction of the primary ore into a metal (Hauptmann 2020:210). The reduction of copper oxides and carbonates did not require slagging practices to be achieved however it could drastically improve the efficiency of the process thereby increasing the yield of metallic copper (Craddock 1995:144-146; Thornton 2009). Evidence for slagging in prehistoric contexts is derived mostly from the recovery of large quantities of slags from metal production sites that are disproportionate to the amount of gangue expected in the primary ore (Craddock and Meeks 1987:191-193; Hauptmann 2007:158). During the Chalcolithic to Early Bronze Age the majority of copper smelting operations typically did not produce substantial quantities of slag with some western European examples being characterised as virtually ‘slag-free’ processes (Bourgarit et al. 2007:3-5; Craddock and Meeks 1987:188). This has been attributed to a range of factors: firstly that metal producers prior to the 3rd Millennium BC mainly exploited high grade copper oxides which did not produce slag (Bougarit et al. 2007; Craddock 1990:69), secondly that the scale of operations were small, intermittent and dispersed and so did not accumulate the larger ‘heaps’ encountered later into the Bronze Age (Hauptmann 2014:92-94) and finally that non-ideal conditions within early furnaces resulted in excessive losses of metallic copper to furnace slags which would then be processed through crushing to retrieve the metal and thus destroyed (Bourgarit et al. 2007:5; Thornton 2009). Most likely all of these factors played a role in the later developments in extractive

copper metallurgy in the drive to improve the efficiency of the process as the scale of operations increased with greater social organisation. Resulting from this, the practice of slagging became widely employed by the fourth Millennium BC at sites such as Shahr-i-Sokta in Iran and later across much of the Near East (Craddock 2000:153-154; Hauptmann 2007:157-158; Hauptmann et al. 2003). The principle ores exploited for slagging purposes during the Bronze Age belong to two mineral groups: copper sulphides and iron oxides. The use of copper sulphides for slagging or co-smelting has been speculated at sites across the Near East dating from the Early Bronze Age onwards (Amzallag 2009:503; Georgakopolou et al. 2011; Hauptmann et al. 2003; Ryndina et al. 1999; Yener et al. 2015). The introduction of copper sulphides through slagging may represent an intriguing first stage of sulphide exploitation prior to the reduction of these ores as the primary source of copper witnessed in Middle to Late Bronze Age production contexts. In the majority of examples for the co-smelting of copper sulphides with oxides, iron-free sulphides such as covellite (CuS) and chalcocite (Cu_2S) were principally used and so it remains uncertain to what degree iron entered into these operations. The addition of iron oxides as slagging agents is well documented in the Near East dating from the early 3rd Millennium BC and the practice was largely popularized in the literature by the type-sites in the Timna valley in southern Israel (Craddock 2000:154; Gale et al. 1990; Hauptmann 2007:157-158; Levy et al. 2002). As discussed previously, increasing iron content in copper alloys and smelting slags have long been associated with the co-smelting of iron oxides with copper oxides with ores such as haematite (Fe_2O_3) and magnetite (Fe_3O_4) being widely distributed and readily reduced into metallic iron (Cooke and Aschenbrenner 1975:252; Craddock and Meeks 1987:188; Wertime and Muhly 1980:24). Slagging remains the putative explanation for the rise of iron contents of metallurgical assemblages from the Early to Late Bronze Age and consequentially is often accredited with the development of an extractive metallurgy of iron in Eurasia (Charles 1980, 165–67; Craddock and Meeks 1987,1988; Pickles and Peltenburg 1998, 79, 90–91; Pleiner 2000, 212–13; Tholander 1982). As is the case for sulphides, slagging with iron oxides could not have lead to the extraction of

practicable quantities of metallic iron without the achievement of sufficient reducing conditions and temperatures, which will be addressed below.

The furnace technologies of the Early to Late Bronze Ages are perhaps the most poorly understood element of extractive copper metallurgy employed in this period (Craddock 2000:157-158; Merkel 1982). The great variety of designs in evidence even from the outset of the period has defied attempts at identification of common features, function and operation (Addis and Artioli 2017; Gilmour et al. 2020; Hein et al. 2007; Pryce et al. 2007:543). Archaeometallurgists have largely relied upon estimations of furnace diameters and heights from the remnants of clay furnace bases and the quantity and dimensions of slagged furnace walls. Furnaces primarily consisting of both substructures and superstructures are reported and in some regions even co-existed as alternate methods of production at different stages of a *chaîne opératoire* (Ackerfield et al. 2020: Erb-Satullo, Gilmour and Khakhutaishvili 2018; Craddock 2000:157-158; Merkel 1982). Nevertheless the construction of larger furnaces and the growing sophistication of forced draught systems by the Late Bronze Age can be inferred from the greater dimensions of furnace bases and the diverse array of ceramic *tuyères* that make their appearance in copper production contexts (Craddock 2000; Gilmour et al. 2020:27; Karageorghis and Kassianidou 1999; Kienlin 2016:129-132; Knapp and Kassianidou 2001:207-209; Wertime and Muhly 1980: 14-18). These larger scale operations would have facilitated higher temperatures of around 1200^{o}C and the maintenance of a strongly reducing atmosphere within the furnace (Crew and Charlton 2007; Kienlin 2016:129-132; Knapp and Kassianidou 2001:207-209; Wertime and Muhly 1980: 14-18). Under these conditions the reduction of iron introduced into the furnace would occur more regularly than in earlier iterations of furnaces utilised in the Early to Middle Bronze Age (Craddock and Meeks 1987:190; Thornton 2009:325). The extent to which LBA metal producers had overcome the physical and chemical hurdles for the extraction of metallic iron through

technical means is unclear. Limited research into the function of furnace technology through simulation or experimental reconstruction holds back any conclusive parallels being drawn between developments in pyrotechnology and the rising iron contents of metallurgical assemblages from the Mid to Late Bronze Age in the Near East. From this summary of the technological and metallurgical precedents that had been established in the Near East by the Late Bronze Age, we can infer the following regarding the potential for the extraction of metallic iron during these operations:

- Considerable quantities of smelted iron were in circulation in the Near East from the 2nd Millennium BC following a tradition of using meteoric iron for elite display.

- The 2nd Millennium BC can be characterised as a period of intensive metallurgical activity in the Near East.

- There is no evidence for the deliberate extraction of iron prior to the late 2nd Millennium BC in the Near East.

- Despite the appearance of worked iron objects, no evidence for secondary production (i.e. smithing, forging, welding) of iron during this period exists nor was it accommodated through craft organisation within 2nd Millennium BC contexts.

- Average iron content in copper alloy artefacts, smelting assemblages, furnace slags and copper ingots in the form of oxides, metallic iron precipitates, sulphides and metal prills rises gradually from the Early to Late Bronze Ages in the Near East.

- The exploitation of mixed sulphide ores, the addition of ferrous oxide ores and advances in pyrotechnology have all been identified as contributing factors to this rise in iron contents apparent by the Late Bronze Age.

It is perhaps surprising that although the extractive copper metallurgy practised in the Near East during the 2nd millennium BC provides the most tangible link to the beginnings of iron use in the region there is virtually no direct evidence for a correlation between the two processes across the entire period (Erb-Satullo 2019:565-566). This raises the question of whether smelted iron in the 2nd Millennium BC was extracted and worked by small specialist producers working tangentially to copper producers. Could developments within an alternative pyrometallurgical process, such as the co-smelting of lead with iron ores or production of speiss from iron arsenides have birthed iron metallurgy in isolation of copper related processes? Such theories envision a scenario of competition between metal traditions to produce iron via trial and error methods originating from multiple pyrometallurgical antecedents prior to the adoption of more singular, efficient bloomery processes. All such hypotheses remain purely in the realm of conjecture and, if a multitudinous origins of extractive iron metallurgy did exist, thus far it has left no visible trace in the archaeological record.

1.8: *Chapter Organisation*

This thesis is organized as follows:

- *Chapter One* – The introduction to the aims and objectives of this thesis and the archaeological and disciplinary contexts of this research.
- *Chapter Two*- A detailed evaluation of the introduction of iron into the chemical processes employed in the extractive metallurgies exploited by copper producers in the Near East during the LBA.
- *Chapter Three*- A detailed appraisal of the physical processes exploited by copper producers and their consequences for the extraction and/or partitioning of iron.
- *Chapter Four*- A methodology for the experimental reconstructions and chemical analysis of smelting assemblages within a crucible and within the context of a full scale furnace smelt.
- *Chapter five*- Metallographic and chemical analysis of the smelting assemblages produced during the experiments and discussion of the results.
- *Chapter Six*- A comparative study of the results of the experimental reconstructions with copper alloy artefacts of the Late Bronze Age Near East and discussion of the implications of the experimental results.
- *Chapter Seven*- Discussion of the development of iron metallurgy in the late second to early first millennium BC in the Near East in regards to established metal production traditions in each region.
- *Chapter Eight*- Conclusions, evaluation of the experimental approach taken and highlighting of areas of promising future research.

Chapter 2.

2.1: *Extractive metallurgy in the Late Bronze Age*

By the late third to second millennium BC pyrometallurgical processes for the extraction of metallic copper through the reduction of copper oxides and sulphides had reached a degree of sophistication in the Near East that is testament to the skill of the practitioners in manipulating furnace conditions through pyrotechnical and chemical means. The employment of various strategies to improve the efficiency of these processes and attain higher yields of metallic copper demonstrates that metal producers had fostered a comprehensive technical knowledge of direct reduction systems and the behaviour of a multitude of minerals in a high temperature reducing environment (Craddock 2000:164; Gilmour et al. 2020; Knapp and Kassianidou 2008:144; Yahalom-Mack et al. 2014). The impetus for the development of highly efficient and controlled smelting operations during the Late Bronze Age was likely driven by the complex relationship between metal producers and social, geological and economic factors. Even at the intra-regional level these metalworking traditions consisted of a significantly diverse range of practices and strategies with the production not only of metallic copper but also of other products such as ochres, speiss, alloying agents and precious metals (Pigott 2003:375; Roberts et al. 2009:1014-1017; Thornton et al. 2009:308; Veldhuijzen and Rehren 2007:190).3 Reconstructing the contexts for the technological development of the metal extraction technologies of the Late Bronze Age has come to the forefront of archaeological investigations in recent years and has proven to be a demanding endeavour requiring the collection of a breadth of information ranging from geological and topographical survey to intensive campaigns of chemical analysis, experimentation and detailed excavation of metallurgical sites (Chiarantini et al. 2009; Erb-Satullo 2019:35-36; Gilmour et al. 2020; Gottlieb 2010; Muhly 2011; Van Brempt and Kassianidou 2016; Veldhuijzen and Rehren 2007). These studies have gradually begun to bear fruit by allowing

archaeologists to define many of the determining factors that shaped the strategies, organisation and technologies employed across the period. This presents a hitherto unprecedented opportunity to explore the nascent technologies and practices that permitted the earliest extraction of metallic iron in the Near East. As these practices were largely determined by the available geological deposits specific to each region, this chapter will first address the types of mineral deposits exploited as a source of copper during the 2nd Millennium BC in the Near East including their geographic distribution, associated geological formations and the consequences these features had for the development of metallurgy within the region. The chemical processes employed in the extraction of copper from these deposits, categorised into two primary groups of the oxides and the sulphides, is presented. An assessment of the presence of iron and its implications in each case is made and finally a secondary group of iron arsenides utilised in speiss smelting and iron oxides encountered in lead smelting is considered.

2.2: *Technological adaptation to ore geology*

Copper is among the most abundant metals residing in the Earths crust, roughly constituting 50 parts per million and an average 0.01% of the outer crust (Killick 2014). In weight, around two hundred trillion tons of copper could be found in the first 1km depth of the crust to the outer surface; two million times more than the reserves of copper estimated from ore bodies exploited in the modern period (Emsley 2003:125; Kesler 2008:257; White 1941:1). Of these the principle minerals containing copper are sulphides occurring as facies with other genetic minerals in mass deposits that account for 80% of modern copper production (Schlesinger et al. 2011:1-4). Exogenous processes leading to oxidation of these sulphides produce the oxide and carbonate family of copper mineralizations though copper can be found in polycrystalline native forms also (see figure 2.1).

Humans likely exploited copper oxides from the Palaeolithic for decorative purposes where they were valued for their greenish-turquoise hue and later began to reduce the ores into small quantities of metallic copper with the application of simple fires and ceramic vessels by the neolithic (Killick 2014:19-20; Wertime 1973:875-876). Possibly as a consequence of the close association of oxide mineralizations with mass sulphide deposits in some regions, ancient populations had begun to smelt copper sulphides such as chalcocite and chalcopyrite from the Chalcolithic period in the Near East (Bourgarit et al. 2007:8-10; Georgakopoulou et al. 2011; Ryndina et al. 1999; Timberlake 2007). The production of metallic copper from sulphides presented the unique challenge of removal of the sulphur before the reduction of the copper from the ore. Geological events of ore genesis within each region accounted for the mineralogy and distribution of ore deposits accessible to ancient peoples. Access to ores in prehistory was mainly dependent upon surficial deposits in secondary zones of enrichment where the softer partially oxidized and eroded (weathered) ores could be mined out with simple tools such as hammerstones and bone picks (Killick 2014:20). These methods were sufficient to benefeciate tons of ore per year and mining by the Late Bronze Age had in some cases become highly sophisticated, intensive and systematic such as in the shaft complexes in the Wadi Arabah valley in southern Israel (Hauptmann 2007:48; Knapp and Kassianidou 2005). Though the exact chemical composition of the ores used in copper production during the Late Bronze Age was highly variable and locally heterogeneous, the most ubiquitous ore minerals can be placed into two groups that were primarily exploited during this period-an oxide group consisting of the carbonates such as malachite or less commonly oxides such as cuprites and a sulphide group of copper sulphides such as chalcocite or covellite and more commonly mixed sulphide minerals such as chalcopyrite (Hauptmann 2007:59-62; Schlesinger et al. 2011:14-15). The local abundance of ore minerals and their purity (a figure estimated today at around 0.5-2% copper on average within an orebody) would have profound consequences for the development of extractive metallurgy across the Bronze Age Near East (Hauptmann 2007: 3-6; Killick 2014:18-21; Schlesinger et al. 2011:1). The great diversity

of operations and the drive to improve upon the efficiency and yield of extractive metallurgical traditions over the period reflected the unique chemical circumstances that local ore sources presented. The mineralogy and chemistry of local ore deposits dictated to a lesser or greater extent the strategies and technologies that arose among local peoples; certain compositions could be propitious and required minimal technological investment while others proved to be exacting in terms of physical and chemical benchmarks to be overcome. Despite this, nearly all the variants of cuprous ore deposits had been successfully exploited by the 2nd Millennium BC with some of the most intensive operations growing up around ore compositions that were technically demanding for extractive metallurgy (see Cyprus, a major exporter of copper alloys from the mid to late 2nd millennium BC)(Knapp and Kassianidou 2005; Van Brempt and Kassianidou 2016). Typically considered the first group of copper ores to be encountered and reduced in prehistory, the oxides or predominantly carbonates of copper will be addressed first.

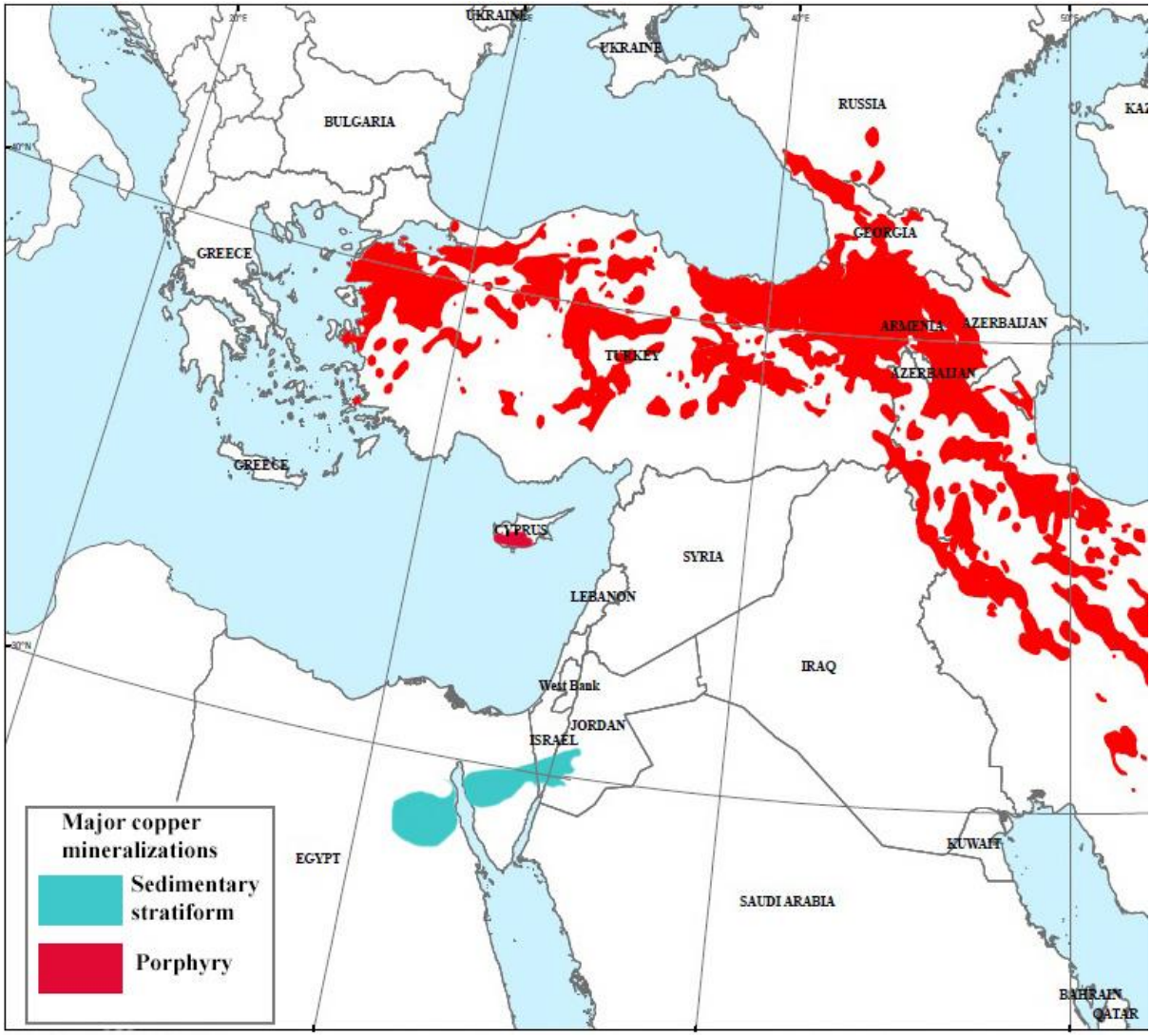


Fig.2.1: Map of Near East showing major copper mineralizations in Porphyry or sedimentary stratiform rock formations. Weathering of porphyry can produce copper carbonates and oxides however the far greater proportion of copper in these deposits is held in sulphides. Sedimentary stratiform rocks including dolomites or limestones become enriched with copper from a parent sulphide deposit by groundwater or hydrothermal action. The red 'belt' or Tethys range extending from western Anatolia through to eastern Iran is visible. Adapted from United States Government Geological survey.

The history of extractive metallurgy in the Near East has long been thought to originate with the collection of easily-reduced copper carbonates such as malachite and azurite which were combusted during a Neolithic experimentation that resulted in the earliest known worked copper, such as that found at Cayönü in Turkey dating to around 8800 Cal BC or at Vinca in Serbia dated to 5000 BC (Garfinkel et al. 2014:3-5; Killick 2014:20; Radivojević 2012; Roberts et al. 2009:1013; Thornton 2010:47). These ores likely originated from surficial deposits that became more widely distributed through erosion and redeposition via hydrological means where they could be easily recognised by their vivid green-blue hue. As profoundly impactful as the early interaction of humans with these minerals would be, initial uses for ores such as malachite or chrysocolla would have been purely decorative as they were soft enough to be worked and could be used as a pigment. The modest thermodynamic requirements for the extraction of metallic copper from these carbonates meant that small quantities could have been produced in a simple operation using a small hearth before later being elaborated upon with pyrotechnical expertise transferable from ceramics production (Wertime 1973:876). Copper carbonate minerals (Malachite $Cu_2CO_3(OH)_2$ and Azurite $Cu_3(CO_3)_2(OH)_2$) form from parent deposits of primary mass sulphides that have become exposed to exogenous hydrological processes. Supergene oxidation of sulphide minerals through leaching by chloride ions in sea water leads to the formation of copper carbonate hydroxides which typically form crystal aggregates or banded crusts (Guilbert and Parks 2007:124-125/774-781). Intrusive formations of copper carbonates could form considerable distances from the parent sulphides as a result of hydrothermal solutions of copper sulphides being carried into the oxide zone and reacting with proximal anions (i.e. silicates and carbonates from limestone) to form copper carbonate or silicate minerals (Dill 2015). The extent of copper carbonate distribution across the Near East as it stood at the outset of human exploitation of these deposits is difficult to assess as most have been extensively worked and the sedimentary rocks that often contain them are prone to erosion through weathering. Modern occurrences and the location of extant mass sulphides that could have been subject to suitable conditions or weathering

can be corroborated by archaeological evidence of mining and ore beneficiation to provide a rough distribution for these deposits. In western Europe, hydrothermal intrusions and oxidation of copper sulphides into malachite, azurite and chrysocolla in veins or open voids between dolomites accounts for the famous Great Orme mine in Britain as well as continental formations in central France, the Iberian massif in Spain and in the Balkans in central Europe such as the Chalcolithic mine of Rudna Glava in Serbia (Filipović 2015; Ixer 2001; Torres-Ruiz et al. 2020). In the Near East the Bronze Age exploitation of copper carbonates in the region is typified by the Wadi Arabah valley paleokarst deposits in Israel. These oxide deposits can be found from Jordan through to Negev and the Sinai and can be described as stratiform mineralizations in sandstone pockets (paleokarsts). Other examples of these deposits mined during the Bronze Age include the Wadi Feinan district of southern Jordan, Bir Nasib in the Sinai and the 3rd millennium BC Old Kingdom workings at Wadi Maghora and Serabit-el-khadim in Egypt (Hauptmann 2007:63-68). Further small deposits in the Upper Euphrates at Keban and into the Zagros rich in native coppers have been speculated to have provided the ores and native metal for the earliest use of copper known in prehistory at Çayönü (Hauptmann 2007:62; Killick 2014:20). The possibility of depletion of copper oxide ores during the course of the Bronze Age is subject to regional variance, at the Great Orme the exhaustion of a rich parallel mineralization of malachite has been offered as a cause for the decline of copper smelting activity at the site around 1400-1300BC (Williams and de Veslud 2019:1188). In contrast, further rich mineralizations that would have been accessible to ancient peoples are still reported in the Faynan and Timna localities despite over four millennia of human exploitation (Hauptmann 2007:68). Though copper carbonates and oxides are known to occur in other regions of the Near East and indeed likely lay in situ with the majority of weathered mass sulphide deposits to some degree, the examples given above represent the most substantial copper oxide deposits for which evidence of intensive exploitation from the Early to Late Bronze Age exists.

As a consequence of the leaching of mass sulphides, these same hydrothermal solutions containing copper sulphides also facilitated the oxidation of iron from the pyrite family of minerals and its deposition in the oxide zone. Forming from ferrous hydroxides, iron oxides such as hematite (Fe_2O_3) or magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) regularly occur alongside copper carbonate mineralizations (Killick 2014:21-22). The karstic deposits found in the Wadi Arabah valley and exploited at Timna for example, were particularly rich in hematites and the typical abundance of ochre (ferric oxides used as pigments) was likely the lure for the first humans to mine these deposits (Hauptmann 2007:69). The common paragenesis of these copper and iron oxide ores has significant implications for the development of extractive metallurgy in the Near East. Co-smelting of copper and iron oxides, whether intentional or not, could be advantageous for the extraction of metallic copper (Craddock and Meeks 1987:188-189). Preferential oxidation of the iron would lower the partial pressure of oxygen in the furnace allowing more of the copper to be reduced into metal; permitting an increased airflow to raise temperatures to facilitate mechanical separation from the gangue (Craddock 1995:148). The co-occurrence of iron and copper oxides within the same orebodies has been described as 'self-fluxing' and past peoples could exploit these properties without necessarily adding extraneous minerals to the ore (Hauptmann 2007:69-70). This phenomenon has been recognised at the sites of Timna and Faynan where the greater abundance of iron silicate slags found at smelting sites in the former locality compared to the latter corresponds with higher iron contents of the local ores at Timna (Hauptmann 2007:78; Gale et al. 1990; Merkel 1983). This theory cannot be applied outside of specific contexts however as the seemingly 'slag-free' exploitation of oxide deposits such as at Ross island, Ireland or Los Millares in Spain from the Chalcolithic period suggests almost total elimination of iron oxides from the furnace charges (Bourgarit et al. 2007:3-5). This raises questions of whether the benefits of co-smelting iron oxides were simply not recognised at this time or if local iron and copper mineralizations were defined into distinct strata and did not become mixed with the primary ore as is the case for karstic deposits (Craddock 1990). By the Late Bronze Age however

exploitation of oxide deposits across the Near East, particularly in the Levant and Sinai regions, had led to the introduction of significant quantities of iron oxide ores into the furnace charges of copper smelting operations. Through the introduction of the furnace and the maintenance of superior reducing conditions amid a rise in temperatures, this may have precipitated the technological and metallurgical developments that permitted the later extraction of iron.

Set against the backdrop of the intensification and wider geographic dispersal of extractive metallurgical practices over the millennia following the first experimentation with copper oxides, past peoples must have encountered and come to exploit the ubiquitous sulphide minerals which account for the bulk of the copper presence in the Upper Crust. Under these circumstances, existing traditions would have been forced to adapt to changes to the ore chemistry in order to achieve equivalent yields of metal (Killick 2014:18-20). The earliest instances of the smelting of sulphides date to the 3rd millennium BC Chalcolithic at sites in the Balkans and Anatolia; appearing to have been co-smelted with oxides (Ryndina et al. 1999; Yener et al. 2015). Sulphides were likely not the primary source of copper in these early smelts, instead acting as a flux through the preferential oxidation of the sulphur and iron contained within though to what degree this was intentional remains uncertain (Ryndina et al. 1999; Lehner 2015). Copper sulphide ores (Chalcopyrite $CuFeS_2$, Chalcocite Cu_2S, Covellite CuS and Bornite Cu_5FeS_4) originate from mass sulphides deposited within the cementation zone by hydrological and magmatic processes such as sulphide deposition, liquid immiscibility, fractional crystallization and lateral secretion (Guilbert and Parks 2007:121-153; Hauptmann 2007:12). As a result of hypogene and mesogene events these formations are frequently massive and despite only a fraction of the total copper contained within reaching the oxide zone they remain the principal source of copper today (Schlesinger et al.2011:1-4). Exogenous events, such as surface erosion and

weathering from hydrological systems, permitted the intensive exploitation of sulphide minerals during the Bronze Age with the formation of 'Gossans' or 'Ore caps' (see figure 2.2) that lay at the surface of mass sulphide formations (Guilbert and Parks 2007:391). Iron is the most ubiquitous metal found in mass sulphide deposits where it forms numerous minerals with sulphur such as pyrite, sphalerite and most significantly for copper production: chalcopyrite ($CuFeS_2$). The composition of chalcopyrite (30.43% iron, 34.63% copper, 34.93% sulphur) meant that iron contributed almost an equal weight to copper in the total charge that was being reduced. In the Near East, copper sulphides that were exploited in prehistory follow a 'belt' of porphyry deposits starting in the west from the Pontide mountains at the northern Anatolian fault and travelling due east to the south Caucasus before turning south-east into the Taurid mountains on the Turkish-Syrian border and further into the Zagros region and central Iran (see figure 2.1). These deposits take the form of ultra-basic ophiolites and pillow lavas originating from volcanic activity at the African-European plate subduction zones (Hauptmann 2007:59; Killick 2014:19-20). Similar formations of exposed copper mineralizations in the pillow lavas of the Troodos district on the isle of Cyprus (see figure 2.3) and at Ergani Maden in Turkey were intensively mined from the 3rd millennium BC (Hauptmann 2007:61; Lehner and Yener 2014; Raber 1987). North into the Caucasus mass sulphides such as the Madneuli deposit in the Bolnisi region of Georgia and ophiolites in Armenia provided the region with a rich source of copper (Erb-Satullo et al. 2017; Galoyan et al.2009; Kuparazde et al. 2008; Popkhadze et al. 2009). As the copper sulphides from these ores were typically polymetallic and interspersed with numerous minerals as a result of paragenesis the copper content by weight of the ore would have been considerably lower than that of oxide ores. At the Iron Age workings at Limni, Cyprus the copper content of the secondary enrichment zone likely to have been mined by ancient peoples was estimated at around 12% whereas oxide ores such as malachite rarely fell below 20% and were often much higher reaching up to 50% (Raber 1987:304). Though depletion of these massive deposits was out of the question for the small scale of prehistoric exploitation, it was possible that the minerals from the

secondary enrichment zone could have been worked out gradually reducing the copper content across the same mass of the charge. This may have been a factor in the development of larger furnaces among sulphide-based practices (Erb-Satullo et al. 2018; Van Brempt and Kassianidou 2016). A bigger furnace that could reduce significantly greater quantities of ore across a greater reaction volume may have been required to produce equivalent yields of metallic copper from poorer ores.

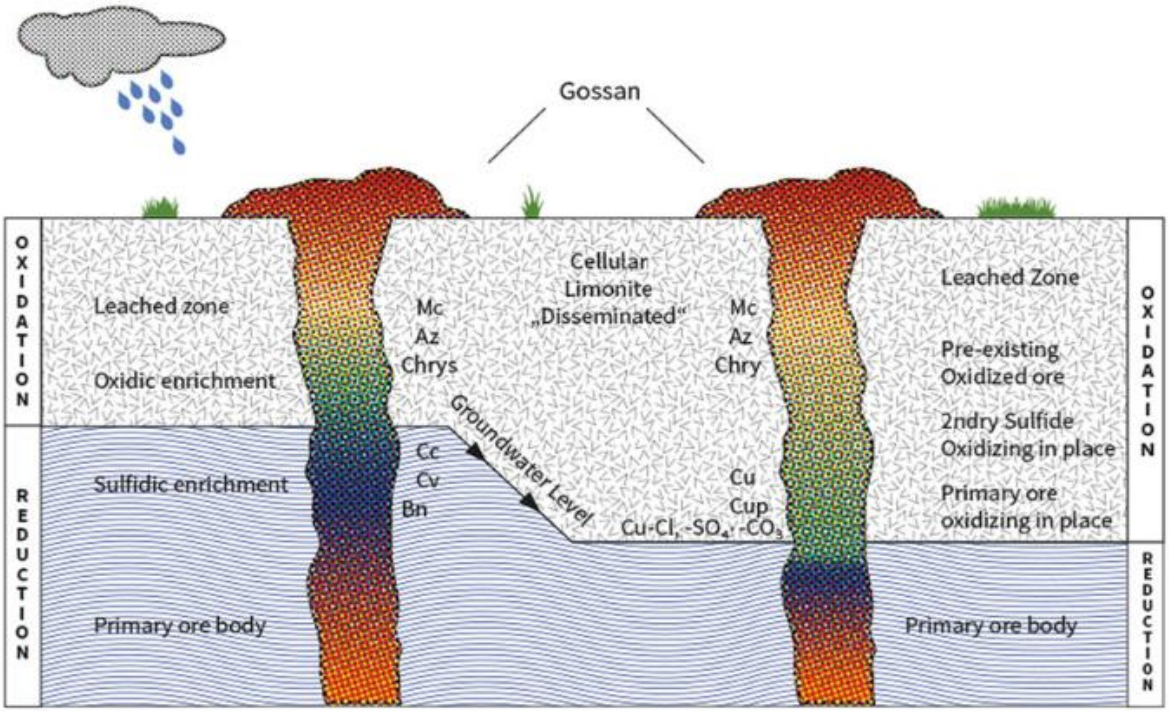


Fig.2.2: Schematic diagram of supergene weathering after cementation of an ore-body to form a Gossan 'cap'. Malachite (Mc), Azurite (Az) and Chrysocolla (Chry) form near the most easily accessible surface. Chalcopyrite (Cc), Covellite (Cv) and Bornite (Bn) form below the oxidation zone which remains enriched in sulphur. Taken from Hauptmann (2020:134).



Fig.2.3: Skouriotissa copper mine situated on the mass sulphide deposit in the north Troodos range, Cyprus. Located 12km due East from the Middle-Late Bronze Age mine at Apliki, supplied by author.

Common to the beneficiation of all copper sulphide ores was the need for removal of the sulphur through oxidation. The practice of 'roasting' the ore, attributed to the presence of 'roasting pits' containing burnt strata and high sulphur contents at some smelting sites and mines, may have been an initial oxidation phase to remove as much sulphur as possible before furnace smelting (Addis et al. 2016; Craddock 1995:157-167; Erb-Satullo et al. 2014: 156). Roasting may not have been a strategy specific to sulphide beneficiation as it has been used to aid in removal of unwanted gangue through heat stress and fracture before the crushing of many different ores from prehistory. Sulphur removal would then continue with a smelting stage leading to the production of 'matte' through fractionation of sulphide phases before a final copper-making stage resulting in 'blister' or 'black' copper named for voids and bubbles caused by escaping sulphur dioxide (Craddock 1995:168-169).

Though a ‘direct to copper’ method may have been feasible with manipulation of furnace conditions, the production of intermediary sulphides presupposes a more technically demanding process than that required to reduce copper from oxides. Tangentially, sulphide smelting constituted a much greater danger to the health of the smelters with the potential inhalation of sulphur dioxide gas. Sulphuric acid would precipitate from the gas from dissolution in the fluids in the throat and lungs causing damage to surrounding tissues. Prolonged exposure would cause respiratory illness and it is likely this danger was recognised to some extent in prehistory (Martin 2017). Nevertheless by the Late Bronze Age sulphides had become the principal source of copper for some of the most intensive metallurgical operations in the Near East including Cyprus, Georgia and Anatolia (Erb-Satullo et al. 2014; Lehner and Yener 2014; Northey et al. 2014; Webb et al. 2006:274-277).

For those metal industries that depended upon sulphide ores as a source of copper, elimination of iron from the furnace charge was impossible through beneficiation as the iron was contained in the primary copper bearing mineral, chalcopyrite, along with copper and sulphur. Iron likely provided a visual clue to prospecting peoples as hydrological weathering of the surface of mass sulphide deposits causes iron oxides to precipitate from the abundant pyrites and chalcopyrites which resulted in the typically reddish appearance of many gossans, such as the ‘kokkinorotsos’ or ‘red rock’ mountain in the Troodos range on Cyprus which was intensively exploited for copper ore during the Late Bronze Age (Guilbert and Parks 2007: 703-708/399-401/451-452; Knapp et al. 2001:208). The toxification of local soils from leached sulphur would have reduced vegetation cover over these conspicuous formations aiding in their discovery (Martin 2017). Iron sulphides constitute over 90% of mass sulphide deposits, predominantly contained within pyrites and sphalerites. Igneous iron minerals such as peridotites and magnetites could be interspersed within the orebody through various exogenous

processes relating to volcanic and ocean crust activity and related hydrothermal systems and also through sedimentation (Killick 2014:19-23). Even the less common copper sulphide minerals such as covellite, bornite and chalcocite which did not contain iron would be found in strata that were enriched with iron oxides and pyrites (Bekker et al. 2010:470). Many of the furnaces discovered within regions where copper sulphides were the primary source of copper are larger than their contemporaries with an estimated reaction volume of up to $0.08m^3$ or 800 litres (Erb-Satullo, Gilmour and Khakhutaishvili et al. 2014, 2017; Hein et al. 2007:142; Van Brempt and Kassianidou 2016). This might be seen as evidence for an emergent strategy to achieve equivalent yields of copper metal from ores that contained less copper than oxides by proportion to iron and sulphur. The production of more slag as a result required management with techniques such as tapping and higher temperatures to improve mechanical separation from the metal. Consequently, the intensification of sulphide exploitation from the Middle to Late Bronze Age has been linked to the increasing average iron content of circulated copper across the period (Cooke and Aschenbrenner 1975:264; Craddock and Meeks 1987:201-202; Muhly and Maddin 1977).

The development of extractive metallurgy in the Near East from the Chalcolithic through to the Late Bronze Age was inextricable from ore geology. The availability and mineralogy of copper, being around 35 times less common within the Earth's crust than iron, determined the geographic distribution and specific chemistry of copper production and to a more variable degree the technological strategies employed. However to see the history of ore exploitation as purely an adaptation to geological circumstances would be to ignore the presence of human agency which permeates technological innovation and production strategies. Achieving a maximum yield of copper may not have been the sole objective of prehistoric smelters nor would it have been an entirely

intuitive process (Timberlake 2007). Social and political considerations, such as adhering to established traditions, could have influenced the organisation and methods employed in the production of copper. The introduction of iron into the pyro-metallurgical operations of Bronze Age metal industries was an inevitable consequence of the paragenetic relationship between iron and copper in geological deposits. Exploitation of these ore deposits engendered a familiarity with iron bearing minerals. The three millennia of experience garnered by the metallurgical traditions of the Near East over the course of the Bronze Age has long been seen as tantamount to the skills required for the successful extraction of iron (Maddin, Muhly and Wheeler 1977; Wertime 1973:885; Wertime and Muhly 1980). The role of ore geology within this transformation of extractive metallurgy cannot be understated. The following paragraphs will examine the chemical processes that were required to extract metallic copper from both oxide and sulphide ores and the presence of iron within these systems.

2.3: *Direct Reduction of Oxides*

The extraction of metallic copper via the reduction of oxide ores in the Bronze Age was facilitated through the firing of the ore within a furnace or crucible with charcoal, which would produce carbon monoxide upon combustion before forming carbon dioxide with oxygen ideally from the ore, thereby reducing the ore and leaving a relatively pure metallic copper (Killick 2014:29-30). Reduction of copper oxides could take place at temperatures as low as 700^{o}C, however by rendering the metallic copper molten at or above a temperature of 1085^{o}C it was possible to further consolidate the copper at the base of the furnace or crucible (Bourgarit et al. 2007:7; Craddock 1995:47; Hauptmann 2007:219). Copper carbonates, produced as precipitates from limestone and copper bearing minerals via hydrothermal processes, would have been the most abundant surficial copper oxide group during the Bronze Age and a principal source of copper for many Near Eastern cultures across the period (Killick 2014:19-25). These ores including malachite and azurite can be converted into copper oxides at temperatures of around 1200^{o}C which could then be reduced by carbon monoxide into metallic copper, water and carbon dioxide:

$$Cu_2CO_3(OH)_2 \longrightarrow 2CuO + H_2O + CO_2$$

Malachite — Copper (II) oxide

$$Cu_3(CO_3)_2(OH)_2 \longrightarrow 3CuO + H_2O + 2CO_2$$

Azurite

$$CuO + CO \longrightarrow Cu^{o} + CO_2$$

Metallic Copper

These operations, using pure copper carbonates, produced almost no slag as demonstrated in the malachite smelting experiments of Coghlan (1939) and by the notable absence of significant quantities of slag at many Chalcolithic to Early Bronze Age smelting sites (Bourgarit et al. 2007:3-4). This has also been attributed to an 'immature' slagging process where excessive copper losses encouraged the retrieval of copper prills by crushing smelting slags, destroying and fragmenting much of the evidence (Bourgarit et al 2007:5). While this may explain the fragmentary and small dimensions of early slags it is still indicative of a simple process reaching low temperatures with variable redox conditions that could not reduce and consolidate a greater mass of copper metal at the base of the furnace. In these circumstances the production of large quantities of slags, which reach free running temperature at around 1200^{o}C, seems improbable (Craddock 2000:154). Chemical analysis of Chalcolithic slags reveals that other than silicates they were mostly composed of magnetite, which supports the interpretation that early furnaces operated at lower temperatures and were more weakly reducing than their later counterparts (Bourgarit et al. 2007:4; Hauptmann et al. 2003:205; Thornton 2009). Craddock also correlates low iron content of contemporary copper artefacts to a minimal-slag process as a consequence of negligible quantities of iron being introduced into and reduced within the system (2000:154). Highly variable iron contents of copper prills from some Chalcolithic slags renders this relationship tenuous and instead points to inconsistent production strategies using differing proportions of iron to copper in the charge and unequal airflow from natural or lung produced draught (Catapotis et al. 2011:72; Day and Doonan 2007:40; Killick 2014:33). Low temperature and short duration smelts forced Chalcolithic metalworkers to collect dispersed copper droplets and melt them in an open crucible, oxidizing most of the present iron and leaving a relatively pure copper (Bourgarit 2019:20). Later pyrotechnological developments allowed for the consolidation of the copper into a single mass at the furnace base reducing the need for amalgamation in a crucible and thus removing less of the iron. By the Middle Bronze Age iron rich slags became increasingly common in smelting assemblages (Bourgarit et al. 2007:3-5; Craddock and Meeks

1987:187-188; Hauptmann 2007:207). This has multifariously been interpreted as a result of improvements in pyrotechnology, the deliberate addition of iron oxides and the working of poorer iron enriched ores upon reaching zones of secondary enrichment (Craddock 2000; Hauptmann 2007:207). The maintenance of temperatures exceeding 1000^{o}C would render more latent iron oxides and silicates within the furnace free-flowing and able to amalgamate however the high viscosity of 'unadulterated' siliceous slags would have been undesirable (Schlesinger et al. 2011:74). Without altering the properties of the slag with additional iron oxides, copper smelters would have been unable to take advantage of the higher temperatures afforded by pyro-technological developments. The sudden onset of mature slagging processes alongside furnaces from the 4th-3rd Millennium BC in the Near East inclines towards an interrelated inception (Amzallag 2009:503-504; Craddock 2000:157-160). Simply the depletion of high grade copper ores or greater reliance upon iron rich deposits cannot be solely responsible for the perceived transformation of smelting practices in the area. Many of the most intensively mined deposits such as at Faynan or Timna in the Near East remained abundant and largely homogenous yet had produced little slag in the Chalcolithic and then much greater quantities by the 3rd and 2nd millennia BC (Hauptmann 2007:232). Pyrotechnical advances and the recognition of beneficial ore composition displayed by the emergent practice of slagging (discussed in the following paragraphs) meant that furnace smelting had supplanted earlier non-slagged operations almost entirely across the Near East by the Late Bronze Age.

2.4: *The role of iron in copper oxide smelting*

Slags are glassy silicates whose main structural component consists of long polyions of acidic oxides, the principal of these being silicas which are found most commonly in metallurgical slags as olivines; a group of metallic (Mg, Fe, Ca etc.) silicates. The high viscosity of these acidic oxides and the low solubility of other acidic oxides (As_2O_3, Sb_2O_3) in them is an undesirable property in a furnace environment as they increase the amount of copper that becomes entrained in the slag and do not remove other unwanted acidic oxides (Schlesinger et al 2011:74). The addition of basic oxides such as calcium and magnesium oxides disrupts these polyion structures and greatly reduces the viscosity of the slag and increases the solubility of acidic oxides. When FeO enters the slag it dissociates into Fe^{2+}, Fe^{3+} and O^{2-} and these free oxygen ions react with bridging oxygen to depolymerize the slag network and lower viscosity (Park et al. 2011:695). The lower melting points of neutral oxides (FeO, Cu_2O) in comparison to silica means their addition would substantially decrease the viscosity of this slag (Bougarit et al. 2007: 7-11; Kaiura et al. 1977:157-158; Schlesinger et al. 2011:74-76). The lower melting point of the most iron-rich olivine member fayalite ($Fe^{2+}{}_2SiO_4$) at 1200^{o}C compared to silica at 1710^{o}C meant that fayalitic slags were an ideal composition for prehistoric furnace smelting as it allows them to be rendered free running, allowing the copper to fall through the slag and collect at the furnace base (Bourgarit 2019:215; Schlesinger et al. 2011:74-75). Also these slags could become highly mobile within the temperature range of the furnace which facilitated removal of the slag by 'tapping' or draining of the furnace. The composition range of iron-rich slags is given in figure 2.4 below:

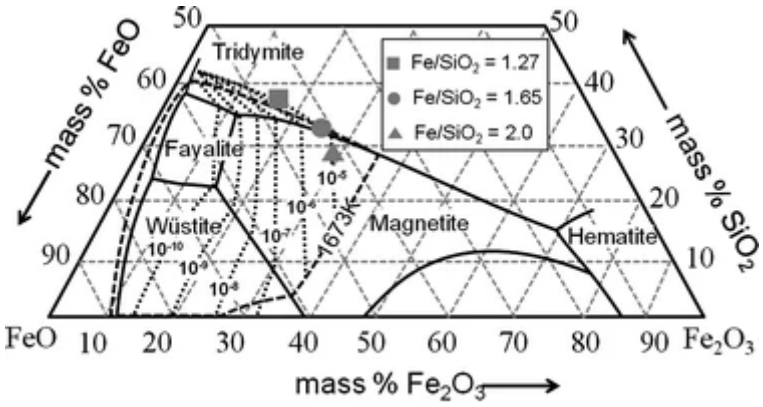


Fig.2.4: Phase diagram and the iso-oxygen potential (dotted lines in powers of 10) diagram of the FeO-Fe_2O_3-SiO_2 slag system. Taken from Park et al. (2011:694).

The production of large iron-rich slag assemblages at the majority of Late Bronze Age Near Eastern smelting sites indicates that significant quantities of iron and silica was being fired alongside the copper oxides (Craddock and Meeks 1978:188; Hauptmann 2007:157-158). In this scenario the iron oxides within the furnace (in this example hematite, Fe_2O_3) preferentially oxidized compared to copper (see figure 2.5) into various iron oxides which would become entrained in the silica to precipitate a fayalitic slag (Park et al. 2011:694). Fayalite precipitates around 60-75 mass% FeO and 20-40 mass% SiO_2:

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

hematite — wüstite

$$2FeO + SiO_2 \longrightarrow Fe_2.SiO_4$$

silica — fayalitic slag

The presence of iron oxides in the slag would also fix the much of the excess oxygen in the furnace with the conversion of iron oxide into magnetite (Fe_3O_4):

$$Fe^{2+} + 2Fe^{3+} + 2O_2 \longrightarrow Fe^{2+},Fe^{3+}{}_2O_4$$

Ferrous iron — Ferric Iron — Magnetite

At these lower viscosities (see figure 2.6), the slag could even be 'tapped' or removed from the front of the furnace while molten greatly reducing the likelihood of copper entrainment. The 'tapping' of the slag could be strategically timed during the smelt to maintain an ideal quantity to lower the partial pressure of oxygen in the furnace while still maintaining high temperatures by preventing the obstruction of air through the *tuyeres* (Bourgarit et al. 2007:3-6; Craddock 1995:31; Veldhuijzen and Rehren 2007). Aside from early instances at Chalcolithic sites in Iran, the practice of tapping seems to have been a universally Late Bronze Age technique that emerged some time after true slagging processes became widespread across the Near East (Addis et al. 2016; Georgakopoulou 2011; Hauptmann et al. 2003; Rehren, Boscher and Pernicka 2012). Evidence for tapping is derived mainly from the presence of so called 'tap slags' which feature flow patterns on the surface lending them a distinct morphology (Bachmann 2016:56; Hauptmann 2020:234).

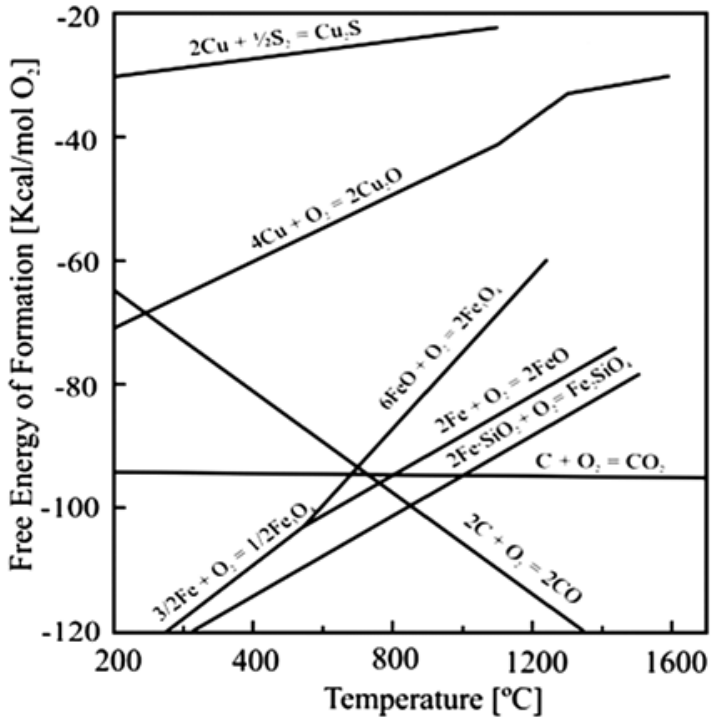


Fig.2.5: Free energy of formation of copper and iron oxides as function of temperature. The lower free energy of formation of iron oxide (FeO) and fayalitic slag ($FeO.SiO_2$) compared to copper oxide (Cu_2O) causes it to form first in the furnace aiding the removal of iron before the reduction of the copper oxide into metallic copper. Taken from Dusan et al. (2009:622).

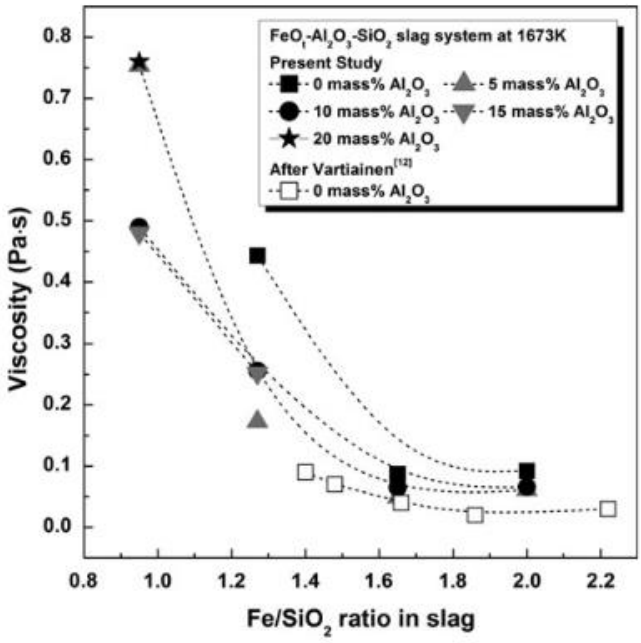


Fig.2.6: Viscosities in the $FeO\text{-}Al_2O_3\text{-}SiO_2$ slag system as a function of Fe/SiO_2 ratio at 1400 °C. Taken from Park et al. (2011:696).

Incontrovertible evidence for the addition of the iron oxides has remained elusive though iron ores have been discovered at copper smelting sites in the Near East from as early as 2100BC in Anatolia and from the Middle to Late Bronze Age at sites in the Levant (Akanuma 2008; Craddock 1995:143; Radivojević and Rehren 2016: 201; Veldhuijzen and Rehren 2009:190; Yalçın 1999:187). Iron bearing minerals such as hematite (Fe_2O_3) or iron hydroxides (weathered hematite and limonite is sometimes called 'tile ore' for its soft brickish appearance and orange colour) are known to occur regularly alongside both sedimentary and metamorphic copper ore deposits leading to the characterisation of them as 'self fluxing' or 'self slagging' (Hauptmann 2020:54-56). At the exemplary sites at Timna, hematite and tile ores were found sorted into piles within Late Bronze to

Early Iron age metallurgical installations at site 30 presumably with the intent of addition to the copper oxide charge (Bachmann 1980:110; Hauptmann 2007:232). A spatial association of iron ores to copper smelting activities is rarely so evident though iron ores can frequently be found in spoil heaps and slag scatters at Middle to Late Bronze Age sites in the Levant, Jordan and the Sinai (Hauptmann 2007:69). In the absence of direct evidence for the addition of oxides, the argument for slagging can instead rely upon chemical analysis of smelting and furnace slags which display higher iron contents from the 3rd Millennium BC onwards in the region (Hauptmann 2007:234; Cooke and Aschenbrenner 1975; Craddock and Meeks 1987). The practice of 'slagging' as evidenced by increasing quantities of iron rich slags at smelting sites dating from the 3rd to 2nd Millennia BC likely originated within a transitional phase of extractive metallurgy in the Near East that accompanied pyrotechnological innovations such as furnaces and bellows (Craddock 2000:157; Hauptmann 2020:203-204; Thorton et al. 2009). Following this phase full comprehension of the behaviour of slags led to the establishment of this practice by the Late Bronze Age.

2.5: *Co-smelting of oxides and sulphides*

Evidence for the co-smelting of copper oxides and sulphides in the Near East from the Chalcolithic has been discovered at sites in the Balkans, Greece, Anatolia, and Iran (Georgakopoulou et al. 2011; Hauptmann et al. 2003; Ryndina et al. 1999; Yener et al. 2015). This phenomenon has been equated to an intermediary stage between oxide smelting and a true matte process that exclusively reduced copper sulphide ores such as chalcocite (Cu_2S) and chalcopyrite ($CuFeS_2$) into metallic copper (Amzallag 2009:503; Bourgarit et al. 2003; Hauptmann et al. 2003; Ryndina et al. 1999; Yener et al. 2015). Though it remains ambiguous whether the co-smelting of copper sulphides with oxides was a natural consequence of exploiting weathered sulphide ores containing mixed deposits or was done deliberately, evidence for stringent beneficiation and sorting of ores even from the Chalcolithic

(sorting pits were found at La Fenestre, France as well as separated caches at Rudna Glava, Serbia) implies there was a general awareness of an advantageous outcome (Bourgarit et al. 2007:5). This process relied upon the oxidation of the sulphur in the copper sulphide (termed 'white metal') to reduce the copper oxide and lower the partial pressure of oxygen in the system:

$$2CuO + Cu_2S \longrightarrow 4Cu^o + SO_2$$

Copper oxide — Chalcocite — metallic copper — Sulphur dioxide

$$2Cu_2O + Cu_2S \longrightarrow 6Cu^o + SO_2$$

Cuprite

$$CuFeS_2 + 5CuO \longrightarrow 6Cu^o + FeO + 2SO_2$$

Chalcopyrite

The number of stages employed in the early instances of co-smelting in the Chalcolithic is difficult to determine however a single stage 'direct-to-copper' process might be inferred from the quantities of intermediary copper sulphides within the smelting slags and frequency of matte in the copper prills (Bourgarit et al. 2003:6; Hauptmann et al. 2003:203-204; Rehren et al. 2016:214). This is born out at Shahr-i-sohkta in Iran, where Hauptmann et al. characterised the co-smelting of sulphides as short duration low temperature operations with minimal charcoal cover providing weakly reducing conditions without prior stages of roasting (2003:205,210-211). The sorting of 'white metal' or copper sulphide matte (Cu_2S) into waste piles, known from modern industrial flash conversion, also points to an incomplete smelting process in which the oxide ores were simply reduced and the smelting finished before the sulphur could be removed from the copper sulphide (see figure 2.7), leaving it as a waste product (Bourgarit et al.2007:10). At Shahr-I Sokta in Iran, both the liquid metal and matte appeared to have been tapped into a pit and the matte broken up to collect the copper as opposed to later processes that allowed for separation of the two phases during the smelt (Hauptmann

et al. 2003). Incidental or not, matte smelting during the Chalcolithic was clearly in its infancy and could not have achieved high yields of copper from exclusively sulphidic ores.

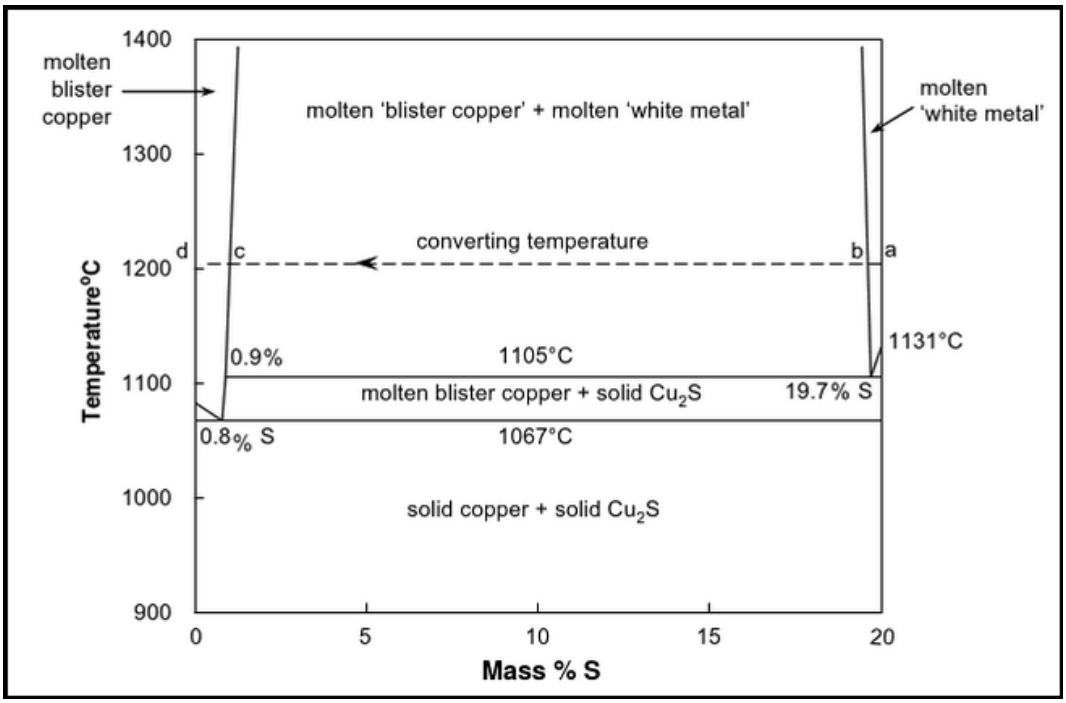


Fig.2.7: Cu-S equilibrium phase diagram showing conversion of copper matte and matte/copper immiscibility as a function of temperature and mass % Sulphur. The 'white metal' (Cu_2S) forms a solution with molten copper at 1131°C and 19.7% Mass S, finally converting into 99.1% molten 'blister' copper at <1% mass S. Taken from Schlesinger et al. (2011:133).

2.6: *Matte Smelting: the extractive metallurgy of copper sulphides*

The introduction of iron into the smelting processes of the Late Bronze Age was not limited to the addition of iron oxides. The exploitation of cupriferous pyrites from sulphide deposits is known from the early 3rd to middle 2nd millennium BC across the Near East and these ores would have provided the primary source of copper for some of the most intensive copper production industries of the Late Bronze Age from Cyprus to Anatolia and the Caucasus (Craddock 1995: 164; Erb-Satullo et al. 2017:175; Karageorghis and Kassianidou 1999:179; Klein et al. 1985; Radivojević and Rehren 2016; Ryndina et al. 1999). As the most abundant copper sulphide mineral in volcanic mass sulphide deposits, chalcopyrite ($CuFeS_2$) provided an almost inexhaustible source of copper across prehistory; with access to the copper contained within these rich ores possibly providing the impetus behind the innovations required to exploit these complex minerals. Modern estimates of the copper content of mass sulphide deposits range from 0.5-10% however the zones of secondary enrichment exploited in prehistory likely exceeded a 12% average, ranging between 8-30% (Raber 1987:304; Schlesinger et al. 2011:2). Even today sulphide ores account for 80% of the world's copper production and many of the mass sulphide deposits worked in the Bronze Age are still exploited today such as the Troodos ophiolite on Cyprus or the Taurus mountains in south-eastern Anatolia (Schlesinger et al. 1999:12). It comes as no surprise that by the Late Bronze Age and into the Iron Age, mixed sulphide ores already accounted for the majority of world copper production (Hong et al. 1996:184). The methods used by prehistoric peoples to smelt mixed sulphide ores (chalcopyrite) remain poorly understood however through analogy with modern industrial processes and the recognition of intermediary stages from ancient and historic sites archaeometallurgists have hypothesized three main production strategies: a direct-to-copper single firing co-smelt, a multi-stage process that can be referred to as 'dead roasting' or 'black copper' smelting and thirdly a matte conversion process (Craddock 1995:149; Rostoker et al. 1989:80-81). These three processes will be discussed over the following pages.

2.7: *Direct to copper sulphide smelting.*

The direct method consists of the single firing of the beneficiated mixed oxide and sulphide ores in a furnace or crucible. Decomposition of the chalcopyrite at temperatures exceeding 600^{o}C causes partitioning of the iron and copper into two sulphide liquids: one being iron rich (pyrrhotite FeS, pyrite FeS_2) and the other copper (bornite Cu_5FeS_4, chalcocite Cu_2S, covellite CuS) rich (Kitakaze et al. 2017:48). As copper reacts preferentially with sulphur when compared to iron (see figure 2.8), the iron sulphide is oxidized first into iron oxide (FeO) and sulphur dioxide off-gas (Rehren et al. 2012:1724). Crushed slag or the gangue originating from the ore produces fluid slag at temperatures just exceeding 1200^{o}C which would absorb most of these iron oxides leaving copper sulphides in a distinct phase (Rostoker et al.1989:74). The remaining copper sulphides could then reduce the oxide ores producing sulphur dioxide off-gas and metallic copper; the copper in turn being converted into more copper oxides to be reduced by remaining metal sulphides and carbon monoxide into metallic copper. An example reaction would be as follows: 33

1) $2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2 \xrightarrow{\text{oxidation}} Cu_2S + 2O_2 \longrightarrow 2CuO + SO_2$

2) $CuO + CO \xrightarrow{\text{reduction}} Cu^{o} + CO_2$

3) $3CuO + FeS \xrightarrow{\text{reduction}} 3Cu^{o} + FeO + SO_2$

4) $2CuO + Cu_2S \xrightarrow{\text{reduction}} 4Cu^{o} + SO_2$

In order to carry out this process within a single firing in the furnace, both an initial oxidizing phase shown in step 1). and following reducing stages (2-4) would need to be achieved within a single operation. This would require strict observation and attention, as strongly reducing conditions during

the initial phase would facilitate the decomposition of the chalcopyrite into a mixed sulphide matte without oxidizing the iron and removing it in the slag (Chiarantini et al. 2009). Likewise if oxidizing conditions were allowed to develop during the reducing stages then the copper oxide would not be reduced and would become entrained in the slag (Schlesinger et al. 2011:73). The direct-to-copper process is rarely entertained in modern industrial methods, as the oxidation of mixed sulphides produces great quantities of iron rich slag which risks entrainment of the metallic copper. In prehistoric smelting, this would have necessitated frequent tapping of the slag out of the furnace during the initial oxidation stage to minimize entrainment and prevent blockage of the *tuyeres*. Only with a high degree of competency in furnace and slag management would this have been feasible if at all; as a generalized model for Late Bronze Age sulphide smelting a multi-stage matte process is favourable.

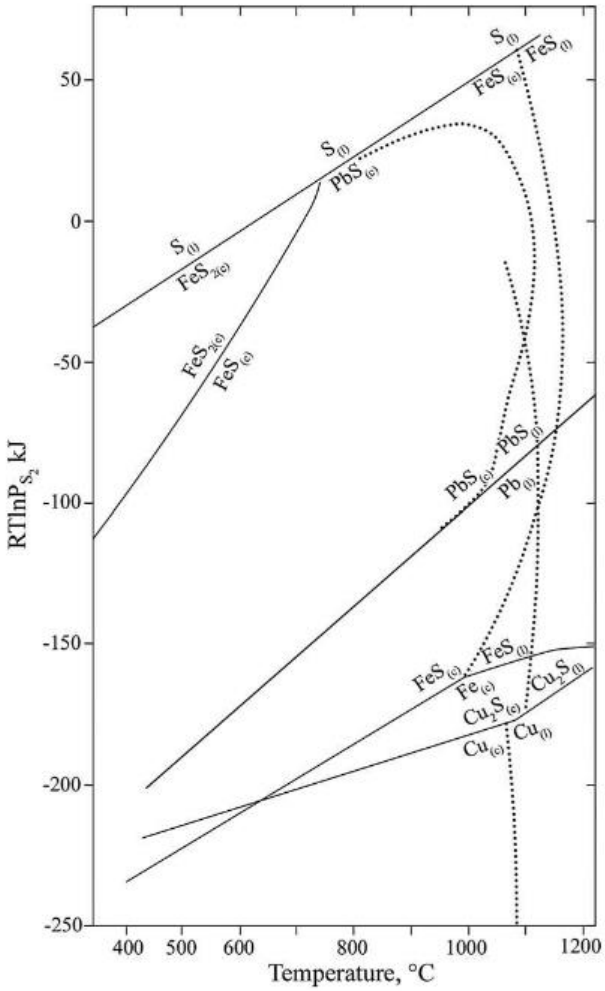


Fig.2.8: Ellingham-style diagram for iron, copper and lead in relation to sulphur. At temperatures above ca. 650ºC, the line for the reaction Cu_2S - Cu is at a lower energy of formation than the line FeS – Fe, suggesting that copper reacts preferentially with sulphur compared to iron. Taken from Rehren et al.2012:1724.

2.8: *Dead-Roasting of sulphides*

The matte process required a complex series of stages of ore beneficiation, reduction and refinement, often repeated successive times (Craddock 1995:165). Named for the metal enriched sulphide phase (matte) produced during at least one initial roasting/smelting stage, this matte would then be recovered and further reduced in a furnace to form metallic copper (Bachman 1982:22; Craddock 1995: 164; Hauptman 2020:147). The objective of the roasting phase is the elimination of some of the sulphur through oxidation and separation of the metallic components from the gangue or unwanted minerals in the ore through heat stress which caused fractures which aided in crushing (Craddock 1995:167). Roasting would leave a highly variable mixture of copper and iron sulphides and oxides which could then be reduced into metallic copper in a final coppermaking stage (Doonan 1994). Roasting could take place within an open fire-pit or a shaft furnace and only required temperatures not far in excess of 600^{o}C (see figures 2.8, p72 and 2.9, p75) and provided higher partial pressures of oxygen than the more strongly reducing environment of a furnace, oxidizing much of the sulphur to produce a sulphur dioxide off-gas:

$$2CuFeS_2 + 3O_2 \longrightarrow Cu_2S + FeS + FeO + CuO + 2SO_2$$

For the 'dead roasting' or 'black copper' procedure this stage would be carried out using the crushed ore or copper matte from matte conversion (described in heading **2.9**) successively until virtually all of the sulphur had been oxidized, leaving relatively pure 'black' copper oxides (Rostoker et al.1989:80). This 'black copper' could then simply be reduced with carbon monoxide through traditional smelting into metallic copper:

$$Cu_2S, FeS + 3O_2 \longrightarrow Cu_2O + FeO + 2SO_2$$

matte *'black' copper oxide*

$$Cu_2O + CO \longrightarrow 2Cu^o + CO_2$$

Descriptions of historic pre-industrial dead roasting or black copper methods demonstrate that it was highly effective in eliminating sulphur and producing pure copper while being fuel intensive (Percy 1861:413). One of the major arguments for dead-roasting in prehistory was made by Eibner (1986) who proposed that the dual furnace installations often encountered in 2nd millennium BC central Europe may have been used to produce matte and then roast it before final coppermaking.

2.9: *Matte conversion*

Alternately 'matte conversion' consists of two phases which may have been achieved within a single smelt or multiple operations: removal of the iron from the matte (slag forming) and conversion of the copper sulphide matte into copper (coppermaking)(Schlesinger et al. 2011:127-129). The first phase relies upon the partitioning of the iron into an iron sulphide phase during the previous roasting stage and early in the matte smelting stage. This is caused by the presence of silica from the gangue which splits the liquid oxy-sulphides into an iron rich matte (FeS) and a slag containing little iron sulphide (see figure 2.10, p76). This facilitated the removal of the iron from the copper, as it preferentially oxidizes over the copper (see figures 2.5, p65 and 2.10, p76):

$$FeS + 1.5O_2 \longrightarrow FeO + SO_2$$

Pyrrhotite *wustite*

$$3FeS + 5O_2 \longrightarrow Fe_3O_4 + 3SO_2$$

magnetite

The iron oxide then reacts with silica to form a fayalitic slag:

$$FeO(l) + SiO_2(s) \xrightarrow{1250^oC} FeO.SiO_2\ (l)$$

silica — *fayalitic slag*

This sequence can be summarized in this schematic reaction:

$$2FeS(l) + 2SiO_2(s) + 3O_2 \xrightarrow{1250^oC} 2FeO.SiO_2(l) + 2SO_2$$

Silica — *Slag*

This process is driven by high partial pressures of oxygen with the iron content of the matte decreasing as the sulphur is oxidized and removed (see figure 2.9).

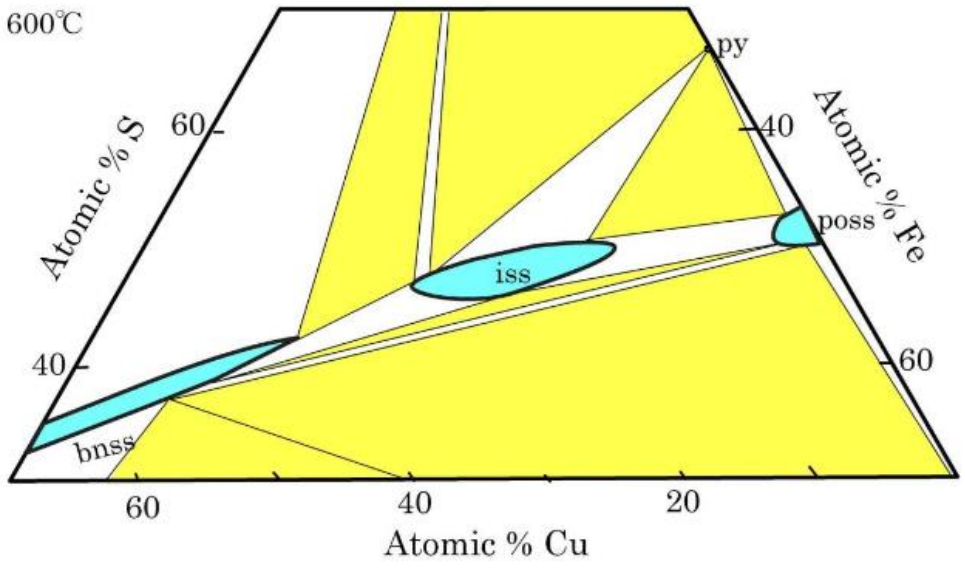


Fig.2.9: Isothermal section in central portion of Cu-Fe-S system at 600°C. At around 550-650°C the Chalcopyrite breaks down into the iss (intermediate solid solution) and sulphur. With a decrease in temperature the central sulphide liquid field decreases in size and the iss becomes more copper rich, forming the copper sulphide 'matte'. The iron sulphide pyrrhotite (poss) also begins to develop around 600°C. Taken from Kitakaze (2017:30).

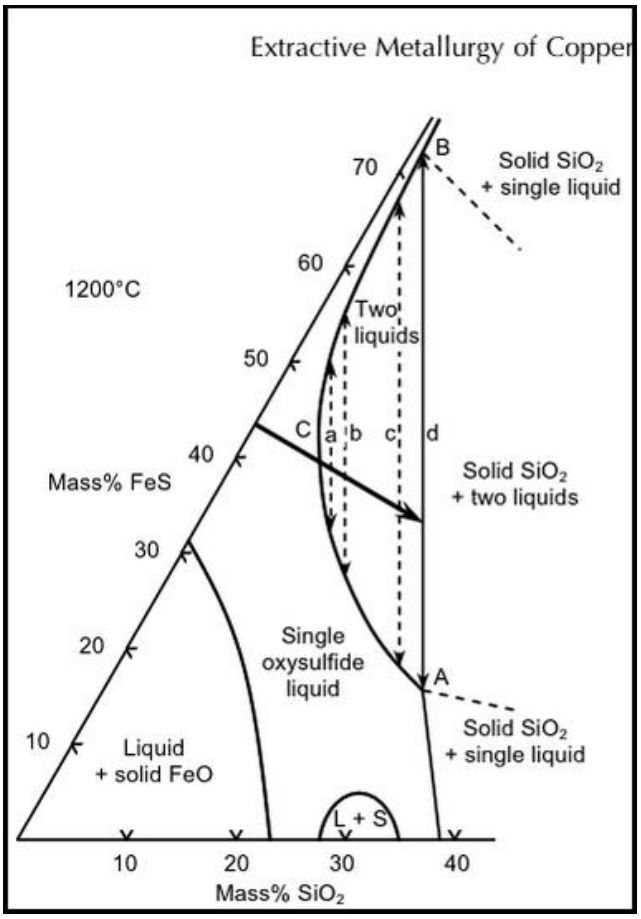


Fig.2.10: Partial phase diagram for Fe-O-S-SiO_2 system showing slag-matte ($Fe.SiO_2$–FeS) immiscibility. Lines *a*,*b*,*c* and *d* represent the equilibrium conditions of the two liquids (slag and matte). The heavy arrow shows that when silica is added to an oxysulphide liquid it splits into iron sulphide rich matte and iron sulphidelean slag. Taken from Schlesinger et al. (2011:74).

By this point the matte consists of relatively pure copper sulphide and an iron rich sulphide. Maintaining an iron-rich matte prevents initial losses of copper into the slag by producing less slag and increasing the volume of low viscosity matte for the copper to be reduced in and sink through

(see figure 2.11). However as the sulphur content of the matte decreases with further oxidation, conversion of the iron sulphide to oxide produces a low viscosity iron-rich slag which prevents the newly oxidized copper from being entrained, allowing it to be reduced and separate cleanly from the slag in the coppermaking phase (Sridhar et al.1997a:195). The further oxidation of the iron in the slag to magnetite (Fe_3O_4) also fixes and lowers the partial pressure of atmospheric oxygen creating more strongly reducing conditions (Schlesinger et al.2011:78). The remaining copper sulphide matte can then be converted into oxides before the final extraction of metallic copper.

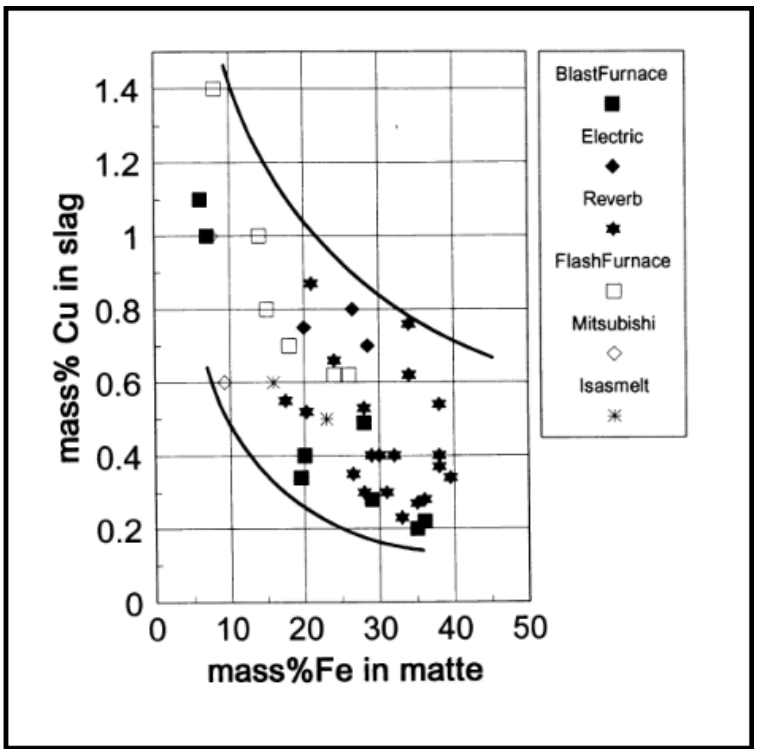


Fig.2.11: Copper content in copper smelting slags in relation to iron content of matte. As iron content in the matte increases, copper losses to the slag decreases. Taken from Sridhar et al. (1997a:194).

The final converting and copper-making phase in the matte process involved the complete oxidation of the sulphur in the copper sulphide matte and the reduction of the remaining copper oxide to produce metallic copper (Schlesinger et al. 2011:127-128). Conversion of the matte requires the presence of oxygen and temperatures of around 1200^{o}C, producing copper oxide (Cu_2O) or 'black copper' which is reduced into metallic copper in the coppermaking phase:

$$Cu_2S + 1.5O_2 \xrightarrow{1200^{o}C} Cu_2O + SO_2$$

$$Cu_2O + CO \longrightarrow 2Cu^{o} + CO_2$$

Once the sulphur content of the matte (white metal) reaches less than 1% it is converted along with copper oxides into metallic copper (see figure 2.7, p69) or 'blister' copper (so named for the blisters and air pockets in the metal caused by the release of SO_2 from the molten metal):

$$Cu_2S(l) + 2Cu_2O(l) \xrightarrow{1200^{0}C} 6Cu^{o}(l) + SO_2$$

The copper oxide is reduced by the carbon monoxide in the furnace and the fixation of oxygen by sulphur in the copper matte would produce sulphur dioxide (Schlesinger et al. 2011:233). When the sulphur in the system reaches below 1%, further oxidation of the metallic copper results in losses to the slag as copper oxides as no more copper sulphide is available to reduce it, so the air flow can cease and the metallic copper is collected from the base of the furnace upon cooling, completing the

operation (Schlesinger et al. 2011:134). Production of copper through the conversion of matte is inherently beneficial (Hauptmann 2020:47; Schlesinger et al. 2011:84-88). Firstly, the low solubility of oxygen and silica in matte (the degree of solubility is greatly reduced with increasing Cu_2S in the matte) reduces the quantity of copper lost as oxides in the slag. Secondly, the low viscosity and higher specific gravity of matte (see figure 2.12, p80) compared to siliceous slags allowed metallic copper dissolved into the matte to separate from the slag without becoming entrained in it, allowing it to settle at the base of the furnace in a consolidated mass. Thirdly, the co-occurrence of copper oxide (Cu_2O) and copper sulphide (Cu_2S) reduces the copper and oxidizes the remaining sulphur simultaneously even under less strongly reducing conditions, reducing copper losses from excessive oxidation and entry into the slag while still facilitating desulphurization. The fixation of excess oxygen, self-reduction and self-fluxing of mixed sulphide ores and the production of low viscosity slags and intermediaries all appear to be features of an autonomic or self-regulatory process however matte smelting and converting takes place across relatively narrow parameters of oxygen partial pressures and iron oxide and silica saturations (see figure 2.14, p81) and would have required advanced furnace and charge manipulation strategies to achieve.

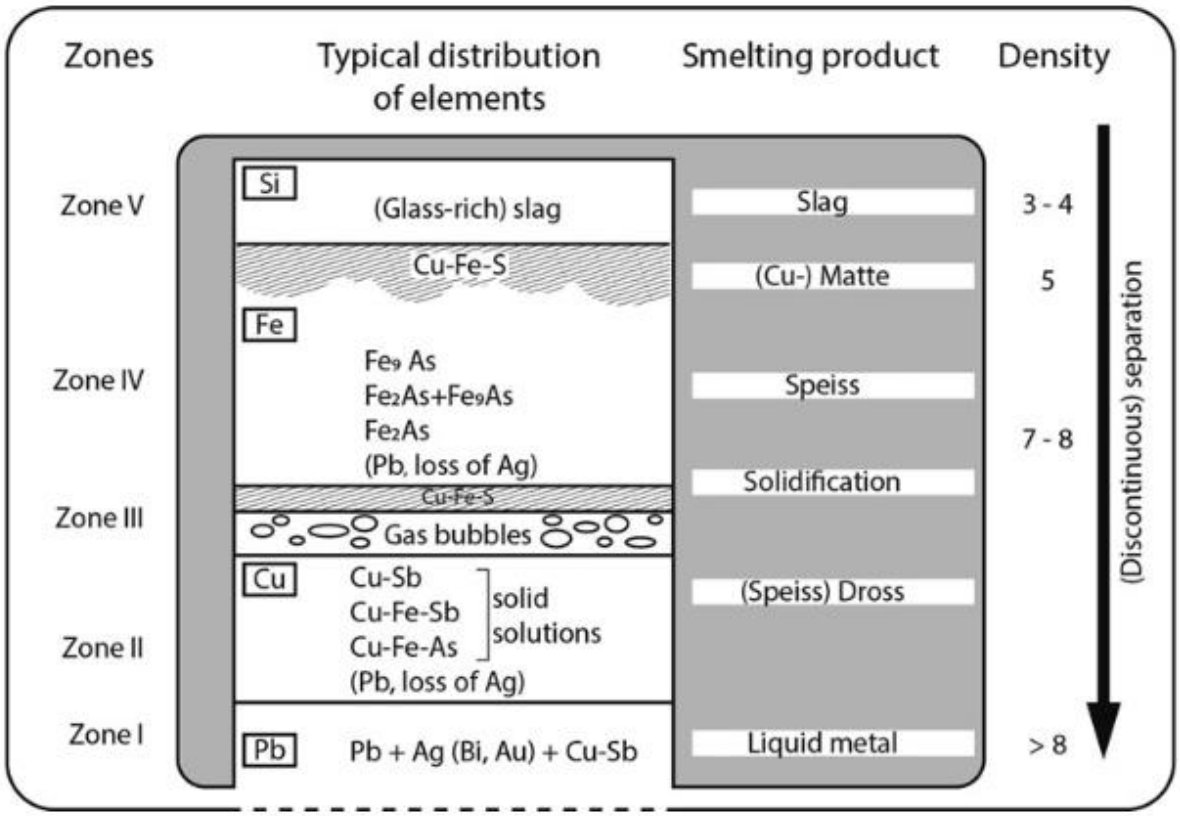


Fig.2.12: Separation of various phases of an ideal copper sulphide ore smelt. The higher specific gravity of the low viscosity matte compared to the slag allows the copper forming within it to sink to the furnace base without risk of entrainment in the slag above. Taken from Hauptmann 2020:271.

2.10: *The Partitioning of iron in Matte smelting*

During the matte process mixed copper-iron sulphides decompose and oxidize partitioning the iron from the copper to form two principal products; iron sulphides and iron oxides. The iron rich sulphide phase or matte is produced by heating chalcopyrite to temperatures as low as 600^{o}C (see figure 2.9, p75), so it is likely that this process began with the roasting of the ore by prehistoric copper producers (Bachman 1982b:22; Hauptmann 2020:312; Ruddle 1953:19; Sridhar et al. 1997A:191). Sufficient oxidation during the roasting stage also removes the sulphur from some of this iron sulphide to produce iron oxides. During the smelting phase, initially the iron sulphides enter the matte or alternatively are further oxidized to produce a fayalitic slag if silica is available. The extent to which

iron enters into the matte as sulphides or into the slag as oxides is dependent upon the partial pressure of oxygen (see figure 2.13) and the availability of silica (see figure 2.10).

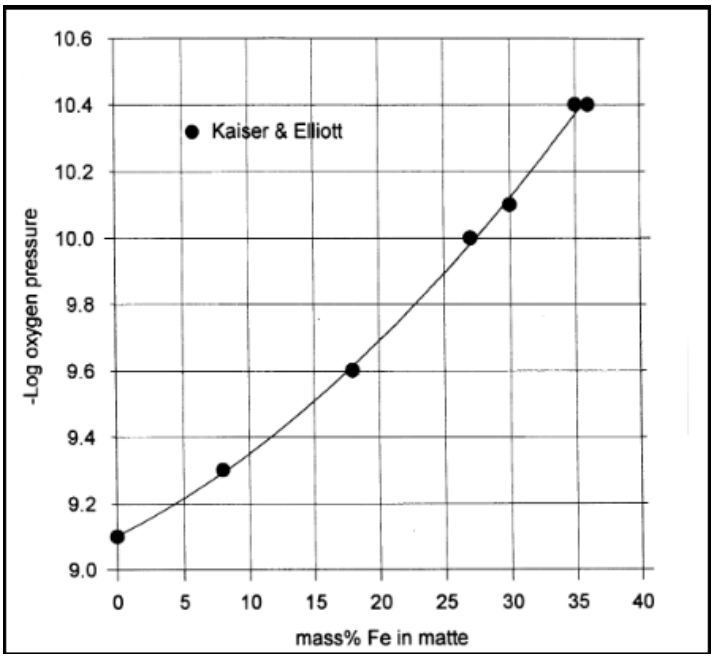


Fig.2.13: Relationship of oxygen pressure and iron content in matte produced at 1250°C. With decreasing oxygen pressure from -9.1 to -10.4 log oxygen pressure the mass % of iron in the matte rises from 0 to 35. Taken from Sridhar et al. (1997a:195).

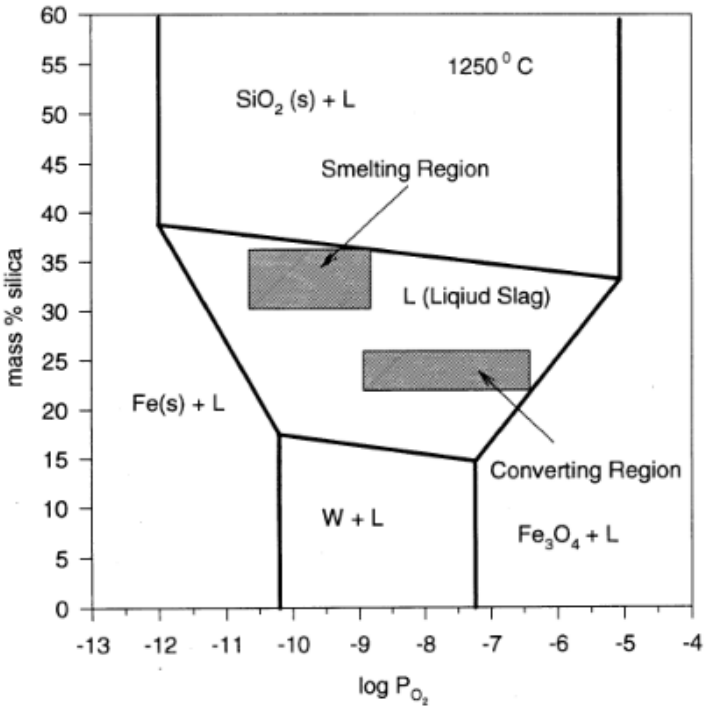


Fig.2.14: Phase relation in the Fe-Si-O system at 1250°C. Copper smelting takes place over a narrow range close to silica saturation at 35-38 mass% SiO_2 in the slag and converting at 22-28 mass% SiO_2. Magnetite (Fe_3O_4) precipitates from around - 7.25 oxygen potential and lower Taken from Sridhar et al.(1997a:195).

As the complete removal of the sulphur from the copper sulphide requires oxidizing conditions the majority of the remaining iron sulphides in the matte are converted to iron oxides (see figure 2.15) and sulphur dioxide gas once the sulphur in the system reaches <1% (Schlesinger et al. 2011:78; Sridhar et al. 1997a:193-194). With increasing oxygen potential the iron in the slag is further oxidized from a ferrous (Fe^{2+}, FeO) to ferric (Fe^{3+}, Fe_2O_3) state until magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$/ Fe_3O_4) is precipitated (see figures 2.14, p71 and 2.16).

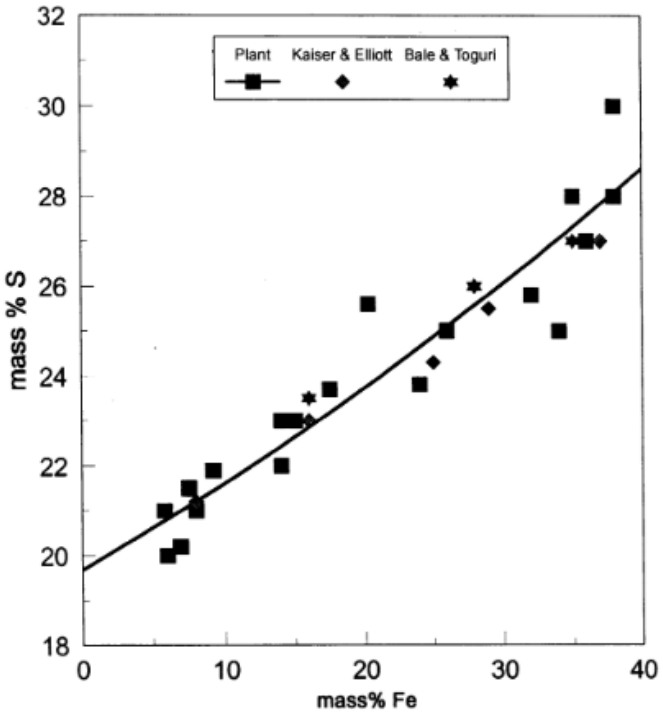


Fig.2.15: Relationship between sulphur and iron content of mattes. Iron content of the matte sharply declines with the decrease of mass % sulphur as both become oxidized preferentially to copper. Taken from Sridhar et al. (1997a:194).

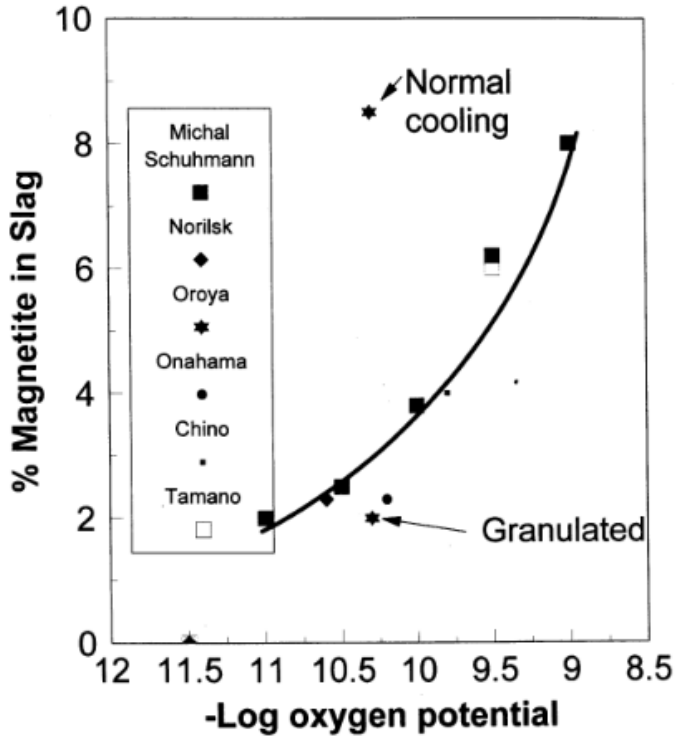


Fig.2.16: Relationship between the magnetite content of slag and oxygen pressure at 1250ºC. The % of magnetite in the slag rises steeply from -11 to -9 log oxygen potential. Taken from Sridhar et al (1997a:195).

With the complete oxidation of the sulphur, more strongly reducing conditions are required to reduce the copper oxide. At lower partial pressures of oxygen in the furnace, the formation of increasing quantities of carbon monoxide reduces the copper oxides to produce metallic copper in a process known as coppermaking (Schlesinger et al. 2011:129-134). These strongly reducing conditions also reduce the iron oxides in the slag starting with magnetite:

$$Fe_3O_4\ (l) + CO\ (g) \xrightarrow{1200^oC} 3FeO\ (l) + CO_2\ (g)$$

magnetite wüstite

As the converting of copper oxide to metallic copper (-9 to -6 oxygen potential) requires less reducing conditions than the reduction of magnetite to wüstite (-10.25 to -7.25 oxygen potential) most matte smelting slags consist of varying proportions of magnetite and wüstite (FeO), favouring magnetite as a general rule (Schlesinger et al. 2011:75).

2.11: *Matte Smelting from the LBA*

Identifying examples of multi-stage matte smelting processes within the archaeological record has proven challenging as each stage is rarely well-defined with mass deposition of smelting assemblages confusing the sequence of production. The bewildering array of intermediary products resulting from the decomposition, oxidation and reduction of complex mixed sulphides renders chemical analysis of the smelting assemblages no less difficult. As such the modern understanding of prehistoric matte processes is mostly analogous drawing on data from the industrial and historical metallurgical literature as well as ethnographic sources (Hauptmann 2020:47; Van Brempt and Kassianidou 2016). The application of these models to prehistoric processes requires the recognition of the various by-products of associated reactions and the state of oxidation of sensitive systems such as the fayalite-wüstite-magnetite complex within the slags (Bougarit 2019:218; Hauptmann 2020:62; Sridhar et al.1997a:195). The concentration and composition of matte trapped in the slag as prills can also be an indicator while slag anatomy provides another means of distinguishing multiple stages of production resulting from variable conditions. Prehistoric matte smelting has often been associated with the binary nature of slags from copper smelting sites in regions rich in sulphide deposits. In general these variants can be described as homogeneous ‘flat’ or ‘cake’ shaped slags and heterogeneous masses containing quartz and various sulphide and metal prills sometimes referred to as furnace slags (Hauptmann 2020:271,312). The first category most likely formed from a liquid and

often retain a meniscus from contact with another phase, possibly metal or matte, in the furnace (Hauptmann 2020:312). The second variants are less clearly identified and are subject to numerous hypotheses regarding their formation or relevance to smelting. Finally descriptions of historic treatment and smelting of sulphides can aid in the identification of products originating from distinct operations such as the 'black copper' which resulted from 'dead roasting' of sulphide ores attested to in historical literature (Bourgarit 2019: 212-217; Percy 1861:413; Rostoker et al. 1989:82).

The most well-studied examples of Late Bronze Age matte smelting in the Near East to date can be found in the South Caucasus and on the island of Cyprus (Gilmour et al. 2020; Van Brempt and Kassianidou 2016). Following claims for widespread metallurgical activity dating to the second half of the 2nd Millennium BC in the south Caucasus region in the 1970s, extensive field survey and excavation was undertaken from 2009 to 2014 to ascertain the nature of the sites which had been tentatively ascribed to early iron smelting (Gilmour et al. 2020; Khakhutaishvili 2009). The results revealed a large number of small smelting sites dating from 1500-600BC dispersed across a wide distribution with an estimated 400 sites situated within the Late Bronze to Early Iron Age in the region (Erb-Satullo, Gilmour and Khakhutaishvili 2014:6-7). These sites typically consisted of one or two pits (see figure 2.17) up to one metre in depth identified as furnaces from vitrified clay lining and small scatters of slags. A forced draught was supplied artificially through complex interlocking *tuyeres* which survive as fragments of flared ceramic nozzles for which their function, while related to the pit furnaces, is thus far ambiguous (Khakhutaishvili 2009:10-14). These furnaces were sometimes accompanied by 'platforms' with burnt substrata. The slags recovered from the smelting assemblages were subjected to chemical analysis and found to have resulted from the smelting of mixed sulphide ores from local polymetallic sulphide deposits to produce copper (Erb-Satullo,

Gilmour and Khakhutaishvili 2014:10-11). Matte inclusions in the slags as well as partially reacted ore fragments contained chalcopyrite, chalcocite, bornite (Cu_5FeS_4), covellite (CuS) and digenite (Cu_9S_5) also occurred frequently. Copper oxides such as cuprite (Cu_2O) and malachite were unusual and formed from post-depositional processes or weathering. This suggests that chalcopyrite formed the principal copper ore in the charges fired in the furnaces. Prills of metallic copper in the slags confirmed the smelting sites as primarily those of copper extraction. The sightly more common occurrence of magnetite in the slags as opposed to wüstite suggests less strongly reducing conditions were achieved in the furnaces which supports this conclusion (Erb-Satullo, Gilmour and Khakhutaishvili 2014:10-11).

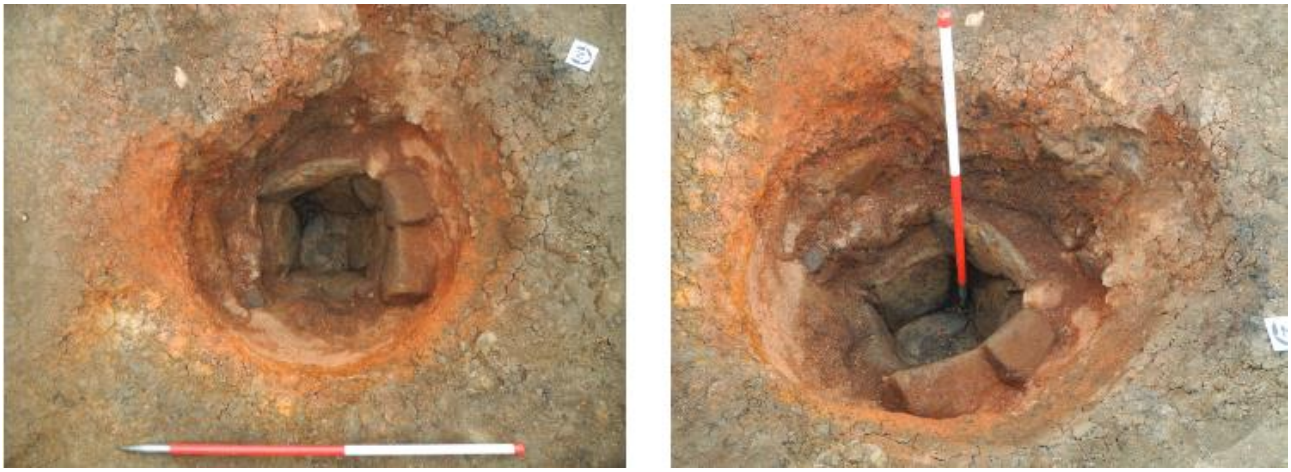


Fig.2.17: Copper smelting furnace from Site 46/ Askana XXVII. The burnt reddish area deliminates the clay lining of the walls. Scale bar is one metre. Taken from Gilmour et al. (2020:28).

Evidence for the multi-stage smelting of mixed sulphide ores at these sites can be inferred from the site organisation and the anatomy and chemistry of the slags. The occasional 'platforms' showing signs of burning that accompany the pit furnaces may have been open roasting areas for the oxidation of the sulphur in the raw sulphide ores. An open firing would have been sufficient to reach the temperatures and partial pressure of oxygen required to remove some of the sulphur and begin to

produce metallic oxides prior to smelting proper (Craddock 1995:167). Secondly, chemical analysis of the slags demonstrated that high copper contents correlated to fewer inclusions of chalcopyrite and vice versa, with a similar pattern reported for pyrite (Erb-Satullo, Gilmour and Khakhutiashvili 2014:9-11). The slags containing iron-rich matte and little copper might be assigned to an initial firing of roasted ores which produced large volumes of liquid matte from which iron entered into the slag, allowing the iron oxides and copper sulphides to mechanically separate (see figure 2.12, p.80). The copper sulphides that had collected at the base of the furnace could have been retrieved after cooling and smelted in the next stage. The prevalence of iron-poor matte (predominantly consisting of Cu_9S_5 or Cu_2S) in the slags containing metallic copper suggests that these copper-rich slags originated from a secondary smelting phase where much of the iron had been oxidized out of the original chalcopyrite ore (Erb-Satullo, Gilmour and Khakhutaishvili 2014:11-12). During this stage the remaining copper oxides and sulphides recovered from the previous firing could be resmelted to produce metallic copper which would become entrained in greater quantities within the more viscous iron-poor slags. The anatomy of the slags also appeared to correspond to a two-part process, with some smaller 'spongy' or porous slags found alongside larger 'dense' slag-cakes which constituted the bulk of the smelting assemblages discovered (Gilmour et al. 2020:29). This first category of smaller slags are heterogeneous and amorphous containing charcoal inclusions that frequently contain half-reacted mineral and rock fragments (figure 2.18, left). The other larger slags or cakes are very homogeneous with few extraneous partially-reacted inclusions within a uniform slag matrix and in one example (see figure 2.18, right) a clear interface between the base of the slag and possibly metal or matte below can be seen. Though the largest of these slag-cakes reach around 20-30cm in width and 10cm in depth, the presence of clear fractures suggests they were broken up upon retrieval of the smelting assemblage. It is plausible that these two slag morphologies belong to two distinct pyrometallurgical processes.

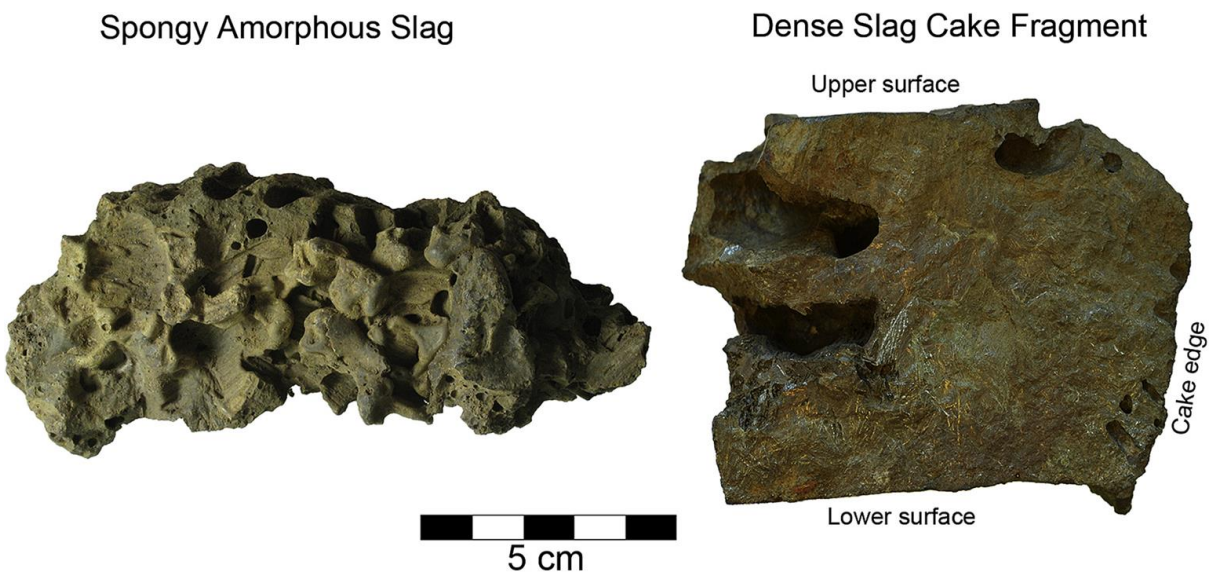


Fig.2.18: Example of the two categories of slags found most commonly. Taken from Erb-Satullo, Gilmour and Khakhutaishvili (2014:151).

The use of technical ceramics at these sites evident from the large quantities of slagged shallow-bowl crucibles found within the smelting assemblages brings another dimension of complexity to these operations (Erb-Satullo, Gilmour and Khakhutaishvili 2015). These crucibles typically measured up to 24cm in diameter with a depth of 5cm or more based upon estimates from fragmentary remains, with an interior volume of just over 1000cm^3. The adherence of many of these ceramic fragments to the furnace slags described above and equivalent chemistries revealed upon analysis suggests that they were placed directly in the furnace to serve as reactor containers in primary smelting operations (Erb-Satullo, Gilmour and Khakhutaishvili 2015:263-264). The presence of copper sulphides and less commonly iron sulphides as well as prills of metallic copper on the slagged surfaces of the ceramics shows that they were in contact with the full suite of intermediary and metallic products involved in matte smelting (Erb-Satullo, Gilmour and Khakhutaishvili 2015:264). Based on rough estimates of the interior volume of these crucibles, they could contain around 5-10kg of chalcopyrite which could yield in excess of 2-3kg of metallic copper excluding gangue within the ores. Overall it appears that these large technical ceramics were employed to contain both ores or matte and prevent the material

becoming attached to the furnace lining or base to assist in retrieval of the metal from out of the pit after cooling (Erb-Satullo, Gilmour and Khakhutaishvili 2015:274).

The authors present three prospective modes of production: a direct-to-copper sulphide and oxide co-smelt, a three-step process to produce matte before dead roasting and crushing it for direct reduction in the furnace and finally roasting of the beneficiated ore before a single firing smelt (Erb-Satullo, Gilmour and Khakhutaishvili 2014:16-18). The first process can largely be dismissed due to the scarcity of copper oxides noted in the major copper deposits of the region which would have been insufficient to supply such intensive production (Popkhadze et al. 2009). The near total absence of oxide ores at the sites or partially reacted fragments encased in the slags appears to confirm their absence from the process (Erb-Satullo, Gilmour and Khakhutaishvili 2014:16). The three-step process is more convincing given the evidence for roasting platforms and the double furnaces found at some sites might point to a dead roasting procedure to convert matte into copper oxide prior to reduction (Erb-Satullo, Gilmour and Khakhutaishvili 2014:17). The lack of substantial evidence for crushing such as hammerstones or fine slags might be explained by a clean matte process which allowed easy retrieval of a distinct matte phase under the slags. The last premise is perhaps most closely reflected by the smelting assemblage and would explain the inter-site variability in the copper contents of the slags. Again the existence of the platforms for roasting the newly beneficiated ore appears beyond doubt and an open fire roast would better account for the semi-reacted ore inclusions and range of minerals encountered in the slags. The greater volumes of toxic sulphur dioxide gas produced during this stage would be dealt with more effectively on an open platform without requiring human proximity to work bellows. Slag morphology and chemistry also substantiates this means of production with the homogenous slag-cakes demonstrating that high temperatures of up to

1250^{o}C or higher were maintained over a long duration to achieve liquidus and complete density segregation (Erb-Satullo, Gilmour and Khakhutaishvili 2014:18). Coupled with the large reaction volume implied by the even burning of the clay lining in the pits and the greater dimensions of the slake cakes; the conditions reached in the furnaces would have been capable of the conversion of matte from the roasted ores across a single firing. The oxygen required to convert the matte was likely supplied through the complex *tuyere* systems in evidence. The main criticism of this explanation is that it doesn't account for the 'spongy' amorphous slags which typically contained more prills of copper metal. It would be extremely unlikely that these slags would form during open air roasting and yet the diminutive quantities in which they are found in comparison to the larger homogeneous cakes suggests they may have been recovered, destroyed and re-smelted in further stages. On the other hand they could simply represent a terminal phase of the smelt following the conversion of the majority of the matte into metallic copper after which more copper would become entrained in the iron poor slags at the base of the furnace during cooling. Inter-site variability might be accounted for by differences between smelters in limiting copper losses and achieving cleaner separations between slag, matte and metal phases (Erb-Satullo, Gilmour and Khakhutaishvili 2014:17).

Matte smelting practices on the isle of Cyprus beginning from the mid to late 2nd millennium BC bear much resemblance to those of the south Caucasus (Erb-Satullo, Gilmour and Khakhutaishvili 2014; Knapp and Kassianidou 2008:144). Island-wide differentiation in social organisation, scale of the sites and pyrometallurgical practices point to a lack of centralization with small social units sporadically exploiting the mass sulphide deposits of the Troodos foothills for copper (Van Brempt and Kassianidou 2016:539; Raber 1989). Smelting sites such as those excavated at Politiko Phorades located at the centre of the island were dispersed, with evidence for roasting found close to the ore

deposits and actual smelting of the ores taking place within the settlement (Knapp and Kassianidou 1998:265). Similar roasting pits found at the site of Almyras were tested using the Moessbauer spectra which confirmed that they did not reach temperatures exceeding 600^{o}C; the expected range for a roasting operation (Fasnacht 2018:254). *Tuyeres* varied with a number of complicated 'double' or 'branched' forms implying differing levels of sophistication or function (Knapp and Kassianidou 1998:260). The slags originating from the smelting activity conform to two main types: large homogenous slag cakes and smaller more porous slags with encased gangue and charcoal speculatively termed 'furnace slags' by the excavators (Knapp and Kassianidou 1998:259). This first category are described as plano-concave in shape with a flat top surface and an original diameter of 44cm and weight of 15-20kg before fragmenting. The consistency of the slag is homogenous and their density and magnetism indicates a high iron content (especially magnetite). Gas vesicles and a large central void are common to all specimens (Knapp and Kassianidou 1998:259). These are striking in similarity to the slag-cakes encountered in the south Caucasus and may have resulted from much the same process; a long duration smelt using roasted ore that converted the matte into metallic copper. The concavity of the slag-bottoms might arise from being situated above the matte during conversion and escaping sulphur dioxide gas could have created the numerous vesicles and large voids visible in the slags. Copper smelting practices were not uniform perhaps as a result of chronological, social or technological disparities between metal producers on the island. At the site of Kalavassos-ayios-Dhimitrios off the south-central coast of Cyprus similar dense homogenous slags (see figure 2.19, left row) were recovered that had flow textures on their upper surface and plano-convex shapes which were associated with tapping of the molten slag into a small pit hence they were named 'tap slags' (Van Brempt and Kassianidou 2016:541). The fragmentary nature of these slags suggested that they had been broken to retrieve matte or metal. The other main grouping of slags found at the site and defined as 'furnace slags' (see figure 2.19, right row) consisted of heterogeneous lumps fused to charcoal and gangue from the furnace. Chemical analysis of these slags identified

frequent inclusions of partially reacted ore and copper-iron sulphides in this latter group in comparison to the tap slags where they occurred to a much lesser extent. Otherwise both slags were largely reciprocal in terms of microstructure (Van Brempt and Kassianidou 2016:545). Metallic copper was also present in both types though was much more pronounced in the furnace slags. Prills of matte trapped within all of the various slags confirmed that both types had derived from a matte smelting process. The authors interpret these variable slags as two different smelting operations possibly relating to an earlier and later metallurgical stage in the site chronology (Van Brempt and Kassianidou 2016:549). The furnace slags would represent an early stage in sulphide smelting which resulted in semi-fused viscous slags that promoted excessive copper losses through entrainment. At a later and more advanced stage, long duration smelting of the sulphide ores at higher temperatures allowed for the tapping of the furnace contents into a pit before allowing it to cool. The slag would then be broken up to recover the matte which would be converted into metallic copper in a final smelt (Van Brempt and Kassianidou 2016:549). Alternatively they propose a theory put forward by Hauptmann (2011) regarding similar furnace slags from the nearby workshops of Kition and Enkomi of the recovery of copper by re-smelting old copper slags. The high copper content of the furnace slags seems incongruous with copper recovery from older slags and leads the authors to conclude that they belong to two distinct practices at different points in time (Van Brempt and Kassianidou 2016:550-551).



Fig.2.19: 'Tap' slag (left) showing profile (top) and cut section (bottom) and 'furnace' slag (right) showing profile (top) and cut section (bottom), note the convex bottom of the tap slag and large voids in bottom section. Taken from Van Brempt and Kassianidou (2016:542).

Investigations into the pyrometallurgical methods employed by Late Bronze Age cultures to extract copper from mixed sulphide ores have made considerable headway even in the last decade. Irrevocable evidence for the primary exploitation of mixed sulphides has been recorded at a greater number of sites which have been mapped and grouped into regional complexes based on survey, excavation and chemical analysis of assemblages (Gilmour et al. 2020). Perhaps the most

unanticipated results of these endeavours has been the intraregional reciprocation of features within Near Eastern smelting assemblages. Shared slag chemistry and morphologies as well as comparable furnace technology provides convincing evidence of the exploitation of the same reaction mechanisms using parallel pyrometallurgical technologies. Notably the clean segregation of furnace contents into fairly homogeneous slags, matte and metal phases indicates that prehistoric matte smelters could achieve high temperatures and strongly reducing conditions across a large reaction volume. This is critical to the evaluation of matte smelting in the following chapter regarding the incidental production of metallic iron.

2.12: *The Speiss must flow: iron from sulpharsenides*

Non-copper related extractive technologies may also have facilitated the direct reduction of iron through the exploitation and beneficiation of iron ores and the skilled manipulation of highly reducing conditions. The production of ferrous speiss or iron arsenides is reported from as early as the 3rd millennium BC in Iran and became widely practised across much of the Near East by the Early to Middle Bronze Age where arsenical bronzes were the chief copper alloy (Oudbashi et al.2020:1-4; Rehren et al.2012; Thornton et al. 2009). The term 'speiss' refers to a family of base metal and ferrous arsenides which could form within the furnace as a result of the exploitation of arsenic rich ores (Thornton et al. 2009:308). Though the deliberate use of speiss as a source of arsenic for alloying copper into arsenical bronzes is a matter of debate, the practice appears to have become established by the Mid to Late Bronze Age with evidence for a trade in speiss 'ingots' in the Balkans and imported fragments discovered in the Cyclades, Turkey and on Crete (Georgakopoulou 2013, 684-685; Horejs et al. 2010; Thornton et al. 2009). Rehren et al. cautiously propose a two stage process for the production of speiss whereby arsenopyrites were subjected to a slightly oxidizing smelting stage to

remove the sulphur, primarily as sulphur dioxide gas and as a liquid iron-sulphide (matte) phase, at temperatures of up to 1200°C (see figure 2.20) to facilitate mechanical separation from the speiss (2012:1723). This first stage would thus avoid the metallic copper forming a sulphide with the sulphur contained within the arsenopyrite that would result from a direct alloying process. In a recent study however, Park and Gelegdorj proved that iron and sulphur are readily removed from high arsenic copper alloys at temperatures of 1000°C as a result of preferential oxidation of iron, sulphur and arsenic over copper and so a direct-to-alloy procedure that avoided this intermediary step is most plausible in regions where local sulpharsenide deposits were exploited (2015:869-871). Similarly, co-smelting experiments of iron and copper bearing sulpharsenides within a crucible have produced excellent arsenical copper alloys that have segregated the majority of undesirable elements into a distinct matte phase (Lechtman and Klein 1999).

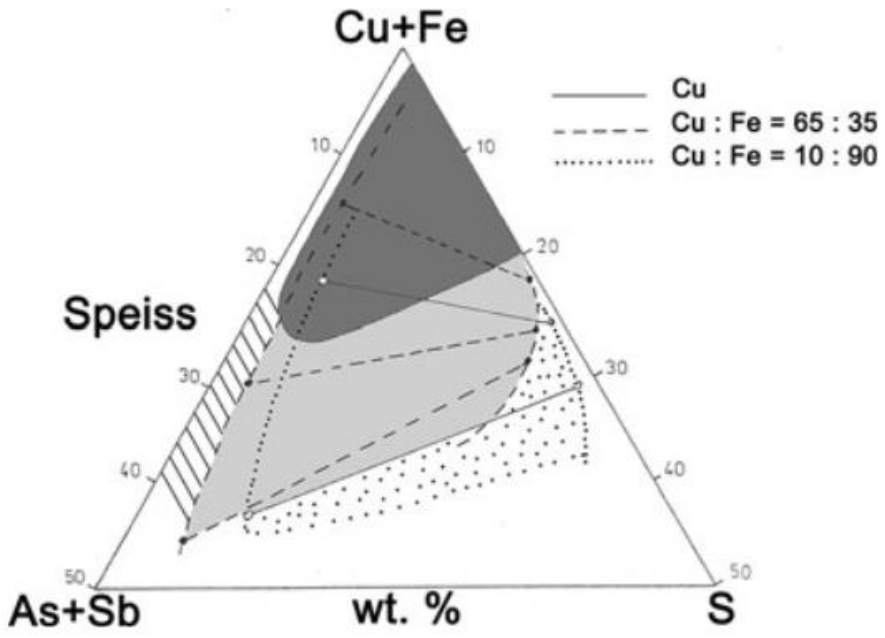


Fig.2.20: The ternary system (Cu + Fe) – (As + Sb) – S at 1200°C showing the miscibility gaps between copper-iron sulphides (matte, dark grey) and the Speiss (As + Sb, light grey) phase. Increasing Fe concentrations enlarges the miscibility gap towards the As-Sb-S line. Taken from Hauptmann (2020:284).

While the technical stages of these operations remain unclear, the extraction of metallic iron through the speiss process seems highly improbable. Both co-smelting of arsenopyrites, represented below, and the production of speiss necessitated the oxidation of iron or the segregation of the iron into the matte sulphide phases:

$$3CuCO_3 + FeAsS \xrightarrow{\text{Heat}} Cu, As + FeO + SO_2 + 3CO_2$$

copper carbonate Arsenopyrite Heat Alloy Iron Oxide

Evidence for copper arsenic prills with an iron content of up to 4.2 wt% from Arisman in Iran lead Rehren et al. to characterise the furnace conditions as strongly reducing, also citing the preferential formation of wüstite over magnetite in some furnace slags (2012:1721, 1725). Overall the mixed picture of both oxidized and reduced minerals found across the total assemblage suggests that the degree to which iron could be reduced through this process was extremely limited (Rehren et al. 2012). As the process appeared to necessitate an initial oxidizing phase to remove the sulphur, much of the available iron would simply form oxides in the slag reducing the partial pressure of oxygen in the furnace and aiding in the reduction of the copper. Only the production of speiss through the smelting of arsenopyrites would introduce a sufficient quantity of iron into the system for it to become reduced in any significant quantities of which most would become inseparable from the matte, slag or copper phases across the short duration of the smelt. This rules out a direct relationship between speiss production and extractive iron metallurgy and also calls into question the possibility of even retrieving speiss from the mixed assemblages of smelting operations. Nevertheless the manipulation of redox conditions to form various intermetallic phases including iron sulphides and oxides in the furnace from as early as the third millennium BC does offer tantalizing evidence of competency not far precluding the extraction of metallic iron.

2.13: *Leading the way? Iron from tin or lead production*

The potential of lead smelting operations to produce iron was first recognised as archaeologically significant in a metallurgical expedition to the Near East in 1962 by esteemed archaeometallurgists Theodore Wertime and Cyril Stanley Smith (Arab and Rehren 2004; Wertime and Muhly 1980:8). At Anjileh in Iran the two discovered a ball of iron weighing almost 360lbs produced by a modern lead smelter which they estimated had fluxed every 6 kilograms of lead ore (cerrusite, $PbCO_3$) with 150g of hematite (Fe_2O_3). This phenomenon was picked up on by later studies that related the lead smelting practices of Bronze Age metalworkers to the early production of iron in those regions (Healy 1982:83; Pickles 1988:10; Shell 1997; Wertime 1973:883). Evidence for the processing and combustion of iron oxide ores alongside lead and tin ores across the period is regularly apparent in Anatolia which has long been associated with the earliest smelted iron. The shared paragenesis of iron (hematite, goethite FeO(OH) and ilmenite $FeTiO_3$) with lead (cerrusite, galena PbS and anglesite $PbSO_4$) ores based upon its chalcophile (affinity with sulphur) nature results in their co-occurrence within many of the principal ore deposits for lead (Hauptmann 2020:86). Tin ore (cassiterite SnO_2, stannite Cu_2FeSnS_4) also frequently occurs alongside iron and lead ores (Hauptmann 2020:102-105). In Anatolia polymetallic ore deposits in the central Pontide and eastern Tauride ranges and to the west were exploited to produce lead as early as the Neolithic at Çatalhöyük IX with early ingots found in mine workings at the Kestel-Göltepe complex (see figure 2.21) and Izmir dating to the third millennium BC (Oy 2017:17-18; Yener 1993:34). At Kestel-Göltepe rich mineralizations of hematite, tin and lead ores had been mined and were sorted into powders at various stages of beneficiation and metallurgical extraction (Adriaens 1999; Earl and Özbal 1996; Yener 1994:24-25).



Fig.2.21: Lead ingot from Göltepe, central Anatolia dating to the early Bronze Age. Taken from Yener (1994:25).

The feasibility of extracting metallic iron during lead and tin smelting operations is best assessed by the thermodynamics of tin and lead ore minerals in comparison to iron oxides. In the case of prehistoric lead smelting, extraction was achieved with the low temperature oxidation (roasting) of an ore such as Galena (PbS) to produce PbO, $PbSO_4$ and PbS. Higher temperatures of just over 900°C would then be generated to reach the melting points of all three products, allowing for a complete reaction during which the lead oxides react with and oxidize the PbS to produce sulphur dioxide and metallic lead:

$$PbS + 2PbO \longrightarrow 3Pb^{o} + SO_2$$

This operation does not require charcoal or particularly high partial pressures of carbon monoxide (favoured at 1200°C) as the lead is primarily reduced by oxidation and removal of the sulphur (Dube 2006:18). Such conditions are not sufficient to extract metallic iron. Unless the roasting products PbS,

PbO and $PbSO_4$ are in stoichiometric proportion to the equation above much of the lead can not be reduced and remains as an intermediary. The historical solution to this was to smelt lead ores with iron which removes oxygen and sulphur from the system to stabilise the reduction of the lead:

1) $PbS + Fe^o \longrightarrow Pb^o + FeS$

2) $PbO + Fe^o \longrightarrow Pb^o + FeO$

According to the above equations the quantity of iron required to reduce the lead is around 23.4 wt. % with the standard free energy change at 900^{o}C for equation 1) equalling about -25 kJ and for equation 2) considerably lower nearing 91.2 kJ (Dube 2006:19). Historical examples of this process co-smelted iron ores with lead ores to produce the iron that would then selectively reduce the lead ores (Dube 2006:19). Charcoal and coal were used to generate temperatures exceeding 1200^{o}C and the high partial pressures of carbon monoxide needed to reduce the iron and liquefy the slag and regulus (metallic sulphides from the gangue). The lead smelter at Anjileh reported by Wertime and Smith was almost certainly an example of this process explaining the maintenance of the large iron 'bear' in the furnace to reduce the lead oxide. Theories for the incidental extraction of iron as a by-product of lead smelting therefore may have been labouring under the false assumption that iron oxides were the intended fluxing agent when in practice metallic iron was used. Since the objective of these historical operations was to produce metallic iron as a flux they likely represent a later development based upon well-established practices for the extraction of iron. Its relevance to the question of the origins of iron metallurgy is dubious and at present only the association of lead and iron ore minerals in deposits exploited from the 3rd Millennium BC offers any tangible support.

The smelting of tin ores was usually facilitated through the reduction of tin oxides in the presence of carbon or carbon monoxide in the contexts of a prehistoric operation:

1) $SnO_2 + CO \longrightarrow SnO + CO_2$

cassiterite — stannous oxide

2) $SnO + CO \longrightarrow Sn^o + CO_2$

Tin

or an overall reaction:

$SnO_2 + 2CO \longrightarrow Sn^o + 2CO_2$

Reduction of the tin oxides begins at around 800ºC however volatilization (evaporation) of stannous oxide (SnO) is reported to occur at temperatures exceeding 975ºC (Berger et al. 2019:303). In the direct reduction method utilised for Bronze Age tin extraction, heating tin ores in a crucible with charcoal could have risked tin losses with the production of stannous oxide as an intermediary followed by excessive heating. The extent to which this is true is difficult to assess however Berger et al. demonstrated that direct reduction of cassiterite with carbon monoxide at temperatures up to 1100-1200ºC recovered ca.90-98% of the tin with less than 10% lost from volatilization in the fume fraction (2019:307). The authors point out that in field experiments representing a closer approximation of prehistoric operations impure tin ores containing iron, aluminium, silicon, niobium and tantalum could increase the production of stannous oxide leading to increased volatilization to as much as circa 70% (Berger et al. 2019:307). An experiment by Earl and Özbal proved this when they reduced a rich tin ore (circa 15% Sn) in a crucible easily maintaining temperatures of 1100ºC using a blowpipe (1996:301). After the firing they collected tin prills from the slag that had formed and recovered 0.175g of metal from an initial charge of 5g of which 10.2% was tin. Metal recovery can be estimated at ca.3.5% leaving 6.7% of the available tin non-reduced which falls in line with the circa 30% average rate of recovery for a prehistoric tin smelting operation (Earl and Özbal 1996:299-301). Chemical analysis of these prills revealed that they contained anywhere from 5.56% iron to as

much as 42.41% however this was shown to be FeO through SEM analysis (Earl and Özbal 1996:301-302). The risk of excessive tin losses at higher temperatures in prehistoric tin extraction precludes any possibility of reducing significant quantities of iron, as shown in figure 2.22.

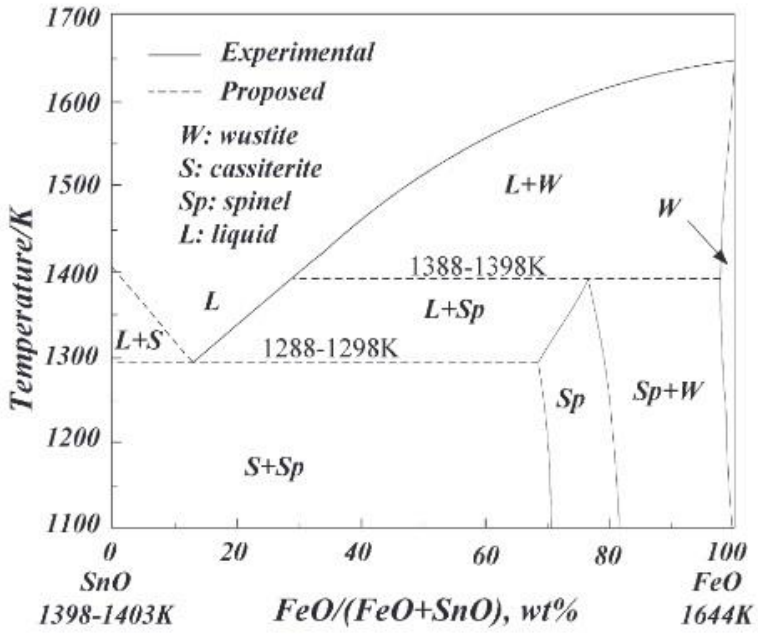


Fig.2.22: Phase diagram of the FeO-SnO system in reducing conditions (CO_2/H_2 9:1). SnO is rendered liquid from 1288-1298K while wüstite only begins to form from 1388-1398K (1100°C) or at >80 wt% FeO. Thus volatilization of SnO starts well below the required thermal parameters for the extraction of metallic iron. Taken from Su et al. (2016:257).

2.14: *Getting iron in: how did iron enter LBA smelting operations?*

In this chapter, the major copper-related extractive metallurgies practised in the Bronze Age Near East have been described in terms of chemical processes and identified in the archaeological record. Of these, based upon the availability of iron in each case, the direct reduction of oxides (**2.3**-**2.4**) and the matte conversion process (**2.9**-**2.11**) are the most favourable circumstances for the potential extraction of metallic iron as a by-product. Either through intentional addition or exploitation of mixed deposits, iron-rich oxidic ores entered in considerable quantities into the copper smelting operations of the Late Bronze Age in an area stretching from Syria to the Sinai and east across to Jordan and Iran (Hauptmann 2007:48). Achieving a strongly reducing environment to reduce the copper oxides would have been the sole objective of these smelts and may well have become sufficient to reduce the iron present. Conversely, matte smelting was employed for perhaps the most intensive metal production of the period such as on Cyprus and in the south Caucasus (Gilmour et al. 2020; Knapp and Kassianidou 1998). Though iron was present in substantial quantities it was contained in sulphides, requiring lengthy oxidation through roasting or re-firing to remove the sulphur (Hauptmann 2020:271). Under these conditions, iron was more likely to become oxidized and enter into the slag before it could be reduced, which was likely the case in dead roasting where a copper oxide was produced before being reduced (Rostoker et al. 1989). For the other processes described here (co-smelting of sulphides, speiss, lead and tin production), these can be characterised by low iron contents and weakly reducing conditions either to avoid volatilization of intended products or from an undeveloped process, making the co-extraction of iron very improbable. Copper oxide and copper sulphide smelting, as the most promising candidates for the co-extraction of metallic iron, will be the focus of this thesis. The physical conditions employed in both processes in terms of temperature and reduction-oxidation (physical in terms of partial pressures of gasses caused by temps, forced or natural draught in the furnace) are discussed in the following chapter and compared to the base requirements for the reduction and extraction of iron from its oxides.

Chapter 3.

3.1: *The extractive metallurgy of iron*

Before addressing the potential for the extraction of iron during Late Bronze age metallurgical operations it is important to define the physical and chemical requirements for the reduction of iron from its oxides into metallic iron. The thermodynamics and kinetics of reduction for iron can be determined in accordance with its atomic structure (Greenwood and Earnshaw 1997:1074-1116). Its 26 electrons are arranged in the $(Ar)3d^64s^2$ configuration and the 3d and 4s electrons are close in terms of energy. This results in four unpaired shells in its three d sub-shells which makes it substantially more reactive than copper which only has one s-orbital electron free with filled d-electron shells making it unable to form metallic bonds with a covalent nature. It is this difference that causes iron to be significantly harder to reduce than copper from its oxides, requiring higher partial pressures of carbon monoxide and greater temperatures before the oxygen will dissociate from the metal. The melting point of iron at 1538^{o}C (see figure 3.1) is lower than other 3d elements due to greater attraction of the d-electrons to the inert core by the nucleus but still considerably higher than copper (1085^{o}C) which can only form relatively weak ionic bonds with the one free electron of the s-orbital. As a first transition series element, the majority of the iron in the Earth's crust exists in various oxidation states (II-VI) but mainly as Fe^{2+} or Iron (II), 'ferrous' oxide or Fe^{3+}, Iron (III) 'ferric' oxide due to the abundance of oxygen (Hauptmann 2020:115). The low energy gap between ferrous (e.g. FeO, wüstite) or ferric (e.g. Fe_2O_3, hematite) oxidation states means that iron oxides are typically non-stoichiometric in composition with ores or products of oxidation being made up of a combination of both forms (for example in $Fe^{2+},Fe^{3+}{}_2O_4$ or magnetite) in differing proportions. In prehistoric extractive metallurgy it is the reduction of these oxides at or above 1200^{o}C, mainly through the oxidation of carbon monoxide into carbon dioxide, that produced metallic iron in the solid state (see figure 3.2).

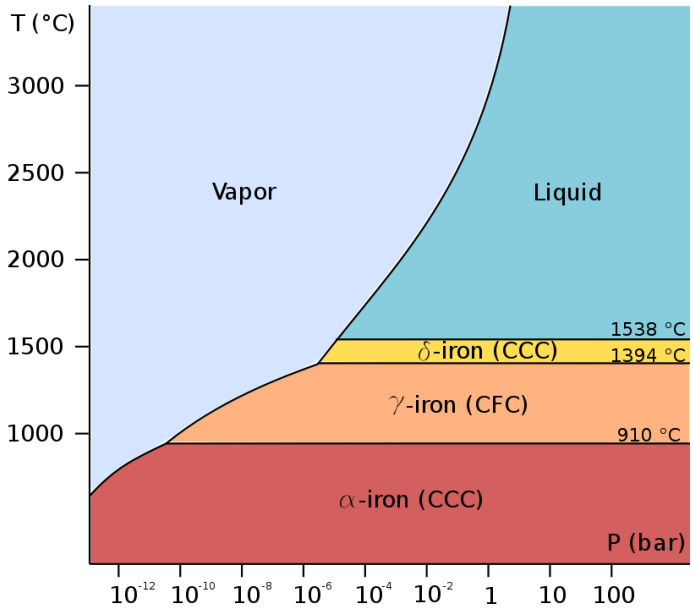


Fig.3.1: States and Allotropes of iron at temperatures up to 4000ºC and pressures over 100 bar. At prehistoric furnace temperatures of 1200ºC the iron would form into the γ-Fe allotrope, transforming upon cooling at 910ºC into α-Fe. Daniele Pugliesi, University of Palermo, Materials Science.

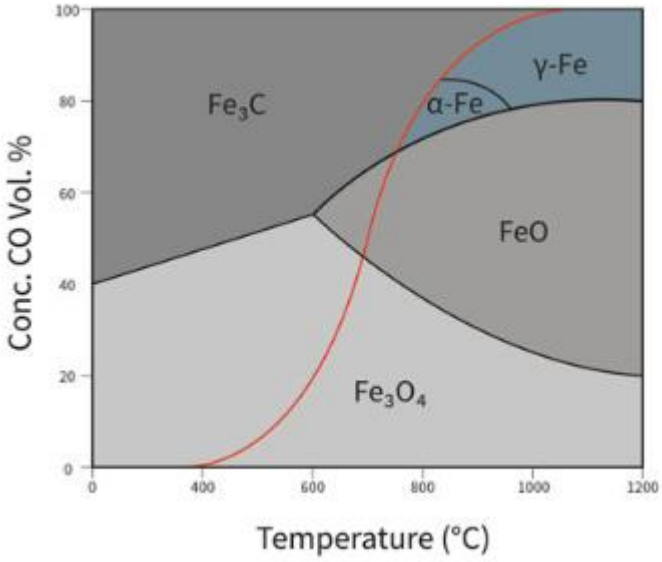


Fig.3.2: Equilibrium diagram showing phases of iron oxides up to the allotropes of iron (α-Fe and γ-Fe) and cementite (Fe_3C). The red line represents the Boudouard reaction: $CO_2 + C$ —— CO and increasing CO concentrations. Taken from Hauptmann (2020:365).

3.2:*The extractive metallurgy of iron within the contexts of a copper smelt*

As discussed in chapter two, iron could be present in significant quantities in both slagged copper-iron oxide and mixed copper-iron sulphide smelting, contributing anywhere from 10-50% of the metal in the furnace charge depending on the ore or extraneous addition (Craddock and Meeks 1987:200). The role of iron in the extraction of copper as defined in the previous chapter can be summarized as two-fold: to reduce the viscosity of by-products namely the slag and matte which lessens the chance of copper entrainment and secondly to fix some of the oxygen in the furnace through preferential oxidation (Killick 2014:32). This permitted higher temperatures to be reached without excessive oxidation allowing for better segregation of the metallic copper from the furnace contents. Both of these functions required the available iron to become oxidized, entering either the slag as various oxides such as wüstite (FeO), magnetite (Fe_3O_4) or spinels ($FeAl_2O_4$ Hercynite) or in the case of mixed sulphides to enter the matte as iron sulphide (FeS, pyrrhotite) before being oxidized in turn and entering the slag (Hauptmann 2020:312). Under sufficiently reducing conditions, which in the context of a Late Bronze Age furnace can be defined in terms of the partial pressure of carbon monoxide, these oxides are reduced into metallic iron and carbon dioxide. Direct reduction of iron-bearing ore minerals in the charge, such as hematite (Fe_2O_3) or the iron sulphide from pyrites was also a possibility however this is less likely during copper smelting for reasons given below. As the temperatures in such furnaces rarely exceeded 1500^{o}C the metallic iron would be reduced in a semi-solid state forming prills within the slag matrix and entering the liquid copper to a lesser or greater extent depending on furnace conditions (Craddock and Meeks 1987:200). Direct reduction of iron-bearing ore minerals within the gangue of mixed copper oxide or sulphide deposits into metallic iron was undesirable for the extraction of copper as it would not produce the low viscosity slags and matte that reduced copper entrainment and promoted slag-matte immiscibility in the case of sulphide smelting. The direct reduction of an iron oxide ore mineral (hematite) into metallic iron can take place at temperatures as low as 500^{o}C but in the contexts of a prehistoric furnace, the Boudouard reaction

($CO_2 + C = 2CO$) requires minimum temperatures of around 700°C (see figure 3.2) and is favoured at 1200°C (Mousa et al. 2013:1085-1088). This would produce the positive to high ratios of CO to CO_2 necessary to reduce the iron oxides (see figures 3.2, p104 and 3.5). Iron ores such as hematite are converted into multiple different oxides that co-exist in varying ratios dependent on temperature and redox conditions prior to reduction into metallic iron:

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

haematite — Magnetite

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$

Wüstite

$FeO + CO \longrightarrow Fe^o + CO_2$

metallic iron

As iron is oxidized preferentially to copper (see figure 2.5, p65) it would have required strongly reducing conditions to be maintained from the outset to extract and prevent re-oxidation of the metallic iron during a firing; such conditions would be in excess of those needed to reduce the copper ores (see figures 3.6 and 3.7). However in prehistoric copper smelting the iron ore was more likely to become oxidized into magnetite or wüstite and enter into the surrounding silica from the gangue or additional material, producing a fayalitic slag ($FeO.SiO_2$) with a high iron content. The high solubility of iron (especially ferrous oxides) in silicate slags can result in iron contributing up to more than 40 wt.% of the total mass upon cooling (Busolic et al. 2011:32-33; Schlesinger et al. 2011:75). In order to produce metallic iron, the magnetite in the slag would have to be reduced at the interface with gaseous pockets in the slag (see figure 3.4) or at the slag surface to wüstite before undergoing further reduction into metallic iron resulting in iron ‘prills’ developing throughout the slag body.

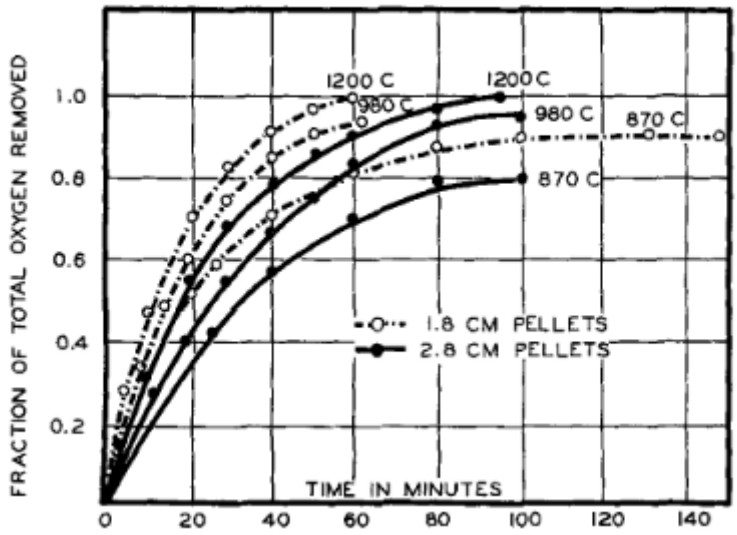


Fig.3.3: Reduction of hematite by carbon monoxide as a function of time and temperature. The hematite is totally reduced at 1200ºC between 60 and 100 minutes. Taken from Kawasaki and Walsh. (1962:49).

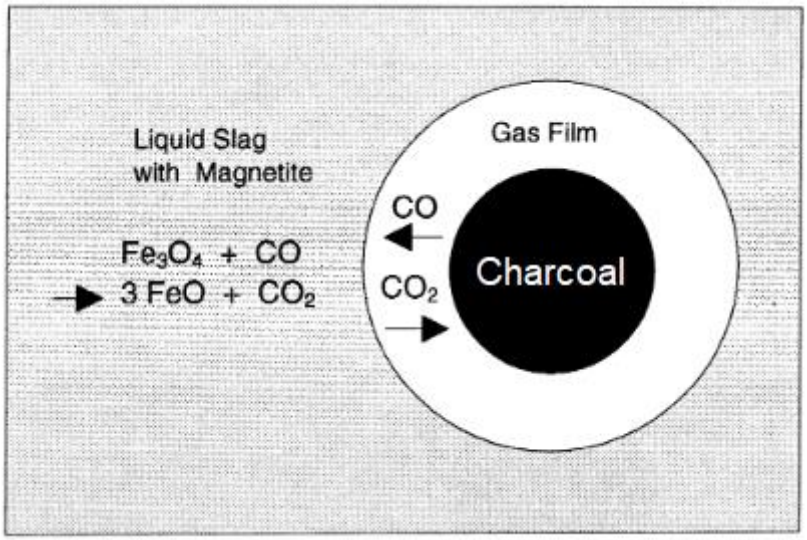


Fig.3.4: Illustration of the magnetite-wüstite interaction with carbon monoxide and dioxide at a slag-charcoal interface. Further reduction of the wüstite would result in metallic iron forming around this interface. Adapted from Utigard et al. (1997:822).

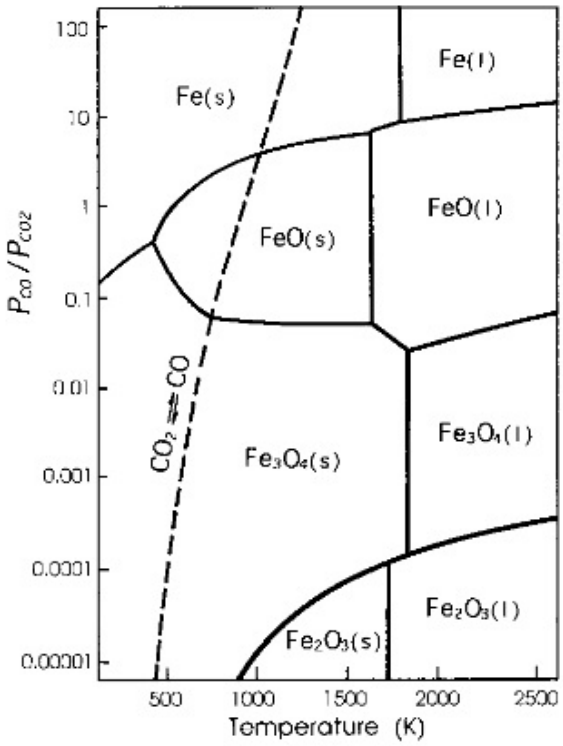


Fig.3.5: Predominance diagram identifying the most stable form of iron in an atmosphere of CO and CO_2 as temperature and the composition of the gaseous phase are varied. The dashed line applies to the equilibrium $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$ at 1 bar total pressure. The Boudouard reaction favours higher partial pressures of CO at 700°C and above at which point wüstite (FeO) and iron (Fe) precipitate. Taken from Treptow and Jean (1998:46).

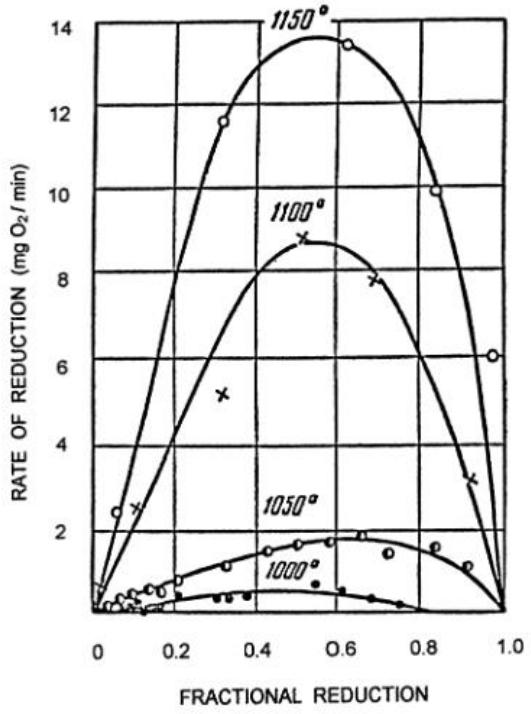


Fig.3.6: Reduction of FeO by carbon in vacuum at different temperatures (in °C). Significant rates of reduction only take place over 1000°C. Taken from L'vov (2000:112).

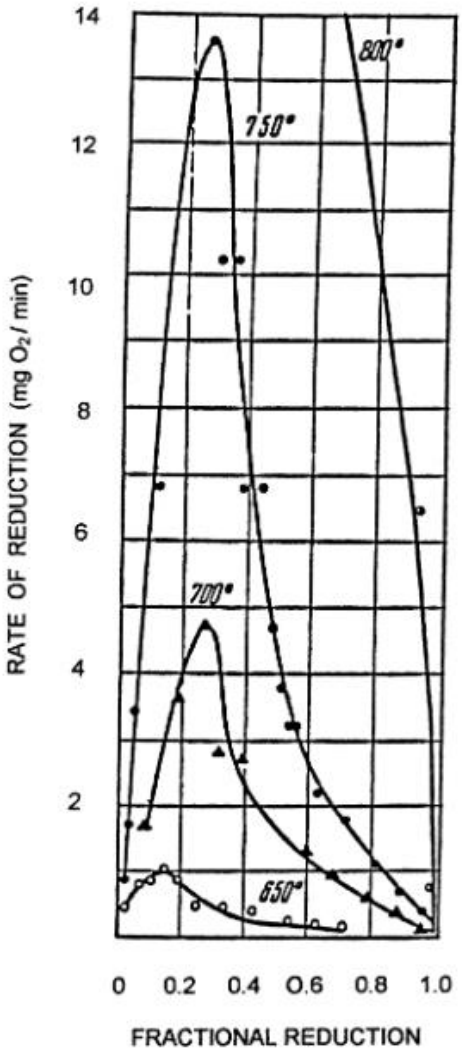


Fig.3.7: Reduction of Cu_2O by carbon at different temperatures (in Celsius). Rates of reduction at 800°C greatly exceed those of FeO, as seen in figure 3.7 above at 1150°C, demonstrating that significantly less reducing conditions and lower temperatures are required to reduce copper oxides compared to iron oxides. Taken from L'vov (2000:112).

For mixed sulphide ores, direct reduction into iron was not possible as both the copper and the sulphur had to be eliminated from the ore: firstly by thermal decomposition of the ore into iron and copper sulphides and secondly through oxidation of the sulphur (Hauptmann 2020:315-317). This could be

facilitated by heating of the ore (chalcopyrite, $CuFeS_2$) at temperatures exceeding 600^oC with sufficient oxygen to produce iron oxides and sulphides described in chapter two as roasting:

$$2CuFeS_2 + 2.5O_2 \longrightarrow Cu_2S/FeS + FeO + 2SO_2$$

chalcopyrite matte

During matte smelting the remainder of the iron sulphides become oxidized with the total removal of sulphur as a result of the similar enthalpies of formation for iron oxide (-272.04 kJ/mol for FeO) and sulphur dioxide (-296.84 kJ/mol for SO_2) (Sridhar et al. 1997a:195):

$$FeS + 1.5O_2 \longrightarrow FeO + SO_2$$

The iron oxide could then be reduced into metallic iron by carbon monoxide in the furnace. Iron oxides produced during this process likely form the primary source from which the metallic iron is extracted; though iron sulphides might also provide a source (Schlesinger et al. 2011:128). The direct reduction of iron sulphide to metallic iron would have required the presence of iron oxide, as demonstrated here:

$$FeS + 2FeO \longrightarrow 3Fe^o + SO_2$$

The formation and reduction of iron oxides within the furnace was likely more prevalent during the matte process than it was for the smelting of copper oxide ores. As the sulphide ore itself contained significant quantities of iron the proportion of iron in the charge was typically much higher than that witnessed in copper oxide smelting (Cooke and Aschenbrenner 1975:264). Secondary enrichment of the ore deposit from the weathering of associated pyrites could also increase the quantity of iron in the charge. This did not necessarily result in more frequent extraction of metallic iron during the

smelting of mixed sulphides however. Multiple stages of oxidation of the ore to remove sulphur coupled with the higher partial pressures of oxygen required to oxidize the remaining sulphur compared to oxide smelting causes a large proportion of the available iron to be converted into magnetite within the slag (see figure 3.7).

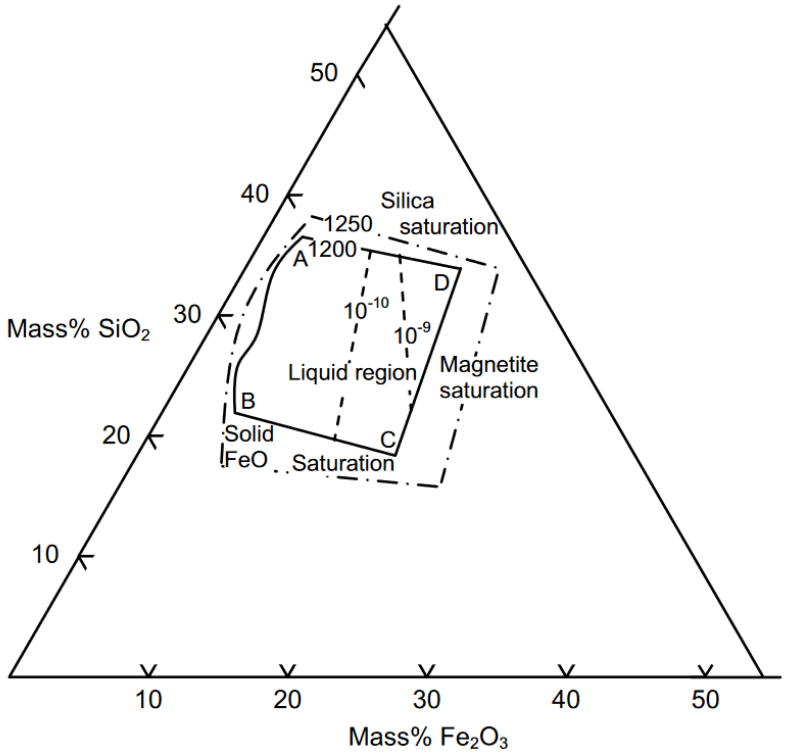


Fig.3.7: Liquidus surface in the binary Fe_2O_3-SiO_2 system at 1200°C and 1250°C. Copper matte smelting operates near magnetite saturation (C-D line). At the bottom checked boundary line the slag is saturated with solid FeO and at the right dissolved FeO and Fe_2O_3 react to form solid magnetite, encouraged by extensive oxidation at lower temperatures. Taken from Schlesinger et al. (2011:78).

3.3: *Furnace Technology of the Late Bronze Age*

The feasibility of extracting practicable quantities of metallic iron during copper smelting operations relies upon the processes of reduction and density segregation, which were determined by the limitations of Late Bronze Age furnaces to sustain sufficient temperatures and a highly reducing atmosphere across a great enough reaction volume. Furnace technologies by the LBA certainly had advanced towards greater dimensions in furnace structure and the introduction of more sophisticated forced draught systems than those observed in the preceding millennia (Craddock 2000; Kienlin 2016:129-132; Knapp and Kassianidou 2001:207-209; Wertime and Muhly 1980: 14-18). Vitrification and heat stress during firing, depositional bias and possibly the practice of destroying furnaces after their use results in the existence of very few examples of complete or semi-reproducible furnaces in the archaeological record of the Late Bronze Age Near East (Craddock 2000:158-160). This has led to the reliance upon indirect evidence from chemical analysis and survey of the associated metallurgical debris to reconstruct the scale and physical conditions employed in LBA copper smelting operations. In recent years these analytical studies have identified a number of general trends in the Late Bronze Age that appear to indicate that contemporary metal industries were capable of sustaining highly reducing atmospheres at temperatures exceeding 1200^{o}C (Gilmour et al. 2020; Berna et al. 2007; Hein et al. 2007). The discovery of increasing iron contents in copper across the late third to early first millennium BC has been cited by many as irrefutable proof that improvements in furnace technology and forced draught systems had led to the reduction of greater quantities of iron and its dissolution into the copper to form alloys, with an iron content of some copper artefacts reported as high as 8 wt.% (Addis et al. 2016:109-111; Cooke and Aschenbrenner 1975:260-264; Craddock and Meeks 1987:193-195; Craddock 2000:153). Both the reduction of the iron from the oxides and the diffusion of this iron into the molten copper required a highly reducing atmosphere and the iron content of the copper increases as a function of temperature; iron solubility in copper beginning at around 1120^{o}C (Turchanin et al. 2003:312-315). Another trend recognised in the LBA

is the production of more vitreous slags found in the slag heaps associated with smelting operations. The vitreous and globular nature of these slags, which are thought to have been produced through the practice of 'tapping' or extraction of the slag from the furnace while molten, required consistently high temperatures exceeding 1200^{o}C (Erb-Satullo, Gimour and Kahkhutaishvili 2014:10; Hauptmann 2020:233-235; Veldhuijzen and Rehren 2007:193-194). The rise in the use of tapping might also indicate a general increase in the scale of copper smelting operations, as greater volumes of ore were being smelted, resulting in an excess of slag which if left in situ would disrupt the airflow across these larger furnaces and cause the temperature to drop below efficient levels (Craddock and Meeks 1987:202; Hauptmann 2020:233). The composition of slags from the Late Bronze Age has also been related to technological advancements in furnace technology by this time. Chemical analysis of these slags has revealed the presence of larger and more frequent inclusions of metallic iron 'prills' and partially reduced iron oxides within them when compared to earlier slags (Erb-Satullo, Gilmour and Khakhutaishvili 2014:157; Rehren et al. 2012:1722-1724). The reduction of greater quantities of iron within these slags is further evidence that LBA furnaces could achieve highly reducing environments across greater volumes of the total mass of the charge. Less prominent yet convincing arguments have also been made based on the greater extent to which furnace linings from the LBA have become vitrified and fluxed by the higher temperatures sustained within the furnace (Hein et al. 2007:145-146). The evidence obtained through these analytical methods lends a great deal of support to the theory that furnace technology, especially during the 2nd millennium BC with the unprecedented deposition of some of the largest slag accumulations in the Near East, had progressed by the Late Bronze Age (Craddock 2000). Though this conclusion may appear to fall foul of technologically determinist narratives, it is worth noting that many of the consequences of these developments were, in the interests of copper smelting, fairly non-advantageous or undesirable such as the dissolution of iron into the copper and the need to tap excess slag. Archaeometallurgists have submitted numerous theories in the literature to explain the growing sophistication of furnaces during the Late Bronze

Age, the most well known being the ore depletion model critically titled ‘the Levantine paradigm’ in its application to the Near East (Thornton 2009). This argument proposes a synthetic model of linear development based upon the depletion of richer ores from the secondary zones of enrichment during the Chalcolithic and Early Bronze Age at sites in the Levant (Amzallag 2009:113-115). The exploitation of less pure and mixed zones in ore deposits resulted in the production of more slag, which necessitated furnaces that could reach sufficient temperatures to render the slag molten and separable from the copper metal (Amzallag 2009::114; Thornton et al. 2010:305). Finally the use of the primary sulphide ores in the deposits required even more extensive slag management resulting in enlargement of the furnaces and more technical sophistication in their operation. Critics of this theory have pointed out that it may serve as an idealized model in the lowlands of the Levant but cannot be applied to many other regions outside of this sphere of influence. Uplands such as in Iran or the Caucasus hosted more dispersed and isolated smelting practices and did not follow a linear developmental trajectory despite primarily exploiting sulphide ores (Thornton 2009; Thornton et al. 2010). Total dismissal of an ore depletion model as a result of these and other incoherences remains unreasonable given the lack of alternatives and the clear (adaptive) relationship between ore compositions and smelting strategies encountered in each region. Instead, a theory combining synthetic and adaptive models may prove a more appropriate contexts for the development of furnace technology from the 3rd to 1st millennium BC in the Near East.

Structures identified as furnaces dating to the Late Bronze Age have been attested to at a number of metal production sites across the Near East in Israel (Berna et al. 2007), Georgia (Gilmour et al. 2020), Cyprus (Karageorghis and Kassianidou 1999:178-180) and the Sinai (Craddock 2000; Yagel and Craddock 2016:40-42). However, the ambiguity of their form as a result of the almost complete destruction of the superstructure typical of these finds, either deliberate or through erosion, has

resulted in a range of interpretations across the literature and a reticence to recreate these furnaces until the pyro-metallurgical processes that underpinned their function is better understood (Craddock 2000:161-162; Hauptmann 2020:460-464). Identification of these structures is further complicated by the inferred multiple stages of copper production ranging from the smelting of ores to the consolidation of the copper in crucibles before casting, all of which utilized some form of furnace. Across the majority of sites, the evidence for LBA furnaces survives as bowl-like depressions or pits that can range from 10-100 centimetres in depth and from 50-100 centimetres in diameter, with superstructures formed of clay and other materials remaining only as burnt rings bordering these depressions and often lining the walls of the pit. As there are few extant examples of these superstructures the total dimensions are open to interpretation, with the deeper pits presumed to have constituted the majority of the body of the furnace and thus requiring a smaller standing structure and the shallower pits to have predominantly consisted of a superstructure to produce the depth of shaft required (Crew and Charlton 2007). The surviving evidence across all sites when taken together supports two common types for smelting furnaces of the Late Bronze Age; the shaft or super-structure furnace and the pit or sub-structure furnace.

The typical shaft furnace towards the end of the 2nd millennium BC consisted of a cylindrical superstructure made with clay, sometimes bolstered by a surrounding stone wall to which the clay would be attached, with a height between 0.5 (see figure 3.8) and 1.5 metres tall (Craddock 2000:160-163; Hauptmann 2007:244-246). The *tuyeres* had to be inserted into an opening just above the base of the furnace and would be angled at a 40-60º declination towards the base of the pit. This format had become well established in Anatolia, Spain, the Alps, Cyprus, Oman and the Levant during the 2nd millennium BC (Craddock 2000:164; Given and Knapp 2003; Hauptmann and Weisgerber 1981; Metten 2004; Rothenburg and Blanco-Friejiero 1981). As the majority of the structure was above

ground, the furnace contents could be tapped through an opening at the base down a decline into a lower pit to cool outside the furnace. The resulting slags display a distinctive flow pattern on their surface that reflects this process (see figure 3.10). The most complete reconstruction of a furnace of this type was based upon fragments found at Agia Varvara-Almyra on Cyprus (see figure 3.9) which dated to approximately 400BC but shared many parallels in the dimensions of the base and wall thickness with Late Bronze Age examples (Hauptmann 2020:304).

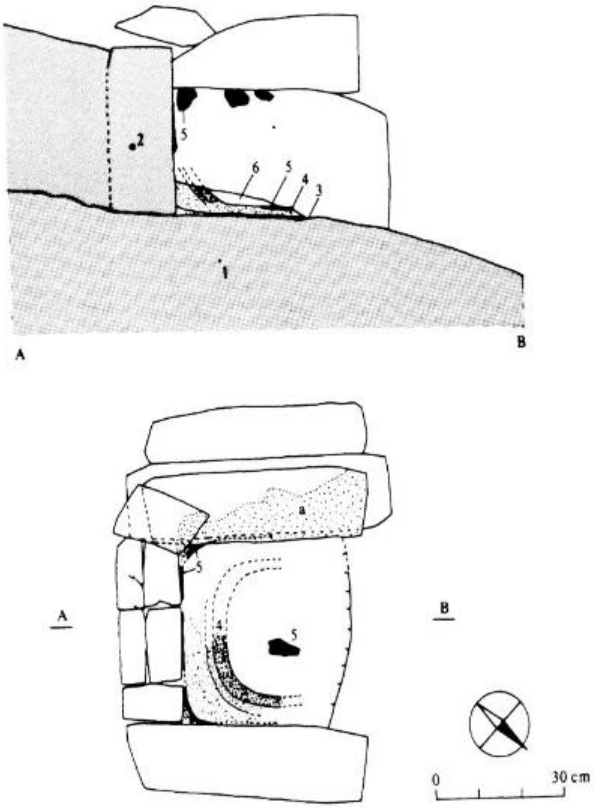


Fig.3.8: Section and plan of copper smelting furnace 7C from Wadi Dara, Egypt. Furnace height is around 50cm with a stone wall and base (numbers 1. and 2.) surrounding a cylindrical clay shaft (numbers 3, 4, 5 above and 4. in plan, below). The furnace was carefully positioned on an incline slope and better survival of the rear clay wall might be evidence of destruction of the front to tap the slag or retrieve the copper. Taken from Craddock (2000:161).



Fig.3.9: Reconstruction of a copper smelting furnace based upon fragments from a c.400BC furnace from Agia Varvara-Alymyra on Cyprus. The height was a little over one metre not including a pit at the base and the *tuyeres* would have been inserted in the opening at the base of the cone. Taken from Hauptmann (2020:304).



Fig.3.10: Copper tap slag from Zahir, Oman c.2200BC. Thin layers overlaying gas pockets and 'rippled' flow texture from successive surges of liquid slag from the furnace are visible. Taken from Hauptmann (2020:234).

Pit furnaces dating to the latter half of the 2nd millennium BC have been discovered most frequently in the Alps and particularly the south Caucasus (figure 3.11) along with a few examples from Anatolia (Addis et al. 2016; Erb-Satullo, Gilmour and Khakhutaishvili 2014; Yener and Lehner 2014). Interpretations of these structures vary across the literature with some speculating that further superstructures (see figure 3.12) encompassed the pits and others claiming they were simply dug into the substrate and lined or based with stone and clay. These pits are deeper than those encountered in examples with obvious superstructures discussed in the previous paragraph, reaching up to a depth of 0.5-1m into the subsoil with a diameter of 30cm or more. The *tuyeres* used for pit furnaces could be complicated (see figure 3.13) in order to provide air flow to the base of the furnace or angle the flow towards a crucible. Tapping of the slag directly from the furnace would have been impossible without containing the viscous contents in a crucible to be retrieved and tipped out while hot, an implausible if not untenable operation in the context of a Late Bronze Age copper smelt. Slags retrieved from pit furnaces are often of the 'cake' type (see figure 3.14) and show flow textures created by contact with surrounding liquid phases and gasses related to cooling within the furnace before being broken up to retrieve the metal.

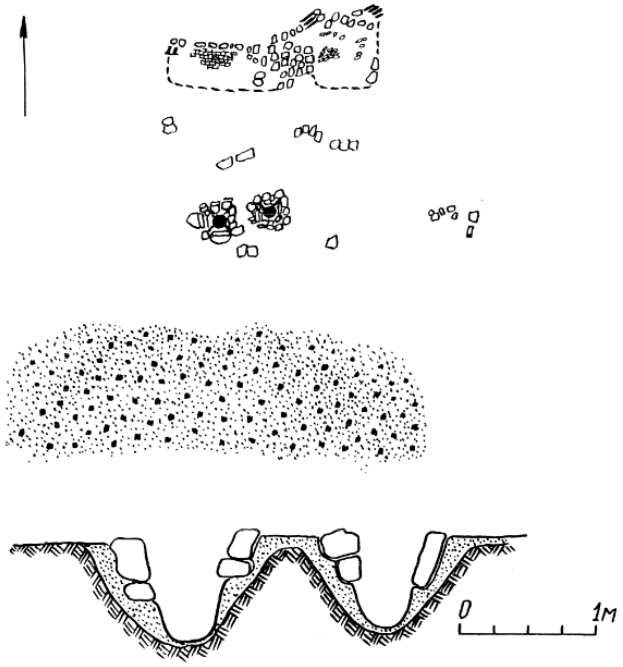


Fig.3.11: Plan and section of copper smelting pit furnaces and workshops from Charnali I, Georgia. Taken from Khakutaishvili (2009:22).

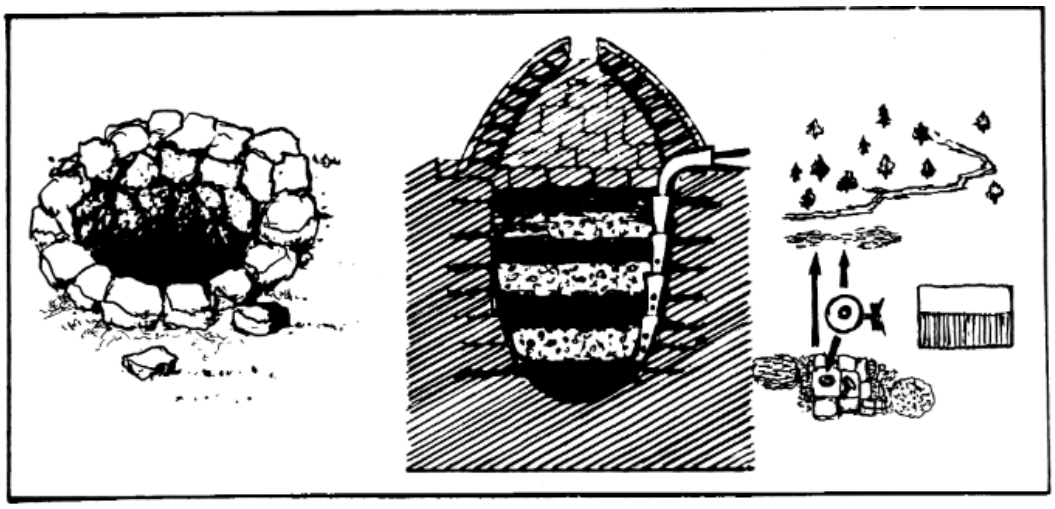


Fig.3.12: Speculative reconstruction of a Late Bronze Age pit furnace from Georgia by J.Mikekadze. The complex interlocking *tuyere* is visible entering the right side of the middle furnace image. No evidence for super-structures in these furnaces has yet been reported. Taken from Khakhutaishvili 2009:116.

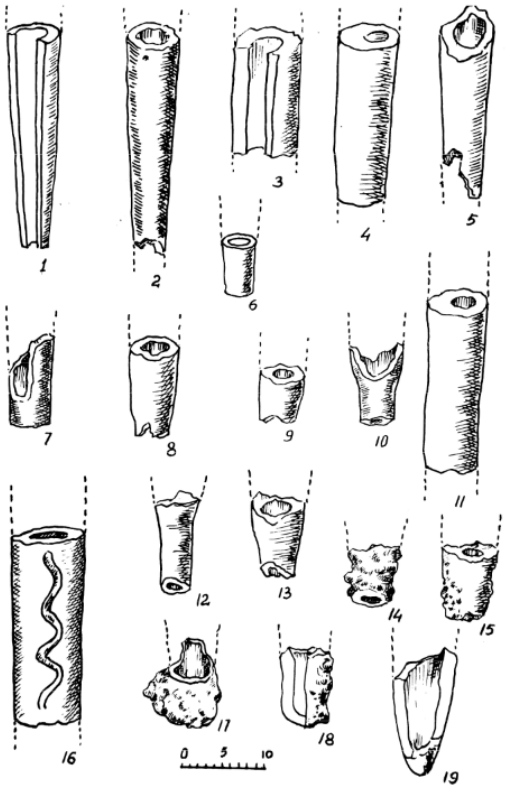


Fig.3.13: Drawings of *tuyere* fragments from copper smelting site Askana III, Georgia. Flared intersections lend some credence to an interlocking system to extend reach into the pit however this may be a misinterpretation of a mass deposition of bellow nozzles. The 'snake' decoration on 16 suggests this piece was intended to be visible during bellow operation. Taken from Khakhutaishvili (2009:63).

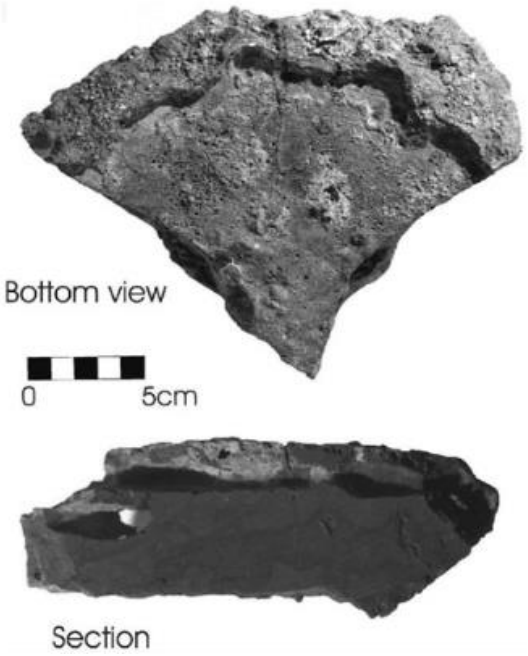


Fig.3.14: Flat slag 'cake' from the site of Politiko-Phorades (c.1650-1550BC), Cyprus. The bottom view, above, shows a meniscus where it lay in contact with a lower liquid phase while cooling. Taken from Hauptmann (2020:231).

3.4: *Bellows: a determining factor in redox and temperature?*

By determining the thermal and redox conditions within the furnace, the provision of a strong air supply without excessive oxygenation is essential for the extraction of metallic copper and iron from their ores (see figure 3.15) (Hauptmann 2020:190,297). Increasing partial pressures of oxygen in the furnace would accelerate the rate of combustion of the fuel (charcoal) and drive up the temperature, which in turn controlled the rate of reduction-oxidation by favouring the Boudouard reaction while providing the oxygen needed to produce carbon monoxide. Both the reduction of oxides into metal, and the conversion of carbon dioxide into carbon monoxide by carbon is endothermic, with the metal oxides becoming less stable with an increase in temperature (Killick 2014:31). This placed a considerable demand on producing a sufficient airflow to provide heat.

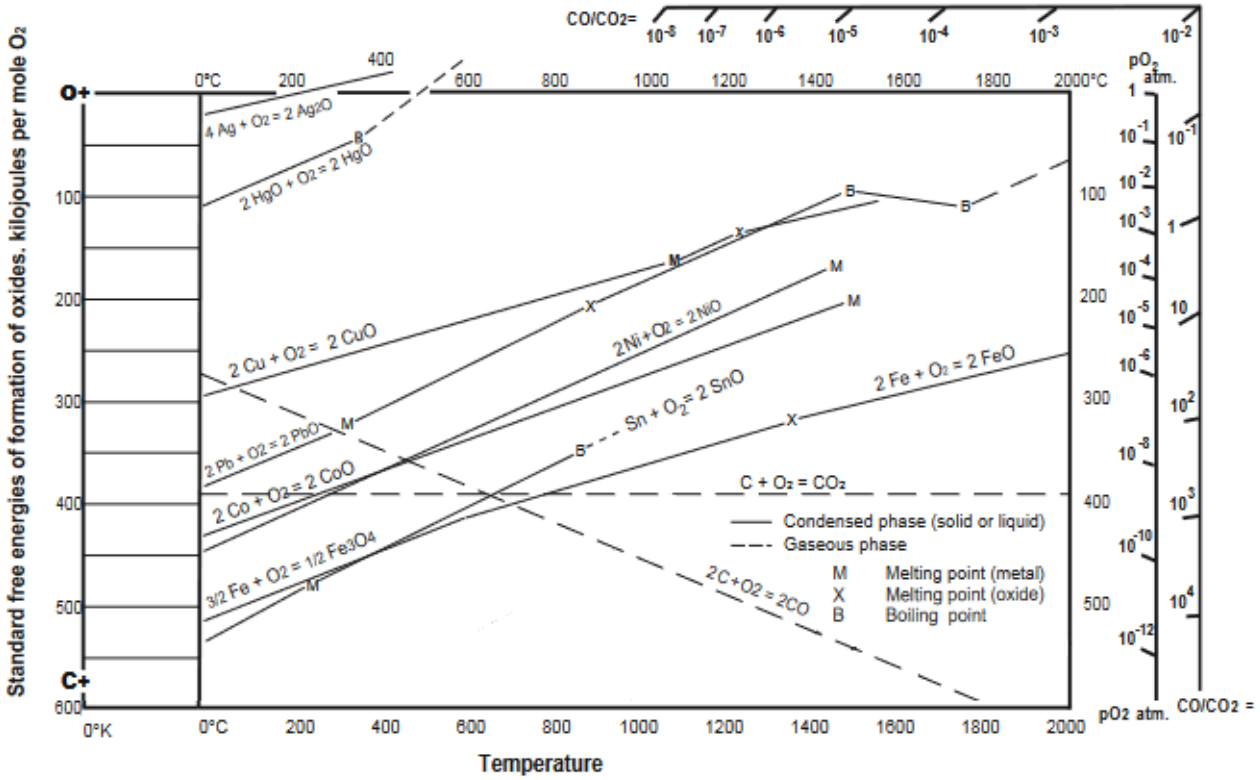


Fig.3.15: Ellingham diagram for the oxides of selected metals and carbon. Plotting a rule from **C+** marked on the *y*-axis to the intersection with the line for the oxide at any chosen temperature and across to the CO/CO_2 ratio on the right of the plot gives the minimum CO/CO_2 required to reduce that oxide into metal at that temperature. At 1200°C Copper (I) oxide (CuO) is reduced at one part CO to 10^3 parts CO_2. At the same temperature, FeO requires five parts CO to 1 part CO_2, a substantial increase. In a prehistoric furnace, this ratio is controlled by the endothermic Boudouard reaction, shown as the negative-sloped dashed line labelled 2C+O2=2CO. Above 700°C, where this line intersects the reaction of carbon and oxygen to produce carbon dioxide, carbon monoxide becomes more stable than carbon dioxide and its partial pressure increases with temperature. To extract metallic iron the airflow into the furnace had to be sufficient to maintain temperatures over 1200°C to favour two endothermic (heat absorbing) reactions: the Boudouard reaction to increase partial pressures of CO and reduction of the oxide by lowering of its stability (Adapted from Killick 2014:30).

As shown in figure 3.15, the pre-requisite conditions for reducing copper oxides require less airflow into the furnace to achieve and could have been provided through human lungs or natural draught i.e.

wind (Killick 2014:31-34; Rehder 1994:346). However by the Late Bronze Age, metal producers in the Near East appear to have recognised technical advantages to achieving temperatures in the furnace reaching and exceeding 1200^{o}C: liquefaction of the furnace contents and increasing the reaction volume (Killick 2014:32-33). By exceeding the melting points of copper (1085^{o}C) and fayalitic slags (1200^{o}C) the mobility of both could be greatly improved, allowing greater density segregation and consolidation into phases upon cooling (Hauptmann 2007:179.246). This would aid in recovery of the copper metal which would not be dispersed throughout the furnace or entrained in the slag. Increases in reaction volumes were a consequence of the adoption of shaft and pit furnaces discussed in **3.3**. These reaction vessels were of greater dimensions than the shallow bowls or crucibles used prior to their adoption and required higher rates of air intake to combust and react the greater mass held as their contents (Craddock 2000:162). The drive to exploit these technical advantages may have been the impetus behind the development of bellows with the unintended outcome of creating more intensely reducing conditions sufficient to extract metallic iron from its oxides.

By the Late Bronze Age intensification of copper production had necessitated the development of forced draught systems with the introduction of bellows and *tuyeres* to direct the blast into the furnace (Craddock 2000:162; Hauptmann 2020:303; Kassianidou 2011). Vitrified *tuyere* fragments begin to appear at sites from the early 2nd Millennium BC and have been found in huge quantities in the metallurgically active regions of Cyprus (Politiko-Phorades), Israel (Wadi Arabah mining complex), the Sinai (Bir Nasib), the south Caucasus (Supsa-Gubazeuli landscape) and over a wide distribution in the Near East (Erb-Satullo, Gilmour and Khakhutaishvili 2014:8; Hauptmann 2020:303; Kassianidou 2011). Though the majority of bellows being produced from organic materials (animal skins) do not survive, evidence for ‘pot bellows’ from Cyprus and the Near East (see figures 3.16 and 3.17) while contentious demonstrates a range of bellow technologies had emerged by this point

(Davey 1979,2021; Kassianidou 2011; Yahalom-Mack 2019). Experimental reconstructions of pot bellows in Sudan, based upon Near Eastern examples by Davey (1979), were reported by Humphris et al. to deliver up to 3 litres of air per stroke estimated on their volume at maximum extension of the hide (2018:405). As these pot bellows were used to smelt iron ore and produced small iron blooms, they clearly provided sufficient air to reduce the iron to some extent (Humphris et al. 2018:406-408). Bellow technology had likely developed in tandem with furnace technology as the greater interior volumes of the furnaces demanded an increased airflow to combust the contents. By far the greatest proportion of bellows and *tuyeres* found at Bronze Age sites are in situ with copper smelting workshops (Hauptmann 2020:303).



Fig.3.16: Ceramic pot bellows from Pancyprian Gymnasium collection. Kassianidou (2011:43).

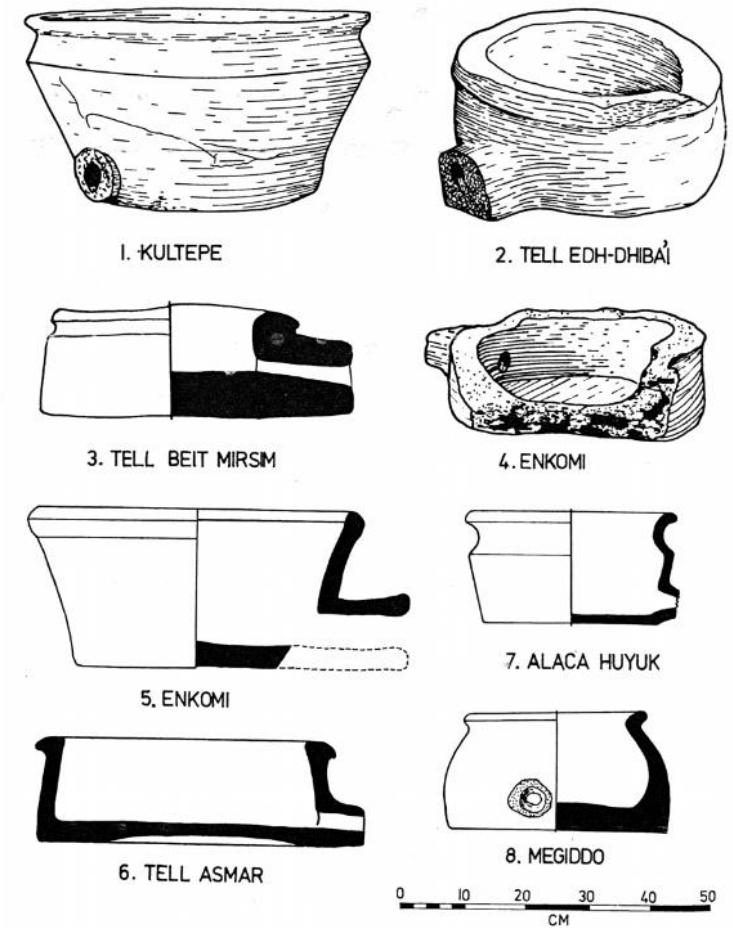


Fig.3.17: Illustrations of Near Eastern pot bellows based on ceramic fragments. Taken from Davey (1979:104).

1.Anatolia, ca.1800BC 2. Iraq, ca.1750BC 3. Israel, ca. 1550BC 4. Cyprus, ca. 1300BC 5. Cyprus, ca.1100BC 6. Iraq, 1860BC 7. Anatolia, 1700-1500BC 8. Israel, LBA-EIA.

As a significant development over lung-powered draught, it is tempting to link the emerging use of bellows in the 2nd millennium BC with the rise of iron contents in contemporary copper alloys (Craddock and Meeks 1987; Rehder 1994:345). While undoubtedly it may have been a contributing factor, it was not until iron was introduced into the furnace in the form of extraneous oxides or mixed sulphide ores that it became available in large enough quantities to be reduced. These practices became established along with the use of the furnace, which itself may have been the determining factor in the development of bellows (Killick 2014:31; Rehder 1994:349). The co-extraction of iron was more likely the result of the convergence of all of these inter-related practices during the 2nd millennium BC in the Near East and may have been unanticipated by smelters.

3.5: *From Theory to Practice: the recovery of metallic iron from a copper smelt.*

As discussed previously, iron oxides were present in substantial quantities during the majority of Late Bronze Age copper smelts, constituting up to a fifth of the total mass of the charge (Craddock and Meeks 1987:191). Reduction of iron oxide requires a carbon monoxide pressure in the order of 0.75 P_{CO}/P_T- (partial pressure of carbon monoxide divided by sum pressure of constituent gases in the reactor) (Busolic et al. 2011:623). The highly reducing atmosphere of a Late Bronze Age furnace should in theory have achieved this pressure and rendered much of the iron present into a metallic state (Killick 2014:32-34). Through the dissolution of carbon and the lower melting points of other impurities in the metallic iron including copper, prehistoric furnaces could have reduced the iron to a semi-molten state from 1200^{o}C allowing a degree of mechanical separation from the slag. Being denser than the slag or matte phases in the furnace, this iron would join the copper in the metal phase at the base of the furnace forming an alloy (Killick 2014:32). This phenomenon has been observed in both modern industrial processes and in reconstructions of prehistoric smelting (Busolic et al 2011; Schlesinger et al. 2011:424; Turchanin et al.2003; Tylecote et al. 1977:309-310). In modern smelting, copper smelting slags can precipitate a Fe-1.9 Cu-5 alloy in the presence of excess carbon (Gonzalez et al. 2004). Tylecote et al. smelted oxide ores from the Wadi Arabah (see figure 3.18) both un-fluxed and fluxed with hematite to produce copper-iron alloys (see figure 3.19) containing between 0.3-2.1% Fe and 23.9-28.9% Fe respectively using a small furnace based upon an excavated example from site 39 at Timna (1977:309-311). The formation of these alloys is caused by over-reduction and would have required a strong air supply to be maintained, as demonstrated by Tylecote and Boydell (1978) in further smelts with Timna ores and other iron-rich copper smelting experiments (Bamberger and Wincierz 1990:133; Merkel 1990:84).

Table 1. Analyses of ores and fluxes used for the work on Timna ores

	Timna nodular ore	Fluxes: Hematite Typical	Hematite Analysed	Hotezel Mn ore	Sand
FeO		nil	0·7	—	—
Fe_2O_3		68·6	73·0	15·10	2·43
SiO_2	43·4	17·0	16·6	5·67	90·30
Al_2O_3	3·1	2·0	1·3	—	4·40
MgO	—	0·5	—	—	—
MnO	—	—	—	63·0	—
P	—	0·002	—	—	
S	0·54	0·17	0·17	—	
H_2O	—		—	—	
CO_2	—		—	—	
CaO	0·084	3·0	1·54	—	0·03
Cu	23·70		0·04	1·01	
Fe	7·29		—	—	
Zn	tr				
As	(500)		(100)	(12·5)	tr
Ni	0·013		0·012	—	tr
Ag	tr		—	—	
Pb	0·045		0·005	—	

( ), p.p.m.; other figures, %.

Fig.3.18: Analysis of major and trace components of the ores and fluxes used in the experimental oxide smelts in a reconstructed furnace. The Timna nodular ores originating from the karstic deposits of the Wadi Arabah notably contain 7.29% Fe, high enough to be considered 'self-fluxing'. Taken from Tylecote et al. (1977:309).

Table 2. Trace and minor element content of copper from Timna oxide ore

No.	Fe	Co	Ni	Mn	Ag	Zn	As	S
7 with Fe Flux	2·1	(62)	(200)	(10)	(500)	(400)	0·31	1·65
	23·9	(130)	(170)	(117)	(194)	(130)	0·36	—
10 with Fe Flux	0·4	(17)	(280)	(5)	(245)	(120)	0·29	1·0
	24·0	(171)	(220)	(211)	(13)	(110)	0·21	—
12 with Mn Flux	0·3	(12)	(400)	(876)	(278)	(90)	0·40	2·05
	26·6	(248)	(360)	1·52	(179)	(300)	0·23	—
13 with Fe Flux	1·2	(33)	(240)	(34)	(237)	(230)	0·29	0·55
	28·9	(213)	(250)	(288)	(109)	(300)	—	—

( ), p.p.m.; other figures ,%.

Fig.3.19: Trace and minor element contents of the copper-iron alloys produced during the experimental oxide smelts using Timna ores. With the addition of hematite flux (which contains almost 10 times more Fe than the Timna copper ores, see figure 29 above) the iron content of the copper multiplies by a factor of 10 or more. Taken from Tylecote et al. (1977:310).

It is possible that with removal of the copper from the furnace, i.e. from tapping, the metallic iron in the slags could separate cleanly and agglomerate into a spongy mass at the furnace base, accounting for the 'bears' seen in historical smelting operations (Craddock and Meeks 1987:200). Evidence for bears from prehistoric smelting assemblages is rare likely as a result of the typically shorter duration and smaller scale of these operations compared to historical smelting however a few examples such as a spongy ferrous lump from Faynan site 1 in Jordan could be infrequent prehistoric counterparts (Hauptmann 2007:208). The discovery of the majority of these masses in waste deposits suggests they were not exploited for metal and were treated as technical 'accidents', a conclusion shared by Sperl in an assessment of Late Bronze Age metallurgical debris in the Alps region (1980:214). However typically upon cooling and the reintroduction of oxygen at the end of the smelt, the remainder of the iron still trapped in the slag or matte phases is rapidly re-oxidized, precipitating from the slag as fayalite, magnetite and other oxides (Busolic et al. 2011:32; Fan et al. 2015:2059; Schlesinger et al.2011:78). Production of copper-iron alloys was therefore more likely and is attested to by a number of Bronze to Iron Age smelting assemblages from sites across the Near East such as Faynan, Timna or Nichoria in Greece (Cooke and Aschenbrenner 1975:251; Hauptmann 2020:357). Evidence for copper-iron alloy production can also be related to the rise in iron contents of copper artefacts from the Middle to Late Bronze Age discussed in chapter one, with the trace amounts of iron being remnants of dissolved iron from the furnace smelt (Craddock and Meeks 1987:187-188; Killick 2014:32).

Assuming that a copper-iron alloy had formed at the base of the furnace, the final product retrieved from the furnace would actually consist of copper with metallic iron inclusions that would precipitate from the alloy during cooling (see fig 3.20). Iron dissolves in copper at 1450^{o}C however the near total miscibility gap causes the metallic iron to separate from the copper into solid phases below this

temperature (see figure 3.21). At the average maximum temperature of 1200°C estimated for an LBA furnace only around 6% iron is dissolved in the copper. At 1100°C the copper already contains as little as 2.8% iron in solution with a precipitated solid phase in the ratio of 28.5/1 copper to γ-Fe. At 1090°C an isothermal reaction (peritectic) between the liquid copper alloy and precipitated iron occurs to give a solid solution containing 96.0% Cu and 4.0% Fe. Around 35% of the already precipitated iron therefore has reacted with the copper assuming an initial 6% iron content in the melt. This process is extremely gradual as it takes place across the peritectic boundary between the precipitated γ-Fe and the molten copper but in the contexts of a furnace smelt it could be completed, resulting in fine dispersal of γ-Fe throughout the melt (Cooke and Aschenbrenner 1975:259). At this temperature the alloy is completely solid and re-precipitation of γ-Fe would proceed as it cools. By 835°C the γ-Fe contains 3.5% copper and below this temperature is transformed into an α-phase with the precipitation of the remainder of the copper in solid solution (Cooke and Aschenbrenner 1975:259; Hansen and Anderko 1958). Finally at 759°C the paramagnetic α-iron is transformed to ferromagnetic α-iron resulting in the magnetism of copper-iron alloys. Though the peritectic reaction of the copper and γ-Fe would rarely be total within the contexts of a prehistoric smelt, the dispersal of the iron throughout the copper to a lesser or greater extent hinders any attempt to recover workable metallic iron from such alloys through mechanical means.

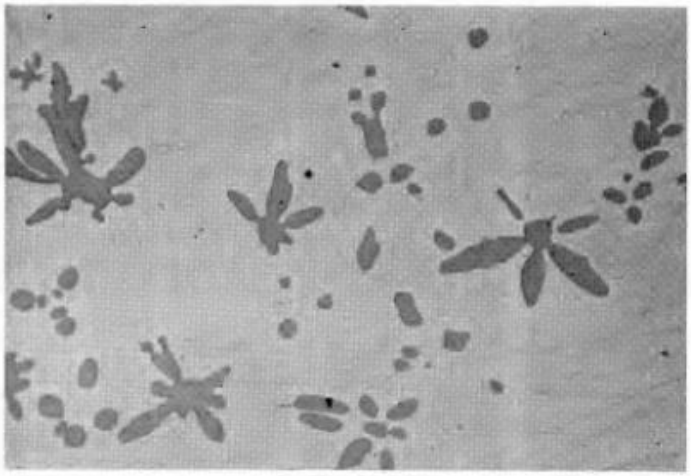


Fig.3.20: Dendritic and spheroidal α-iron (dark grey) in copper, x120 magnification. Taken from Cooke and Aschenbrenner (1975:258).

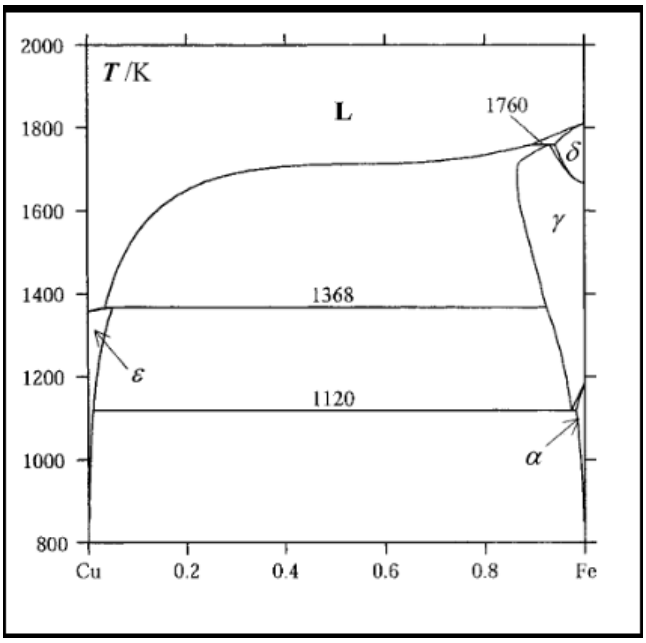


Fig.3.21: Copper-Iron phase diagram based on a thermodynamic model with optimized set of paramaters. The temperature range for a prehistoric furnace is 800-1200°C across which there is total copper-iron immiscibility. Iron on the right forms a γ phase from 1120°C before transforming into an α-phase at lower (1090°C) temperatures. Taken from Turchanin et al. (2003:315).

Recovery of practicable metallic iron was therefore dependent upon the elimination of copper from the iron. In both modern industrial operations for recovery of iron from copper slags and historical processes this could be achieved with further heating in the presence of carbon (Busolic et al. 2011:33; Tylecote et al. 1977:331). This process is facilitated by very low solubility of carbon in copper in contrast to the solubility of both copper and carbon in the iron-rich alloy. The solubility of copper in the alloy decreases with increasing carbon content (see figure 3.22), driving out the copper and leaving relatively pure α-iron (see figure 3.23). The molten copper could then mechanically separate from this iron to leave a porous mass of iron in solid state not unlike a bloom encountered in prehistoric iron smelting.

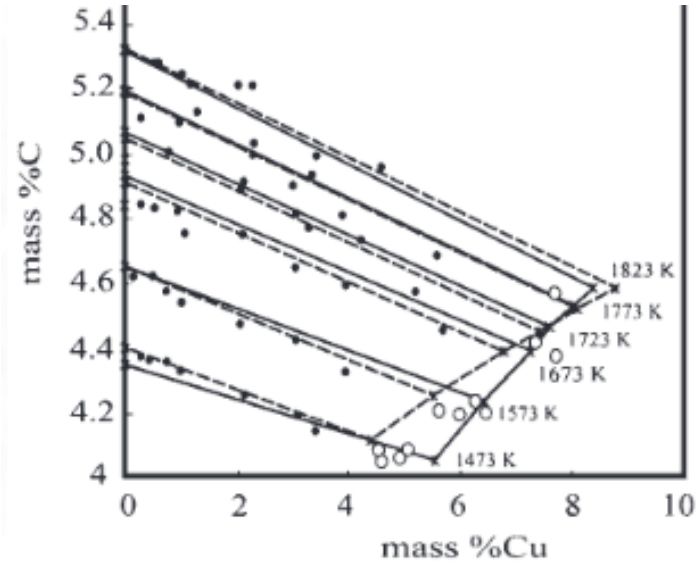


Fig.3.22: Solubility of carbon in the Fe-Cu-C system as a function of copper content at given temperatures. At the bottom line of 1473K (1200ºC), around the expected maximum temperature of a prehistoric furnace, copper content decreases from around 6 to 0% with an increase of carbon from 4 to 4.4 %. Taken from Busolic et al. (2011:33).

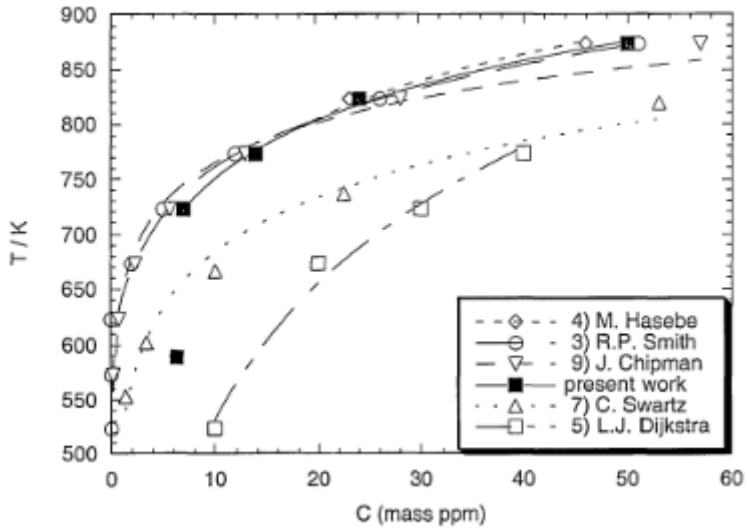


Fig.3.23: The solubility of carbon in α-iron in equilibrium with cementite (Fe_3C). In the expected range of 900 K (626ºC) and over for a prehistoric furnace, carbon solubility levels off to around 50 mass ppm or 0.5% mass carbon in the iron upon cooling. Taken from Bonnentien and Bigot (2000:78).

Modern industrial processes for the recovery of iron from copper flash smelting slags have exploited this reaction mechanism by heating slags to working temperatures of 1450^{o}C with the addition of coke or carbon monoxide gas producing a copper rich iron alloy through selective reduction (Busolic et al. 2011:35; Sanchez et al. 2004). This alloy is then further reduced with the addition of coke in a second step forming two metal phases, consisting of an iron rich alloy containing 97% iron and 3% copper and a copper rich alloy containing 95% copper and 4% iron. With the addition of 75% of the stoichiometric carbon required to reduce the iron the copper content in the metal phase decreases to 13-18% and with the addition of 150% of the carbon this falls to between 6-20% (Busolic et al. 2011:35). Through this method iron with a purity of up to 98.1% can be obtained from a copper-iron alloy (Sanchez et al. 2004). The extent to which this can be achieved within a prehistoric furnace is highly dependent upon the presence of carbon (carbon monoxide) which acts as the rate limiting factor in the removal of copper from the iron and sustaining temperatures to allow mechanical separation of the two metal phases. As the density of copper (8,944 kg/m^3) is not an order of magnitude much higher than iron (7,860 kg/m^3), density segregation is very gradual especially given that the iron remains in solid state. Clean separation of the iron and the copper would require a long duration of the firing exceeding the time needed to reduce and consolidate the copper. During cooling, the reduction of the air flow would also lower temperatures and the partial pressure of carbon monoxide allowing some re-uptake of the molten copper into the solid iron. Production of iron from matte smelting of mixed sulphides would be even more difficult requiring the elimination of sulphur, which is both deleterious to the properties of iron and greatly increases copper solubility in the Cu-Fe-S system (Kitakaze et al. 2018:61). High sulphur content in iron produced a material termed hot short, which upon heating would fracture along grain boundaries. The extent to which copper-iron alloys can be cast or worked due to the irreconcilable melting points of the two metals is also dubious (Craddock and Meeks 1987:201). Thus it seems improbable that a suitably pure iron for working could be produced from a single copper smelting procedure. Tylecote and Boydell demonstrated this

in the contexts of a prehistoric furnace when they took a 2:1 copper-iron alloy from a smelt using fluxed Timna ores and melted it in a crucible with crushed charcoal. (Tylecote and Boydell 1978:49-54). They were able to isolate metallic iron with only 0.5% copper and worked it into a 400g billet. Similarly, Shell was able to produce a small quantity of metallic iron from a small scale two step matte and alloy smelt in a crucible (1997:122-123). Historical precedents for the production of iron from copper smelts are rare with one example of an iron bloom documented at the Mamluk (1250-1500AD) copper smelting camp at El-Furn in Jordan and also a description of the process by Georgius Agricola in his treatise on 16th century metalworking practices *De Re Metallica* (Hauptmann 2007:207). Agricola relates to us that:

> *'But to iron ore that is cupriferous…we must break it up by dry stamps…we must also roast it, so that the other metals and noxious juices may be exhaled; and we must wash it, so that the lighter parts may be separated from it. Such ores are smelted in a furnace similar to a blast furnace, but much wider and higher, so that it may hold a great quantity of ore and much charcoal…from this kind of ore once or twice smelted they make iron which is suitable for reheating in the blacksmith's forge'* (Hoover and Hoover 1950:423).

The exact material specified in the passage 'iron ore that is cupriferous' is somewhat ambiguous though the term 'ore' seems to rule out copper slags and the later mention of 'noxious juices' likely references sulphur dioxide gas indicating that this was a method to extract iron from chalcopyrite ores. The preparation of the ore, roasting and long duration of smelting in a large furnace appear to have been necessary stages in the extraction of iron from these ores. The application of this process to prehistoric practices is limited as Agricola stresses that a 'much wider and higher' furnace is required to contain large quantities of charcoal and ore, possibly to drive up temperatures to render the iron more molten to facilitate separation from the slag and copper. Such a furnace was beyond the technical abilities of Late Bronze Age metalworkers to reproduce though the small scale extraction of iron from mixed sulphide ores using a similar *chaîne opératoire* cannot be ruled out.

Extracting iron from the furnace in a metallic form presented no less a challenge for the established metal industries of the Iron Age. The solution was to render the iron molten enough with a strongly reducing environment and temperatures of up to 1400^{o}C for a length of time over which the iron would consolidate as a 'bloom', which would attach to the furnace lining above the *tuyère* in the hottest part of the furnace (Hauptmann 2020:364). The bloom would then be taken out of the furnace at full heat and beaten or 'wrought' to expel the aggregate slag which would have remained molten (the melting point of fayalitic slag is around 1200^{o}C, although it can be lowered with the addition of neutral oxides) for long enough to remove much of the slag from the bloom resulting in a billet of workable iron with a heterogeneous carbon content (Crew 1991:24-26; Schlesinger et al. 2011:74). Assuming that a bloom could have formed within a particularly strongly reducing and hot furnace during copper smelting, it is unlikely that Late Bronze Age smelters could have successfully retrieved and worked it. The maintenance of temperatures exceeding 1200^{o}C that could both render the slag and metallic iron semi-molten over a period of segregation would have been required to produce a workable bloom of metallic iron within the furnace. Reduction of the iron oxides does not begin until the copper content of the slag has been reduced to as low at 0.5% as a result of the lower thermodynamic stability of copper oxides, until which point the iron content in the slag remains stable, so this may have required a longer period of firing than typically necessitated by copper smelting (Busolic et al. 2011:32-35; Schlesinger et al. 2011:78-79). As the primary objective of Late Bronze Age smelting was to produce metallic copper, which was reduced into a fully molten state at temperatures exceeding its melting point of 1084.62^{o}C, it was unnecessary and possibly counter-productive to attempt to extract the metal at full heat. Exposing the molten copper to oxygen would have caused some of it to re-oxidize and the only way to extract the hot dense liquid copper from the furnace would have been to 'tap' it through an opening at the base of the furnace into a declined pit. Instead, the furnace was typically allowed to cool while maintaining a fairly reducing environment to prevent re-oxidization, and the copper was removed in a solid form which could then be melted in a

crucible, allowing the slag and other impurities to settle on the surface through density segregation (Hauptmann 2020:299-300). This layer could then be 'skimmed' off the surface of the crucible leaving the metallic copper for use in casting or possible alloying to produce bronzes (Craddock 1995:34-48). Any metallic iron bloom that had formed in the furnace during copper smelting would thus have likely been subjected to cooling and re-oxidation of the surrounding environment before being discovered by the smelters. Without the expulsion of the slag through beating of the bloom at high temperatures, the iron mass would contain a large number of slag inclusions and other impurities from the furnace that would not be amenable for working. The subsequent removal of this slag would be difficult to achieve in a hearth, which would be unsuitable for bringing the iron mass up to temperatures exceeding 1100-1200^{o}C. It can be surmised that both the formation of an iron bloom during copper smelting and its extraction from the furnace during Late Bronze Age copper smelting is extremely doubtful (Killick 2014:34). How the bloomery process could have developed from the more likely production and extraction of copper-iron alloys during the Late Bronze Age remains unclear and may have resulted from the gradual elimination of copper in the ores of the furnace charge until the iron could form into a bloom without entrainment in the copper.

The production of great enough quantities of workable iron to sustain the manufacture of the considerable number of iron artefacts dating to the second millennium BC through extraction from copper-iron alloys is therefore hard to determine (Waldbaum 1999; Yahalom-Mack and Eliyahu–Behar 2015). The iron oxides would likely have had to form a considerable proportion of the total charge before an appreciable quantity of iron could be recovered and may have relied upon successive firings of the same material and the gradual accumulation of metallic iron in the furnace. The actual yield of workable metallic iron from a single smelting operation would have been diminutive, though this in many ways might be expected given that iron in the Late Bronze Age was typically used for

small scale decorative articles which expressed both the esteem in which it was held by elites and the value that it held as a metal in limited circulation (Erb-Satullo 2019:6-8; Wertime and Muhly 1980:18-21). With the manufacture of larger artefacts from iron, mainly implements of display such as daggers and short swords, from the late second millennium BC, it can be inferred that this process may have become more efficient or that the welding together of the iron from successive smelts may have provided enough workable iron to produce these objects (Pigott 1981:82-84; Sherratt 2000:97-98; Yalçın 1999:188). While the recovery of some form of metallic iron from copper smelting operations may have been plausible, the purity of the iron would have directly impacted upon its properties as a material. The principle impurities that it would become contaminated with during these smelts are copper and sulphur and both would be severely undesirable in an iron alloy. This might explain the hesitance to replace copper alloy implements wholesale with iron until the mid-1st millennium BC in the Near East as the impurities in early iron made it difficult to work (Erb-Satullo 2019:7-8).

3.6: *Getting iron out: iron extraction during LBA smelting operations*

The chapter began with a commentary on the extractive metallurgy of iron, establishing how greater physical boundaries, namely temperature and related reduction-oxidation conditions, had to be overcome to extract metallic iron when compared to copper. Pyrometallurgical developments across the 3rd to 2nd millennium BC in the Near East such as furnaces with greater reaction volumes to accommodate larger charges of ores and fuel, forced draught systems such as bellows and *tuyeres* and an increase in the proportion and quantity of iron-bearing minerals introduced into the furnace have all been identified as contributing factors towards overcoming these physical boundaries with the result of more frequent iron extraction across the period. This may correlate with rising iron contents of smelted copper alloys during the 2nd millennium BC in the archaeological record for the Near East and even the presence of metallic iron in some exceptional copper iron alloys from the Levant region (Craddock and Meeks 1987; Gale et al. 1990). Copper-iron alloys may have been an undesirable and unanticipated consequence of the convergence of technical developments in copper smelting driven by an increase in the scale and ease of production these new strategies afforded. Theoretical models for the production of iron during copper smelting should not be conflated with the actual results of prehistoric smelting which can be highly inconsistent with variable conditions and sub-optimization being introduced through differences in skill, perception and local materials and resources (Pleiner 2000). The reduction of iron was also considerably more difficult to achieve in the contexts of prehistoric furnace smelting and technical investment into reaching and maintaining sufficient conditions was largely unnecessary for the production of copper. The evidence presented over the previous chapters appears to affirm that the necessary chemical and physical pre-requisites for the extraction of iron had been achieved within the contexts of Near Eastern copper smelting in the 2nd millennium BC. In the following chapters this hypothesis will be tested in a series of experimental reconstructions informed by the evidence presented here regarding Late Bronze Age smelting practices in the Near East.

Chapter 4.

4.1: *Experimental design: the case for an inductive approach*

Essential to our understanding of the earliest production of iron in the Late Bronze Age Near East is to establish whether metallic iron could have been extracted during copper smelting operations. In chapter one, an appraisal of the archaeological evidence for metallic iron in association with copper smelting in the region revealed that at present it is insufficient to address this question. Given the absence of evidence for the extraction of iron it is necessary to recreate the conditions of contemporary copper smelting and reproduce a metallic assemblage on which to base a conclusion. This approach can be characterised as inductive and it is for this reason that an experimental methodology was adopted. Ethnography, while a viable alternative for testing archaeological theory in a dynamic setting, is primarily useful in exploring the environmental and social contexts behind technology (Ferguson 2010:2). In corroboration with experiment this can produce complimentary research which can reveal technological, social and environmental aspects of past material cultures, such as the study of iron smelting techniques in Tanzania undertaken by Schmidt (1978) described in chapter one, **1.6**. The use of ethnographic sources was not appropriate for this study as it was important to recreate as close an approximation of the conditions experienced in Late Bronze Age copper smelting as possible in order to estimate the real outcome of such operations in relation to iron production. Introducing variables not derived from the archaeological record and taken from ethnographic sources may have obfuscated this outcome, especially given the lack of close contemporary analogues in modern day copper smelting. The application of the singular social and environmental contexts that could be explored in ethnographic sources to the vast diversity encountered across the Late Bronze Age Near East is also very limited. In inductive experiment, where the objective is to produce a hypothesis based upon the outcome of specific circumstances or conditions, strict control of variables to test the assertion made in an initial hypothesis is not necessary

(Schenck 2011:90). Actualistic experiments are thus ideally suited to the inductive process where less control over a greater number of variables is expected or probable and the emphasis is placed upon reflecting the actual materials and conditions that constituted past operations. Another key advantage is the generation of a complete production assemblage for analysis, which are rarely if ever recovered intact in the archaeological record (Ferguson 2010:3; Outram 2008:3). The successful employment of actualistic experiment to inductively resolve a technological question is exemplified in the serial smelting experiments conducted under Peter Crew at Plas Tan y Bwlch, Wales (Crew 2013). Spanning several decades from 1983 to 2007, up to 100 iron smelting and iron-working experiments were carried out to produce slags for comparison to Iron-Age slags recovered from local excavations (Crew 2013:25). As these experiments sought to infer the conditions under which the excavated Iron-Age slags formed, they represent one of the most substantial attempts at inductive archaeological experimentation to date. Both primary and secondary production of iron was investigated, with experiments for bloom refinery utilising the iron blooms produced from the iron smelting experiments, offering an insight into a process that would not be possible without this co-ordination between experiments (Crew 2013:36-37). The techniques and furnaces used were based upon prehistoric and medieval examples with many of the participants drawing on knowledge gained directly from excavations of iron-working sites in the area for instruction. Integration of this data with previous experimental and historical work allowed for more accurate reconstructions of the technology which was crucial for producing a slag assemblage that correlated closely with the slags from excavated sites (Crew 2013:25-29). Perhaps the most striking aspect of this experimental work was the emphasis upon repetition, with 50 iron blooms being produced over the course of 100 smelting experiments (Crew 2013:46-47). Though it stands as an impressive achievement, of greater significance for the participants were the frequent failures and limited nature of successes (Crew 2013:47). Crew acknowledges that: “A single experiment, successful or not, gives useful data but it is necessarily of limited value” and concludes that: “It can only be said that the methods used in

antiquity have been reproduced in a satisfactory manner when the problems...have been resolved but, above all, with a high degree of reproducibility." (2013:47). Consistent results from experiments can be expected to more closely approximate the operations carried out in the past especially from sites or among cultures that saw continuous production cycles over successive periods (Crew 2013:47; Outram 2008:4). Reproducibility is therefore a good base objective for experimental design and practice. The contribution that reflection can make towards achieving this is invaluable and Crew cites numerous mistakes, ranging from the early use of high-grade ores prior to the development of skills to make the best use of them and the miss-use of resources to explore the smelting of hard-rock ores, which was based on insufficient archaeological evidence to be helpful (2013:46). It is these considerations made in hindsight that can prove indispensable to future research initiatives while providing an insight into the production strategies of past peoples.

The experimental methodology adopted in this thesis aims to adhere to the principles discussed in chapter one, **1.4** and largely follows the pattern outlined in the series of experiments described by Peter Crew (2013), detailed above. In chapters two and three, an appraisal of the archaeological record and comparison with modern commercial and academic data was undertaken to establish the conditions that would be reproduced during the experiment to simulate Late Bronze Age copper smelting in the Near East. This included the reconstruction of furnaces of the dimensions and materials used contemporarily in their construction, which can be seen to parallel the work of Crew and his use of data derived from excavated furnaces (2013:28-29). As an exploratory exercise, a single variable was controlled across all the smelts and melting and casting of ingots: iron content either in the charge or alloys respectively. Since a controlled variable was introduced, the experiments incorporated a preliminary laboratory stage, to provide a strictly controlled basis for comparison to

the full scale smelts. Repetition, although not on the scale envisioned by the Plas Tan y Bwlch experiments, was achieved with the completion of six field smelting operations and three casting operations across which consistent results were obtained. The manipulation of the controlled variable, iron content, provided a broad spread of data suitable for comparative study which may have proven more valuable than simply repeating the process successively. Peter Crew summarised the strengths of this experimental design in the following: "The combination of good archaeological evidence, giving the basic criteria to underpin the experiments, with the results of experiments then providing data for more informed archaeological interpretations gives a 'virtuous circle.' (2013:28). It is hoped that by emulating this design the work presented here has contributed towards a 'virtuous circle' in experimental copper and iron metallurgy which can help bring resolution to an often neglected and ambiguous transitional period. The series of experiments designed and carried out to this end are summarized in Table II on page 141 and are discussed throughout this chapter.

Experiment	Charge Contents					
Crucible smelting (**CRS, Appendix A**). Methodology and analysis given in **4.2** and **5.2** Heating to 1200°C for one hour in a graphite crucible with 2kg of crushed charcoal.	**1) CRS-1** Hematite, Fe_2O_3: 1.0kg. Malachite, $Cu_2CO_3(OH)_2$: 1.0kg. Macrograph series: HM1402A		**2) CRS-2** Chalcopyrite, $CuFeS_2$: 2.0kg Macrograph series: HM1403A		**3) CRS-3** Hematite, Fe_2O_3: 2.0kg. Macrograph series: HM1401A	**4) CRS-4** Copper slag: 2.0kg. Macrograph series: HM1286B
Furnace Smelting (**CUFE, FE, CUFES)** Firing in a reconstructed Late Bronze Age furnace (**Appendix B**) for a period of 6-12 hours. Methodology and Analysis: **CUFES: 4.6** and **5.3, Appendix C, I-II** **FE: 4.8** and **5.4, Appendix CIII-IV** **CUFE: 4.10** and **5.5, Appendix D, I-VIII**	**1) CUFES** Chalcopyrite,$CuFeS_2$: 30.0kg. Micrograph series: CUFES-1	**2) FE** Hematite, Fe_2O_3: 30.0kg Micrograph series: FE-1	**3) CUFE-1** Copper (II) Oxide, CuO: 12.0kg. Hematite, Fe_2O_3: 8.0kg. Micrograph series: CUFE-1	**4) CUFE-2** Copper (II) Oxide, CuO: 16.0kg Hematite, Fe_2O_3: 4.0kg. Micrograph series: CUFE-2	**5) CUFE-3** Copper (II) Oxide, CuO: 4.0kg. Hematite, Fe_2O_3: 16.0kg. Micrograph series: CUFE-3	**6) CUFE-4** Copper (II) Oxide, CuO: 8.0kg. Hematite, Fe_2O_3:12.0kg. Micrograph series: CUFE-4
Crucible copper melting at 1200°C and ingot casting (**CUIN)**. Methodology and Analysis given in **4.12** and **5.6** **Appendix EI-II**	**1) CUIN-1** Copper/iron metal from smelt 6, CUFE-4: 2.5kg. Micrograph series: CUIN-1		**2) CUIN-2** Copper/iron metal from smelt 4, CUFE-2: 2.4kg. Micrograph series: CUIN-2		**3) CUIN-3** Copper/iron metal from smelt 5, CUFE-3:3.2kg. Micrograph series: CUIN-3	

Table II: A table of experiments including crucible and furnace smelting and melting and casting of ingots with sample series from the analysis.

4.2: *Preliminary crucible smelting* (**CRS-1,2,3,4**)

An initial series of crucible smelts were undertaken prior to the reconstruction of the prehistoric furnaces and full-scale smelting experiments which will be described later in the chapter. The objective of these experimental smelts was to investigate the behaviour of iron within crucible charges of various compositions related to copper smelting operations, when subjected to a highly reducing atmosphere at a temperature of up to 1200^{o}C. For this purpose a graphite crucible of the dimensions 12x14cm was filled with a 4kg charge and heated to 1200^{o}C for a period of one hour (see figure 4.1 and 4.4) after a 15 minute pre-heating stage in a gas burner furnace (see figures 4.2-4.3). A total of four charges of differing compositions were fired successively after cooling and removal of the previous material (see figures 4.5-4.6). The first charge (**CRS-1**) consisted of 1kg of malachite (tumbled stones, botryoidal in origin), 1kg of hematite (crushed pellet) and 2kg of crushed charcoal to simulate the smelting of oxide ores. The second charge (**CRS-2**) consisted of 2kg of chalcopyrite and 2kg of crushed charcoal to simulate the smelting of mixed sulphide ores. The third charge (**CRS-3**) was made up of 2kg hematite (crushed pellet) and 2kg of charcoal as a control for the extraction of iron within the crucible process and the final charge (**CRS-4**) contained 2kg of iron rich copper slags and 2kg of crushed charcoal to test the plausibility of extracting iron from copper slags. The crucible smelting assemblages, consisting of the copper and iron oxide smelt, the chalcopyrite smelt, the iron rich copper slag smelt and the iron ore smelt were cut into cross-sections and mounted in 7 to 10cm long and 5 to 10cm wide resin blocks to prevent further fragmentation and for ease of grinding. After mounting in resin the cross-sections were ground using wet aluminium oxide paper up to 800 grit before further grinding from 1000 to 7000 grit using wet silicon carbide paper. The cross-sections were then photographed using an inverted scope Nikon epithot to produce 1.5 objective macrographs.



Fig.4.1: Crucible filled with a charge of charcoal and chalcopyrite.



Fig.4.2: Crucible at the start of heating in the furnace.



Fig.4.3: Crucible up to temperature at 1200^{o}C after 40 minutes heating.



Fig.4.4: Crucible and chalcopyrite contents after heating.



Fig.4.5: Sintered metallic mass from malachite and hematite co-smelt.

Red-brown **c**opper 'spheres' are visible under the black oxides.



Fig.4.6: Reverse side of mass from figure 54. Light grey inclusions in the copper (red-brown) appears to be iron.

4.3: *Evaluation of experimental crucible smelts*

Though the crucible smelts were designed to act as a controlled microcosm the very limited scale and duration of each experiment made their application to prehistoric smelting processes seem dubious. After comparison to the data from the furnace smelting experiments this initial assessment was shown to be unfounded with the results closely mirroring those acquired from full scale and long duration smelting. This correlation between small scale laboratory smelting and full-scale furnace smelting experiments is borne out in the crucible experiments conducted by Tylecote and Boydell (1978) and the later furnace smelts of the same ores carried out by by Merkel (1990) which produced copper-iron alloys of similar composition (Craddock 2000:154). In all of the smelts the temperatures reached in the burner furnace, which according to an internal thermometer fluctuated around 1200^{o}C, were sufficient to render the charge into a mostly coherent hemispherical mass at the crucible base with much of the charcoal surviving as inclusions. For experiment CRS-1, the malachite had very clearly been reduced into reddish metallic copper upon cooling, with 'patches' of brassy to silver-white metal across the surface. CRS-2 was the most fragmentary assemblage and was a dark glossy black. Yellow streaks of a powdery material, identified as sulphur, formed a rim around the inside of the crucible walls. CRS-3 and CRS-4 appeared as porous black masses with charcoal inclusions, however CRS-3 retained its heat for longer and was considerably easier to remove from the crucible.

4.4: *Reconstruction of a prehistoric furnace*

Prehistoric furnaces in Eurasia have received considerable attention from archaeometallurgists since their positive identification in the late 19th century (Cleere 1972; Coghlan 1956:88). Attempts to categorise these furnaces into typologies have been met with scepticism in the literature, as these categories have been criticised as being too broad and biased by depositional factors which make interpretations of the original furnace structure contentious (Cleere 1972:23-24; Dungworth 2015; Hauptmann 2007: 246-247; Tylecote et al. 1971:245-247). Rather than relying upon the interpretation of the remains of prehistoric furnaces many studies have instead focused upon the types of slag produced by these furnaces and the process by which the slag was removed during firing (Veldhuijzen and Rehren 2007:193; Cleere 1972:22; Pleiner 1989:29-41). Tap slags, slag cakes or blocks and cinder have all been linked to various furnace functions and layouts (Hauptmann 2020:301-305). As the evidence for Late Bronze age furnaces, discussed in **3.3** p112, remains fragmentary and ambiguous, experimental reconstructions have often relied upon the more complete assemblages dating to the Iron age right up to pre-industrial examples for instance in central Africa (Childs 1991). Despite the apparent diversity in furnace construction and the methods used to remove slag, the process of smelting iron (bloomery production) remained consistent across the Iron Age up until the medieval era (Hauptmann 2020:364-365). The furnaces employed were based largely upon the well established ceramic and stone constructs employed to smelt copper in the previous millennia (Craddock 2000:162; Wertime and Muhly 1980:50). This is perhaps evidenced most clearly with the example of ca.500BC copper-smelting furnace from Varvara-Almyra in Cyprus, whose conical upstanding clay walls and *tuyere* opening just above the base closely resemble contemporary iron furnaces (Hauptmann 2020:304). The similarities were no doubt born out of a necessity of function as both operations typically required a broad walled shaft of sufficient height and depth to hold a large charge of charcoal and ore without obstruction of the passage (Craddock 2000:162; Tylecote et al. 1971; Wertime and Muhly 1980:48-51). In terms of dimensions, Iron Age shaft furnaces had a

diameter in the range of 25cm minimum up to 50cm or greater in some cases, and the depth of the shaft (the height of the furnace walls combined with the depth of the excavated pit at the base of the shaft) could range from 50 to 200cm in extreme cases (Cleere 1972:24-25; Craddock 2000:162; Crew 1991:22-23; Tylecote 1971:343). The thickness of the furnace walls depended on the materials used in their construction, but were usually found to be no less than 10cm thick as they had to retain structural integrity while enduring the corrosive process of smelting and providing insulation to maintain internal temperatures. Air flow in Iron Age furnaces, introduced through the single or multiple *tuyeres* via forced draught using bellows, has been calculated at around 0.3 cubic metres (300 litres) per minute which would sustain the combustion of the charge at a temperature of around 1200^{o}C and up to 1500^{o}C immediately surrounding the *tuyeres* (Crew and Charlton 2007; Sauder and Williams 2002; Tylecote et al. 1971; Tylecote 1981; Rehder 1994:346). The scale of iron smelting operations in terms of the total mass of the charge fired in the furnace varied depending on the purity and type of ore being reduced. Through a series of experimental smelts using shaft furnaces, Tylecote estimated that smelting a 100kg 3:1 charge of charcoal and iron ore would produce a 16kg bloom of iron which when consolidated into a billet would weigh around 10kg (1971:347). Further experimental reconstructions of these processes have yielded similar results, successfully reducing around 60% of the available iron from the ore (Crew 1991:34-35; Sauder and Williams 2002:126). Given these parameters for the construction and operation of Late Bronze to Early Iron Age furnaces; the author undertook the reconstruction of a prehistoric furnace at Wytham woods wood-yard in Oxford, with a further six furnaces built over the course of experimentation at Wytham and Lincoln following the destructive removal of the smelting assemblages from the previous structures. The furnaces (see figures 4.7 and 4.8) were constructed upon the foundations of a hole dug 10cm deep into the ground with a 45cm diameter. The furnace walls were coil built using a mixture of local clays, fine ballast and straw to produce a circular shaft with a height of 90cm and a total diameter of 70cm (see figures 4.9, 4.10, 4.11 and 4.12). The diameter of the interior chamber was 40cm and the

walls had a thickness of 15cm. A *tuyere* was cut at the base of the rear of the shaft with a diameter of 4cm and a 10cm high opening at the front of the shafts base was left to allow access to the chamber after firing. In terms of materials about 75-100kg of clay with sand and straw mixed in was required per furnace which remained consistent.



Fig.4.7: First reconstructed furnace in situ at Wytham Wood-yard.



Fig.4.8: Furnace interior.





Figures 4.9 (left) and 4.10 (right): Coil building of the furnace walls. Clay, sand and straw mixture tubes were worked by hand before being laid onto the surface and kneaded to shape, overlaying one another.



Fig.4.11: Building of the furnace base. The clay mixture tubes are visible left, with the foundations with frontal opening of the furnace laid, right.



Fig.4.12: Constructing the upper chamber. Thickness of the walls at around 10cm was maintained towards the top of the shaft.

4.5: *Furnace technology and pyrotechnical considerations*

As the only reconstructive element of the smelting experiments it was important that the materials and design of the furnace were as authentic as could reasonably be expected in a modern context (Crew 2013:28). Thus clays dug from natural deposits which were then manually prepared by stamping and kneading straw and coarse sand into the mixture were used as the structural material for the furnaces. Each furnace (there were six in total) was an entirely hand built structure using half-coils of manually prepared clay, eschewing an exact method of construction using pre-fabricated concrete rings or even a metal or wooden template to build the clay around. This introduced inconsistency across all of the structures which mostly manifested itself in the varying diameters and shape of the upper chamber furthest from the more easily and accurately measured furnace base. This did not have any clear impact upon the performance or function of the furnaces with the charcoal and ore being able to pass through without any blockages though prehistoric furnaces were probably built with more regularity of structure given the greater skill and experience of prehistoric smelters (Crew 2013:28-29). In terms of overall dimensions it is difficult to assess how accurate the height of the furnace walls can be in a reconstruction in relation to prehistoric examples which are never fully intact. Based on an interior diameter of >30cm that was defined with the laying of the furnace base a height between 70-80cm remained stable even with a wall thickness of >5cm and allowed for a conical shape without too much constriction in the upper chamber. The semi-failure to tap the slag through the entrance that had been built into each furnace may have related to the structure and the distribution of heat in the furnace. The furnace floor was always built with a steady incline (around 20^{o}) running from the exterior at the front of the furnace towards the *tuyere* at the back of the interior to promote the flow of the slag out of a frontal opening. This opening measured about 10cm wide and 5cm in height. In practice the slag had already begun to re-solidify around the front opening which greatly limited the amount of slag that could exit with no more than a few short runnels ever forming on the exterior slope. This may have been caused by the use of a removable clay ‘bung’ from the

beginning of the firing which alternately could have been emplaced after a certain duration to prevent the slag building up behind the frontal opening and cooling down. Of course this could have affected the conditions in the furnace by introducing more oxygen, driving up temperatures and encouraging more oxidation of the contents. It is also not definite whether the slag would have become hot enough to remain liquid and exit down the exterior slope simply as a result of removing a possible obstacle. Crew highlights this challenge, stating: "An important aspect is to anticipate when the furnace needs tapping and if the opening of the arch is delayed for too long, the slag can freeze in the base of the furnace, usually against the arch blocking, thus making subsequent removal difficult" (2013:31). Management of slag in the furnace was a continuous effort with blockages of the *tuyere* usually occurring in the opening few hours of the firing and requiring mechanical removal. If similar events did occur during prehistoric smelting, which most likely produced more slag by firing larger charges of ore with a higher silica content, this problem must have been much more severe. It is perhaps unsurprising that prehistoric smelters developed a much greater competency at tapping than displayed in the experiments presented here as it would have been instrumental in producing good yields and maintaining furnace function (Crew 2013:31).

The use of an electric blower was a matter of some debate at first but eventually became a necessity based on very limited manpower available for the experiments as a result of COVID restrictions. Testing of the blower with an anemometer gave a reading of 0.3 m^3 per minute which was equal to estimates for a range of ancient bellow types such as pot and goatskin bellows and even blowpipes as well as the rates estimated by other experimental smelts such as those carried out by Peter Crew in Snowdonia (Crew 2013:29-30; Kassianidou 2011; Rehder 1994). Excluding the use of double bellows attached to T-section nozzles, most prehistoric bellows would have ceased air flow at constant intervals as air was forced back into the vacuum caused by increasing the interior volume

before pressure was applied to push the air out of the nozzle and through the *tuyere*. During this downtime it has been hypothesized that the interior pressure of carbon monoxide would increase as it would not be forced upwards and out of the furnace opening by the expansion of incoming cool air (Crew 2013:43-46). This would produce more strongly reducing conditions in comparison to the constant air delivery afforded by an electric blower. A counter-argument to this might be that higher pressures of oxygen delivered at a constant rate would favour the Boudouard reaction and increase the pressure of carbon monoxide in the furnace while raising temperatures which aids in separating the furnace contents into phases. This must be balanced against greater rates of corrosion of the furnace walls which can reduce the thickness to such an extent that structural integrity is compromised and the walls no longer provide adequate insulation. In the experimental smelts the loss of a great deal of material from the furnace walls in some places (usually the area immediately above the *tuyere* and midway up the front of the furnace) left a thickness of no more than 4-5cm, a common event recognised by Crew in many of the smelting furnaces used in his experiments (2013:30-31). Extending the duration of the smelts by a number of hours could have potentially resulted in structural collapse. This led to the destruction of most of the furnaces after a single firing as they did not survive the percussive force required to fragment and remove the slags and furnace content that was fused to the furnace walls. The successful production of reasonable to good yields of metal in all of the furnaces suggests they were efficient and suitable for smelting which may be as close an approximation to prehistoric furnaces and smelting operations that can be expected given the huge disparities in perception and skill between ancient and modern smelters (Crew 2013:46-47).

4.6: *Experimental smelting of mixed sulphides* (**CUFES-1**)

For the smelting of a mixed sulphide ore (chalcopyrite, $CuFeS_2$), a roasting stage and subsequent matte smelting stage was planned based upon the findings discussed in chapters two and three. The objective of these experiments was to observe any partitioning and extraction of iron during the smelting of a mixed sulphide ore. To this end 30kg of exceptionally pure chalcopyrite, sourced from the Nussir deposit from central Norway with an estimated 7 wt.% copper content (see figures 4.13,4.15) was prepared in a preliminary roasting stage (Dhar et al.2019:382). The ore was roasted at a temperature of an estimated 600-750^{o}C within an iron container (see figure 4.14). The roasted ore was then crushed and 5kgs were mixed with 30kg of charcoal to form an initial charge which was placed in the pre-heated furnace and fired with the use of a forced draught from an electric blower. The front opening of the furnace was sealed with clay before firing. The furnace shaft was kept full with the addition of charcoal and roasted ore across the duration of the firing, and the draught was maintained for just over eight hours over which time 77kg of charcoal in total was combusted in the furnace (see figures 4.16-4.17). After this time the draught was stopped and the seal on the front opening was removed to allow slag to leave the chamber and to investigate the production assemblage following a period of cooling. The production assemblage was retrieved from the furnace after 24 hours. Initially a further copper-making smelt had been intended with the aim to extract iron during this operation however the first matte smelt met with mixed success owing to low-grade modern ores and a short duration of firing from which only very small quantities of matte could be recovered. The second attempt, detailed here, was substantially more productive with the formation of a layer of matte at the base of the furnace estimated around 3-4kg in weight. Unfortunately a copper-making experiment could not be reproduced within the time-scale available for this project.

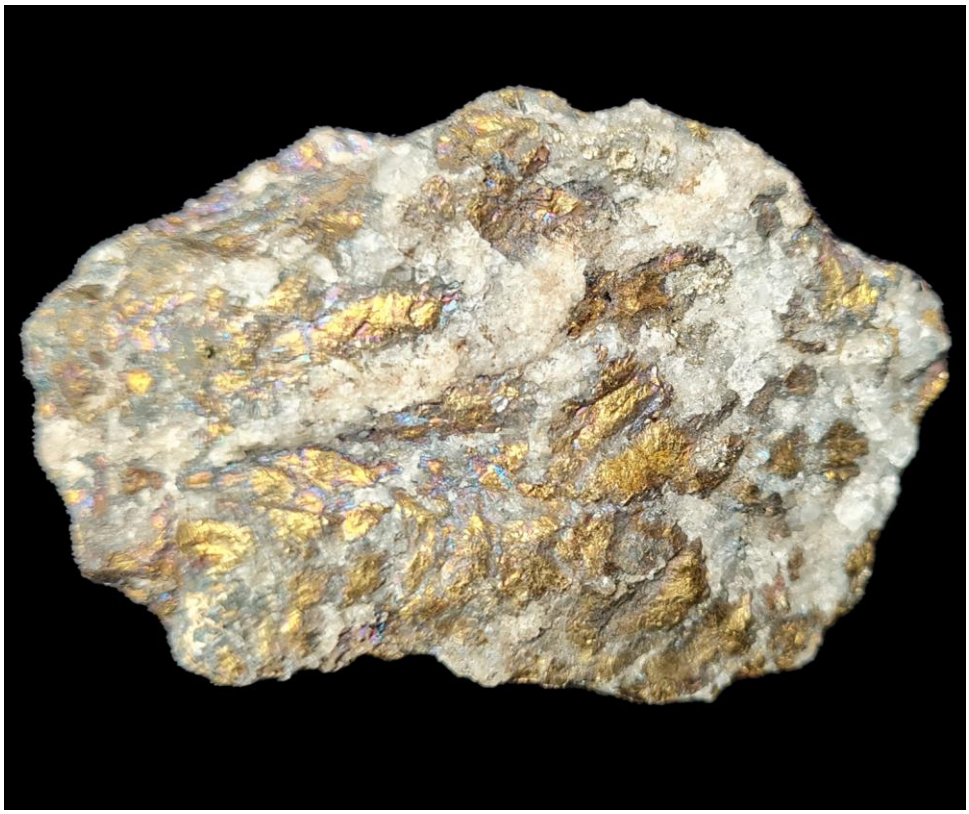


Fig.4.13: Chalcopyrite ore from Norway. Chalcopyrite (lustrous yellow) in quartz (white).



Fig.4.14: Roasting of the mixed sulphide ore.

	N-NE	N-OW	Cp	Cc	Bn
Minerals		Wt.%			
Chalcopyrite	0.02	3.5	92	3.2	2.1
Chalcocite	2.1	0.01	1.02	93.2	2.9
Bornite	8.5	9.2	0.61	1.2	90.9
Calcite	40.5	9.0	1.78	1.9	3.1
Dolomite	12.3	20.9	2.10	0.2	0.1
Quartz	12.3	29.8	0.8	0.08	-
Microline	-	5.8	-	-	-
Muscovite	5.1	4.1	-	-	-
Albite	17.6	15.1	-	-	-

Fig.4.15: Mineralogy of two Nussir ore samples (N-NE, N-OW) obtained through optical microscopy, SEM, XRD, XRF, LECOsulfur, ICP-OES methods (taken from Dhar et al. 2019).

Fig.4.16: Schedule of roasted mixed sulphide ore and charcoal addition to furnace over duration of firing.

Time (hrs:mins)	Forced Draught	Charcoal Added (total kg)	Roasted ore added (total kg)
00:00	Started	10	0
00:25		14	2
00:32		18	4
00:46		22	6
00:59		26	8
01:13		28	10
01:22		30	12
01:47		34	14
02:12		36	16
02:28		40	18
02:36		44	20
03:09		48	22
03:37		52	24
03:42		56	26
04:18		60	28
05:26		68	30 (End of Ore)
07:47		72	

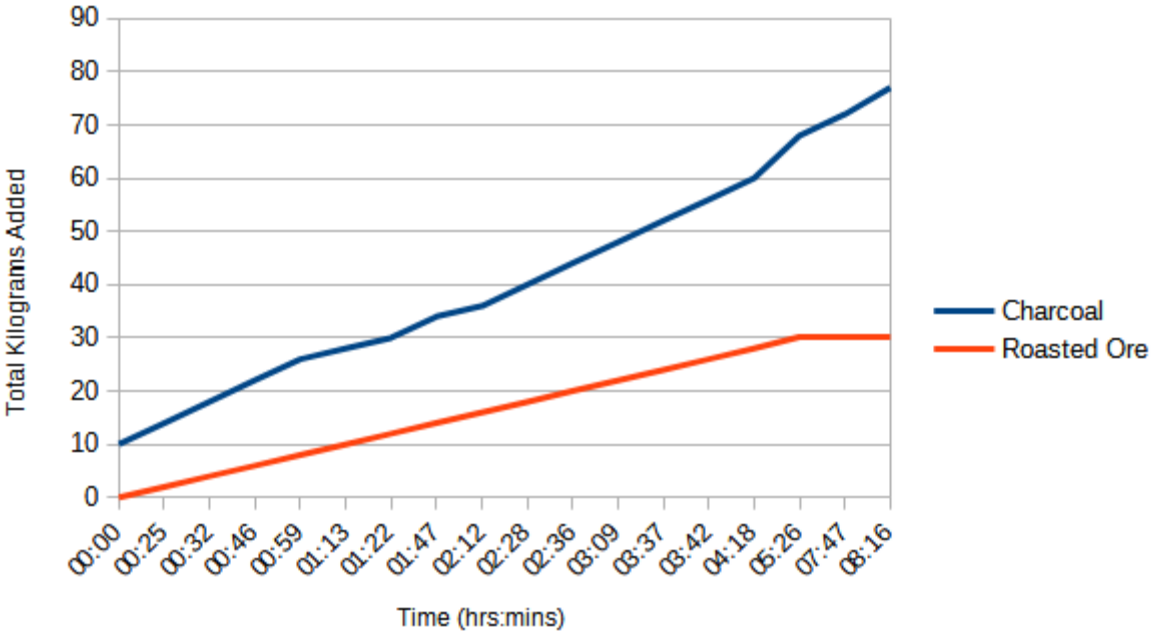


Fig.4.17: Addition of charcoal and roasted ore (chalcopyrite) to furnace over duration of firing.



Fig.4.18: Firing of the furnace two hours after ignition.

Evacuation of the furnace was carried out in two stages, with the material above and surrounding the *tuyere* removed first and the denser material below removed last (see figure 4.20). The first layer removed consisted mostly of furnace slags, vitreous furnace lining and cinder. The lower layer consisted of a more homogenous and denser 'cake' which was termed the 'matte cake' for analytical purposes.



Fig.4.19: Furnace interior following the first removal of material. The *tuyere* is located on the left of the chamber and the front opening is located on the right. The furnace lining was heavily vitrified and removal surrounding the *tuyere* was destructive. Note the green colouration of the left upper chamber; copper carbonate formation from oxidation of the copper higher in the furnace.



Fig.4.20: Slag ‘cake’ containing the matte as it lay in situ at the base of the furnace (fragment of rear wall is visible at the top of the image). The furnace walls at the base had become unusually thin at no more than 4cm, tentatively attested by the author to be the result of increased corrosion as a result of sulphur content. Could this be a cause for the frequent use of pit and stone lined furnaces for sulphide smelting in regions such as the Alps or Caucasus?

The materials collected from the mixed sulphide ore (chalcopyrite) smelt were identified as furnace slags, vitrified furnace lining, cinder and a dense slag and matte 'cake' which was retrieved from the base of the furnace. Four sections were cut from the material retrieved from the base of the furnace identified as the slag/matte 'cake' using a rock saw. These sections were then ground successively at increasing grits with wet aluminium oxide paper up to 900 grit, with a final silicon carbide 1000 grit paper used. Photographs of these sections were taken a Nikon D850 camera. Five samples measuring <3cm were then cut or removed from these sections and mounted in resin before being ground up to 1200 grit using wet aluminium oxide and silicon carbide paper. The samples were then polished using aluminium oxide powder at 1µ up to 0.3µ. An Olympus BX53M TRF-S microscope and Olympus DP74 camera were used for chemical analysis and the production of micrographs of the smaller sections.

4.7: *The smelting of copper sulphides from an experimental perspective*

The extraction of copper from sulphidic ores remains one of the most poorly understood processes in prehistoric metallurgy in spite of their economic importance as the most abundant source of copper in the Earths crust (Hauptmann 2020:45, 339). Though sulphide smelting in prehistory can be identified with a high degree of certainty based on the quantity of matte inclusions in copper slags, local sulphide deposits and also divergent slag morphologies from those found in oxide smelting; the process itself is obscured by incomplete smelting assemblages in mixed waste deposits (slag scatters and heaps) which do not clearly pertain to a particular operation or stage in extraction (Van Brempt and Kassianidou 2016; Gilmour et al. 2020). Though experimental archaeology is ideally suited to bridge the gap between a theoretical and conceptual understanding of sulphide smelting and its practical application in prehistoric operations, the extractive metallurgy of sulphides has been widely

neglected by the discipline. The reasons for this have never been openly addressed and seem mostly to relate to the perceived complexity and ambiguity of sulphide smelting which makes reconstructing the process difficult; a good example of the false and harmful assumption that experimental archaeology merely replicates past technologies rather than seeking to determine how they functioned through experimentation using a range of parameters. Prehistoric copper extraction from the smelting of sulphides thus represents an increasingly unique opportunity for experimental archaeology to address fundamental questions about a technological process that can be regarded as virgin soil as far as previous studies extend. A recent example can be found in the smelting experiments undertaken by Rose et al. (2020) based upon chalcopyrite ores and smelting technologies of the Bronze Age Eastern Alps. The objective of these experiments was to address how isotopes of copper behave during the roasting and smelting of these ores to aid in isotopic provenance studies which could link copper alloy artefacts to the more technically demanding processes required to smelt copper from sulphidic ores (Rose et al. 2020:77).

The experimental methodology chosen for the mixed sulphide (chalcopyrite) smelt presented in this thesis was designed with virtually no preconceptions of stages or distinct technical operations. The crucible smelt that preceded the full-scale furnace firing was useful in determining the suitability of the ore for smelting and the creating of a consistent phase of matte with a total absence of visible copper was an early indicator that copper extraction would require at least two firings notwithstanding other intermediate technical stages. This contrasts with Rose et al. who chose to base their experiments on the Bronze Age site of St Johann im Pongau in Austria due to the presence of well documented ‘roasting beds’ which suggested an oxidation stage was employed providing a typical example of a two-step process (2020:78). The vast differences in scale between the crucible experiment and a furnace smelt did not favour a simple upscaling of the same methodology given the

chalcopyrite could not equal the charcoal in weight across the volume of a furnace. As a result the furnace firing was mostly structured along practical lines based on the volumes of the reconstructed shaft furnace. A quantity of 30kg of chalcopyrite was estimated to roughly occupy the 30cm^3 reactor volume in the lower chamber of the furnace without producing excessive amounts of slag. This represents an increase of 50% weight in ore compared to the 20kg of ore in the charges fired by Rose et al. in pit furnaces of the dimensions 40x45cm^2 and a height of around 100cm (2020:83). An initial open roasting of the ore was carried out, which can be inferred in prehistory from the presence of roasting pits discussed in chapter two but that is also a common process in general ore beneficiation to aid in crushing and mechanical removal of some of the gangue. The ore used for the smelt could reasonably be considered authentic as a terrestrial chalcopyrite ore containing circa 10% Cu, matching the expected purities of prehistoric deposits, with quartz as the other major constituent which is frequently encountered in the majority of world sulphide ore deposits. Of course in such an ore the proportion of iron to copper is stoichiometrically determined with some fluctuation dependent on inclusions of other iron or copper sulphide minerals. Exploitation of very similar ores in the Late Bronze Age can be seen in the large quartz inclusions and partially reacted chalcopyrite ores in slags on Cyprus, the south Caucasus and the Alps (Gilmour et al. 2020; Rose et al. 2020:80; Van Brempt and Kassianidou 2016). Roasting followed no predetermined duration and temperatures could not be controlled in the contexts of an open wood fire. Rose et al. reported temperatures reaching 650^{o}C in an open roasting of chalcopyrite using dried wood obtained from readings from a thermocouple, which may be an indication of the temperatures achieved in this roasting (2020:83). The fire was allowed to take its natural course until the fuel had been combusted though observations of heat stress in the ore which created popping and cracking noises as the ore fragmented coupled with the smell of sulphur in the smoke was a progress indicator, an observation also made by Rose et al. (2020:83). It is hard to imagine much deviation from this in prehistoric practices other than in scale and duration which almost certainly would have been greater while producing the same result (Rose et al. 2020:83).

The smelting of the ore was conducted along much the same lines as experimental bloomery smelting with gradual addition of the ore with the charcoal during firing to ensure the contents were consistently brought up to temperature and the upper chamber in the furnace was not over-filled with slag or ore which could block the descent of the rest of the charge. A similar regime was adopted by Rose et al. who added ore to the furnace every 15 minutes over a 3 hour period (2020:85). The duration of the firing was not time or fuel constrained and was allowed to continue for many hours after all of the ore had been added to grant sufficient time for the furnace contents to separate into phases, with the draught ceasing after 8 hours similarly to the 9 hour blowing duration chosen by Rose et al. (2020:83). Visual or sensual cues as to the progress of the smelt came with the end of the sulphuric odour in the smoke quite shortly after the final addition of the ore and a barely perceptible greenish-yellow tinge to the flame in the final hours. Temperatures in the furnace were frequently assessed on the basis of the colour of the interior which in the lower chamber can be described as yellow to white which changed to an orange to red heat in the upper chamber. Thermocouples situated between the double *tuyeres* in the furnaces used by Rose et al. recorded temperatures of up to 1500^{o}C with thermocouples placed around the central chamber recording <1200^{o}C (2020:85). The authors initial concerns that this might exceed the temperatures that were achieved in a prehistoric furnace as a result of the constant delivery of air from the electric blower instead of the intermittent blast expected from a lone bellows can be offset by the failure to tap the slag contents. An attempt to tap the furnace slag down the decline built from the furnace floor and through a pre-made entrance in the front of the furnace was made around 4 hours into the firing. Removal of the bung revealed that the furnace slag had already partly solidified behind the entrance blocking any molten slag from escaping while indeed being immobile itself. In comparison to the developed practices of the Late Bronze Age which produced large slag assemblages with flow textures showing considerable mobility, the temperatures reached during the experimental smelt were actually inferior and could not bring as large a volume of material to liquidus. This was a pattern that would be repeated across all of the

smelts and it reinforces interpretations of slag tapping in prehistoric smelting as indicative of sophisticated high temperature operations. The use of the electric blower also raises questions over the possibility of introducing too much oxygen into the furnace during firing in an error known as 'over-blowing' (Crew 2013:30). This is less problematic or even advantageous at least during the initial stages of matte smelting which aims to oxidize and remove the sulphur in the ore as sulphur dioxide gas. During the firing this was mainly judged based on the quantity and density of smoke in the furnace and the colour of the flames in the top opening. At all times the pressure of carbon monoxide in the furnace interior was presumed to be quite high with large volumes of smoke being emitted throughout the smelt and the telltale opaque yellow-orange to reddish colour of the flames. The rate of fuel consumption after the initial filling of the furnace with charcoal seemed to increase over the first 5 hours of smelting before the entire contents were brought up to temperature which then required less fuel to be sustained in the final few hours. At the end of the smelt the burning down of much of the charcoal showed that the slag had become fused to the interior of the furnace walls and since tapping was not possible it would have to be allowed to cool before retrieval of the assemblage. Cooling of the furnace contents could not be done rapidly with water or sand for safety reasons. This is very clearly a possible departure from prehistoric practices which in some cases are asserted to have tapped the entire furnace contents into pits (see Arisman in Iran or LBA Cypriot smelting from Rehren et al. 2012 and Kassianidou and Van Brempt 2016 respectively) however destructive retrieval of matte or metal from cool furnaces is well-attested also from fragmented and crushed slag and furnace remains at many smelting sites (Gilmour et al. 2020; Knapp and Kassianidou 1999). After the contents had cooled the retrieval of the smelting assemblage necessitated the destruction of the furnace as the slag had become inextricably fused to the furnace walls. The main visual cue for the matte phase was a much more porous surface to the slag where it had lain on the furnace floor, becoming mixed with larger quartz inclusions visible as white specs. The slag to matte ratio was heavily skewed towards slag with the matte weighing an estimated 5-6kg which in a follow

up matte conversion or coppermaking smelt would be too small to form the total charge for copper extraction. Rose et al. were able to produce an estimated 5.5kg of matte out of a 20kg charge of ore which is consistent with these results suggesting ores of a similar composition were subjected to equivalent conditions (2020:84). This may have resulted from inefficiency of the smelt however it is also possible that a 30kg charge of sulphide ore was much smaller than the mass of ore used in prehistoric sulphide smelting. If so, the methods used to manage much larger volumes of slag by prehistoric practitioners can be speculated to have been very sophisticated, requiring a high degree of technical accomplishment. The later correlation of the features of the experimental production assemblage to many of the slags presented in the literature on Late Bronze Age sulphide smelting is encouraging with perhaps the limited separation of the matte into a phase distinct from the slag being the most disparaging factor. Rose et al. were only able to achieve a larger matte phase in one out of five experiments, demonstrating the challenge that this poses to modern experimental smelters (2020:84). Retrieval of the matte from the slag would have been quite arduous almost requiring a chiselling action though it did in some places break away cleanly from the slag as larger fragments. As an example of one of a very few complete production assemblages from an intermediary stage in sulphide smelting using prehistoric methods this data could be applied to analytical and experimental research into the sulphide smelting process or used to predict and identify the associated products that have been recovered from the archaeological record in relation to a formative event.

4.8: *Experimental smelting of iron oxide* (**FE-1**).

The objective of this smelt was to produce a bloom of metallic iron in a successful reconstruction of an iron smelting operation. The results of this experiment acted as a control and basis for comparison with the mixed copper and iron oxide experiments, while also demonstrating the reduction of an iron oxide into metallic iron using the chosen methodology. A total charge of 30kg of naturally occurring hematite from Cumbria, UK was prepared by crushing the ore into a fine shale-like consistency. A furnace of the type detailed earlier in this chapter was built and fired prior to the experiment (see figure 4.21) and charcoal was ignited at the base of the furnace before the front was sealed with clay and it was filled with charcoal. A forced draught was provided by an electric blower and across a 7 hour period the 30kg charge of crushed hematite and 115kg of charcoal was added to the furnace at intervals (see figures 4.22-4.23). At the end of this period the forced draught was stopped and the furnace front was opened to attempt to retrieve the bloom. Slag fused to the walls of the furnace proved difficult to remove while hot in low light conditions and so the furnace was filled with charcoal and allowed to cool for 12 hours after which the smelting assemblage was retrieved (see figures 4.24 and 4.25).

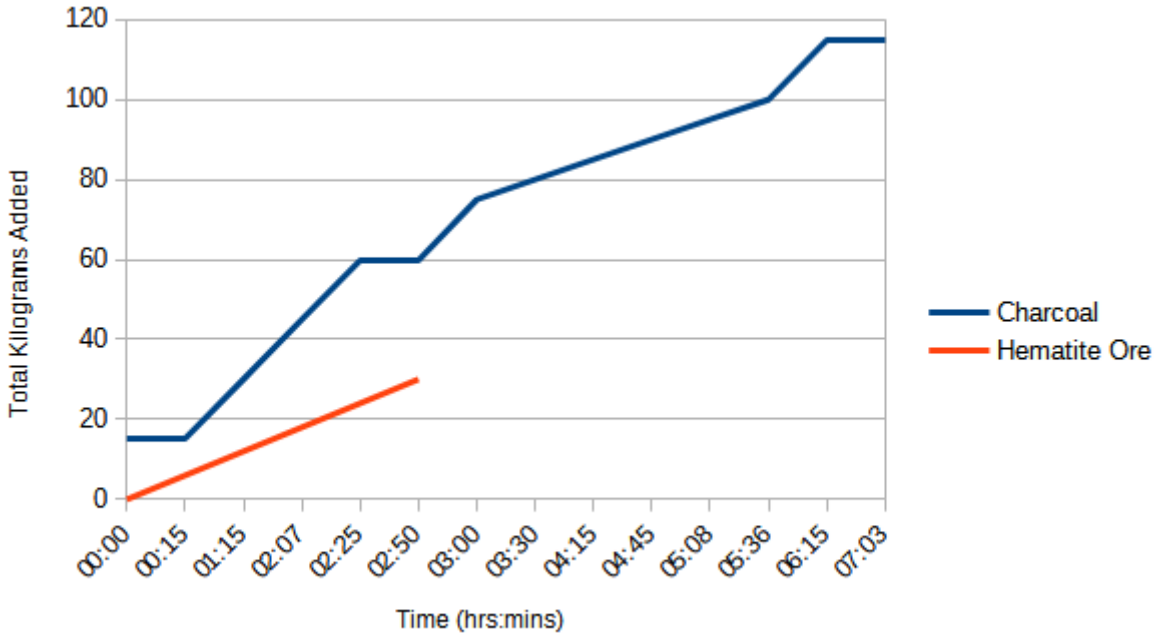


Fig.4.21: Addition of charcoal and hematite to the furnace over duration of firing.

Time (hrs:mins)	Forced Draught	Charcoal Added (total kg)	Iron Ore added (total kg)
00.00	Start	15	0
00.15		15	6
01.15		30	12
02.07		45	18
02.25		60	24
02:50		60	30 (end of ore)
03:00		75	
03:30		80	
04:15		85	
04:45		90	
05:08		95	
05:36		100	
06:15		115 (end of charcoal)	
07:03	End		

Fig.4.22: Schedule of charge addition to furnace over the duration of firing undertaken 3/08/2020.



Fig.4.23: Firing of the furnace, 3/08/2020.



Fig.4.24: Furnace interior following smelt.



Fig.4.25: Front of the furnace during attempted retrieval of the smelting assemblage.

The entire smelting assemblage consisted of furnace slags, particularly heavy and dense slags, vitrified furnace lining and cinder. No 'bloom' was visible however this was to be expected as the furnace slags had not been hammered while hot to consolidate any iron contained within. The densest and most heavy slags from the furnace displaying a light grey lustre were cut into cross-sections using a rock-saw and ground up to 1000 grit using wet aluminium oxide and silicon carbide belts on a bench sander. These sections were photographed using a Nikon D850 camera. Three smaller <2cm samples (Fe-1, Fe-2 and Fe-3) were cut from these sections and mounted in resin and ground up to 1200grit using wet silicon carbide paper and polished on a wheel using 1µ aluminium oxide powder followed by 0.3µ powder. An Olympus BX53M TRF-S microscope and Olympus DP74 camera were used for reflected light microscopic analysis and the production of micrographs.

4.9: *Evaluation of iron smelting experiment*

The full scale furnace smelt of iron ore (hematite) was undertaken to trial the production of iron in a furnace of the same specifications used in the later mixed sulphide and oxide smelting experiments and using a charge of similar size. As such it was not a reproduction of a smelting operation based on an example from the archaeological record of which many examples can be found in the literature (Crew 2013; Humphris et al. 2018). This may have been a determining factor in the failure to extricate a proper bloom from the furnace while hot which had been the intention. The fairly short duration of the smelt at seven hours was at the minimal end of most estimates for bloomery smelting however this seemed appropriate given the smaller charge size at 30kg and excessive slag in the furnace chamber began to obstruct the *tuyere* in the final hours, an issue noted by Crew (2013:30). The furnace contents proved impossible to remove as they had adhered to the furnace walls and after cooling the retrieval of dense and lustrous, porous grey 'slags' was the only indication that iron had been

produced. Initial interpretation of this material concluded that it may have been cast iron caused by excessive temperatures from over-blowing of the furnace via the electric blower which was a concern early into the campaign of experimental smelts. If this had been the case it would have brought the relevance of the data acquired into question as it is improbable that Late Bronze Age furnaces achieved temperatures that could partially or fully liquefy iron and allow >10% of carbon to become dissolved in it. Later analysis, which is shown in the following chapter, confirmed that this was a misidentification and the furnace design and system of forced draught did not need to be reconsidered. Vitrification of the furnace walls, which had lost in some regions up to half of their thickness, suggested much of the material in the slag that had proven so difficult to remove had originated in the clay and sand of the furnace walls. Crew estimated that only around 7.5% of the slag originated from furnace clays however this appeared to be much higher during this smelt (2013:35). Furnace slags came in two varieties of a dark black vitreous slag and also a heterogeneous slag with white quartz and coarse pebble inclusions possibly from the clay or furnace floor substrate. A mixed light grey cinder which was lighter and more porous than other slags was also present.

4.10.1: *Experimental smelting of mixed copper and iron oxide* (**CUFE-1**)

The following four experiments consisted of the co-smelting of a mixture of copper and iron oxides in a 20 kilogram charge of varying composition within a reconstructed furnace. For each experiment the charge was made up of a total of five parts towards which copper and iron oxides contributed towards the total weight in the ratios of 1:4, 2:3, 3:2 and 4:1. This methodology was chosen as 20 kilograms of material was a manageable quantity in terms of reducing the likelihood of blockages in the furnace interior and interference with the *tuyere*, for ease of retrieval of the assemblage following each experiment and to provide as wide an array of ratios without smelting such diminutive amounts

of either oxide that losses to the slag would render their reduction undetectable in the assemblage during analysis. The objective of these co-smelts was to reduce copper and iron oxides into metallic copper and iron and to produce an assemblage for chemical analysis to form the basis of an investigation into the chemical and physical processes that the iron present in a co-smelt with copper oxide is subjected to at differing proportions in the charge. For the first copper and iron oxide co-smelt, a twenty kilogram charge was prepared consisting of 8 kilograms of crushed iron ore from Devon, UK (hematite) to 12 kilograms of copper oxide (CuO flake) in a 2:3 ratio. A furnace was built and fired prior to the smelt, with the 20 kilogram charge added and 67 kilograms of charcoal being combusted in the furnace over a period of eight hours (see figures 4.26-4.27). An attempt to tap the furnace was made three hours into the firing however molten copper had run to the opening and solidified preventing evacuation of the slag. At the end of this period the electric blower was turned off and the front of the furnace was opened for retrieval of the smelting assemblage, destroying the furnace in the process (see figures 4.28-4.29).

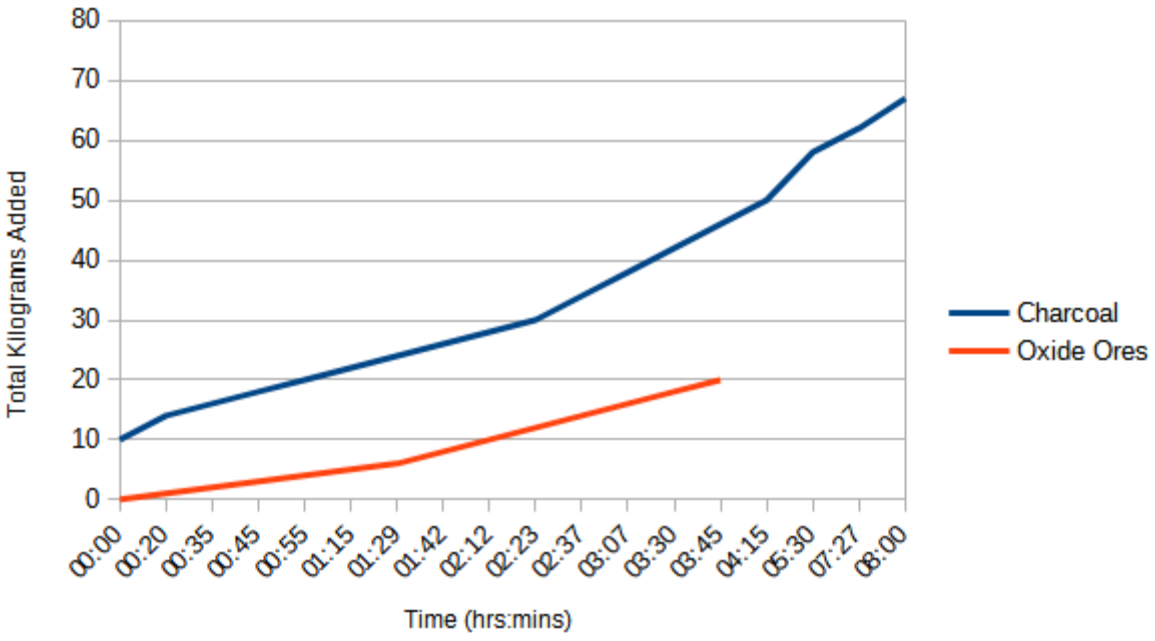


Fig.4.26: Addition of charcoal and oxide ores to the furnace over duration of firing.

Time (hrs:mins)	Forced Draught	Charcoal Added (kg)	Oxide ore added (kg)
00:00	Started	10	
00:20		14	1
00:35		16	2
00:45		18	3
00:55		20	4
01:15		22	5
01:29		24	6
01:42		26	8
02:12		28	10
02:23		30	12
02:37		34	14
03:07		38	16
03:30		42	18
03:45		46	20 (end of Oxides)
04:15		50	
05:30		58	
07:27		62	
08:00	Stopped	67	

Fig.4.27: Schedule of 2:3 iron oxide to copper oxide smelt 08/09/2021.



Fig.4.28: Furnace during smelting, 08/09/2021.



Fig.4.29: Fragmented furnace shaft with smelting assemblage attached to the base. Note the reddish-brown metallic copper lower-centre, 09/09/2021.

4.10.2: CUFE-2

For the second experiment, a 20 kilogram charge consisting of copper oxide and iron oxide was prepared in the ratio of 4:1 respectively, resulting in 16 kilograms of copper oxide (CuO flake) being added to 4 kilograms of iron oxide (Fe_2O_3 pellet). This experiment most closely approximated the iron content of a typical slagged copper smelting operation at around one fifth of the total charge (Craddock and Meeks 1987:180). A furnace of the specifications detailed earlier in the chapter was built and fired prior to the experiment. The furnace front was sealed and the base was ignited before the forced draught was started. The 20kg charge of oxides was added and 72kg of charcoal was combusted in the furnace over a period of over nine hours (see figures 4.30-4.31). The furnace was then allowed to cool for 12 hours before retrieval of the smelting assemblage, during which the furnace was destroyed (see figures 4.32-4.33).

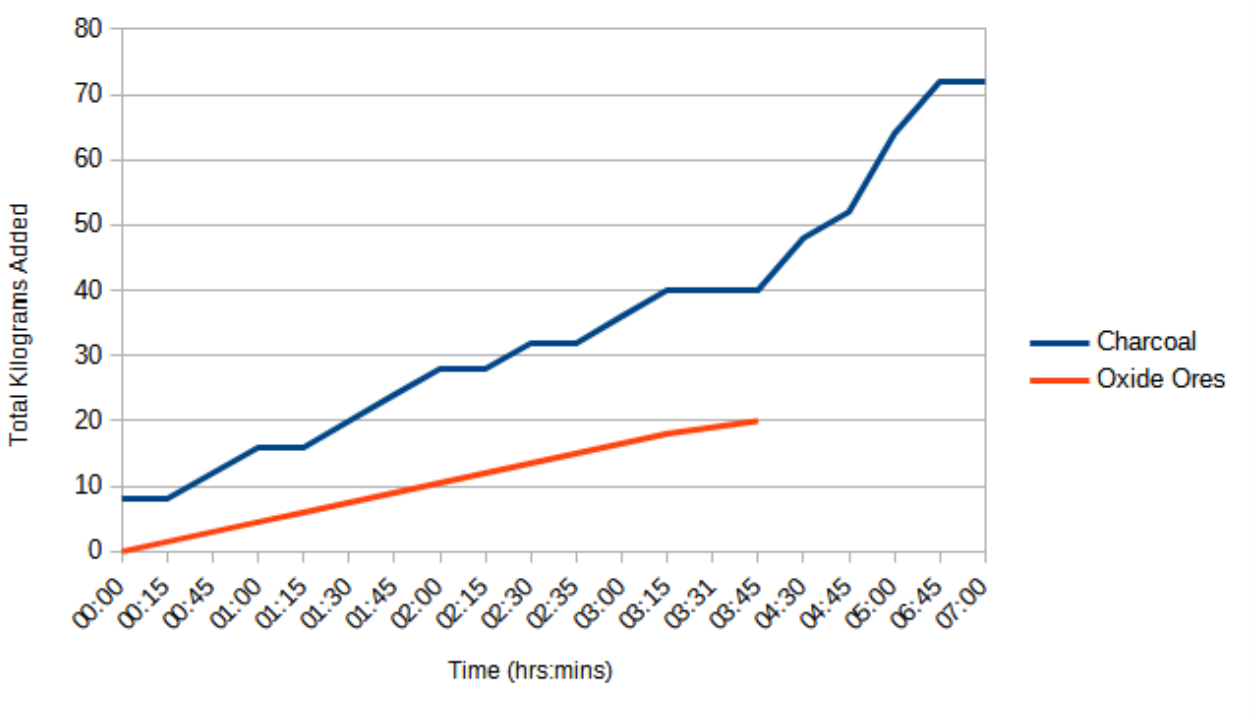


Fig.4.30: Addition of charcoal and oxide ores to the furnace over duration of firing.

Time (hrs:mins)	Forced Draught	Charcoal Added (kg)	Oxides added (kg)
00:00	Started	8	
00:15			1.5
00:45		12	3
01:00		16	4.5
01:15			6
01:30		20	7.5
01:45		24	9
02:00		28	10.5
02:15			12
02:30		32	13.5
02:35			15
03:00		36	16.5
03:15		40	18
03:31			19
03:45	Stopped (blockage)		20 (end of oxides)
04:30	Started (cleared)	48	
04:45		52	
5:00		64	
06:45		72	
07:00	Stopped		

Fig.4.31: Schedule of 4:1 copper to iron oxide smelt 22/09/2021.



Fig.4.32: Furnace during smelting, the greenish flame shows copper reduction. 22/09/2021.



Fig.4.33: Furnace during retrieval of smelting assemblage.

4.10.3: CUFE-3

For the third experiment a 1:4 mix of 4 kilograms of copper oxide (CuO flake) and 16 kilograms of iron (II) oxide (Fe_2O_3 powder) was prepared to form a 20 kilogram charge. A furnace was built and fired prior to the experiment (see figure 4.36) and following ignition 54 kilograms of charcoal was combusted in the furnace over a period of over 7 hours to which the ores were gradually added (figures 4.34-4.35). An attempt to tap the furnace was made at the end of this period (see figure 4.37). The furnace was allowed to cool for twelve hours before retrieval of the smelting assemblage, which necessitated the destruction of the furnace.

Time (hrs:mins)	Forced Draught	Charcoal Added (kg)	Oxides Added (kg)
00:00	Started	6	
00:06		10	3
00:36		14	6
00:46		18	8
01:11		22	10
01:51		26	12
03:01		30	14
03:36		34	16
04:06		38	18
04:35		42	20(End of Oxides)
05:21		46	
07:36	Stopped	54	

Fig.4.34: Schedule of 1:4 copper oxide to iron oxide smelting experiment.

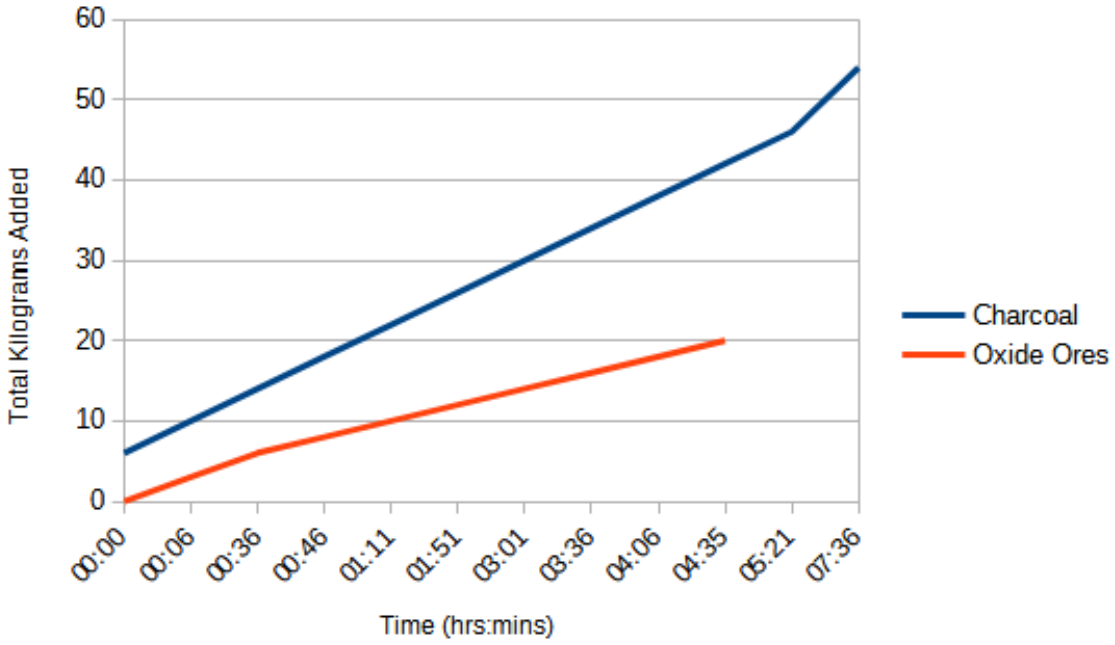


Fig.4.35: Addition of charcoal and oxide ores to furnace over duration of firing.



Fig.4.36: Furnace during smelting experiment, 09/10/2021.



Fig.4.37: Front opening of furnace during retrieval. A red-brown copper runnel is visible, centre.

4.10.4: **CUFE-4**

For the fourth and final smelting experiment in the series a 3:2 mix of 12 kilograms of iron oxide (Fe_2O_3 powder) to 8 kilograms of copper oxide (CuO flake) was prepared. A furnace was built and fired prior to use and after ignition of the base the forced draught was started and over a period of ten hours (see figures 4.38-4.39) the 20 kilogram charge was added along with 69 kilograms of charcoal. After four hours an attempt to tap the slag was made with limited success as it had quickly cooled towards the furnace front (see figure 4.41). At the end of this period the furnace was destroyed and the contents removed while at a yellow heat and beaten (see figure 4.43) to expel slag before being allowed to cool as a novel effort to consolidate any metallic iron present into a bloom.

Time (hrs:mins)	Forced Draught	Charcoal Added (kg)	Oxides Added (kg)
00:00	Started	8	
00:10		10	2
00:50		12	4
01:20		16	5
01:44		20	6
02:35		24	7
03:00		26	8
03:20		28	9
03:30		30	10
03:50		32	11
04:05		33	12
04:20		34	13
04:40		35	14
05:05		36	15
05:25		37	16
05:50		40	17
06:10		43	18
06:35		46	20 (End of Oxides)
07:50		49	
08:00		61	
09:00	Stopped	69	

Fig.4.38: Schedule of 3:2 iron oxide to copper oxide smelting experiment, 22/10/2021.

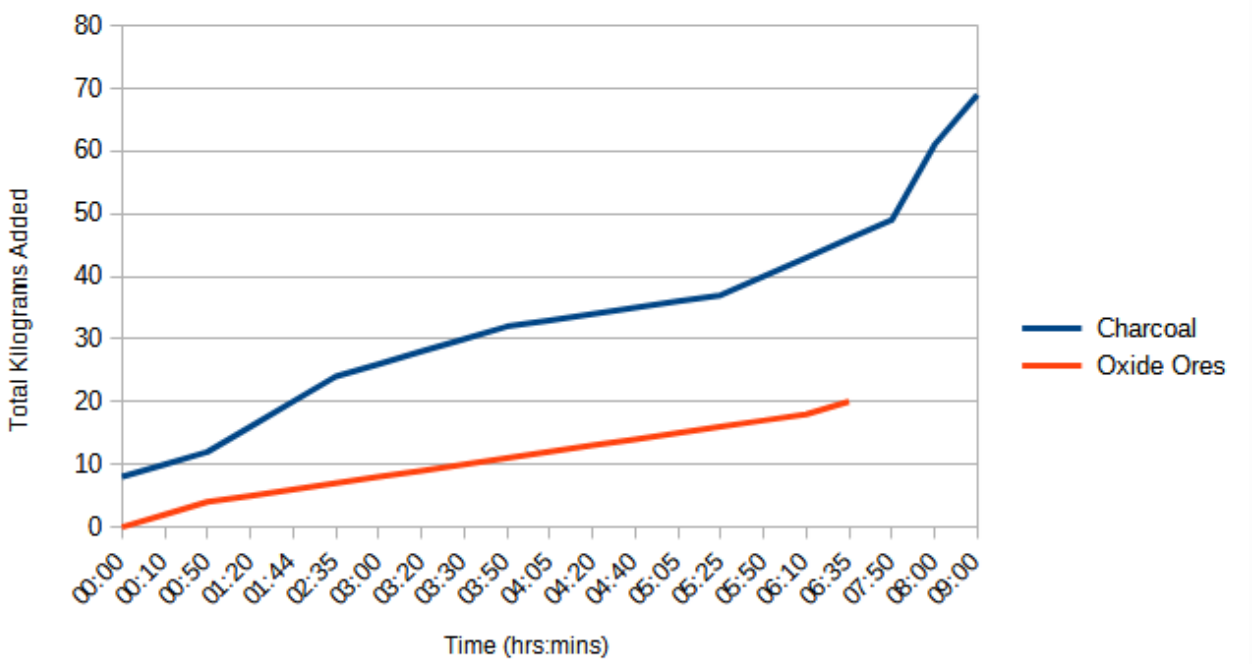


Fig.4.39: Addition of charcoal and oxide ores to furnace over the duration of firing.



Fig.4.40: Furnace during smelt, 22/10/2021.



Fig.4.41: Front opening of furnace during ‘tapping’ showing runnels of slag, 22/10/2021.



Fig.4.42: Furnace prior to retrieval of the smelting assemblage, 22/10/2021.



Fig.4.43: Beating of the furnace contents to expel slag, 22/10/2021.

For all of the furnace smelts in the copper and iron oxide series the smelting assemblage consisted of metal and dense slags from the base of the furnace, overlaying slags, vitrified furnace lining and cinder with very small quantities of ‘tap’ slags or runnels. The metal and slag phases from the base were cut on a rock saw into cross sections and ground up to 1000 grit using wet aluminium oxide and silicon carbide belts on a bench sander. These sections were photographed using a Nikon D850. Samples measuring <3cm were then cut from these sections and mounted in resin before being ground up to 1200grit using wet aluminium oxide and silicon carbide paper. The samples were then polished using aluminium oxide powder at 1µ up to 0.3µ. An Olympus BX53M TRF-S microscope and Olympus DP74 camera were used for reflected light optical microscopic analysis and the production of micrographs.

4.11: *The smelting of copper and iron oxides from an experimental perspective*

After the metals such as tin, arsenic or lead used in alloys with copper to make bronzes, iron is by some margin the next most common component in prehistoric copper. It is somewhat surprising then that comparatively little analytical or experimental research into copper-iron alloys has been submitted into the literature on prehistoric cuprous metallurgy. With the exception of the experimental smelts undertaken in the wake of the archaeological expedition and large-scale excavation at Timna (Gale et al. 1990; Merkel 1982; Tylecote and Boydell 1978) the co-smelting of copper and iron oxide ores in equable proportions has not received any attention from either the archaeological literature or experimental archaeologists. The reasons for this probably stem from the continuing lack of indisputable evidence for deliberate fluxing or slagging of copper smelting using iron ores. Also the hypothetical uptake of iron in copper during the more sophisticated extractive operations of the Middle to Late Bronze Age has been widely accepted and most analytical or provenance studies into cuprous metallurgy are content with this theoretical evaluation (Craddock and Meeks 1987:202). In isolation the prehistoric methods for extracting copper or iron from their oxidic ores is well studied and has been carried out and reported in great detail in numerous experimental projects though studies into the smelting of copper oxides in larger furnaces are uncommon. The main limiting factor in experimentation using copper oxides is economic as copper retains a high market value and even synthetic ores are expensive in comparison to iron ore (the CuO catalyst flake used in this study was up to three times the cost of the iron ore used). Acquiring geological deposits is virtually prohibitive in cost at the larger scale which restricts experimentation with authentic ores to exceptional occasions when the ores can be obtained personally at deposits in protected heritage sites such as at Timna. With the majority of the oxide co-smelting experiments presented here producing yields of around 5-10kg of copper in consolidated masses this can definitely be considered the greatest scale of experimental copper smelting conducted in a reconstruction of prehistoric methods, with most experiments in the literature consisting of much smaller controlled

smelts in laboratories or in bowl or shaft furnaces (Timberlake 2007: Lechtman and Klein 1999) not exceeding 40cm^3 in volume. This has provided new insights into what a Late Bronze Age smelting and metal assemblage might look like prior to the destructive acts of retrieval and intensive re-melting and casting into ingots and artefacts that accompanied the extensive trade in copper across the Near East during the 2nd millennium BC.

As was the case for the sulphide smelting experiment, the methodology was designed with few notions or guidelines though from the outset achieving a yield of copper metal from a single firing of the oxides was expected. The experimental crucible smelt confirmed that an oxidic ore could be readily reduced even over a short period given sufficient temperatures and a strongly reducing environment. At this small scale it was possible to use semi-precious malachite in contrast to the furnace smelt where an artificial ore was prepared. The use of a synthetic ore was the most major deviation from prehistoric smelting and clearly differed from natural deposits in two ways that are relevant to smelting: the low or non-existent quantities of silica in the ore and the higher proportions of copper. Prior to the experiments these differences were expected to manifest as a greater copper to slag ratio in the furnace. Copper losses in the slag due to a more viscous slag in the absence of large quantities of silica were a potential risk. The addition of silica by mixing the synthetic ore with sand was considered but initially dismissed on the basis that silica content in ore deposits is so variable and could have been much lower than modern industry standards during their exploitation in prehistory. Ultimately this decision was vindicated after retrieving the slag and metal assemblage from the first smelt of which slag made up the greater proportion by weight and copper losses in the slags was minimal. Evidently the sand and silts in the clay of the furnace walls, which became heavily vitrified and often reduced in thickness with the loss of material into the slag, provided enough silica to produce adequate amounts of slag. The occasional blockage of the *tuyere*, which required forceful

removal using a metal pole at times, suggested there was a maximum slag content in the furnace without significantly impacting the efficiency of internal combustion. The greater copper component in the artificial ore may have increased copper yield in comparison to equal quantities of a natural ore. This partly influenced the limiting of the charge to a 20kg total which could have contained almost twice as much copper than the same weight of ore from a naturally occurring deposit. The copper component in the experimental smelt, which used a smaller charge, should have remained consistent with prehistoric smelting where the firing of upwards of 30 to 40kg of ore would be more probable. Tapping of the furnace was attempted for all of the oxide smelts with mixed and always ineffectual results for which a number of possible causes can be discerned. Firstly, the temperature across the entire reaction volume in the lower chamber of the furnace may have been insufficient to keep the entire slag assemblage molten especially towards the front entrance. While the furnace interior ran at a yellow-white heat for much of the firing period and the slag was clearly vitreous and rendered free-running the solidification of the slag at the front opening during tapping suggests temperatures were much lower furthest from the *tuyere*. As mentioned for the previous smelts, this is a problem that Crew claims never to have fully resolved even over 100 smelting experiments (2013:31). By closing the frontal opening at the start of the firing this may have trapped the liquid slag behind it allowing it to cool and solidify where it prevented more of the slag from escaping. The blocking up of the front entrance was done to maintain carbon monoxide pressures in the furnace interior however this may not have been necessary during the initial hours of firing. Instead removal of the gangue by allowing the slag to empty from the furnace may have been the priority for prehistoric smelters before blocking the opening and reducing the remaining metallic oxides. It is also possible the experimental furnaces may have had too large an interior volume to maintain at temperature. Adhesion of the slag to the furnace walls, which made retrieval of the metal difficult, must have been in part a consequence of the majority of the silica in the slags originating from the walls. With the addition of much more silica this may have been less pronounced and would have

reduced the entrapment of material inside the furnace allowing more of the slag to escape during tapping. Nevertheless the efficiency of the smelt in terms of metal yields was not noticeably impacted by these factors. Furnace operation was managed in much the same way as for the sulphide smelt with fuel consumption varying slightly across all of the smelts mostly due to periodic blockages causing the temporary cessation of the forced draught. In general the rate of fuel consumption increased immediately after the addition of all of the ore into the furnace before levelling out when this material had been brought up to temperature. Across the smelts a higher proportion of copper oxide in the charge corresponded to greater fuel consumption, with the 4:1 copper to iron oxide smelt consuming the most charcoal at 70kg; 20% more than that used for the 4:1 iron to copper smelt. This may have been a result of more efficient reduction of the copper in the presence of more iron oxide which acted as a flux and lends credence to the suggestion that extraction of iron is more economical than the extraction of copper (Horne 1982). Retrieval of the metal from the furnace required destruction of the furnace for each smelt as the slag had become fused to the furnace walls. Copper was clearly visible at the base of the assemblages from the numerous runnels of 'springy' grey-black oxidized metal with a globular network that was distinct from the smooth vitreous slags. Hammering of the smelting assemblage quickly fractured and loosened much of the slag from the metal phase which being more ductile remained intact allowing a fairly clean separation. The production of iron was not visually apparent from the metal assemblages though the strong attraction of a magnet to the metal from each smelt provided an easy non-destructive confirmation that iron or possibly magnetite had entered into the copper (see figure 4.44). For prehistoric smelters visual clues for iron in the copper would probably not be revealed until the metal was re-melted and a large amount of crucible slag formed on the surface of the molten metal (Craddock 2000:162). This may be an underestimation of the observational skills of past practitioners who may have recognised different densities, the slightly more brassy colour of the copper and given time and exposure to damp the beginnings of orange rust in the metal. The significance of the mixed copper and iron oxide smelts lies with the

regular production of a large consolidated yield of copper in contrast to smaller scale experiments which often produce numerous droplets and prills that need to be collected (Lechtman and Klein 1999; Timberlake 2007). These more limited experiments clearly cannot represent the greater scales of Middle to Late Bronze Age copper smelting in the Near East which in some regions operated at an order of magnitude above that of the preceding Chalcolithic. This provides an opportunity to engage with and analyse a metal and smelting assemblage that more closely approximates those that would have been produced in the intensive smelting landscapes of the Near East during the late 2nd millennium BC.



Fig.4.44: Spherical silver magnet (centre) attracted to the reddish-grey copper metal from the furnace. Taken 9/09/2021.

4.12: *Copper ingot production*

Crucible melting of copper either for refinement (for which there is little evidence) or casting purposes was a procedure that must have been carried out regularly by the Late Bronze using the raw copper that had consolidated at the furnace base following smelting (Hauptmann 2020: 307-309,317-318). As discussed in chapters two and three, re-melting of the copper would have exposed the iron contained therein to further oxidation allowing for mechanical removal from the molten surface in a layer of slag (Craddock 2000:162). Even low iron content in copper alloy artefacts of the LBA might therefore be indicative of much higher iron content in the raw copper from the furnace. In order to assess the iron losses in raw furnace copper alloys during the crucible melting process, samples of copper metal were taken from three of the furnace assemblages and rendered molten in a graphite crucible at just under 1200^{o}C for 15 minutes (see figures 4.45-4.46). The molten copper was then cast in an ingot mould. The first sample weighing 2.5kg was cut from material from the fourth smelt in the copper-iron oxide series (CUFE-4) produced using a 2:3 ratio of copper oxide (CuO) to iron oxide (Fe_2O_3) respectively. The second sample weighing 2.4kg was cut from the metal of the second smelt of 4:1 copper oxide to iron oxide (CUFE-2). The third sample weighing 3.2kg was cut from material from the third smelt of 1:4 copper oxide to iron oxide (CUFE-3). Small samples (<3cm) were cut from the ingots with a hacksaw, mounted in resin and ground up to 1200grit using wet aluminium oxide and silicon carbide paper before being polished on a wheel with aluminium oxide powder at 1µ up to 0.3µ. The ingots were then photographed using a Nikon D850 camera and micrographs were taken using an Olympus BX53M TRF-S microscope and Olympus DP74 camera. Macrographs at 1.5x magnification were obtained using an Epiphot inversed microscope.



Fig.4.45: Removal of surface slag and impurities from molten copper following crucible heating.

Experiment was carried out at Sutton Castings, Southwell, Nottingham 11/03/2022.



Fig.4.46: Casting of molten copper into an ingot. The cooled black surface slag is shown below.

Chapter 5

5.1: *Analysis of experimental smelting assemblages*

Archaeometallurgists have embraced a breadth of analytical techniques over the course of the latter half of the 20th century that have had profound implications for the discipline, with the most successful projects integrating this data with material from the archaeological record and detailed spatial plans of smelting assemblages to provide new insights into the technological strategies employed by past cultures (Killick and Fenn 2012:566-567; Veldhuijzen and Rehren 2007:196-198). Experimental archaeology presents a rare opportunity for analytical studies as the material represents the total production assemblage of a smelting operation prior to removal of the metallic and non-metallic material and destruction of the structural context of the furnace itself. The relation of this material to particular regions within the furnace interior provides an insight into the 'anatomy' of a smelt in three dimensional space which is usually only recoverable from archaeological contexts through slag morphology. As the conditions of an experimental smelt are controlled and recorded, the results of the analysis of the production assemblage can be related directly to physical and chemical conditions reproduced in the furnace and to an exact period of time over which the smelt took place. Applying the appropriate analytical techniques for the study of this material is crucial for reproducing a set of data that can contribute towards fulfilling the objectives of the experimental research. As the objective of this campaign of experimental smelts was to investigate whether practicable quantities of metallic iron could be produced and recovered from Late Bronze Age copper smelting operations, the analytical methods chosen were optical microscopy of cross-sections of the metallic assemblages and photography of cross-sections of the production assemblages. X-ray Fluorescence spectroscopy was also employed to provide quantitative analysis of copper and iron and their ratios in the copper and iron oxide co-smelting material and ingots.

Reflected light microscopy using a metallographic microscope was selected as an accurate method for examining expected metallic microstructures across samples with a range of compositions while also providing high resolution photomicrographs to clearly demonstrate apparent metallic phases in the thesis (Leng 2013:1). This technique was also chosen to contribute towards an analytical methodology that incorporated photography, macrographs and micrographs of the assemblages and samples to produce a more representative dataset which tied into a hypothesis that iron metallurgy may have developed as a result of human observation of visible phenomena during copper smelting in the Late Bronze Age Near East. The primary objective of the metallographic analysis of the samples was to identify metal (copper and iron) phases in the assemblages recovered from the furnace smelting and casting experiments. In metallography, metal phases are distinguished by the tendency of atoms of metals to bond closely in typically regular arrangements termed a crystal lattice. These units are characterised by their formation, for example copper forms a face-centred cubic lattice while the α-Fe iron allotrope forms into a body-centred cubic structure. Metals consist of repeating series of these lattices so are described as having a polycrystalline structure. Across the structure each crystal lattice has alternate planes of orientation in relation to the other resulting in grain boundaries where they meet. The grain is a zone which has a single orientation. These grains and grain boundaries are visible at magnification under a reflected light microscope and are referred to as microstructures (Hauptmann 2020:435). It is through optical identification of these microstructures that the phases of metal can be observed. Of course optical microscopy is not limited to analysis of metals and was employed by the author for the analysis of metallic oxides and sulphides and siliceous slags.

Quantitative analysis utilizing methods such as Scanning Electron Microscopy, X-Ray Diffraction, X- Ray fluorescence, Electron Microprobe Analysis and ICP Mass Spectrometry has often been used

in concert with metallographic techniques (Henderson 2013:208). These techniques are often employed due to being non-destructive in comparison to quantitative metallography which often requires larger samples (Hauptmann 2020:438). Thus the data provided by these techniques is immensely useful for comparative study with the large body of analytical data that has been generated over the past half century for archaeological artefacts and materials. Portable X-ray fluorescence (p-XRF) analysis was used to produce a dataset from the experimental smelting assemblages which formed a basis for comparison with the data available for 2nd millennium BC copper alloys from the Near East. Portable XRF provided the most accessible technique available due to constraints on use of the Dyson-Perrins RLAHA facilities during renovation and COVID. The samples mounted and ground for metallographic analysis were also well-suited for p-XRF sampling and allowed for direct correlation between the metallographic and quantitative analyses. This method proved sufficient to provide good quantitative data on the major copper and iron metal phases in the samples.

All identifications were made in reference to Bernhard Pracejus (2015) "*THE ORE MINERALS UNDER THE MICROSCOPE AN OPTICAL GUIDE"* and to Bachmann (2016) "*The Identification of slags from archaeological sites".* The reference collection provided by Pracejus (2015:XVII) represents samples from naturally occurring ore minerals that were not derived from the artificial contexts of smelting so were compared to the examples presented by Bachmann (2016) in archaeological slags. Taken together these references were used to inform the analysis of the experimental samples. Dr Peter Northover and Dr Brian Gilmour were also consulted on the copper-iron alloy, ingot and slag samples. Images from all samples are listed in the Appendices I-V.

5.2: **CRS-1,2,3,4** *Crucible smelting assemblages*

The surfaces of all four assemblages can be described as a 'sintered' mass which largely retains the hemi-spherical shape of the interior of the crucible (see figures 5.1 to 5.3). Small lumps of charcoal have become embedded within the mass, which itself is considerably porous or 'blistered' most likely from the escape of gasses within the crucible during the firing. The copper and iron oxide crucible assemblage contains a considerable quantity of metallic material (see figure 5.1), namely a brassy red-brown copper with white-silver inclusions tentatively assigned as iron. The chalcopyrite crucible assemblage consists of brassy yellow lustrous material threaded with dull grey 'veins' (see figure 5.2). The iron ore smelting assemblage can be described as rings and prills of whitish-silver metal (iron) surrounding interfaces with charcoal and slag inclusions (see figure 5.3). The iron rich copper slag assemblage had become a fused mass largely resembling a dark black silicate slag however small prills of a brassy metal are visible (see figure 5.4).

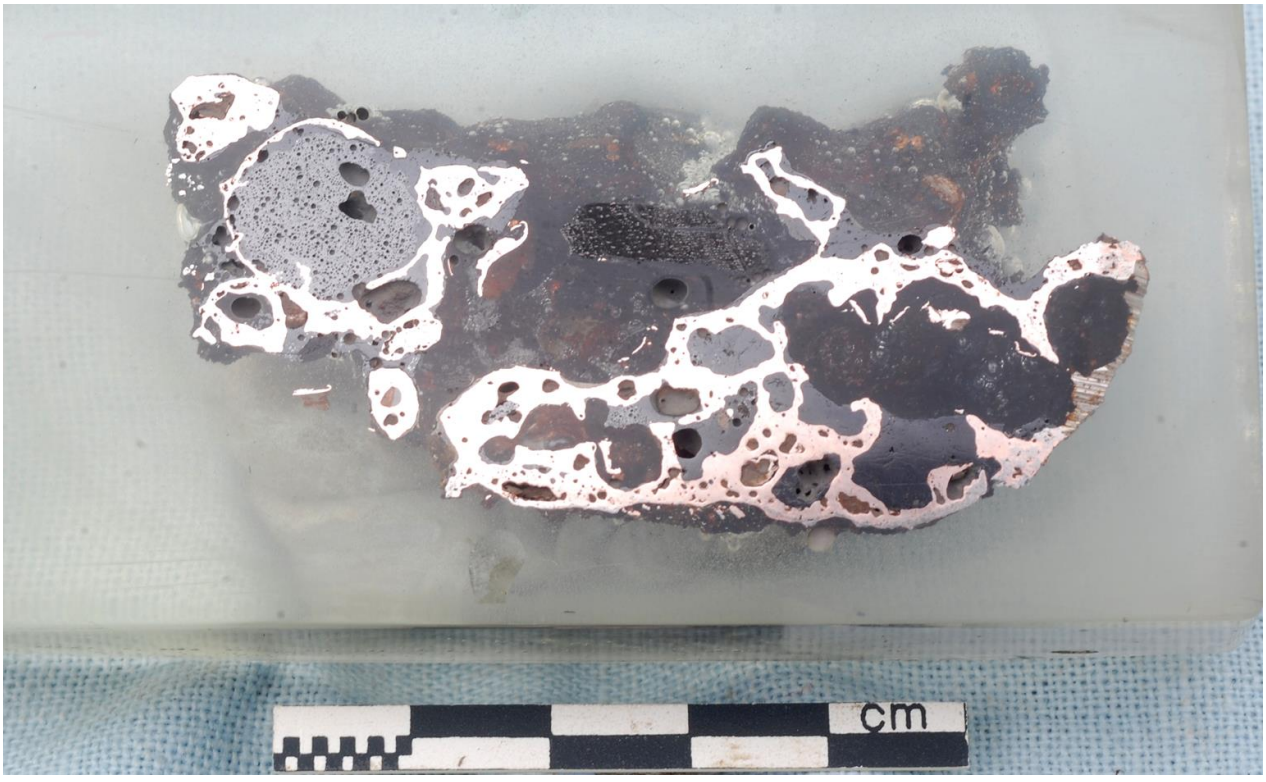


Fig.5.1: Cross section of copper oxide and iron ore crucible assemblage after mounting.

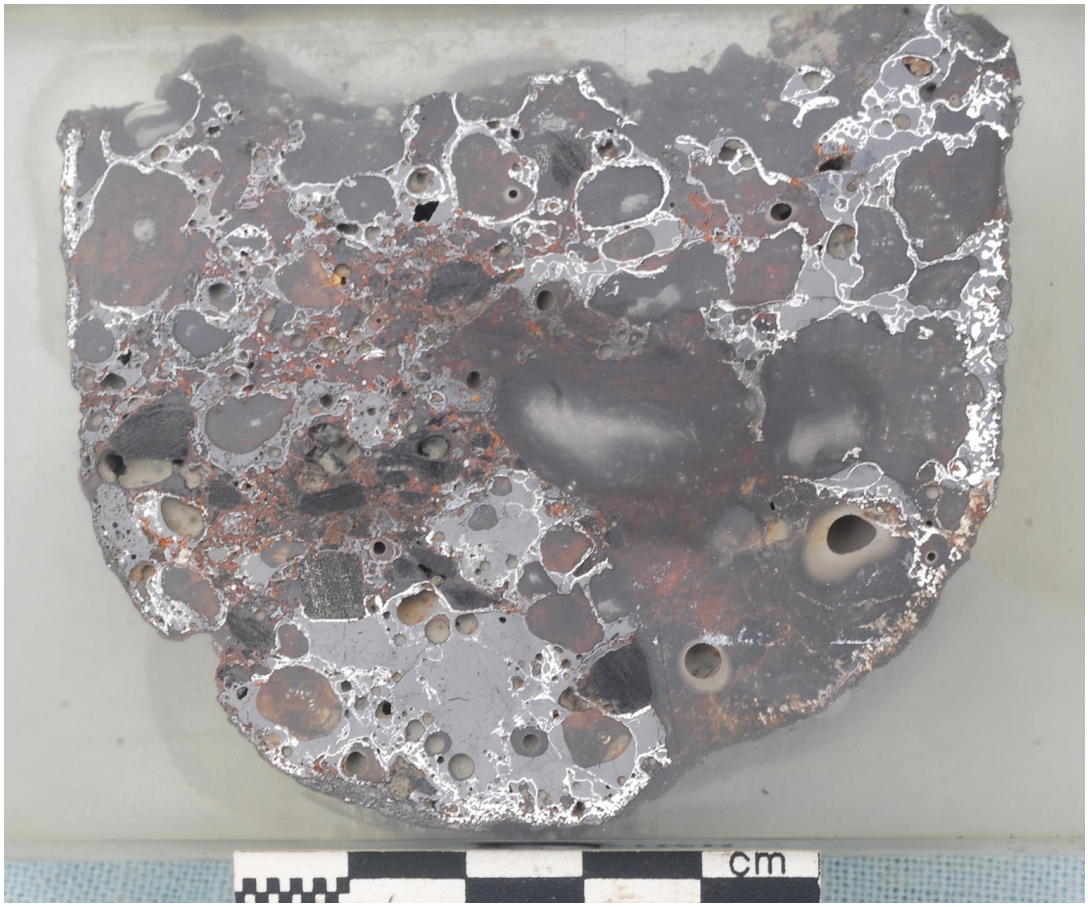


Fig.5.2: Cross section of iron ore (hematite) crucible assemblage after mounting.



Fig.5.3: Cross section of mixed sulphide (chalcopyrite) crucible assemblage after mounting

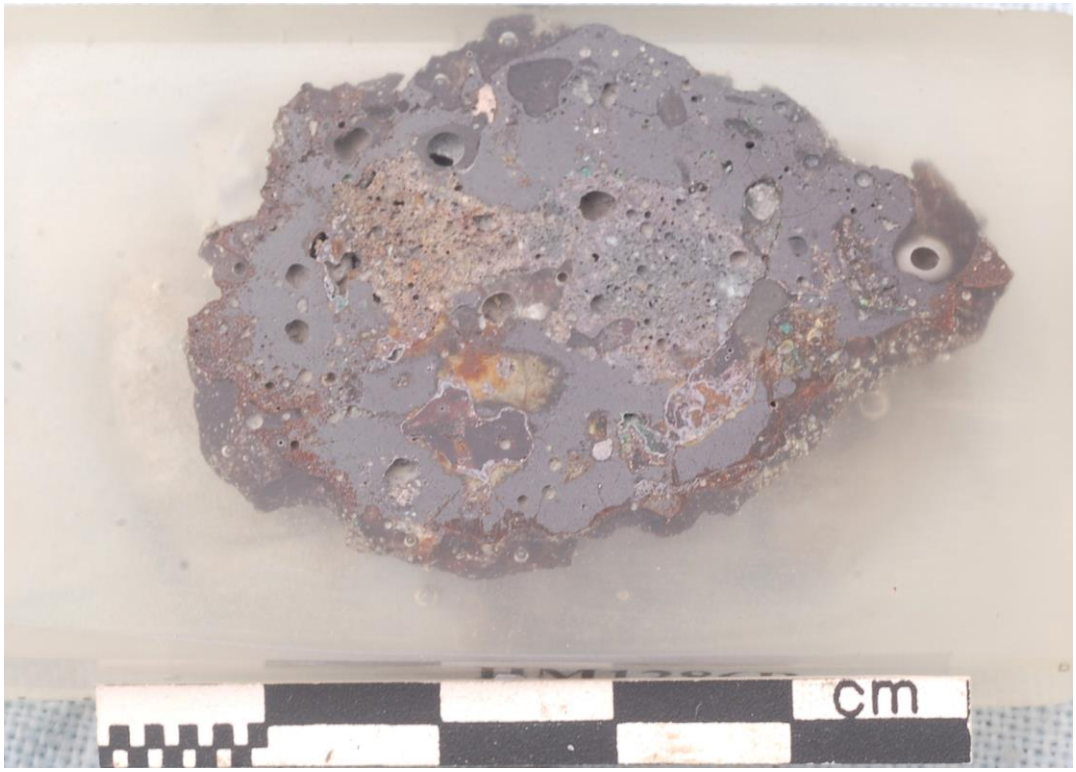


Fig.5.4: Cross section of copper slag crucible assemblage after mounting.

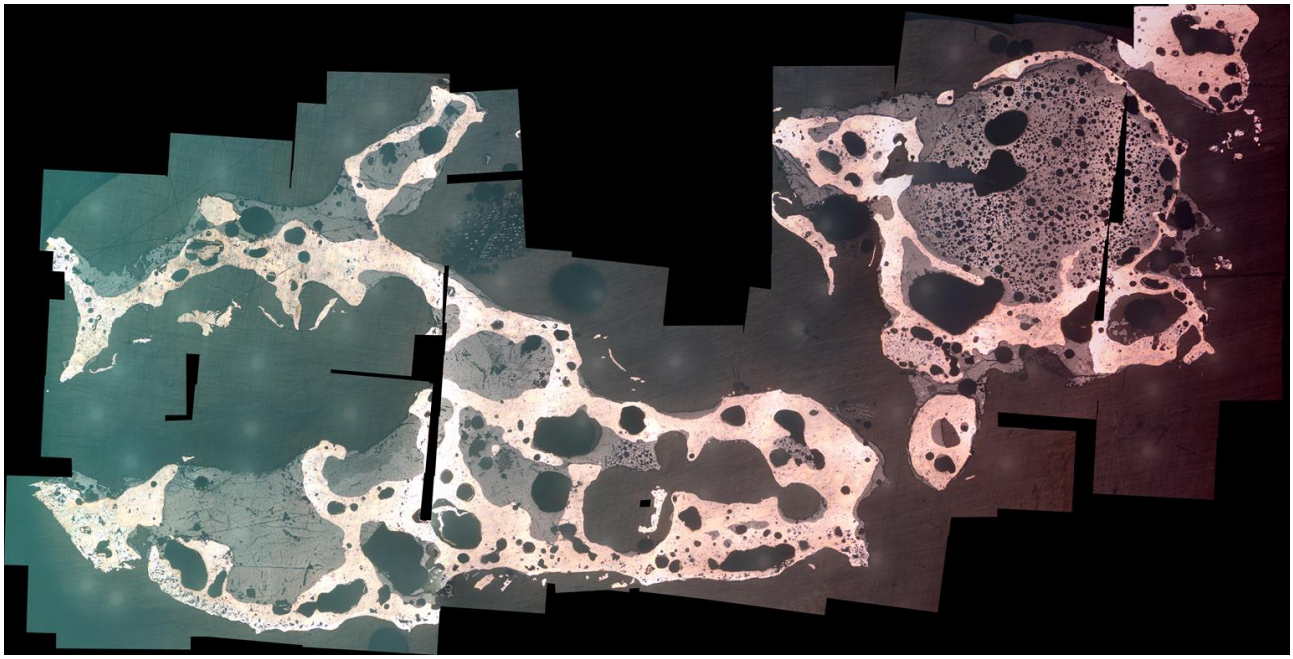


Fig.5.5: Macrograph of cross section of mixed copper and iron oxide crucible assemblage, x1.5 objective. Red-brown copper with bright white inclusions (iron).

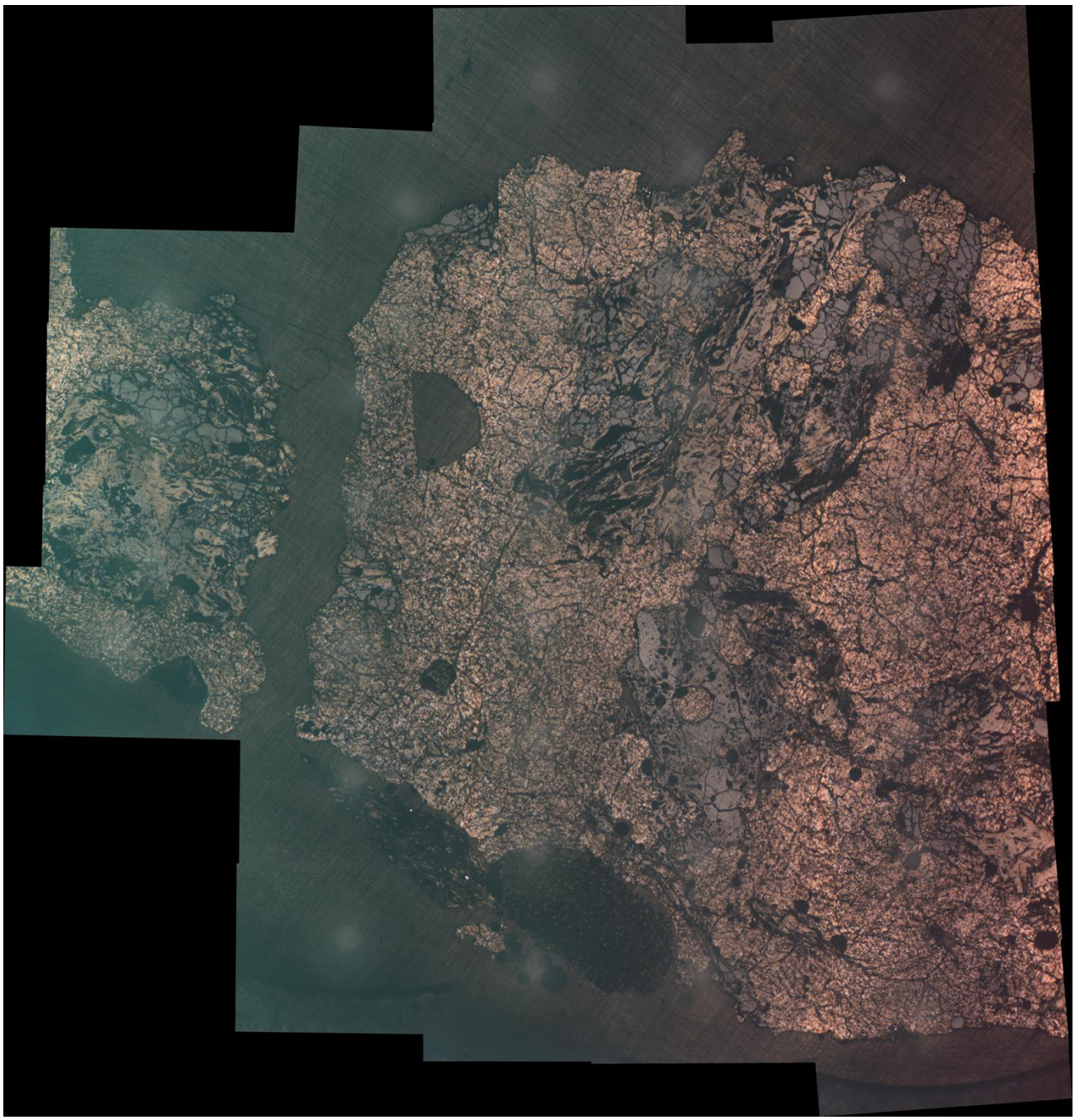


Fig.5.6: Macrograph of cross section of mixed sulphide assemblage, x1.5 objective. A network of brassy yellow grains of chalcopyrite threaded with dull grey copper sulphides.

5.3: **CUFES-1** *Experimental mixed sulphide smelt: Metal, Matte and slag assemblages*

Two assemblages were recovered from the 'cake' that had formed at the base of the furnace during the mixed sulphide smelt which were cut into four sections (see figure 5.7). Within this cake two distinct phases can be identified; a porous dark grey material veined with a brassy-yellow semi-reflective 'metal' containing infrequent copper prills and large quartz inclusions and an overlaying dense and dark grey slag that was mostly homogeneous with occasional prills of white metal and large voids. Orange-brown rust from surface oxidation in this slag revealed the presence of some iron and some black charcoal is visible where it became trapped in the mass. Taken as a whole the assemblage very much resembled the slags of the south Caucasus and on Cyprus discussed in chapter two in terms of quartz inclusions, voids and consistency.

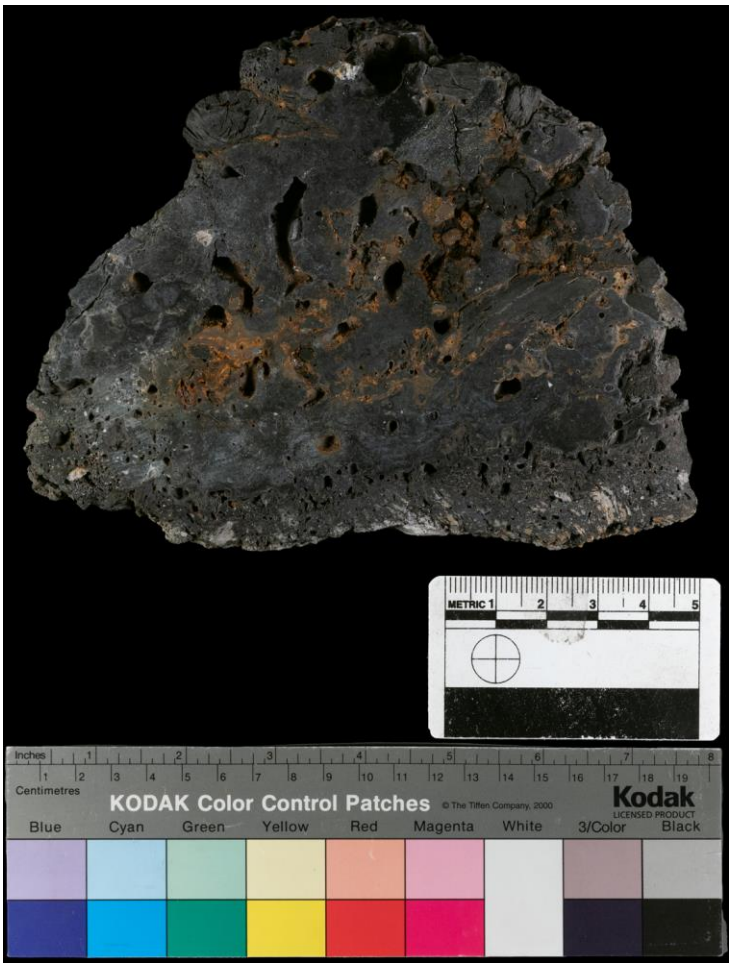


Fig.5.7: First section of slag/matte 'cake' from mixed sulphide smelt. Assemblage is orientated as it lay on the furnace floor. Brassy-yellow veins are visible within the bottom fifth of the assemblage with interspersed white quartz inclusions likely from the ore gangue. Light grey metallic prills surrounded by orange rust are visible in the dark grey slag, centre.

Smaller sections for analysis through optical microscopy were selected from two main 'metallic' features identified on the large sections; the veined and porous material termed 'matte' (see figures 5.12-5.13) and the light grey-white metallic inclusions in the slag (see figures 5.14-5.15).

As described in chapter 2 (**2.6**), *matte* is a material that consists of various metallic sulphides originating from a parent ore such as chalcopyrite. The relationships of minerals in the copper-iron-sulphur system are complex and many remain uncertain especially at low temperature. This is caused by extensive solid solutions, non-quenchable phases, persistent metastability and number of phases which complicate the breakdown of sulphide fields during cooling (UCL-mineralogy of sulphide minerals). During roasting and smelting of the ore, thermal decomposition (the stability limit of chalcopyrite is <547^{o}C) causes the ore mineral to split into various sulphides along the miscibility gap in the Cu-Fe-S system, before precipitating from solid solutions upon cooling (Kitakaze 2018:24). Over temperatures of 400^{o}C, three extensive solid solution groups are present which are relevant to the extraction of metallic copper from these ores:

- Copper-rich: Bornite-Chalcocite-Digenite solid solution (*bnss*)
- Iron-rich: Pyrrhotite solid solution (*poss*)
- Intermediate: Intermediate solid solution (*iss*)

The relative compositions of these solid solutions can be represented on ternary phase equilibria diagrams for the Cu-Fe-S system (see figures 5.8-5.9):

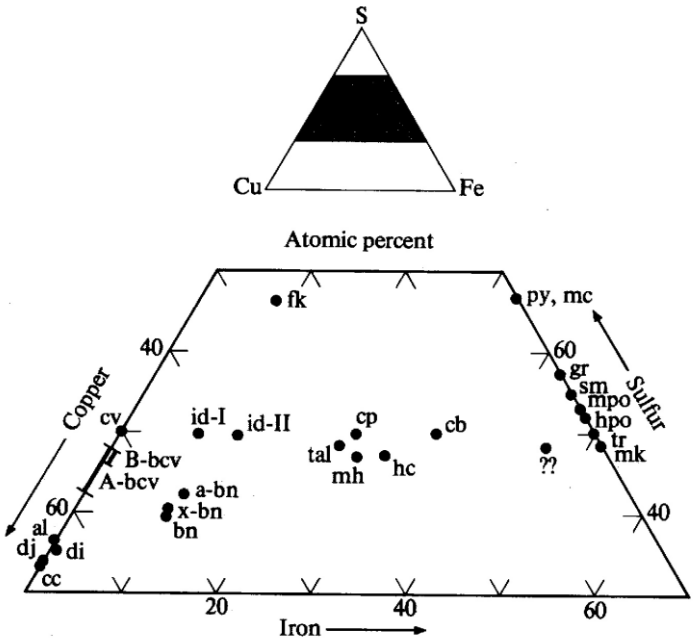


Fig.5.8: Minerals reported in the Cu-Fe-S system. Abbreviations: **cp:** chalcopyrite **cc:** chalcocite, **dj**: djurleite, **al:** anilite, **cv**: covellite, A-B **bcv:** blue remaining covellite, **bn** (x,a): bornite, **id** (I,II) idaite, **tal**: talnakhite, **mh**: mooihoekite, **hc**: haycockite, **cb**: cubanite, **py**: pyrite, **mc**: marcasite, **gr**: greigite, **sm**:smythite, **mpo**: monoclinic pyrrhotite, **hpo**: hexagonal pyrrhotite, **tr**: troilite, **mk**: mackinawite, **fk**: fukuchilite. (UCL-mineralogy of sulphide minerals).

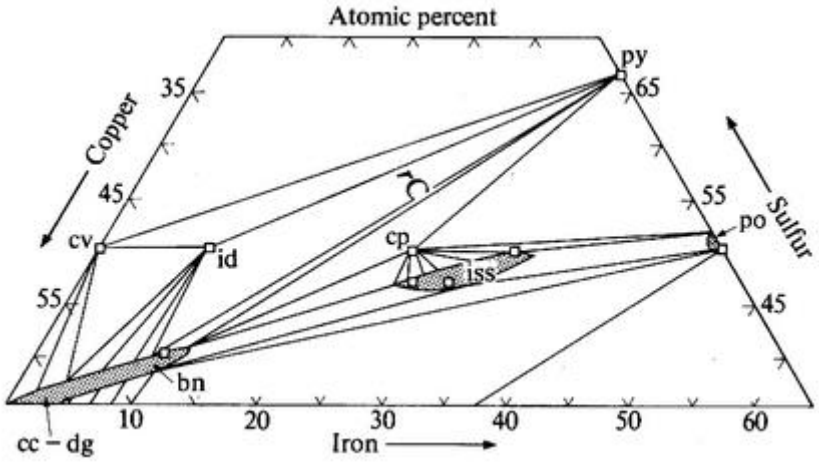


Fig.5.9: Phase relations in the central portion of the Cu-Fe-S system at 400°C. Solid solutions are marked by the grey fields with the bnss in the bottom-right, iss centre and poss mid-right. See figure 5.8 for abbreviations.(UCL-mineralogy of sulphides).

The *bnss* (bornite-chalcocite-digenite solid solution) is largely composed of copper-rich sulphides such as bornite (Cu_5FeS_4) and chalcocite (Cu_2S) and represents a ternary extension of the high digenite (Cu_9S_5) solid solution of the Cu-S system (UCL-mineralogy of sulphide minerals). Below 435ºC the high-digenite solid solution converts to more sulphur rich compositional ranges. At low temperatures (see figure 5.10) the stable sulphides belonging to this system include covellite (CuS), anilite (Cu_7S_4), djurleite ($Cu_{1.97}S$) and chalcocite (Cu_2S). The bnss contains the most desirable sulphides in matte smelting as these form the principle source of the metallic copper during matte conversion.

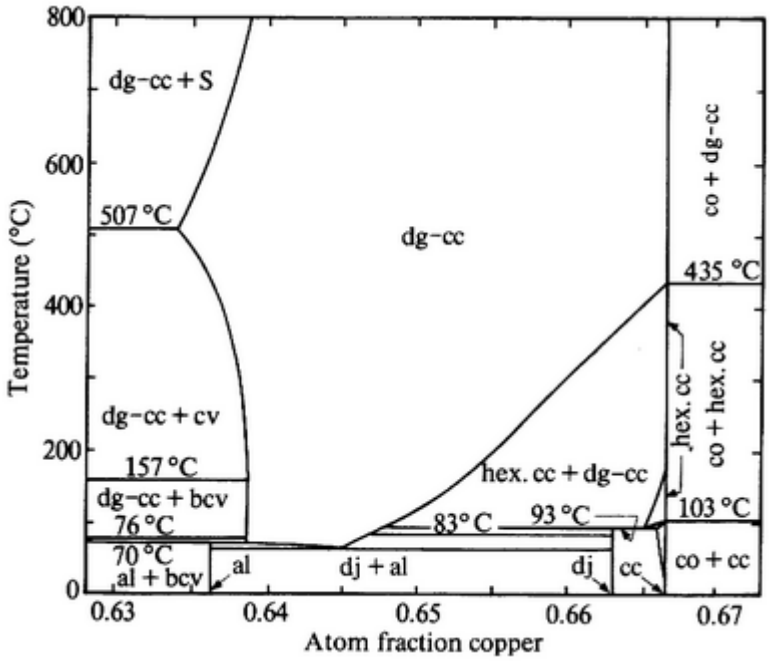


Fig.5.10: Phase relations of condensed phases in the central portion of the Cu-S system. See figure 5.8 for abbreviations. (UCL-mineralogy of sulphide minerals).

The *poss* (pyrrhotite solid solution) contains the iron-rich sulphides and as discussed in **2.6** p.71, during matte smelting the presence of silica causes the oxysulphides to split between iron matte (FeS) and an iron-rich slag. Below 300ºC the composition of pyrrhotite is enigmatic and upon cooling it can exsolve pyrite (FeS_2) and other iron-rich phases (UCL-mineralogy of sulphide minerals).

The *iss* (intermediate solid solution) occupies the central portion of the Cu-Fe-S system and contains a range of minerals which are sulphur deficient compared to chalcopyrite ($CuFeS_2$). In matte smelting the *iss* develops as a result of the oxidation of some of the sulphur from the chalcopyrite and represents an intermediate step of decomposition of the ore that begins with roasting. Below 300°C, the *iss* and *bnss* fields break down into low temperature copper-iron sulphide phases and phases related to chalcopyrite (talnakhite, mooihoekite, haycockite) however the phase relations remain uncertain. Possible phase relations at 25°C are presented in figure 5.11:

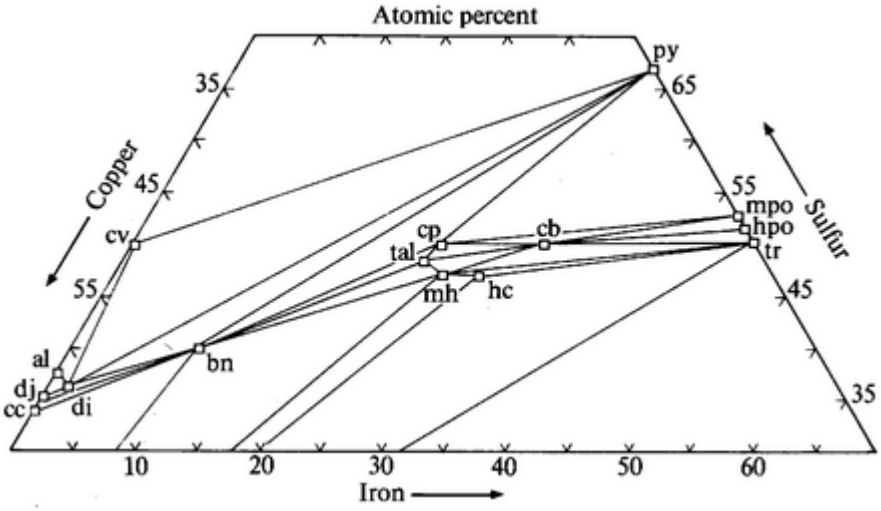


Fig.5.11: Possible phase relations of the Cu-Fe-S system at 25°C. Abbreviations as for figure 5.8. Sulphur deficient minerals of the iss relating to chalcopyrite are shown, centre (UCL-mineralogy of sulphide minerals.)

Final composition of the matte at room temperature is linked to enigmatic phase relations with numerous intervening factors involved during cooling (UCL-mineralogy of sulphide minerals). The copper and iron sulphides contained in matte encompass a range of compositions. Furthermore, the products of matte smelting are anthropogenic and not minerals by strict definition (Rose et al. 2020b:11). In order to address these complications, the analyses presented here will instead identify **copper-rich** (originating from the *bnss*), **iron-rich** (originating from the *poss*) and **intermediate** and ore related (originating from the *iss*) sulphide phases in the samples. As the most relevant groupings to prehistoric copper matte smelting, this should aid in the presentation of this data.

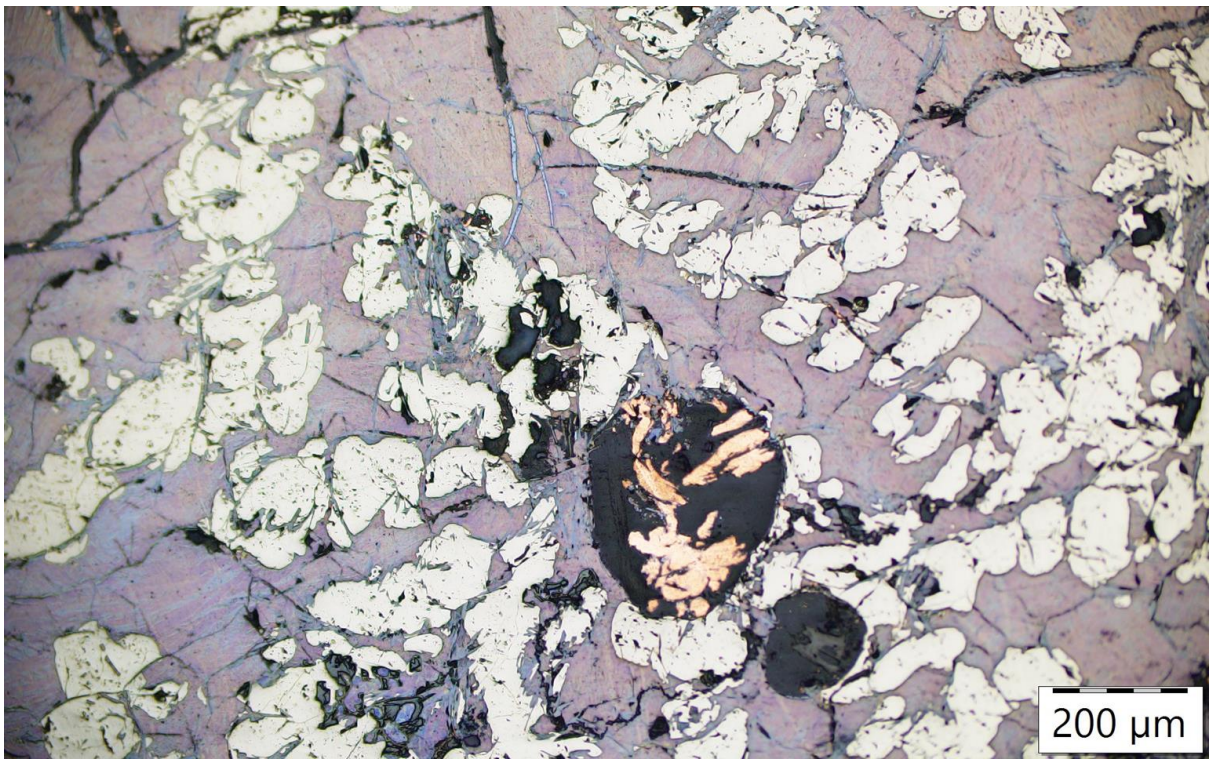


Fig.5.12: Micrograph of 'matte' sample CUFES-1-1, x10 mag. Copper-rich (pink, blue-grey) sulphides with iron-rich (white-cream) sulphides and copper (red-brown, centre).

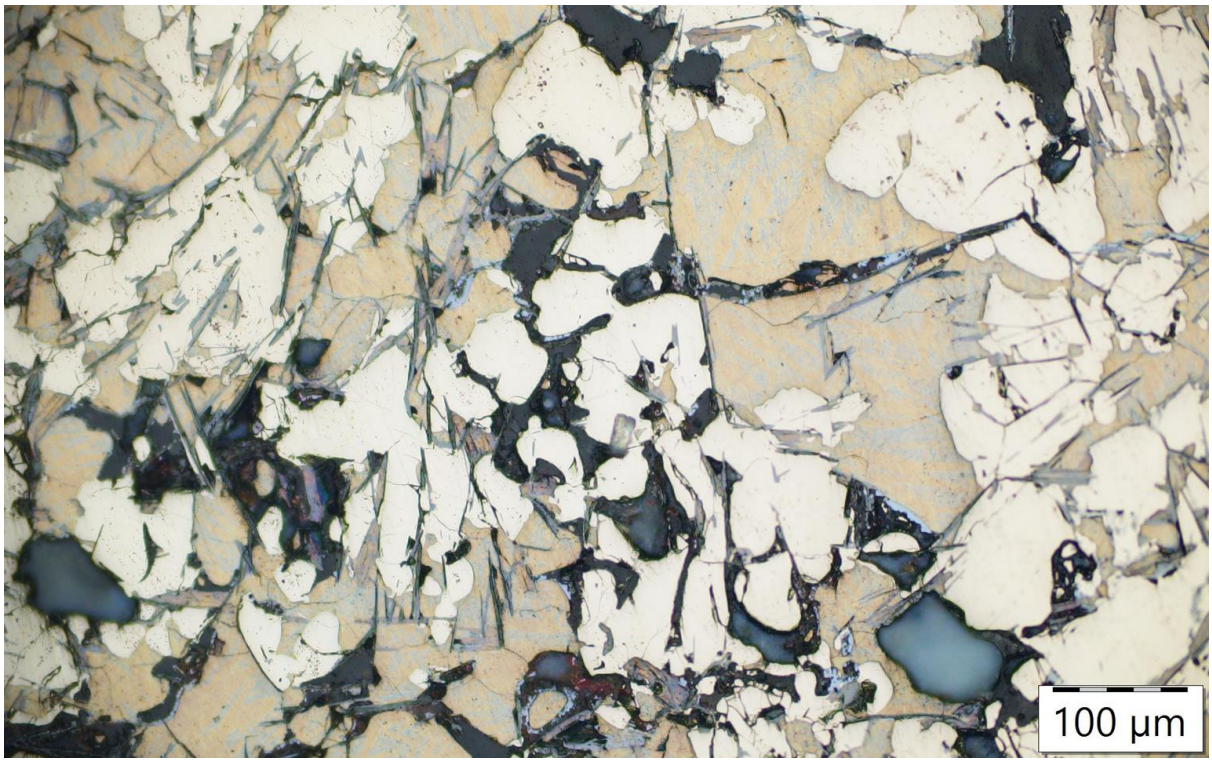


Fig.5.13: Micrograph of matte samples CUFES-1-3, x20 mag. Intermediate (yellow) sulphides veined with copper-rich (blue-grey) sulphides and large inclusions of iron-rich (white-cream) sulphides.

Matte sample CUFES-1-1 shown in figure 5.12 is primarily made up of copper-rich sulphides. Further removal of the sulphur through oxidation and reduction of copper oxides is evident from the copper metal prill in the centre and the small voids from escaping sulphur dioxide gas. Iron-rich inclusions may be iron-sulphide remnants from the ore. Sample CUFES-1-3 in figure 5.13 is considerably more iron-rich with large iron-rich inclusions surrounding the intermediate sulphide which is veined with small copper-rich sulphides and copper prills. These micrographs illustrate the variability of matte composition as the (chalcopyrite) ore decomposes and the iron and copper is partitioned by the Cu-Fe-S miscibility gap. Sample CUFES-1-2, taken from a silver metal prill found in the centre of the slag (see figure 5.7) is shown in figures 5.14-5.15. The large iron-rich sulphide phase contains vesicles of copper-rich sulphides and copper metal and is an indication of the composition of iron rich mattes prior to oxidation of the iron. These prills closely resemble the 'white metal' mentioned by Bourgarit et al. (2003) regarding Chalcolithic fahlore smelting in France, possibly explaining its deposition as waste material in the context of copper smelting.

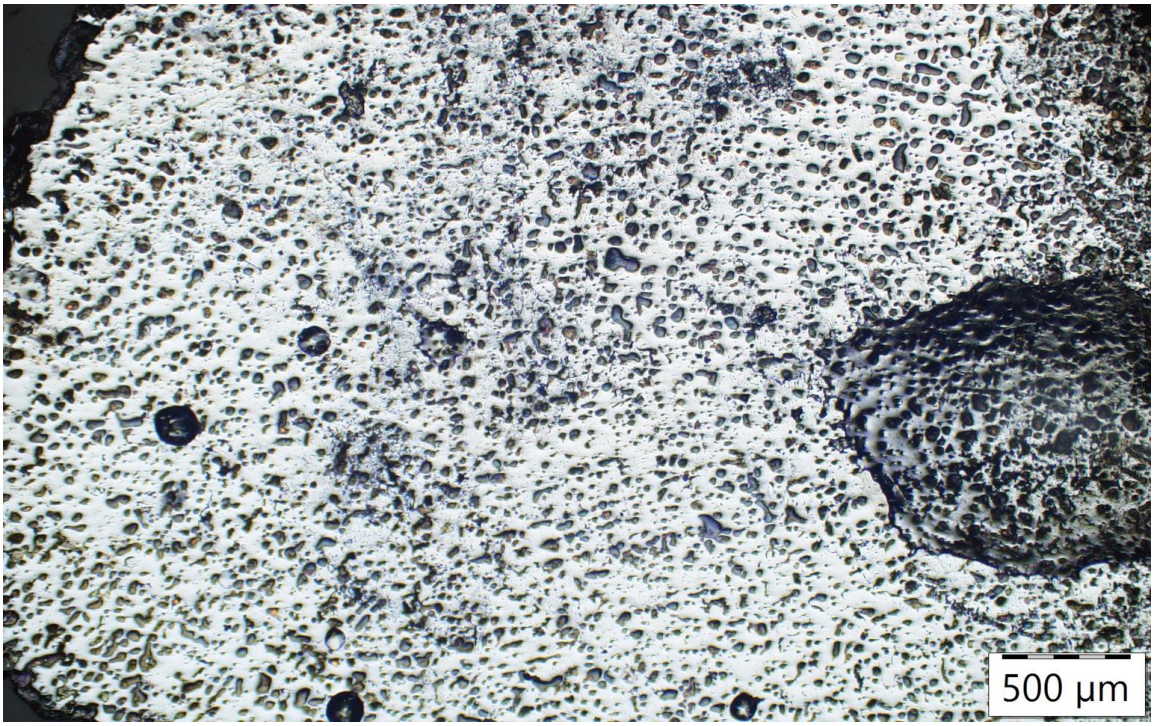


Fig.5.14: Micrograph of sample CUFES-1-2, x4 mag. Large iron-rich sulphide phase (white-cream) with copper rich vesicles (grey).

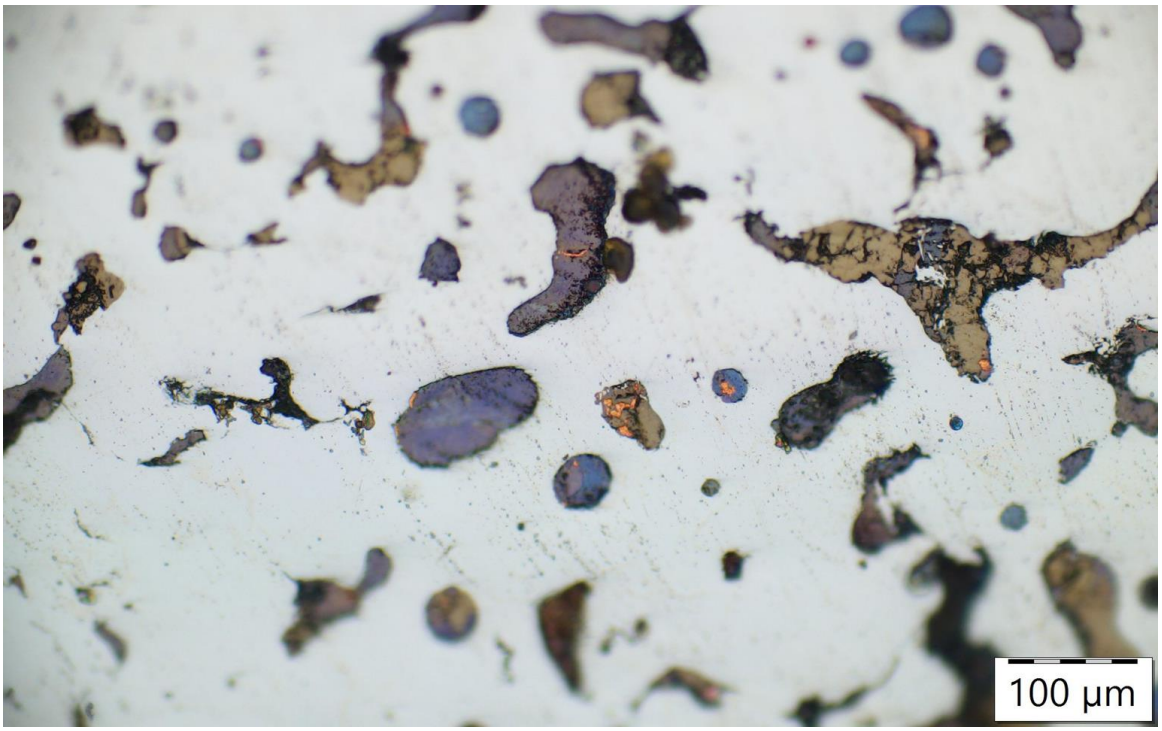


Fig.5.15: Micrograph of sample CUFES-1-2, x20 mag. Large iron-rich sulphide phase (white-cream) with vesicles of copper-rich sulphides (blue-grey) and copper prills (red-brown).

5.4: **FE-1** *Experimental iron oxide smelt: Metal and slag assemblages*

The production assemblage from the iron oxide (hematite, Fe_2O_3) smelt resembles a dense and heavy black slag with a fine porous texture and shiny grey lustre (see figure 5.16). No iron is visible on the surface however oxidation over a short time produced a lot of orange rust. Cross-sections of three pieces were cut which revealed interlacing iron metal in a 'proto-bloom' contained in a dense dark grey and black slag (figure 5.17) with some large quartz inclusions.

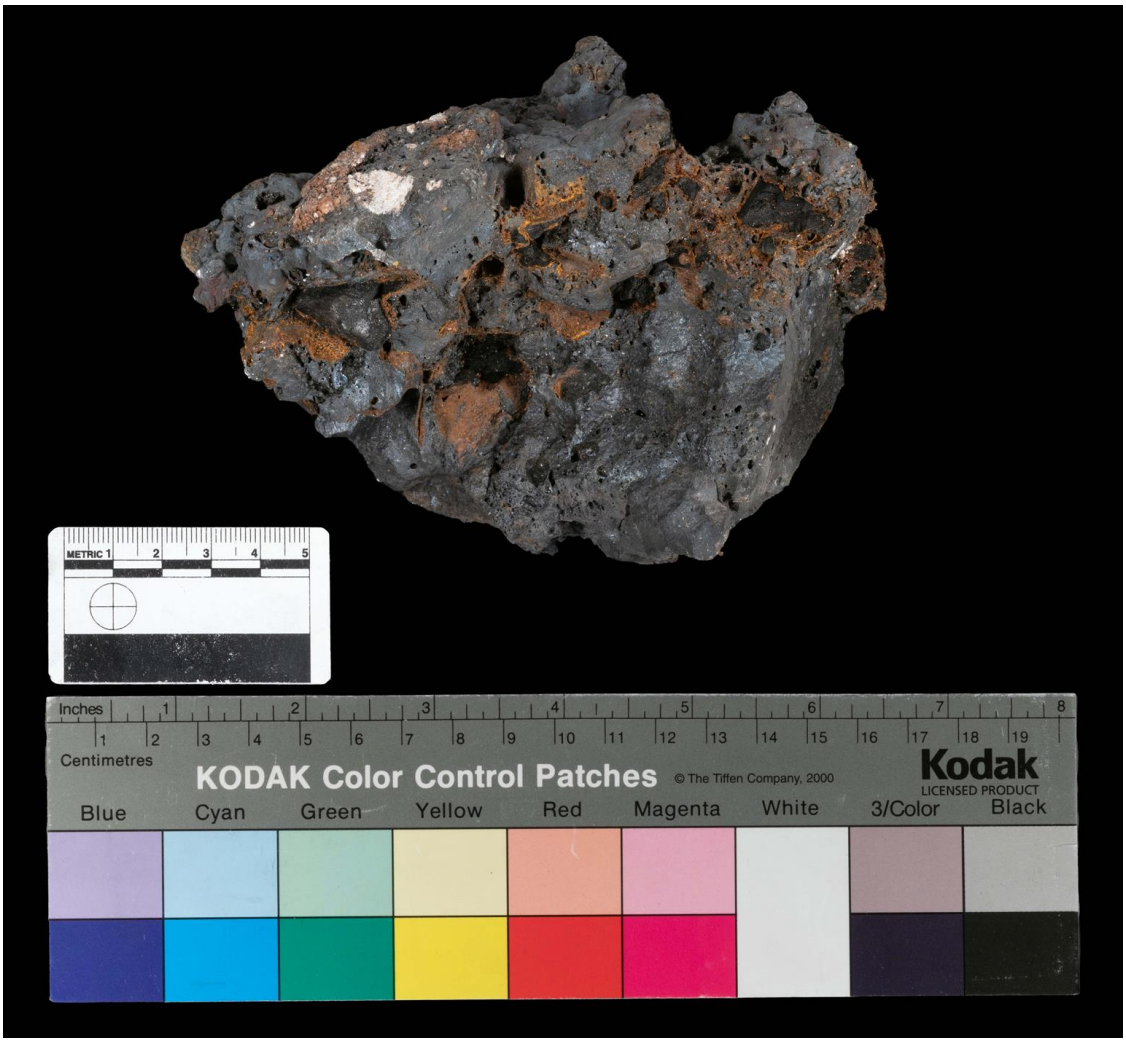


Fig.5.16: Rear of hematite smelt cross-section. Lustrous and porous grey slag with trapped charcoal (black) with surrounding rust (orange). The large white inclusions are quartz.

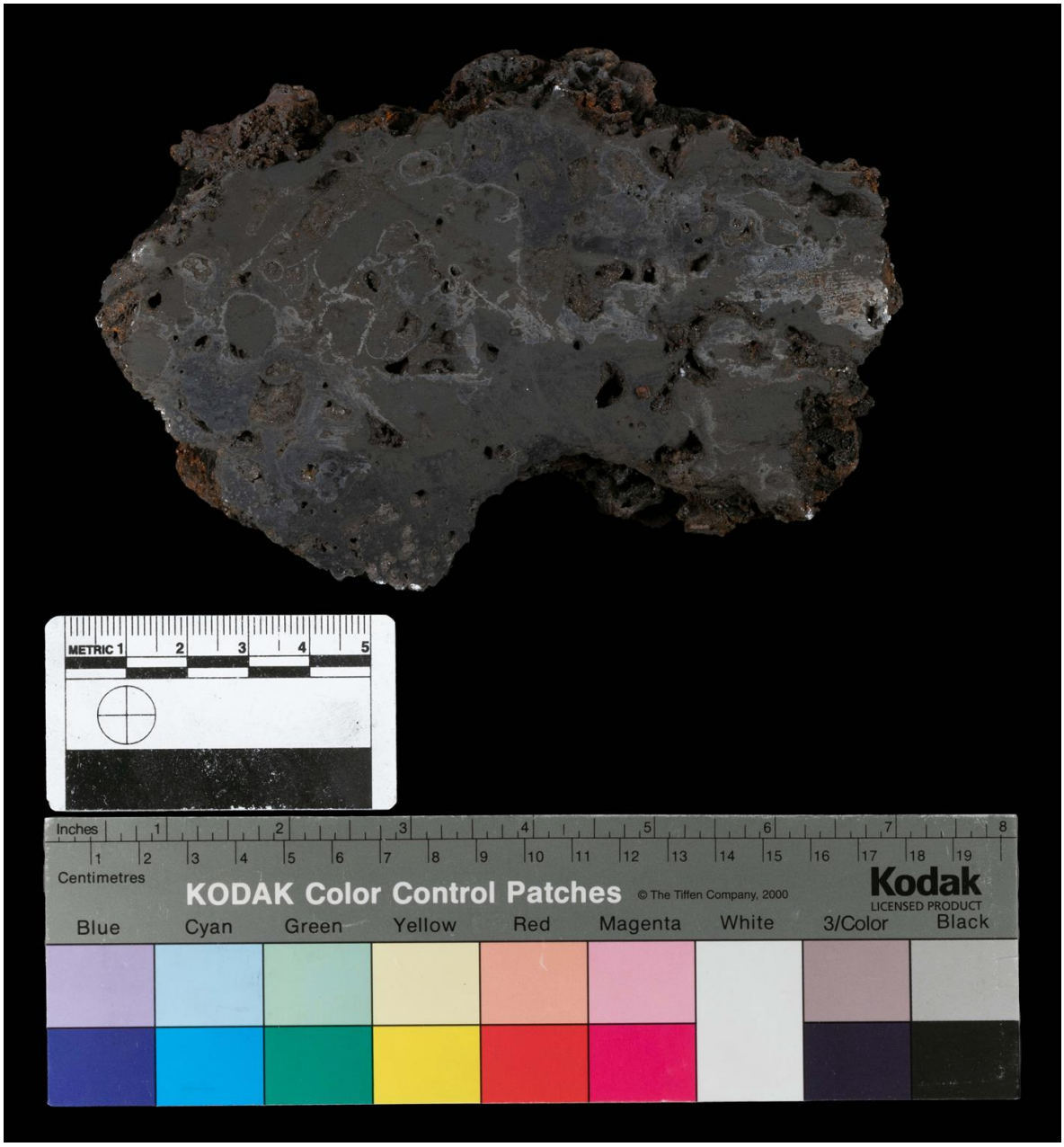


Fig.5.17: Cross-section of iron oxide production assemblage. Light grey reflective iron metal, often banding charcoal inclusions, in a dense black slag. Beating at high temperatures may have consolidated much of this metal into a bloom.

From the six cross sections three small (<3cm) samples were cut and prepared for optical microscopic analysis. These samples revealed an abundance of iron oxides in the slag and their reduction into spongy ‘networks’ and prills of metallic iron contained throughout (see figures 5.18-5.19). This is consistent with the formation of the spongy metallic mass for which bloomery smelting is named after and recognised in prehistoric iron production. Dendritic forms of wüstite indicate a more highly reducing furnace environment which led to reduction of the oxides into metallic iron.

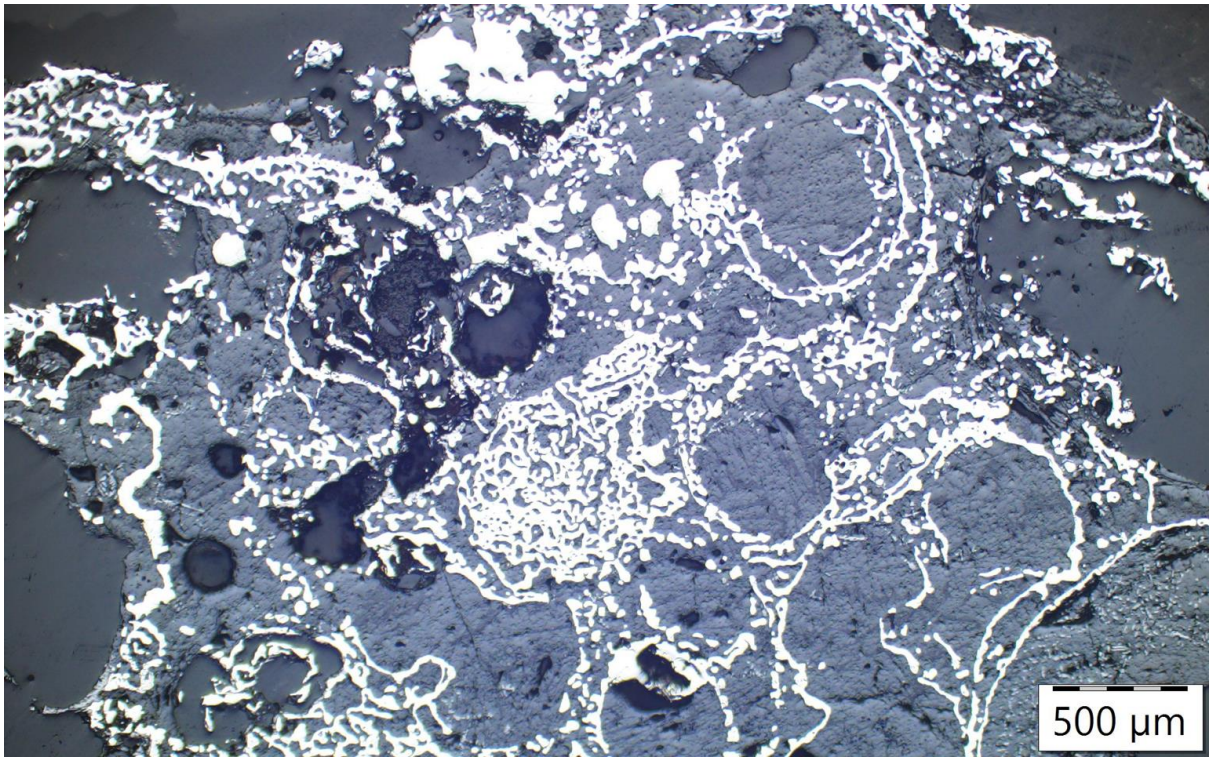


Fig.5.18: Micrograph of sample FE-01, x4 mag. Strands and meshes of metallic iron (white) interspersed through light grey fayalite and dark grey olivines.

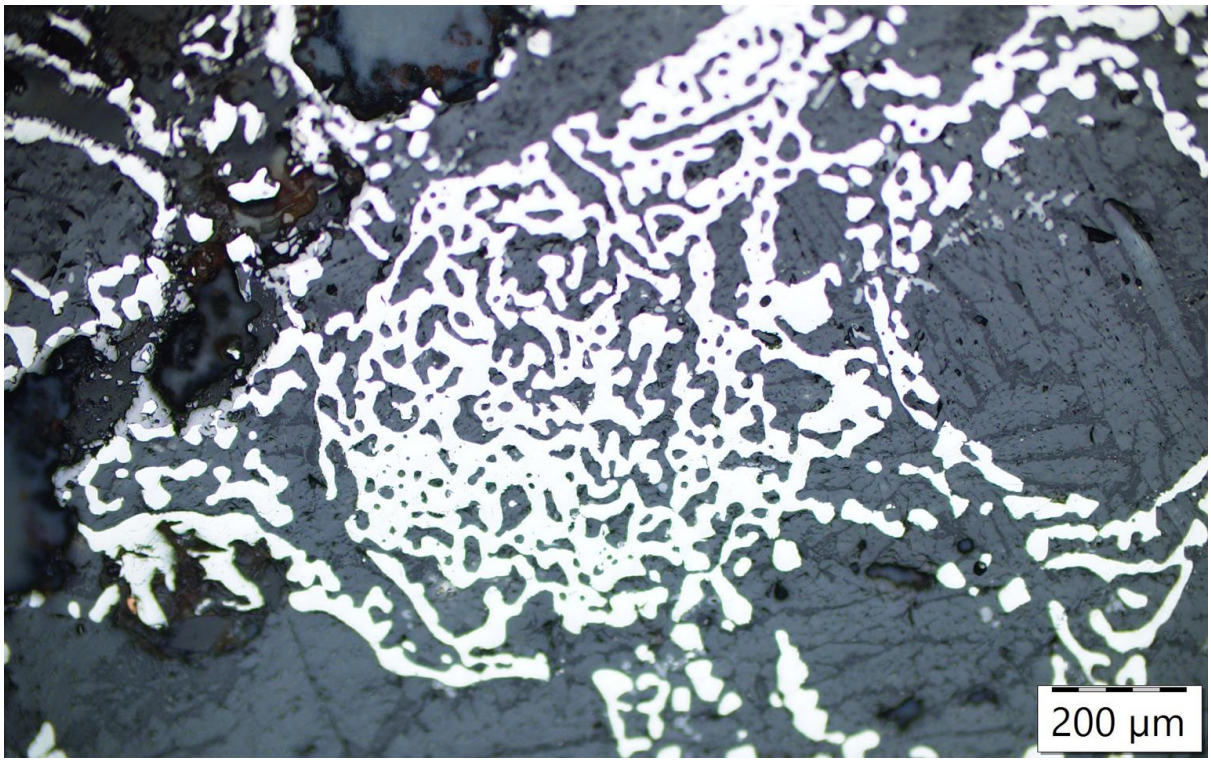


Fig.5.19: Micrograph of sample FE-01, x10mag. Small 'micro-bloom' of metallic iron (white) with 'fingers' of light grey fayalite in dark grey olivine.

5.5: *Experimental copper and iron oxide smelts: Metal and slag assemblages*

The production assemblages of the copper and iron oxide smelts mostly consist of semi-amalgamated copper metal that contains some light-grey reflective inclusions with accruing dense black slag. At their bases the copper had run freely into numerous runnels as it had flowed over charcoal and hard detritus on the furnace floor. Clean segregation of the denser copper on the bottom and the lighter slag on the top was both very apparent in some examples and less so in others and in some of the larger intact pieces the round hole through which the air inflow from the *tuyeres* had entered still survived. As will become apparent in the following figures, the metal contains differing proportions of iron to copper based upon the quantities of both contained in the furnace charge.

5.5.1: CUFE-1

For the first smelt containing a 3:2 mixture of copper oxide to iron oxide in the charge, the cross sections (see figure 5.20) show large predominantly copper metal phases in a dark smooth slag with many smaller copper prills throughout. Large charcoal inclusions had become entrenched in the copper which given more time could have more completely settled at the furnace bottom.

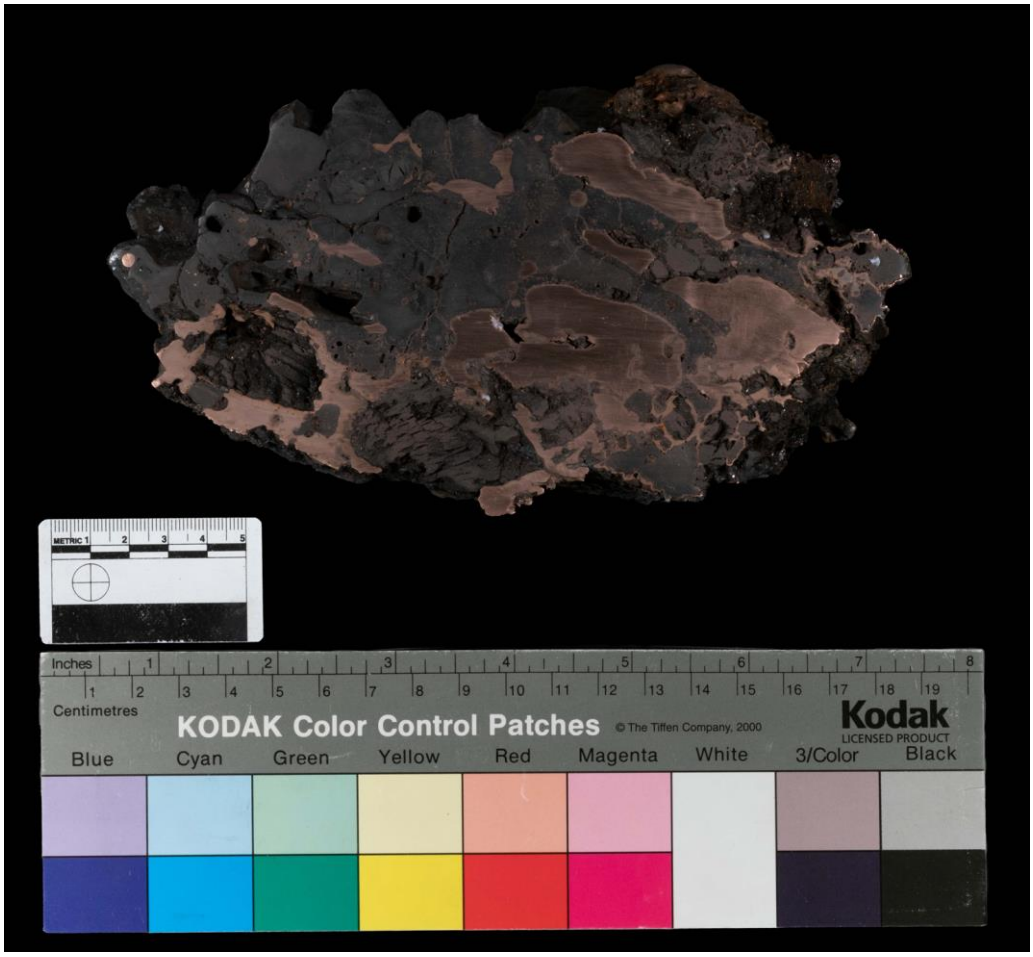


Fig.5.20: Cross-section of 3:2 copper to iron oxide production assemblage as it sat in the furnace. Major copper phases (red-brown) in dark smooth slag with entrained charcoal (black).

The major features visible in the microscopic analysis of two metal samples from this assemblage are widely distributed intrusions of α-iron phases of variable size and form within the copper (see figures 5.21-5.23). Much of the iron has collected into large prills however much finer dispersals of iron are present in all of the copper (see figure 5.24). Very little copper appears to be contained within the iron and there are virtually no iron oxides and only small quantities of cuprite (Cu_2O). The slags that

had become attached to the copper (see figures 5.25-5.26) contain large concentrations of magnetite (Fe_3O_4) and wüstite (FeO) with some entrained copper prills.

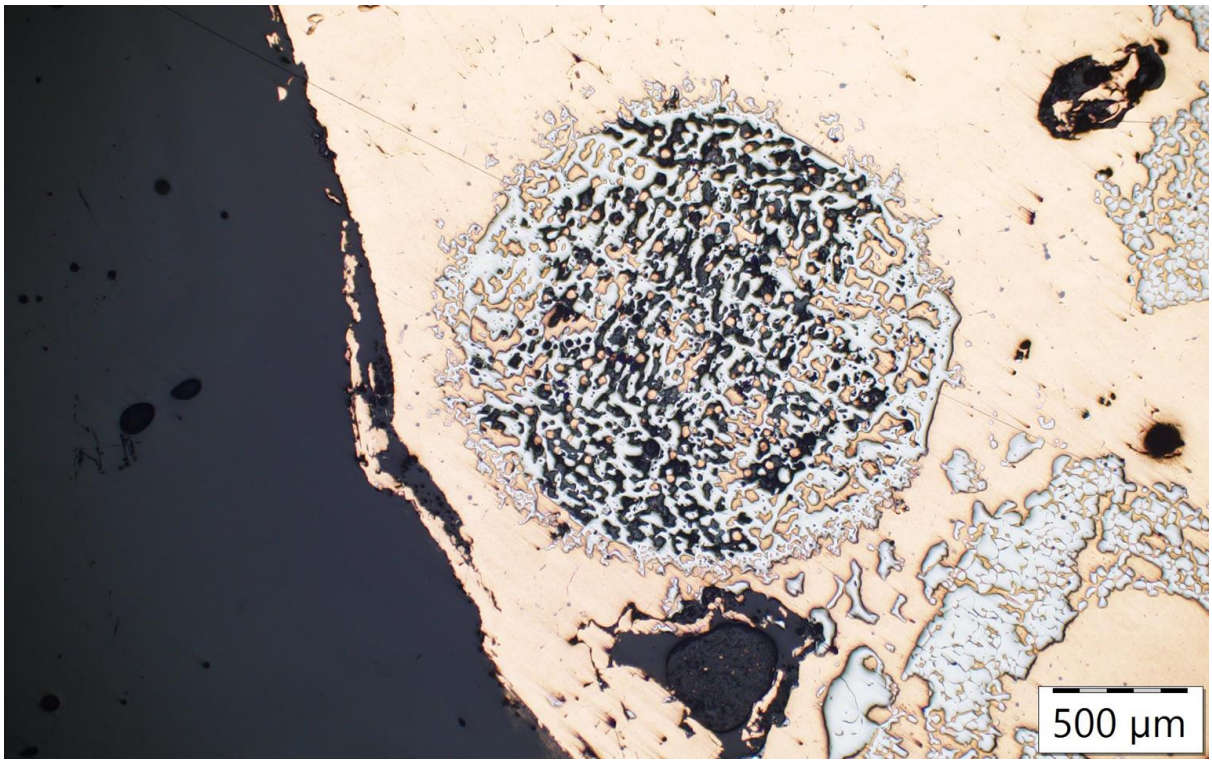


Fig.5.21: Micrograph of CUFE-1-1, x4 mag. Agglomeration of metallic iron (white) in copper (pink -brown).

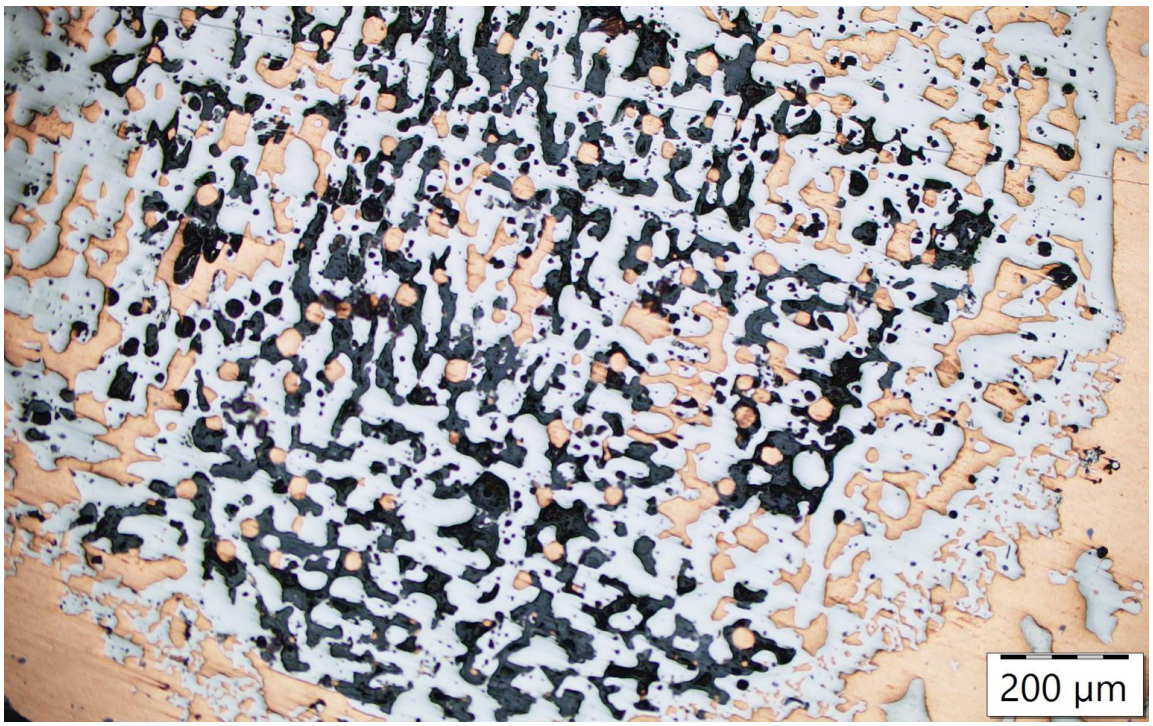


Fig.5.22: Micrograph of prill in figure 5.17, x10 mag. Iron (white) agglomeration in copper (pink-brown).

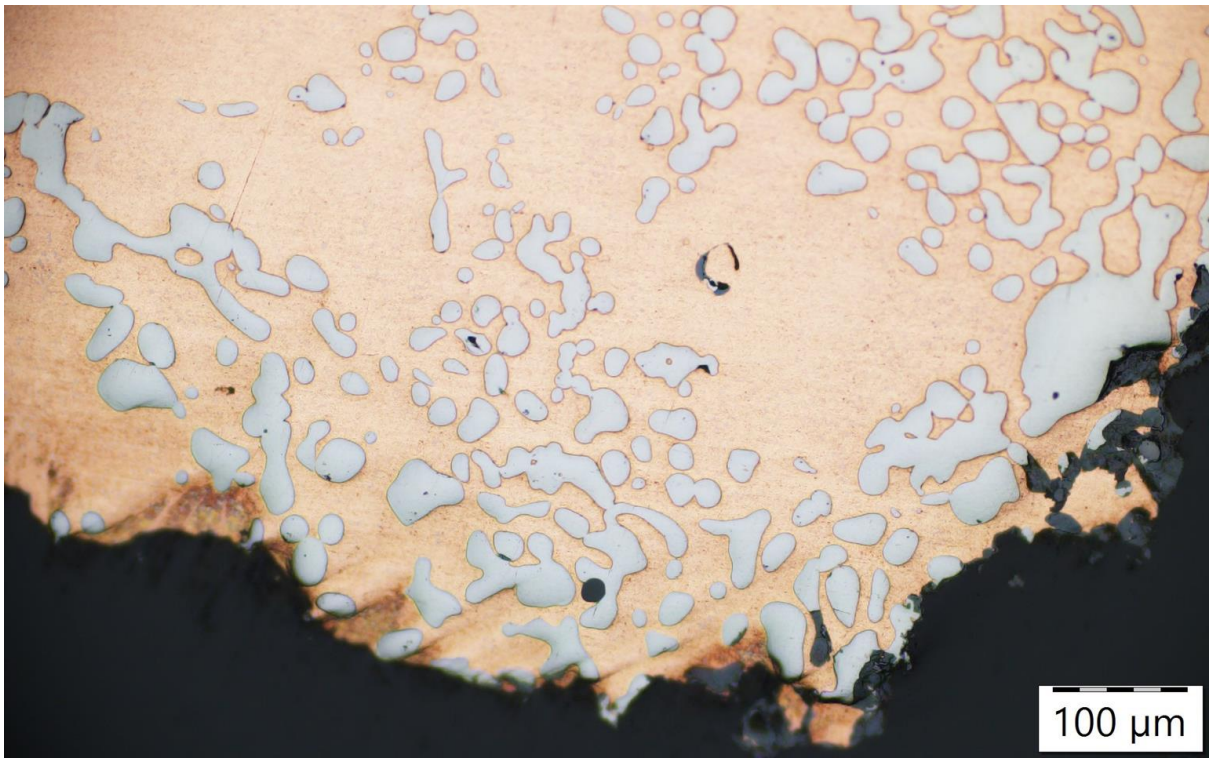


Fig.5.23: Micrograph of CUFE-1-2, x20 mag. Metallic iron (white) in copper (pink-brown).

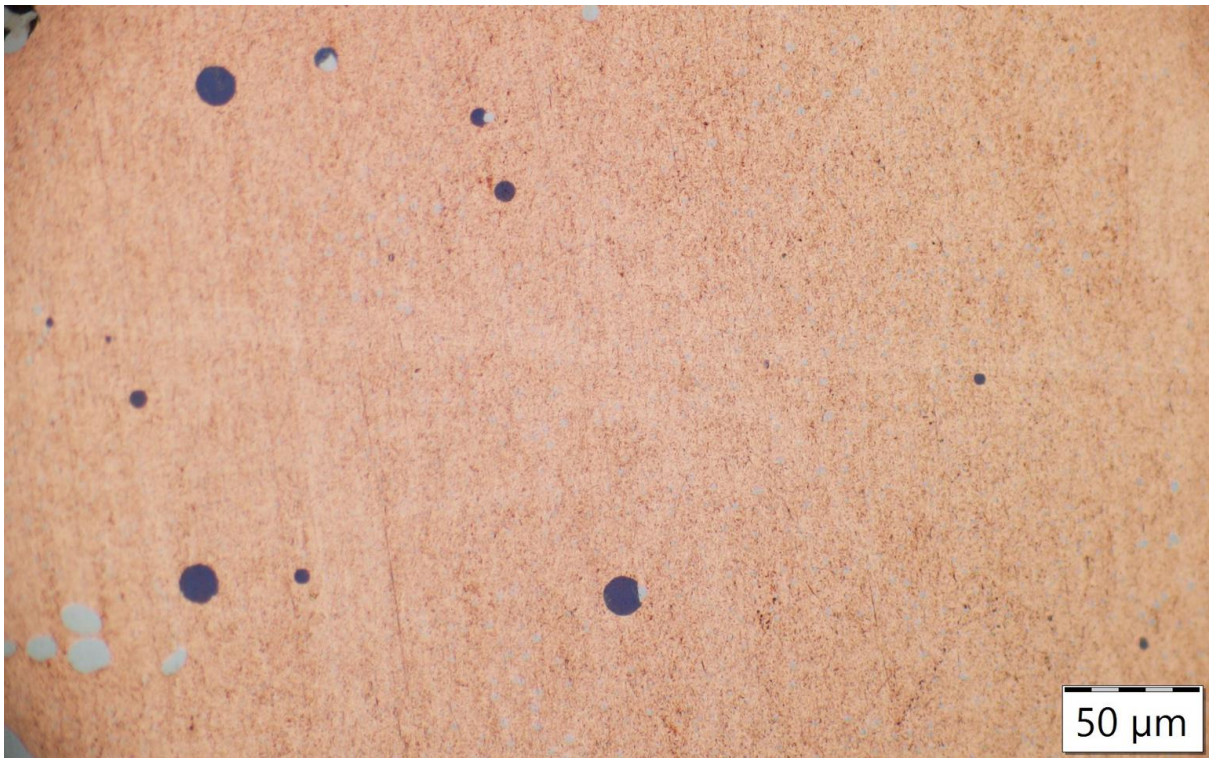


Fig.5.24: Micrograph of CUFE-1-1, x40 mag. Fine spherical iron (light grey) in copper (red-brown).

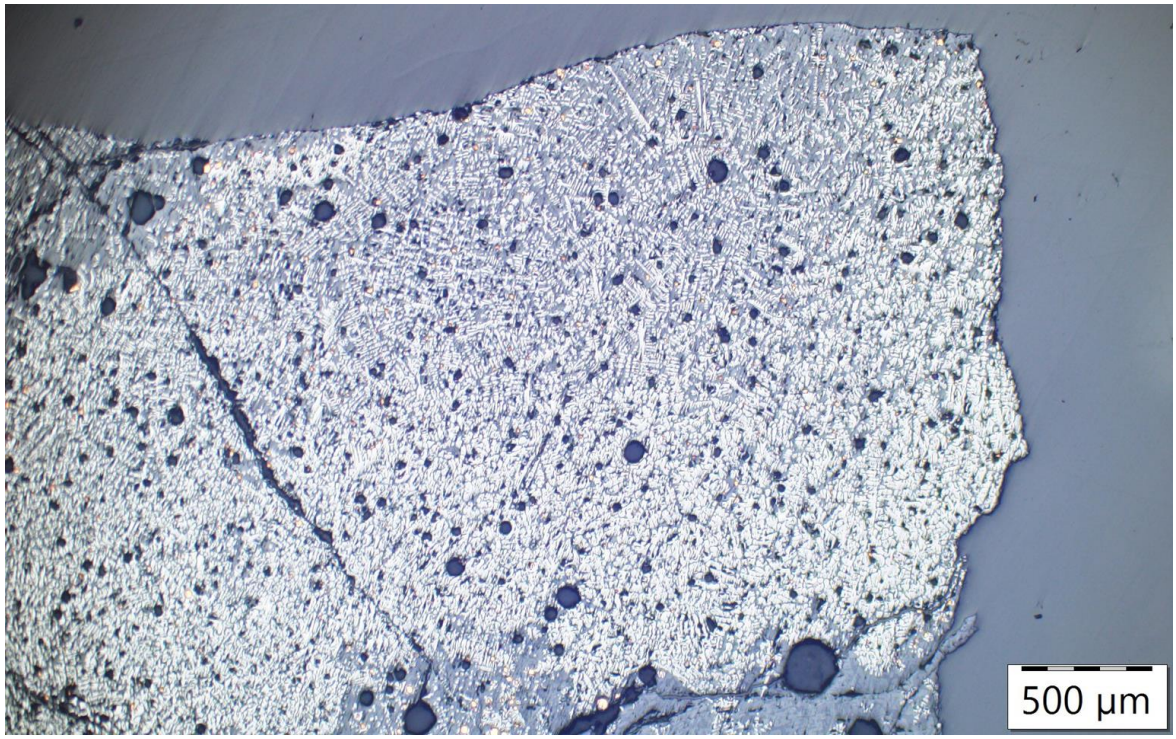


Fig.5.25: Micrograph of CUFE-1-3, x4 mag. Dendritic magnetite (light grey) with globular wüstite (white) and fayalite (grey) in a glassy matrix (dark).

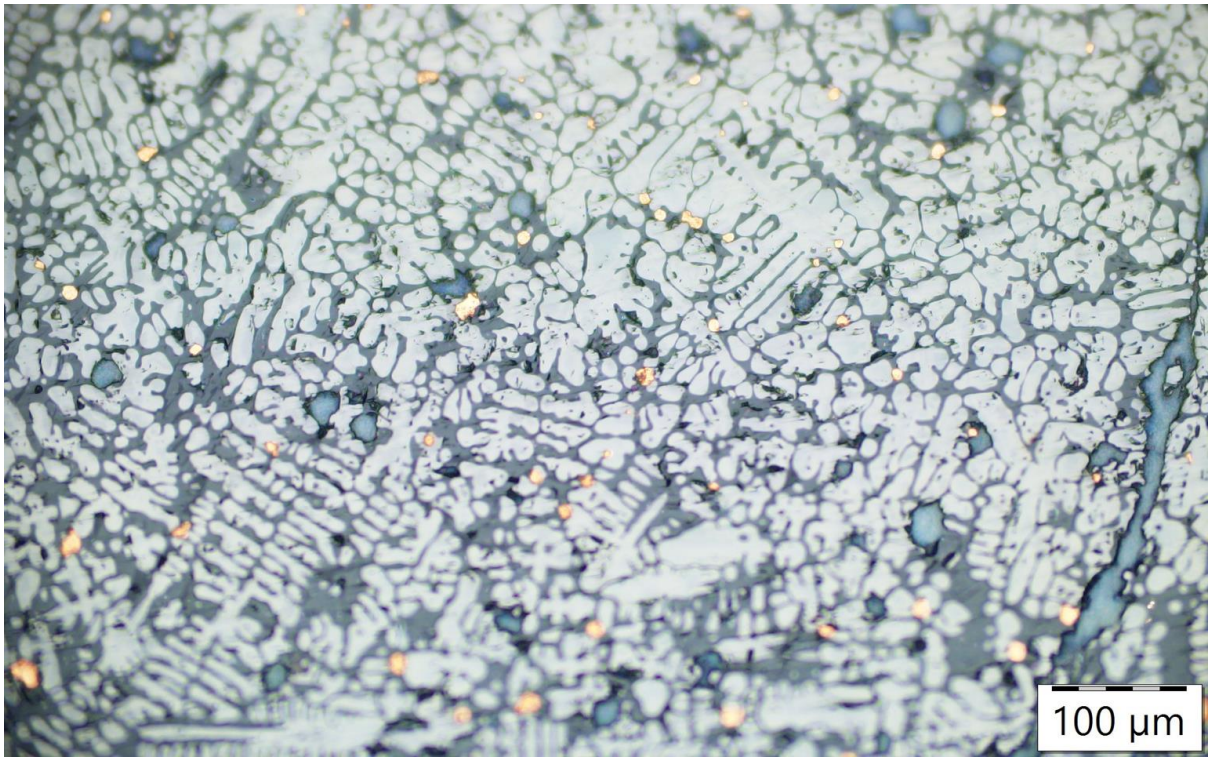


Fig.5.26: Micrograph of CUFE-1-3, x20 mag. Dendritic wüstite (light grey) and copper prills (pink-brown) in fayalite (grey).

5.5.2: CUFE-2

The assemblage retrieved from the 4:1 copper oxide to iron oxide smelt is perhaps the best example of a copper smelting assemblage produced in terms of metal-slag phase separation (see figure 5.27-5.28). A glassy black slag overlays a well defined copper metal phase which had formed a clear meniscus between layers. Some charcoal had become encased in the copper which was otherwise largely free of any inclusions including the light-grey metal observed in the metal of the previous smelt, moulding to the concave furnace floor. The superior separation of the copper metal from a particularly vitreous slag indicates ideal parameters for copper smelting were achieved with near peak efficiency of extraction and consolidation.

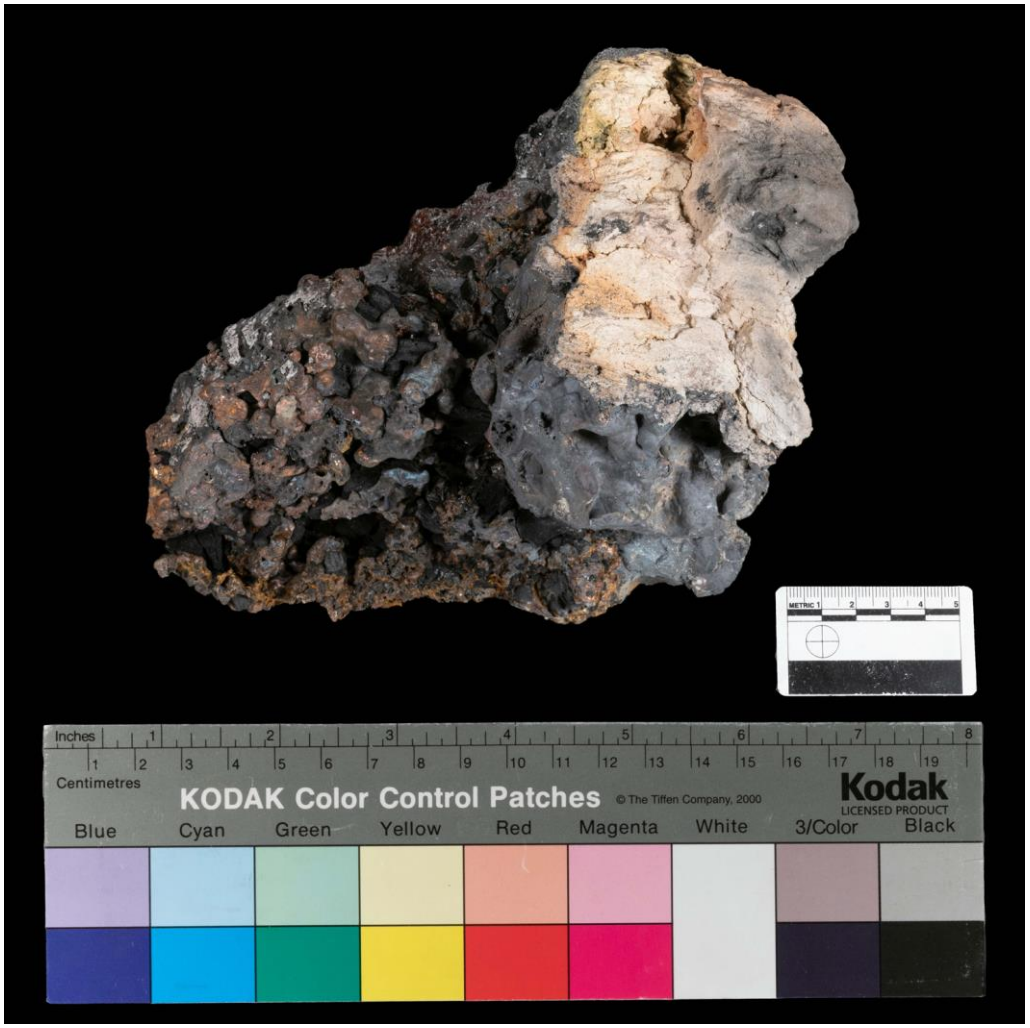


Fig.5.27: Rear of cross-section showing furnace lining (yellow) and copper (red-brown to grey).

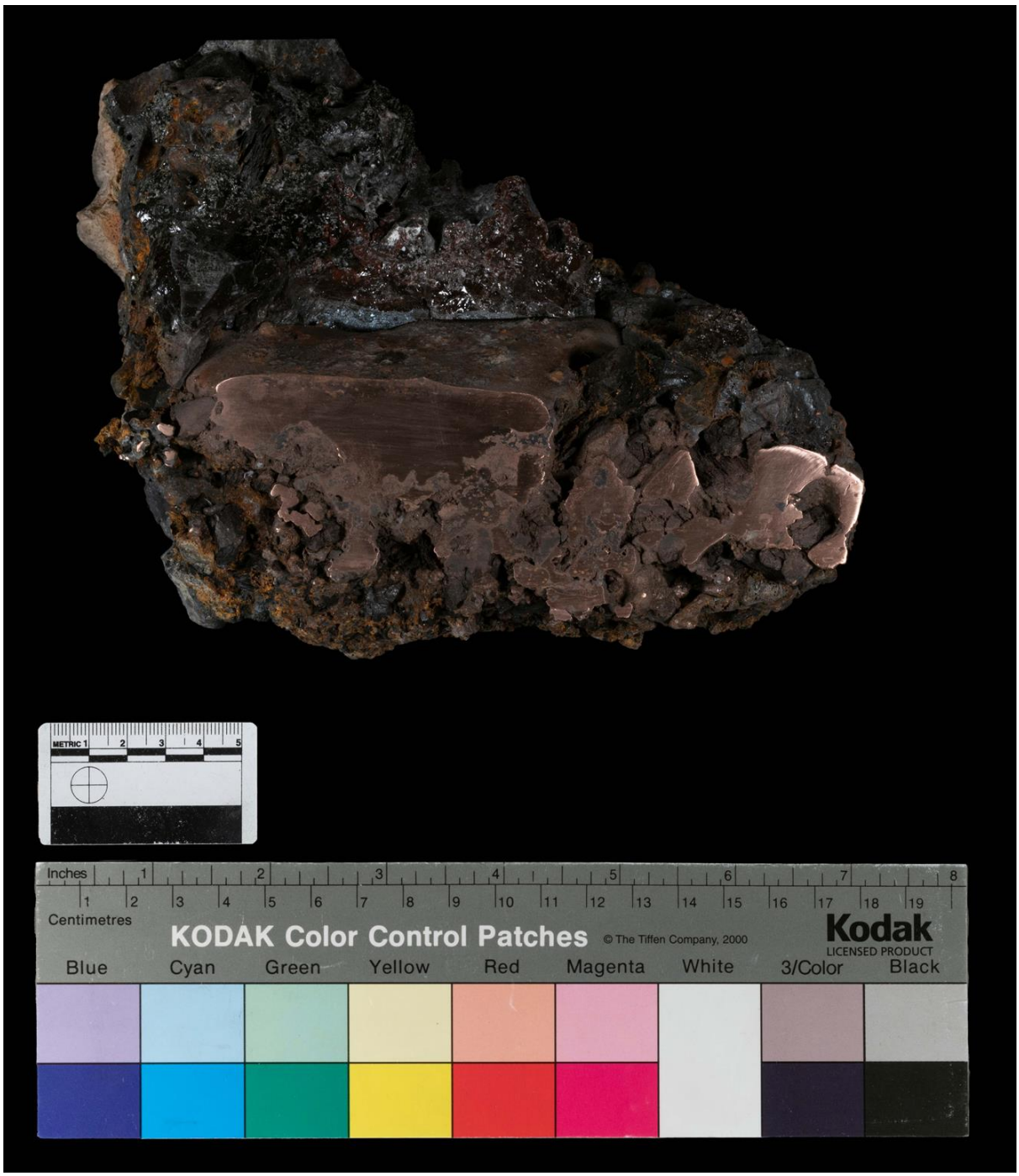


Fig.5.28: Cut-face of cross-section of the 4:1 copper to iron oxide smelting assemblage as it sat in the furnace. Copper (red-brown) showing a clear meniscus on the top surface over which the glassy black and red-brown tinged slag lay. The top-left yellow ceramics is remnants of the furnace wall. Orange rust is also visible revealing the presence of iron.

The metal samples of the second oxide smelt consisting of the 4:1 mixture of copper to iron oxides are of a much more homogeneous copper with smaller but widely dispersed iron inclusions (see figures 5.29-5.30). Larger prills are less frequent and occur in particularly iron-rich regions of the copper (see figure 5.31-5.32). The slags contain less wüstite typically and more magnetite (see figure 5.33) within the fayalite along with many copper prills.

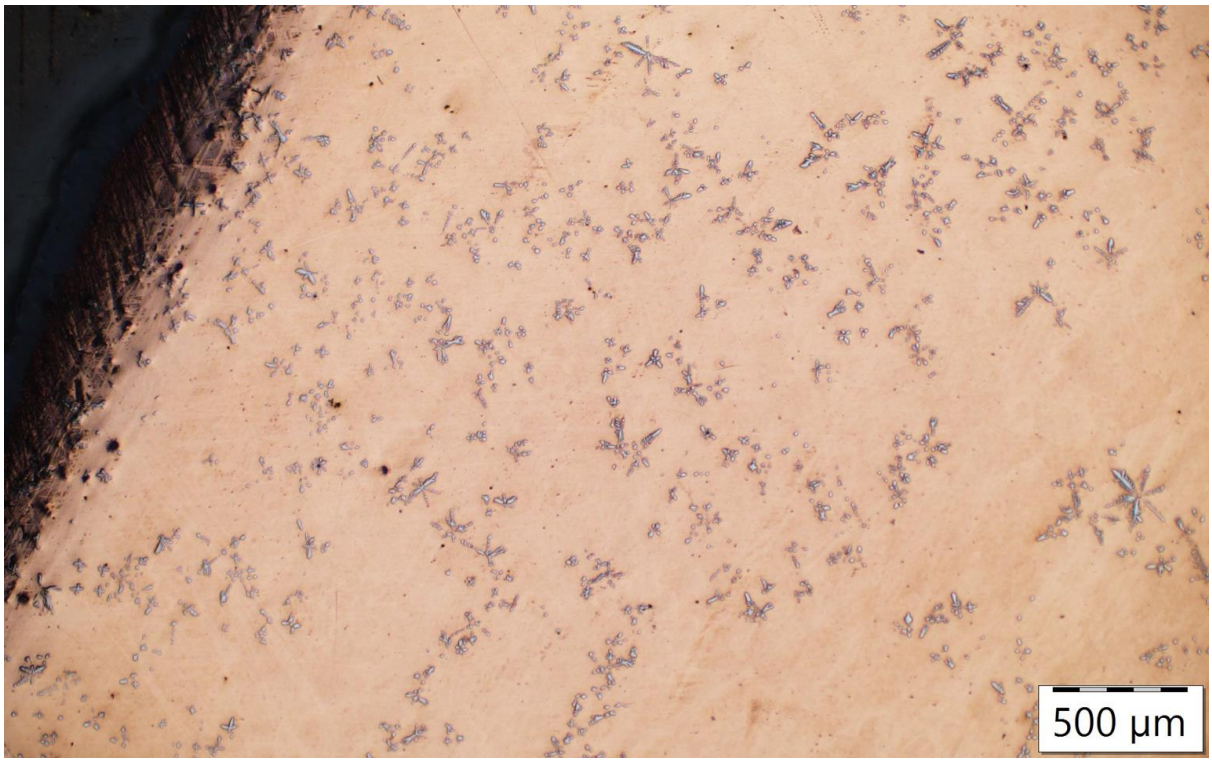


Fig.5.29: Micrograph of CUFE-2-5, x4 mag. Fine dendritic iron (white-grey) in copper (red-brown).



Fig.5.30: Micrograph of CUFE-2-2, x20 mag. Nearly pure copper (red-brown).

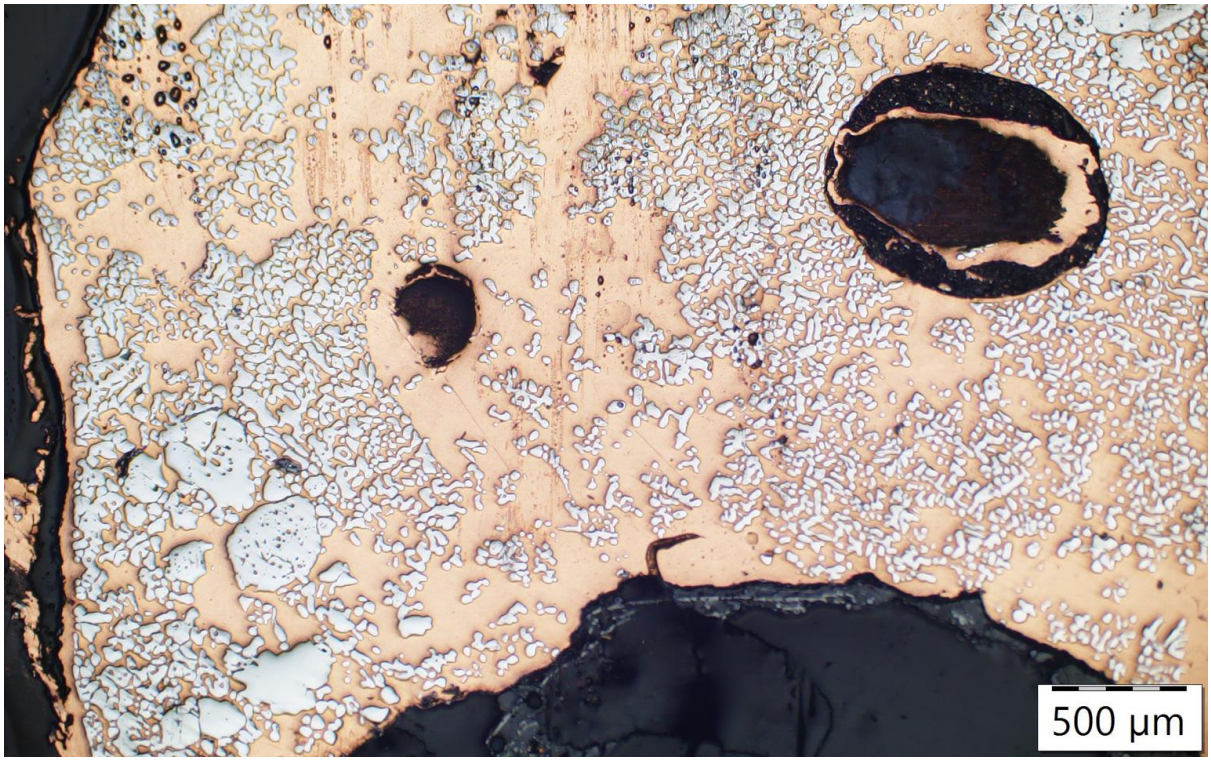


Fig.5.31: Micrograph of CUFE-2-4, x4 mag. Iron inclusions (white) in copper (red-brown).

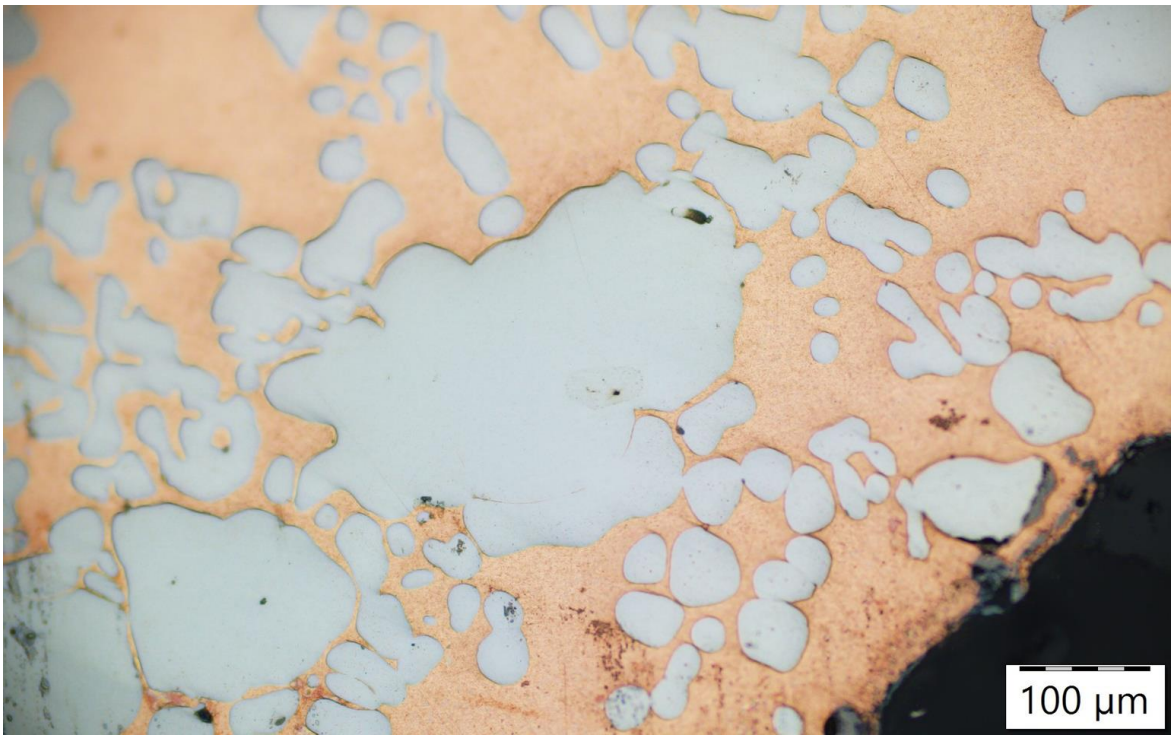


Fig.5.32: Micrograph of CUFE-2-4, x20 mag. Metallic iron prills (white-grey) in copper (red-brown).

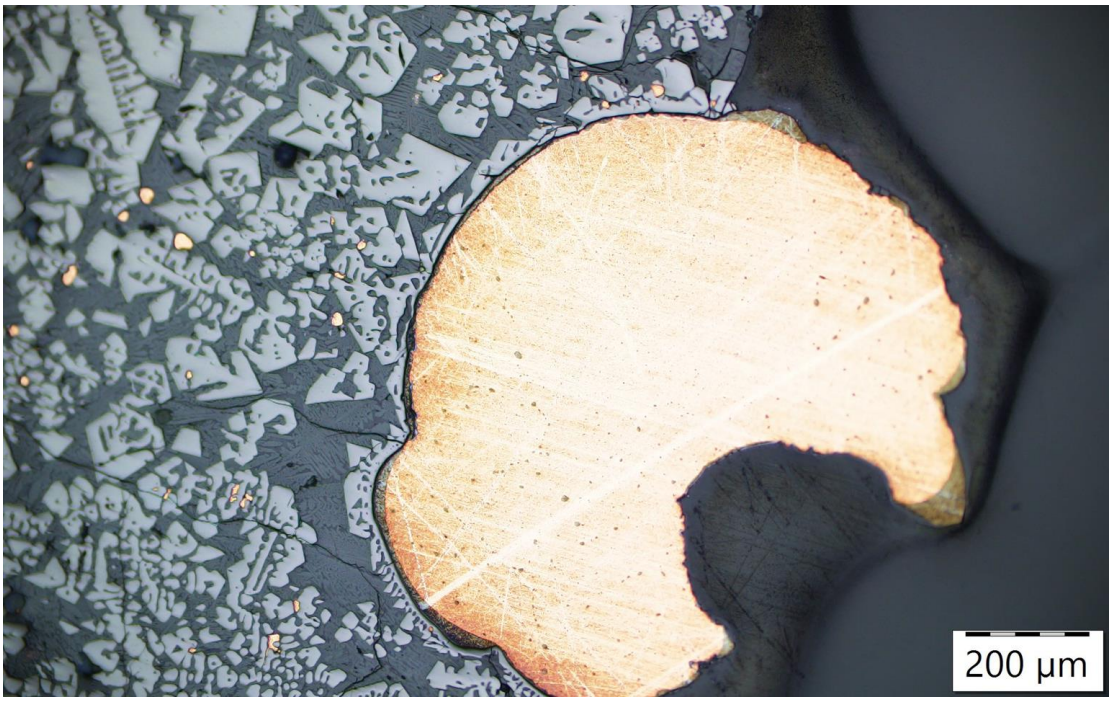


Fig.5.33: Micrograph of CUFE-2-1, x10 mag. Large copper prill (red-brown) surrounded by magnetite (light grey) and fayalite (grey).

5.5.3: CUFE-3

The 4:1 iron to copper oxide smelting assemblage was composed of a dense and glassy black slag containing silver-grey metal with little separation of the two phases. The metal appeared to be mostly iron 'banded' with red-brown copper (see figure 5.34) and smaller copper prills were visible across the slag.

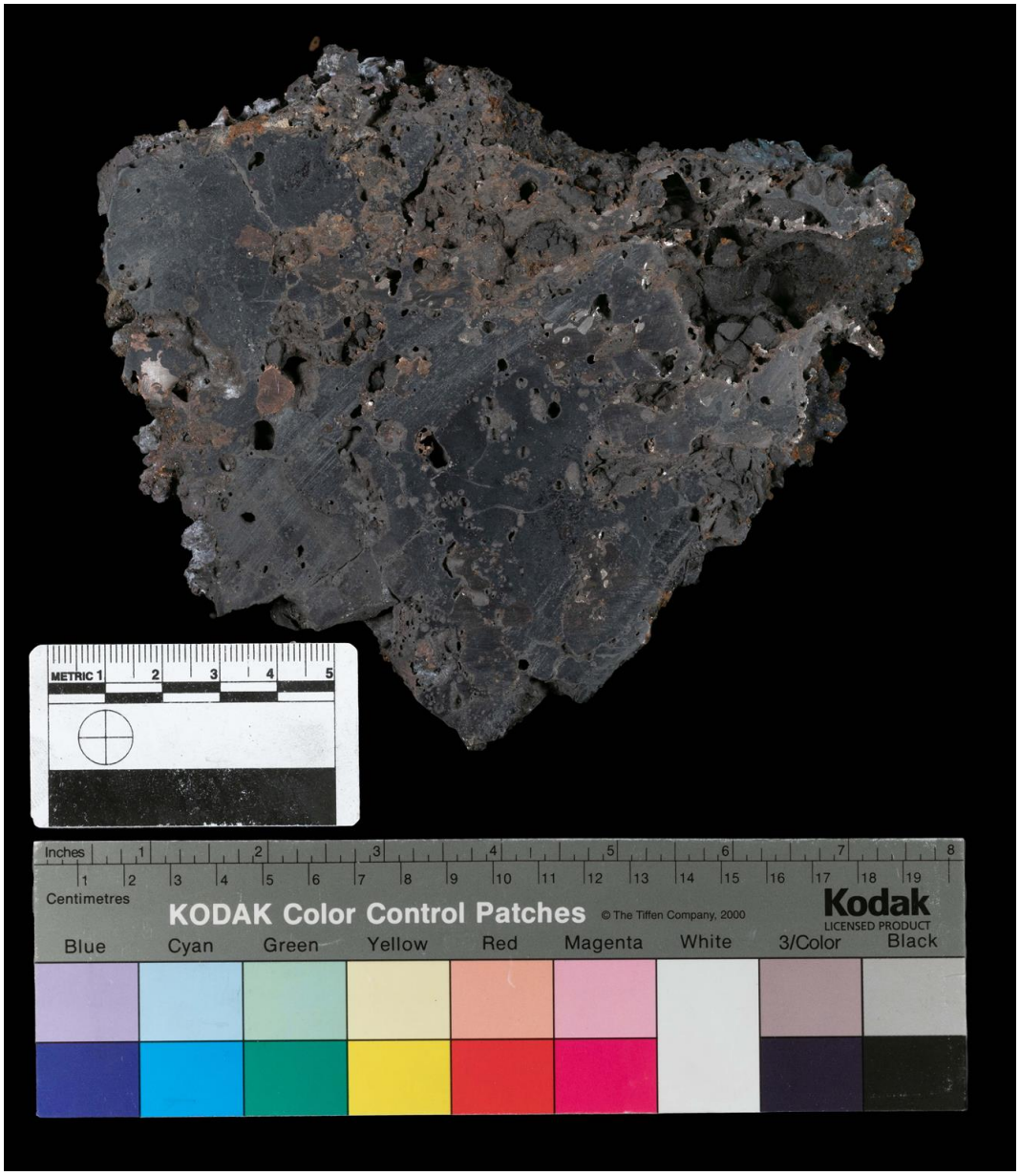


Fig.5.34: Cross-section of 4:1 iron to copper oxide smelting assemblage. There was little clear separation between the iron (light grey) banded with copper (red-brown) and the slag (dark grey).

As might be expected, metallic iron is abundant in the metal samples in large formations and in equal or greater proportions than copper (see figures 5.35-5.37). The slags can be separated into two categories; the first being similar to previous examples (see figure 5.38) and containing iron oxides with fayalite and the latter being an extremely vitreous and homogeneous silicate slag with small inclusions of metallic iron (see figure 5.39).

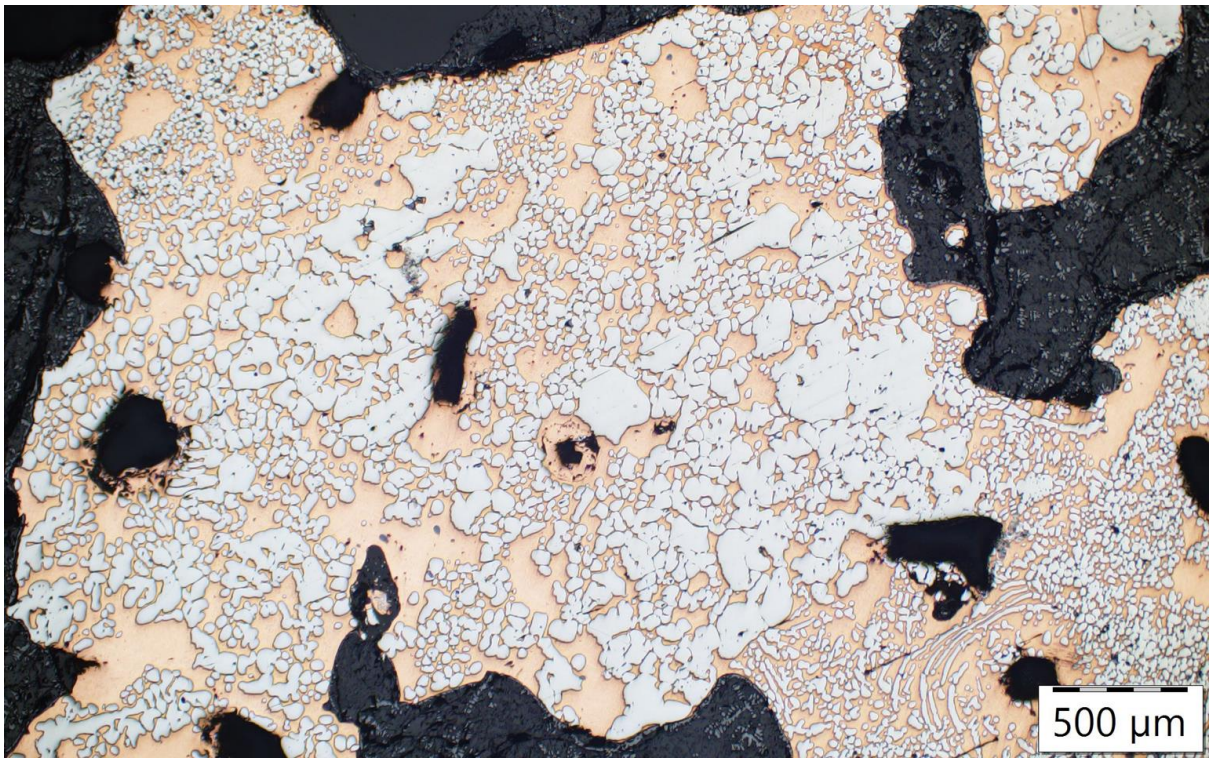


Fig.5.35: Micrograph of CUFE-3-5, x4 mag. Abundant metallic iron (white) within copper (red-brown). Dendritic wüstite (light grey) is visible in the surrounding glassy matrix (dark grey).

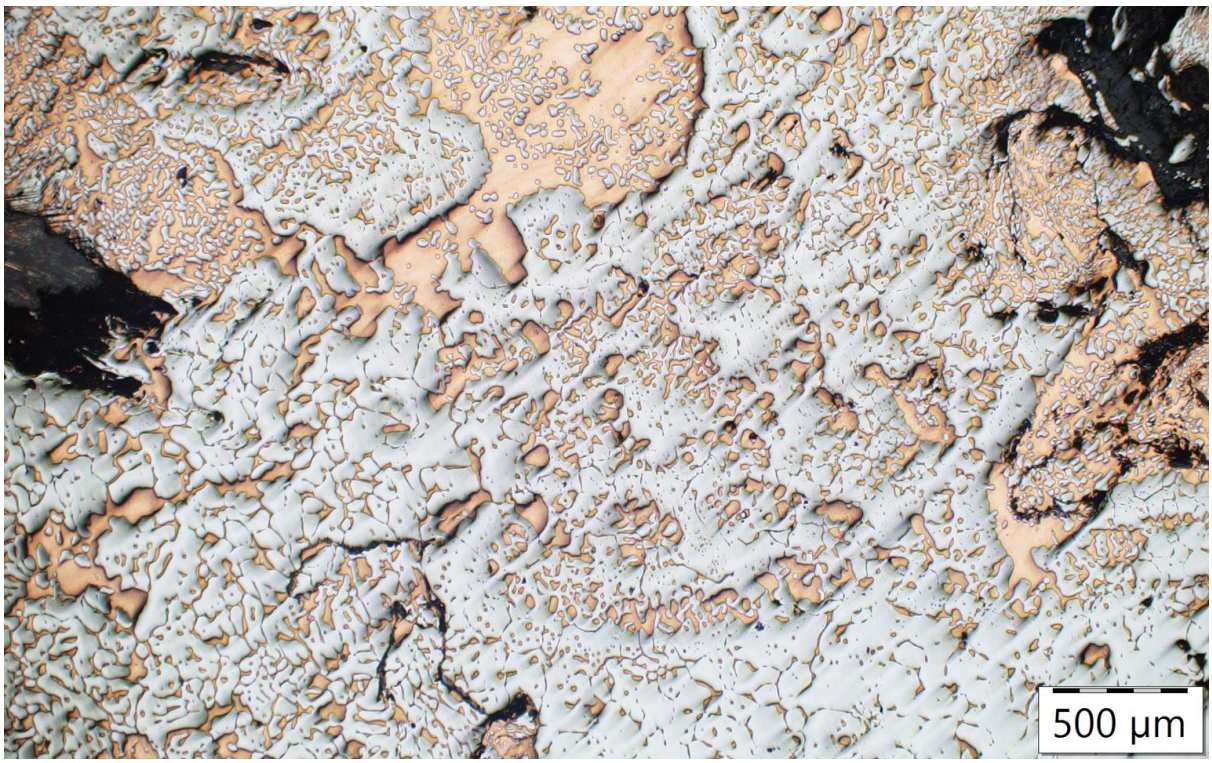


Fig.5.36: Micrograph of CUFE-3-6, x4 mag. Dense formation of metallic iron (white) in copper (red -brown).

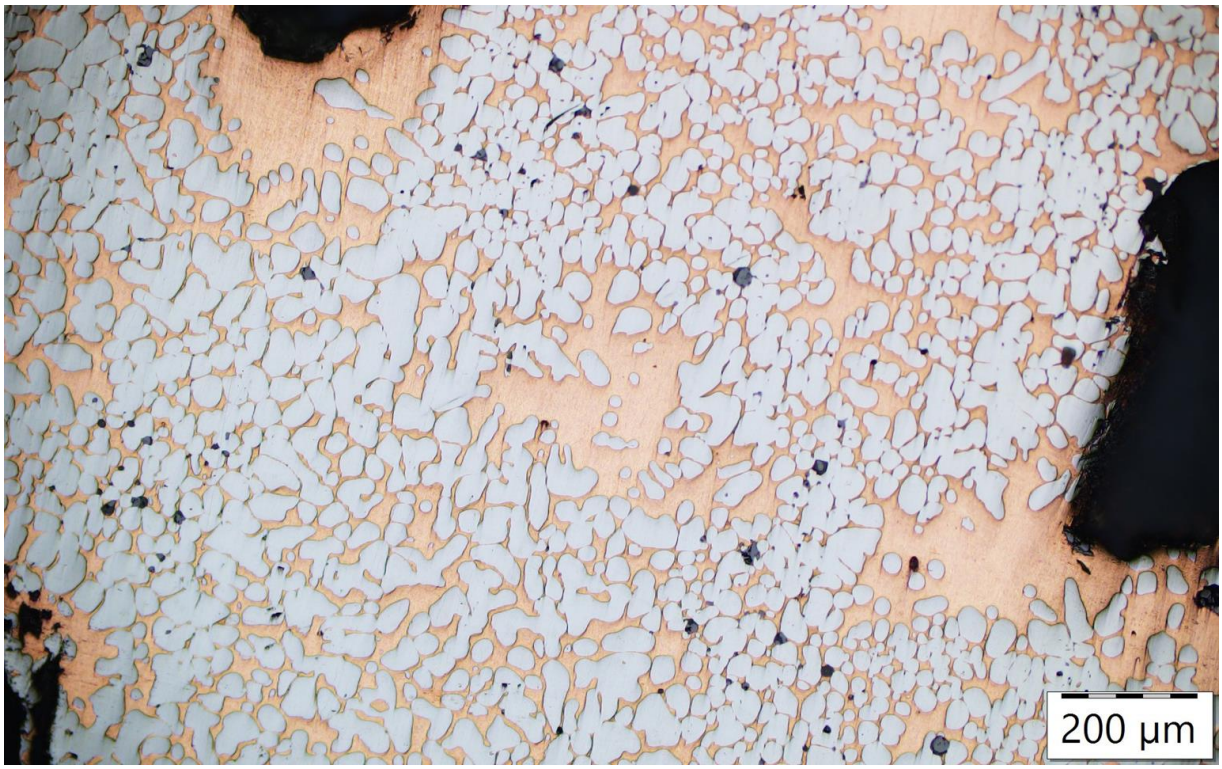


Fig.5.37: Micrograph of CUFE-3-5, x10 mag. Densely packed iron (white) in copper (red-brown).

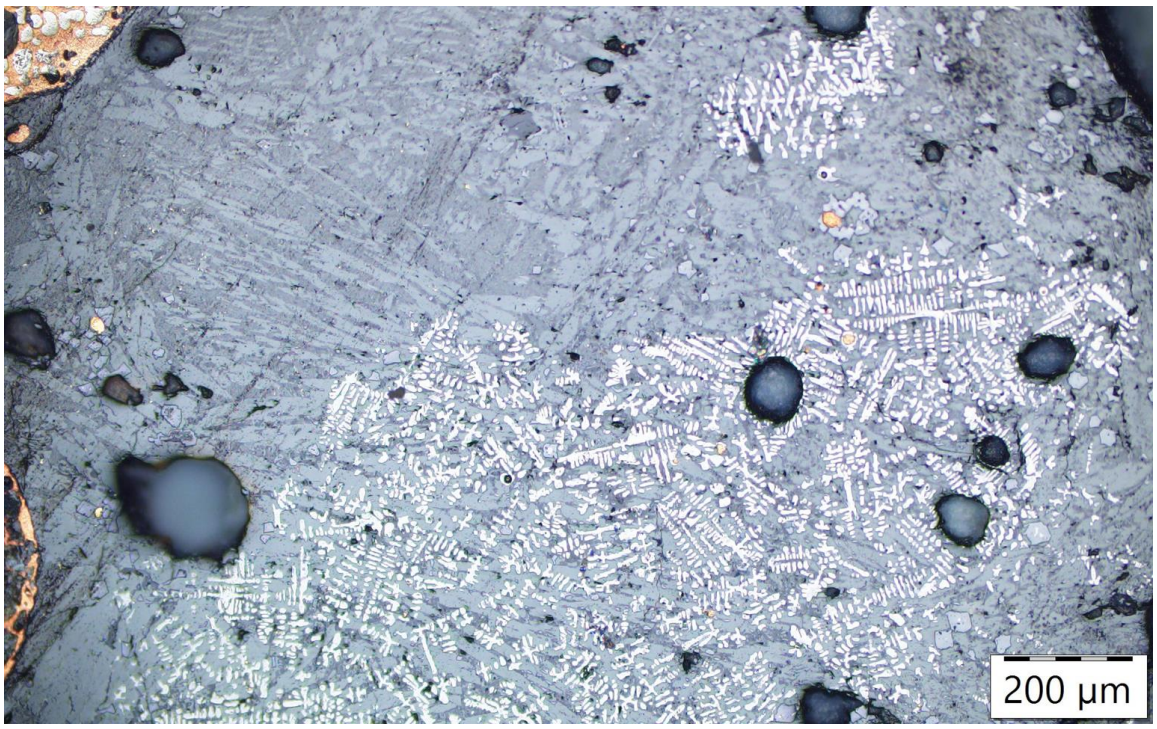


Fig.5.38: Micrograph of CUFE-3-7, x10 mag. Dendritic wüstite (white) among laths of fayalite (grey) with copper prills (red-brown). Iron (white) in copper is visible, top-left.

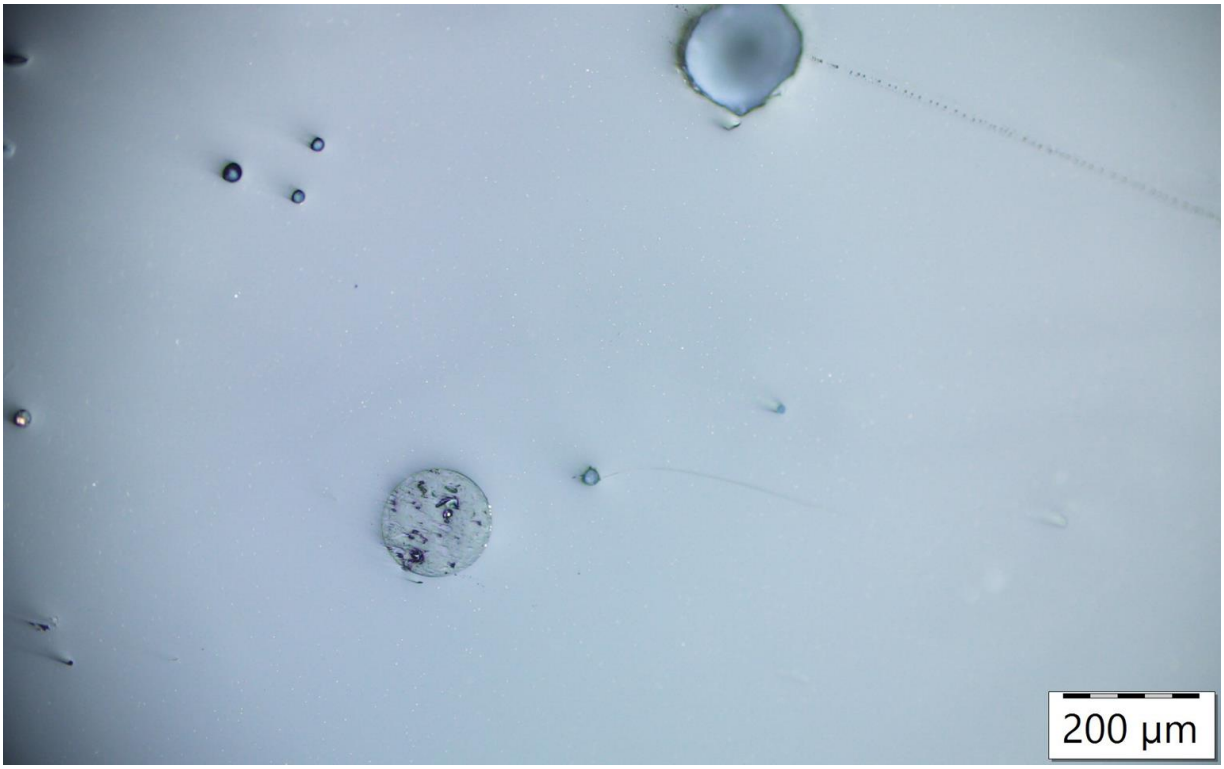


Fig.5.39: Micrograph of CUFE-3-1, x10 mag. Silica (light-grey) with tiny iron inclusions (white).

5.5.4: CUFE-4

The production assemblage from the final smelt (see figure 5.40) using a 2:3 proportion of copper to iron oxide consisted mostly of copper with multiple small and large light-grey metal inclusions. Unusually the *tuyere* opening had survived which was surrounded by copper and dark slag.



Fig.5.40: Cross-section of 2:3 copper to iron oxide smelt. *Tuyere* entrance is visible, centre with light grey iron to the right and copper (red-brown) surrounding it. Position is inverted in photo.

The metal samples of the 2:3 copper to iron oxide assemblage display almost as much metallic iron in the copper as observed for the previous 4:1 iron to copper smelt (see figures 5.41-5.44). The slag (see figure 5.45) is comprised of iron oxides with prills of metallic iron within a dark grey silicate slag.

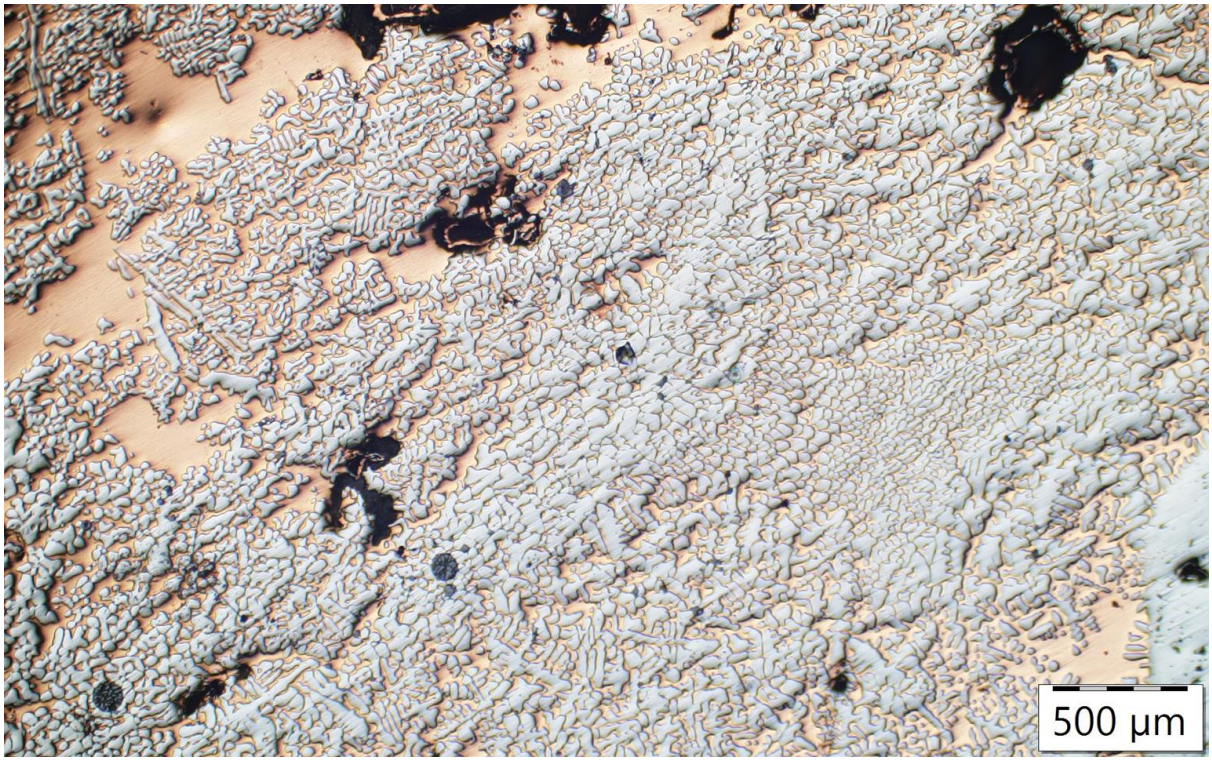


Fig.5.41: Micrograph of CUFE-4-3, x4 mag. Extremely dense metallic iron formations (white) in copper (red-brown).

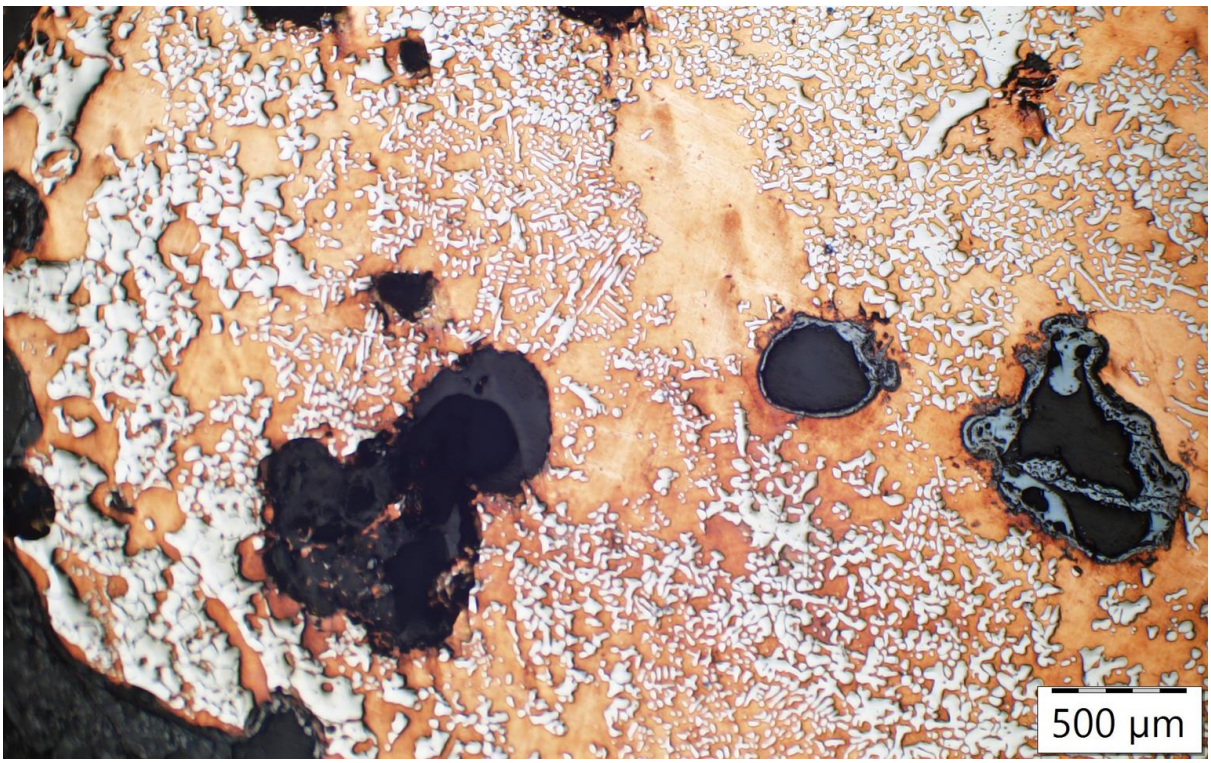


Fig.5.42: Micrograph of CUFE-4-1, x4 mag. Metallic iron (white) in copper (red-brown).

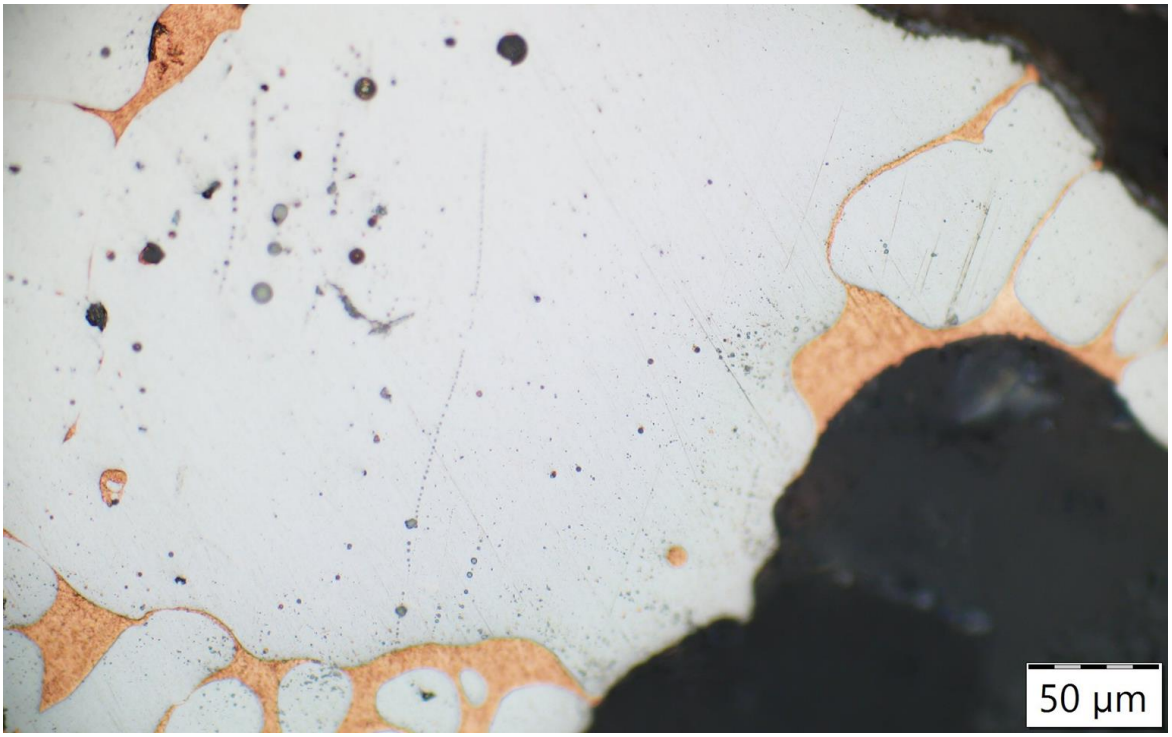


Fig.5.43: Micrograph of CUFE-4-2, x40 mag. Metallic iron prill (white) with copper (red-brown).

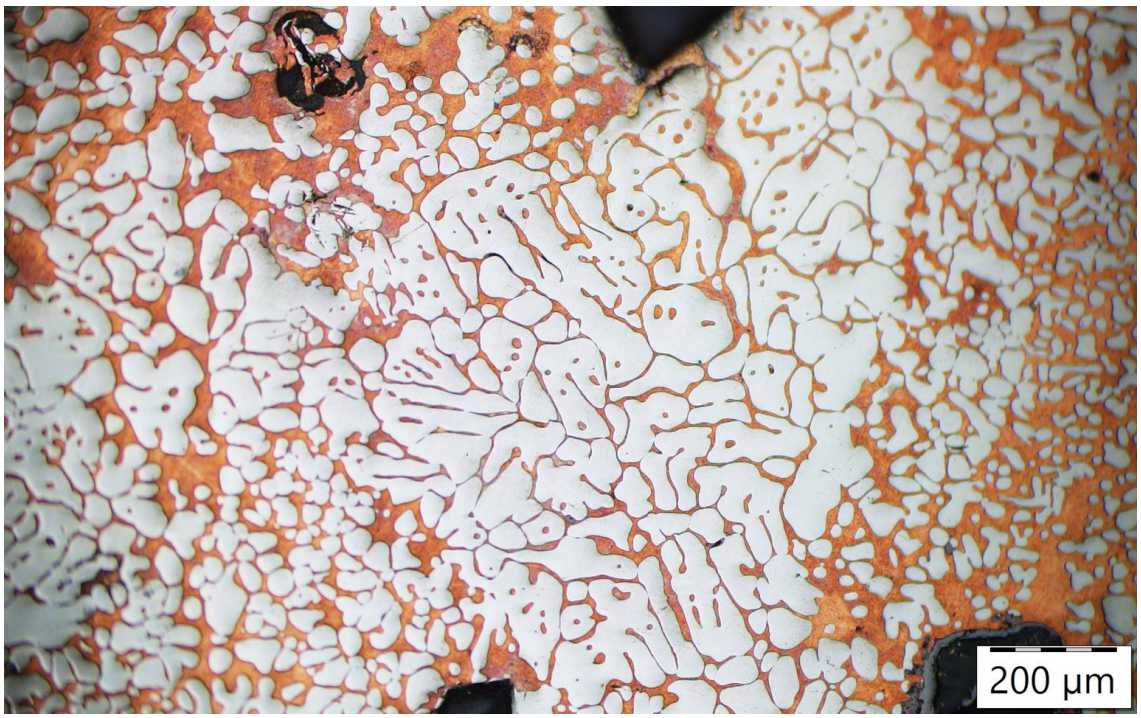


Fig.5.44: Micrograph of CUFE-4-1, x10 mag. Metallic iron (white) in copper (red-brown).

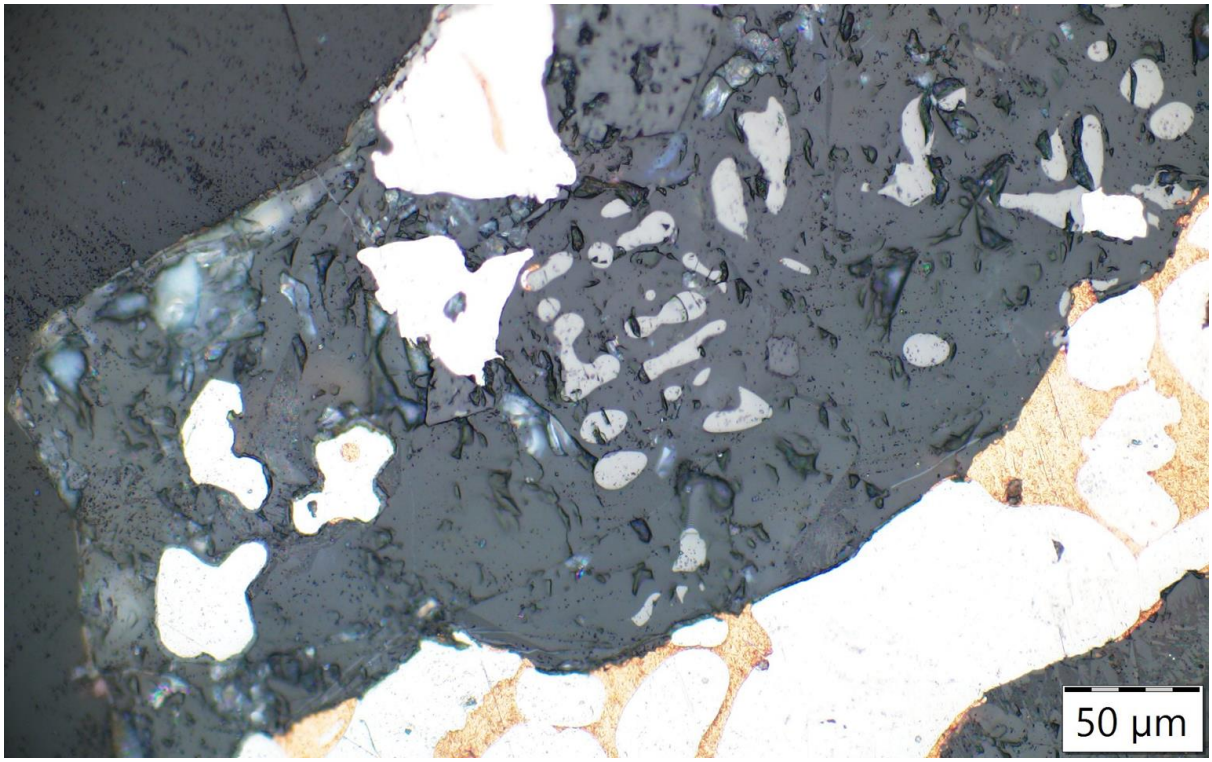


Fig.5.45: Micrograph of CUFE-4-2, x40 mag. Metallic iron prills (white) and wüstite (light-grey) in dark grey slag. More copper-iron biphasic alloy is visible bottom mid to right.

5.6: **CUIN-1,2,3** *Copper ingot assemblages.*

The metal used to produce the ingots was taken from the smelting assemblages of the fourth (2:3 copper to iron) oxide smelt, the second (4:1 copper to iron) oxide smelt and the third (4:1 iron to copper) oxide smelt.

5.6.1: **CUIN-1**

Starting with the first ingot (made using 2:3 copper to iron oxide metal) the metal fragments (see figure 5.46) consisted mostly of red-brown copper and some light-grey inclusions presumably of iron. Rivulets and runnels of copper were visible in most pieces as well as some red cuprite along with attached dark grey slag. The ingot (see figure 5.47) was comprised of a 'brassy' yellow copper with spots of rust and some silver surficial colouration probably from copper oxide formation (CuO).

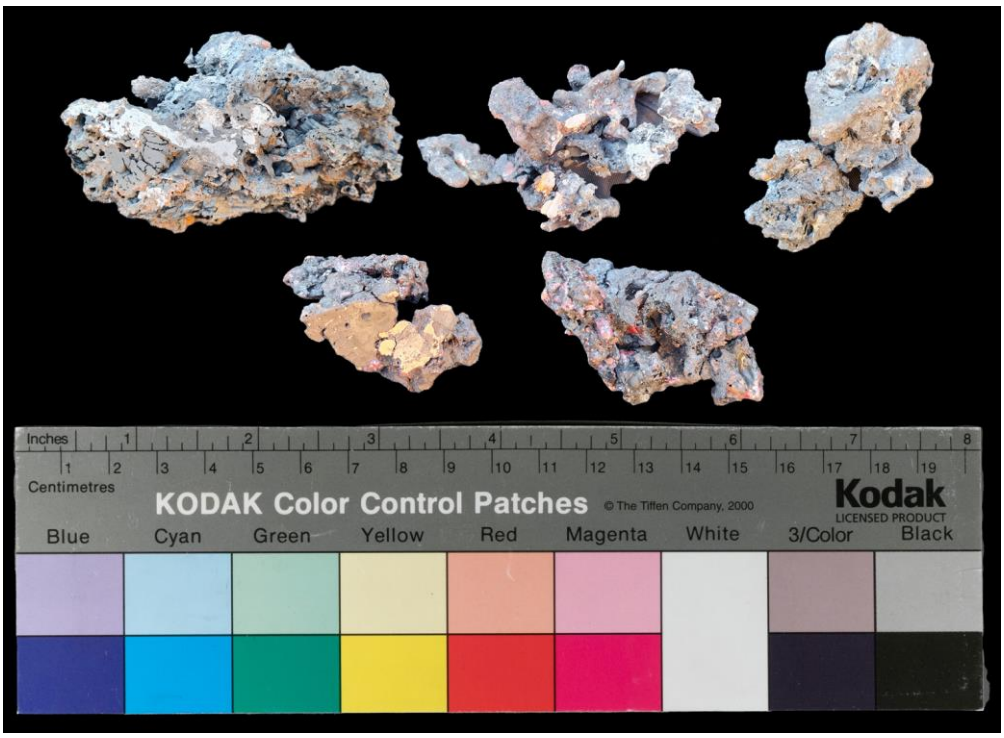


Fig.5.46: Metal pieces used in the CUIN-1 crucible melt from the 3:2 iron to copper oxide smelt. Total weight was 2.5kg, the pieces contained iron (white) and copper (red-brown).



Fig.5.47: CUIN-1 ingot. 'Pale' or brassy copper with spots of orange rust and silver to dark grey colouration on the surface. Section for sampling was cut from bottom right corner.

Microscopic analysis of a cut section of CUIN-1 (see figures 5.48-5.49) showed the significant presence of metallic iron in both widely dispersed small spherical inclusions and much larger inclusions visible to the naked eye. Large vesicles from escaping gases were common and the copper itself had still cast tightly to the surface of the mould with a reasonable degree of fluidity despite being so rich in iron.

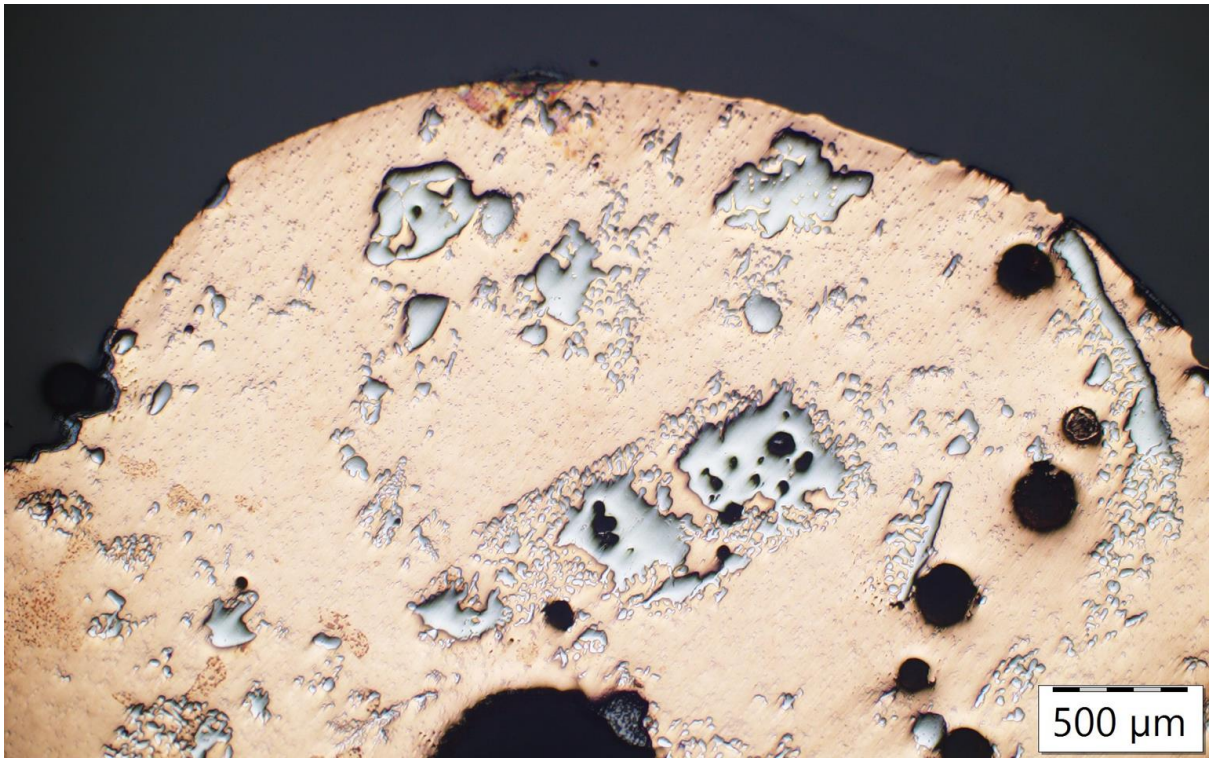


Fig.5.48: Cut section of CUIN-1 ingot, x4 mag. Metallic iron (white-light grey) in copper (red-brown).

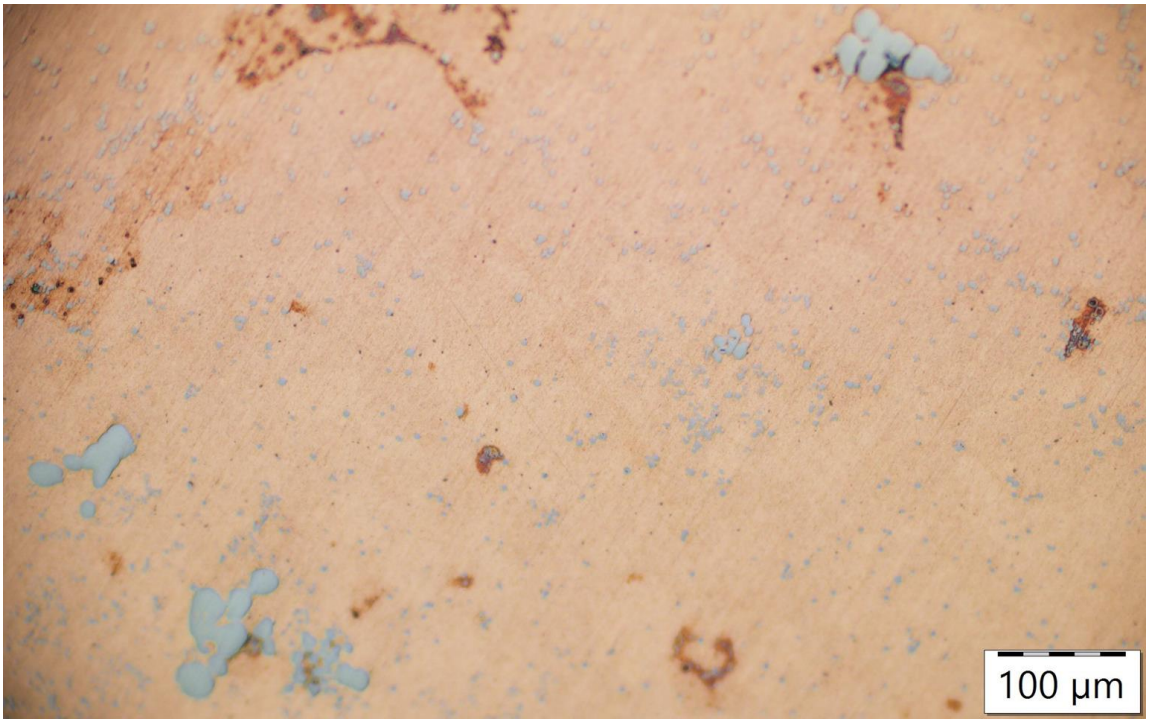


Fig.5.49: Cut section of CUIN-1, x20 mag. Small spherical iron (light grey) in copper (red-brown).

5.6.2: CUIN-2

The metal used to produce the second ingot from the 4:1 copper to iron oxide smelt was more homogeneous being mostly red-brown copper with dark black slag attached (see figure 5.50). Some small light grey iron inclusions were visible on the coppers surface, which started to rust. The ingot was mostly copper with a red-brown colouration and no obvious iron inclusions again with some silver-grey colouration on the surface.

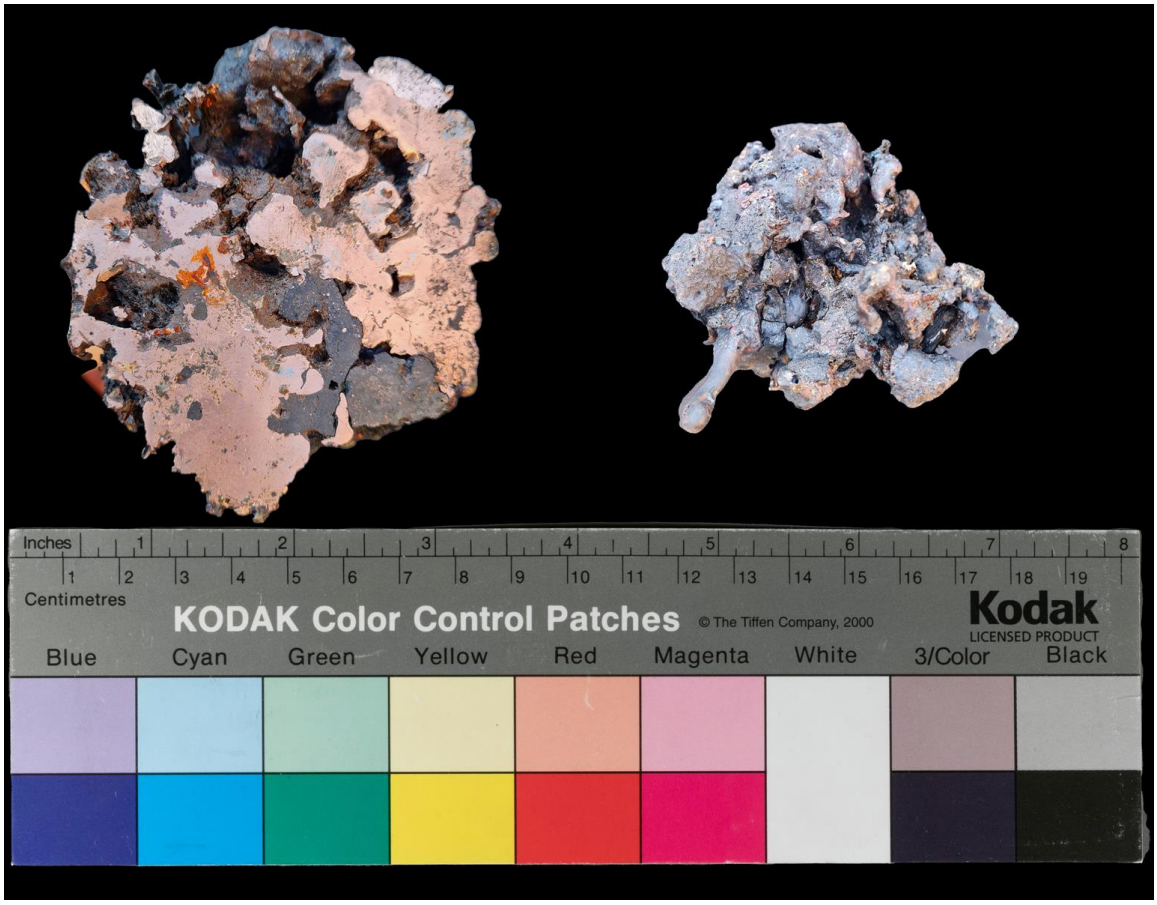


Fig.5.50: Metal used for CUIN-2 ingot. Copper (red-brown) and some iron (light grey) with dark grey slag. Orange rust surrounding an iron inclusion is visible on the left piece, centre.



Fig.5.51: CUIN-2 ingot. Ground surface centre-right shows reddish-brown copper with no obvious iron inclusions. Black to silver surface colouration from oxide formation.

The cut-section of the CUIN-2 ingot (figures 5.52 and 5.53) appeared to contain no iron inclusions with only pure red-brown copper visible as well as vesicles from gas bubbles. Occasional inclusions of dark grey may have been some cuprite from oxidation of the copper or entrained slag.



Fig.5.52: CUIN-2 ingot, x4 mag. Virtually pure metallic copper (red-brown).



Fig.5.53: CUIN-2 ingot, x40 mag. Metallic copper (red-brown) with no visible iron.

5.6.3: **CUIN-3**

For the final ingot using the 4:1 iron to copper oxide production assemblage, the metal used (see figure 5.54) was clearly mixed with light-grey metallic iron and red-brown copper visible throughout. Orange rust was present across most surfaces with small amounts of dark grey slag attached. The ingot (see figures 5.55-5.56) was strikingly different from the previous examples with a large lump of blistered copper and dark grey slag attached to the upper side of the ingot, which was brassy yellow in colouration. Orange rust quickly became prevalent across the surface. The ingot also failed to cast to the mould, only succeeding in two corners and becoming broken up by intervening slag over the rest of the casting.

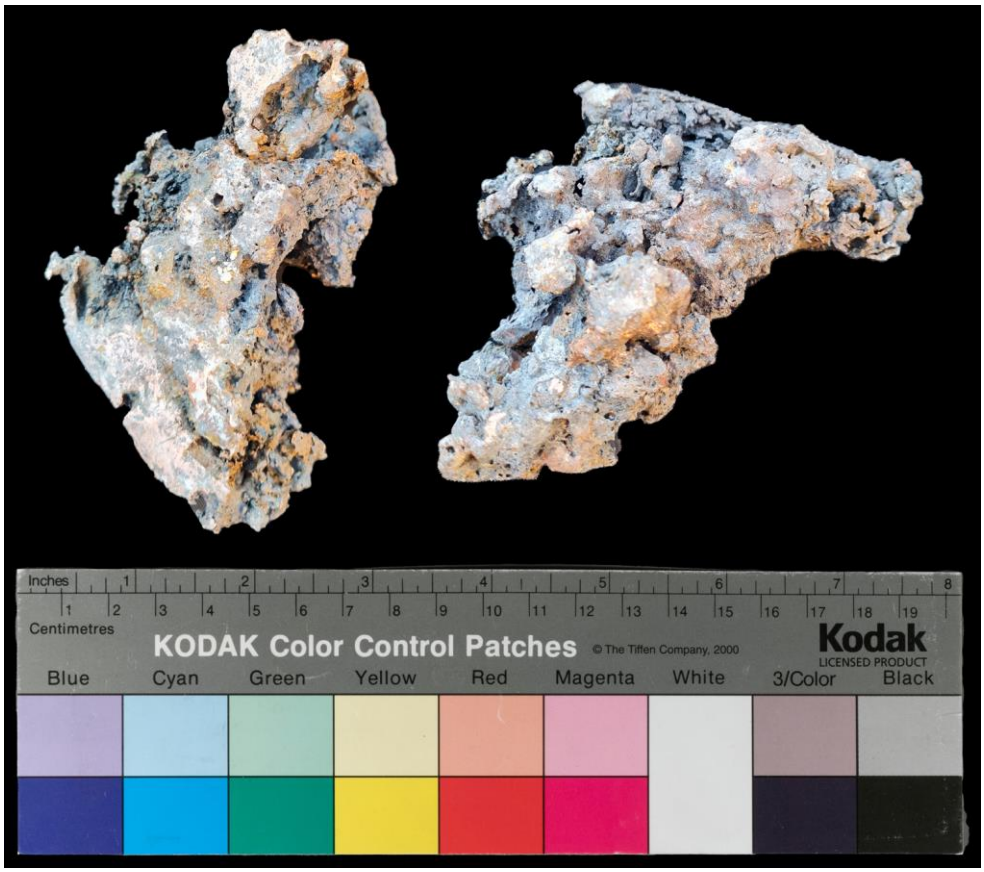


Fig.5.54: Metal used for the CUIN-3 ingot. Predominantly iron (white) with some copper (red-brown).

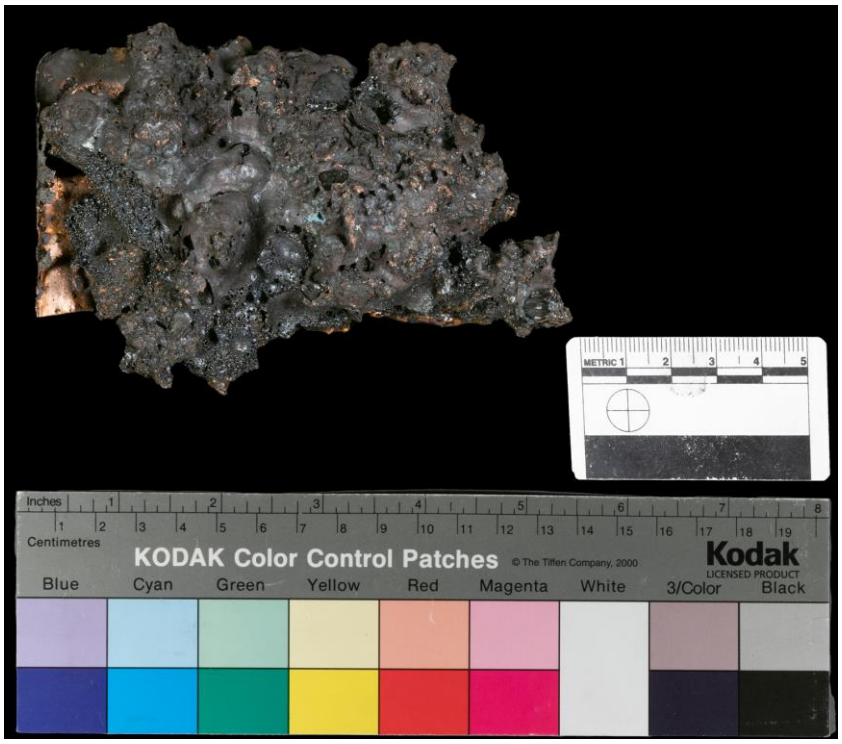


Fig.5.55: Ingot CUIN-3. Dark grey blistered slag and red-brown copper on the surface of the ingot.

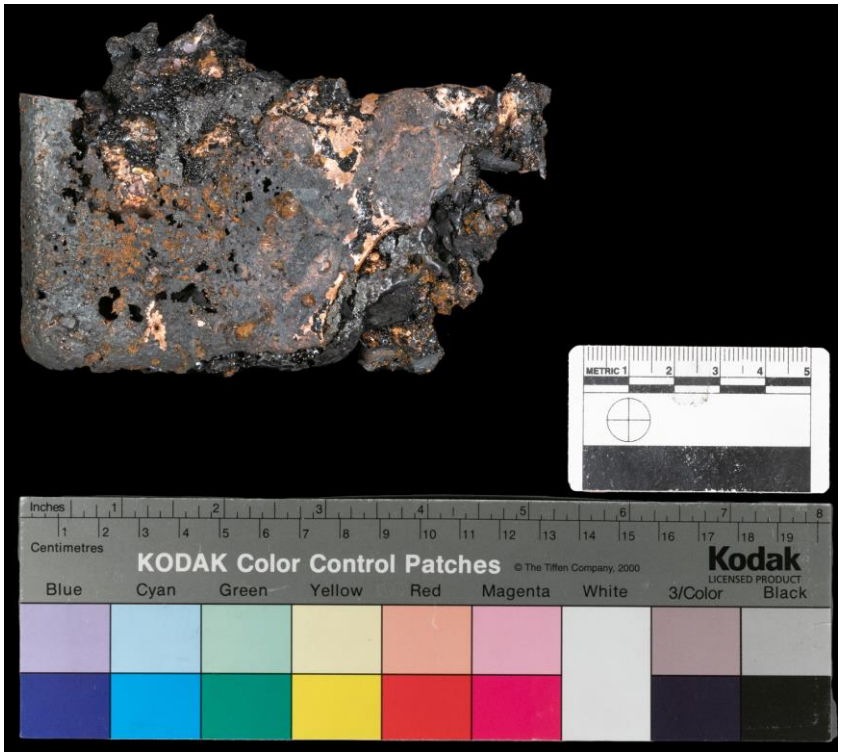


Fig.5.56: Ingot CUIN-3, reverse side. 'Pale' brassy red-brown copper with black oxidation and accruing slag. Many spots of orange rust are visible. The failure to cast into a complete ingot shape reveals the detrimental effect of iron on the properties of copper.

The final ingot produced using the 4:1 iron to copper oxide assemblage closely resembled the first ingot with a wide distribution of fine iron inclusions and infrequent prills (see figures 5.57-5.58).

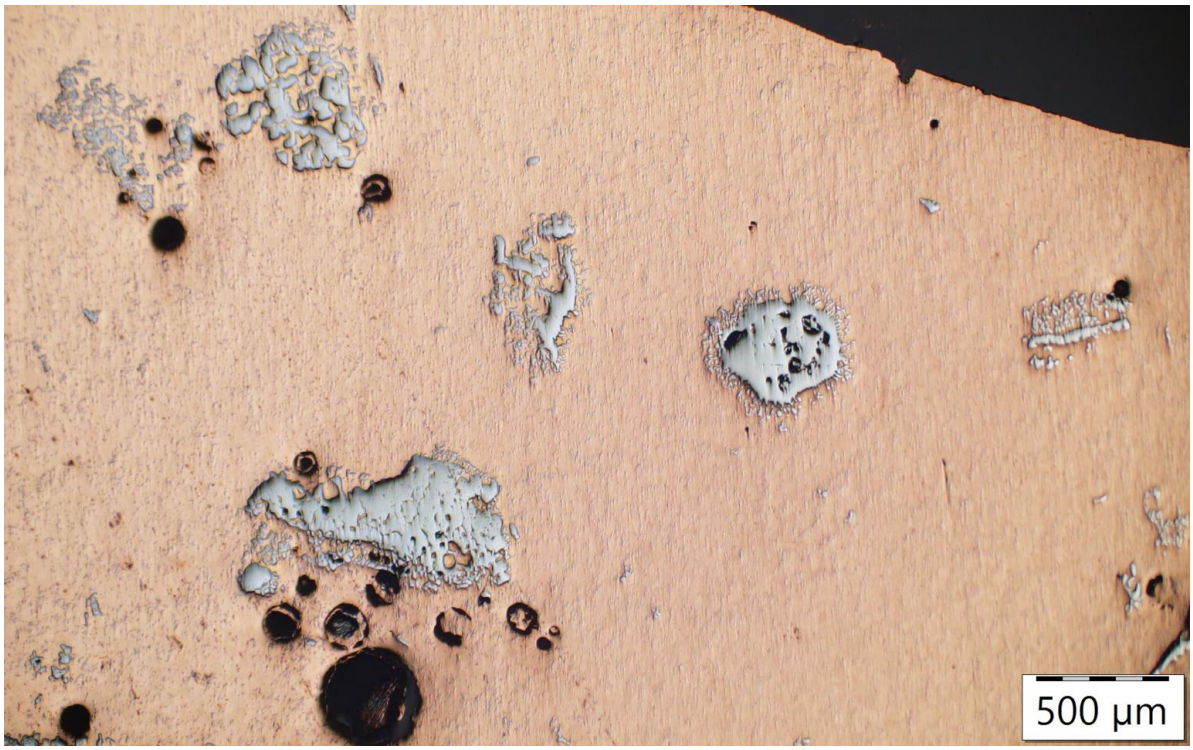


Fig.5.57: CUIN-3 ingot, x4 mag. Fine dispersed inclusions and prills of iron (grey) in copper (red-brown).



Fig.5.58: CUIN-3 ingot, x10 mag. Fine spherical inclusions and prills of iron (grey) in red-brown copper.

5.7: *XRF analyses of metal assemblages from experimental smelting*

A chemical analysis of the sections presented in the micrographs earlier in the chapter was made using a portable X-ray fluorescence instrument (Bruker S1 Titan) to measure the content by wt% of copper and iron in the samples and is presented in the following table. This method was chosen as an accurate means of assessing the content of copper and iron within the prepared and mounted cut-sections from the micrographic analysis given the low detection limits of the handset and opportunity for multiple sampling from ease of use. The use of the cross-sections ruled out any errors from surficial enrichment that can be problematic in p-XRF analysis of metals (Orfanou and Rehren 2015). The size of the mounted sections (<3cm) allowed for five samplings at different locations on the sections from which an average content by wt. % was calculated and is presented here. Considerable variability in iron and copper content in the sampling based on localized formation of the metal phases must be taken into account and give only approximate values for the entire heterogeneous metal assemblages.

Section No.	Cu (wt. %)	Fe (wt. %)
CUFE-1-01	87.2	12.3
CUFE-2-05	96.2	3.59
CUFE-3-06 (Fe rich)	18.9	78.4
CUFE-3-06 (Cu rich)	59.2	39.7
CUFE-4-03	65.1	34
CUFES-1-1	72.5	26.5
CUFES-1-4	18.7	67.7
CUIN-1-1	87.4	12.4
CUIN-2-1	97.5	2.25
CUIN-3-1	90.9	8.73

Fig.5.59: Table of copper and iron contents of sections from experimental production assemblages determined by p-XRF.

Chapter 6.

6.1: *Iron from copper: implications of experimental smelts*

Iron has long been recognised as one of the chief 'impurities' present in copper alloy artefacts (Cooke and Aschenbrenner 1975; Craddock and Meeks 1987; Merkel 1985). Given the results of the experimental reconstructions detailed in chapters four and five, this is perhaps unsurprising. Significant quantities of metallic iron were reduced and rendered into the copper metal for all four of the oxide smelts and iron sulphides still formed a large component of the matte prior to further copper-making. The smelting method used for the experiments can reasonably be characterised as efficient with consolidation of most of the copper into a main metal or matte phase in the furnace and production of iron-rich and vitreous low-viscosity slags. The failure to produce a large iron bloom during the iron ore smelt using an approximate process suggests that it was far less proficient at extracting metallic iron than copper. Yet with the potential for so much iron to enter into the metal phase, the management of iron in the furnace must have been a necessity for efficient copper extraction operations which aimed to produce good yields. Excessive iron could have been detrimental in a copper alloy and so avoidance of this undesirable outcome must have been preferable especially given the lack of evidence for intensive refinement of copper during the Late Bronze Age in the Near East (Hauptmann 2020:317). If large amounts of iron can enter into the copper metal in the furnace it seems improbable that so little would remain in the copper alloy artefacts of the period. Craddock and Meeks recognised this disparity, stating: "...the question should be why do most copper alloy artefacts from the Bronze Age on contain so little iron?" (1987:192). That Late Bronze Age smelters in the Near East must have regularly produced copper containing metallic iron, either to a greater or lesser degree than demonstrated in these experiments, appears to be beyond question. The ramifications of the experimental results for copper production during this period will be explored in this chapter.

6.2: *Iron from Sulphides: smelted iron in the LBA Eastern Mediterranean and south Caucasus*

Reconstruction of prehistoric sulphide and matte smelting has always been fraught with difficulty regarding interpretation of the evidence available from smelting assemblages and in carrying out these more complex and technically demanding procedures in experiments (Rose et al. 2020:97; Rostoker et al. 1989; Timberlake 2007:33). This is no doubt the cause of the marked dearth of archaeological and experimental data on the process in comparison to most other prehistoric extractive metallurgical operations. While the experimental smelt (**CUFES-1**) detailed in chapters four and five may go some way to address this shortcoming evidently it raises as many questions as it provides answers. Even so there were some compelling parallels between the experimental assemblage produced and with those found in the archaeological record for Late Bronze Age sulphide smelting in the Near East. The assemblage also closely resembled those produced by Rose et al. (2020) in their experimental smelting of chalcopyrites in a Bronze Age pit furnace based on an example in the Eastern Alps. As the smelt encompassed only the first two intermediate steps of matte smelting according to the multi-stage theory (Craddock 1995:147) it presents the opportunity to analyse the material that in a prehistoric context would have been collected and destroyed in further smelting operations to produce copper. This is particularly significant for understanding the partitioning of iron prior to conversion of the matte into copper, which may have been a limiting factor in its reduction and entry into the copper.

The mixed sulphide crucible smelt (CRS-2) can be viewed as a microcosm of the later furnace smelt and in many ways achieved the same outcome of a consolidated matte phase containing copper and iron sulphides over a much shorter duration and with minimal production of waste products in the form of slag. The bands of silver-grey copper sulphides surrounding the grains of yellow chalcopyrite

and iron sulphides that are visible on the cross-section (figure 5.6, p.198) highlights the partitioning of the metals following the decomposition of the ore at temperatures of 600^{o}C and higher. The almost total lack of any slag in the crucible assemblage must have been a consequence of very little silica availability suggesting the chalcopyrite ores did not contain much gangue. In the absence of silica to produce a slag, the matte should still contain most of the iron from the ore which may make it atypically iron rich compared to the matte products used in both modern industrial and prehistoric coppermaking processes (Craddock 1995:151; Schlesinger et al. 2011:74-76). The production of a matte phase in a crucible demonstrates that the first stage in sulphide smelting could be done in a relatively simple operation that could have been carried out by Chalcolithic smelters, as suggested by Bourgarit et al. (2007:10) and Rostoker et al. (1989).

Analysis of the production assemblage from the experimental mixed sulphide smelt (CUFES) defined two major phases of slag and a denser matte which contained most of the metal in sulphides. The breaking down of the chalcopyrite into iron rich and copper rich sulphides, both of which are present in significant quantities in the matte, likely began during the initial roasting (Doonan 1994). Rose et al. found that chalcopyrite, quartz, bornite and the iron oxides magnetite and hematite were the major components of the ore after roasting in a similar procedure used by the author (2020a:92). After smelting at higher temperatures (>900^{o}C) this process continued with the desulphurization of the ore progressing until a matte phase, containing copper-rich and iron-rich sulphides (see figures 6.1 and 6.2) and a dense slag were produced. This is caused by the presence of silica (SiO_2) in the gangue (mostly quartz) which promotes slag-matte immiscibility (see figure 2.10, p.76) causing the iron to partition between the matte and slag which then separated into phases according to different specific gravities in the furnace and slag viscosity (Hauptmann 2020:284; Schlesinger et al. 2011:74). This

should result in the production of an iron sulphide rich matte and iron sulphide lean slag, which in the experimental samples certainly appears to be the case.

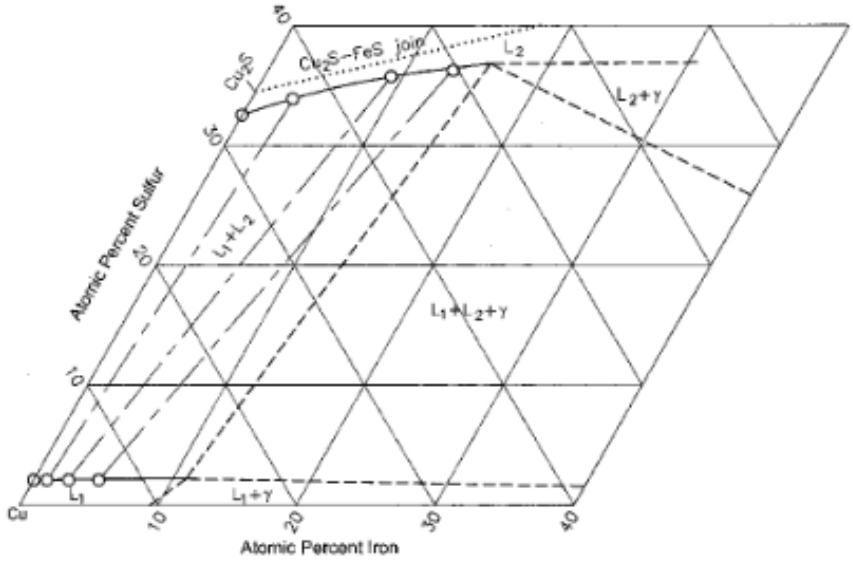


Fig.6.1: Cu-Fe-S partial isothermic section at 1200ºC. With removal of the sulphur to <35 atomic percent the sulphides split into Cu_2S and FeS which at >10 atomic percent iron results in one copper rich liquid sulphide (L_1), an iron-rich liquid sulphide (L_2) and an iron-rich solid sulphide (γ). Taken from Raghavan 2004:451.

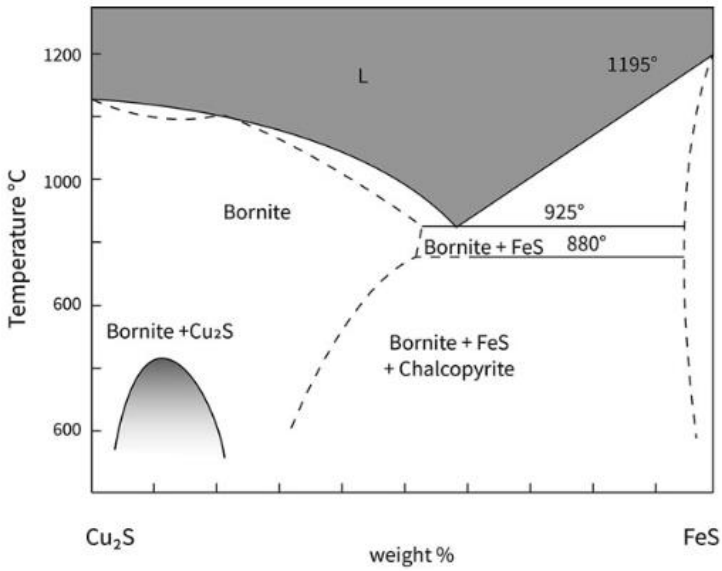


Fig.6.2: Composition of mattes in Cu-Fe-S system. Chalcopyrite co-exists stably with bornite, pyrrhotite and chalcocite in the matte. Taken from Hauptmann 2020:278.

Copper prills trapped in the matte (see figure 6.3) may have resulted from the reduction of copper oxides produced during the roasting stages. The association of the copper prills with the copper-rich sulphide phases shows how reduction of the copper progressed with the removal of sulphur and iron from these phases. General estimates of the sulphur content of the matte based upon the copper and iron sulphides present would put it around 20-35 mass% which may be higher going into conversion of the matte into copper than in modern industrial processes which begin at 20 mass% and lower (Schlesinger et al. 2011:134). This appears to correlate with the results Rose et al. obtained for sulphur contents of matte shown in figure 6.4 (2020a:93).

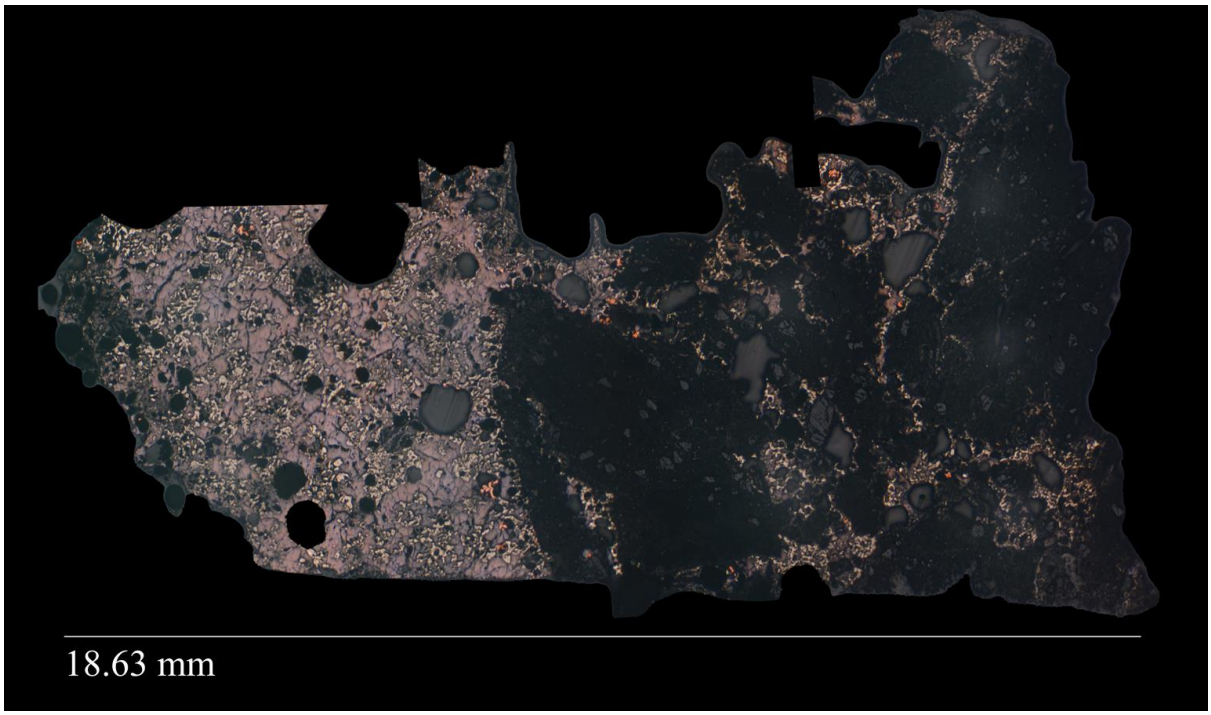


Fig.6.3: Macrograph of CUFES-1-1, x1.5 mag. Pink-blue copper-rich sulphides with brassy-yellow iron -rich sulphides and red-brown copper prills.

The results of the p-XRF analysis (figure 5.59, p.237) confirm the findings from optical microscopic analysis of the partitioning and removal of some of the iron from out of the original chalcopyrite ore and into the slag. Comparison of compositions for the experimental matte assemblage with the stoichiometric compositions of copper and iron in chalcopyrite reveals that the matte has become particularly copper-rich while the smaller prills of iron sulphides are iron-rich. The copper content of sample CUFES-1-1 at 72.5 wt.% is considerably higher than in chalcopyrite which contains 34.5 wt.% copper. As the production of a copper-sulphide rich matte phase is the objective of this stage in matte smelting the experiment displays a good degree of success. The iron content of this sample at 26.5 wt.% was also lower than in stoichiometric chalcopyrite suggesting some of the iron may have been partitioned out of the matte (Haldar 2016:14). Some of this iron appears to have entered into an iron-sulphide rich phase as prills in the slag which are represented by the compositions given for sample CUFES-1-4. The 67.7 wt.% iron to 18.7 wt.% copper marks these prills out as clearly distinct from the copper matte but also heavily enriched with iron in comparison to the original ore. The reason for the separation of these iron-rich sulphides from the matte is unclear but may involve the lower density of pyrite at 5g/cm^3 causing it to form in the slag above the copper sulphides like chalcocite with a density of 5.6g/cm^3 (Bachmann 2016:24). Estimating the total weight of the matte phase at around 6kg, the matte would contain about 4.3kg of copper sulphides and 1.6kg of iron sulphides in a ratio of 3:1 at this stage of production though in actuality the non-stoichiometric ore composition reduces this considerably. Assuming these sulphides were 100% chalcocite (Cu_2S) and pyrite (FeS_2) the 4.3g of copper sulphide would contain 3.5kg of copper and in the 1.6kg of iron sulphide there would be 736g of iron in a ratio of 5:1. In comparison to the values presented by Rose et al. in figure 6.4, sample CUFES-1-1 is both more copper-rich (with the exception of the S2p3c4-m sample) and iron rich (with the exception of the S4f1 samples)(2020a:93). This may be a result of more selective sampling of metal-enriched matte introduced by the p-XRF method opposed to the

powdered samples produced for the XRD analysis carried out by Rose et al. (2020). In both datasets the pattern of copper enrichment and sulphur and iron removal is clearly evident however.

Sample	Material	Experimental set-up	Cu	Fe	S	Total
Cpy6	Ore		21.0	22.7	24.3	101.6
S2f1-m	Matte	Shaft furnace	28.3	30.0	18.3	98.1
S2p1a-m	Matte	Pit furnace	54.3	17.9	19.0	100.7
S2p2-sm-m	Matte	Pit furnace	51.8	17.7	19.1	100.8
S2p3-m	Matte	Pit furnace	59.0	16.0	21.8	98.2
S2p3c1-m	Matte	Graphite crucible	56.1	18.1	20.0	97.4
S2p3c2-m	Matte	Graphite crucible	55.4	19.0	22.4	98.7
S2p3c3-m	Matte	Graphite crucible	58.2	16.3	21.9	98.6
S2p3c4-m	Matte	Clay crucible	73.9	1.34	18.0	95.5
S4f1-m (bulk)	Matte	Shaft furnace	22.8	27.0	16.0	94.0
S4f1-m2-1	Matte	Shaft furnace	40.1	31.2	23.7	96.9
S4f1-m4	Matte	Shaft furnace	37.7	32.2	22.5	93.8
S4p1-m-1	Matte	Pit furnace	57.5	14.1	22.1	95.8
S4p2-m	Matte	Pit furnace	49.0	22.8	15.5	92.6
S4p2c1-m	Matte	Graphite crucible	56.2	15.1	20.7	99.0
S4p2c2-sm	Matte	Graphite crucible	63.0	12.9	19.9	97.7
S4p2c3-sm	Matte	Clay crucible	65.7	3.07	18.1	89.1

Fig.6.4: Copper, iron and sulphur concentrations by wt. % of the chalcopyrite ore and matte produced in the experiments conducted by Rose et al. (2020:93).

The production of large quantities of slag caused by the oxidation of iron-rich sulphides would be a certainty in further coppermaking smelts using the matte obtained from this experiment. The production assemblage for the experimental sulphide smelt (**CUFES-1**), described in chapter 5, seems to closely resemble the 'furnace' and 'spongy' varieties of slags reported by Kassianidou and Van Brempt (2016) and Erb-Satullo, Gilmour and Khakhutaishvili (2014) from smelting sites in Cyprus and the south Caucasus. Rose et al. also produced slags that closely resemble these and the experimental slags presented in this thesis (2020). All of these slags featured the quartz inclusions found in the experimental slag as well as the large voids, prills of matte and some copper metal. If these pre-historic slags did derive from similar processes to those employed in the experiments of

Rose et al. (2020) and in this thesis, then the hypothetical formation processes of the prehistoric slags described by the following authors are not entirely correct. The conclusions of Kassianidou and Van Brempt (2016) regarding copper sulphide smelting on Cyprus are the least coherent with the data produced during this experiment. Rather than originating from two distinct phases of copper sulphide exploitation within the chronology of the site as argued by the authors; instead an argument can be made on the basis of the experimental assemblage that the two different slag types, furnace slags and cakes, derived from two firings during the same copper extraction operation (Van Brempt and Kassianidou 2016:553). In this scenario the 'furnace' slags were actually produced from the initial smelting of a roasted chalcopyrite ore before being recovered and broken to retrieve the matte. A correlation between the Cypriot 'furnace' slags and the experimental assemblage can be drawn with both containing large quartz inclusions from the ore gangue and very similar proportions of copper and iron sulphides (see figure 6.5) showing the same degree of decomposition of the original mixed sulphide ore.

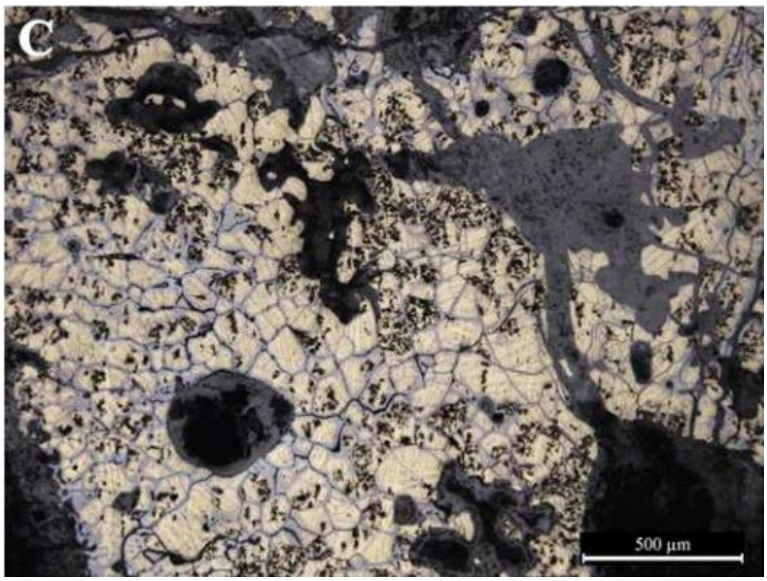


Fig.6.5: Large Cu (chalcocite, light grey in fractures) and Fe sulphide phases (pyrrhotite and chalcopyrite, light yellow) in furnace slags from Kalavassos-ayios dhimitrios, Cyprus. Taken from Kassianidou and Van Brempt (2016:548).

Of the three potential methods for smelting sulphides offered by Erb-Satullo, Gilmour and Khakhutaishvili (2014) the closest approximation to the experimental smelt was the first option given which required three stages. In the first stage the ore would be smelted to produce an iron-rich matte, which would then be collected, crushed and roasted in a second stage to convert the copper into oxide for a final coppermaking stage. The authors note two main discrepancies between this theorised process and the slags from sites in the south Caucasus; no clear bulk chemical differences between copper rich and copper poor slags and the more frequent occurrence of copper metal in slags from some sites compared to others (Erb-Satullo, Gilmour and Khakhutaishvili 2014:156-157). The data from the experimental assemblage (CUFES) may alleviate these incoherences with a multi-stage process and instead point to the partial roasting of the ores prior to matte production and finally conversion of the matte into copper. Using this model, the spongy slags would have resulted from the smelting of part-roasted chalcopyrite ores with copper prills developing based upon the degree of oxidation the ore was subjected to in the roasting step. Copper prills were visible in differing quantities in most of the experimental matte and slag samples and could have resulted from the reduction of oxides produced during the roasting stage. This would go some way to explaining the inter-site variation in copper content of the Georgian slags but also their largely indistinguishable bulk chemical content as both would derive from the same matte smelting process. Similar sulphide phases observed in both the Georgian (see figure 6.6) and experimental slags supports this hypothesis.

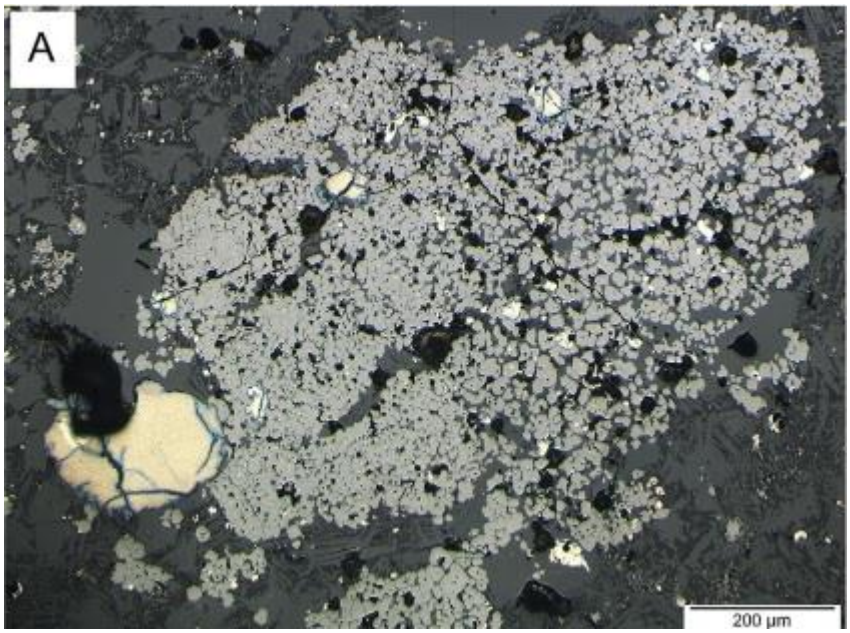


Fig.6.6: Prill of Fe and Cu sulphide (pyrrhotite light yellow, chalcopyrite rich yellow and chalcocite, blue-grey) in a south Caucasus copper smelting slag. Taken from Erb -Satullo, Gilmour and Khakhutaishvili (2014:152).

As the experimental assemblage only represents the product of the first two intermediate stages it does not allow for the application of a complete production model to Late Bronze Age sulphide smelting in the Near East. However the material from these sites will largely be the waste from the final copper-making smelts during which the copper metal was produced and the rest of the furnace contents discarded. Since no slags even remotely resembling the flat and homogeneous slag cakes identified from all of these sulphide smelting sites were produced during the experiment it is reasonable to suggest that they belong to a different and most likely later stage of production. This stage would have involved the smelting and conversion of the matte produced along with the 'furnace' or 'spongy' slags into metallic copper. The formation of the 'flat' or 'dense' slag 'cakes' noted in the Cypriot and south Caucasus slag variants during this matte conversion would explain the absence of similar slags in the experimental smelt. Rose et al. (see figure 6.7) suggest that these slags originated

from a coppermaking stage using a matte ‘cake’ or larger consolidated matte phase from which the flat slags would develop at the slag-matte interface, though they were unable to produce matte in this way (2020a:97). Therefore the ‘bowl-rim’ slag anatomy would probably have arisen as a result of sitting on top of the newly formed molten copper or matte during matte conversion at the base of the furnace. Unfortunately no direct correlation between these distinctive slags and the experimental assemblage can be made until further smelting experiments with the matte retrieved from the assemblage are carried out however the production of an intermediate product is greatly informative and lends support to a two stage process of matte production followed by conversion of the matte into copper resulting in two slag types at these sites.

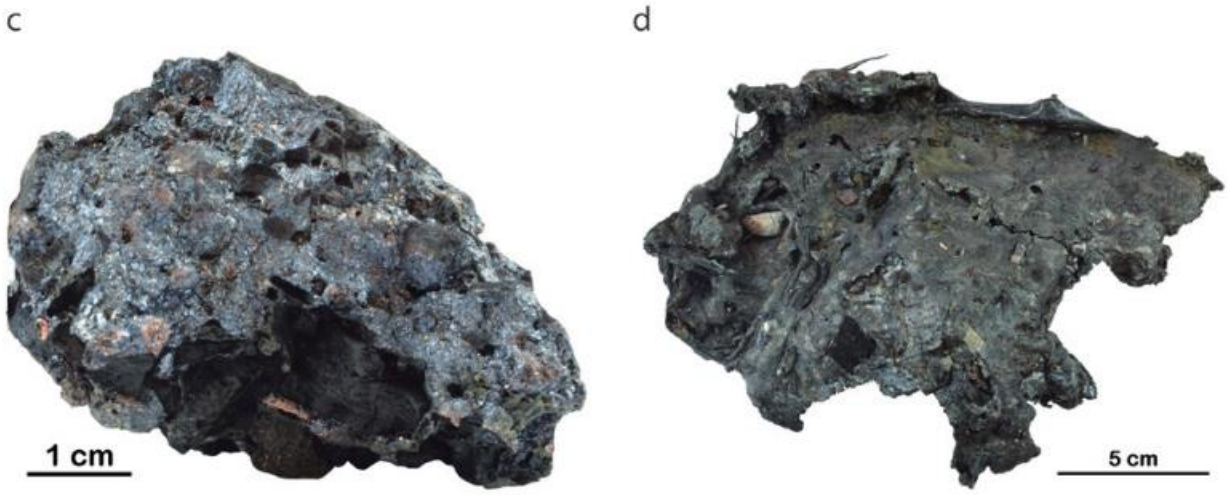


Fig.6.7: Experimental smelting assemblages produced by Rose et al.: C-matte with accruing slag and charcoal D-slag ‘plate’. The dull grey lustre of the matte in C as well as the glassy slag and large quartz inclusions in D closely resemble features of the experimental assemblage produced for this thesis (taken from Rose et al. 2020:88).

The results of the analysis of the experimental assemblage show that metallic iron was clearly not produced during the partial roasting or matte production stage. This is to be expected given the

strongly oxidizing conditions required to favour the removal of the sulphur from the metals. Also reduction of iron during mixed sulphide smelting should not have begun before oxidation of the copper sulphides into oxides and reduction of these into metallic copper given the preferential bonding of iron to oxygen and copper to sulphur (Rehren et al. 2012:1724). What is observable is the partitioning of the iron from the mixed sulphide ore (chalcopyrite, bornite) into iron sulphides such as pyrite (FeS_2) and into oxides which entered into the slag. The tendency of some of the iron sulphides to collect in concentrated prills within the slags above the more copper rich matte phases may have been a result of the slag forming around these iron-rich sulphides more rapidly with their oxidation, causing them to become entrained sooner and higher in the furnace near the air inflow. Even accounting for this unanticipated separation of some of the iron sulphide from the matte, the abundance of pyrites in the matte suggests that it remains very iron-rich prior to conversion into copper. Whether this would have necessitated further oxidation through roasting of the matte to remove the iron and produce the 'black copper' oxides before coppermaking remains contentious. In chapters two and three, the benefits of an iron rich matte were discussed in full but can be summarized as providing both a low viscosity medium for the copper metal to sink through and escape entrainment in the slag and as a flux aiding in the reduction of the copper oxides. Removal of the iron from the matte in a roasting stage was likely undesirable in the contexts of a prehistoric smelt where copper losses to viscous slags were an ever-present risk and improving the reducing conditions in the furnace was economical.

Though the experimental sulphide smelt did not produce metallic iron, the presence of metallic iron in copper sulphide smelting slags from some Late Bronze Age sites can be extrapolated to the data produced here. Wüstite (FeO) in smelting slags is one of the primary indicators that sufficiently

reducing conditions were reached in a furnace to potentially produce metallic iron (Hauptmann 2020:268). It is known in small quantities in sulphide smelting slags on Cyprus from the 1700-1300BC site of Politiko Phorades and in some of the copper slags of the south Caucasus (Erb-Satullo, Gilmour and Khakhutaishvili 2014:156; Knapp and Kassianidou 2008:143). Evidence of iron sulphides in iron smelting slags in the Caucasus region (see figure 6.8) also lends credence to the extraction of metallic iron from sulphide or mixed sulphidic-oxidic ores. While the perennial question of whether iron was produced during mixed sulphide smelting is still far from a resolution, the removal and oxidation of the large proportion of iron from these ores required to extract the copper continues to attract attention in studies into the innovation of iron technology (Erb-Satullo et al. 2020; Kassianidou 1994).



Fig.6.8: Iron, arsenic (light-grey), copper (yellow) and wüstite (grey) in slag (dark grey) from a smelting slag from Mtsvane Gora, south Caucasus. Taken from Erb-Satullo et al. (2020:10).

6.3: *Iron from Oxides: the case for smelted iron in the LBA Near East*

The adventitious production of metallic iron from the smelting of mixed oxidic ores has continued to intrigue archaeometallurgists since the possibility was first raised by Beno Rothenberg after the discovery of a number of 'cupriferous' iron objects were discovered in a metal cache in a New Kingdom Egyptian Temple at Timna (Gale et al. 1990; Merkel and Barrett 2000:59). Bias introduced by the analysis of surface samples led to the mistaken assertion that the copper in these iron artefacts had derived from co-smelting and not from post-depositional processes as was proven later, causing the theory to lose traction in recent years following a brief period of interest (Merkel and Barrett 2000). Despite the experimental production of copper-iron alloys (Bamberger and Wincierz 1986; Merkel 1990; Tylecote and Boydell 1978) and even the isolation of metallic iron from such alloys in a crucible (Tylecote and Boydell 1978) the lack of a direct link to prehistoric smelting has limited the discussion and application of this data to the archaeological record. Reconstructing the physical and chemical circumstances for the production of copper-iron alloys within the context of a Late Bronze Age copper smelt has provided an opportunity to assess the potential of contemporary operations to extract metallic iron based upon charge composition from local ores, furnace technology and technical skill. The data from these experiments is also applicable to mixed sulphide smelting which after the removal of the sulphur relies on the reduction of copper oxides to produce metal and subsequently could have begun to reduce any iron oxides present also. The behaviour of any metallic iron produced in tandem with the copper in the furnace should be constant between oxidic ore co-smelts and mixed sulphide ore smelting. The conspicuous presence of iron, noted as large (>4cm) inclusions of grey metal down to mottling from micro-inclusions throughout the experimental assemblages, could not have gone unnoticed by Late Bronze Age smelters, becoming particularly apparent during the casting of such alloys with the rapid oxidation of the iron and it may have been these initial encounters that set the stage for the development of true iron metallurgy.

The mixed copper and iron oxide (malachite and hematite) crucible smelt (CRS-1) successfully reduced the majority of both the copper and iron into a metallic state which became mixed in the metal phase at the base of the crucible. Upon first reflection the entrainment of the iron in the copper appeared to be simply a result of the small volume of the crucible and short duration of the smelt not providing enough room or time for the two metals to separate according to their only marginally different densities. Given the same phenomenon was observed in the furnace smelting assemblages, where the reaction volumes and duration were much greater, this outcome actually appears to be inherent to the co-smelting process itself. Unlike the furnace smelts the crucible process used a 1:1 composition of iron to copper ore which works out to slightly more iron present (about 700g out of 1kg of hematite) compared to copper (580g out of 1kg of malachite) excluding gangue. More iron lost to oxidation during the crucible smelt levelled out this slight disparity to produce a near 1:1 copper-iron biphasic alloy. The iron was readily reduced at 1200^{o}C evidenced by the hematite crucible smelt (CRS-3) which suggests sufficient carbon monoxide for reduction was produced by the combustion of the two kilograms of charcoal in the crucible. The smelt confirmed the findings of Tylecote and Boydell (1978) of the production of copper-iron alloys using mixed oxides in a crucible (ores local to Timna in their case) which does not appear to be confined to furnace smelting.

Production of metallic copper during all of the experimental smelts was efficient with >80% of the available copper from the copper (II) oxide reduced into metal and consolidated into a main phase for each smelt (approximately estimated at 8kg in CUFE-1, 10kg in CUFE-2, 3kg in CUFE-3 and 5-6kg in CUFE-4). Losses of copper to entrainment in the slags was minimal with typically small and dispersed prills being frequent but diminutive in terms of mass and largely irretrievable. The most striking feature of the copper metal is of course the abundant intergrowth of metallic iron in α-phase

visible across all of the smelts in numerous formations ranging from dendritic to spheroidal and striated macro and microstructures (Bachmann 2016:31; Cooke and Aschenbrenner 1975:257-260). The near total immiscibility of copper and iron at room temperature (figure 3.21, p.129) is clearly evident in the formation of the separate α-phase iron with room temperature saturation of iron in the copper fixed around 0.2 wt.% (Hutchison and Reekie 1951). A fair degree of consistency in the redox conditions and temperatures reached in the furnaces for the smelts is implied by the iron content visible in all of the assemblages which appears to vary primarily on the basis of the charge composition and not furnace operation where more fluctuation would be expected. The first question to address is why the majority of the metallic iron entered into the copper and not the slag. In bloomery smelting the extraction of the iron in a single workable mass is reliant on the formation of the 'bloom', a porous spongy mesh of α-iron that would form around charcoal and slag boundaries, just below the *tuyere* (Hauptmann 2020:365). The melting point of iron at 1538ºC or slightly lower in the variably low carbon ferritic bloom could not be reached in a prehistoric furnace and so the iron remained in solid state and would not consolidate on the furnace floor like copper. Despite this no bloom had formed in any of the experimental smelts, even with a 4:1 charge composition of hematite to copper oxide (CUFE-3). Appreciable quantities of iron were produced which should have been sufficient to form a small to medium bloom in the furnace. Three possible causes have been identified and will be explored in the following paragraphs.

The first possibility for the entry of iron into the copper is through dissolution and later precipitation of the iron at room temperature. Craddock and Meeks claim that with the solubility of iron in copper of around 6% at 1200ºC there would have been: "...ample opportunity for the copper to pick up iron whilst the small droplets drained slowly through the iron-rich slag" (1987:192). While this would

explain the consolidation of the iron alongside the copper at the base of the furnace a major shortfall of this argument is the far greater quantities of iron present which easily exceed the 6% that could have been dissolved in the copper. This theory cannot even account for the second experimental smelt using a 4:1 mix of copper to minimal iron oxides (CUFE-2) which only in some regions (see figures 5.29-5.30, p218. and 6.9, below for comparison) displayed the <6% precipitation of small iron inclusions that might be expected, with larger and more frequent inclusions being found elsewhere in the assemblage. Also the prills of copper caught in the slag were mostly free of iron (see figure 5.32, page 220) and surrounded by iron oxides such as magnetite suggesting that the slag formed in the more oxidising parts of the furnace where reduction of the oxides into metallic iron was less likely. It is improbable that the molten copper could have picked up the large quantities of iron present through absorption from the slag during percolation to the furnace floor.

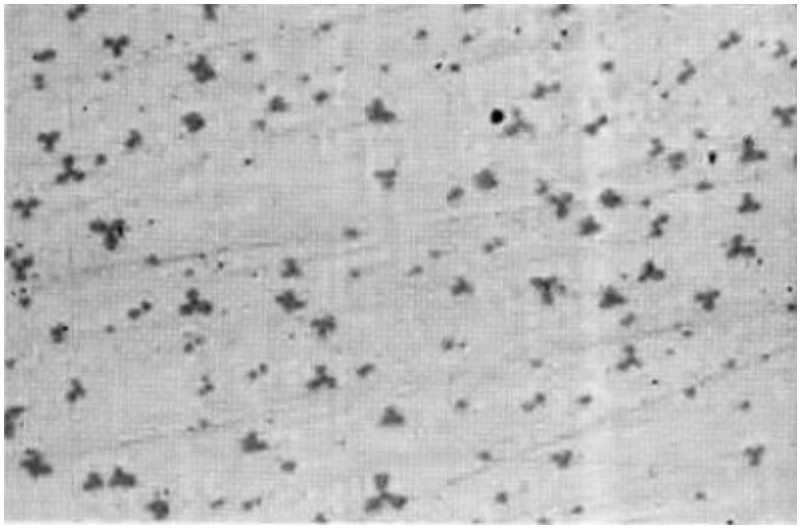


Fig.6.9: Laboratory prepared alloy. Dark grey α-iron precipitated from the copper. Taken from Cooke and Aschenbrenner (1975:258).

The close densities of copper and iron which can be translated into a specific gravity of 8.95 for copper and 7.85 for iron may limit the extent to which the two can separate in the context of the furnace (Bachmann 2016:31). Thus once both metals have sunk beneath the lighter slag they would enter into a more or less contiguous metal phase. Though this theory goes some way to addressing this phenomenon, it does not factor in the two different states of the metals, with iron remaining in solid state and copper reaching liquid state at 1200^{o}C. The mobility of the iron while in solid state would be much lower than the molten copper which over the limited duration of the smelt should facilitate more segregation between the metals with more of the iron becoming trapped and oxidized in the slag. Also a difference of one in the specific gravities of materials in the furnace is usually proficient for separation into distinct phases as is the case with slag and matte, matte to speiss and speiss to metal shown in figure 2.12, p80.

The final explanation is the formation of metallic copper and iron in the same and most reducing region of the furnace causing the two to become mixed instantaneously. In this theory, the newly reduced metallic iron would form directly in the nascent copper as intergrowths of γ-iron and α-iron within the most reducing region of the furnace. Generally this region, which can be defined as the area/volume that has the highest partial pressure of carbon monoxide, is located immediately around and just below the *tuyere*. This is caused by the acceleration of the Boudouard reaction (reaction of carbon dioxide with carbon to produce carbon monoxide) from the higher partial pressure of oxygen and combustion of the charcoal. Within this zone the simultaneous reduction of the copper and iron would also raise the partial pressure of carbon dioxide (from carbon monoxide taking up the oxygen removed from the metal oxides) in a positive feedback loop, increasing the rate of the Boudouard process. The dispersal of the solid state iron in the molten copper could increase its mobility and

facilitate its consolidation at the base of the furnace. Consequently the presence of copper may actually improve the yield of metallic iron and limit losses to the slag in comparison to a pure iron oxide smelt. The rate of re-oxidation of the iron trapped in the copper would also be greatly lessened. Analysis of the experimental assemblages appears to confirm this with the iron and copper phases being closely associated with the region around the *tuyere* which has been preserved in some of the slags such as in figure 5.40, page 225. The 'proto-blooms' (see figure 5.21, p213) and spherical appearance of many of the larger α-iron inclusions also supports this theory over precipitation of the iron from a copper-iron solution. Analysis of the iron inclusions confirmed that they contained little to no copper and no copper had precipitated from the iron. The solubility limit of copper in iron is considerably lower than iron in copper at furnace temperature (see figure 6.10) and drops off to virtually 0% at room temperature which explains why so little copper was picked up or retained by the iron as it formed in tangent.

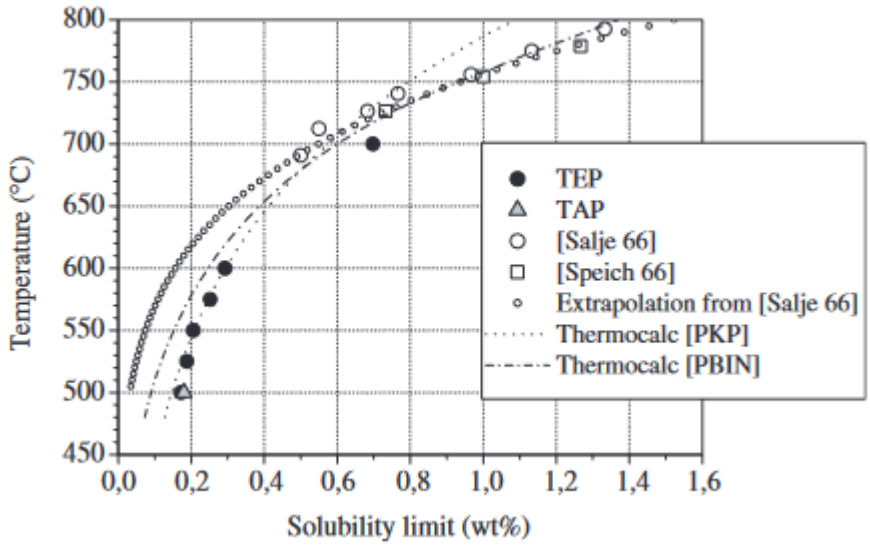


Fig.6.10: Solubility limits of copper in iron at 800-450ºC. Copper solubility in iron gradually decreases from only 2-3% at 1200ºC to a sharp decline around 600ºC to almost zero past 450ºC. Values given are for a pure iron, the copper would be even less soluble in the furnace iron which might contain carbon and other impurities. Taken from Perez et al. (2005:2207).

If the findings of the experimental copper and iron oxide smelts can be summarized as the simultaneous reduction of oxides into metallic copper and iron and their consolidation into a single bimetallic phase within the furnace, what connotations does this have for prehistoric but especially Late Bronze Age copper smelting? Firstly it may be helpful to compare the experimental ore compositions to oxidic ores that were exploited from prehistory. Using the example of Tylecote and Boydell (1977), their chemical analysis of an oxidic Timna copper ore contained around 76.5% (weight percent) copper and 23.5% iron in its metallic component, in a ratio of about 3:1. To find the closest approximation from among the furnace smelts the stoichiometric proportions of copper and iron in the artificial experimental ore needs to be calculated. For the first smelt (CUFE-1), using a 3:2 ratio of copper (II) oxide or CuO and hematite (Fe_2O_3), 63.1% was Cu and 36.7% was Fe in a ratio of about 2:1. The second in this series of smelts (CUFE-2), using a 4:1 copper to iron oxide charge composition translates to about 82% copper to 18% iron or a ratio of about 5:1. The third smelt (CUFE-3) using a 4:1 ratio of iron to copper oxides comes to 83.5% Fe to 23.8% Cu or a 3:1 ratio and the fourth smelt (CUFE-4) consisting of a 3:2 ratio of iron to copper oxides contained 56% Fe to 43.2% Cu or roughly a 1.5:1 ratio. By subtracting the experimentally obtained percentages from those of the Timna ores the second smelt using the 5:1 ratio of Cu to Fe shows the smallest disparity of plus and minus 5.5% for iron and copper in the Timna ore respectively. Using the results of the p-XRF analysis of sample CUFE-2-05 taken from the second 4:1 copper to iron oxide smelt in comparison to the values obtained by Tylecote and Boydell (1977) for copper-iron alloys produced by smelting Timna ores (see figures 3.18-19, p126) the degree of correlation between the smelts can be assessed. The authors report an iron content in the copper alloys from the un-fluxed smelting experiments in the range of 0.3 to 2.1 % Fe. (Tylecote and Boydell 1977: 310). Sample CUFE-2-05 was shown to contain 3.6% Fe, a difference of 1.5-3.29 %. While the Timna ores contained more iron than in the artificial charge for this smelt, the higher iron content in the experimental copper compared to the copper produced by Tylecote and Boydell suggests the experimental smelt in the larger furnace

reduced the iron more efficiently allowing more to enter into the alloy (1977:309). This is before taking into account the stoichiometric iron content of both charges; the artificial charge contained 2.8 kg of iron in the 4kg of hematite added to the charge in contrast to the Timna ore of which only 1.45kg out of 20kg of ore would be iron and 4.7kg would be copper. A difference of 1.5-3.29% might then be expected given the artificial ore contained 1.35kg or nearly double the amount of iron indicating the two smelts were in fact close in efficiency of iron extraction. Overall the data from the second oxide smelt seems to comply with that obtained from the unfluxed smelting of oxides from a mixed orebody exploited from the Late Bronze Age. Taken together a copper-iron alloy with an estimated 1-3.5% iron content would predictably have been produced by the unfluxed smelting of these ores.

The deliberate addition of iron oxides as fluxes which has been inferred from Late Bronze Age smelting sites across the Near East and notably at Timna is best reflected by the experimental assemblages for the first (CUFE-1) and fourth (CUFE-4) mixed oxide smelts. The first oxide smelt, containing 9.6kg of copper and 5.6kg of iron, produced a copper-iron alloy with 12.3% iron content or 700g of iron out of 6 kilograms of metal. The fourth oxide smelt with a charge consisting of 8.4kg of iron and 6.4kg of copper produced an alloy containing 34% iron or 2kg out of 6.4kg of metal. Through comparison to the experimental smelting of Timna ores with the addition of hematite carried out by Tyelcote and Boydell (1977) it appears that their data for the iron content of copper-iron alloys falls between the two values for the first and fourth experimental smelts. Iron contents in the range of 23.9 to 28.9% suggest that more iron was available or reduced in the Timna experiments than in the first experimental oxide smelt (CUFE-1) and slightly less than the fourth oxide experiment (CUFE-4) which lies closest with a difference of 5% more iron than the most iron-rich experimental Timna alloy. Assuming that the experimental furnaces and methods used by Tylecote and Boydell

(1977) were not greatly more reducing or efficient than those used in the experimental oxide smelts, a charge consisting of almost equal parts iron to copper oxides would most closely have approximated the iron content in the resulting alloy observed in their smelts. The iron enrichment of the copper in the fluxed Timna ore smelts compared to the unfluxed smelts ranges from over 10 to 80 times greater (see figures 3.18-3.19, p126). In the experimental oxide smelts the iron produced for smelts one and four contains around 4 to 10 times more iron than in the second smelt which is closest to the unfluxed Timna examples. The difference in iron enrichment between the fluxed Timna ore smelt and the experimental smelts is probably a consequence of the much more variable iron content across all of the unfluxed Timna smelts producing a wider discrepancy with the results of the fluxed smelts. The most iron-rich of the unfluxed copper-iron alloys was just over 10 times more enriched than the fluxed smelts which correlates well with the data from the experimental smelts. The reason for this variance may be greater heterogeneity of the Timna metal samples, which Tylecote and Boydell specify had mostly formed as prills and not a consolidated metal phase during their experiments (1977:311). This heterogeneity was also present in the experimental oxide production assemblages as evidenced by the micrographs in chapter 5 and in figures 6.11-6.12. Limited but robust sampling of the experimental alloys demonstrated that the single values presented in figure 5.59, p237 are in accordance with an average copper and iron contents for the entire metal assemblages and can be corroborated with the results of the optical microscopic analysis. In conclusion the iron contents of the metal assemblages produced during the first and fourth experimental oxide smelts using a 3:2 and 2:3 copper to iron oxide charge composition respectively can determine the expected range for alloys produced in a fluxed Late Bronze Age copper oxide smelt using the Timna ores. This range can be defined as an iron content in the copper-iron alloys of anywhere between 5 to 34%.

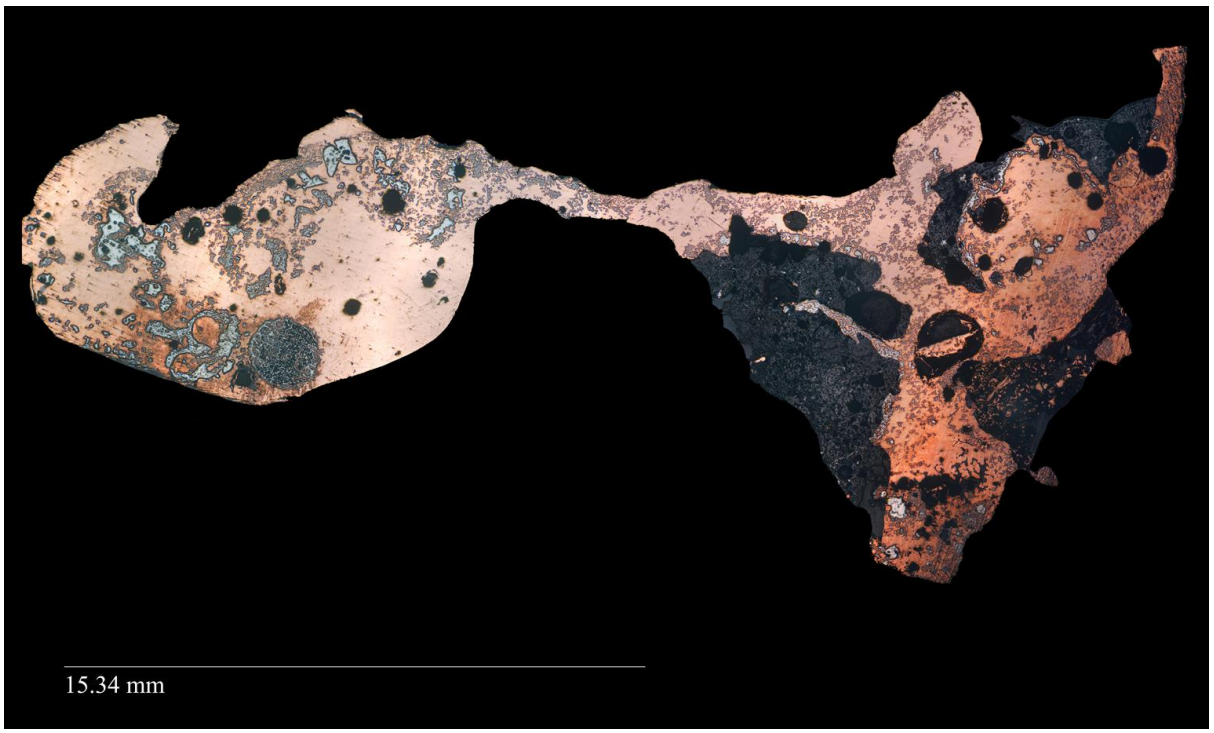


Fig.6.11: Macrograph of CUFE-1-01, x1.5mag. The small sphere of iron in figures 5.21-5.22, p213 is visible, bottom centre of the left formation.

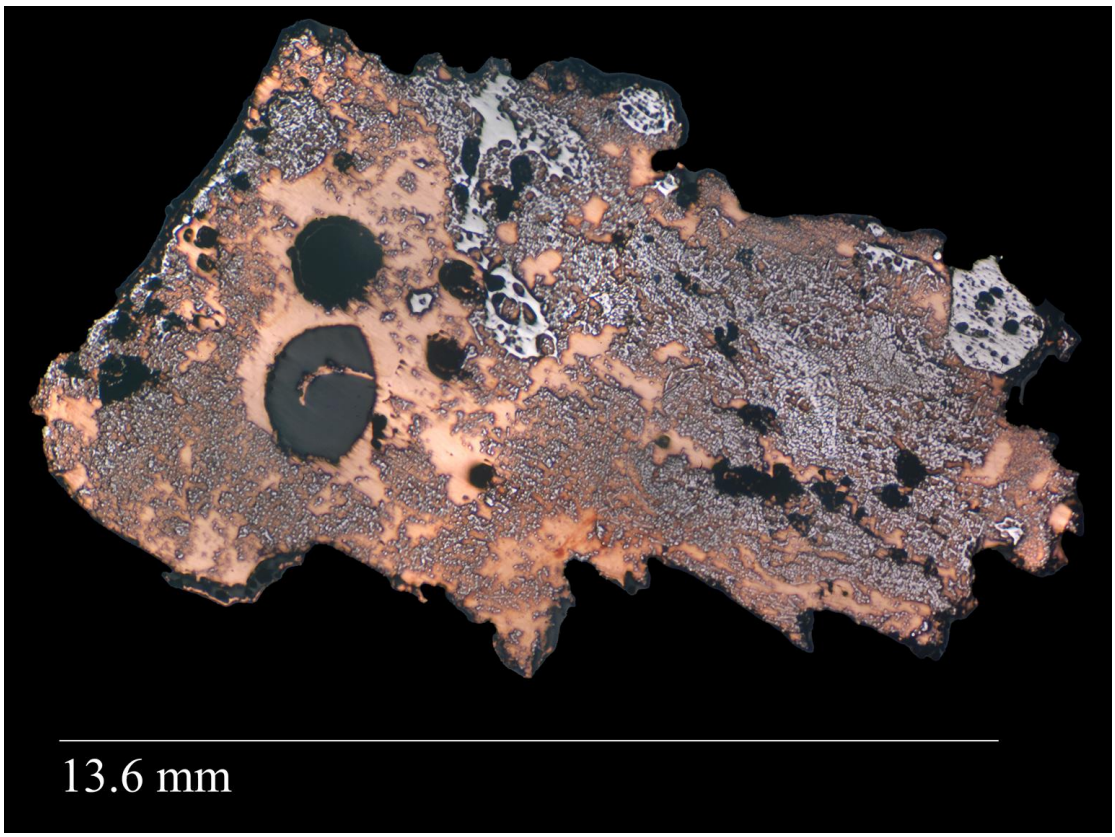


Fig.6.12: Macrograph of CUFE-4-3, x1.5mag. Dispersal of iron within the copper is very variable.

The recovery of raw copper prior to casting or refinement at smelting sites is rare and often restricted to small copper prills trapped in slags. This limits comparison of the experimental data to the primary products of prehistoric smelting. Fortunately spills of raw copper found at site 3 at Timna provides a unique opportunity to assess the correlation between the mixed oxide experimental smelts presented here and the raw products of a Late Bronze Age smelting operation. The site underwent multiple phases of occupation and construction over a century of habitation from the 13th to 11th centuries BC but was most metallurgically active during the first half of the 12th century (Yagel et al. 2016:46). These spills, located in a smelting and storage installation (see figure 6.13), may have been considered waste material or were being stored prior to re-melting and casting into an ingot of which two rare examples were found in situ (Yagel et al. 2016:46).

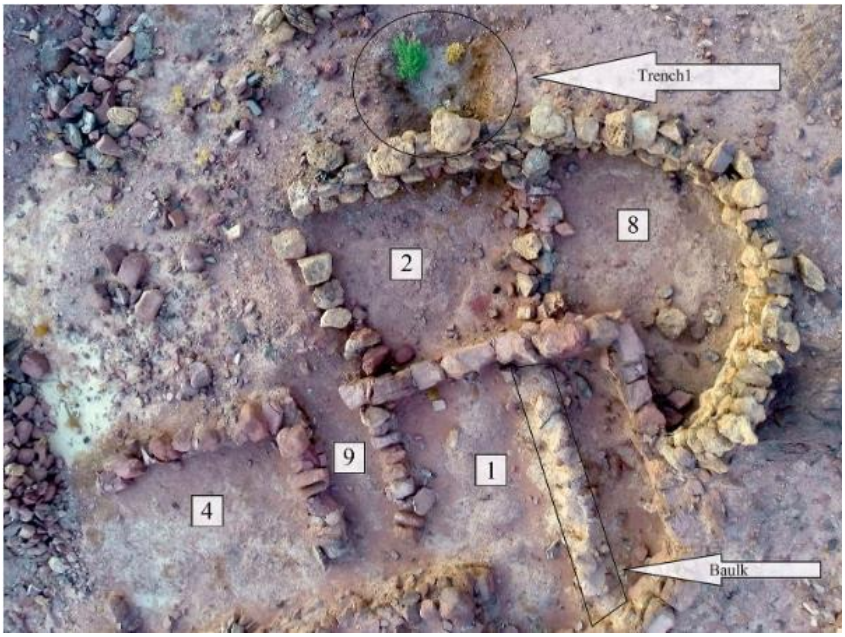


Fig.6.13: Structure 1, Site 3 at Timna, Israel. Numbers are areas excavated in the 1989 field season and trench 1, dug in 2014. Metal spills came from rooms 8 and 2. Taken from Yagel et al. (2016:41).

From the table in figure 6.14, the iron contents of the copper fluctuates between 0.33% up to 9.72%. The presence of quite low iron contents in some of the copper suggests the entire assemblage was not wastage but actually being stored after collection for melting into an ingot which is in-keeping with the characterisation of the structure as a 'logistical headquarters' for the site by Yagel et al. (2016:48). These iron contents correlate closely with those obtained for the furnace copper obtained in the first and second experimental oxide smelts which used a charge composition of 3:2 and 4:1 copper to iron oxides respectively. Similar proportions in the Timna ores smelted at this site and others in the area can be predicted and as will be explored later in the chapter, the high iron content of the 'bun' ingot is typical of these finds across the eastern Mediterranean.

Sample No.	Description	Cu (wt%)	Fe (wt%)
346	Raw Copper	98	1.85
329	Raw Copper	90	4.1
345	Raw Copper	85	7.15
347	Raw Copper	87.5	5.5
348	Raw Copper	90	0.33
349	Raw Copper	94	0.51
350	Raw Copper	89	2.9
351	Raw Copper	83.5	9.72
353	Raw Copper	92	2.52
354	Raw Copper	90	4.84
355	Raw Copper	89	0.72
331	'Bun' shaped ingot	96	2.7

Fig.6.14: Iron and Copper content of metal items found in structure 1, site 3. Adapted from Yagel et al. (2016:47).

The third oxide smelt (CUFE-3) which fired a 4:1 charge of iron oxide to copper oxide produced what should be described as an iron-copper biphasic alloy that unsurprisingly was the greatest outlier in terms of composition and bears no comparison to any Late Bronze Age assemblage. Two values were given in the p-XRF analysis table in figure 5.59 on page 237 for iron and copper contents as both more iron and copper rich regions of the sample were apparent (see figure 6.15). The 20kg charge, containing a stoichiometric 11.2kg of iron and 3.2kg of copper, was smelted to produce an iron-copper alloy (based on sampling of the iron rich region) composed of between 3.5-4.7kg of iron and 1-2.3kg of copper.

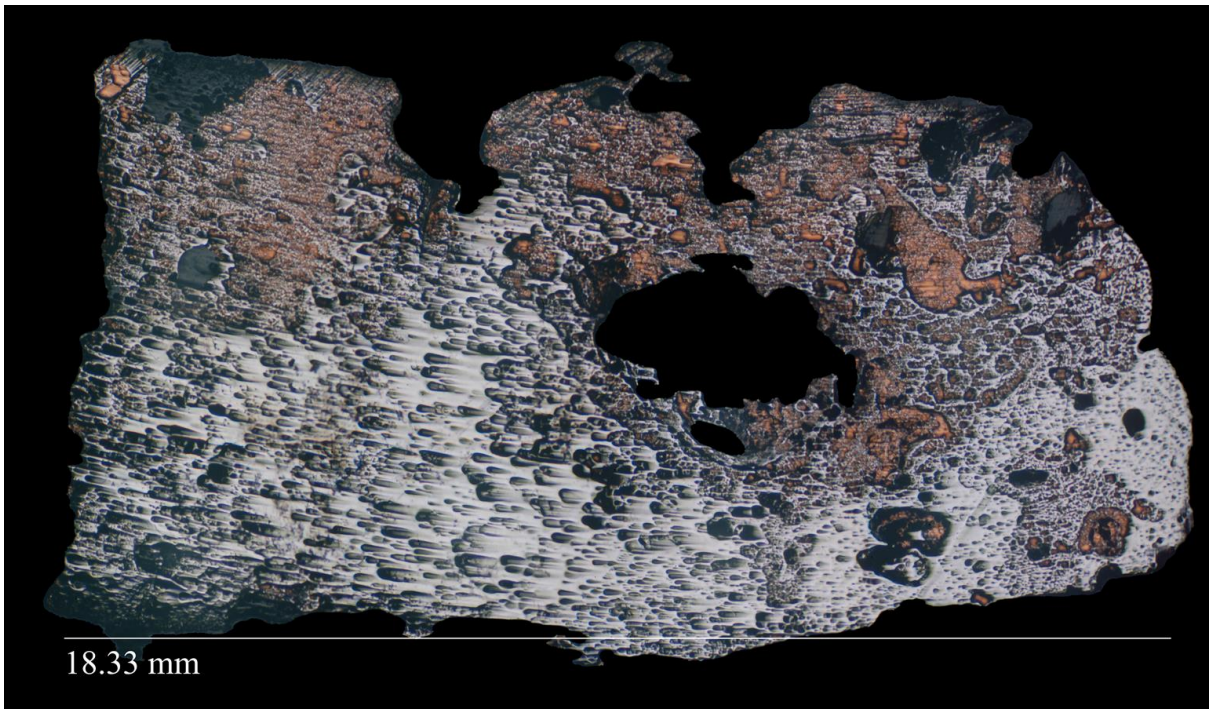


Fig.6.15: Macrograph of CUFE-3-06, x1.5 mag. Large iron phases (white) contained up to 78.4 wt.% iron with copper rich regions (red-brown) containing as little as 39.7 wt.%, almost half.

This quantity of iron is equal to a small to medium bloom in bloomery iron smelting and displayed a greater degree of consolidation and separation from the slag than might be achieved in a proper bloom. Reduction of about two thirds of the available iron and three quarters of the copper into metal suggests the smelt was quite efficient and the assemblage probably represents close to the highest content of iron that a copper-iron alloy can be enriched with using prehistoric smelting methods. Perhaps the main question raised by this smelt is why a bloom still did not form in the furnace despite significant quantities of metallic iron being produced? The failure of the small amount of copper to separate even from the much larger phases of α-iron must be a consequence of both metals forming simultaneously in the same region of the furnace discussed earlier in the chapter. Even over a long firing duration the solid α-iron must have prevented the molten copper from escaping through it to the base of the furnace. Such large amounts of iron could not derive from precipitation in solution from the copper upon cooling when the maximum solubility of iron in copper is only around 6% at 1200^{o}C. The lack of any copper precipitates in the iron reaffirms that the iron has remained in solid state and is likely quite pure. The possibility of similar iron-copper alloys being produced as a final preliminary stage prior to true bloomery smelting is intriguing however contemporary iron artefacts containing more than 10% copper are yet to be discovered.

Much of the data from the experimental oxide smelts can also be applied to the coppermaking or matte conversion stage of mixed sulphide smelting. In this step metal oxides produced by the oxidation of the sulphur from the sulphides would be reduced into metal via the same process used in the smelting of oxide ores. All the physical and chemical events witnessed in oxide smelting and subsequent products therefore apply to this stage of sulphide smelting allowing for direct comparison once sulphur has been virtually removed from the system. The proportion of iron to copper in 6

kilograms of the matte produced during experiment CUFES was estimated roughly at 5:1 copper to iron or 3.5kg of copper to 736g of iron. If this is scaled up to reflect the 20kg charges fired in the experimental oxide smelts then the furnace would contain about 11.6kg of copper and just over 2kg of iron taking into consideration the removal of some of the iron sulphide from the matte phase as prills in the slag. The charge composition of the second oxide smelt (CUFE-2) of 2.8kg of iron and 12.8 kg of copper contained a difference of 350g or 12.5% more iron and 1.15kg or 9% more copper than the matte in a theoretical 20 kilograms. This being so the composition of a copper-iron alloy produced through the smelting and conversion of the matte to metal should be roughly equivalent to the alloy made in the second smelt (CUFE-2) of 96% Cu to 4% Fe rounded up. The removal of sulphur via oxidation would oxidize much of the available iron which could also become trapped in the slag so lower quantities in the final alloy would be highly probable. Iron contents in the region of <2% for copper produced via mixed sulphides is a reasonable estimate. The production of copper alloys with >10% iron from mixed sulphide smelting could only occur with the inefficient partitioning of the iron in the matte or the failure to separate the copper-rich and iron-rich phases during collection and processing of the matte for conversion into copper. Regardless of this, the smelting of mixed copper sulphides in regions such as the south Caucasus or Cyprus must have contributed to the more or less universal rise in iron contents of copper alloy artefacts from the Middle to Late Bronze Ages in the archaeological record for the Near East (Cooke and Aschenbrenner 1975; Craddock and Meeks 1987; Hauptmann 2020:406).

6.4: *Getting it out: crucible processing*

Even supposing that most of the iron-bearing metal was recovered from each smelt, removal of the iron during secondary processing of the raw copper through oxidation during crucible melting, casting and working would have been carried out intensively in successive stages. During the production cycle of a Late Bronze Age copper alloy artefact four such stages, not necessarily sequential or separate, could have been carried out: ingot making, alloying and casting with a possible fourth stage: recycling (Hauptmann 2020:383). By far the greatest proportion of copper alloys in the archaeological record is made up of these secondary products following repeated exposure to oxygen and high temperatures during processing into various artefacts. Relating these objects for which there is a wealth of chemical analytical data to the less available primary metallic products from smelting is crucial for estimating the scale of iron extraction during copper production. The production of ingots for transport from the raw furnace copper may have been one of the first operations that the metal was subjected to following its extraction in the furnace. Any iron present during this process would be exposed to temperatures up to 1200^{o}C sufficient to render the unalloyed (before addition of tin, lead or arsenic) copper molten and free-flowing for casting without flaws in the mould (Hauptmann 2020:464). At this temperature in the open air environs of the crucible and casting mould much of the iron would be subject to oxidation on the surface of the molten copper. In the final experiment (CUIN 1-3) listed in chapters four and five the raw metal from three of the mixed oxide furnace smelts was used to produce three ingots for chemical analysis. The first ingot (CUIN-1) was produced by melting and casting 2.5kg of metal from the fourth oxide smelt (CUFE-4) in a graphite crucible to create a 754g ingot, the second ingot (CUIN-2) weighing 1.214kg was made using 2.4kg of metal from the 2nd oxide smelt (CUFE-2) and the third (CUIN-3) using 3.2kg of metal from the 3rd oxide smelt (CUFE-3) weighed 556g. The melting of the copper required heating at just over 1200^{o}C for about 15 minutes in a blast furnace before the slag on the top of the metal was skimmed off and the contents were poured into the mould and allowed to cool gradually. While the use of a graphite crucible and

blast furnace means that a direct parallel to prehistoric processes was not achieved, the possible introduction of carbon from the graphite could have occurred from the presence of charcoal in a prehistoric crucible hearth. The furnace environs may have been slightly more oxidizing in the blast furnace with the absence of carbon monoxide however. The results of the chemical analysis of these smelts will be discussed in the following paragraphs.

The first ingot, the sample from which is shown in figure 6.16, underwent a marked reduction in iron content compared to the sample of furnace metal it was produced from of over 20 wt.%. Despite this drop it remained very rich in iron at 12.4 wt.% with visible large inclusions surrounded by smaller dispersed spherical iron. The more even distribution of iron in the copper may be caused by the settling of the metal throughout the molten copper without obstruction by material in the furnace or inconsistent redox conditions causing the formation of α-iron in different parts of the metal phase in the furnace. Weight loss of over half of the furnace metal samples during casting into an ingot or a reduction by 1.7 kilograms from the removal of slag and impurities such as iron is considerable. Estimates of the iron content of the metal assemblage for the fourth smelt of 2kg of iron out of a 6kg total and for 69g of iron out of a 556g total in the ingot shows that the iron to copper ratio changed from 2:1 copper to iron in the furnace copper to 7:1 in the ingot.



Fig.6.16: Ingot sample CUIN-1, x1.5 mag. Larger inclusions surrounded by smaller aggregations of iron (light grey) in copper (pink-brown).

The second ingot (see figure 6.17), produced from furnace copper containing only 3.59% iron, was only reduced to 2.25% iron, 1.34% less. The greater mass of the ingot at 1.214 kilograms despite being produced from 100g less furnace metal than the first ingot demonstrates how much iron had contributed towards the mass of metal from the fourth smelt in comparison to the second smelt. The metal from the second smelt lost about 1.2kg during re-melting in the crucible, 500g less than that removed from the metal of the fourth smelt which contained 30.4% more iron though some of this material may have been other impurities from the slag. The estimated mass of iron in the ingot is 27g.



Fig.6.17: Ingot sample CUIN-2, x1.5mag. Virtually no iron is visible in the copper (pinkish-brown) even at high magnification (x40), see chapter 5 p234.

The third ingot (see figure 6.18) using the most iron-rich furnace copper from the 3rd oxide smelt contained 8.73% iron or a reduction of almost 70% in comparison to the most iron-rich value taken for the furnace metal sample. Despite beginning with the most amount of material at 3.2kg, the resulting ingot was only 556g in weight and by far the smallest, reinforcing the trend witnessed across all three ingots of the reduction in weight from the oxidation and removal of the iron. This oxidation was apparent with the large mass of attached and blistered slag visible on the top of the ingot which had disrupted the flow causing an incomplete casting. The slag that was detached from the metal during the skimming produced small beads of metallic iron and must have been extremely rich in iron oxides. Though it is less than half the weight, the third ingot contains 48g of iron, nearly double that of the second ingot.

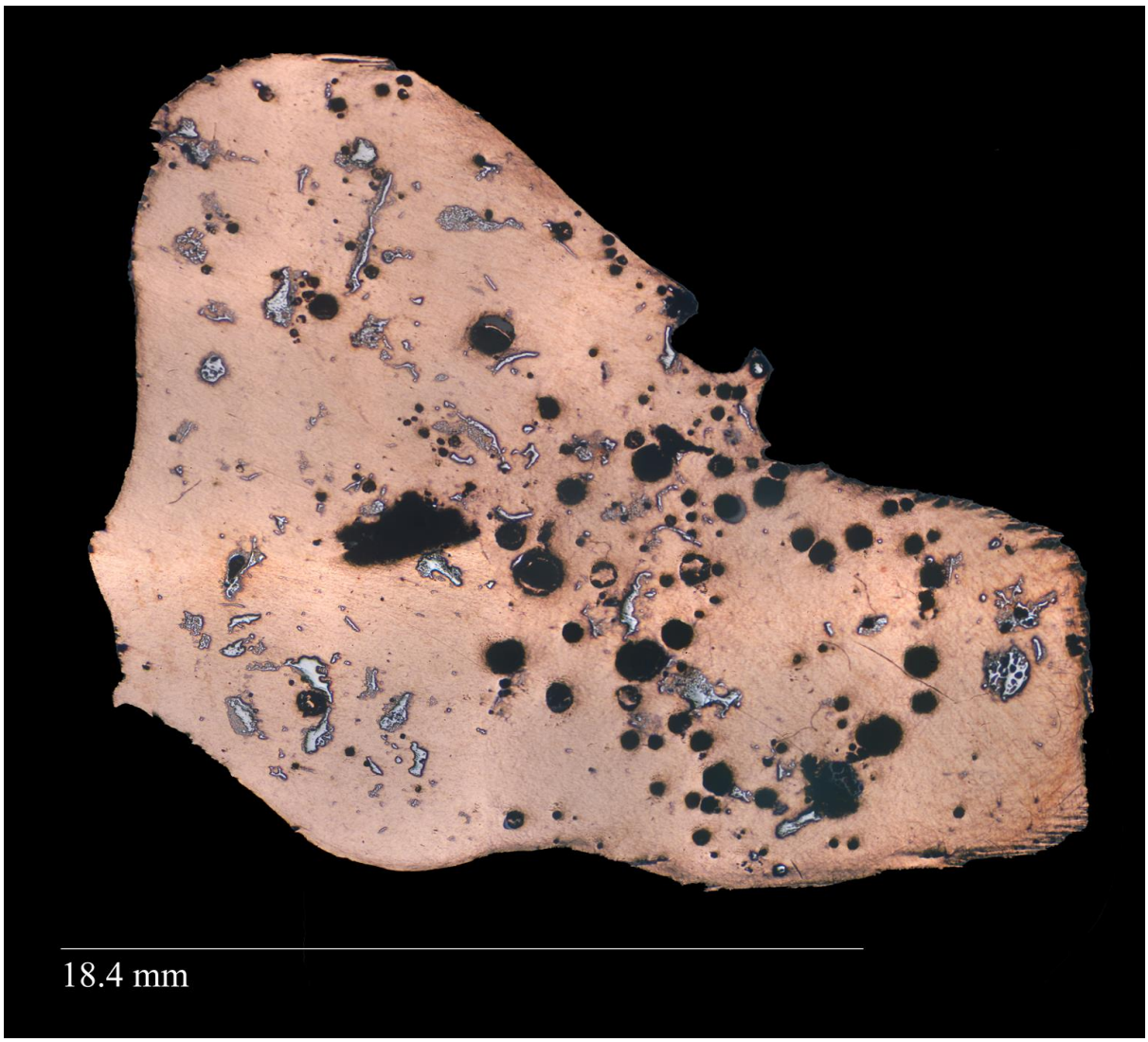


Fig.6.18: Ingot sample CUIN-3, x1.5mag. Distinctly less iron inclusions (white-light grey) dispersed in the copper (pinkish-brown) than in ingot one (CUIN-1).

Comparative analysis of the ingots reveals both shared and distinct features which, having all been produced in the same controlled conditions, must relate to the composition of the furnace metal they were cast from. For all the ingots a reduction in weight correlates positively with the reduction in iron content and the copper content was raised variably across the board. The drop in iron contents was consistent for ingots one and two (CUIN-1 and CUIN-2) with a 21.6% decrease or 36% of the content in the first ingot compared to the metal from CUFE-4 and a 1.34% decrease to 37% of the original iron content of CUFE-2 in the second ingot. As the rate of reduction did not drop below 35% for the

second ingot, diminishing returns in the removal of iron at low percentages/proportions in the copper suggests that further reduction would be more arduous, requiring higher partial pressures of oxygen. This procedure is often referred to as refining based on modern industrial processes but a lack of evidence for its application in prehistoric copper production suggests either that it was rarely done or that the process was archaeologically indistinguishable (Hauptmann 2020:317). This may account for the survival of iron and indeed sulphur in many Middle to Late Bronze Age ingots and copper base artefacts as the contents could not be decreased further than a few percent from melting and casting (Craddock and Meeks 1987:188). This is in stark contrast to the third ingot (CUIN-3) which saw a just under 70% decrease in iron contents compared to CUFE-3; retaining only 11% of the iron content in the furnace metal. This loss of iron was so excessive that the third ingot contained 3.67% less iron than the first ingot even though the furnace copper had begun with 44.4% more iron than the metal used for the first. The variable rates of oxidation seemed to impact the casting process where ingots one and two cast tight to the mould with no visible flaws in spite of a difference in iron content between them of 10%, whereas ingot three failed almost entirely to cast. The oxidation of such large quantities of iron in the furnace metal was clearly disruptive in the casting process which marks such iron-rich alloys out as being extremely undesirable as a raw smelting product going into processing. This goes some way to validating the general assignment by both excavators and archaeometallurgists of very iron rich copper alloys as waste materials exemplified at the Late Bronze to Early Iron Age sites at Timna (Gale et al. 1990:184; Hauptmann 2020:357). That being said an alloy very similar or even less rich in iron than the first ingot was recoverable though it would require re-melting to consolidate this into a proper ingot for casting purposes. The wide range of values for iron content in the material from the metal spill at Timna with some containing as little as 0.33%, shown in the table in figure 6.14 on p263, also disparages this notion. Worth noting is that the large mass of crucible slags removed from the surface of the molten metal during the third crucible melt contained multiple spheres of metallic iron of variable size upon cooling. These must have formed from the reduction of

the abundant iron oxides in the slag and suggests the blast furnace interior was fairly reducing though charcoal trapped in the furnace metal may have supplied excess carbon monoxide gas. These small pellet sized spheres might be sufficient to use as beads or possibly could have been beaten into a small length of wire though they are unknown in prehistoric crucible slags (Hauptmann 2020:225). In the iron rich ingots CUIN-1 and CUIN-3 larger inclusions of α-iron were visible though smaller than in the furnace copper with a more regular dispersal of small spheres of iron which may have developed as the iron became more evenly distributed in the molten copper during the crucible melt. In the CUIN-2 ingot the 2.25% of iron was virtually invisible with a presumed 0.2% being dissolved in the copper at room temperature and the other 2% being so finely dispersed it was undetectable. For the prehistoric metal producer this copper would be considered pure enough for casting or alloying. In short the ingot experiments have shown that furnace copper containing anything from 2 to more than 70% iron could be melted into an ingot containing less than 10%.

Late Bronze Age production of ingots is typified by the well studied ox-hide ingot trade originating on Cyprus which saw the wide distribution of distinctive hide-shaped copper ingots across the eastern to central Mediterranean from the 16th to 12th centuries BC (Mair 2009:11-14). The presence of copper sulphides in the ingots and their association with the sulphide smelting practices of Cyprus indicates that the ores used to produce them came from mixed sulphides and predominantly chalcopyrites mined from the Troodos pillow lavas found to the west and centre of the island, confirmed by isotopic studies (Hauptmann et al. 2002: 5-8; Mangou and Ioannou 2000). Weighing up to 30kg the oxhide ingots were probably produced using material from multiple smelting operations using a number of crucibles holding smaller quantities of metal. Recreations have been attempted in experiments seeking to reconstruct the process used in their production with much success (Hauptmann et al. 2016;

Hauptmann 2020:464-465). Iron contents range from 0.89% to 30ppm though are typically >0.2% in oxhide ingots (Begemann et al. 2001; Gale and Stos-Gale, 1987; Hauptmann et al, 2002; Kassianidou, 2009; Mangou and Ioannou 2000). Given the results of the experimental sulphide smelt where a copper alloy containing 2-4% iron was predicted from the smelting of the matte; a reduction of the iron content to >0.2% during melting into a large ingot with a longer period of oxidation falls within expectations. Ingots produced in regions that primarily exploited mixed sulphides have also been found to contain <2% of iron such as those belonging to the Late Bronze Age period in the South Caucasus shown in the table in figure 6.19 (Beridze et al.2018:67).

Description	**Inventory No.**	**Lab No.**	Fe (wt%)	Cu (wt%)
Complete hemispherical copper ingot	3-1976:1	HM1022a	2.68	96.1
Half hemispherical copper ingot	3-1940:2	HM1023a	0.76	98.9
Hemispherical copper ingot minus edge	3-1935:5	HM1024a	1.02	98.7
Segment of copper ingot	3-1939:4	HM1025a	0.39	99.1
Segment of copper ingot	3-1976:3	HM1026a	0.14	99.6
Rough sector of copper ingot	3-1940:8	HM1027a	1.19	98
Rough sector of copper ingot	3-1976:14	HM1028a	1.68	97.5
Complete small hemispherical copper ingot	3-1976:13	HM1031a	0.11	99.7
Sector fragment of copper ingot	3-1939:9	HM1032a	0.74	98.3
Mostly complete hemispherical copper ingot	3-1978:6	HM1033a	2.07	97.7
Edge fragment, hemispherical copper ingot	?1700 series	HM1037a	0.84	98.4
Edge fragment, hemispherical copper ingot	3-1976:11	HM1038a	0.89	98
Cut quadrant of flattish copper ingot	3-1976:1	HM1039a	1.09	98.4

Fig.6.19: X-ray fluorescence analyses of copper base ingot samples from Tsageri Museum, Lechkumi. Fe content varies from 2.68 to 0.11wt%. Adapted from Beridze et al.(2018:67).

Iron rich copper base ingots dated to the Late Bronze Age have been identified at sites across the eastern Mediterranean where a high iron content has been linked to a plano-convex (see figure 6.20) or ‘bun’ style of ingot (Mangou and Ioannou 2000; Yahalom-Mack et al. 2014:170). These ingots can contain anywhere from 4% to 0.1% iron (see figure 6.21) with extreme outliers reaching 25% iron content. The discovery of these ingots at Timna and Hazor in Israel but also in the Sinai suggests that they were produced from the smelting of the mixed oxide ore deposits found in the region as karstic inclusions in the local dolostones. The correlation between the high iron contents of these ingots and the ingots produced from the production assemblages of the experimental mixed oxide smelts demonstrates how the copper could become particularly enriched with iron during these operations. These ingots could have been produced with metal containing 3% to >70% iron depending on the degree of oxidation in the casting stages based on the experimental results.

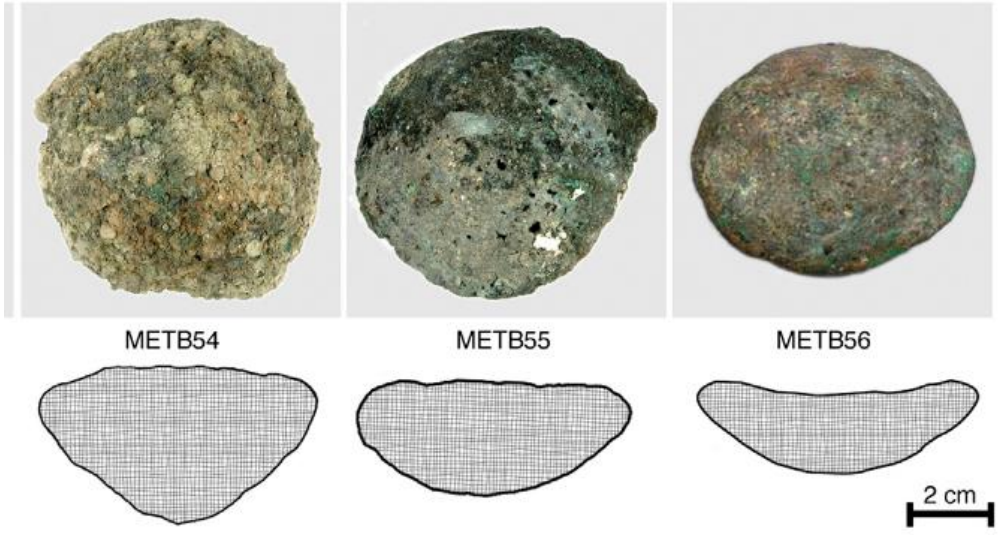


Fig.6.20: Copper ingots from Hazor. Taken from Yahalom-Mack et al. (2014:163).

Ingot Code.	Site	Ingot Type	Fe	Cu
METB31	Timna, Site 2	Plano-convex	2.49	87.8
METB32	Timna, Site 2	Plano-convex	1.86	90.1
METB33	Timna, Beer Ora	Plano-convex	1.83	86.5
METB34	Sinai, Bir Nasib	Plano-convex	25	56
METB35	Deir Alla, Jordan	Plano-convex	1.48	91.9
METB52	Hazor, Israel	Bar-shaped	0.41	92
METB53	Hazor, Israel	Ring-shaped	3.23	92.6
METB54	Hazor, Israel	Plano-convex	0.69	93.5
METB55	Hazor, Israel	Plano-convex	0.8	90.1
METB56	Hazor. Israel	Plano-convex	0.46	92.4
METB67	Hazor, Israel	Plano-convex	0.14	86.8

Fig.6.21: Iron and copper composition of ingots from the Levant and Sinai obtained from ICP. Ingots METB54-56 are shown in figure 6.19. Adapted from Yahalom-Mack et al. (2014:162, 170).

The iron in many of these plano-convex or bun shaped copper ingots is formed into the dendritic 'flowers' or intergrowths which precipitate from the copper upon cooling. One such growth in ingot METB53 from Timna was analysed by Yahalom-Mack et al. (2014:166) and found to have 53.1% iron content, confirming the presence of metallic iron in α-phase reported by Roman in many of the Timna ingots (1990). Similar iron rich formations are noted throughout the ingots and range from 69% to 1.4% iron content (Yahalom-Mack et al. 2014:166). The similarity of these iron inclusions with those in the copper of the second smelt is striking and raises the question of whether these ingots

were produced directly in the furnace at the base. The melting of large volumes of copper sometimes in multiple crucibles required prior to casting would be a significant investment in fuel and energy and so producing an ingot directly in the furnace would be more economical than a proceeding casting stage. This would limit the exposure of the iron to oxidation at high temperature. In any case the use of raw furnace metal in excess of 70% iron or likely nearly any composition with a greater proportion of iron to copper, can safely be dismissed on the basis that such high quantities of iron heavily disrupts the casting process as seen in the third experimental ingot. The ingot from Bir Nasib (METB34) with 25% iron content is remarkable and may represent the maximum iron contents that a copper ingot can contain and still be cast, though it might also have been made directly in the furnace. Data from the archaeological record and the experimental reconstructions shows that even quite low iron contents in copper base ingots could have derived from iron-rich smelting where the charge was composed of a ratio of up to two parts iron to three parts copper oxides or more in rare cases. Higher iron contents in ingots produced from the smelting of mixed oxides opposed to those produced from mixed sulphide smelting suggests that iron was more frequently extracted and separated into the copper during oxide smelting.

6.5: *Redox conditions within the furnace: what the slags can tell*

Slag petrography has been used with increasing interest in the field of archaeometallurgy to infer furnace conditions, charge compositions and formation events and to inform reconstructions of pyrometallurgical processes (Hauptmann 2020:217; Killick 2014:30-31). For the purposes of investigating iron extraction during copper smelting operations, the occurrence of metallic iron in the slag and the proportion of its oxides in the oxygen-sensitive wüstite-magnetite system bear closest attention in regards to the redox conditions in the furnace (Hauptmann 2020:268). The vitreosity of the slags also helps define the interior maximum temperatures of the furnace with more glassy slags being produced at higher temperatures from 1200^{o}C and up (Hauptmann 2020:267). In the slags of the mixed oxide smelts there are three main features: olivines intermixed with fayalite, metal oxides and copper prills (see figures 5.25, 5.26 on page 215, 5.33 on page 220 and 5.38, 5.45 on pages 224 and 228 respectively) and silica rich glassy slags with small iron inclusions (see figure 5.39, p224). In this first category wüstite was very prevalent in the slags of all four oxide smelts as seen in the dense formations of white dendrites in the micrographs. Less frequent instances of angular magnetite in the slags such as that shown in figure 5.45, p228 suggests the redox conditions in the furnace interior were highly variable and operated close to the wüstite-magnetite boundary around 11 log oxygen potential (see figures 2.16, p83 and 6.22-6.23, below). Prills of metallic iron in these slags is unsurprising though the majority were located close to the slag-metal interface, probably towards the most strongly reducing regions in the furnace (see figure 6.24). The high concentrations of wüstite in these slags are slightly atypical for copper smelting slags which under the less reducing conditions required for copper extraction should favour precipitation of magnetite. Nevertheless they closely match many of those from Timna and iron prills are known in copper slags from regions such as the south Caucasus and Cyprus (Erb-Satullo, Gilmour and Khakutaishvili 2014; Kassianidou and Van Brempt 2016).

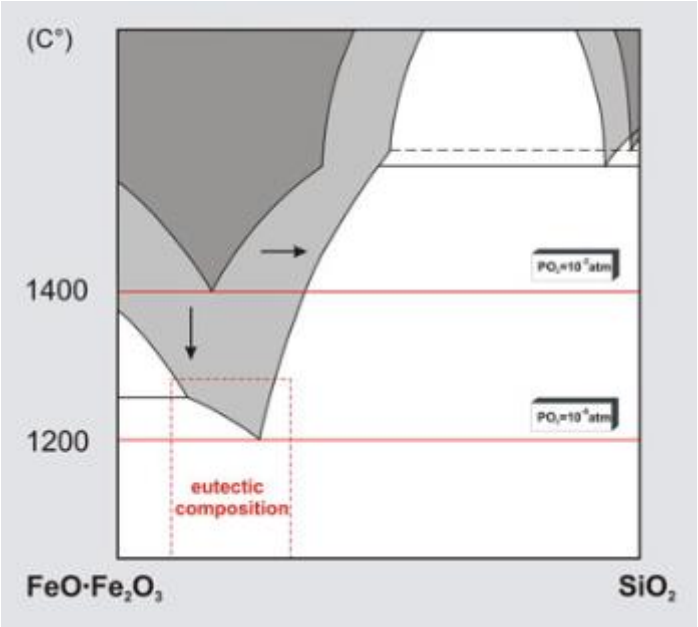


Fig. 6.22: The binary system FeO/Fe_3O_4-SiO_2. Fe^{2+} rich (wüstite) silicate (light grey) melts at temperatures around 1200°C and forms a limited range of compositions under strongly reducing conditions ($pO_2=10^{-9}$ atm, bottom red line). Taken from Hauptmann (2020:196).

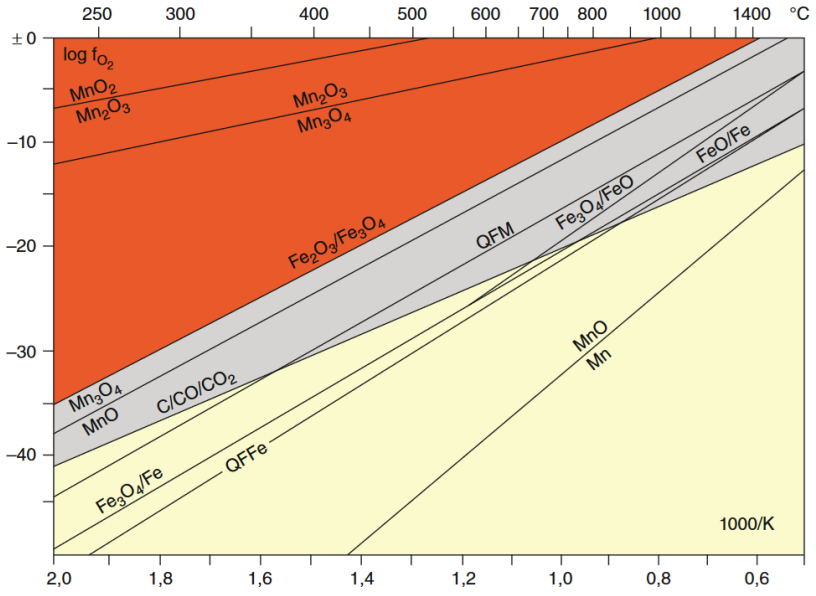


Fig.6.23: Formation of iron oxides as function of partial oxygen pressure Fe_3O_4/FeO begins at 1200°C around -11 pO_2. Taken from Hauptmann (2020:193).

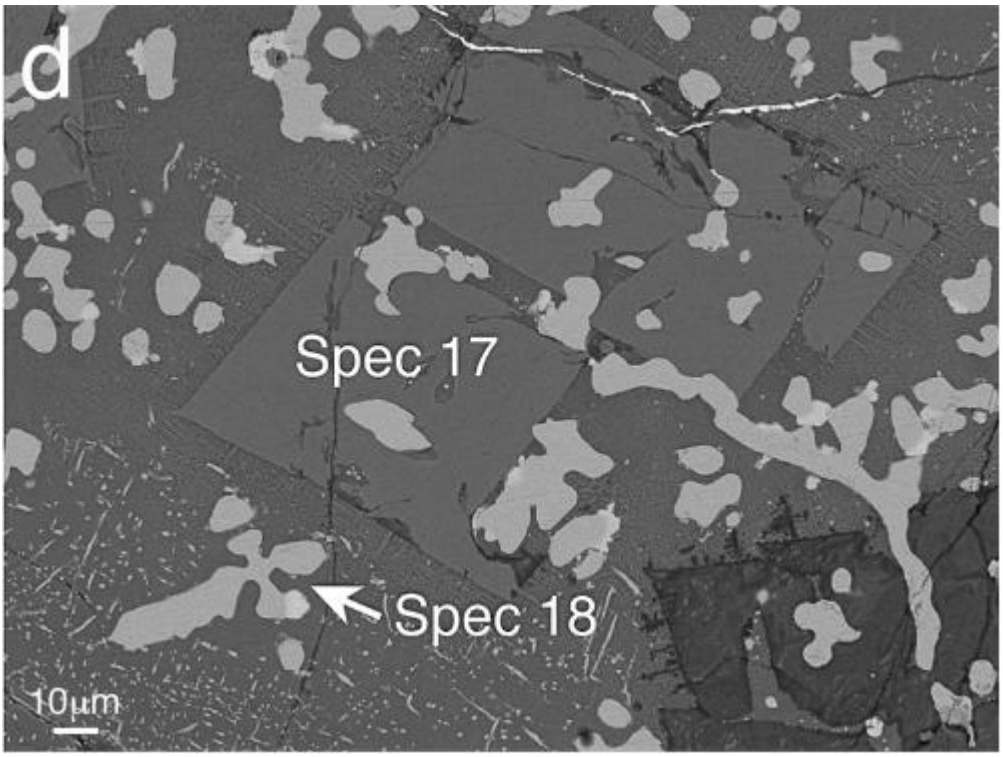


Fig6.24: SEM BSE image showing microstructure of adhering slag on METB53 ingot from Hazor. Globular iron (light grey) containing 69% iron in a glassy slag matrix (dark grey). The cuboid crystals are $Al.SiO_2$. Taken from Yahalom-Mack et al. (2014:168).

The more unusual variant of slag shown in figure 5.39 on page 224 appears to mostly consist of silica with a dispersal of very fine spherical iron. A few small inclusions of fayalite were present but infrequent in the homogeneous matrix of the slag. These slags were probably formed in the hottest part of the furnace as their melting points would remain high (pure silica reaches liquidus at 1710^{o}C) given they contain so few metal oxides or other impurities to lower it. The homogeneous and glassy appearance of the slags also points to their formation at high temperatures that probably exceeded 1200^{o}C and up to 1400^{o}C. Similar slags found in the archaeological record are usually associated with iron smelting due to the absence of copper prills, oxides or sulphides, high iron content and the high temperatures needed to produce them (Hauptmann 2020:247). The production of small quantities of this slag during the most iron rich experimental oxide smelt is not exceptional though it provides

an interesting parallel with some iron smelting slags in the south Caucasus which have been classified as tap slags (Erb-Satullo, Gilmour and Khakhutaishvili 2020:408). These slags from the classical/hellenistic period site 83 in the Khobi-Ochkhomuri area in Georgia shared the rounded iron inclusions in an extremely vitreous slag (see figure 6.25) composed mostly of silica and aluminium in a glassy phase (Erb-Satullo, Gilmour and Khakhutaishvili 2020:408). It may be possible that this type of slag is formed as a result of similar technical operations of the furnace, shared chemical compositions in the ore or gangue or even by the low proportion of copper in the charge during smelting for both the Georgian slags and the experimental oxide smelting assemblage.

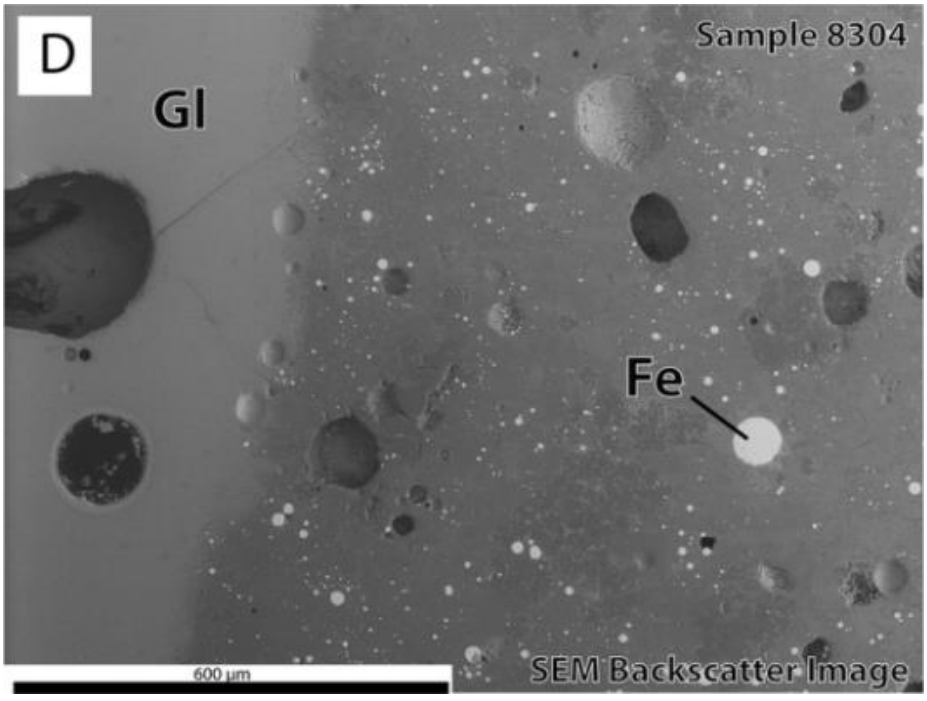


Fig.6.25: Microstructures of classical/hellenistic slag from site 83. Spherical iron (white) in a glassy phase (grey) resembles the glassy slag produced in mixed oxide smelt three, CUFE-3-1a. Taken from Erb-Satullo, Gilmour, Khakhutaishvili 2020:408.

6.6: *Estimating the output in metallic iron of LBA copper smelting*

As we've seen, iron could be produced in quantities ranging from 0.1 of a percent up to over half of the total metal production assemblage in a Late Bronze Age copper smelt. How frequently this occurred is hard to assess and would have been variably affected by factors such as the particular charge composition of each operation based on beneficiation and ore geology as well as the skills and intentions of the smelters. Still the general rise in iron content of copper base alloys and especially ingots witnessed from the Middle to Late Bronze Ages suggests that iron was extracted and caught in the copper with some regularity (Craddock and Meeks 1987). If this was true of a single smelt, how much iron could have been produced over the course of successive smelting over the long chronology of copper production in many regions such as at Timna, Cyprus or the south Caucasus? Estimates for the lifetime output of metal from smelting sites or complexes have often been made in the literature based mostly on the volume of slag heaps found in conjunction. By working out the volume of slag produced by one smelt this figure can be divided by the total volume in a slag heap to roughly determine the number of smelting operations it represented and hence how much copper would have been produced according to predicted yields in a single smelt. By applying these estimates to the results of the experimental oxide smelts and the analytical evidence for iron in Late Bronze Age copper it is possible to obtain a rough figure for the total weight of iron produced in the raw copper over the course of the site chronology. As the values obtained in the experimental smelts correlate the most with mixed oxide copper production at the sites in Timna, Israel and with the mixed sulphide smelting in the south Caucasus, sites from these two regions will be used with reference to similar traditions in other regions.

The long exploitation of the karstic oxide ore deposits of the Wadi Arabah valley at Timna has been recognised since an archaeological expedition in 1959 headed by Beno Rothenberg surveyed slag scatters, mines and smelting installations (Rothenberg 1990). Multiple phases of exploitation and occupation of the area beginning from the Chalcolithic and peaking with the influence of the New Kingdom of Egypt (1550-1070BC) represented by Egyptian wares but especially the Temple of Hathor, which was explicitly linked to metallurgical activity, proved challenging when constructing site chronologies, many of which remain disputed still (Rothenberg 1990:149-152; Yagel et al. 2016:33-34). Brief interludes in metallurgical activity and occupation in the area has helped define the main periods of smelting which fall within the Ramesside dynasties of the New Kingdom followed by abandonment with the withdrawal of Egyptian control before being re-established in the early Iron Age. In recent years greater success in characterising these phases of activity has been achieved using slag morphology, site comparison and implied production strategies from the sites in conjunction with accurate calibrated carbon dates. Yagel et al. have thus constructed a profile for a Late Bronze Age smelting site in the region as an undefended cluster of small structures (lack of defensive walls and earthworks in comparison to EIA phases) with small scale smelting indicated by slag scatters with fewer mounds or heaps (2016:46-47). The majority of sites that fit this description are located to the north of the Arabah valley in viewing distance of one another as opposed to those of the early Iron Age which lie mostly in the southern end. In all, five sites belonging to this phase have been identified (sites 2,3,13,14 and 15 see figure 6.26).

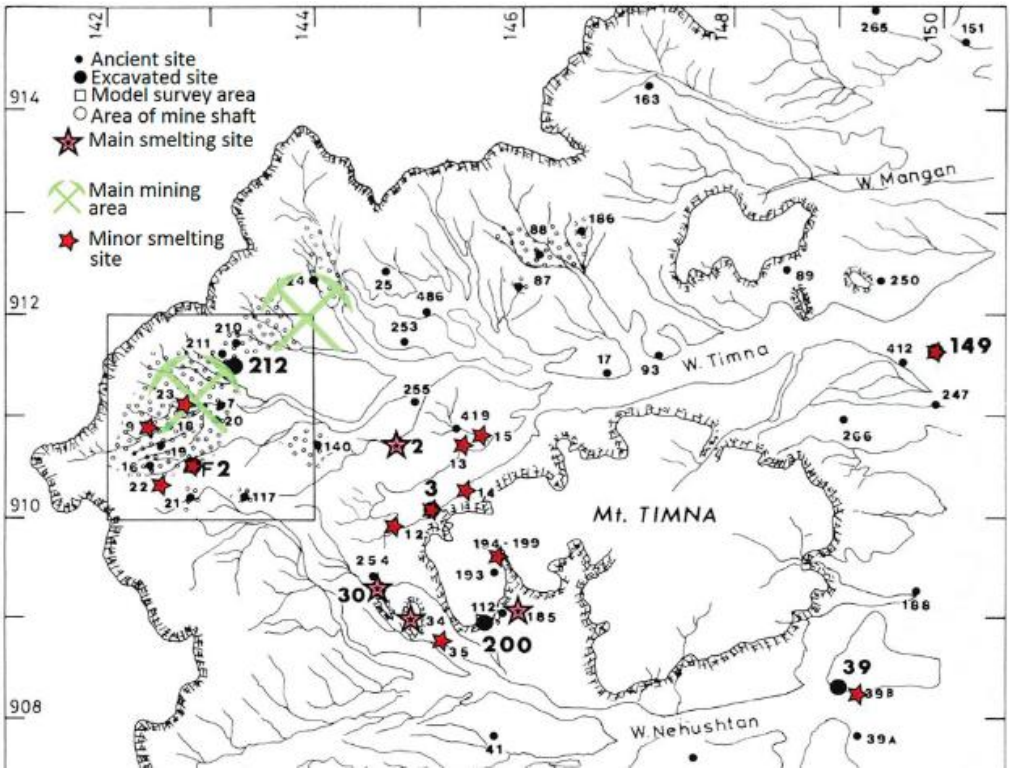


Fig.6.26: Site map of the Timna valley as recorded by the Arabah expedition 1959. LBA sites 2,3,13,14 and 15 can be seen in the centre, just north of the western spur of Mt. Timna. Adapted from Yagel et al. 2016:35.

Evidence for the extensive exploitation of local deposits in the numerous mines in close proximity and the yields acquired of around 2-3kg of copper in the experimental reconstructions of Merkel (1989) and Tylecote et al. (1977) has been used to provide estimates for the output in copper of a single smelting site in the region. A quantity of 120 tons of copper per smelting site produced during the Ramesside phase was predicted which when applied to the five smelting sites identified by Yagel et al. (2016:47) brings the total output of copper to 600 tons over 100 years (1184-1145BC) of operation (Hikade 1998:48). As the Late Bronze Age sites were typically smaller than later sites in the area, a more conservative figure of 400 tons may be more accurate however the number of sites and long exploitation of the mines speaks to considerable intensity in metallurgical activity. As was shown earlier in the chapter, the iron content of furnace coppers produced in the LBA phase at Timna was highly variable (see figure 6.14, p263) however the iron content of an ingot cast from this material

at 2.7% implies an average content of over 4% at minimum based on the second experimental ingot casting (CUIN-2). Taking a value in the middle of the range of 4-10% at 7.5% should provide a reasonable basis for estimation. This returns a total weight of about 30 tons of iron out of 400 tons of metal produced over a hundred year period, or 305 kilograms a year. Though this may be an overestimation of more heavily slagged or primitive smelting operations where iron losses could be greater, the production of iron somewhere in the hundreds of kilograms each year illuminates the scale at which iron was being extracted and had to be managed going into subsequent casting and alloying processes. Though the smelting activity at Timna was most pronounced during the penultimate period of the LBA with a revival in the 10th century BC, the smelting of mixed oxides at sites in the region with older chronologies suggests appreciable quantities of iron were produced as early as the Middle Bronze Age. At Wadi Nasib in the Sinai, a mining and smelting camp occupied since the reign of Amenemhet III (1842-1794BC) and worked up until the New Kingdom period, production of up to 5,000 tons of copper has been estimated based on the large slag heaps (Hikade 1998:46). Though the intensity of copper production at the site was not consistent, this amounts to an average of about 7.5 tons of copper made each year over a 650 year occupation. Based on the exceptional ingot from the adjacent site of Bir Nasib containing 25% iron, across a 200 year period over the Late Bronze Age around 1,500 tons of copper was produced along with 375 tons of iron (Yahalom-Mack et al. 2014:170). A more modest estimate of average iron contents of around 12%, which may be an underestimation since an ingot will be less rich in iron than a furnace copper, would reduce this to 180 tons or a single ton each year which is still considerable. Iron was indisputably the second most major metal after copper being produced at Late Bronze Age sites in the mixed oxide smelting camps of the Levant and Sinai region. Iron must have been regularly encountered by the smelters and close attention paid to its management and possible exclusion by sorting or refinement. By the dawn of the first millennium BC iron became a metal that these metallurgical traditions would have been wholly familiar with.

Determining the output of metallic iron for the smelting of mixed sulphides is far more ambiguous. The exposure of the iron to the higher oxygen potentials needed to remove the sulphur and the apparent mechanical separation of some of the iron sulphide away from the matte in the slag contribute towards higher losses than observed in oxide smelting. Copper yields are also difficult to estimate as the matte smelting process is only partly understood and very little experimental reconstruction of the matte conversion or coppermaking stages has been undertaken. The proportion of copper metal to slag produced in the furnace from mixed sulphide smelting is also potentially skewed towards slag with the association of more gangue, trace metals and iron content reaching over a third of the ore, with weathering increasing this, that is common in polymetallic mass sulphide deposits. One solution to this is to take an alternate approach using estimates of the Late Bronze Age trade in copper which is well documented in both textual sources and the archaeological record for the island of Cyprus. The well preserved shipwrecks of Uluburun and off Cape Gelidonya carried up to 10 tons of copper in >350 ingots which supports textual sources in the Amarna archives detailing the importation of over 800 ingots over a thirty year period into Egypt (Kassianidou 2013:51-52). These ingots, often in the oxhide form, roughly correspond to around 30kg in weight and if their shape does correspond to the means of casting using four crucibles (see figure 6.27) then a single smelt might produce around 7-8kg of copper metal (Hauptmann et al. 2016). If each ingot required around four furnace smelts to produce, 350 ingots would have required 1400 separate smelting operations to be carried out. Assuming that the decentralised copper smelting complexes on the island had all contributed towards this number with each camp providing something like 50 ingots or 1.5 tons of copper this may have been feasible within the span of a year (Kassianidou 2013:52). Based on the iron contents of the second mixed oxide smelt (CUFE-2) which was found to be closest to the predicted iron contents in the copper produced using mixed sulphide ores, nearly 400kg of iron would have been produced each year on Cyprus. Much of this iron may have existed as sulphides in matte phases, which further complicates bulk estimates of iron output from sulphide smelting. In the 354

oxhide ingots recovered from the Uluburun wreck alone the weight of iron would equal 70kg based upon the iron content of Cypriot oxhide ingots recovered in the Levant (Yahalom-Mack et al. 2014:170). Analyses of these oxhide ingots has shown that matte inclusions are common though small amounts of precipitated α-iron do feature as <10% of the total iron content. Taking this into account the Uluburun copper haul could contain around 5-7kg of metallic iron and this may well have been higher in the original furnace copper (Hauptmann et al. 2002:15-18). The rise in the manufacture of iron daggers on the island during the penultimate years of the late Cypriot era (1200-1050BC) coincides with the height of copper production on the island and this no doubt was facilitated by long experience with iron in the smelting furnace in the years prior.



Fig.6.27: Experimental casting of copper oxhide ingot using four crucibles containing <8kg of copper each. Taken fron Hauptmann et al. (2016:756).

The final copper producing region for comparison is the south Caucasus which in the Late Bronze Age period saw the exploitation of the polymetallic sulphide deposits of the Caucasus range (Erb-Satullo, Gilmour and Khakhutaishvili 2014). Following widespread survey from 2010 to 2014 in the area, copper production was revealed in the presence of multiple dispersed sites of slag scatters and smelting installations along inclines and ravines that did not appear to be centrally organised (Erb-Satullo, Gilmour and Khakhutaishvili 2017:8-9). Based upon the slag scatters and heaps at each site, an average weight in slag of around 13000-17000kg was obtained which when compared to the densities of single slag cakes approximated 770 separate firings (Erb-Satullo, Gilmour and Khakhutaishvili 2017: 11). An average site chronology extending to about 25 years works out at around 30-40 smelting operations conducted each year. Translating this quantity of slag into metal produced is difficult especially for mixed sulphide smelting. Using the production of 6kg of matte from 20kg of ore during the experimental sulphide smelt (CUFES-1) as a foundation, the firing of almost double this quantity of ore per smelt which could be expected in a prehistoric context would produce 12-15kg of matte. From this quantity of matte a yield of around 5-10kg of copper is very likely. Thus in the span of a year the expected yield from 30 firings at one of these smelting camps in the south Caucasus would equal a few hundred kilograms of copper metal though this may be an underestimation. Of this annual yield in metal, based on the results of the mixed sulphide (CUFES-1) and second mixed oxide (CUFE-1) smelting experiment, about 4.5 to 8kg would be iron. Again, most of this iron may have been contained in sulphide or matte inclusions however small quantities of metallic iron may have precipitated in the copper which is visible as iron prills in some copper slags from the region (Erb-Satullo, Gilmour and Khakhutaishvili 2014:152). The extent to which iron was recognised by Late Bronze Age smelters in the south Caucasus remains an enduring question after early assertions of the rise of extractive iron metallurgy in the region; even so it is clear that by the early 1st millennium BC copper and iron metallurgy were both practised in a shared metalworking tradition (Erb-Satullo et al. 2020).

6.7: *Metallic iron from copper smelting: workable or not?*

Even if the extraction of significant quantities of metallic iron during copper smelting operations of the Late Bronze Age was proven beyond doubt; the implausibility of extricating it from the copper limits any potential role it could have had in the development of iron metallurgy (Wertime and Muhly 1980:12). The formation of the iron in a γ and α-phase in the nascent copper during smelting discussed earlier in the chapter seems to eliminate any possibility of a pure amalgamation of iron approaching a bloom forming in the furnace. Under these circumstances it is easy to dismiss any possibility of these extremely iron rich copper alloys or indeed copper rich iron alloys being worked in the manufacture of an object. This may not necessarily be the case as both constituent metals largely retain their properties in biphasic alloys. In a study into the work hardening behaviour of a biphasic copper-iron alloy at low temperatures, Yamashita et al. (2021) performed neutron diffraction measurements on a cold-rolled sample of the metal during tensile tests at 293K or about 20ºC. The commercially prepared cold-rolled alloy (Cu-40 mass% Fe, CFA-60 see figure 6.29) contained 40% copper and 60% iron which is almost equal proportions to the average obtained across the two samples taken for the third experimental mixed oxide smelt (CUFE-3) of 39.05% copper to 58.75% iron. The results are shown in the table (figure 6.28) below:

Test temperature	σ_{macro}^{YS}	σ_{macro}^{UTS}	σ_{Cu}^{YS}	σ_{Fe}^{YS}
293 K	258 MPa	338 MPa	41 MPa	517 MPa
150 K	334 MPa	436 MPa	44 MPa	691 MPa

Fig.6.28: Yield stress (YS *macro*), tensile strength (UTS *macro*) and yield stress of each constituent phase (YS *Cu* and YS *Fe*) at 293K or 20ºC. Taken from Yamashita et al. 2021:4.

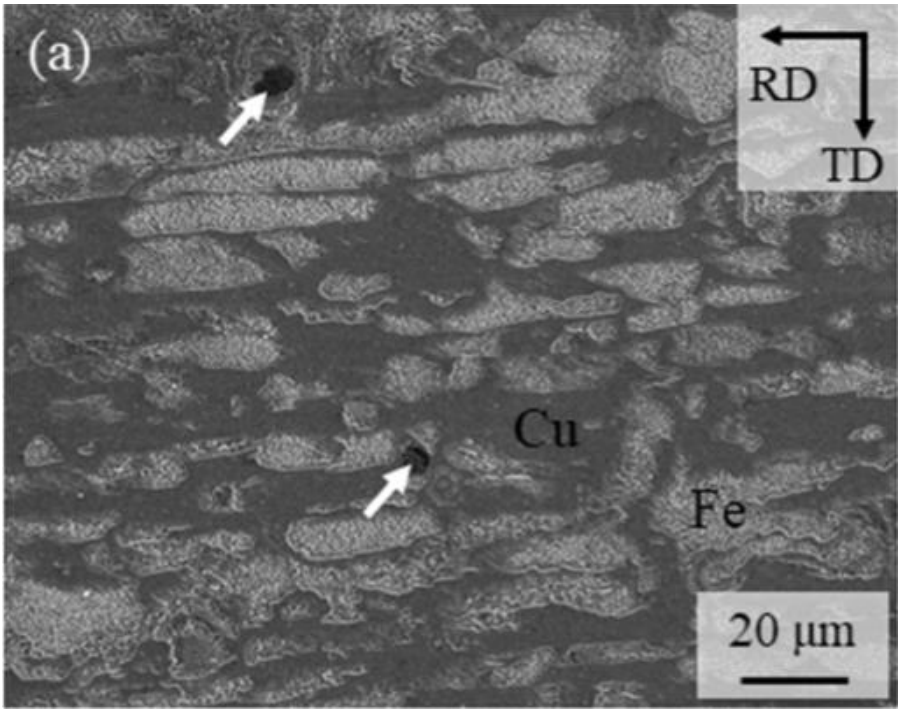


Fig.6.29: Microstructure of the test alloy in an SEM image. Horizontal elongation of the iron phases (light grey) in the copper (dark grey) was caused by cold-rolling (rolling direction is shown by the arrow marked RD). Tensile loading (direction that the exerted pressure was applied from) is shown in the arrow marked TD. Taken from Yamashita et al. 2021:4.

An overall tensile strength of 338 MPa at room temperature shown in the table in figure 6.28 actually exceeds that of pure copper (137 MPa) and is close to non work-hardened arsenical and tin bronzes. Iron also improves the yield strength of the copper considerably (below the yield strength the behaviour of the material is elastic and it will return to its original shape when the pressure is no longer applied, above this pressure it will undergo plastic deformation). The increase in strength is caused by the phase stress in the iron which increases with a reduction in temperature however the rate of work hardening was higher in the copper which also increased at lower temperatures (Yamashita et al. 2021:9). At high temperatures the alloy could become less stable with the reduction of phase stress in the iron and lower rates of work-hardening in the copper. In a limited test of the copper-iron alloy produced in the third experimental oxide smelt (CUFE-3), the author beat a

fragment of the metal into a flat disc (see figure 6.30) at a low red heat (around 600-700ºC). The metal remained cohesive and held a shape with few fractures. This suggests that the tensile strength of such alloys during forging at low heats remains sufficient to shape the metal. At higher temperatures required for advanced forging and particularly welding, it is unclear how these alloys would behave and whether the copper would disrupt the welding of the iron along grain boundaries. More thorough experimental and analytical work is needed to clarify the practical feasibility of forging and welding copper-rich iron alloys into useable objects, tools or even blades. As no Late Bronze Age artefacts made from copper-iron alloys with >20% iron have ever been found their use in any capacity remains purely theoretical.

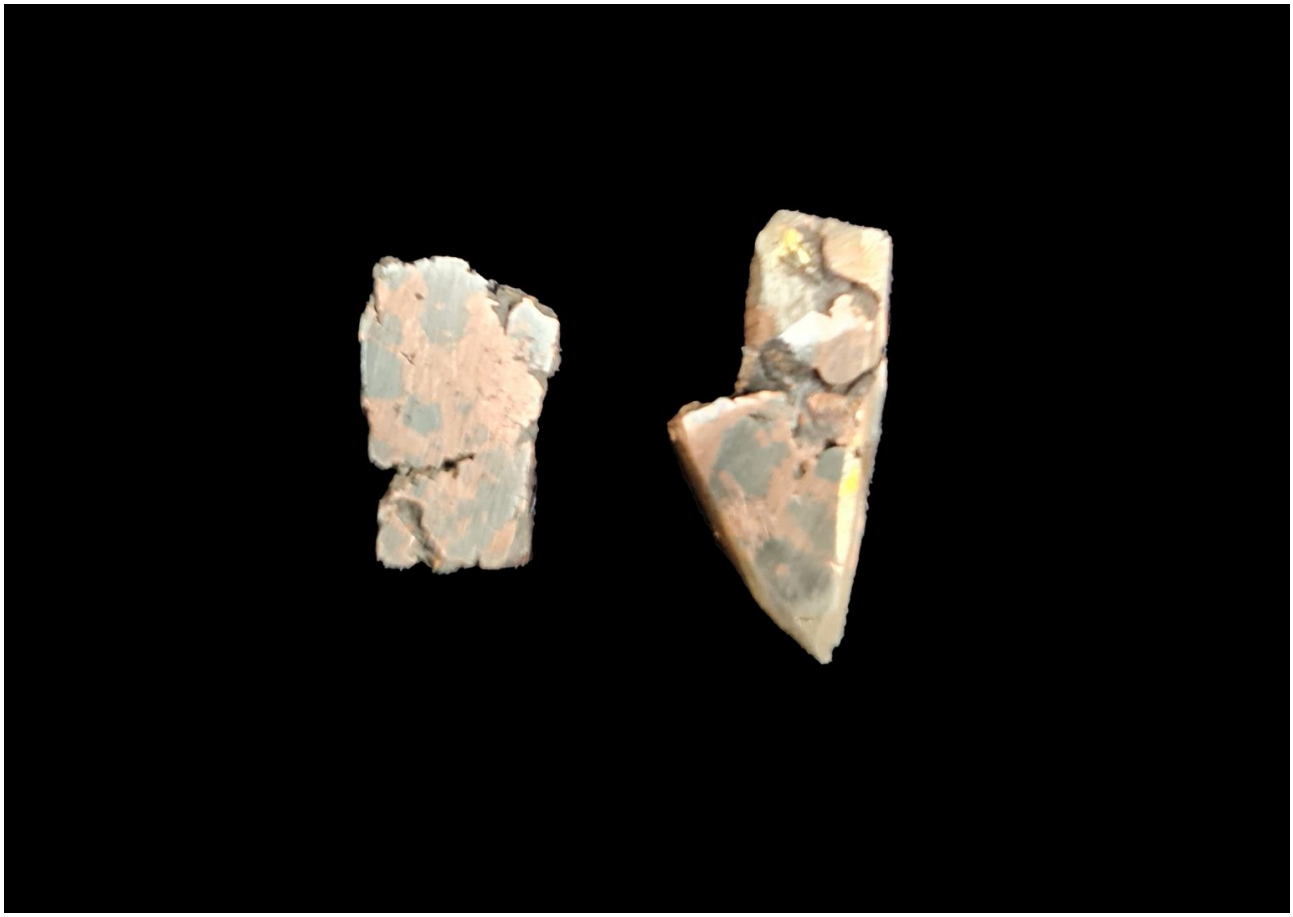


Fig.6.30: Copper-iron alloy from smelt CUFE-3 flattened into a 1mm thick square, left and arrowhead, right through beating at red heat. Iron (grey) is visible in the copper (pinkish-brown).

6.8: *Two for one: Implications of iron extraction during copper production*

Analysis of the alloys produced during the experimental smelts in chapters four to five revealed that substantial quantities of iron were partitioned into the matte during mixed sulphide smelting or became reduced and entered into the copper during oxide smelting. This has a number of implications for current understandings of Late Bronze Age copper production in the Near East, which are as follows. As an intermediary product in an inferred two-step smelting process, the matte would have been the primary source of iron during the final coppermaking stages of mixed sulphide smelting and would have contributed to the iron content in resulting copper alloys. In mixed oxide smelting, direct reduction of the iron oxides resulted in large phases of metallic iron to become entrained within the copper metal to a variable degree based upon the proportions of iron and copper in the charge. Iron content far surpassed that expected from the precipitation of the iron from the molten copper and reduction of both the copper and iron oxides must have been simultaneous within the more reducing region of the furnace. During casting the iron contents of furnace coppers were drastically reduced through oxidation of the iron though not lower than <2 wt. % in a single casting operation. Slag analysis suggests the experimental furnace smelts fell within expected ranges for temperatures and redox atmospheres during Late Bronze Age copper smelting. These conditions were sufficient to reduce iron though may have been sub-optimal compared to prehistoric iron smelting. The output in metallic iron at Late Bronze Age production sites in the Near East, estimated through comparison to the experimental results, suggests iron could have been the next major metal after copper to be produced in the region albeit as a biphasic alloy with copper. While there is little evidence for the use of copper-iron biphasic alloys suggesting they were simply discarded or processed through casting, their properties are amenable to a degree of working that could have fulfilled minor decorative or functional roles. Iron extraction is likely to have occurred far more frequently during copper production than previously anticipated, raising the possibility of a gradual conception of iron metallurgy among copper-related technological traditions.

Chapter 7

7.1: *From Copper to Iron: A holistic argument*

Over the previous chapters the extraction of metallic iron during non-ferrous metallurgical practices has been theorised with the most favourable circumstances being considered to have arisen during copper smelting. Experimental smelting of mixed oxide and sulphide ores was undertaken and the production assemblages were analysed with the results being explored in the previous chapter with reference to the archaeological record. From the evidence presented thus far it can be surmised that the extraction of metallic iron must have occurred with relative frequency in the contexts of Late Bronze Age copper smelting in the Near East. Nearly all of this iron was interspersed within the same metal phase as the copper in the furnace and in many cases would have required further pyrometallurgical operations to be removed before a desirable copper or indeed iron alloy could be produced. In certain instances this iron would have been visible as white-grey inclusions in the copper and surface oxidation and corrosion as orange rust would reveal its presence in an iron-rich copper alloy. More often the iron would be contained in matte, oxide or sulphide prills that would be undetectable to the smelter or metalworker. Barring the production of a mass of pure iron from an unanticipated event in the furnace such as the historical 'bear' phenomenon; how then does the incidental rise of iron contents in copper lead to the invention and innovation of extractive iron metallurgy?

The processes of 'invention' and 'innovation' are pivotal in conceptualising technological change among past and present cultures and have attracted a great deal of attention across the social sciences (Erb-Satullo 2020:36-37; Killick and Fenn 2012; O'Brien and Shennan 2010:3-4; Pollard and Gosden 2021:45-46;). Clear definitions for invention and innovation have proven elusive with interpretations

and application of both terms differing between authors (Killick and Fenn 2012:565-566; Roberts and Radivojević 2015:300). Often they are defined in descriptive rather than specific terms, for instance Pollard and Gosden frame both as: "...Individual inspiration giving rise to invention, to the responsive mode of problem-solving as the driver for innovation" (2023:45). These descriptions can be formalized such as in the definition given by Roberts and Radivojević: "Invention is frequently defined as the discovery of a new idea, material or process, deliberately or by chance...When an invention affects the evolution of the system and is successfully transmitted within a population, and beyond, it becomes an innovation" (2015:300). Amongst these descriptions common strands can be found which form a base conceptualisation of these processes:

- Invention is the novel application of a concept into practice which is unprecedented for an individual or within a cultural or technological context.
- Innovation is the transmission and adaptation of this practice among populations as a consequence of its invention.

Opinion on what exactly constitutes invention can range from an idea (Schiffer 2011:36) to recognition of advantageous phenomena (Shortland 2004:1) and the manifestation of a concept into a process (Erb-Satullo 2020:38). The impracticability of demonstrating invention in the archaeological record has long been recognised along both theoretical (Roberts and Radivojević 2015:301) and practical lines of reasoning (Schiffer 2009:239-241). These limitations are largely imposed by the reliance of archaeologists upon assessment of the material record. Conceptualised as an 'idea' prior to human action, invention cannot exist in a physical sense (Roberts and Radivojević 2015:301). Alternatively, if invention represents a novel idea put into action, by necessity it must be a lone event within time and space which is unlikely to be perceptible in the fragmentary material record (Schiffer 2009:240). This has naturally caused archaeologists to approach the topic of invention with reluctance (Roberts and Radivojević 2015:302) however its significance for

understanding human cognition (deBeaune 2004; Wadley 2013) and agency (Frieman 2021) in a cultural context continues to be of relevance. Innovation comprises two processes that represent the spread of an idea or practice borne out of invention: firstly through transmission to and adoption by new populations and then through adaptation of the invention by the host population to fulfil a desired outcome (Erb-Satullo 2020:38). Innovation provides far more tangible evidence of technological change through the repetition and reciprocation of a process after it has come into practice, causing it to have a greater physical and social impact which leaves a deeper impression upon the material record (Walsh et al. 2019). This is integral to archaeological research which is based upon interpretation of physical remnants of human activity to make inferences about technological change and diffusion (Pollard and Gosden 2023:46). A productive approach to the study of invention has been to incorporate it into a wider system of innovation as a hypothetical starting point for the process of technological change (Erb-Satullo 2020:38; Roberts and Radivojević 2015:301). In this scenario, an act of invention would be indicated by the absence of technological or cultural elements that are characteristic of a system of innovations that appear later in the archaeological record (Pollard and Gosden 2023:47; Roberts and Radivojević 2015:301). Innovation should not be conflated with technological progress or risks falling back into synthetic or 'evolutionary sequence' models that ignore human choice in adoption and adaptation of technology (Erb-Satullo 2020:40). Here archaeomaterials (Erb-Satullo 2020:38) and experimental archaeology (Killick and Fenn 2012:566; Roberts and Radivojević 2015:301) can play a major role in reconstructing the technical and physical contexts of innovation and in demonstrating its absence or presence in the archaeological record. In this chapter, the topics of invention and innovation will be discussed in relation to the development of iron metallurgy among the metal using cultures of the Late Bronze Age Near East as an example of the utility that experimental and materials approaches can bring to studies of technological change.

7.2: *The Advent of Iron: ancient or modern invention?*

The invention of the extractive metallurgy of iron as an unanticipated consequence of copper production during the Bronze Age has been the subject of internecine debate among archaeometallurgists. It has been long been argued (Rickard 1939; Pleiner 2000; Wertime and Muhly 1980) that the physical and chemical parameters for the extraction of iron could only have been overcome through the technical skills and pyrometallurgical developments hosted within the copper extraction traditions of the Bronze Age. Perhaps more significant still, the technical understanding of the behaviour of iron and its ores within various redox and thermal conditions must seemingly have been fostered within copper smelting contexts in the absence of alternative parallel technologies or circumstances. Often termed the 'adventitious' or 'incidental' invention of iron, from its beginnings in the latter half of the 20th century this theory hinged upon analogy with pre-modern industrial processes (Gale at al. 1990; Tylecote and Boydell 1977; Wertime and Muhly 1980: 14). A phenomenon witnessed in historical slagged smelts, the consolidation of excess metallic iron in a furnace into a conglomerate known colloquially as a 'bear' or 'salamander' was construed as a possible provenance for early smelted iron or at least the metallurgical basis for the development of iron extraction techniques in the Bronze Age (Craddock and Meeks 1987: 200; Gale et al. 1990:185; Percy 1861:435; Wertime and Muhly 1980:13-15). The excess metallic iron could derive from the gradual reduction of extraneous iron-bearing minerals in non-ferrous metal smelting and was common in middle-eastern lead smelting which had been heavily fluxed with hematite (Wertime and Muhly 1980:13). Similar occurrences were witnessed in copper smelting, such as at a smelter in Talmessi, Iran which in an expedition to the region in 1968 was reported to produce these iron 'bears' regularly by Tylecote (Arab and Rehren 2004). With the excavation of the remarkable metallurgical complexes at Timna in Israel during the late 70s to 80s arguments for the co-development of iron metallurgy from copper extraction strategies were renewed (Gale et al.1990). In an analysis of 'cupriferous' iron objects (see figure 7.1) found in the 'Temple of Hathor' at Timna initially dated to

the Egyptian New Kingdom period (1570-1057BC), Gale et al. concluded that the high copper content (between 0.1-0.5%) may have derived from slagged copper smelting using the local hematite rich ore deposits: "Iron artefacts dating between 1318 and 1156 BC, found both at Site 2 and at the site of the Hathor Temple contain noticeable amounts of copper. There is a strong indication that the iron used to make these artefacts was produced locally as an adventitious by-product of copper smelting" (1990:189). These conclusions were supported by the correlation between the lead isotopic ratios of local ores and the artefacts (Gale et al. 1990:189-190).

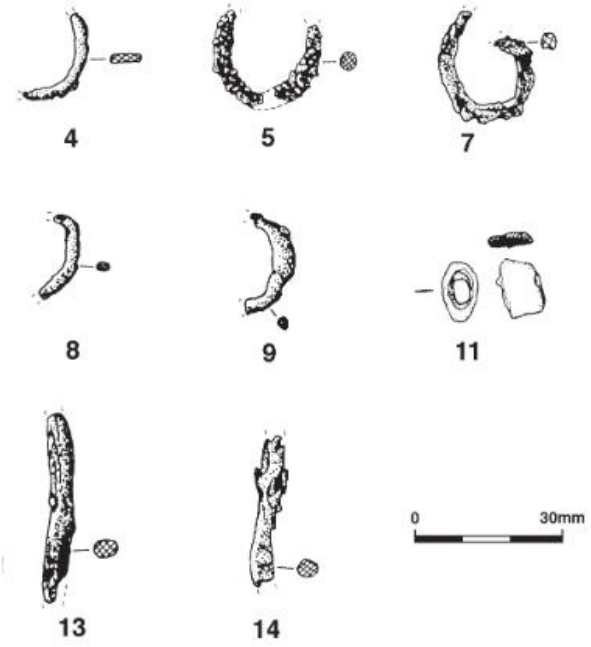


Fig.7.1: Illustrations of eight 'cupriferous' artefacts analysed by Gale et al. (1990) and later Merkel and Barrett (2000), recovered from the Temple of Hathor, Timna. They consist of heavily corroded pins, bracelets, beads and rings, some with gold embellishment marking their status in elite display. Taken from Merkel and Barrett (2000:60).

These sentiments became mirrored in studies of early iron metallurgy among contemporaneous practices of neighbouring regions in the eastern Mediterranean and Iran (Kassianidou 1994; Moorey 1999; Waldbaum 1999:30). With the completion of seminal works on the origins of iron metallurgy (Hauptmann 2007; Pleiner 2000; Wertime and Muhly 1980) this theory came under increasing

scrutiny as these books sought to foster a comprehensive understanding of prehistoric smelting processes. Wertime's 'The Coming of the Age of Iron' (1980), Craddock's 'Early metal mining and production' (1995) and Pleiner's 'Iron in Archaeology' (2000) all claimed that deriving metallic iron from the contexts of a prehistoric copper smelt was implausible. Discrepancies in the analogies with historical processes were stressed as insurmountable; for instance the 'bears' encountered in pre-modern Asia were noted to contain many impurities along with small amounts of copper and would not have been workable without significant refining, a process that was thought to have been too arduous and technically demanding even for Late Bronze Age metallurgists (Craddock 1995:255; Wertime and Muhly 1980:14-15). The role that such impracticable anomalies could play in the beginnings of iron metallurgy was therefore unclear. In a definitive statement on the matter, Craddock concluded that: "Not until the copper, together with other elements such as sulphur which are likely to have been present if the route to iron really was via non-ferrous metals and their ore deposits, were entirely eradicated from the charge would it have been possible to smelt an iron that was itself sufficiently pure to forge into a usable metal" (1995:255). Upon revisiting the evidence from Timna in an EPMA (electron probe microanalysis) analysis of the original copper-iron artefacts studied by Gale et al. (1990), it was found that depletion of the copper content towards the core of the artefacts to expected levels for smelted iron ruled out an indisputable origins within copper smelting operations (Merkel and Barrett 2000:64). Instead the results gathered by Gale et al. were probably caused by surface enrichment of the iron objects from the decomposition of surrounding copper artefacts which were picked up by surface XRF analysis and erroneously assigned to a common provenance (1990; Merkel and Barrett 2000:64-65). Revised dates obtained in the past decade for the majority of sites at Timna place them no later than 1147BC squarely within the early phases of the eastern Mediterranean Iron Age which further diminishes their significance as an early origins of iron extraction within Bronze Age practices (Yagel et al. 2016:46). Curiously the rediscovery of copper-iron alloys (with iron contents exceeding even the 6% that can precipitate from a copper solution

upon cooling from 1200°C) across many of the sites during revisitation demonstrates that reduction of metallic iron and its uptake within the copper may have been more widespread and frequent than initially thought (Yagel et al. 2016:49-50). The metallic iron within the copper may owe its survival to the lack of refinement of copper alloys at the Timna complexes which avoided oxidation of the iron in a crucible melt. Copper smelting at Timna was likely limited by local fuel resources to production of copper alloys in the form of raw ingots straight from the furnace which were traded and refined elsewhere in Egypt which did not have a scarcity of fuel (Yagel et al. 2016:50). It is uncertain whether this process was capitalized upon by the smiths at Timna to produce smelted iron however the lack of evidence for refining processes suggests the metal was not treated further and was simply exported in this form to be purified elsewhere. Moreover iron production would not be considered novel given the revised dates of the sites, though it may be an improvised minor scale production to exploit an emerging market in iron. Theories for the 'adventitious' production of iron and subsequent invention of iron metallurgy have ultimately proven inconclusive. This has likely arisen out of a failure to identify the complicated array of cultural, social and technological factors at play over the course of the 2nd millennium BC in the Near East. If iron metallurgy was discovered through adventitious means within copper smelting, without reconstructing the technical contexts of discovery as they pertain to human recognition and exploitation of phenomena this would remain purely speculative. Experimental reconstructions, such as those presented here, present an opportunity to explore these contexts and shed new light on an old topic.

7.3: *Direct to iron? Smelted iron in the contexts of a copper smelt*

One of the greatest challenges to revealing invention in the archaeological record is to reconstruct the circumstances of an invention from a material context (Roberts and Radivojević 2015:303). Schiffer presents three methodological steps towards resolving this issue: "First, search for those archaeological deposits that might retain high-resolution evidence of inventive activities as in the primary refuse of highly mobile peoples...Second, develop models by employing research strategies such as ethnoarchaeology, computer simulation, experimental archaeology, modern material culture studies and historical research...Third, formulate research questions in behavioural-not archaeological context-terms" (2010:236). The importance of archaeomaterials approaches for addressing the first step is stressed by Roberts and Radivojević who claim that: "...the approach taken in materials science seeks instead to identify and investigate anomalies, thus enabling the evidence of inventions to be evaluated more easily" (2015:301). In chapters two and three, the discussion of copper-alloy related smelting practises presented a number of anomalies apparent in the archaeological record of the Late Bronze Age Near East based on archaeomaterials research which can be summarized as follows:

- There is a general rise in iron contents of copper-alloy artefacts between the Middle-Late Bronze Age in the Near East.
- Iron-bearing minerals were exploited more intensively and increasingly formed a greater component of the charge in copper smelting across the period.
- The introduction of larger furnaces and forced draught through bellows produced more strongly reducing conditions and higher temperatures, evident in slags.

These anomalies form a contexts for the hypothetical invention and innovation of iron metallurgy among copper-producers in the Near East. In the second step, a model that explains the circumstances of invention within these contexts needs to be developed, which in this thesis has been attempted

through experimental archaeology. Experimentation as a means to explore the circumstances of invention as it pertains to the observation and recognition of exploitable phenomena has been promoted frequently in the literature on technological change in past societies (Killick 2014; Mesoudi and O'Brien 2008a; Schiffer 2010). The strengths of experimental approaches lay in their capacity to reconstruct technologies and practises based on data obtained from archaeomaterials studies, as discussed in chapters one and three. Bearing this in mind, what model can be developed to explain the invention and innovation of iron metallurgy from the copper smelting practises of the LBA Near East based upon the experiments presented in this thesis? From analysis of the experimental metal assemblages, substantial quantities of metallic iron was reduced during mixed-oxide smelting and entered into the copper. A smelted iron content of less than 5 wt.% in the copper is virtually invisible to the naked eye as the precipitation of the 6 wt.% of iron that can be dissolved in copper at 1200ºC creates widely dispersed minute dendrites or spheres of iron. This suggests that smelting operatons that employed a charge with a copper to iron ratio of 4:1 (demonstrated in CUFE-2) are unlikely circumstances for the invention of iron metallurgy. Infrequent larger prills or amalgamations of the α-iron can exist but there is no way of discerning whether these consist of iron. Until the iron content of the copper reaches 10-30 wt.% it can mostly be observed in the brassy-yellow tone of the copper. A charge composition between 3:2 and 2:3 parts copper to iron would produce copper with an iron content between 10-30 wt.% at which point the brassy colour and more frequent inclusions of iron could have become recognisable to the smelters. As the content of iron approached 50 wt.% larger formations and phases of α-iron would become easily perceptible and possibly extractable however this would require the proportion of iron in the charge to exceed copper by two times as much or higher. From this a model can be devised in which the realisation of iron extraction during copper smelting proceeded in three stages. In the first or incidental stage, copper producers smelted copper with an iron content between 10-30 wt.% from a charge with roughly equal or slightly lesser parts copper to iron content. In an evolutionary scheme this can be considered fortuitous observation or the

point at which an exploitable phenomenon becomes apparent (Boyd and Richardson 1988:42). Such charge compositions and alloys certainly appear to be in evidence in the Near East at Timna in the Sinai (Tylecote and Boydel 1977; Yagel et al. 2016;46), in Anatolia (Gailhard 2014:153) and across the wider region as indicated by iron content of ingots discovered across the eastern Mediterranean (Yahalom-Mack et al. 2015:167). During this stage the presence of the iron must have been recognised but was not acted upon with casting of the furnace copper being sufficient (see chapter 6, **6.5**) to produce the desired copper. At this stage it becomes necessary to address whether Late Bronze Age metal producers were even capable of identifying or characterising iron during a period when iron was extremely rare and inaccessible for the majority of the populace (Erb-Satullo 2019:559). Purely along linguistic and terminological lines it appears that iron both meteoric and smelted had been defined and even described based on its properties within the languages of the New Kingdom Egyptian (bỉ3-nỉ-pt, 'iron from heaven'), Hittite (*AN.BAR* 'iron metal') and later Assyrian (*amūtu* 'bloom iron') dynasties some time during the second millennium BC (Cavaignac 1934; Siegelová, and Tsumoto 2011; Wainwright 1934; Yalçin 1999:178-180). The appearance of iron and related terminology in these languages has often been conflated with emerging iron production in Hittite Anatolia without taking into consideration the contexts of the written records it has been derived from (Bjorkman 1973:112; Cordani 2016; Maxwell-Hyslop 1972; Waldbaum 1974). Often serving diplomatic or religious functions, it is improbable that these texts used terminology that had developed among metal producers. It is also unclear how these few instances of iron terminology, though coined by influential powers of the age, could relate to the material understanding of iron of Near Eastern metal producers both within and outside these spheres of influence. Iron likely represented an entirely novel material to the majority of Late Bronze Age metalworkers. This leads to the second or exploratory stage during which accidental or intentional smelting of extremely iron-rich charges resulted in the production of copper with >50 wt.% iron content resulting in large phases of metallic iron being produced that could potentially be exploited as a source of iron. In evolutionary

theory this stage could be described as goal-directed experimentation and represents an intent to produce iron prior to the establishment of efficient production pathways (Basalla 1988:18). Evidence of this is unsurprisingly rare given how such high iron contents were undesirable in copper during casting and economically wasteful. Apart from the exceptional example of the Bir Nasib ingot containing 25 wt.% iron (prior to casting the furnace copper could have contained upwards of 50 wt.% iron) this stage remains hypothetical but could have facilitated the circulation of small iron goods prior to direct bloomery smelting. In the final or innovative stage, a technological, social or cultural stimulus may have provided the impetus to finally remove copper from the charge and to exclusively produce iron. This can be seen to reflect the cascade model of Schiffer (1996, 2005a) which posits that once a technology became established e.g. production of metallic iron, new practises were proliferated to eliminate performance problems (i.e. removal of copper-bearing minerals from the charge) in order to better achieve this new objective. In simple terms, this process derives from a stimulus (transmission) and a response (adoption and adaptation) which are concepts central to understanding innovation. Therefore this stage will be discussed throughout the rest of the chapter. Returning to Schiffer's three step scheme in revealing invention in past societies, the final step was to formulate research questions in a behavioural and not an archaeological context (2010:236). This aspect of behavioural archaeology has been criticised as being isolationist from other approaches (Erb-Satullo 2020:40). This need not be the case as behavioural themes are already explored through archaeomaterials and experimental methods, shown in the work presented in this thesis. Questions of 'how' and 'why' are intrinsically related to behaviours of past peoples in response to physical phenomena and it is these questions that archaeological science is primarily concerned with.

7.4: *Old dog new tricks: adaptation of pre-existing extractive technology.*

In chapters three and four many technological developments unrelated to the deliberate extraction of iron were highlighted that proved to be determining factors in the incidental production of iron and may have laid the pyrotechnical and geochemical foundations for the true iron smelting traditions that emerged during the 1st millennium BC in the Near East. These developments achieved by the Late Bronze Age can be summarized as follows:

- **Furnace technology**- Clay or stone built structures that could hold fuel and ore in the tens of kilograms and bring a large reactor (volume of>20cm^3) up to temperatures of 1200^{o}C and higher.
- **Technical ceramics and bellows**- Sophisticated built-to-purpose ceramic *tuyeres*, nozzles and bellows were a Late Bronze Age investment into forced draught to provide higher and more consistent temperatures.
- **Technical strategies**- technical operations such as tapping became widely employed to improve the efficiency of pyrometallurgical processes at greater scales.
- **Exploitation of iron ores**- The mining and deliberate addition of iron ores as fluxes or to produce less viscous slags became more prominent.
- **Matte smelting**- The extraction of copper from purely sulphidic ores with the production of an intermediate product had developed from earlier co-smelting of sulphides and oxides.

The continuity in the use of this technology for iron smelting seen in the designs of bloomery furnaces, technical operations like the use of bellows or tapping and in some regions the exploitation of iron-rich ore deposits remains the most convincing evidence for the development of iron metallurgy within preceding copper production traditions (Craddock 2000:164; Erb-Satullo 2019). If metal producers in the Near East were aware of iron and had the technology to extract it, this raises of question of why wasn't iron produced at scales equalling copper sooner than the Late 2nd to Early 1st Millennium BC? To address this question the technical and technological strategies required to produce iron need to be examined and compared to those employed in copper smelting. From this we can infer what innovations were necessary to permit the extraction and production of iron in great enough quantities to fulfil roles of utility traditionally occupied by copper alloys.

The first and most obvious difference is the charge composition, with total exclusion of copper-bearing minerals being perhaps the first priority in early attempts to produce bloomery iron. As demonstrated during the experiments, even one parts copper to four parts iron in the charge can disrupt the iron through entrainment in the copper and prevent the formation of a bloom. Depending upon local geological deposits this may have not been straightforward, for instance in the mixed karstic deposits of the Wadi Arabah valley in Israel so called 'tile' iron ores were interspersed with copper oxides (Hauptmann 2007:48). Metal producers who exploited mixed sulphide ores such as on Cyprus or the Caucasus might also have relied upon mixed sulphide and oxide ores retrieved among the 'gossan' ores situated atop mass sulphide deposits (Erb-Satullo et al. 2020; Kassianidou 1994:75-76). In other geological settings this may have been much less problematic such as in Anatolia where readily-reduced high quality haematite ores and also magnetite sands were available without intrusive copper or sulphur (Yener et al. 2015).

By the late second millennium BC, smelting practises in the Near East had clearly achieved sufficiently reducing environments at the necessary temperatures to extract metallic iron though much less effectively than the extraction of copper. Of the two most iron-rich smelting experiments (FE-1, CUFE-3) less than a tenth of the iron content of the ore was estimated to have been extracted as iron, which was virtually inseparable from accruing slag. How might yields of iron be improved within these smelting contexts then? As discussed in chapter three, furnace dimensions and forced draught technology that was commensurate with that employed in the Iron Age had already become established in this period (Craddock 2000:164). Alternatively new strategies regarding the technical operation of a smelt may have been needed to overcome the difficulties of producing iron in the furnace. In theory, the duration of firing in prehistoric iron smelting was longer than that required for copper smelting due to the metallic iron remaining in solid state within the temperature ranges of the furnace (Hauptmann 2020:360). This causes entrainment and much lower mobility, extending the time required for the iron to consolidate into a semi-cohesive mass compared to copper, which once molten could flow into a complete mass in the furnace due to shared density (Hauptmann 2020:310, 364). The duration of successful experimental iron smelts carried out in shaft furnaces is typically around the ten hour mark or over, perhaps demonstrated most clearly in the fifty experiments by Crew (2013) that produced large (>4kg) iron blooms. This most likely exceeded the necessary duration required to consolidate molten copper in the furnace during copper smelting. A second and unique technical strategy that needed to be developed in the production of bloomery iron was the removal of the bloom at heat from the furnace and the percussive expulsion of slag and welding of the porous iron mesh into a billet (Hauptmann 2020:366). This represented an arduous and delicate operation that risked damaging the furnace in comparison to allowing the furnace to cool before collecting the copper metal with no such difficulties. This process is often avoided even by competent experimental smelters who instead recover the bloom cold from the furnace and subject it to re-heating and refining, a practice that is less fuel-economic (Crew 2013:36).

Once the iron was produced, fashioning it into the various forms needed to fulfil functions that copper alloys had occupied presented a challenge that smiths would spend arguably the next millennia to overcome (Maddin et al. 1977:124). Basic comprehension of the properties of iron based on complex factors such as forge welding (Li et al. 2014) and the eutectic properties of carbon-iron alloys (steel) was required before iron could even begin to displace copper-alloys in similar roles (Erb-Satullo 2019:577). Developing these technical skills was the purview of the smith and will be discussed later in the chapter with the evidence for secondary production during the Early Iron Age in the Near East; yet it was not achieved in isolation of primary production of iron during which the iron may have been vetted for its quality and carbon content requiring an appreciation of its properties right from its conception (Erb-Satullo 2019:577; Pleiner 2003:185; Tylecote et al. 1971). Each of these factors can be viewed as components which along with the technological developments of the Late Bronze Age formed the greater whole required to establish true iron metallurgy across the Near East. This collection of technical and technological components to innovation has been described as a 'recipe' which Schiffer and Skibo defined as "...(1) a list of raw materials...(2) a list of tools and facilities used...(3) a description of the specific actions undertaken in the technological process, and (4) the contingent rules used to solve problems that may arise." (1987:597). In this case, (1) would be the exclusive use of iron-bearing ores, (2) the furnaces and bellows re-purposed from copper smelting, (3) the technical operations of furnace firing, bloom extraction and smithing with (4) representing tapping of the furnace contents and other technical means to encourage efficient furnace operation. As a recipe these components can be categorized as either 'ingredients' (ores, furnaces, bellows) or rules (firing temperatures and redox conditions, bloomery extraction, duration) however these rules are not instructions and can be achieved through many different means and configurations, accounting for the apparent diversity of technological practises throughout human history (O'Brien and Shennan 2010:8). Only after the complete recipe for iron metallurgy had been established could iron begin to displace copper alloys.

7.5: *The search for iron: diffusionist approaches*

In the absence of direct evidence for the co-production of iron during copper smelting greater emphasis was placed upon locating instances of the earliest smelted iron and correlating it to local geological or technological circumstances that could have permitted the inaugural extraction of iron. With the most extensive archaeological and historical record for smelted iron in the 2nd and 3rd millennia BC Anatolia was naturally a prime candidate (Veldhuijzen et al. 2012; Yalçın 1999; Yener 2010). Classical and Hellenistic texts such as the Argonautica by Apollonius of Rhodes (Bittarello 2016) or the Parian texts (3rd century BC, in Rickard 1939) placed the discovery and mastery of iron metallurgy within the central and northern Anatolian plateau at the hands of a tribe called the Chalybes. These and other contemporary 3rd century BC texts by Aristotle (*De Mirabilibus Auscultis*) and Theophrastus (*On Stones*) claimed that the Chalybes produced iron from black sands with an "attractive" quality hence those rich in magnetite which is naturally magnetic (Gailhard 2012:153-54). As magnetite sands are readily reduced into metallic iron at 1200-1300°C with self fluxing silicas intermixed, as demonstrated by Tylecote who managed to extract metallic iron from two samples of black sea littoral magnetite sands in a crucible, this appeared an ideal contexts for incipient iron extraction practices (Gailhard 2012:154; Piaskowski 1983:337; Tylecote 1981). This was deemed by many to be a resolution to the question of the origins of iron metallurgy in Eurasia, with the influential 'The Coming of the Age of Iron' by Theodore Wertime and James Muhly stating "...we make so bold as to suggest that the first systematic production of iron and steel technologies thus derived, occurred precisely where the Greek authors said it occurred, namely the northern reaches of Anatolia and Paphlagonia in modern Turkey...the area in which the Hittite empire lay." (1980:18). This has remained the prevailing view among archaeometallurgists although the lack of evidence for primary iron smelting sites or for the exploitation of magnetite sands of the Black Sea littoral has cast doubt on the technological origins of iron if not the location (Gilmour, Khakhutaishvili and Erb-Satullo 2014:137-138; Yener 2010:185). Alternative processes such as lead smelting or speiss production

have instead been posited as the technological foundation for extractive iron metallurgy in the region (Akanuma 2006; Lehner and Yener 2014; Powell et al. 20201; Yener 2010). In prioritizing singular cultures as an origins for iron metallurgy based on an assessment of their capacity to overcome perceived material and technological constraints, this view has ignored the cultural and social contexts of technological innovation, an issue highlighted by Gamble (2007:61). One approach to reconstructing these contexts for technological innovation is social constructionism which correlates technical choices with cultural and social factors to explain why some technologies are adopted and others rejected (Childs 1991; Killick 2004; Lechtman 1996; Thorton et al. 2009). This is significant for understanding the broader patterns of adoption and adaptation of technology that proceed from invention as part of the innovative process.

The experimental and archaeological evidence discussed in this thesis has taken the onus away from the primary production of iron which clearly could have been achieved during the 2nd millennium BC. As an example the earliest evidence for the indisputable production of smelted iron comes from an 11th century BC workshop at Phokaia in western Anatolia which contained smelting installations with associated ironworking debris (Yalçin and Özyiğit 2013:240-243). Yet in the neighbouring regions of the Levant or the south Caucasus clear evidence of iron smelting doesn't appear before 900BC with the major expansion occurring almost 400 years later than at Phokaia (Erb-Satullo et al. 2020; Yahalom-Mack and Eliyahu-Behar 2015). All of these regions hosted comparable metal industries which rules out a purely technical disparity between them that delayed the implementation of the technology. Arguments for a shift in the metals trade and economy based upon a Late Bronze to Early Iron Age shortage of copper base alloys with the disruption of trade networks and centralised administration have been repeatedly postulated and revisited over the past century (Erb-Satullo and Walton 2017:11; Pickles and Peltenburg 1998; Mirau 1997; Muhly 1982; Snodgrass 1971:231). A

rise in the recycling of bronzes and more frequent deposition of the metal in hoards during the Late Bronze Age across the Mediterranean basin was interpreted as a reaction to stress in the metal economy whereby extra precaution was taken to ensure a local supply of metal would be available in the advent of a collapse in trade (Knapp 1988:152). These shortage theories in application to a wider regional synthesis have been met with numerous discrepancies relating to the upscaling of production of copper base alloys in the penultimate period of the Late Bronze Age (Erb-Satullo 2019:580-583). On Cyprus, bronze production had reached unprecedented highs at the end of the Late Cypriot era (1200-1050BC) and in the Wadi Arabah the intensification of copper smelting during the early Iron Age (1200-700BC) suggests the trade in copper alloys may have been at risk of market saturation and not privation (Ben-Yosef et al 2012; Karageorghis and Kassianidou 1999; Yahalom-Mack et al 2014). Similarly access to tin for alloying copper into tin bronzes did not become restricted based upon the continuity in tin contents of early Iron Age bronzes from across the eastern Mediterranean and Levant (Charalambous 2014; Pickles and Peltenburg 1988; Waldbaum 1999). This leaves the monopolization of iron which has traditionally been associated with the Hittite kingdoms of Anatolia (Muhly 1983). Prima facie this theory has much to recommend it from the wealth of textual evidence and smelted iron artefacts, unparalleled elsewhere, discovered in Anatolia during the 2nd Millennium BC in the major Hittite phases of occupation (Siegelova and Tsumoto 2011; Yalçın 1999). If the Hittites had exercised a monopoly on iron which was lost with the collapse and total annexation of their empire by the Neo-Asyrians from 1200 to 700BC then rapid development of iron metallurgy might be predicted in neighbouring regions with the migration of ironworkers (Muhly et al. 1985). A review of the spread of iron from newly emergent production sites in these regions instead points to a piecemeal and gradual adoption that was not a reaction to an external stimulus but to transformations in local economies, settlement patterns and production strategies (Erb-Satullo et al. 2020; Pleiner and Bjorkman 1974:307; Yahalom-Mach and Eliyahu-Behar 2015). The concept of a monopoly also loses technological credibility given the widespread production of metallic iron during copper smelting

operations of the Late Bronze Age that can be inferred from the experimental smelts described in chapters 4-6. It is hard to conceive of metalworkers in neighbouring regions to Anatolia remaining incapable of producing iron while under economic pressure by elites that would otherwise be forced into unequal trade with the Hittites (Cordani 2016). If technological and economic factors were not a barrier to the adoption of iron metallurgy in the Near East, instead it may reflect social or cultural changes that influenced metal producers to choose to make iron (Pfaffenberger 1992:282).

If iron production reflected the choices of metal producers in the region, emphasis can be placed upon the establishment of practises for secondary production, which can be defined as the acts of smithing, forging and welding of iron, as the determining factor in the rate of adoption of the technology. Production of iron prior to developing the skills to work it within a tradition would have been counter-productive. Evidence from Early Iron Age sites across the Near East has revealed a close relationship between copper and ironworking which may have been an attempt at diversification of products by metalworkers to exploit changing demand in the trade of metals (Erb-Satullo 2019:583-588). With the co-manufacture of copper and iron goods these pioneers set the stage for the development of advanced smithing skills that led to the deliberate use of carbon steels, piling of iron structures and forge welding that elevated iron and its properties above those of copper alloys. The most well studied examples come from the Levant where iron metallurgy appears at settlement sites like Tel Hammeh as early as 900BC and becomes widespread in large urban sites such as Tel Beth-Shemesh and Ashkelon by 700BC (Erb-Satullo 2019; Veldhuijzen and Rehren 2007:191; Yahalom-Mack and Eliyahu-Behar 2015). Sites such as Tel Hammeh were continuously settled from the Late Bronze Age through to the Early Iron Age with iron smelting being prevalent in the Early Iron Age phase (940-850 cal BC) which contained up to 700kg of slags that were estimated to have been produced over a

100 year period (Veldhuijzen and Rehren 2009:191,193). Local hematite ores from deposits at Mugharet el'warda were used as a source of iron and a total of 50-100kg of iron could have been produced each year that the site operated (Veldhuijzen and Rehren 2009:193). Recent discoveries of iron smelting activity from urban sites in Israel dating to the late 9th century BC seem to reveal a gradual transition to the production of iron alongside co-existing bronze industries (Buminovitz and Lederman 2012; Gottlieb 2010;Greer 2014:596; Veldhuijzen and Rehren 2007; Yahalom-Mack and Eliyahu-Behar 2015). The metallurgical assemblages from these sites consist of furnace remains, ores, slags and vitrified ceramics and there is evidence for primary and secondary production with the latter being particularly intensive within larger urban centres such as at Ashkelon and Tel Beth Shemesh (Buminovitz and Lederman 2012:13-15;Erb-Satullo and Watson 2017; Veldhuijzen and Rehren 2007:199). Continuity of Bronze industries alongside the newly established iron industries can be witnessed across many of the sites in Israel though there is great local and regional variation between sites. The later persistence of bronze production in northern Israel and resistance to the total displacement of bronze for utilitarian use can be seen by the much greater quantities of bronze objects recovered from northern sites compared to southern sites (Gottlieb 2010:292-293). Primary production of iron has been recognised at urban sites including Megiddo, Tel Dan, Hazor, Yoqneam, Taanach, Tel Rehov, Tel Es-Safi and Beth Shean (Gottlieb 2010; Yahalom-Mack and Eliyahu-Behar 2015). These sites display variable characteristics both in terms of technological choices and in the persistence of bronze smelting. At Megiddo, a city from which a large quantity of metal artefacts ranging from tools to decorative pieces were recovered, the location of iron production assemblages within the courtyard of a large public building contrasted with the domestic setting of contemporary bronze industries (Gottlieb 2010:91; Yahalom-Mack and Eliyahu-Behar 2015:291). A similar disparity between these two industries is apparent at the sites of Tel Rehov and Tel Hazor; at Tel Rehov the furnace assemblage and iron smelting debris was located within a public sanctuary and at Hazor a similar assemblage was found over the remains of previous bronze working activity

indicating the deliberate abandonment of bronze by an established smithy which later moved into the centre of the acropolis during a period of expansion in the 9th century BC (Yahalom-Mack and Eliyahu-Behar 2015:290-293). Examples of secondary production workshops within urban centres have been excavated at sites in Syria (Tel Fukh Fawqani, Tel Ahmar and Tel Afis), Jordan (Tel Es-Sadiyeh) and Israel (Tel Es-Shari'a) which might provide evidence of the stockpiling of iron to be processed within specialised workshops controlled by centralized administrations (Erb-Satullo and Walton 2017; Veldhuijzen and Rehren 2007:191). Evidence for iron smelting and secondary production in southern Israel was recovered from the sites of Beersheba and Arad dating to 1000-900BC. These sites are characterised by the wholesale abandonment of bronze with copper objects representing only 10% of the total metal finds (Gottlieb 2010:95-7). The primary purpose of these workshops was the production of utilitarian tools, making them perhaps the earliest well-studied contexts for iron tool production from Israel. Technological choices in the construction of furnaces and especially the shape of *tuyères* also display a surprising degree of diversity given the youth of iron extraction techniques and their rapid adoption from what is often assumed to be a single point of origin. These features are frequently shared across settlement contexts leading to various interpretations of them as cross-cultural contacts, permanent bases for itinerant smiths or remnants of bronze working traditions before their standardisation by central authorities (Erb-Satullo and Walton 2017:16-18; Veldhuijzen and Rehren 2007:199). These interpretations remain purely speculative until furnace assemblages from these sites can be identified with greater precision yet they represent a period of changing strategies and re-organization of metal production before facing standardisation in the 9th century BC. Of particular significance in the Levant is the continued use of local oxidic ore deposits which had seen previous exploitation during the Late Bronze Age as a source of copper ores but also for iron ores for production of ochres and slagging of copper smelts. Based on the experimental oxide smelts it is easy to speculate that these metal producers had drawn upon long experience and practice with iron from iron-rich copper smelts to exploit an emerging demand for

iron by developing new production strategies. The co-production and manufacture of copper alloy and iron goods has also been recently reported in the south Caucasus (Erb-Satullo et al. 2020). At a fortified hilltop site at Mtsvane Gora metallurgical debris was found dating from the 8th to 6th centuries BC. Most of the metallurgical activity was confined to secondary production resulting in the deposition of hammerscale, smithing slags and plano-convex slag cakes that may have been hearth bottom slags (Erb-Satullo et al. 2020:4-5). Analysis of smithing slags, which were identified on the basis of their proximity to hearth structures and the presence of both magnetite and wüstite which may have been caused by the variable redox conditions of an open hearth, showed that they contained prills of both iron and copper. High arsenic and tin contents in the copper supports the deliberate addition of these agents to produce a range of copper alloys (Erb-Satullo et al. 2020:8-10). Mixed pyrite ores in association with the hammerscale, smithing slags and hearths pointed to the exploitation of nearby polymetallic sulphide deposits and mining implements such as hammerstones and antler bone picks confirmed this (Erb-Satullo et al. 2020:4-9,13). This raises the intriguing possibility that iron production in the south Caucasus also co-existed with and was propagated by established copper alloy producers who continued to rely upon local polymetallic sulphide ore deposits as a source of copper and iron. This opens up regions where sulphide deposits were primarily exploited to the co-existence of copper and iron production (e.g. Cyprus) similar to that witnessed in the Levant where oxidic ores were used as a source of copper and iron (Kassianidou 1994). For the populations of the Late Bronze Age Near East, the decision to adopt iron metallurgy following its invention was largely determined by cultural and social factors and not technological ones. The proficiency with which metalworkers were able to innovate to produce and fashion the new metal is testament to skills honed over the previous millennia; long before the decision to adopt iron was taken.

7.6: *Metalmorphosis: the transition to iron*

"For here now is the Age of Iron. Never by daytime will there be an end to hard work and pain, nor in the night to weariness, when the Gods will send anxieties to trouble us"

- Hesiod *The works and days/theogeny/The shield of Herakles.*

Even since the classical period the use of iron by man has been seen as marking a distinct epoch forever sundered from the brazen age of heroes and kings that came before it. The hard labours of men necessitated by the acts of smithing and forging were now required to fit this unyielding metal to purpose. The artistry of carving moulds and the elegance of casting was discarded and in its place the brute pragmatism of the smith became the order of the day. Economy, the preserve of lesser men and not the Kings who had received tribute in the eras prior, now dictated the scale and expertise displayed by the smith who was perceived with grudging respect and not the abject wonder of ages past. Such evocative and dramatic sentiments may seem out of place in the rational and empirical study of archaeometallurgy however an ideological divide in the perception of copper and iron technology remains pervasive throughout the discipline to this day. This can perhaps be seen most clearly in past and present studies into the adoption and transmission of iron technology in western Europe and the Near East where debate continues to revolve around economy, environmental and climatic change and societal collapse at the end of the 2nd millennium BC (Horne 1982; Mirau 1997; Negbi 1998:201; Pigott 1982; Sheratt 2000; Snodgrass 1971:231; Veldhuijzen 2012). Evidence for continuity between copper and iron production and working across the late 2nd and early 1st millennia BC shows that in many regions of the Near East the well established metalworking traditions of the Late Bronze Age were not displaced but had adapted to changing societal perceptions of materiality by employing iron in the manufacture of implements and artefacts. Now that questions relating to the innovation of iron metallurgy in the Near East are beginning to be addressed, archaeometallurgists must now examine its consequences.

The consequences of innovation range from technological to cultural and social changes which are progressively more difficult to determine archaeologically (Erb-Satullo 2020:42). While these changes can be beneficial or disadvantageous for the host culture; in most instances they are transformative (O'Brien and Shennan 2010:228; Schiffer 2005). Such transformations, for example the centralisation of metalworking at Early Iron Age Megiddo in Israel (see p.304), often manifest through their impact upon a society (Erb-Satullo 2020:43). As the primary focus has been to establish the technological elements that permitted the innovation of iron in the Near East, assessing the societal impact that iron metallurgy had in the region falls outside the scope of this thesis. Instead a comparison of the properties of early iron with those of copper alloys will be made to assess the technological impact the new metal may have had.

Bronzes can be referred to as a family of copper alloys, a number of which were exploited for their ductility, malleability and hardness by populations in the millennia following the first deliberate extraction of copper around the late 6th and early 5th millennium BC in the Near East (Roberts et al. 2009:1014). Various forms of copper would have been encountered before its deliberate extraction in the form of malachite, used for beads and as native copper, a naturally occurring conglomerate of pure copper from geological deposits which was used for ornamentation (Maddin et al 1980:223). The ductility and hardness of bronze could be controlled through the use of different alloying elements in varying quantities and by work hardening the material (see figure 7.2), which through plastic deformation of the crystalline structure of the metal would increase the hardness and decrease the ductility (Bhadeshia and Honeycombe 2017:23-31; Buchwald 2005:74-75; McKerrell and Tyelcote 1972:210). Work hardening could be relieved through annealing the metal or achieving an even temperature just below its melting point throughout the metal before allowing it to cool

gradually. In the Early Bronze Age the addition of arsenic to copper may have been incidental from its presence in the same ore body. By the Late Bronze Age copper producers possessed considerable skill in casting and working Bronze, and were certainly aware of the advantages of different alloying agents and the process of annealing (Thornton et al. 2009:308-309). Alloying agents were traded over long distances in the form of speiss (iron arsenides) and tin to make bronzes which can be seen in the rare instances of tin ingots at sites such as a shipwreck off Israel's Carmel coast and speiss residues and fragments in a crucible at the Middle Kingdom site of Buhen in Egypt (Davey et al. 2021; Galili et al. 2013). The addition of lead to increase molten mobility greatly aided casting, while the use of tin or arsenic vastly improved the tensile strength and hardness of copper.

Bronze Alloy (% wt.)	Work-Hardened	Tensile strength (Mpa)	Hardness (VPH)
Arsenical Bronze (1-7% As)	No	386-442	53-125
	Yes	537-792	185-263
Tin Bronze (1-9% Sn)	No	400-448	60-85
	Yes	496-965	170-250
Tin Bronze (10-18% Sn)	No	413-641	70-120
	Yes	620-1054	150-250
Pure Copper	No	137	50
	Yes	164-262	115

Fig.7.2: Table of the tensile strength and hardness of various copper alloys (Buchwald 1990; Lechtman 1996).

The properties of iron are primarily manipulated through its relationship to carbon in the alloy known as steel (see figure 7.3), which contains around 0.2 to 1.8% carbon. Iron with a carbon content of over 2% is known as cast iron. With such high carbon content the crystalline structure of cast iron contains both body and face centred cubic phases which causes it to lose ductility however the lower melting point (1100-1200^{o}C) meant it could be reduced to a molten state and cast in moulds, a practice used in China from the 8th century BC (Angus 2013:4-38; Qiang and Huang 2021). Through heat treatment, the iron-carbon structure could be manipulated to produce different properties in a high carbon or eutectoid steel (0.8% wt. carbon). Rapid cooling of steel at a red heat, known as quenching, produced a remarkably hard but brittle material. Annealing, or the gradual cooling of steel from a red heat, resulted in ductile yet soft steel (Buchwald 2005:65). The first exploitation of the eutectoid phases of steels is a matter of intense scrutiny, the early claims of quench hardening of iron knives from Cyprus dating to the 11th century BC appear to be anomalous and the practice was not widespread until the advent of consistent carbon steels in the second half of the 1st Millennium BC (Buchwald 2005:72; Maddin 2011; Tholander 1971:15-22).

Iron /carbon Alloy	Tensile strength (Mpa)	Hardness (VPH)
Ferrite (pure iron 0% carbon)	82	80-120
Pearlite (0.8% carbon)	434-690	250-300
Martensite (0.5-1.8% carbon, quenched)		200-800
Bainite (0.5% carbon, slack quenched)		200-400

Fig.7.3: Table of the tensile strength and hardness of iron in its hypoeutectic (Ferrite), eutectic (Pearlite) and hypereutectic (Martensite and Bainite) phases with carbon (Bhadeshia and Honeycombe 2017; Buchwald 2005:75).

The displacement of bronze by iron around 1100-800BC has been widely accredited to the superior properties of iron especially when alloyed with carbon to make steel; the principal alloy of iron that would result from the reduction of the iron ore using a high carbon fuel such as charcoal (Craddock 1995:210; Waldbaum 1999:27-28). The most significant advantage of steel over bronze is its greater hardness. The two hardest bronze alloys produced during the Bronze Age; arsenical bronze and tin bronze; could be cold forged to a hardness of 177 VPH and 230 VPH respectively (Buchwald 2005:44-47). By comparison, early Egyptian and Assyrian low-carbon (0.2-0.6% content) steels dating to 800-580BC varied between 116-187 VPH with later high carbon non-tempered steels reaching between 200-400 VPH (Bhadeshia and Honeycombe 2017:23-31; Buchwald 2005:74-75). Early wrought iron and steel was not vastly superior in terms of hardness than the tin bronzes of the LBA though it had the potential through the controversial theory of carburization, fuel intensive if deliberate or anomalous if incidental, to achieve up to two times the hardness. Caburization, or 'case-hardening' of iron through heating with carbon over a long duration is hotly disputed as uptake of the carbon by the iron occurs only very gradually at the surface before ceasing without becoming more widely dispersed. More likely, the bloom that formed during smelting would variably become enriched with carbon, demonstrated by Crew with the production of carbon-heterogenous bloom iron (Crew 1991). Tempering of a homogenous carbon steel could also improve the hardness up to a value between 500-1000VPH; evidence for the heat treatment of steels during the Early Iron Age is limited and debatable given the very limited instances where a homogenous steel was produced that could benefit from the process, the earliest examples coming from Cyprus and Israel circa 1100-900BC (Maddin et al 1985:43-46; Waldbaum 1999:34-35). Conversely, the disadvantages of iron in comparison to copper alloys are numerous. In the manufacture of tools and objects that would undergo stress, work hardened iron could achieve a tensile strength of 689Mpa while cold forged bronze could reach in excess of 827Mpa, making bronze considerably more durable and without the potential for stress fracture induced by slag stringers trapped in the wrought iron (Maddin et al

1977:124). The primary disadvantage that metallurgists would have initially encountered is the difficulty of extracting iron from the slag with its melting point of 1538^{o}C being beyond the capabilities of the Bronze Age furnace to achieve which meant that iron could not be separated by density into a distinct phase below the slag (Haynes 2011:4.121-4.123; Craddock 1995:140). Early wrought irons were of wildly varying quality depending on the degree to which adhering slag could be expelled or manipulated into 'stringers' by the smith, thus ameliorating their deleterious qualities for the material (Pleiner 2003). The expulsion of slag required heating the entire mass of the bloom to welding temperature which was unlikely to be achieved in a smithing hearth after primary production, resulting in significantly more labour for the smelter (Crew 2013:36). By comparison copper alloys could be rendered totally molten at temperatures as low as 800^{o}C and separated from the gangue resulting in a pure material which could be collected after cooling, transported and recast immediately (Hauptmann 2020:383). The lower melting points of copper alloys also permitted the recycling of objects through a simple operation whereby an object or fragments were melted in a crucible and recast. Wrought iron was impossible to cast at these temperatures and only after the introduction of up to 2% or more carbon could iron be cast with a melting point between 1150-1200^{o}C (Craddock 1995:329). Copper alloys would clearly have competed favourably with iron in the creation of utilitarian objects; their greater ductility, ease of repair, attractive quality and considerable hardness when cold worked along with the ability to recycle and cast them into a vast range of pre-designed shapes would have been as invaluable an asset during the Early Iron Age as it was during the Bronze Age. The adoption of iron likely preceded its technological impact which came later with the technological breakthroughs in the use of steels.

Chapter 8. Conclusions.

8.1: *Closing remarks*

By the 2nd millennium BC, developments within extractive metallurgical practises in the Near East gave rise to the unanticipated reduction and production of metallic iron alongside copper. Exploitation of iron-rich mixed ores and newly emergent production strategies that increased reaction volumes, generated more intensely reducing environments and achieved temperatures that could render the copper and gangue material molten all contributed towards this unprecedented phenomenon. The extent to which this occurred across the Near East was dependent upon intraregional differences in local geology and production strategies. To the north in Anatolia, the south Caucasus and on Cyprus mixed copper-iron sulphidic ores from volcanogenic mass sulphide deposits were intensively exploited to produce a copper and iron sulphide-rich intermediate product termed matte. In the south, mixed copper and iron oxide deposits from dolostone deposits were exploited from Egypt across to the Levant and Jordan to produce copper through direct reduction of oxides. Iron-rich charges were favoured in the smelting practises of both traditions to promote the viscosity of the matte or slag which improved upon the yields of copper and the ease of retrieval. This encouraged the frequent reduction and entrainment of metallic iron in the copper metal; though to a lesser degree in mixed sulphide smelting which necessitated greater oxidation to remove the sulphur. Extraction of iron during these processes may have become so prolific that it could already be considered the second major metal produced after copper centuries before its adoption, constituting a total weight in the tonnes. Re-melting of these copper-iron alloys for casting into ingots resulted in rapid oxidation of the iron into oxides which could be removed from the molten copper, leaving only the iron that was soluble in copper at room temperature as it could not be removed without arduous refinement. This had significant implications for technological change in the region towards the latter half of the 2nd

millennium BC. The most tangible of these consequences was the production of copper-base artefacts with gradually increasing iron contents towards the end of the period. The anomalous production of metallic iron in the furnace may have been the catalyst for early experimentation and ultimately the innovations that permitted the exclusive production of iron. The capability of metal producers across the Near East to produce iron may well have preceded its eventual spread and adoption with the emergence of iron-working traditions and socio-cultural re-organisation during the Late 2nd to Early 1st millennium BC creating a demand for the new metal that had not been present earlier. Following the adoption of iron, its technological impact was limited prior to the development of comprehensive iron-working skills and an understanding of its eutectic properties in steels. Iron, that had once been the providence of the heavens, was now squarely in the grasp of man to whose history it would become indelibly forged.

8.2: *Experimental perspectives*

One of the most valuable exercises that is promoted through experimental approaches is that of reflection. Not only is this required to assess the validity of the hypothesis in light of the results; it provides an opportunity to explore what we thought we knew, what we have come to know and how we might come to learn more about it. In chapters two and three a theoretical framework was applied to the question of co-extraction of iron during copper smelting that proved to be largely accurate but could not predict the extent of the phenomenon. Appraisal of the archaeological record could not corroborate theory due to the potentially anomalous nature of the evidence and lack of a basis for comparison. This was the gap to be bridged via experimental reconstruction. Estimating the success of the experimental methodology must be relative; as a series of inductive experiments the objective was to reproduce smelting events and assemblages for observation and analysis to inform a new

hypothesis. As an example, the iron smelting experiment (FE-1) was a dismal failure in relation to the successful bloomery smelting campaigns of Crew (2013). Yet in relation to Late Bronze Age copper smelting, the results provided a tantalizing insight into sub-optimal conditions in the smelting of iron and an expectation of outcomes for copper-iron co-smelting. Rather than dwell on the methodology it might be more productive to ask what the variable acting as the control was supposed to achieve in terms of knowledge and whether it did so (Schenck 2011:89). As the primary variable controlled across the experiments, varying iron contents by proportion of the charge was done to address the extent to which iron could be reduced in prehistoric copper smelting operations. In producing an array of remarkably complete smelting assemblages control of the variable can certainly be considered a success. Analysis of these assemblages revealed correlations between both ancient and modern processes and also between the more tightly controlled laboratory experiments and the actualistic furnace smelting highlighting the utility of both methods. By providing a robust dataset, the experiments can provide an invaluable source of comparison for assessing the impact of technological developments during the 2nd millennium BC in the Near East. So how might we come to learn more? Three obvious areas requiring future research are matte conversion or coppermaking experiments at furnace scales, copper-iron alloy refinement and experimental or simulated smelting in furnaces of different dimensions. Matte conversion experiments would allow for comparison of the iron contents of furnace copper with those of copper-base artefacts of sulphidic provenance. Copper-iron alloy refinement to demonstrate whether iron could be extricated from copper from co-smelting assemblages may reveal a link between early smelted iron and copper smelting practises during the early to middle 2nd Millennium BC prior to convincing evidence for iron smelting. Simulated smelting in furnaces of different dimensions could establish just how significant a factor the enlargement of furnaces was in the production of iron. This work could contribute much towards the ‘virtuous circle’ started here.

8.3: *Getting lost in the details: challenging micro-analytical approaches with macro methodology.*

The use of materials science has seen wholesale adoption within the wider discipline of archaeological science. A host of techniques, some adopted and many others specifically developed, have seen application to almost every facet of the archaeological record. Optical microscopy, chemical analysis and SEM imaging have all seen frequent employment in tackling a range of archaeological topics. Archaeometallurgy has perhaps been one of the greatest beneficiaries of materials science where non-destructive methods for reviewing microstructures such as crystalline phases or the identification of minerals for slag chemistry have been instrumental in propelling the subject beyond the scientific vagaries of analogy and field observation that it relied upon in the early 20th century. As with all good things people rarely give way to introspection to question what the consequences of a new development might be, a pattern that so far describes the progress of materials analysis in archaeological studies. The role that materials science has played since the mid-20th century in the study of prehistoric metallurgy cannot be understated and it has been used in conjunction with theoretical models such as the Ellingham and phase diagrams in countless studies to reconstruct pyrometallurgical processes and formation events based on analysis of archaeological assemblages. Widespread usage should not be conflated with success however and the pessimist might point out that very few of the pressing archaeological questions raised early in the last century have been resolved with the onset of methodologies borrowed from materials science. In archaeometallurgy perhaps the major flaw of the materials science approach has been the emphasis on micro-analysis which pertains to those analytical techniques that allow for the chemical identification and quantitative analysis of small amounts of substances that fall outside of visual acuity due to sampling size, magnification and resolution. Examples include reflected light microscopy, SEM imaging and bulk quantitive analysis methods and relates not only to the analytical methods employed to produce sets of data in the study of archaeological assemblages but also to the

modes of presentation chosen to display this data and to offer interpretations on in the format of scientific articles and publications. Both as a means of analysis and for the presentation of data these techniques may be inappropriate and could cause either the analyst or the readers at large to form mistaken assumptions or views based on insubstantial or misleading evidence. This issue mostly derives from the sampling of only a small fraction of the complete assemblage which can exaggerate the significance of otherwise anomalous or inconsequential features that may be presented in isolation of the wider contexts of the material. In answer to this the methodology presented in this thesis has employed low magnification macrographs and the photography of large sections through metallurgical assemblages in order to produce a complete and representative dataset with attention paid to the spatial relationship of different phases and macrostructures and its relevance to ancient peoples. This is especially useful in the study of experimental archaeology where the experience of an assemblage that falls within the range of human perception is important for gaining new insights into the technological process. In conjunction with the microscopic metallographic analysis, this provides a comparative dataset that rules out anomalous findings in favour of features that are consistent across the entire assemblage. This may go some way to avoiding mistaken assumptions based on non-representative datasets while trusting reasonably in the accuracy of the data acquired by such methods.

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