THE STRUCTURE AND CONSTITUTION OF

ARCHAEOLOGICAL FERROUS PROCESS SLAGS

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SUMMARY

Slag, unlike metallic iron and ore, is generally abundant on
early ironworking sites, but paradoxically has received scant attention.
This study attempts to correct the imbalance by determining the quantity
and quality of information obtainable from archaeological slags
concerning ore sources and smelting techniques.

Detailed investigations have been made of slags from various
localities, dating from early Iron Age to early medieval. Archaeological
and geological details of the investigated sites put the results in
context. The variety of furnace types is noteworthy and a high level of
technology before the Roman conquest is indicated. Slag was probably
raked from some furnaces. Early iron production was not confined to
areas with major ores and minor ironstones were exploited for a variety
of reasons.

Research into the reduction of iron ores is considered in the
light of its relevance to slag formation.

Slag petrography, investigated by X-ray diffractometry, optical
and scanning electron microscopy and electron probe micro-analysis,
and slag chemistry, determined mainly by X-ray fluorescence spectrometry,
are discussed with reference to phase diagrams. The mineralogical
compositions and textures of the slags show no consistent patterns
which can at present be related to ore source, furnace type, production
technique, or date.

Arguments against the use of trace elements and in support of the
choice of certain minor oxides (i.e. MnO, MgO, TiO_2, V_2O_5 and Al_2O_3)
for the provenancing of ferrous materials are given. Simple two
component plots using these oxides show some differentiation of
geographically separated samples, but the best results are obtained by
considering all five together. The use of ratios allows direct
comparison of ore and slag and multivariate statistical analysis permits
all ten ratios of the five oxides to be considered simultaneously. Of
the three techniques applied to the data, discriminant analysis has
proved most valuable for determining ore source.

Key words: Archaeometallurgy, iron-slags, petrology, ore provenancing

Acknowledgements

Syndre hyght Scoria and is the fylth of yren that is clensyd therefro in fyre. Anon., 1398.

CHAPTER 1

INTRODUCTION AND THE STATE OF THE ART

1.1 Opening remarks

In the past archaeologists have tended to dismiss slag as 'industrial waste' and have paid little more attention to the furnace remains, but increasing   interest in industrial archaeology in recent years now means that ancient technology is considered almost as important as the art and architecture. Early interest in ancient ironworking techniques appears to have been minimal, although Graf Wurmbrandt must have been an exception, as it is reported that towards the end of the nineteenth century he succeeded in producing smithable iron in a reconstruction of Roman period furnaces found at Hüttenberg, Austria.[1]   In 1958, Gilles experimented with a shaft furnace based on La Tene age remains in Siegerland,[2]   while in England, Wynne and Tylecote used a bowl furnace reconstruction.[3] Since then, similar experiments have been carried out all over Europe.

In addition to the production of iron, archaeometallurgical research in the field of ferrous metals has tended to concentrate on the metallography of artifacts, with a view to investigating the method of manufacture. Some work has also been done on the problem of provenancing iron objects. Little serious study of slags has been undertaken however, despite the fact that on most ironworking sites furnaces are poorly preserved and samples of ore and the iron produced are rare, whilst accumulations of slag may be very large. Morton and Wingrove showed that slags were potentially very informative,[4,5] and

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Sperl, having suggested a system for classifying slags, attempted to relate slag typology to process.[6]

Apart from the publications of Morton and Wingrove and Sperl, there is little in the literature on the subject of archaeological ferrous process slags and it became clear that here was scope for a detailed study. The generally well-documented material in the national collection of archaeological slags, housed at the Ironbridge Gorge Museum, formed the basis of the present investigation, with further material being obtained from current excavations as well as experimental smelts in furnace reconstructions.

1.2 Methods

The gross mineralogies of the slags were determined by X-ray diffraction, while the detailed mineralogical compositions and textures were investigated by the microscopic examination of thin and polished sections. The scanning electron microscope was used to elucidate the fine-scale textural details and proved useful for the semi-quantitative analysis of individual phases. Accurate analyses of the minerals were carried out using the electron probe micro-analyser. The chemical compositions (major and minor elements) of the samples were determined using X-ray fluorescence and atomic absorption spectrophotometry, the proportions of ferric iron being found by a standard wet chemical method.

The geological background of this author suggested that the type of approach used in igneous petrography could equally well be applied to slags. The relationship between the chemical composition and mineralogy of the slags was therefore studied using the appropriate phase diagrams, and the actual crystallization sequences, as determined

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from thin and polished sections, were compared with the crystallization paths predicted from phase diagrams.

The relationship between the chemistry of ores and slags is also of interest, in particular because of the possibility of determining ore source from the slag composition. For this reason this study concentrates mainly on sites where ore samples were excavated or where the ore source can be predicted with a reasonable degree of confidence. In Northamptonshire, a more detailed examination of the possible ore sources was undertaken, the various ironstones being sampled to investigate their nature and variability. The ironstones' chemistry and mineralogy were determined using X-ray fluorescence analysis, atomic absorption spectrophotometry and X-ray diffraction, supplemented in some cases by microscopic examination of thin sections and qualitative analysis using the scanning electron microscope. The compositions of ores and slags have been compared both qualitatively and quantitatively.

1.3 Outline of thesis

The archaeological and geological settings of the investigated samples are described in detail in Chapter 2 so that the results of this study can be evaluated in the light of known facts about furnace types, sophistication of associated settlements, availability of ore, etc. In Chapter 3, the literature on the reduction of iron ore, with particular reference to work on bloomery furnaces, is appraised and interpreted with regard to the formation of slag. Chapter 4 sets out the results of the mineralogical investigation of the slags. The provenancing of ores on the basis of slag composition is dealt with in Chapter 5. Various techniques for multivariate statistical analysis

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are described and the results of their application to the data evaluated. This is followed by a discussion on the factors affecting such provenance studies. The conclusions are given in Chapter 6 and finally, possible directions for further work suggested in Chapter 7.

Appendix A lists the code numbers of the slags used in this work and those used by the Ancient Monuments Laboratory and the excavators, naming the site and giving the furnace type where known. The electron-probe micro-analyses of individual phases within the slags are contained in Appendix B and chemical analyses of the investigated material are to be found in Appendix C.

1.4 The state of the art

A brief review of the present state of research into bloomery slags and the bloomery process in general is necessary in order to set this thesis in its proper perspective, but fuller discussions of many of the topics covered are more relevantly addressed in the appropriate chapters.

Experimental smelts in furnace reconstructions, such as those of Gilles,[2] Wynne and Tylecote,[3] Tylecote et al.,[7] Cleere,[8] Straube[1] and Pleiner,[9] have provided details of the factors affecting the bloomery process and give some information on the course of the smelt, and it is clearly useful to have some idea of the conditions under which slag is likely to have formed when attempting to interpret its composition and mineralogy. The systematic investigations of Wynne and Tylecote using a bowl furnace and of Tylecote et al. using a slag-tapping shaft furnace are of particular value because they established the optimum operating conditions in each case. Their experiments show how sensitive the process is to

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variations in temperature, blowing rate, ore and charcoal size, etc. That the early ironworkers knew how to control these factors is a measure of their skill. In contrast, the generally low yields of these and other experimental furnaces suggests a certain lack of expertise on the part of their modern-day operators and this should be borne in mind when comparing the products of these experiments with excavated material. It is understandable, but unfortunate as far as the present work is concerned, that detailed examination of the products has tended to concentrate on the metallic portion whilst the slags have been less thoroughly investigated. Analysis of the chemistry and mineralogy of slags formed under well-defined conditions would have been invaluable for direct comparisons with archaeological samples. Some of the conclusions reached by the operators of experimental bloomery furnaces are of use when interpreting excavated remains. For instance, it has been found that a single tuyere and efficient top insulation give the best results in a 9 inch diameter bowl-furnace,[3] that the Ashwicken-type shaft furnaces were probably not designed to operate using induced draught[7] and that a consumable stopper of turf or peat for the tapping arch of a shaft furnace enables slag to be removed continuously and without loss of heat, thus improving the furnace's efficiency.[8]

Further details about the operation of bloomery furnaces can be obtained from observations of recent or present-day 'primitive' practice. Some of the reports, by people with no metallurgical background or at least no experience of the bloomery process (e.g. the publication by Bellamy[10] and some of the information quoted by Percy[11]), should be interpreted with caution, as should those based on past practice specially revived for the sake of the observers

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(e.g. the work of Pole[12] and of Avery and Schmidt[13]). Many ethnographic accounts either contain scant information about the smelting products or omit such details entirely. In contrast, the more comprehensive work of Todd[14] (see also Todd and Charles[15]), based on the current practice of the ironworkers of the Dimi tribe in southwest Ethiopia, provides a large amount of metallurgical detail. However, only three samples of furnace slag were chemically analysed by Todd, one also being examined mineralogically (this was the only sample later thought to represent true furnace slag). Six chemical analyses of ore were made, but no clear information was given about their mineralogical composition, nor was the field relationship between the limonite and magnetite ores elucidated and it was not ascertained which ores were used to produce either the investigated slags or the iron objects. In view of Todd's interest in the possibility of provenancing iron objects on the basis of their slag inclusion compositions, the number of analyses made seems rather small and the lack of precision over the ores is regrettable. A further criticism of this and similar ethnographic studies is that the observations of the process were made from the point of view of a modern metallurgist; little attempt seems to have been made to establish how the ore was found, what criteria were used in the selection of pieces to be smelted or why certain procedures were followed. Such information could have provided an insight into the prospecting methods of the early ironworkers and might have provided clues as to the reasoning behind some of the inferred technological changes.

Percy, in the mid nineteenth century, also reported on contemporary bloomeries in India, Borneo and Africa, but his main contribution to the knowledge of the bloomery process was his own observations of the

Catalan Furnace and his detailed discussion of Richard's and Francois's work on the subject.[11] This is dealt with more fully in Chapter 3.

Reports of excavations at archaeological ironworking sites are adding to the body of knowledge about the variety of furnace types used and slowly a picture is being built up of the possible procedures used (e.g. work of Cleere[16]). As roasting hearths, smithing hearths, anvils, etc. are being recognized,[17,18,19,20] the general level of technology at different periods and in different areas is beginning to be understood. In addition, as more sites are investigated, some understanding is gained of the evolution of furnace designs and the relationship between the different types. The archaeological literature has therefore enabled the samples studied and the sites from which they were obtained to be seen in a wider context. The reports dealing specifically with the investigated sites are dealt with in Chapter 2.

Only a small amount of research has concentrated on archaeological slags. The innovative work of Morton and Wingrove,[4,5] which involved detailed chemical and mineralogical analysis, showed that slags were potentially very informative and the approach of these authors has been used in much subsequent research.[6,7,14,15] Unfortunately, Morton and Wingrove's confusion over the actual rather than theoretical appearance of anorthite and the order of crystallization of the minerals has also persisted in the literature and some of their inferences, based on limited data, have been shown by the present study to be inapplicable to other sites and different ore types (see Chapter 4). Morton and Wingrove's work is nevertheless an important milestone in archaeometallurgical research. Sperl[6] proposed a classification scheme for slags based on their morphology, which

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appeared to be largely determined by the furnace type and process, but his attempt to relate the chemical and mineralogical compositions to the defined slag types was unsuccessful. However, although a large number of slags from iron smelting, smithing and refining and from copper smelting were superficially examined, only twenty were chosen for detailed chemical and mineralogical analysis. For slags from so many different processes and dates ranging from several centuries BC to c. 1500 AD, twenty samples seems an extremely small number to base any conclusions on. This interesting line of research was followed up in the present study (Chapter 4). Bachmann has also attempted to provide a system for identifying archaeological slags, but this is somewhat generalized as it covers both copper and iron working.[21] The author's expertise is evidently in the field of non-ferrous metallurgy and some of the information on iron slags is not of such a high standard as that on the copper slags. His discussion of the typology of iron slags is for instance based uncritically on that of Sperl.[6] In addition leucite, commonly found in iron smelting slags, has been omitted from the list of phases occurring in slags, whilst the descriptions of the photomicrographs of iron slags in his 'catalogue' of different slag types are confusing. Similarly, Bachmann's proposed computer program for assignment of ternary phase diagrams to analytical data of silicate slags does not include the system $Al_2O_3-SiO_2-FeO$, the one system found to be most generally applicable to the iron smelting slags of this study. The usefulness of the program is therefore limited to slags with a generally higher CaO content than the ones investigated here. The rigorous approach of this author does however set a standard which all archaeometallurgists ought to aim for and which has hopefully been achieved in the present work.

As part of her research, Todd reduced samples of iron ore using hydrogen at temperatures between $1100^{\circ}C$ and $1300^{\circ}C$.[14] The resultant slags, even the ones produced from ores typical of those exploited by the early ironworkers, have mineralogies dissimilar to excavated bloomery slag, whilst the detailed analyses of the slag inclusions in the iron also appear to show phases not normally encountered in archaeological material. It is possible that the strongly reducing atmosphere had some influence on the phases which appeared. Unfortunately, the lack of overall chemical analyses of the slags and the absence of details on the relative proportions of the phases mean that the work is only of limited value for comparison with archaeological material.

A few attempts have been made to provenance ironwork. Haldane[22] made trace element analyses of samples of pre-Roman ironwork, together with their contained slag inclusions, from sites in Somerset. A statistical grouping technique was applied to the data and four groups were found which were considered to be significant with regard to provenance, but no attempt was made to relate these groups to any of the likely ore sources because sufficiently detailed ore analyses were lacking. In a similar study, Hedges and Salter[23] determined the compositions of slag inclusions in Iron Age 'currency' bars from three locations and statistical analysis of the data established that the three groups were chemically distinct, but again the absence of suitable ore analyses for comparison prevented the authors from determining ore sources. The work of Haldane and Hedges and Salter shows that it should be possible to provenance ironwork on the basis of its chemistry, in particular the trace element content. However, it would only be possible to use such an

approach if the trace element composition of the likely ores had been throughly investigated.

Todd had a number of reservations about the utility of trace elements for provenancing ironwork and her research, which involved the analysis of ore, slag and slag inclusions in iron, led her to conclude that the study of major and minor element compositions of slag inclusions should enable iron objects to be provenanced. She doubted whether a complete correlation was possible between the compositions of roasted ore, slag and slag inclusions, but she only used a visual comparison of the compositions and it is possible that a statistical treatment would have given clearer results. The work of these authors is relevant to the provenancing of ores on the basis of slag composition and is more fully discussed in Chapter 5.

In conclusion, it can be said that there is a dearth of information on archaeological bloomery slags and it is hoped that this thesis goes some way towards filling the gap.

CHAPTER 2

SITES INVESTIGATED : GEOLOGY AND ARCHAEOLOGY

2.1 Introduction

A study of slag mineralogy is clearly of greater value if it is
known what type of furnace the slag was produced in and at what period.
The scale of the ironworking operations and the type and sophistication
of associated settlements may also provide clues about the probable
level of technological expertise relative to other contemporary sites.
Lack of geological knowledge on the part of archaeologists as well as
geologists' lack of experience in archaeological matters has caused
some confusion in the past about possible sources of iron ore. This
chapter therefore describes in detail the archaeological and geological
contexts of the material investigated so that the results of this study
can be properly evaluated.

For the two main areas studied (Northamptonshire and the Weald),
a brief outline of the geology is given and probable ore sources
discussed in general terms. For each site, the archaeological setting
is then sketched and the provenance of samples detailed. Brief
descriptions of slag and ore (where found) are followed by an evaluation
of local ironstones. A similar pattern is followed for sites outside
these areas. The slag mineralogy is dealt with in more detail in
Chapter 4, whilst the provenancing of iron ores on the basis of slag
composition is given a more quantitative treatment in Chapter 5.

2.2 The Northamptonshire Area

2.2.1 Geological setting

The Jurassic rocks in this part of eastern England have a NE-SW outcrop pattern and young southeastwards, dipping at around $\frac{1}{2}^{\circ}$. The dominant feature is the Lincolnshire Limestone escarpment, the basal Rutland Formation being widely preserved on the dip slope. The thin but rich Ironstone Junction-Band, extensively exploited by early iron workers, is developed at the contact between the Lincolnshire Limestone and the Rutland Formation. To the west of the Lincolnshire Limestone escarpment outcrops the stratigraphically lower Grantham Formation and Northampton Sand Formation, the latter including the Northampton Sand Ironstone (Figure 2.1), which has been commercially important in the very recent past. Both the Grantham Formation and Rutland Formation, particularly in its lower part (Stamford Member), contain leached sands, silts and muds whose refractory properties were recognized by the early smelters and which are still being worked today. A simplified stratigraphic column with brief descriptions of the main lithologies is given in Figure 2.2 and a map of the area showing the outcrops of the Northampton Sand Ironstone and the Ironstone Junction-Band is shown in Figure 2.3.

Mineralogically, the Northampton Sand Ironstone consists principally of chamosite (an iron alumino-silicate, $(Fe_4^{II}Al_2)(Si_2Al_2)O_{10}(OH)_8$) and siderite ($FeCO_3$). The dominant lithology is a sideritic chamosite oolite (nomenclature of Taylor[24]), i.e. ooliths of chamosite set in a siderite spar groundmass. However, the groundmass may also be entirely or partly of chamosite mud or calcite spar and less commonly, the ooliths may be of limonite or kaolinite. Ooliths may

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in places be absent, giving rise to siderite, calcite or chamosite mudstones. Quartz sand is particularly abundant around the margins of the field, sometimes in sufficient quantity for the rock to be classified as a sideritic sandstone, etc. A stratigraphic succession of - five lithological groups has been recognized,[24] each group being defined by its dominant rock types (Table 2.1). In general, workable ironstone is confined to the Main Oolitic Ironstone Group and the Upper Siderite Mudstone-Limestone Group.[25]

At outcrop, the ironstone is characteristically weathered in the form of boxstones, that is it has a cellular appearance with dense box 'walls', usually of goethite, surrounding softer, less iron-rich cores. Intense weathering results in the breakdown of the original iron minerals to a mixture of limonite and kaolinite. Limonite is a mixture of hydrated ferric oxides, whose main constituent appears to be goethite ($\propto Fe_2O_3.H_2O$), although the material is generally poorly crystalline. Migration and concentration of the ferric oxides then leads to the development of boxstones. Even at depth, the ironstone may be weathered, the degree of weathering depending largely on the thickness and permeability of the solid cover, although the presence of joints is also important. Some lithologies are more susceptible to oxidation than others and this is well illustrated by material collected at Brookfield Cottage Pit. Here the overlying strata total 18 m and there is in addition a variable thickness of Boulder Clay, yet some of the beds show a boxstone weathering pattern while others are unweathered. Petrographically, the samples range from fresh sideritic or sideritic chamositic chamosite oolite to limonitic sideritic chamosite kaolinite oolite. Detrital quartz and feldspar are low (1-2%) while bioclastic

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debris is variable, ranging from 1% to as much as 10%, and a variety of intraclasts occur in some samples. A small proportion of euhedral magnetite ($\sim$2%) was identified in one of the most highly weathered samples.

The chemical composition of the Northampton Sand Ironstone is variable, depending on lithology, but in general it is lean, the iron content of workable stone ranging from 28-35 wt %.[25] However, comparison of the analyses of boxwalls with those of relatively unweathered cores of some Brookfield Cottage samples (Appendix C) illustrates that weathering results in loss of lime and magnesia and relative enrichment of iron. The ore obtained at outcrop by the early ironworkers is therefore likely to have been much richer than that recently quarried from beneath a thick overburden. The iron content of Northampton Sand Ironstone fragments from the Stamford excavations (48 and 49 wt % Fe in roasted and raw bulk samples respectively) supports this. Weathered ironstone also has the advantage that any sulphur originally present as pyrite (FeS_2) has been removed by oxidation. Few full analyses of Northampton Sand Ironstone are available, but it appears that the relatively high contents of P_2O_5 (average 1.6 wt %[25]) and V_2O_5 (generally > 0.1 wt %) are characteristic.

The Ironstone Junction-Band (Figure 2.4) is a thin seam (approximately 20 cm thick, but may be as much as 80 cm) of nodules and occasionally tabular masses composed mainly of hydrated ferric oxides. This ironstone was believed by Judd[26] to be present at the base of the Rutland Formation (his Upper Estuarine Series) even where it oversteps the Lincolnshire Limestone's margin, south of a line through Draughton, Kettering and Oundle. Hollingworth and Taylor[25] were also of this opinion, although Taylor in a later work[27] states

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that the ironstone is "rarely present and never as well developed" to the south of the limestone's margin. Bradshaw[28] has reported that in deep boreholes (> 40 m) iron is present mainly in the form of finely divided pyrite plus occasional siderite nodules, the former being particularly abundant at the base of the Rutland Formation. This suggests that the ferric hydroxides of the Ironstone Junction-Band are the result of Pleistocene or Recent weathering and the ironstone is therefore only likely to have developed where the Rutland Formation overlies the relatively permeable Lincolnshire Limestone. Oxygenated waters circulating through the joint system of the limestone would have oxidised the pyrite, the overall reaction being:

$$4FeS_2 + 15O_2 + 10H_2O \rightarrow 2Fe_2O_3.H_2O + 8SO_4^{2-} + 16H^+$$
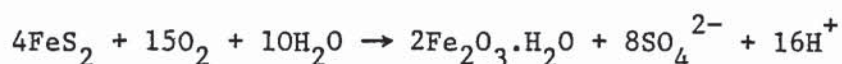
Reaction of SO_4^{2-} with dissolved Ca^{2+} results in the formation of gypsum ($CaSO_4.2H_2O$), which is commonly associated with the Ironstone Junction-Band, occurring as euhedral crystals (selenite) or as veins cutting through the nodules. Concentrations of pyrite, often around organic debris, would have become centres of oxidation and the resultant compositional gradients would have been conducive to the formation of discrete nodules.[28]

XRD analyses show the nodules to consist mainly of goethite, although lepidocrocite ($\gamma Fe_2O_3.H_2O$) is a common accompaniment and is sometimes the dominant mineral. About half of the samples contain varying proportions of haematite. No jarosite has been detected, although Bradshaw reported this mineral from his material.[28]

Internally, the nodules may be massive or concentrically-banded with alternating red and orange or red and purple bands. Less commonly, the structure of wood fragments may be preserved. Sometimes the iron

minerals completely replace parts of the underlying Lincolnshire
Limestone, the ooliths and fossil debris still being clearly
recognizable. The replaced oolitic limestone is however quite distinct
from the microscopic spherulitic texture which is displayed by
many of the samples examined. In thin section, the texture is most
clearly seen in the less well-cemented areas (Figure 2.5), i.e. in
those areas where individual spheruliths have not grown together.
The colour banding shows the shape of the growth fronts and indicates
that the texture has not arisen by oxidation of original sphaerosiderite
(small radiating clusters of needle-like siderite crystals). Nucleation
may have occurred on finely-divided organic material or at tiny clusters
of pyrite crystals, of the order of a few microns across.

Chemically, the Ironstone Junction-Band is rather variable
(Appendix C), as might be expected from late diagenetic nodules which
have grown in differing lithologies. Silica and lime contents are
particularly variable, the former depending greatly on the proportion
of quartz silt or sand in the host sediment and the latter depending
on the amount of unaltered limestone still present or on the degree of
veining by gypsum. Very low P_2O_5 contents (usually 0.05 wt % or less)
are nevertheless characteristic.

Ironstone (i.e. fragments of Northampton Sand Ironstone) is
recorded from the Boulder Clay over much of the area, although it
is usually subordinate in quantity to Bunter quartzite, flints, etc.[27]
Fresh exposures of Boulder Clay have been examined at Wakerley, Brookfield
Cottage and Great Oakley Northampton Sand Ironstone pits and it is
apparent that carbonate nodules (i.e. siderite + calcite), probably
from Upper Jurassic clays, are also abundant and may constitute up to
a half of the large clasts. Intense weathering has resulted in the

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formation of a thick goethite shell which spalls off easily.
Although it is unlikely that ferruginous material from the Boulder
Clay constituted a principal ore source, it is possible that such
ironstone was used to supplement ore from another source. Irregular
pits at the Great Oakley site may have been dug to exploit this
ferruginous material.[29] Chemical analysis of weathered carbonate
nodules (Appendix C) shows that they are rich in CaO and P_2O_5, but
it is probable that the goethite shells contain only a very small
proportion of these oxides.

Both Judd[26] and Hollingworth and Taylor[25] referred to the
frequently large amounts of ancient slag found in Northamptonshire
and Rutland, but these accumulations were unfortunately rarely dateable
and no effort was made to determine whether the ore had been obtained
from the Northampton Sand Ironstone or the Ironstone Junction-Band.
Artis, in his book 'The Durobrivae ...',[30] figured a Roman period
furnace discovered in Bedford Purlieus as well as an example of the
nodular iron ore which was smelted. Ancient pits in the wood go down
to the Ironstone Junction-Band and there is little doubt that this
was the source. Recent excavations have revealed either similar
quarry pits or fragments of Ironstone Junction-Band at other Iron Age
and Roman period ironworking sites in the area (see below). In
contrast, although it has been stated that the Northampton Sand
Ironstone is known to have been worked in Roman times,[25] the only
real evidence is presented by Judd,[26] who in his discussion of this
ironstone referred to mounds of slag and ore (some of it crushed and
roasted) associated with Roman pottery and coins in Oundle Wood.
No recent excavations have proved the early exploitation of the
Northampton Sand Ironstone and the available evidence suggests that the

Ironstone Junction-Band was preferred in the Iron Age and Roman periods. However, the Northampton Sand Ironstone was used in the Saxo-Norman period at Stamford. Furthermore, documentary evidence[25] shows that ironworking was an important industry in Northamptonshire in medieval times and it has been suggested that the district of Rockingham Forest vied with the Weald of Kent and Sussex in iron-producing.[26] It is probable that such a large-scale industry was based on the more extensive Northampton Sand Ironstone rather than the Ironstone Junction-Band, although little is known about the post-Roman history of ironworking in this area.

2.2.2 Wakerley[31]

NGR SP 941983, Figures 2.6 and 2.7

Situated on the south side of the Welland valley, the ironworking remains are associated with an Iron Age settlement, the site of which continued to be used in the Roman period. The earliest boundary, on the southwest side of the site, consisted of a line of post holes paralleled by a discontinuous ditch which contained slag as well as pottery dated as second or early first century B.C. This boundary was succeeded by a sequence of ditched enclosures spanning the period from the first century B.C. to the late third century A.D. A number of hut circles and pits, as well as two furnaces associated with Belgic pottery provide evidence of the Iron Age occupation, while Roman period remains include an aisled barn, three pottery kilns, corn-drying ovens and various hearths.

Two smelting furnaces and four hearths/furnace bases were excavated within the enclosures, but most of the remains lie to the south (Figure 2.7). Three furnace types have been recognized. The

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first type, for which there is no direct dating evidence, was
poorly-preserved and consisted of a relatively large diameter (60-
130 cm) flat-bottomed circular pit, cut 10-20 cm deep into the
limestone bedrock and estimated as being at least 20-30 cm below the
contemporary ground surface. The pits were lined with a thin (2-10 cm)
layer of clay, but in only one example (F770) was there any evidence
of superstructure, tentatively identified as 'part dome-shaped'.[31]
There was no evidence of slag tapping, but extensions to the furnace
pits were probably used for raking out the slag. The second type,
for which there is some evidence of a Belgic date, consisted of a
clay shaft 30-40 cm in diameter, constructed in a pit up to 100 cm
in diameter and 40-75 cm deep. In three examples, an arch ~ 35 cm
high had been preserved intact and in view of the restricted space
in the pits it is probable that the slag was raked out through the
arch rather than tapped. Some of the pits themselves had semicircular
or horseshoe-shaped fired clay linings which cannot be directly
related to the much smaller diameter clay shafts within them. These
may represent a modification of the Type 1 furnace, possibly
transitional between Types 1 and 2. The third furnace type, one
example of which was firmly dated as Roman period, was a shaft-furnace
constructed on the surface and provided with a large slag-tapping
channel. The shafts were of a similar size to those of the Type 2
furnaces. Both varieties of shaft furnace were relined, but there is
no evidence for this in the Type 1 furnace.

Samples of slag were obtained from the earliest boundary ditch
and from furnaces 2 and 4 on site 4 (Type 2 and Type 1 furnaces
respectively; neither were directly datable). A further slag sample
and two samples of ore were obtained from the fill of the ditch around
the first enclosure (pre-Roman). The slags are greyish olive to dark

grey in colour, with a crystalline fracture; moderately dense to dense, they contain some small vesicles. All show some signs of viscous flow. Under the microscope the samples display a variety of textures. Fayalite (50-60%) may be in the form of long laths arranged sub-parallel or in radiating bundles, or it may be massive. Wüstite dendrites (15-40%) may be long and fine or short and thick. Only a small amount of glass is present (~ 2%), but hercynite and leucite may constitute much larger proportions. A few grains of metallic iron are generally present. Surprisingly, all but one of the samples showed one or more chilled surfaces on the polished sections. This evidence for rapid cooling (see Chapter 4) supports the inference that the slag was raked out of the furnaces. No tap slag from the excavated area was available, but whilst investigating the line of the Ironstone Junction-Band outcrop along the edge of Wakerley Great Wood (east of the site, around SP 956987), large quantities of tap slag were found in the fields. Although somewhat scattered by ploughing, the main concentration was at the top end of the fields near the wood and the slag most probably derives from one or more furnaces positioned close to the Ironstone Junction-Band outcrop. There is no dating evidence, but the presence of Roman period slag-tapping furnaces at the nearby Wakerley site gives reason to believe that this slag is also of the same date. Other concentrations of slag have been reported in the fields to the south of the site.[32] Mineralogically, the slag is closely similar to the slags from the non-tapping furnaces, with ~ 60% fayalite and 35% wüstite, the remainder consisting of leucite, hercynite and glass. A few metallic iron grains are also present. A number of chilled surfaces are visible on the polished section.

One of the ore samples examined was half of an unroasted nodule

showing concentric red and purple colour banding and its appearance
suggests an Ironstone Junction-Band origin. The other sample, two
fragments consisting of a porous mixture of haematite and magnetite,
could have been obtained by roasting the former. Situated on a
broad band of Lincolnshire Limestone, the settlement was positioned
between outcrops of the two main ironstones of this region (Figure
2.6). Capping the hill is a patch of Boulder Clay, also containing
some ferruginous material which could have been exploited. Samples
of the Ironstone Junction-Band, which here is typically in the form
of reddish-purple or orangey-red nodules, often concentrically colour-
banded, were collected from the field brash along the edge of
Wakerley Great Wood. Four samples were separately analysed. The
Northampton Sand Ironstone was quarried until 1978 and the Wakerley
site itself was destroyed by the operations. Samples of this ironstone
were obtained from the north-west corner of the quarry (at SP 941984),
close to the former position of the site. The ironstone showed some
boxstone development and the boxwalls only were collected as it was
considered that these would be more representative of the highly
weathered material which would have been found at outcrop. A gull
in the Lincolnshire Limestone, exposed in the quarry face, was filled
with Chalky Boulder Clay containing abundant ferruginous nodules and
flints in roughly equal proportions. The nodules consisted of
concentrically banded limonite and probably formed by weathering of
siderite nodules.

The chemistry of the excavated ores most closely resembles
that of the Ironstone Junction-Band (Appendix C), particularly in the
low V_2O_5 and P_2O_5 contents. The Ironstone Junction-Band was probably
the major ore smelted, but it is possible that other ironstones (in

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particular Boulder Clay nodules, see Chapter 5) were also added on occasions. The chemistry of the slag is rather ambiguous since it cannot as a whole be compared directly with the compositions of the three possible sources.

2.2.3 Great Oakley[29]

NGR SP 881866, Figure 2.3

Approximately 1.5 km north-east of the village of Great Oakley, the remains of a furnace and a smaller circular hearth were found associated with two semi-circular structures and a number of pits containing pottery sherds and one piece of slag. A fragment of cinder was also found in a trench forming part of one of the structures. Radiocarbon dates from charcoal in some of the pits suggest an age around 800 B.C., which is very early and is particularly significant in view of the associated ironworking. All that remained of the furnace was a reddened oval depression, 80 x 55 cm in diameter and 10 cm deep, containing a few fragments of slag, some with fired clay attached. The furnace was positioned at the bottom of a shallow southwards trending valley with the dated features lying on the higher ground to either side. The source of the stream, which now rises in the valley just south of the site, was apparently further north during the Iron Age as a modern drainage trench a few metres away from the furnace revealed a large accumulation of slag, presumably in the old stream course. No dating evidence was obtained from either the furnace or the stream course, but the slag found in one of the pits was identical in outward appearance and mineralogy to that which had been dumped in the stream.

The slag, in the form of large (up to 25 cm across) irregularly

shaped lumps often bearing charcoal impressions and attached pieces
of heavily slagged fired clay, was all furnace slag. This and the
lack of any identifiable tap slag are consistent with the furnace
remains. The slag from pit F22 and three fragments from the stream
course were examined microscopically. Freshly fractured surfaces
show the slag to be dark grey in colour and coarsely crystalline.
Both polished sections and thin sections reveal textures consistent
with slow cooling. Fayalite ($2FeO.SiO_2$), which comprises 55% of
the slag, tends to be massive and commonly shows wüstite exsolution.
A hercynite type spinel ($\sim$15%) either forms intergrowths with the
fayalite or occurs as euhedral crystals. There is 25% wüstite,
mostly in the form of large thick dendrites. Leucite, often showing
wüstite exsolution, and some glass is also present. One large piece
of slag (GO 792017) shows more distinct signs of flow. A polished
section reveals evidence for more rapid cooling than the rest of the
examined slag: the fayalite occurs as randomly oriented generally
skeletal laths, there is a higher proportion of glass (15%) and
a chilled surface is present. Perhaps this slag escaped from the
furnace somehow.

In the vicinity of the Great Oakley site there are no obvious
ore sources. The Northampton Sand Ironstone here lies beneath 20 m
of overburden, the nearest outcrop being 1 km to the north (around
NGR SP 883878) and of limited extent. The Ironstone Junction-Band
at the base of the Rutland Formation outcrops 1 km to the south east
in the Harper's Brook valley (around SP 890857). The Boulder Clay
on which the furnace was built does contain some ferruginous material:
ellipsoidal pyrite-bearing carbonate (calcite + subordinate siderite)
nodules derived from Upper Jurassic clays have developed a thick

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(up to 1.5 cm) goethite crust during weathering; also present are irregular masses of cellular goethite, presumably weathering products of the clay matrix.

In an attempt to identify the ore source, the slag and fragments of ironstone found on site, as well as local Boulder Clay nodules were examined and analysed using X-ray diffraction and X-ray fluorescence. The ironstone collected on site consists of goethite with minor lepidocrocite, either forming unstructured masses or displaying a spherulitic texture. This latter texture and the presence of lepidocrocite, which is rare in weathered Northampton Sand Ironstone, suggest that the ore source was the Ironstone Junction-Band. Samples of this ironstone collected from Brookfield Cottage Pit (SP 925937), Wakerley Great Wood (SP 956987) and Woodside Quarry, Wansford (Tl 063990) for instance are virtually identical both in appearance and mineralogy to the ironstone found on site. The composition of the slag is closely comparable with that of the ironstone found on site (Appendix C) and the latter must therefore be representative of the ore used. The high P_2O_5, V_2O_5, K_2O and Al_2O_3 and rather low iron content of the Northampton Sand Ironstone precludes this being a possible source. Similarly, the low iron and relatively high phosphorus content of the Boulder Clay material as a whole and (unless the ironworkers rejected the cores of the carbonate nodules) the excessively high CaO and related MgO argue against its use as an ore in this case. Comparison with other analyses of Ironstone Junction-Band shows that this is most closely similar to the slag and ore. The mineralogy, chemistry and texture of the majority of ore fragments therefore indicate that their source was the Ironstone Junction-Band and this was presumably obtained in the Harper's Brook valley.

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2.2.4 Bulwick [32]

NGR SP 929939 (Site 1) and SP 926937 (Site 2), Figures 2.3 and 2.6

The stripping of topsoil prior to quarrying the Northampton Sand Ironstone at Brookfield Cottage Pit west of Bulwick revealed two groups of furnaces and channel hearths. The best preserved furnace (furnace 1 on Site 1) consisted of a clay shaft of 25 cm internal diameter and wall 15 cm thick, with a gently sloping slag-tapping channel 135 cm long and 45 cm wide. There was evidence for two periods of use. The other furnaces on this site and on Site 2 were generally poorly preserved but appeared to be of the same design as that described. There is no direct dating evidence, but a few unstratified sherds of Roman pottery and the similarity to the Roman period slag-tapping furnaces on the Wakerley site suggest that these furnaces also date from the Roman period.

Only one piece of tap slag, from the area of furnaces 1 and 2 on Site 1, was available for examination. In cross-section six separate flows could be identified, each with the characteristic ropy upper surface which indicates that the slag from each tapping cooled completely before the next influx. Freshly fractured surfaces are greyish-green in colour and crystalline, with only a few very small vesicles. Microscopic examination shows that the slag consists mostly of close-packed, often skeletal, fayalite laths. Very little wüstite is present ($\sim$ 5% in total) and primary dendrites are small and confined to patches of glass. Wüstite also occurs as exsolution rods in the fayalite and as films of close-packed globules at chilled surfaces. There is approximately 10% spinel, this being mostly hercynite, in the form of intergrowths with fayalite or euhedral crystals.

The furnaces were constructed on the clays, silts and fine sands of the Rutland Formation which are here ~3 m thick. The Ironstone Junction-Band is 0.6-0.8 m thick and is in the form of large masses up to 1 m across. This ironstone would have outcropped downslope, just a little to the south, but there is evidence that the ore and probably also the overlying refractory clay were obtained from shallow pits near the furnaces.[32] The Northampton Sand Ironstone lies beneath 18 m of solid cover plus a variable thickness (0-10 m) of Boulder Clay. The nearest outcrop lies 1.7 km to the east and its use in these furnaces is improbable.

Although in this particular case there is little doubt which ore was smelted, the exposures in the quarry afforded an opportunity to collect ironstone samples for comparison with the slag and with material found at other sites. Samples from the Ironstone Junction-Band were obtained at the edge of Mavis Wood around SP 925937. Eastwards, the Rutland Formation was overlain by an increasing thickness of Chalky Boulder Clay, the top 2-3 m of which contained relatively abundant ellipsoidal nodules (15-30 cm across and 50-100 cm apart). These nodules, consisting of a thick goethite shell around a less weathered core of calcite and siderite, were sampled around SP 928941. Samples of the partly weathered Northampton Sand Ironstone, showing a variety of facies, were also collected from the floor of the quarry near this location. The composition of the slag is not closely comparable with any of the three ironstones sampled (Appendix C), although the low V_2O_5 and P_2O_5 content is most consistent with an Ironstone Junction-Band source (see also Chapter 5).

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2.2.5 Brigstock

NGR SP 963859, Figure 2.3

A large fragment of slag (20 cm long) was found in the upper part of the fill of a drain gully, sealed by the entrance metalling to a second to third century A.D. Romano-British shrine.[33] No furnaces were discovered in the excavation, nor were there any other signs of ironworking, but a large isolated fragment of slag is unlikely to have been transported far. Concentrations of mostly Romano-British pottery sherds in the surrounding fields provide evidence of other activity during this period.

The slag, which is dense and bears numerous charcoal imprints, appears to be a typical furnace slag. Fractured surfaces show it to be mostly coarsely crystalline and the colouring is patchy, varying from greenish grey to dark grey. It is highly vesicular, with vesicles ranging up to several millimetres across. Under the microscope, the fayalite appears as large (up to 2 mm long) subhedral laths separated by patches of glass, leucite, or leucite/fayalite intergrowth. The wüstite ($\sim$30%) is in the form of short thick dendrites and isolated globules. There is also approximately 15% hercynite present, occurring mainly as euhedral crystals.

The shrines were constructed on Boulder Clay and the nearest outcrops of ironstone (both Ironstone Junction-Band and Northampton Sand Ironstone) are in the Harper's Brook valley 2 km to the west. Alternatively, though perhaps less likely, ferruginous nodules within the Boulder Clay may have been exploited and smelted close to the shrines. The high P_2O_5 content of the slag (2.27 wt %, see Appendix C) argues against an Ironstone Junction-Band source, whilst the high

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V_2O_5 content (0.13 wt %) is more consistent with the Northampton Sand Ironstone. The problem of provenancing the ore on the basis of the slag composition is dealt with further in Chapter 5.

2.2.6 Blind Eye Quarry[34]

NGR TF 002148, Figure 2.3

The remains of at least three furnaces, dated as second century A.D., were discovered during sand and gravel extraction at a pit near Pickworth variously known as 'Blind Eye Quarry' or 'Lincolnshire Gate Pit'. Two were well preserved and excavation revealed that they were clay-lined shafts, a metre or more high, built into a bank. Colour banding of the clay suggested that the furnaces had been re-lined and the final internal diameter was 30 cm. A single opening served for blowing air in (experimental work using a reconstruction of this furnace type suggested that a forced draught would have been necessary[7]) and for tapping slag into the pit in front of the furnace.

Two fragments of slag from the site were examined: one (610135) was only $\sim$ 1 cm thick and had a smooth upper surface, indicating its highly fluid nature on tapping, and the other (610134) was of the more typical ropy form. The fragments are similar in their mineralogical composition and texture, consisting largely of long subhedral fayalite laths exhibiting considerable wüstite exsolution. The small amount of primary wüstite ($\sim$ 1% in 610135 and $\sim$ 5% in 610134) is concentrated mostly at chilled surfaces but also occurs as a few small scattered dendrites. The 5-10% glass appears as elongate patches between the sub-parallel fayalite laths. Hercynite (approximately 5%) is mostly concentrated at the edges of the fayalite laths and is in the form of euhedral crystals or a graphic intergrowth

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with fayalite. A small amount of interstitial leucite is visible immediately beneath the cooling surfaces.

X-ray fluorescence analyses (Appendix C) show the two samples to be very similar chemically and the difference in their fluidity on tapping is therefore thought to be the result of temperature differences rather than compositionally controlled variation in viscosity. The published analysis of a slag sample from this site[34] shows that some of the slags contained less iron than those discussed above, although the deficiency was probably not sufficient to cause a significant increase in viscosity.

No ore samples were available for study and a ferruginous nodule analysed for Tylecote[34] was evidently unrepresentative of the ore smelted. The nearest outcrop of Northampton Sand Ironstone is 4.4 km due south near Little Casterton and is therefore unlikely to have been the source of the ore. In contrast, because the glacial sands and gravels in which the furnaces are constructed rest on an isolated patch of Rutland Formation, the Ironstone Junction-Band outcrop actually rings the furnace site (Figure 2.3). This ironstone is particularly well-developed on Ryhall Heath just to the south east. and could have been obtained only 100 m from the furnaces. Now no longer exposed in the immediate vicinity, samples of Ironstone Junction-Band were collected from Holywell Quarry (New Quarry), Clipsham (1.5 km to the north west). Here the ironstone appeared to form large masses up to 1 m across, although slumping had obscured all the in situ material. Some of the masses, orange-yellow in colour and consisting of approximately equal amounts of goethite and lepidocrocite, proved to be leaner than the reddish-purple variety which consisted of poorly-crystalline hematite, with lesser amounts

of goethite and lepidocrocite (63.2 and 83.2 wt % Fe_2O_3 respectively).

The analyses of material from Holywell Quarry compare closely with

those of the investigated slags (Appendix C) and there can be little

doubt that the Ironstone Junction-Band was the source of the ore

(see also Chapter 5). There is no clear evidence that the richer

material was preferentially smelted. Finally, although there are

areas of Boulder Clay 400 m to the north west of the site, it is

unlikely that any attempt was made to exploit the ferruginous material

within it when a much richer and more consistent source was closer

at hand.

The furnaces were probably located on the sands and gravels

because the ground was better-drained than the surrounding clay. It

is also possible that the nature of the substrate influenced the

furnace design. Here, as at Ashwicken,[35] the presence of moderately

well-consolidated sands enabled the ironworkers to carve the shafts

out of a solid bank. Such furnaces would probably have been more

permanent than the free-standing clay shafts found elsewhere in the

Northamptonshire area. Furnaces of a similar design were widely used

in nineteenth century India, these being built into a clay bank, but

in the wetter north-west European climate clay banks would not have

dried sufficiently and this furnace type is therefore likely to be

confined to localities with consolidated sands. It is interesting to

note that the Type D Wealden furnaces of Gibson-Hill[36] were built

into a low 'clay' bank, specially prepared and with a fine sandy

texture quite unlike that of the Weald Clay. This specially prepared

material presumably dried better than the local natural clay.

2.2.7 Stamford[34,37]

NGR TF 03150720 (Co-op site), Figure 2.8

Excavations at Stamford, combined with research into the early development of the town, indicate that a period of intensive iron-working at least partly preceded the establishment of a planned Danish burh. Both commercial and archaeological excavations have revealed considerable quantities of slag, cinder and ore fines at a number of sites in the eastern part of the old town; furnace remains have been found at the corner of St Georges Street and St Leonards Street and on the north side of the High Street (Co-op site), while four hearths, interpreted as roasting hearths, were discovered on the south side of the High Street. An archaeomagnetic date in the first half of the eleventh century was obtained for the furnace at the Co-op site, whilst the pottery suggests a date from the late ninth to early eleventh century. This furnace was poorly preserved, only surviving to a height of 18 cm. All that remained was a D-shaped hollow, 36 cm by 32 cm internally, cut into the natural clay and with a 3-8 cm thick lining of a different clay. A tapping hole 11 cm by 13 cm in the curved part of the furnace led into the tapping pit, a heat-hardened hollow $\sim$1 m long. The poor preservation makes interpretation of the remains difficult and it has been suggested that the furnace was either a bowl or a low shaft type, although the latter seems more likely in view of its small internal dimensions.

Samples of slag were obtained from the tapping pit of the furnace (no. 630532), from Pit B (No. 700130; the function of the pit is uncertain, but it was apparently contemporary with the furnace and a nearby roasting hearth) and from Layer 6B in cutting IV (No. 700128;

Layer 6B probably represents the clearance of topsoil from an adjacent area and is assumed to postdate the destruction of the furnace by a number of working seasons). All three samples have the ropy upper surfaces typical of tap slags. Freshly broken surfaces are crystalline, dark grey or greenish-grey in colour and with a few small vesicles. Microscopic examination of thin and polished sections shows that the three samples are closely similar in their mineralogical compositions and textures. All contain 50-55% fayalite and 20-30% dendritic wüstite, although the proportion of the minor components varies (see Table 4.1). The fayalite mostly occurs as skeletal laths, with some subhedral laths showing wüstite exsolution; in sample 630532 the laths have grown together to a greater extent than in the other two samples. All three slags show chilled surfaces and in 630532 and 700130 compositionally zoned spinels and small amounts of leucite are associated with these features. Hercynite, occurring as an intergrowth with fayalite and as occasional euhedral crystals in 630532 and 700130, is absent from 700128.

Microscopic examination of an ore fragment (No. 700075, from layer 6D, which has been interpreted as the base of an ore dump) shows it to be a fine quartz sandy sideritic chamosite oolite which has been partly weathered to limonite and kaolinite. Investigation of a number of ironstone fragments from the layers postdating the furnace revealed that their petrography was similar to 700075, although packing of the ooids is variable and occasional pieces should be classified as oolitic mudstones.[37] The petrography and boxstone weathering pattern indicates a Northampton Sand Ironstone provenance and it is likely that the ore was obtained from the extensive outcrops along the escarpment south of the River Welland. As a result of

faulting outcrops a little nearer the ironworking site are small and close to river level and may have been obscured by slumping.

X-ray fluorescence analyses of slag samples 630532 and 700130 are closely comparable with the composition of the ore found on site (Appendix C) and there are no grounds to suggest that any other ore was used or that flux was added.

The reasons for carrying out the smelting north of the river rather than close to the main outcrop are uncertain. The establishment of the industry pre-dated the planned Danish burh and its defences but an earlier settlement may have influenced the location of the industry. Alternatively, there may have been political reasons since in the tenth century the river formed a boundary between the Danish settlement to the north and an 'English' settlement to the south. However, it is interesting to note that the spur on which the Danish burh stood is capped by clays of the Rutland Formation, at the base of which is the Ironstone Junction-Band. It might have been this ore which initially attracted ironworkers to the site.

2.2.8 South Witham

NGR SK 929205, Figure 2.3

Excavation of a Preceptory of the Knights Templar near South Witham revealed a quantity of metal working waste. Iron slag was apparently plentiful and a partially worked bloom was also discovered. It has been suggested that much of the slag is forging slag,[38] although some tap slag and a small piece of boxstone-weathered oolitic ironstone were found associated with the primary range, adjacent to the aisled hall. This material has been dated as c. 1170-1225. No

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furnace remains or hearths were found during the excavations.

The slag is dense and has a well-developed ropy upper surface
and a flattened lower surface. It is mid grey in colour and shows a
crystalline fracture. A few large vesicles are visible. The
mineralogical texture is typical of rapidly-cooled slags, with
bundles of long (up to 1 mm), partly skeletal fayalite laths radiating
down from two separate chilled surfaces. Approximately 15% of
wüstite is present, mostly in the form of long fine dendrites.
Hercynite ($\sim$ 5%) occurs as euhedral crystals and occasional intergrowths
with fayalite. Small amounts of interstitial leucite, zoned spinels
and angular magnetite dendrites are associated with the chilled
surfaces. There is also approximately 5% glass present.

In hand specimen and microscopically, the ore fragment appears
similar to the material found at the Stamford excavation and identified
as weathered Northampton Sand Ironstone. The Northampton Sand
Formation outcrops   400 m to the south of the site and although
this may have been mostly obscured by the Boulder Clay cover, it
could have been exposed in the valley of the River Witham. There
are large rafted masses of ironstone in the Boulder Clay approximately
4 km to the west of the site and it is possible that similar masses
near the site were exploited. The composition of the slag (Appendix
C) is consistent with analyses of the local Northampton Sand Ironstone
(from Colsterworth and Cottesmore) given by Todd[14] and the relatively
high MgO and CaO contents of the slag (MgO 1.73 wt %, CaO 4.89 wt %)
suggest that the ore was moderately weathered.

2.3 The Weald

2.3.1 Geological setting

The Wealden formations, earliest Cretaceous in age, form the central part of a broad east-west trending anticlinorium extending between south London and the south coast. The rocks therefore young both northwards and southwards and the structure and alternation of dominantly sandy and dominantly clayey formations combine to give the Weald its character. The stratigraphy is illustrated in Figure 2.9. The Hastings Beds Group have been interpreted as the deposits of a variable salinity coastal mudplain with lagoons and sandy watercourses.[39] Uplift of the blocks around the basin caused the channel networks to merge into a single sandy braidplain during the deposition of both the Ashdown Beds and Lower Tunbridge Wells Sand Formations. The overlying Weald Clay accumulated when the London and Kent blocks, which had previously supplied sediment, became less active and the sea encroached from the north west.[39]

There are no major ironstones in the Weald, but ferruginous horizons, many of ore quality, are common. The most abundant variety of ironstone is a nodular or tabular siderite developed within the more argillaceous lithologies and often referred to as 'clay ironstone'. Perhaps the most important examples, from the archaeological viewpoint, are those in the lowest 15 m of the Wadhurst Clay, as they have evidently been extensively worked in the past (Figure 2.10 a and b). Topley[40] noted that the more ferruginous sandstones within the Hastings Beds Group also seem to have been worked and it is recorded that iron was mined briefly in the mid nineteenth century from the Ashdown Beds at Snape Wood (NGR TQ 633308).[41] Finally limonitic concretions (locally called 'crowstone', 'ragstone', etc.) formed

by the weathering and recementation of ironstones at or near the ground surface may also have been exploited.[42,43]   Such concretions are fairly common, though sporadic in their occurrence, on the outcrop of the Wealden formations. A fragment of this material analysed by Worssam and Gibson-Hill[43] proved to be highly siliceous and would probably have been unsuitable for smelting in a bloomery unless charged with a richer ore. However, the composition of such concretions is variable, depending on the quality of the original ironstone and on local conditions and it is likely that some concretions would have been richer than that analysed.

In contrast with the Northamptonshire area, the history of the exploitation and smelting of ironstones in the Weald has been extensively researched. Straker's contribution[42] is outstanding and the continuing work of the Wealden Iron Research Group is adding to the constantly growing body of data.

2.3.2 Garden Hill[44]

NGR TQ 444319, Figure 2.11

Excavations at the eastern end of the Garden Hill earthwork, which has proved to be an Iron Age hill fort, have revealed remains ranging from Mesolithic to Romano-British in age. The main settlement spans the period from the mid first century B.C. until at least the mid third century A.D. and ironworking on a relatively small scale appears to have been carried out, though perhaps sporadically, throughout. The earliest evidence of ironworking is a forging hearth which has an archaeomagnetic date in the latter half of the first century B.C. Close to this forging hearth and perhaps contemporary with it are two other small hearths and a furnace, 1 m in diameter,

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which has been likened to the furnaces found at nearby Cow Park.[17]
Two smaller diameter ($\sim$ 30 cm internally) furnaces 30 m to the north
east of these features have later, though less precise, archaeomagnetic
dates (one is dated as 50-200 A.D., the other c. 50 B.C. to 200 A.D.).
Little remained other than the furnace bases and tapping pits, but
both have been interpreted as being of the low shaft type.[45]
Two roasting hearths, one dated as mid third century A.D., and
accumulations of ironstone and slag have also been discovered. Although
the ironworking appears to have been on a small scale here, it has
been suggested that in the second century A.D. the Garden Hill
settlement was a managerial centre for a number of nearby bloomeries
such as those at Pippingford and Cow Park.[45,46]

Slag from all three furnaces and from the fills of two of the
rampart quarries have been examined. Although the slag petrography
is variable, there are no really distinctive differences between
slags from different periods and furnace types (see Table 4.1 for
mineralogical descriptions). Only one sample of definite tap slag,
from the tapping pit of one of the shaft furnaces, was available for
examination. In hand specimen it is medium grey and moderately dense
with a ropy upper surface. Under the microscope it can be seen that
the long skeletal fayalite laths ($\sim$ 55%) are arranged in slightly
radiating bundles perpendicular to one of the edges, providing
evidence that a chilled surface existed just beyond, but no chilled
surfaces are visible on this (or any other) section. There is
approximately 30% wüstite present in the form of long, randomly
oriented, dendrites which are smaller and finer near the edge
assumed to have been chilled. Glass containing small fayalite
crystallites constitutes the remainder of the section, apart from a

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few globular or dendritic metallic grains which may have been
molten at the time of tapping. Furnace slag from the same furnace
shows a higher proportion of wüstite ($\sim$50%), this being coarsely
dendritic. The fayalite ($\sim$40%) appears mostly massive in polished
section, broken only by irregular patches of glass ($\sim$ 7.5%), although
in thin section separate randomly oriented laths can be distinguished.
The fayalite is non-skeletal and shows some wüstite exsolution.
Small amounts of hercynite and leucite are discernible. Furnace
slag from the possible Iron Age furnace differs from the above in
showing very little primary wüstite (1-2%) and very little glass,
leucite being the main interstitial material. Fayalite is in the form
of long laths arranged in close-packed sub parallel bundles and showing
abundant wüstite exsolution. The texture is similar to that of a
slag fragment obtained at the Pippingford bloomery site. Material
from the lower levels of the rampart quarries (dug in the late Iron
Age and infilled mainly during the Romano-British period) show
mineralogical compositions and textures between the Romano-British tap
slag and the earlier furnace slag, yet all appear similar in hand
specimen, most closely resembling furnace slag.

The site is located on a strong feature formed by a band of
massive sandstone within the Ashdown Beds Formation. The local
sandstones of the Ashdown Beds has been identified as the source of
much of the ironstone found on site.[47] As a result of weathering,
concentrations of limonite are built up along joints and bedding-
partings in the same manner as boxstone formation. However, the quartz
sand content may still be high and careful selection would be
required if such an ironstone were to be a viable ore source.
Rejection of a certain proportion of the material collected as ore

might account for the fact that several tonnes of ironstone remained and much of it had apparently been used to level part of the site before the ironworking activities had ceased.[46] Examination of a fragment of ferruginous sandstone with a boxstone development along one edge showed that the boxwall contained some sand-free layers, but these would have been inseparable from the remaining much sandier portion. Two other fragments of boxwall, one raw and one roasted, also proved to contain a large amount of silica (42.8 and 31.6 wt % respectively) and were therefore rather lean. In contrast, a roasted fragment of boxstone-weathered 'clay ironstone' contained only 8.0 wt % silica.

A comparison of the slag analyses with those of the ores (Appendix C) shows that the compositions of the samples from the Romano-British shaft furnace are not consistent with their production from either the boxstones from the sandstones or the clay ironstone. The compositions of the remainder of the slags however correspond closely to that of the clay ironstone. It is therefore suggested that the major ore source was an argillaceous band (or bands) within the Ashdown Beds, although some ironstones from the sandy lithologies may have been added to the charge of the shaft furnaces. Finally, a small fragment of limonite oolite was also selected for further investigation by the archaeologists. Although rare in the Hastings Beds, thin ($\sim$ 5 mm) layers of chamosite ooliths have been reported from the Tunbridge Wells Sand in a borehole at Warlingham, Surrey.[48] The Lower Tunbridge Wells and Ashdown Beds Formations have been interpreted as having accumulated under similar conditions[39] and it is conceivable that chamosite ooliths occur in both; subsequent weathering would have resulted in limonitization of the ooliths. The chemistry of the excavated fragment is unlike the other ores or slags

(note the particularly high alumina content, Appendix C) and in view
of this and the probably very limited extent of such a lithology, it
is unlikely to represent a significant ore source.

2.3.3 Millbrook[49]

NGR TQ 441296, Figure 2.11

The excavation of a pipeline trench led to the accidental discovery
of an ironworking site approximately 600 m to the north of the Mill
Brook, in the upper part of a tributary valley. On an artificially
levelled working area were the remains of a smelting furnace and two
hearths as well as an accumulation of slag. An archaeomagnetic date
in the ninth century A.D. was obtained for the furnace and this is
supported by the presence of Saxon pottery. The furnace remains
consisted of a hollow, approximately 1 m in diameter, with sloping
sides and a slightly deeper excavation, 0.33 m across, in the middle.
The total depth remaining was 0.62 m. The possibly domed super-
structure had either collapsed or been destroyed and the hollow was
filled with fragments of fired clay. Part of the furnace wall had
remained in situ and showed evidence of at least three relinings.
There were no proper facilities for tapping slag and the presence of
both irregularly-shaped pieces and small furnace bottoms suggests
that some of the slag may have been raked out while the rest accumulated
in the furnace.

The furnace bottoms, mostly of a roughly oval shape with
maximum diameter of 15-17 cm, vary from dense and homogeneous to
highly vesicular with inclusions of charcoal, flint and occasionally
fired clay or unreduced iron ore. Both the furnace bottoms and
irregular fragments show a crystalline fracture and although some

pieces are coarsely crystalline, with fayalite laths 7 or 8 mm long,
many are finely crystalline and surprisingly equigranular. Microscopic
examination of several samples reveals that fayalite, although sometimes
skeletal, tends to be in the form of elongate euhedral crystals rather
than laths and thus more closely resembles the usual naturally-occurring
olivines. This probably reflects the small degree of undercooling
experienced (see Chapter 4). The slag's mineralogical composition is
variable, some samples consisting only of euhedral fayalite (70-75%)
set in glass containing tiny laths of the same mineral, whilst others
contain up to 50% wüstite in the form of thick dendrites or isolated
globules, the fayalite ($\sim$30%) forming intergrowths with hercynite
($\sim$15%) and leucite and glass occurring interstitially. Large proportions
of magnetite have been detected in some samples[50] and this combined
with the form of the fayalite, implies that temperatures at the
bottom of the furnace were rather low. The variability of the slag's
mineralogy may be a reflection of the variations in furnace conditions
from smelt to smelt and this in turn perhaps reflects a lack of skill
on the part of the operators. However, the slag chemistry is very
variable (Appendix C; other analyses are to be published)[49] and
this is the main reason for the mineralogical differences in the slag
samples. Several different ironstones, some from far afield, were
found on site (see below) and this explains the chemical variation of
the slags. The ironworkers therefore did not necessarily lack expertise
and they may in fact have been consciously experimenting to find the
best charge for their furnace.

The predominant variety of ironstone found at Millbrook is a
boxstone weathered nodular siderite typical of the clay ironstones
so well-developed in the lower part of the Wadhurst Clay Formation.

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The furnace is sited on the Ashdown Beds Formation near the crest of the Crowborough Anticline and conseqeuntly the younger Wadhurst Clay Formation outcrops both to the south (at a distance of 3-4 km) and to the north (approximately 6.5 km). Just less than 1 km to the southeast of the site, near Nutley, is a lenticular clay body up to 7.5 m thick within the Ashdown Beds. Numerous pits on the eastern side of the shallow valley at TQ 44822856 strongly suggest former working of ironstone within the clay.[51]   It is therefore possible that the clay ironstone found at Millbrook was locally-derived. Fragments of 'Cyrena' (i.e. Neomiodon)-rich lumachelle collected around the furnace have been roasted and now consist of haematite and magnetite, though the matrix is likely to have been calcite or siderite mudstone, perhaps secondarily enriched with iron as a result of weathering. This lithology is probably from the Wadhurst Clay Formation. Other ironstone fragments are more difficult to provenance. Some of the pieces consist of fragmented nodular limonite re-cemented to form irregular lumps. Superficially they resemble the 'crowstone' or 'ragstone' found in many parts of the Weald, but they contain flint pebbles and therefore derive from outside the Wealden outcrop. Pieces of dark reddish purple sandy ironstone containing pebbles of flint and some siltstone also cannot be locally-derived. This lithology may be from the northern margin of the Weald, as similar materials occur there in the Drift deposits and soils on the Lower Greensand and upper part of the Weald Clay outcrop.[52]   The flint pebbles within some of the ironstones provide a simple explanation for the large quantities of flints found on the site and even within some of the slags. There is no reason to suspect that the flints were deliberately added to the charge and most were no doubt removed from the ore when it was crushed after being roasted.

2.3.4 Furnace reconstructions

An account of the furnace reconstructions built and worked by
Mr R. Adams properly belongs to this section on Wealden archaeology
and geology. Adams has attempted to reproduce in every detail the
ironworking methods used at Wealden sites such as that of nearby
Garden Hill. The furnaces, situated in a clearing in the woods next
to a small stream, were made of clay (Ashdown Beds Formation) dug from
a pit on the site. The early furnaces were constructed of air-dried
blocks, sealed by smearing wet clay inside and out, as this ensured
that the structure dried sufficiently in a fairly short time. Later
furnaces were of a monolithic construction, being built of well-
rammed clay. The charcoal was made on site from branches cut in the
surrounding woodland (predominantly beech; the charcoal has been
estimated as 95% beech[53]). Clay ironstone, obtained from Sharpthorne
brickworks, West Hoathly, (TQ 374330; lies 6 km west of the site and
exploits Wadhurst Clay) and also from Herstmonceux (TQ 634142; 25 km
south east, again in Wadhurst Clay), was initially roasted in the
charcoal pit to conserve fuel, but it was later found that better
results were obtained when the containers (large paint tins) holding
the ore fragments were heated in an open fire. The roasting was
followed by crushing and sieving. The first batch of material examined
was from a furnace based on the second to third century remains at
Garden Hill. Built of air-dried clay blocks, the internal diameter
of the shaft was $\sim$30 cm and overall height $\sim$1.5 m (Figure 2.12).
The tap-hole was closed during blowing by a piece of turf which was
removed every 15-20 minutes to allow the slag to be tapped. Air was
blown in by a large pair of bellows at a rate of 0.005 $m^3 s^{-1}$. The
charcoal to ore ratio was 4:3 and 22 kg of ore were charged during the

four hour blowing period. Unfortunately, the air-rate was too high and very little iron was produced. The presence of primary magnetite in the form of skeletal crystals and angular dendrites in both tap slag and furnace slag provides evidence of oxidising conditions within the furnace. Fayalite occurs as euhedral skeletal laths and slightly elongate crystals, randomly oriented and suspended in a glassy matrix. The texture suggests that in both cases the slag was initially well above its melting point and underwent rapid cooling. Furnace slag from a smaller shaft furnace ($\sim$ 23 cm internal diameter, 100 cm high) of a monolithic construction was also examined. This slag was variable, one fragment closely resembling slag from the larger furnace, with the exception that two small patches of rounded ?wüstite dendrites were observed within the glass, whilst the other fragment contained only a very small amount of magnetite ($\sim$ 1%), this being seeded around another euhedral spinel (probably hercynite) within the glass phase. A single pot bellows was used to blow the furnace, but as might be predicted from the slag mineralogy, conditions were *too oxidising and only traces of iron were found*. Finally, slag from a 44 cm diameter non-tapping furnace, based on the remains found at Millbrook, was analysed. 22 kg of clay ironstone were smelted and 3 kg in total of crushed flint were added to see whether its presence affected the process. Little iron was produced (0.1 kg) and although no furnace bottom was formed (Adams considers this was because only one tuyere was used),[53] the slag did resemble some of that found at Millbrook.

The slag analyses are closely comparable with those of the ironstone (Appendix C) and this supports the hypothesis that it should be possible to provenance ores on the basis of slag composition. The ironstone is rather lean, although the high loss on ignition shows that it would be considerably improved on roasting.

For the purposes of comparison, slag from a preliminary smelt
in a 'bowl' furnace, using ore from West Hoathly, was examined.
Built and operated by Mr R. Clough at the Institute of Archaeology,
the furnace was similar to that used by Wynne and Tylecote[3] for
their experiments. Unfortunately, very little iron was produced and the
presence of primary magnetite indicates that furnace conditions were
insufficiently reducing. Slag from the middle of the furnace and from
just below the tuyere was vesicular and contained fragments of charcoal.
Both pieces consisted of randomly oriented skeletal fayalite laths
(45-50%) set in glass. Unusually, both also contained euhedral crystals
of leucite and whilst the K_2O contents are fairly high (1.93 and 2.27 wt %)
they are unremarkable and it is likely that furnace conditions were a
strong influence on the early appearance of this mineral (see Chapter
4). The slag composition is closely comparable with that of the West
Hoathly ore, with the exception of the CaO and K_2O contents.
Contamination of the slag by charcoal ash is the most probable cause
of the discrepancy (see Chapter 5). The slags from all of the furnace
reconstructions are low in iron compared with the excavated slags and
the high fuel to ores ratios used in the experiments must be
responsible.

2.4 Ramsbury, Wiltshire[54]

NGR SU 272715, Figure 2.13

Excavations at a site in the High Street, Ramsbury, revealed
a Saxon ironworking site. On an artificially levelled working area
were found the remains of at least two non slag-tapping 'bowl'
furnaces and an unusual type of domed furnace provided with slag
tapping facilities. The furnaces occur at different stratigraphic

levels, the slag tapping furnace representing a slightly later phase of activity than the other two; radiocarbon dating places the site in the late eighth to early ninth centuries A.D. Other ironworking remains include ore roasting hearths, smithing hearths, a sarsen stone evidently used as an anvil, and layers of charcoal, ore fines and slag, the disposition of which were considered to show evidence of cyclical activity.[54] The three furnaces had been re-lined many times (12 distinct linings could be discerned in the case of the slag tapping furnace) resulting in a considerable reduction in volume as well as a change in internal shape. Stake holes within the two bowl furnace hollows suggest that these furnaces had domed clay superstructures, initially supported on a framework of stakes and woven withies, like that at Minepit Wood.[55] Apart from the modification of having a back wall built of Roman bricks and clay, the slag-tapping furnace's superstructure was presumably constructed in a similar fashion.

Two samples of slag for chemical and mineralogical analysis were taken from a furnace bottom 45 cm x 20 cm x 20 cm. Apart from its large size, the slag block was similar to the furnace bottoms from other sites, bearing charcoal impressions and showing signs of viscous flows on the surface. The slag petrography is variable and apparently reflects differences in cooling rates of different portions of the furnace bottom as it accumulated. Fayalite (35-55%) varies from massive to randomly-oriented euhedral laths, while wüstite (10-35%) may occur as thick rounded dendrites and globules or may be absent in some areas. There is approximately 10-15% leucite present, generally forming rounded patches showing wüstite exsolution, or intergrown with fayalite. A small amount of hercynite (2-3%) also forms intergrowths with fayalite. The matrix contains abundant tiny skeletal

laths of fayalite. A polished section of a fragment of tap slag revealed a typical texture, the upper surface showing evidence of chilling and the main body of the slag consisting mainly of randomly oriented skeletal fayalite laths and fine wüstite dendrites. Glass, hercynite and leucite are minor phases and there are also a few grains of metallic iron.

The ore found on site, some of which had been roasted, mainly consists of boxstone-weathered nodules of siderite microsparite containing approximately 5% very fine quartz sand. The site, in the valley of the River Kennet, lies on a thin layer of gravelly sediment which rests on Upper Chalk (Figure 2.13). There is no obvious source of sideritic ironstones close by. Concretionary ironstones have been recorded from Eocene strata (especially the Reading Beds and Lower Bagshot Beds), the nearest sizeable outcrops of which lie 5 km south of Ramsbury. The stratigraphically younger Clay-with-Flints also contains local developments of ferruginous nodules, and Osborne-White[56] notes that 'a good deal of concretionary iron ore', formed in situ, was exposed in old diggings in Savernake Forest 6-7 km southwest of the site. A single piece of sandstone found on site proved geologically distinctive. The coarse and well-rounded quartz grains cemented by purplish iron oxides are regionally unique to the Lower Greensand, which outcrops some 30 km to the west, around Seend. More iron rich lithologies within this formation have been exploited since the Roman period,[57] but no such material, characteristically consisting of coarse rounded grains of limonite and glauconite cemented by siderite,[58] was discovered in this excavation. The occurrence of a fragment of sandstone from the Lower Greensand, perhaps from the Seend area, suggests that another source of siderite microsparite nodules, namely

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the Red Nodule Beds of the Upper Oxford Clay,[59] could also have been utilized. These also outcrop some 30 km west of Ramsbury (see Figure 2.13).

2.5 Bulbourne Valley, Hertfordshire[60,61]

NGR SP 9907 to 9211, Figure 2.14

Recent excavations in the Bulbourne Valley between Tring and Berkhamsted have revealed evidence of a flourishing iron industry in the late Iron Age and Romano-British period. Four slag-tapping shaft furnaces, one surviving to a height of 60 cm, were discovered during the building of Bridgewater School, Berkhamsted.[60] The furnaces were of an unusual construction, the 8 cm thick clay walls of the shafts (28 cm internal diameter) being supported and/or insulated by a surrounding wall, 15 cm or more thick, of hard packed chalk fragments. Gibson-Hill's Wealden shaft furnace Type E [36] shows some similarities, although this variant is characterized by having up to one third of the shaft set below ground level, whilst the Berkhamsted furnaces are built at the surface. Belgic potsherds were found in the tapping pits of three of the furnaces and four Iron Age cremation burials were also discovered, although these presumably predate the ironworking since it is unlikely that burials would have been located so close to furnaces in operation. Apart from the design of the furnaces, which is commonly regarded as a Roman Import (see, for instance the comments of Cleere in the Dellfield report),[60] there seems to be no reason to suggest that they are Romano-British rather than Iron Age. Two other furnaces of the same design and construction, discovered during work on the Tring bypass (SP 934107), are undated. Features described as 'furnace bowls' were found at the Romano-British settlement at The Cow Roast (as

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well as more than 2 tonnes of slag) and at Boswick Lane, Dudswell,
the latter site yielding artifacts dated as Flavian to late third
century A.D. Again chalk was associated with the furnace remains. Tap
slag was also excavated at the Northchurch Roman villa[61] and at Grove
Road, Tring, this being tentatively dated as Romano-British.[62]

Slag from the Bridgewater School site, the three separate sites
at The Cow Roast and the Northchurch villa has been examined. Variably
vesicular, the slag is dense, dark grey to black in colour and with a
coarsely crystalline fracture. All the fragments are tap slag, displaying
the characteristic ropy upper surface, except in the case of one thin
piece which has a flat upper surface and was presumably very fluid when
tapped. Three pieces contain a few small fragments of flint, but
since the sites are either on chalk or Clay-with-flints, this lithology
is extremely common and could easily have been incorporated into the
furnace charge by accident.

Under the microscope, the slag's mineralogical composition and
texture is surprisingly variable, but most polished sections show
chilled surfaces and lath-like fayalite which is sometimes skeletal
but more commonly subhedral and with wüstite exsolution. Primary
wüstite is present in amounts varying from 2-20% and is often patchily
distributed. One of the Northchurch slags resembles those from the
furnace reconstructions (Subsection 2.3.4) in containing primary
magnetite and it can be assumed that furnace conditions were similarly
insufficiently reducing (see also Chapter 4). Magnetite is sometimes
present as an oxidation product at chilled surfaces, while leucite,
hercynite and an iron rich spinel may also be observed associated
with these features.

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The geological setting is similar to that at Ramsbury, the sites lying on Chalk, with no obvious local ore sources. The Bulbourne Valley is cut through the chalk of the Chiltern Hills; in the valley bottom are Pleistocene river gravels and Recent alluvium, while the hills are capped with 'Clay-with-flints' and some isolated outliers of Eocene strata. The 'Clay-with-flints' as mapped in this area (Geological Survey 1" series, Sheet 238) is considered to have formed when the thin layer of Reading Beds (Eocene) overlying the Chalk became weathered and affected by periglacial and karstic disturbance, with the incorporation of insoluble residues from the Chalk.[63] The resulting deposit was more aptly referred to as 'Plateau Drift' by Avery.[64] Pockets of relatively unaffected Reading Beds may still be found beneath the Plateau Drift. Seams of ironstone within the Eocene strata are reported from Cowcroft, Chesham[65] and it is likely that similar seams, either in situ in isolated patches of Reading Beds or incorporated into the Plateau Drift, occurred on the hills above the Bulbourne Valley. In addition the Plateau Drift would have contained marcasite nodules from the Chalk, probably heavily weathered so that much of the original sulphide would have been oxidised and the sulphur lost. Ferri-magniferous concretions, considered to have formed pedogenetically during a period of sub-tropical weathering (probably during the middle Devensian or Ipswichian interglacials), are also found within the subsoil horizons of the clayey Plateau Drift,[63] but neither these nor the other ironstones are likely to have occurred as large accumulations. The Lower Greensand around Heath and Reach, ~14 km to the north-west, consists of large-scale cross-bedded sands, variably cemented by iron oxides. Ironstones from this formation have been used at sites elsewhere (e.g. All Cannings Cross, Wiltshire[66])

and could have been exploited here, although the transport of ore over such distances is unusual in this early period.

Samples of ironstone from the Lower Greensand were collected from quarries at SP 929241 (dark purple nodules scattered on the top surface of the sands where the topsoil had been removed) and at SP 927290 (mostly thin shells of goethite which had formed around burrows, logs and other organic material). X-ray fluorescence analyses show that these could constitute a viable ore, but some of the slags have a high MnO content (Appendix C) inconsistent with the use of these ironstones. The composition of material found with the slag, i.e. two marcasite nodules (thoroughly roasted before analysis) and a hollow limonite nodule (assumed to be weathered marcasite) does not compare closely with the slag analyses either. However, in view of the variable and sometimes very high MnO content of the slags, material from the Plateau Drift is the most likely ore source. It is of interest to note that the possibility of successfully smelting highly weathered iron sulphide nodules has been confirmed by the experiments of Clough.[67]

2.6 Caerwent, Gwent

NGR ST 470905

The site, at the corner of Pound Lane, Caerwent, was excavated in 1946, with some further work carried out in 1954. Occupying the western portion of Insula VII, immediately west of the forum of the Roman town of Venta Siluram, the remains have been interpreted as a sequence of shops, houses and workshops ranging from late first century to the fourth century A.D. Despite the urban setting, iron smelting and smithing was apparently carried out here in the late first, early second and fourth centuries, some of the slag being

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utilized as road metalling in the surrounding streets. No smelting furnaces were discovered, although there were a number of hearths, evidently connected with the ironworking.

Slag, found stacked on a round hearth of the fourth century, was examined microscopically. It consisted of ~45% skeletal fayalite laths with ~30% variably distributed wüstite dendrites set in glass. Other fragments of tap slag from the site show less glass (5-10%) and correspondingly more wüstite and fayalite, but none of the sections revealed minor phases such as hercynite and leucite.

No ore was available for examination, although a few fragments of limonite were recorded by the excavators. Given that the slag is very iron-rich, the minor oxide content is low and this suggests a lean ore, whose gangue consists of little other than silica. The town of Caerwent is situated on a spread of gravelly material between the second and third terraces of the Nedern Brook, this in turn resting on Triassic strata. There are no obvious local sources of ironstone, although the rich goethite and hematite deposits of the Forest of Dean lie 20 km to the north-east and similar ores on the edge of the South Wales coalfield outcrop some 35 km west-south-west. Comparison with published analyses shows that the composition of the slag is consistent with its having been produced from such ironstones, although the transport of ores over these distances does not seem to have been the usual practice during the Roman period.

2.7 Discussion

The furnace remains on the sites studied were generally poorly-preserved, but these meagre remains and the few furnaces which were better-preserved indicate a great variety of designs and construction methods. Some of the differences may be the result of variation in

construction materials locally available, others may have arisen
because of variations in the nature of the ground on which the furnaces
were built, whilst some must represent technological improvements.
The furnaces at Berkhamsted provide further evidence, supporting that
from the Weald, [36] that slag-tapping shaft furnaces were in use before
the Roman Conquest. The design of the ?domed and sunken-shaft furnaces
at Wakerley suggest .that slag was raked out in a viscous state and
the present author believes this was fairly common practice; it is not
necessary to assume that non-tapping shaft furnaces were of the slag-
pit type. Furthermore, the raking-out of slags suggests a likely
evolutionary step between non-tapping and tapping furnaces.

The investigated sites also illustrate that the production of
iron was not confined to areas with major iron ore deposits such as
Northamptonshire and the Foest of Dean. The study of the
Northamptonshire area (and the Millbrook site) has shown that the most
obvious ore sources in the eyes of a modern metallurgist were not
necessarily the ones exploited. A detailed knowledge of local geology
can often help to determine which ironstones were used and in most
cases it should not be necessary to conclude that the iron working
at a particular locality was based on an unknown deposit which was
worked out. One can only speculate about the prospecting methods
used by the early ironworkers, but they appear to have been efficient.
In the Northamptonshire area, the early preference for the Ironstone
Junction-Band rather than the Northampton Sand Ironstone may be due to
several factors. As discussed in Subsection 2.2.1, even when
weathered the Northampton Sand Ironstone is generally leaner than the
Ironstone Junction-Band but there is no reason to believe that the
furnaces and smelting techniques, at least in the Roman period, were

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inadequate to cope with this. Indeed Tylecote et al.[7] successfully smelted Northampton Sand Ironstone in their reconstruction of a Roman period shaft furnace. Clearly, it would have been more difficult to quarry the Northampton Sand Ironstone than to extract the nodules of the Ironstone Junction-Band from their soft host sediments and this must have been one of the criteria for choosing the latter. The early ironworkers were probably also influenced by colour, for the dark reds and purples of the Ironstone Junction-Band give it the appearance of being richer than the brown-weathering Northampton Sand Ironstone. The local geomorphology may also have been an important factor; over much of the area the Ironstone Junction-Band tends to cap hills, occurring immediately above the sparsely-vegetated Lincolnshire Limestone, while the Northampton Sand Ironstone outcrops only on the lower slopes of valleys and may well have been obscured by slumping and perhaps by dense vegetation.

Finally, plotting the major components of the slags on the FeO-Al_2O_3-SiO_2 and FeO-anorthite-SiO_2 ternary phase diagrams (see Chapter 4 for details) indicates melting temperatures of 1100-1200°C for the great majority. Only four samples (WAK 48A, Caerwent, Brigstock and Millbrook E) plot between the 1200 and 1250°C isotherms. These figures are consistent with the operating temperatures generally assumed for bloomery furnaces.

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CHAPTER 3

REDUCTION OF IRON ORE IN BLOOMERY FURNACES

Experiments involving reconstructions of bloomery furnaces have
been carried out in a number of countries (see for instance Table XIX
of Tylecote et al.[7]). The main aim of most of these studies has been to
find out how the various furnace types were operated, but some research
has been directed towards particular aspects such as the direct
production of steel.[1,9] Tylecote et al.[7] have made a more thorough
investigation of the variables affecting the bloomery process in shaft
furnaces (see Chapter 1) and their work is of particular value. Much
experimental work has also been done on the reduction of iron ores and
the kinetics of reduction have been extensively investigated (see
for instance the review of von Bogdandy and Engell[69]). Most of these
studies have involved pure iron oxides and hydrogen, rather than
carbon monoxide, has commonly been used as the reducing gas. It is
therefore difficult to apply the results of such work directly to the
bloomery process.

Discussions on the mechanism of reduction in bloomery furnaces
have already been published,[7,13,70] but a re-examination of the
reduction process, particularly with regard to the formation of slag,
is considered to be of use in the context of this study. Although of
an early date, the methical observations of Richard[71] and Francois[72]
on the operation of the Catalan 'forge' are of great value in such a
study. The Catalan 'forge', in use until the end of the nineteenth
century in the Pyrenees, was an evolved form of bloomery furnace.
Approximately twice the size of the great majority of its medieval
counterparts (see for instance Tylecote's[73] figure 50), it was blown

by a water-powered blowing machine (a 'trompe' or 'tine', for details see Percy[11]) and the descent of the ore and formation of the bloom were controlled to some extent by the smelters, but despite these differences it provides a useful analogy for earlier bloomeries. Richard[71] and Francois[72] examined the contents of such furnaces, which had been working under the same conditions and extinguished at successive intervals during smelting. Francois published a detailed account of his investigations (this has been extensively quoted in Percy's work[52] and it is the latter which has been used as the course for the present study) and his descriptions of the microscopic appearance of the ore as it undergoes reduction are of particular interest as they provide information about the reduction process in ores containing gangue.

Limonite or fairly friable goethite/lepidocrocite (referred to by Percy[11] as 'brown haematite') was the ore type preferred for smelting in the Catalan furnace, but siderite and hematite were also used. Percy noted that the 'brown haematite' became dehydrated at fairly low temperatures, becoming porous and fissured and such ores would therefore also have been ideal for use in early bloomeries. Ferrous carbonate decomposes less easily than the ferric hydroxides (dissociation temperatures are approximately 580 and 350°C respectively, although the latter may be considerably lower, depending on crystallinity and amount of silica present; initial porosity is also important) and whilst this was not too serious a problem in the Catalan furnace, where residence time could be controlled, most early bloomeries probably did not have a sufficiently high column of ore to allow efficient calcination. Sideritic ores would therefore generally have required pre-roasting and there is evidence for this at both of the investigated sites where siderite was smelted (i.e. the Romano-British site at Garden Hill and the middle Saxon site at Ramsbury). It should

be noted that ores composed mainly of ferric hydroxides were also roasted, e.g. at Wakerley (Iron Age to Romano-British) and Stamford (Saxo-Norman). In these cases the roasting would have improved the reducibility of compact pieces and, as Tylecote et al.[7] pointed out, would also have made the ore lumps easier to break up. Francois[72] emphasised that ores were not satisfactorily reduced if they were too compact, or if there was too little silica or too much lime in the gangue for the formation of a suitable slag.

For ease of reference, Francois divided the Catalan furnace into different regions (Fig. 3.1) corresponding to the various stages of ore reduction occurring towards the end of a well-conducted smelt. The actual extent of these regions was obviously very variable. In region 1, the ferric hydroxides were dehydrated and the ore lumps became highly fissured. The surface of the lump and the fissure walls were quickly reduced to magnetite by the action of carbon monoxide and generally the ore was sufficiently porous to be completely converted to magnetite before reduction to wüstite and iron commenced. Sometimes however the ore was too compact and did not become fissured and in these cases concentric layers of reduction products formed. In region 2, the commencement of reduction to metallic iron was observed and Francois recorded the development of a skin around the lumps composed of an aggregate of particles of iron and 'imperfectly formed slag'. This skin attained a thickness of 1-3 mm in the lower part of region 2 and was also seen to extend down into the cracks. Chemical analyses of ore fragments from the middle and lower parts of this region showed that the proportion of FeO to Fe_2O_3 increased, whilst the free silica (originally present as quartz) entered into combination. Lean et al.,[74] when investigating the reduction of jaspilite (a fine-grained hematite-quartzite), found that fayalite ($2FeO.SiO_2$) formed by a solid state

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diffusion reaction at temperatures as low as $650^{\circ}C$ and it must have been this reaction which was occurring during the ore's descent through region 2. The formation of fayalite would tend to slow down the reduction rate.

Both Francois[72] and Richard[71] noted the presence of large quantities of carbon powder in the flame. They assumed that it was finely-divided charcoal, but Morton and Wingrove[70] thought that the carbon resulted from the reaction $2CO \rightarrow C+CO_2$. This reaction is rapid at $500^{\circ}C$ and in the blast furnace results in substantial deposition of carbon both on the surface of the ore and in fissures. Morton and Wingrove provided evidence for this reaction in a medieval bloomery, but they were uncertain as to its general occurrence and extent. It is likely however that with the short columns of ore and relatively brief residence time in the upper parts of the furnace, the deposition of carbon would not have been extensive in most early bloomeries.

Francois[72] reported that the metallic envelopes of the ore lumps continued to develop in region 3 and here the temperatures were high enough to allow them to weld together at their points of contact. Lower down in this region, at an estimated temperature of $1000^{\circ}C$, the ore lumps become rounded as their interiors grew pasty. At this stage, a liquid slag started to separate, forming between the metal envelope and the pasty interior and tending to ooze out through pores in the iron. Within the iron skin, this slag was said to be a dirty greenish yellow colour and of a fayalitic composition (Percy[11] consistently referred to the slag composition as being that of a tribasic silicate, $3RO.SiO_3$ but later stated that this was the composition of olivine, which is actually $2RO.SiO_2$). In the region between the metal and the pasty interior, the slag was described as very liquid, chocolate brown

in colour and containing branching microscopic particles of iron which grew more abundant towards the interior. Both the slag and the pasty core apparently contained "microscopic shots of iron" as well as gas bubbles, although the description of the iron as branching and its distribution in the slag gives cause to suspect that it was actually wüstite rather than metallic iron (but metallic iron <u>may</u> show a branching form and this has been observed in the investigated slags; Fig. 3.2). The metallic envelopes of the ore lumps had branching projections on their inner surfaces and apparently thickened by growth of these. The iron evidently contained carbon and Percy stated that it frequently had "the aspect and grain of white cast-iron".[11]

There are a number of points in these detailed observations which are difficult to interpret in the light of present knowledge. The appearance of a very fluid slag of fayalite composition at around $1000^{\circ}C$ is unlikely and it must be assumed that either the temperature estimate was too low or the slag was of a lower melting point composition than pure fayalite, containing an excess of FeO and probably having been fluxed by other gangue components or by the fuel ash. Francois[72] and Percy[11] took the gas bubbles in the pasty interior of the ore lumps to be evidence of the penetration of reducing gas and the escape of gaseous products. However, although CO could have diffused in through the porous layer of iron, it is unlikely to have penetrated the apparently continuous slag film or to have reached the centre of the pasty mass. Sufficient carbon may have been deposited in fissures to enable further reduction of the ore's interior. Experimental work[75,76,77] has shown that at temperatures above $900^{\circ}C$, the amount of direct reduction by the reaction $Fe_nO_m + {_m}C$

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= nFe + mCO would have been minimal but this would have initiated the chain of reactions: $mCO + Fe_nO_m = nFe + mCO_2$

$$mCO_2 + mC = 2mCO \qquad \text{(Boudouard reaction)}$$
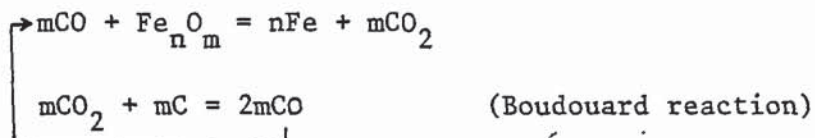
This provides a possible mechanism for the internal reduction of ore lumps even when a continuous film of slag is present. However, it is doubtful whether much carbon would have been deposited so far into the interior of the ore fragments. It also seems unlikely that such a mechanism was the principal means for completing reduction as it would have been so dependent on the structure of the ore after dehydration or calcination and on the amount of carbon initially deposited. A more probable explanation is that the ores, which were mostly sufficiently porous to be completely reduced to magnetite, were on their descent reduced to wüstite throughout. Further reduction, with nucleation and growth of metallic iron, would then have proceeded and whilst this would have occurred most extensively at the surface, the high porosity would have enabled iron to form at numerous nucleation centres within the body of the lump. This might account for the presence of Francois's "shots of iron" in the slag and pasty core if these were truly iron and not wüstite. By this stage, the ore would have descended to the higher temperature zones and the slag would have begun to liquate. The partially reduced core (consisting of FeO and $2FeO.SiO_2$ plus the remainder of the gangue components), which had itself become semi-fused, could then have started to dissolve in the liquid slag. The branching form of the metallic envelope's inner surface indicates that it grew by addition of iron ions and electrons which had diffused through the liquid slag. The slag itself must therefore have been reduced, probably both by CO gas and by decarburization of the metal. Experimental work on the reduction

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of iron from slag has been ambiguous and von Bogdandy and Engell[69] stated that it was not possible to decide whether the reduction of slag droplets as they trickle down inside the blast furnace takes place predominantly by reaction with coke or with CO. However, direct reduction in the case of slag beneath a porous iron shell is unlikely to have been significant because there would have been minimal contact between slag and charcoal. The observed high carbon content of the iron at this stage indicates that the overall rate of carburization and diffusion of carbon through the metal was equal to or slightly more rapid than the rate of decarburization. Experimental work[78] has confirmed that the rate of diffusion exceeds that of the reaction with the slag.

According to Francois,[72] in region 4 of the Catalan furnace, where the temperature was estimated as $1200-1300^\circ$C, the reduced ore lumps became flattened and all the iron particles welded together to form an iron sponge, whilst the fully liquid slag separated out. Once the slag had separated, further carburization of the upper part of the bloom could occur by the action of CO gas and by contact with charcoal, although the lower part tended to be decarburized at the same time by reaction with the basic slag beneath. The implication of these observations is that carburization and decarburization were actively occurring even when the bloom had formed and also that decarburization occurred as much as a result of slag/metal reactions as by oxidation in the tuyere zone. Tylecote et al.[7] placed much more emphasis on decarburization by oxidation and also stated that: "no change in carbon content of the bloom as a whole can take place during this stage ...". It is difficult to decide how important such reactions were in early bloomeries as their rate would have been dependent

on temperature and the amount of contact between slag and metal and between metal and CO or charcoal. Some reduction of the slag by charcoal at the bottom of the furnace probably occurred, as is shown by the polished section of slag from the bowl furnace reconstruction (Fig. 3.3), but this would not have been significant.

The reduction of the greillade (ore fines) in the Catalan furnace followed a similar path to that of the lump ore. In region A of Francois, calcination and reduction predomina ted; in region B reduction proceeded and the formation of slag began; in region C further reduction and liquation of the slag occurred. This sequence of events took place more rapidly than in the lump ore, but reduction was not complete and the first slags to be tapped were always very iron rich. The function of the greillade appears to have been to quickly form some iron which acted as a 'collector' for the iron reduced from the lump ore, thus allowing the formation of a sound bloom in the correct place. The rapid formation of a liquid slag would also have helped to protect the iron as it passed through the tuyere zone. It is likely that ore fines introduced into earlier bloomeries would have had a similar effect and it is interesting to note that Tylecote et al.[7] found that the best charge for their experimental shaft furnace consisted of ore ranging in size from fines to ~12 mm.

In early bloomeries, the reduction of ore and formation of slag must have followed a very similar course to that in the Catalan process. The detailed observations of Richard[71] and Francois[72] serve to emphasise the importance of the quality of the ore, which must ideally have become fissured and/or highly porous on dehydration or calcination to allow complete reduction. The amount and type of gangue present

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was also very important. Some appreciation of the bloomery operators'
skill can be gained, since it is clear that for efficient reduction the
early formation and separation of slag had to be avoided, hence the
descent rate of the ore needed to be controlled. For a given furnace,
the rate of blowing and the rates of charging ore and fuel would have
had to be carefully balanced and even the amount of charcoal put in
before the first lot of ore was probably important. If slag started
to form too early, the bloom would have been small and the remainder of
the ore would have been incorporated into the slag instead of being
completely reduced, thus making the slag extremely iron rich. As Morton
and Wingrove[5] pointed out, the wüstite content of the slag is therefore
to some extent a reflection of the ironworkers' skill. It should
however be realized that low losses of iron to the slag cannot be
directly used as the criterion for judging the competence of the early
bloomery operators. For instance, Tylecote et al.[7] found that slags
containing less than 45% FeO produced from Northamptonshire ores were
not easily tapped on account of their high viscosity at the operating
temperatures of the furnace. The amount of iron in bloomery slags
must therefore be the result of a compromise between high yields and
the need for low melting point, low viscosity slags.

CHAPTER 4

SLAG PETROLOGY

4.1 Introduction

Morton and Wingrove[4,5] first investigated archaeological slags in
terms of their mineralogy a decade ago and their approach has been used
in the course of much subsequent research.[6,14,79,80] The observed
mineralogy of Roman slags, i.e. wüstite ('FeO'), Fayalite ($2FeO.SiO_2$)
and glass, was taken as confirmation of the validity of plotting the
bulk compositions on the anorthite ($CaO.Al_2O_3.2SiO_2$)–FeO–SiO_2 'ternary'
to obtain melting temperatures. These authors also suggested that the
generally smaller proportions of wüstite in Medieval slags compared to
those of the Roman period (causing them to plot further away from the
FeO apex of the 'ternary') was a reflection of the improvements in
technique with time, leading to greater efficiency of furnace operation.
In addition, Morton and Wingrove found their Medieval slags from lean
Carboniferous ores to be characterized by the presence of the spinel
hercynite ($FeO.Al_2O_3$), whereas those from the rich (i.e. low gangue
content) hematite ores of the Lake District were similar in mineralogical
composition to the Roman slags they had investigated.

Widening the scope of Morton and Wingrove's work, a group of
researchers in Austria attempted to use observed mineralogy as a
criterion for classifying slags (see Sperl[6]). They examined a large
number of slags from iron smelting, smithing and refining processes as
well as from copper smelting. Dating from several centuries B.C. to
around 1500 A.D., this material was obtained from excavations in Austria
and Italy. Eighteen of the ironworking slags were chosen for detailed
mineralogical analysis. In a publication arising from this research,
Reimann and Sperl[79] noted that they found great difficulty in

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determining the crystallization sequences on the basis of the
observed structures. They concluded that the variety of structures
related to the variety of process-steps preceding solidification. In
a later publication Sperl[6] aimed to relate the mineralogies to
particular processes, but whilst he had proposed a classification of
slags on the basis of outward appearance, which seemed to be largely
process-dependent, he found it difficult to relate the mineralogical
composition and structure to slag morphology. In broad terms, only
three types of slag structure were considered to be recognisable:

(i) Fayalite slags containing wüstite and glass

(ii) Glassy slags with small proportions of fayalite and metallic
iron

(iii) Iron-rich slags with a high metallic content in addition to
glass and fayalite.

None of these types was found to be confined to any one category or
set of related categories in the proposed scheme of classification.

Todd,[14] after studying ore, slag and slag inclusions in metal from
a contemporary bloomery in Ethiopia and from a Roman site in Britain
(Longthorpe, Northants.), concluded that there is no complete
correlation possible between the compositions of the roasted ore,
furnace slag and the individual phases present in the slag.

The research of these authors has suggested that the mineralogical
composition and texture of archaeological slags was influenced by such
factors as ore composition and production technique. In the case of
the latter, relationships with furnace type and with date (since
techniques must have changed through time) might be expected and
variation in process-steps, giving rise to differing conditions before

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and during slag solidification might also be recognisable. The present work was undertaken to investigate the extent to which slag mineralogy reflects these factors. The study has been confined to smelting slags in order to limit the number of processes which have to be taken into consideration. A detailed comparison of mineralogical compositions and textures is therefore justified. Slags from Early Iron Age, Roman and some later sites (see Chapter 2) have been examined, using optical microscopy (both reflected and transmitted light) and X-ray diffraction (XRD), scanning electron microscope (SEM) and electron microprobe analysis. A description of the mineralogical composition of the slags is followed by an evaluation of the factors affecting mineralogy. The compositions of the individual phases and the significance of the compositional variation are then discussed. Finally, the mineralogical structures are described and interpreted.

4.2 Mineralogical composition

4.2.1 Microscopical investigation of mineral suites

Brief descriptions of the mineral suites observed, with approximate percentage figures indicating the overall mineralogical compositions, are set out in Table 4.1. The percentage estimates were made on polished sections with the aid of diagrams originally published by Shvetsov[81] and using the assumption that the area covered by each mineral is directly proportional to its volume. Difficulties are encountered when anisotropic phases (i.e. those with one or two dimensions greater than the other(s), e.g. fayalite, particularly in its lath-like habit) show a preferred orientation. In addition, it was found difficult to estimate the proportions of minerals occurring as fine intergrowths (e.g. intergrowths of hercynite or leucite with fayalite). As might be expected, fayalite, wüstite and glass are the

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major components, fayalite and glass being ubiquitous and wüstite

absent from only one archaeological slag. 'Glass' refers to the

interstitial material which has obviously solidified last; it is not

intended as an accurate description of that material's state (see

sub section 4.4.6). Perhaps more surprising is the presence of

hercynite ($FeO.Al_2O_3$) and leucite ($K_2O.Al_2O_3.4SiO_2$) in the majority of

slags. Magnetite occurs in several slags, but generally only in small

quantities and its common association with chilled surfaces (see sub

section 4.4.7) strongly argues that in these cases, it is a result of

superficial oxidation of the slag after it left the furnace. Also

associated with these chilled surfaces in some slags are spinels, of

hercynite composition at the core, but with more iron-rich rims, and

tiny lath-like crystals rich in calcium. Finally, tiny anhedral

crystals of a phase high in calcium and phosphorus have been observed

within patches of leucite in a few samples. Metallic iron is common

in slags of all periods regardless of furnace type and its usually

irregular form suggests that it was present as solid grains suspended

in the liquid slag. There is evidence that the iron was molten in

a few cases.

4.2.2 X-ray diffraction analysis

The results of the X-ray diffraction analyses of the slags is

summarised in Table 4.2. The method is not very sensitive, particularly

for determining relative proportions of minerals, since the main

fayalite peak (2.501 Å) is close to the main magnetite peak (2.532 Å)

and a major wüstite peak (2.49 Å; $^I/I_1$=80). In addition, another major

wüstite peak (at 1.523 Å; $^I/I_1$=60) coincides with an important fayalite

peak (1.523 Å; $^I/I_1$=70). Further, fayalite belongs to the orthorhombic

system and shows a large number of reflections, many of them of

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relatively high intensity, and these may mask peaks of minerals present in small quantities. The X-ray diffraction traces were obtained for angles of 2θ between 10° and a minimum of 75° using Co Kα radiation with an Fe filter. The peaks were indexed using the Powder Diffraction File compiled by the Joint Committee on Powder Diffraction Standards.

The X-ray diffraction analyses at least serve to confirm the identity of the major minerals observed in thin and polished sections. This particular analytical technique is probably of greater value when the identity of the iron oxides is in doubt, as in Millbrook E, where a small amount of an anhedral phase, associated with leucite and of slightly higher reflectivity than the wüstite dendrites, was tentatively identified as magnetite. X-ray diffraction analysis supported this identification. Although small amounts of leucite and hercynite were commonly observed in polished section, X-ray diffraction analysis failed to detect the former and only rarely detected the latter. This is because the high level of background radiation masks small peaks (even some fayalite peaks with a low relative intensity cannot be distinguished). Sperl[6] reported possible traces of anorthite and also suggested that many of the unindexed peaks may be attributed to the iron hydroxide (a corrosion product) seen under the microscope. In the present study, no peaks were observed corresponding to either anorthite or iron hydroxide. In view of the high level of background radiation, it seems unlikely that small quantities of anorthite, indiscernible in thin section, would actually be distinguishable on an X-ray diffraction trace, whether of primary origin, or a devitrification product of the glass, as Sperl suggested.

When there is partial or complete solid solution between endmembers

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of a mineral group, X-ray diffraction analysis can indicate the approximate composition of the member under invesitgation. In the two slags in which hercynite was positively identified, it was found that the peaks are consistently 0.02 $\overset{o}{A}$ higher than they should be for pure hercynite, i.e. there is a shift towards the magnetite peaks (see Table 4.3). The spinel is therefore more iron-rich than pure hercynite and should ideally be written as $FeO.(Fe_2O_3, Al_2O_3)$.

4.2.3 Factors affecting mineralogical composition

A comparison of the mineralogies of the investigated slags has revealed no consistent trends and it must be concluded that the mineralogical compositions do not directly reflect either the supposed furnace type or the period in which they were produced (compare Appendix A, which lists furnace type and date for each slag, with Table 4.1 which summarises their mineralogy; further archaeological details are given in Chapter 2). Some tap slags for instance contain only a small proportion of primary wüstite (e.g. Roman period slags from Bulwick, Blind Eye Quarry and some of those from Berkhamsted), but this is not a general feature and is not age related, the Saxo-Norman Stamford slags and medieval South Witham slags containing a much higher proportion than the Roman ones quoted above. There is also no clear relationship with the scale of the iron smelting operations although it might be expected that a large-scale operation where iron was regularly produced would have been run more efficiently than a small unit producing iron sporadically or perhaps just once. However, scale is difficult to assess since the furnaces excavated at the investigated sites have either been single or in small groups and even when several such groups are clustered together (as at Berkhamsted and in the area around Bulwick), their contemporaneity has not been

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established. Leucite is apparently less common in tap slags than in furnace slags, although this might be partly due to the variation in texture. In furnace slags, it is mostly present as irregularly-shaped patches whereas in tap slags it generally occurs interstitially as fine to very fine intergrowths with other minerals and may be difficult to distinguish from glass (see sub section 4.4.5).

The absence of a clear relationship between the observed mineralogy of slags and either their age or the type of furnace in which they were produced suggests that the mineralogy depends largely on chemical composition. The composition of the ore should be reflected in that of the slag and should therefore directly influence mineralogy. Morton and Wingrove[5] showed that the presence of spinels (usually hercynite) in medieval slags produced from 'lean' Carboniferous ores of the Midlands, West Yorkshire and Kent distinguished them from slags produced from the rich Lake District haematite ores. According to the authors, the small proportion of gangue in the Lake District ores is reflected in the very small amounts of phases other than wüstite, fayalite and glass which were found in the slags produced from them. Morton and Wingrove also considered that such slags would be similar to those of the Roman period, since the Romans tended to exploit only rich ores.

In the present study, slags of varying periods have been examined. They are derived from different geographical locations where a variety of different ores were available (see Chapter 2). Ranging from lean chamositic-sideritic oolites of the Northampton Sand Ironstone and the nodular siderites of the Wadhurst Clay Ironstone (averaging 50-60% 'Fe$_2$O$_3$') to the somewhat richer goethite-lepidocrocite nodules from the Ironstone Junction Band of the Rutland Formation (averaging

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70-80% Fe_2O_3), the variation in composition of these ores might be expected to be reflected in the mineralogies of the slags. However, if only those sites are considered where ore samples were excavated or where the source of the ore is reasonably certain (see Table 4.4), all the ores have a similar iron content (~70% 'Fe_2O_3'; the iron has been calculated as Fe_2O_3 for easy comparison), except the Wadhurst Clay Ironstone which is somewhat leaner. Before any comparisons are made, it should be noted that the proportion of volatiles is variable, so that the iron content of raw ores is not a particularly accurate reflection of the amount of gangue. It should also be remembered that the ironstones, whether excavated with the slag or locally derived, may nevertheless be unrepresentative of the ore used. Ore fragments are rarely found in any abundance on ancient ironworking sites and it is almost impossible to be certain that those samples were not rejected for some reason or were not mixed with other material from a different source.

The iron content of the ores under discussion is slightly higher than the Bourne Pool and Rushall ores analysed by Morton and Wingrove,[5] but those authors would presumably still have predicted the presence of spinel in the slags. The relationship between the proportion of Al_2O_3 in the ores and the amount of hercynite observed in the slags is less predictable however (see Table 4.4). Compare, for instance, the Stamford material with that obtained from the reconstructions: the raw Stamford ore contains 3.65% Al_2O_3 and the slag showed no hercynite in one sample but 15-20% in another, while the Wadhurst Clay Ironstone contains an average of 3.54% Al_2O_3 yet most of the reconstruction slags contain much less than 1% spinel and in RR1 and RR2 this is an extremely iron-rich variety (72% 'FeO', compared with the stoichiometric value for hercynite of 41%). The occurrence of leucite similarly

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cannot be related to the content of K_2O in the ores. All the ores, and the Ironstone Junction-Band in particular, contain little K_2O yet leucite is present in varying amounts (0-20%) in slags from all the sites referred to in Table 4.4 except Bulwick. It might be thought that since both hercynite and leucite contain relatively high proportions of Al_2O_3 (59% in pure hercynite and 23% in pure leucite), the two phases would be 'competing' for the available Al_2O_3, but there is no evidence for a mutually exclusive relationship and there is always abundant alumina remaining in the glass. The presence of the calcium-rich crystallites and the calcium-phosphorus phase also appears to be independent of ore type, as they occur in slags produced from a variety of ores in different geographical areas (see Table 4.1).

To summarise, although Morton and Wingrove[5] were able to relate ore composition to slag mineralogy in their study, no clear relationship was found for the material under investigation. This suggests that although large variations in ore composition are directly reflected by slag mineralogy, there are other factors which influence slag composition (and hence mineralogy). Further treatment of this subject is given in Chapter 5. In addition, for any given slag composition, the rate of cooling determines textures and may also affect the mineralogy. Certain textures displayed by some slags also suggest that the gas phase can also influence mineralogy. These points are enlarged upon in Section 4.4 of this Chapter. Morton and Wingrove[5] suggest that in general the Romans used only rich ores and the slags consequently tended to show a simple 'ideal' mineralogy of wüstite + fayalite + glass, but in the present study it has been found that a wide variety of ore sources were exploited during the Roman period (and earlier) and the mineralogy of these slags is no less complex than

that of later material. It is also clear that when ores from different sources are chemically similar, it may be very difficult to identify which one was used simply on the basis of the slag. This problem is the subject of Chapter 5.

No clear relationship exists between slag mineralogy and either age, furnace type or ore source for the material investigated in the present study. At this point, it is necessary to try to evaluate the effect of the slag composition itself. The best method available for predicting mineralogy is the application of equilibrium phase diagrams to the data, but a number of problems are involved. Firstly, for this technique to be valid, the slags must have passed through a liquid state. None of the slags of this study contain high temperature phases, nor do they appear to show the heterogeneity in mineralogical composition and structure which might be expected if they had not been completely molten and they therefore seem to meet the first requirement. Although at the high temperatures of contemporary iron- and steel-making processes, a close approach to equilibrium is often realized, at the much lower temperatures of the bloomery[7,73] equilibrium cannot be expected to be attained. Furthermore, the often very rapid rate of cooling would have prevented equilibrium crystallization. Phase diagrams are therefore not directly applicable to bloomery slags. In addition, the bloomery process was not necessarily a closed system as further charges of ore and charcoal could be added during smelting and the slag could be continuously drained from the bloom either by formation of a furnace bottom beneath the metal sponge or by tapping. As the slag cooled it could also be partly oxidised, either inside the furnace on cessation of blowing or, if tapped, on contact with the air outside. Sperl[6] also suggests that moisture in the slag channel may be

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responsible for some oxidation of tap slag, although no mechanism is suggested. Slag solidifies and cools so rapidly on tapping that any oxidation is superficial (the mineralogical evidence for this is discussed in a later sub-section) and this, combined with the fact that surface moisture would be lost by evaporation on contact with the very hot slag (it seems unlikely that much, if any, steam so generated would penetrate into the possibly still liquid centre of the slag), suggests that moisture in the slag channel probably does not cause significant oxidation. Finally, phase diagrams of necessity only deal with a limited number of components and the few that have been formulated for three or more components of relevance to bloomery slags are complicated. Slags consist of a complex mixture of many oxides. Minor components may not be accommodated in the lattices of the major minerals crystallizing out and so become concentrated in the remaining liquid. In addition, rapid non-equilibrium cooling is equivalent to fractional crystallization in that instead of being able to react with the liquid, the first-formed crystals are effectively removed from the system by having layers of a different composition precipitated round them. As crystallization proceeds, the composition of the remaining liquid may therefore alter dramatically and the phase diagram most relevant to the original bulk composition may be inapplicable to the late-stage liquids.

Providing the limitations of the technique are fully considered, the application of phase diagrams to the bulk compositions of slags can provide useful information regarding the mineralogy of slags.

Iron oxide and silica are the two major components of all the slags investigated, while alumina and lime are the most important minor

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components. Full analyses of all the slags are presented in Appendix
C. If only iron oxide and silica are taken into consideration, the
oxidation state of the iron affects the phases formed and the slags
should therefore be interpreted in terms of the $FeO-Fe_2O_3-SiO_2$ system
(Fig. 4.1). Chemical analysis shows the slags contain a small
proportion of Fe^{3+} relative to Fe^{2+} ($\frac{Fe_2O_3}{FeO}$ does not exceed 0.3L and
is usually much less) and the extreme left hand side of the ternary
is therefore the most relevant part. However, the quantity of Fe_2O_3
determined may not represent that originally present in the slag.
Morton and Wingrove[4] argued that in the strongly reducing conditions
within the furnace, the proportion of Fe^{3+} is likely to have been
negligible and suggested that oxidation on tapping was responsible
for the Fe^{3+} found on analysis. This point is significant when
estimating melting temperatures or assessing the relationship of
mineralogy to process, but is less important when assessing the
relationship of mineralogy to bulk composition; in the latter case, the
proportion of Fe^{3+} determined will only complicate interpretation if
post-solidification oxidation has occurred. Weathering is the most
likely cause of such oxidation. Although Morton and Wingrove[4] found
no evidence for oxidation during burial of a fragment of Roman slag,
Sperl[6] did identify weathering products (mainly ferric hydroxides)
in his samples and the yellowish-brown infillings of pores and cracks
commonly observed in thin sections of the material under investigation
indicate that it too has undergone some oxidation. However, the
effects of weathering are likely to be superficial because of the slow
rate of solid state diffusion and the overall Fe^{3+}/Fe^{2+} ratio should
not be seriously affected. In addition, the TEMA mill used in sample
preparation carried a warning that prolonged grinding (i.e. for more

than 45 seconds) may cause oxidation and in this case the grinding times of 25-35 seconds used should have avoided this problem. It is not known whether the 20 minute periods required for powdering samples in the small ball mill were sufficient to cause significant oxidation.

In brief, the proportions of Fe^{3+} determined for the slags in this study are relatively small and may originally have been even smaller, depending on the degree of post-solidification weathering and perhaps on the grinding method. It is therefore reasonable to begin the interpretation of the mineralogy simply in terms of the $FeO-SiO_2$ system. Phase relations in this system can be conveniently shown on a pseudo-binary as determined by Bowen and Schairer[82] (Fig. 4.1). It can be seen from this diagram that slags containing 29.5 wt% SiO_2 (i.e. the stoichiometric value for fayalite) or less should crystallize as a mixture of wüstite and fayalite and most slags conform in that wüstite and fayalite are the main constituents. Some slags (NOR. 1, Millbrook D and all those from furnace reconstructions) contain just over 30% SiO_2 and these should theoretically crystallize a very small proportion of tridymite in addition to fayalite (which is the primary phase). Tridymite has not been detected and in these particular slags the excess SiO_2 has given rise to an increase in the proportion of glass compared with the other slags (see Table 4.1). It would also be predicted from the simple $FeO-SiO_2$ system that slags containing more than 29.5 wt% SiO_2 should not contain any wüstite, but in practice, these 'high silica' slags do contain magnetite. It can be seen from Figure 4.2 that these slags fall into the fayalite-magnetite-tridymite stability triangle of the $FeO-Fe_2O_3-SiO_2$ system, hence iron oxide is stable as a separate phase in slags which contain an excess of SiO_2 over the fayalite composition.

Alumina is an important component, generally occurring in much higher proportions than the other minor oxides (see Appendix C). It would therefore now be valuable to consider the slag mineralogy in terms of Al_2O_3 as well as iron oxides and silica. The Al_2O_3-FeO-Fe_2O_3-SiO_2 system is highly complex (see Fig. 4.3) and as in the previous case, it is convenient to ignore the small proportion of Fe^{3+}. The phase relations in the system FeO-Al_2O_3-SiO_2 are presented in Figure 4.4; the compositions of the slags are also shown. Most of the slags plot in the wüstite-fayalite-hercynite compatibility triangle and, except for three samples, they contain all three phases as would be predicted. No hercynite was observed in Caerwent (31), GH2 (19) or NOR 2 (62) and it is significant that these three have the lowest alumina contents (2.46, 2.95 and 1.74 weight % respectively compared with an average of 5.04 wt%). It is possible that hercynite is present, but in such small quantities that it is undetectable. In view of the predicted crystallization paths (see Fig. 4.5) and the absence of any other alumina-rich phases, it seems more probable that the alumina remained in the final liquid which solidified as glass rather than the ternary eutectic of hercynite + wüstite + fayalite. Microprobe analysis of the glass (see Appendix B) supports this hypothesis.

One sample (Millbrook E, no. 56) falls in the fayalite-wüstite$_{ss}$ area (a small proportion of alumina is soluble in wüstite) and should consist only of these two phases. However, despite the extremely low alumina content (0.81 weight %), some hercynite was observed in two polished sections. As it is unlikely that both sections are unrepresentative, the presence of hercynite indicates non-equilibrium conditions (the general furnace temperature was possibly only a little

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higher than the slag liquidus). The alumina was not accommodated in the wüstite lattice and therefore remained free to form other phases. Unlike the three slags discussed above, the proportion of glass is very small (estimated as 2%) so that some hercynite might be expected to have crystallized from the last liquid before final solidification.

A few slags fall outside the wüstite-fayalite-hercynite and fayalite-wüstite$_{ss}$ compatibility triangles, four plotting in the fayalite-hercynite-iron cordierite compatibility triangle and five in the fayalite-iron cordierite-tridymite compatibility triangle. From the 'ternary' (i.e. Fig. 4.4) it can be predicted that the maximum amounts of cordierite and tridymite which should crystallize from these slags is 23% (in 16) and 6% (in 52) respectively, yet neither phase was detected in any of the samples. Eight of the slags contain particularly high proportions of glass (average 35%) and since all plot in the fayalite primary phase field, they presumably solidified before the liquid composition reached the peritectic (in the case of 15, 51 and 57) or even the cotectic (in the case of 11, 14, 32, 50 and 52). It appears that the higher silica slags are more prone to solidify as glass than those richer in iron, a tendency noted in modern acid slags. Although cooling rate must have some effect on the proportion of glass, it is significant that all but two of these particular samples are furnace slags and have cooled relatively slowly. The presence of some magnetite and other spinel in these slags also suggests that the system was out of equilibrium and this may have suppressed crystallization of cordierite and tridymite. Even if the system $FeO-Fe_2O_3-Al_2O_3-SiO_2$ is considered (see for instance the work of Muan in J. Am. Ceram. Soc. 1957[83]), there seems to be no other explanation for the presence of iron oxide and spinel and the absence of cordierite and/or tridymite.

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One slag (61) plots very near the boundary of the wüstite-fayalite-hercynite compatibility triangle and it appears that in this case a slight shift from equilibrium has caused it to crystallize these three phases, plus a 'normal' amount of glass, rather than fayalite, hercynite and cordierite, as would have been predicted.

In terms of quantity, CaO is second to Al_2O_3 in its importance and its possible influence on mineralogy should be evaluated. Reimann and Sperl[79] and Sperl[85] used the $CaO-FeO-SiO_2$ 'ternary' (Fig. 4.6) to compare mineralogy with composition. All the iron oxide was assumed to be FeO and 'CaO' includes all oxides except FeO and SiO_2. No justification for this method was given and it seems strange to add all the remaining acid and basic cations together in these circumstances, particularly since the proportion of alumina is far from negligible, often greatly exceeding that of CaO. Sperl[85] plotted both the chemical compositions of his slags and the calculated proportions of the phases anorthite, wüstite and fayalite on the $CaO-FeO-SiO_2$ ternary and concluded that there is little correlation between the two, except in the iron-rich apex. In view of the compositions of the slags, such an approach seems to be of very limited value for the comparison of mineralogy and composition.

Morton and Wingrove[4] suggested the use of the $CaO.Al_2O_3.2SiO_2$ (anorthite)-SiO_2-FeO plane of the quaternary system $CaO.Al_2O_3.SiO_2$-FeO in order to consider bloomery slags in terms of their four main components (see Fig. 4.7). The authors argued that any Fe_2O_3 present in the slag resulted from oxidation after tapping and for their purpose (which seems to be mainly the determination of melting points), the calculation of all iron oxide as FeO was therefore justified. This method is useful

providing there is not a large excess of Al_2O_3 over CaO or vice-versa.
To take an extreme example, analysis (i.e. calculated tap analysis)
number 7 of Morton and Wingrove showed 0.37% CaO and 13.52% Al_2O_3 and
calculating this as they described gives 1.84% anorthite, 46.62% SiO_2
and 33.59% FeO, with an excess of 12.89% Al_2O_3, which they assumed
to have dissolved in the 'anorthite' (the anorthite was equated with
the glass phase). In this case, the anorthite-SiO_2-FeO 'ternary' is
inadequate for determining phase relations or melting temperatures.
In their later work on medieval bloomery slags[5], Morton and Wingrove do
acknowledge that two samples containing 14.50 and 13.57% Al_2O_3 and
1.13 and 2.70% CaO+MgO respectively (they consider that adding MgO to
CaO in molecular proportions will ensure calculation of the maximum
percentages of the constituents) are more accurately represented on the
Al_2O_3-SiO_2-FeO ternary rather than on the anorthite-SiO_2-FeO diagram.

Providing the compositions can reasonably be represented on the
anorthite-SiO_2-FeO diagram, Morton and Wingrove's method is a valid
means of considering bloomery slags in terms of their four main components.
However, in trying to justify the use of this 'ternary', the authors
have made the error of expecting actual mineralogy to conform with that
calculated. Line traces of the phases present in one of their samples,
made using an electron microprobe analyser, revealed that the glass
contained Ca, Al and Si with a small proportion of iron. Morton and
Wingrove regarded this as confirmation that the glass was anorthite.
Had a full analysis been carried out, it is likely that significant
quantities of other oxides (e.g. K_2O, P_2O_5) would have been found,
although the authors would perhaps have argued that these would all be
dissolved in the 'anorthite'. The glass results from solidification of
the final liquid and therefore must contain all the oxides which have

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not been accommodated in the lattices of the minerals which have previously crystallized. If that glass approximates to the composition of anorthite, then the slag can conveniently be represented on the anorthite-SiO_2-FeO 'ternary', but the glass is not anorthite as such. In their calculations of mineralogy, Morton and Wingrove first determined the proportion of anorthite, then assumed that the maximum amount of fayalite is formed from the remainder of the SiO_2 plus the FeO, and if any FeO remains, this represents the proportion of wüstite. Taking this reasoning to its logical conclusion, the authors appear to have assumed that the amount of CaO and/or Al_2O_3 determines the proportion of glass and that this in turn determines the proportion of fayalite, whilst the presence of wüstite depends on there being an excess of FeO over that required to form the fayalite. These assumptions cannot be justified. The authors' confusion is further illustrated by their uncertainty as to whether anorthite (i.e. the glass) forms before hercynite.[5] Subsequent authors[6,7,14] continue to use the term 'anorthite' when referring to the glass phase and it appears that Morton and Wingrove's confusion has persisted in the literature.

The slags of the present study have been plotted on the anorthite-SiO_2-FeO diagram (Figure 4.6) after the method of Morton and Wingrove.[4] All fall in the fayalite primary phase field, except 9 and 92 which plot in the hercynite primary phase field and 7, 31 and 56 which plot in the wüstite primary phase field. It is also noticeable that the slags from furnace reconstructions (11,14,15,50,51, 52 and 57) and NOR 1 (32) plot in a group, separate from the majority of the slags and further away from the FeO apex. The pattern is therefore almost identical to the plot on the FeO-Al_2O_3-SiO_2 'ternary' (compare Fig. 4.4). This indicates that the compositions of these slags can be equally well

represented on either of the two phase diagrams, although in the experience of the present author, the latter is easier to use for predicting mineralogy. Estimates of melting temperature for the majority of the slags are the same (i.e. between 1150 and 1200°C), whichever diagram is used, although the reconstruction slags plot at slightly lower temperatures (1100 to 1150°C) on the anorthite-SiO_2-FeO 'ternary'.

A computer programme is now available to aid in selection of the most applicable ternary phase diagram for a particular analysis.[79] Five ternary systems (Al_2O_3-anorthite($CaO.Al_2O_3.2SiO_2$)-FeO, anorthite-SiO_2-FeO, anorthite-wollastonite($CaO.SiO_2$)-FeO, gehlenite($2CaO.Al_2O_3.SiO_2$)-wollastonite-FeO and anorthite-gehlenite-FeO) within the quaternary system CaO-FeO-Al_2O_3-SiO_2 were chosen as being widely applicable to silicate slags and the computer programme will select the most relevant one on the basis of the bulk analysis of a slag. In order to include minor oxides, the quaternary system is actually expanded to CaO(+BaO+Na_2O+K_2O)-FeO(+MnO+MgO)-Al_2O_3-SiO_2.

The discussion above has shown that the major mineral phases can usually be accurately predicted by plotting the three or four most abundant oxides on either the Al_2O_3-SiO_2-FeO or anorthite-SiO_2-FeO 'ternaries'. The usefulness of the CaO-SiO_2-FeO system is considered to be very limited. In some cases the FeO-Fe_2O_3-SiO_2 phase diagram is a valuable additional ternary for interpreting mineralogy. However, the presence of the potassium alumino-silicate phase observed in many of the slags, or the calcium phosphate mineral also seen in some, would not be predicted from these ternaries which are of necessity a simplification of the real situation. It is evident that crystallization of the major phases (wüstite, fayalite and also hercynite) which hold only small proportions of other oxides in solid solution causes the remaining liquid composition to become so enriched in minor oxides that

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the above ternaries are no longer valid and the last liquid must be considered in terms of other systems.

An indication of possible liquid composition after all, or almost all, the major phases have crystallized can be obtained by using estimated mineral percentages (based on examination of thin or polished sections) in conjunction with chemical analyses. The method is illustrated in Table 4.5 for two examples, chosen at random. The liquid composition so calculated is only a rough estimate because of inaccuracies in estimating volume percentages of minerals from polished sections and because the extent of substitution in the different phases is difficult to take into account. The subject of substitution is further discussed in the following section. It is nevertheless apparent from Table 4.5 that K_2O, P_2O_5 and CaO are significant components of the remaining liquid. Unfortunately little is known of the phase relationships in systems including these oxides and FeO, SiO_2 or Al_2O_3. However, the system CaO-iron oxide-P_2O_5 has been investigated because of its relevance to the basic bessemer process and work has also been done on the system $K_2O-Al_2O_3-SiO_2-FeO$.[86,87] In the case of the latter system, phase equilibrium diagrams are available for the ternary subsystems $K_2O-SiO_2-Al_2O_3$, $K_2O.2SiO_2-FeO-SiO_2$ and for leucite($K_2O.Al_2O_3.4SiO_2$)-fayalite-SiO_2. The common occurrence of leucite, often as an intergrowth with fayalite, in the slags studied suggests that the leucite-fayalite-silica system is the most applicable. A particularly interesting feature of the ternary, shown in Fig. 4.8, is the relatively large area of low temperature (as low as $1120^{\circ}C$) liquid immiscibility, the two liquids being in equilibrium with crystals of fayalite or tridymite (or both along the conjugate line A-A^1). The extent of the associated immiscibility volume in the quaternary

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K_2O-FeO-Al_2O_3-SiO_2 is not well known, although it does not intersect any of the three faces of the tetrahedron represented by the ternaries K_2O-FeO-SiO_2, FeO-SiO_2-Al_2O_3 or SiO_2-Al_2O_3-K_2O. To return to the leucite-fayalite-silica system, the immiscibility region encompasses liquids with compositions ranging from approximately 52% FeO, 43% SiO_2, 2.5% K_2O, 2.5% Al_2O_3 to approximately 10% FeO, 74% SiO_2, 8% K_2O, 8% Al_2O_3 and it is therefore possible that some evidence for immiscibility may be found in the interstitial glass of bloomery slags.

The possible 'late liquids' calculated for RAM 5 and GO 4 have been plotted on the leucite-fayalite-SiO_2 ternary, using a similar method to that used by Morton and Wingrove[4] for the anorthite-FeO-SiO_2 diagram. In this case, the maximum amount of fayalite was first determined, followed by the maximum amount of leucite and these figures were then rounded up to 100% with the remainder of the SiO_2. The RAM 5 liquid plots on the leucite-fayalite cotectic and leucite-fayalite intergrowths have been observed in polished section (see following subsection). The GO 4 liquid falls in the two liquid region, although no evidence for immiscibility has been microscopically observed in this slag.

Liquid immiscibility is also a feature of the CaO-FeO-P_2O_5 system. The two liquid field is large and extends right into the FeO apex (see Fig. 4.9a), although work by Oelsen and Maetz[88] suggests that the presence of even small amounts of SiO_2 causes contraction of this field (see Fig. 4.9b). This is particularly significant for bloomery slags as a high proportion of SiO_2 is to be expected in late liquids. It should also be noted that the two liquids exist at temperatures ranging from just under 1300°C to over 1600°C, i.e. higher temperatures than those expected in normal bloomery operation. In terms of their

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CaO, P_2O_5 and FeO contents, the late liquids calculated for RAM 5 and GO 4 plot in the two liquid field of Fig. 4.9a, although their high proportions of SiO_2 (approximately 50 wt%) would presumably cause the disappearance of this field. No information is available about the phases which might precipitate from liquids containing all four oxides. It is also uncertain whether the presence of K_2O and Al_2O_3 would enhance or suppress the tendency to form two liquids although there is also an immiscibility gap in the system $K_2O-P_2O_5-FeO$. No clear evidence for immiscibility has however been found in either thin or polished sections and the occurrence in some slags of a crystalline phase containing high CaO and P_2O_5 within areas of leucite (see Fig. 4.20 and text of following section) suggests that no separation has occurred in these particular cases at least.

4.3 Compositions of individual phases

It has been argued in the previous section that a reasonably accurate indication of the gross mineralogical composition can be obtained by the application of certain phase diagrams to the bulk compositions of slags. The prediction of phases appearing at a late stage in crystallization is more difficult, partly because of the complexity of the late liquids and the lack of information on systems including oxides such as K_2O and P_2O_5 and partly because of the difficulties encountered in trying to estimate the compositions of these liquids. One problem is the substitution of minor components into the major phases. Fayalite, wüstite and hercynite are all end-members of solid solution series and their crystal lattices are also able to accommodate limited quantities of oxides other than those showing continuous substitution. It would therefore be useful at this stage to assess the compositional variation shown by the individual phases.

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The compositions of the phases have been investigated using the electron probe micro-analyser and the scanning electron microscope with a Kevex attachment. The former instrument has a wavelength-dispersive X-ray spectrometer which enables the proportions of elements to be determined to an accuracy of approximately 0.1 wt%. The Kevex attachment of the SEM has an energy-dispersive X-ray spectrometer and permits qualitative analyses of phases; its great advantage is the speed with which the analysis can be carried out and recorded. Further details of these techniques and tables of the electron probe analyses are given in Appendix B.

4.3.1 Fayalite

Fayalite is the major phase in all the slags investigated. This mineral is so named because it was believed to occur in the volcanic rocks of Fayal Island in the Azores, although ironically it is now believed that the 'rock' analysed was actually slag, carried as ship's ballast and dumped on the island. Fayalite is the iron end-member of the olivine group, which shows continuous variation from $2FeO.SiO_2$ to $2MgO.SiO_2$. There is also a limited replacement of (Mg,Fe^{2+}) by Mn in most natural olivines, while in synthetic systems it has been found that there is complete solid solution between $2FeO.SiO_2$ and $CaO.FeO.SiO_2$ (kirschsteinite or iron monticellite; see Fig. 4.10), which also has an olivine type structure.[89]

As might be expected, although most slags contain little MgO, this is found to be concentrated largely in the fayalite. One of the most striking examples is RAM 5: the fayalite has an average content of 2.85% MgO, while wüstite, hercynite and glass contain averages of 0.13, 0.30 and 0.02% MgO respectively (the bulk analysis of the Ramsbury slags shows 1.08% Mg). The average MgO content for all the fayalites

investigated (62 in all) is low: $\bar{x}$ = 1.12, although there is a wide variation (sample standard deviation, σ = 1.01). Even within the different source areas MgO values fluctuate and this probably reflects local variation in the MgO content of the ores. The averages and standard deviations for several minor oxides are shown in Table 4.6.

MnO shows a similar behaviour to MgO, but has slightly higher averages, although once again the content varies greatly. The overall pattern of MnO contents in the fayalite appears related to that shown by the ores, these having a higher (but still very variable) content of MnO than MgO.

It can be seen from Table 4.6 that, in contrast to the pattern shown by MgO and MnO, the mean CaO contents of the fayalites in Wealden and Northamptonshire slags are less than those for their respective ores, although the variation in this oxide is so great as to make the averages practically meaningless. The CaO content of slags may not be directly related to that of the ores (this is discussed in Chapter 5) and other external factors may account for some of the variation in the fayalite composition. However, the average CaO content of the olivines is also less than that determined for the whole slags (for Wealden slags, $\bar{x}$ = 3.36, σ = 1.18, n = 8; for Northamptonshire slags, $\bar{x}$ = 1.71, σ = 1.28, n = 7). This suggests that the calcium does not preferentially substitute in the olivine lattice, but is either taken up by other minerals or remains in the liquid, at least until a late stage. The solid solution series between fayalite and kirschsteinite indicates that calcium is relatively easily accommodated in the olivine lattice and it might be assumed that the proportion of calcium in fayalite must therefore be related to the amount of competition from other calcium-containing minerals. However, neither wüstite nor hercynite can

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take up significant quantities of calcium, while the high calcium
phases only crystallize out at a very late stage and cannot affect the
fayalite composition. The calcium must therefore remain in the liquid
and electron probe microanalyses of the glass phase (see Appendix B)
confirms this. The ionic radius for Ca^{2+} (1.20Å for its common 8-fold
co-ordination, but a little less for octahedral co-ordination in olivine)
is greater than that for Fe^{2+} or Mg^{2+} (0.86 and 0.80Å respectively in
octahedral co-ordination[90]) and this plus the reluctance of Ca^{2+} to
enter six-fold co-ordination probably explains the unexpected rejection
of calcium from the olivine lattice. An examination of individual
fayalite analyses shows that there are exceptions to this general
pattern, some showing high calcium contents (e.g. 5.65 and 4.80 wt%
CaO in two fayalites from GH 653a) and others showing very variable
composition (e.g. in GO4, where CaO was determined as 2.60 wt% in one
olivine and 0.44% in another).

Evidence has been obtained that as crystallization proceeds,
there is an increase in the degree of substitution of Ca^{2+} for Fe^{2+}.
Kevex analysis of an olivine in GH 653a showed that at the centre of
the crystal, the composition is near 'normal', but towards the edge,
there is a marked increase in Ca-content and olivine crystallites
in the glass are similarly close to the kirschsteinite end-member of the
$2FeO.SiO_2 - CaO.FeO.SiO_2$ solid solution series (see Fig. 4.11). There
is a melting point minimum in that solid solution series of 1117°C
at a composition of 81% $2FeO.SiO_2$, i.e. 64.4% FeO, 29.9% SiO_2 and
5.7% CaO (see Fig. 4.10). It could therefore be predicted that even
if fractional crystallization occurred, liquids with CaO contents
between 0.0 and 5.7 wt% (this includes all the slags under investigation
except RR1 and Millbrook D) should not precipitate olivines with amore
calcic composition than that of the minimum point. GH 653a is not the

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only slag to show this phenomenon, Kevex traces for GH1, GH2 and GH 631 showed generally low-calcium large olivines while crystallites in the glass were highly calcic (see Fig. 4.12). Slags WGW and GHR4 also show a trend towards more calcic olivines later in the crystallization although this is far less marked than in the examples quoted above. The evidence of GH 653a, GH 631, GH1 and GH2 indicates that the rapid crystallization shifts the system far from equilibrium, with the result that the olivine is initially calcium-poor, giving rise to calcium enrichment of the remaining liquid. This process apparently continues until a fairly late stage in crystallization, 'overshooting' the minimum point so that the late liquids contain more than 5.7% CaO and the olivines crystallizing from them are far more calcium-rich than predicted. There is no evidence to suggest that a specific CaO content of the liquid is reached before precipitation of calcium-rich olivine occurs; in the case of GH 653a, the change from calcium-poor to calcium-rich olivine appears abrupt, but in other slags (e.g. GHR4) where the trend is less marked the transition is evidently gradual. The electron probe microanalyses were generally made with the beam focussed on the centre of the olivine crystals in an attempt to avoid penetration of the beam through a thin edge and into the phase beneath. The EPMA results therefore do not clearly reflect the variation shown by the Kevex analyses; however, the variation in olivine composition noted in some samples (e.g. GO4) and the often low CaO contents in others (e.g. RR1, which contains 5.75 wt% CaO overall, but shows an average of only 1.34 wt% in the olivines) give support to the idea of early calcium deficiency followed by late stage calcium enrichment in non-equilibrium conditions. Although this coring effect seems confined to Wealden slags (apart from a slight calcium enrichment of the olivine in WGW), this is not related to ore or slag composition (see Appendix C).

In this context, it is interesting to note that Todd[14] reports an olivine containing 12.90 wt% CaO in a Roman slag (bulk composition CaO 2.33 wt%) from Northamptonshire, although there is no information as to which part of the crystal was analysed. The amount of coring evidently depends on crystallization rate, but the Wealden slags show no significant differences in their textures compared with other slags and no special conditions before or during crystallization are implied. The restriction of coring to Wealden slags is therefore apparent rather than real and it is fortuitous that reasonable analyses for crystallites and the edges of large crystals were only obtained from these samples.

Alumina is also present in small proportions (generally much less than 1 wt%) in the olivines. There is no recognisable pattern to its distribution and no apparent relationship with ore composition. The amounts of Al_2O_3 are consistent with those reported for natural crystals and it presumably substitutes for SiO_2 rather than the basic cations. Two analyses, one from NOR 1 and one from WK/AV, show relatively high alumina contents (3.46 and 3.70 wt% respectively), but in these isolated cases it is possible that the beam hit the edge of a hercynite intergrowth (although admittedly, none were observed microscopically in the former).

In natural olivines, tiny dendritic octahedra and opaque plates and wedges may occur oriented parallel to the (001) or (100) planes of the host crystal. They have apparently exsolved on cooling and in some cases have been shown to be magnetite or chromite.[89] Low temperature oxidation (i.e. 500-800°C over a period of several days) of iron-rich olivines has also been shown to give rise to well-oriented hematite- or magnetite-like precipitates, in the form of thin needles ~ 50-100Å apart and separated by amorphous silica.[91] Increasing the

temperature results in an increase in the size of the oxide grains. Reimann and Sperl[79] and Sperl[6] report the presence of 'unmixed' fayalites in some of their slags; these apparently contain wüstite, with the appearance of tiny dots or lines in polished section, generally concentrated towards the middle of the host crystal. Iron oxide is also commonly found within the fayalites of the slags under investigation (see Table 4.1 under 'wüstite') and a typical example is shown in Figure 4.13a. The iron oxide's appearance in two dimensions indicates that it is in the form of rods or elongated blebs, in this case mostly oriented perpendicular to the length of the fayalite crystal. In thin section, the rods can occasionally be seen to be joined into a comb-like form by other rods, or perhaps plates, perpendicular to them (see Fig. 4.13b; this appears similar to the plates of dendritic 'iron ore' exsolved from olivine figured by Hatch, Wells and Wells,[92] Fig. 132, and to the 'graphic' magnetite exsolution from olivine figured by Grapes[93]). This rod or plate-like iron oxide has the same reflectivity as the primary wüstite in polished sections, and in an attempt to identify it positively, some samples were etched. The etchant was a saturated solution of stannous chloride in 10% HCl, diluted with methanol, which should etch wüstite whilst leaving magnetite unaffected. While much of the iron oxide was etched, some showing random distribution remained unaffected, and the test therefore does not show unequivocally that this iron oxide is wüstite. It seems unlikely that both oxides are present, although it should be noted that the Fe_2O_3 content of liquids in the system $FeO-Al_2O_3-SiO_2$ in equilibrium with liquid iron can range from approximately 4.5 to 2.5% for liquids containing 20–30% SiO_2 respectively,[94] and it is not known how sensitive the etchant is to the amount of Fe^{3+} in wüstite. The results of the etching combined with the evidence of the reflectivity suggest that the iron oxide within

these olivines is wüstite rather than magnetite. The commonly high proportion of this iron oxide, its relatively large size and probability that it is wüstite, as well as the absence of associated silica all indicate that it is unlikely to have been produced by the oxidation mechanism investigated by Champness. It also seems unlikely to represent a cotectic intergrowth of fayalite plus wüstite since no fayalites have been observed with the wüstite concentrated only around the edges, a situation which might be expected to occur when the liquid falls in the fayalite primary phase field in such a position that the liquid composition moves towards the wüstite-fayalite cotectic on crystallization. Instead, the wüstite rods invariably form a 'spine' along the length of the fayalite laths, often giving way towards the edges to fayalite-hercynite intergrowths (see Fig. 4.14a), although wüstite can also occur within areas of such intergrowths (Fig. 4.14b). Exsolution of the wüstite on cooling seems to be the most probable explanation for its occurrence and the consistency of its orientation within the olivine tends to support this.

4.3.2 Wüstite

Although very common in bloomery slags, wüstite (ferrous oxide) is rare in nature, only forming and being preserved when low P_{O_2} conditions combine with rapid cooling. Its only natural occurrences are in some volcanics and in fusion crusts of meteorites.[95] Wüstite has a range of compositions, but this apparently does not cover the composition of the stoichiometric compound FeO, the oxygen content being in excess of the stoichiometric value, 22.27 wt%,[96] i.e. it is a defect lattice. The rather low totals for some of the electron probe micro-analyses of wüstites (Appendix B) are probably explained by the fact that the iron had to be calculated as FeO, it being difficult to take into account the

proportion of any 'extra' oxygen in the lattice. In synthetic systems 'FeO' forms solid solution series with MnO and with MgO and natural wüstite showing a variable MgO content has been reported.[95] Electron probe micro-analysis of wüstites in the investigated slags show that the extent of substitution of Mn and Mg for Fe^{2+} is very small, the average MnO content being 0.50 wt% (σ = 0.28, n = 37) and the average MgO content 0.06 wt% (σ = 0.06). There is no apparent relationship between the content of these oxides in wüstite and either the ore or slag composition. While the trends for MnO and MgO in wüstite and fayalite are generally the same, this is not always the case, and there is also no evidence for higher contents of the two oxides in the wüstites from those slags which should precipitate wüstite as a primary phase (e.g. WK-AV, GH1, Caerwent). Competition from fayalite or possibly hercynite therefore does not seem to be an important influence. Within each sample, the MnO and MgO contents of the wüstite are relatively constant and it is possible that a major control is the slag temperature; the liquidus temperature for both solid solution series increases progressively with increase in MnO or MgO.

The proportions of Mn and Mg are too low to show on a Kevex trace but the element which does appear is titanium. Electron probe micro-analyses show an average of 0.82 wt % TiO_2, but the content is variable (σ = 0.41) and shows no clear relationship with the composition of ores, slags or other phases. In the synthetic system 'FeO'-TiO_2 in contact with metallic iron,[97] there is no solid solution between the end-members and a eutectic exists between FeO and an intermediate compound, $2FeO.TiO_2$ (Ülvospinel). The presence of titanium in wüstite, although common, is therefore difficult to explain in terms of the published data, but defects in the FeO lattice presumably allow this substitution

to occur. If titanium is present as Ti^{4+} (although this is not
necessarily the case; see for instance the arguments of Fine & Arac[98]
in their work on the effects of minor constituents on the liquidus
temperature of synthetic blast furnace slags), then a smaller proportion
of this would be needed to satisfy the electron balance than of Fe^{3+}.

Vanadium is sometimes present in more than trace amounts (i.e.
greater than 0.1%), particularly in the wüstites of slags from the
Northamptonshire area (including Stamford) and Ramsbury, but like
titanium there is no clear explanation for its distribution. The
electron probe micro-analyses also show the presence of small but
variable proportions of Al_2O_3 and SiO_2 in wüstite (for Al_2O_3, $\bar{x} = 0.60$
wt %, $\sigma = 0.33$; for SiO_2, $\bar{x} = 0.48$ wt %, $\sigma = 0.28$; n = 37 as before).
It is perhaps significant that those samples showing the highest contents
of Al_2O_3 and/or SiO_2 in wüstite are those in which the dendrites are
particularly fine and it is possible that these values do not represent
Al and Si substituted in the 'FeO' lattice, but indicate a slight
penetration of the electron beam into the surrounding phases.

4.3.3 Magnetite

Magnetite ($FeO.Fe_2O_3$) is present in several slags, but occurs as
a primary phase in only one archaeological specimen (NOR 1) and in some
of the material from furnace reconstructions. It is a member of the
spinel group of minerals, a group covering a wide range of compositions.[99]
Above 858°C, there is a complete solid solution series between
magnetite and hercynite ($FeO.Al_2O_3$) although below this temperature,
exsolution of one phase from the other occurs and in natural crystals
only small amounts of Al substitute for Fe^{3+}. Calcium, manganese and
magnesium may replace Fe^{2+} to a limited extent, although continuous

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substitution of Mg for Fe^{2+} to $MgO.Fe_2O_3$ (magnesioferrite) is possible.
Titanium is easily accommodated in the magnetite lattice and there is
a complete solid solution series between magnetite and $2FeO.TiO_2$
(Ulvospinel), $2Fe^{3+}$ being replaced by $Fe^{2+} + Ti^{4+}$. Vanadium may also
replace Fe^{3+}. Electron probe micro-analyses of primary magnetites in
the slags studied show fairly high proportions of Al and Ti (for Al_2O_3,
$\bar{x}$ 4.66 wt %, σ = 1.29; for TiO_2, $\bar{x}$ = 3.46 wt %, σ = 1.16; n = 11).
Only very small amounts of Mn and Mg are present (for MnO $\bar{x}$ = 0.67
wt %, σ = 0.30; for MgO $\bar{x}$ = 0.23 wt %, σ = 0.17) and the contents in
NOR 1 are significantly lower than in GHR 1 and GHR 4 ($\sim$ 0.2 wt % MnO
and negligible MgO in the former and 0.8 wt % MnO and 0.3 wt % MgO
in the latter two samples); this is probably a reflection of the ore
compositions. A small proportion of vanadium is found in all the
magnetites ($\bar{x}$ = 0.59 wt %, σ = 0.19). The analyses also show a very
variable amount of SiO_2. The average content is 1.61% but is so
variable that, as in the case of wüstite, it may represent 'interference'
from the surrounding phases rather than actual substitution. The
skeletal nature of the magnetites in GHR 1 and GHR 4 and the small
size of those in NOR 1 makes this a distinct possibility.

4.3.4 Hercynite and other spinels

Hercynite ($FeO.Al_2O_3$) is found in many of the slags of this study.
Like magnetite, it is a spinel group mineral, but differs in its
distribution of two-and three-valent cations (hercynite is a normal
spinel, while magnetite is a reverse spinel). There is a complete
solid solution series between hercynite and $MgO.Al_2O_3$ (spinel _sensu_
stricto) and as discussed above, there may be extensive substitution of
Fe^{3+} for Al, although there is complete solid solution between hercynite
and magnetite at high temperatures. The composition of the hercynites

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is remarkably constant, regardless of ore source or furnace type (for FeO, $\bar{x}$ = 50.07 wt %, σ = 2.65; for Al_2O_3 $\bar{x}$ = 43.10 wt %, σ = 2.14; n = 21 as analyses from GHR 4 and GH 671 have been excluded, the former because the iron analysis is inaccurate and the latter because the SiO_2 content is very high). Using the standard method for calculating the chemical formula of minerals set out in Table 4.7 (this is explained fully in Appendix 1 of Deer, Howie and Zussman's 'Introduction to the Rock Forming Minerals'[99]), it can be seen that the ions as calculated do not fulfil the requirement for $16R^{3+}$ and $8R^{2+}$. This indicates that a certain proportion of the iron (perhaps a quarter to a third) must be present as Fe^{3+} in all the hercynites examined. The shift shown by the peaks on the XRD trace towards those for magnetite is consistent with this result. The apparent constancy of composition regardless of furnace type is therefore even more remarkable, as similar conditions for each case are implied.

The proportion of titanium is generally relatively high, although variable from slag to slag and is apparently independent of ore source ($\bar{x}$ = 1.61 wt %, σ = 0.86; n = 24). Minor amounts of MnO, MgO and V_2O_5 are also commonly present (these average 0.64, 0.44 and 0.44 wt % respectively, although proportions vary greatly). Some SiO_2 (usually ~0.5%) generally appears in the analyses and Si may replace Al. In GH 671 however, SiO_2 is apparently very high (up to 5.58 wt %) and it seems unlikely that Si substitutes to this extent. Kevex analyses also reveal chromium in minor or trace amounts in hercynites from several slags, e.g. Brigstock, ST 700130, RAM 1 and GH 666.

The three analyses from GH 631 are unusual in showing a range of compositions for hercynite, from the usual spinel for these slags (i.e. 51.68 wt % FeO, 41.99 wt % Al_2O_3) to a composition nearer hercynite

sensu stricto (43.96 wt % FeO, 48.69% Al_2O_3). The euhedral spinels commonly found immediately adjacent to cooling surfaces also show variation in composition. This may be revealed by colour banding running parallel to the crystal faces, particularly good examples of which are displayed by samples ST 700130 and ST 630532 (see Fig. 4.16). Kevex analyses of the former show that as crystallization proceeds, the spinels become progressively more iron-rich, the higher iron bands appearing paler and more reflective in polished section. There is also a progressive reduction in Ti, V and Cr, this being a reflection of the very small proportion of these elements in the liquid initially.

Two of the reconstruction slags, RR1 and RR2, contain spinels rich in iron and with an extremely high proportion of TiO_2 (for 'FeO', $\bar{x}$ = 71.69 wt %; for Al_2O_3 $\bar{x}$ = 12.29 wt % and for TiO_2 $\bar{x}$ = 11.13 wt %; n = 3). It is clear from the calculation of the chemical formula (Table 4.7) that about half the iron must be present as Fe^{3+}. The composition is consistent with the results of phase equilibrium studies in the ternary system $FeO-Fe_2O_3-TiO_2$, which show that magnetite (solid solution) is the primary crystalline phase in the composition range 0-12 wt % TiO_2. This spinel is therefore a titaniferous magnetite. It also contains relatively high vanadium (V_2O_5 averages 1.83 wt %) and a little Mn and Mg (MnO averages 1.15 wt %, MgO averages 0.16 wt %).

4.3.5 Leucite

Although leucite has been reported from medieval slags,[5] the potassium alumino-silicate phase in the slags of this study was not immediately identified as such. Initial electron probe micro-analyses showed that the compositions did not correspond to that for leucite

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($K_2O.Al_2O_3.4SiO_2$, i.e. 21.6 wt % K_2O, 23.4 wt % Al_2O_3, 55.0 wt % SiO_2), the K_2O values being too low and the proportions of SiO_2 and Al_2O_3 slightly too high. In addition, a small amount of FeO (2%) was consistently present. It was eventually noticed that potassium was 'boiling out' under the electron beam and the counts for this element were decreasing significantly in a matter of seconds. The volume of the mineral depleted in potassium then also showed falsely high values for Al_2O_3 and SiO_2. The problem was overcome (although not entirely satisfactorily) by either using a small area raster or by analysing for potassium first, counting for ten seconds only, then moving the beam to other areas for the other elements. All the analyses of this phase are included in Appendix B for comparison, although only those for GH 671, GH 631 and the later four of WK K(4) are accurate. The analyses cited compare closely with those appearing in the literature for natural crystals.[100,101] Roedder[86] suggests that there is at least a partial solid solution series between $K_2O.Al_2O_3.4SiO_2$ (leucite) and $K_2O.FeO.5SiO_2$, but there is no evidence for such substitutions occurring in the leucites investigated. In fact, like fayalite, the leucite commonly contains abundant tiny rod-shaped wüstite grains which again appear to be the result of exsolution on cooling (see Fig. 4.17; X-ray maps showing the distribution of the major oxides are included for comparison). The wüstite rods do not appear to be so well oriented as in the fayalite, but this is probably because the structure of leucite is more complex, being based on an alumino-silicate framework.

4.3.6 Minor phases

The occurrence of crystallites of calcium-rich olivine and kirschsteinite in some slags (e.g. GH1, GH2, GH 653a, etc. has already been discussed. Kevex traces of probable kirschsteinite crystallites

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in GH2 and GH 653a show the peak heights in the order Fe > Ca > Si, but analyses of other crystallites (e.g. in GH 653 a and GH 631) show Fe > Si > Ca, and in the latter a relatively large proportion of Ti is also present (compare Figs. 4.11 and 4.12 with Fig. 4.18). Very few electron probe microanalyses of these minor phases were carried out because the small size of the crystallites made them difficult to locate and the probe beam invariably penetrated the surrounding phases, giving false readings. Despite this, two analyses from RR1 are reasonable (Appendix B), though one from RAM5 is ambiguous. The crystallites in RR1 are lath like and in the back-scattered electron image of the scanning electron microscope appear a darker grey than fayalite (Fig. 4.19). They are composed of 41% FeO, 24% SiO_2, 12.5% Al_2O_3, 12% CaO and 7% TiO_2 (compare with the Kevex trace of crystallites in GH 631). Calcium rich pyroxenes from slags have been reported in the literature,[7,102] but the low SiO_2+Al_2O_3 content of this phase indicates that it is unlikely to be a pyroxene of any kind. The composition does not correspond to anorthite or to any of the commonly-occurring calcium-rich phases of blast-furnace slags (such as dicalcium silicate) and its identity remains a mystery at present. Schürmann and Winterfeld[103] discovered a phase in the course of their work on the $CaO-FeO-Fe_2O_3-SiO_2$ system which they were unable to identify and while this may have no relevance to the crystallites described above, it is at least consoling that other workers have similar problems!

Kevex analyses of small anhedral crystallites occurring within the leucite of GH 631 and GH 671 (see Fig. 4.20) show them to contain high calcium and phosphorus, with minor peaks for Si, Al, K and Fe some or all of which may be a result of the beam penetrating the surrounding

leucite. Electron microprobe analyses of similar calcium-phosphorus

phases in RAM 1 and GH 671 are somewhat ambiguous, but that for WAK K(4)

corresponds well with an analysis of manganapatite[104] ($[Mn,Ca]_5[PO_4]_3$ F;

MnO 7.6%, CaO 46.5%, P_2O_5 42.0%, F 3.0%), taking into account the

fact that Fe may also substitute for Ca, and OH^- and/or CO_3^- may

substitute for F. Apatites (basically $Ca_5(PO_4)_3$ plus a monovalent

anion, but showing variable composition) occur as accessory minerals

in almost all igneous rocks and their presence in some slags is

therefore not unlikely. In view of the association of this calcium-

phosphorus phase with leucite, it is interesting that the particular

association of apatite and leucite in certain igneous rocks has been

noted in the literature.[101] The composition of the crystallite in

WAK K(4) does not correspond to any of the phases in the system

$CaO-P_2O_5-FeO$, although if it were assumed that Fe can substitute

extensively for Ca in these phases the combined molar proportions

of FeO+CaO to P_2O_5 (0.896:0.280) are not far from the ratio of CaO

to P_2O_5 in the compound $3CaO.P_2O_5$ (Todd[14] reports $3CaO.P_2O_5$ in slag

produced during laboratory reduction of ore from Colsterworth).

However, although not previously reported from slag, the present

author would identify this phase as apatite rather than $3CaO.P_2O_5$.

It should be noted that although the calcium-rich crystallites

and the calcium-phosphorus phase were observed in only a few slags,

their small size means that they could easily be overlooked and they

may actually occur more frequently than appears to be the case.

4.3.7 Glass

All the slags investigated contain some glass and it is clearly

an important component of bloomery slags. As can be seen from

Appendix B, the analyses of glasses are often more inaccurate than for other phases, generally totalling less than 100%. A number of difficulties were encountered when trying to determine the glass compositions. Firstly, many of the slags are weathered and in thin section it can be seen that the glass phase is invariably the worst affected, in extreme cases appearing dark brown and almost opaque. This corrosion of the glass, as well as causing oxidation of Fe^{2+} and Mn^{2+}, may also lead to loss of some oxides (e.g. the alkali oxides), probably leaving this phase with a small-scale porosity. In addition, some elements are 'boiled out' of the glass under the electron beam. Potassium is particularly badly affected and presumably any sodium present would also be lost (the latter element has only rarely been detected, but whether this is because it is absent or easily lost is uncertain). Both of these factors would result in analyses totalling less than 100%. Other inaccuracies are caused by the presence of crystallites in the glass. The analyses show that the glass is very variable in composition and may even vary within samples. This variation is to be expected since the glass results from solidification of the remaining liquid and contains all the oxides not accommodated in the lattices of the crystalline phases, furthermore as the network of crystals is built up, barriers to liquid movement and to diffusion are created, leading to heterogeneity of the glass. Possible small scale heterogeneity is also seen in some samples, the glass appearing patchy in the secondary electron image of the scanning electron microscope or the electron probe microanalyser, although because of the small scale no satisfactory analyses have been made (see Appendix B). Such patchiness may however be a result of partial devitrification.

4.3.8 Metallic iron

The metal grains within several of the slags have been analysed
using the electron probe microanalyser, and as might be expected, the
iron is very pure (Appendix B). The phosphorus content is generally
very low and to some extent this reflects the low phosphorus contents
of the ores but may also be a result of de-phosphorising reactions.[105]
It is interesting to note that the P_2O_5 contents of the /metallic grains in slags from the
reconstructed shaft furnace are relatively high (0.26, 0.09, 0.47
and 0.18 wt % respectively in four separate grains from slag GHR 4)
whilst slags from the reconstructed bowl furnace using the same ore
shows negligible phosphorus content in the metallic inclusions. This
probably reflects the higher temperatures attained in the former
furnace. The carbon content is very variable and some of the grains
have evidently been molten (Fig. 4.21).

4.4 Mineralogical structures – description and interpretation

4.4.1 Fayalite

Drever and Johnson in their work on the crystal growth of forsteritic
(i.e. magnesium-rich) olivine in magmas and artificial melts[106] concluded
that the morphology of individual crystals is extremely sensitive to,
and dependent on, the physical and chemical environment at their point
of growth and olivine of almost any shape or size can crystallize.
The fayalitic olivines of the investigated slags generally appear lath-
like, although more equant crystals do occur (Fig. 4.22a). Despite
the rapid cooling, which might be expected to result in a mass of tiny
crystals, the fayalites are generally large (commonly ~1 mm long in
tap slags and often 2 mm or more in furnace slags). This suggests that

nucleation was centred on very few sites and possibly indicates that the liquid was actually well above its melting point. Nesbitt[107] postulates that supersaturation (i.e. supercooling) prior to nucleation of a superheated liquid (i.e. one that is initially almost free of nuclei) provides the conditions required for the rapid growth of relatively few large crystals. A skeletal development is commonly shown by the fayalite (Fig. 4.22b) and this is also characteristic of rapid crystallization, when the diffusion rate is too slow to cope with small, but rapidly growing crystal faces and preferential growth of corners and edges occurs, since these can collect material diffusing in over a wider volume.

Other laths are non-skeletal and these frequently display an oriented wüstite exsolution. This again appears to be a result of the very rapid crystallization, and suggests the initial precipitation of a phase richer in iron than fayalite, which on cooling exsolves wüstite. Eutectoidal decomposition of a ferrous silicate phase to fayalite + wüstite could produce such a texture and parallels exist in igneous rocks, e.g. the inversion of a monoclinic pyroxene, pigeonite $2(MgO,FeO,CaO).2SiO_2$, to an orthopyroxene accompanied by exsolution of a second monoclinic pyroxene, augite $CaO(FeO,Mg)).2SiO_2$. However, the binary system $FeO-SiO_2$ shows only a simple eutectic between wüstite and fayalite and another between fayalite and tridymite; no other ferrous silicate should form. There is therefore no obvious mechanism by which wüstite might exsolve, unless the fayalite lattice itself is less well-ordered at high temperatures and can accommodate an excess of FeO.

Skeletal fayalite and non-skeletal fayalite with wüstite exsolution are occasionally found together and the overall physical

conditions or chemical composition therefore do not determine which type is formed. Fayalites showing wüstite exsolution are known to have been analysed accurately in only one sample (GH 671) and these are not significantly different in composition from skeletal olivines in other slags (e.g. in GHR 4); there is clearly no special relationship between the composition of the actual mineral and its form.

(Fig. 4.23a)

Fayalite laths may occur in parallel or sub-parallel bundles/or there may be a random distribution of large laths, with many tiny parallel laths in the triangular spaces between them (see Fig. 4.23b). Nesbitt[107] describes olivine showing identical textures in Archaean ultramafic rocks (i.e. rocks particularly rich in ferromagnesian minerals) in Australia. This author found that over a distance of approximately 0.5 m, the texture commonly changed downwards from fine random laths (his 'radiating spinifex' texture) through coarser random laths to coarse parallel bundles (his 'plate spinifex') and hence the control on the structure is presumably physical rather than chemical. A similar control can be assumed for the slags of this study. The more common of the two textures in the investigated slags is that of parallel or sub-parallel laths and this is often related to the presence of chilled surfaces.

In the more slowly-cooled slags, the rate of diffusion was evidently sufficient to permit some lateral growth of the laths, with the result that the fayalite is rarely skeletal and the original lath-shape is only recognisable in polished section by the presence of elongated patches of glass oriented roughly parallel to one another. In extreme cases, the fayalite may appear massive, broken only by occasional patches of glass showing no distinct pattern, although

the distribution of exsolved wüstite may indicate the original shape
and orientation of the individual crystals (e.g. in GO4, see Fig. 4.24).
In thin section this massive fayalite may often be clearly seen to
consist of coalesced laths, although in rare cases the fayalite is
anhedral (e.g. in parts of WK K(4) and ST 630532, see Fig. 4.25).

4.4.2 Wüstite

Wüstite ranges from long fine dendrites through shorter thicker
dendrites to isolated globules and very short thick dendrites.
There is a tendency for wüstite to occur as long fine dendrites in
those slags showing clearly lath-shaped fayalite, but there are
exceptions and there may be abrupt transitions from one form to another
when no change is shown by the associated fayalite. Except in the rare
cases where wüstite is confined to the glass phase (e.g. Bulwich slag),
the dendrites and globules are randomly oriented, cross-cutting the
fayalite laths (see Fig. 4.26). This suggests that the wüstite
crystallized before the fayalite, yet only four slags (WK-AV, No. 7;
GH1, No. 18; Caerwent, No. 31; Millbrook E, No. 56) plot in the
wüstite primary phase field of the $FeO-SiO_2-Al_2O_3$ ternary (7, 31 and 56
also plot in the wüstite primary phase field of the anorthite-FeO-
SiO_2 ternary). Of these, WK-AV plots very close to the wüstite-hercynite
cotectic and only a very small amount of primary wüstite would be
predicted yet it contains approximately 40%, and the other three slags
also contain high proportions of this phase (approximately 50, 35 and
55% respectively) in the form of short thick dendrites and globules.
The structure and mineralogical composition of GH1, Caerwent
and Millbrook E therefore conform to that predicted from the phase
diagram. In these three slags, as in nearly all the others, not only

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does the wüstite cross-cut the fayalite structure but there is also very rarely any sign of thickening of dendrites in the glass phase. In fact, fayalite crystallites are sometimes nucleated around the lobes of primary wüstite projecting into the glass (see for instance Fig. 4.11). This implies that there is a 'flush' of wüstite precipitation as the liquid begins to cool and practically all the primary wüstite observed crystallizes at this point. Any excess 'FeO' not taken up by the fayalite or hercynite which subsequently crystallizes must remain in the liquid which finally solidifies as glass. Occasionally, crystallites of wüstite are recognisable within the glass, suggesting that a second phase of wüstite precipitation can occur. The texture displayed by a slag not included in this study, where the primary wüstite dendrites are completely surrounded by fayalite (no other wüstite being present; see Fig. 4.27), supports this hypothesis. All the wüstite in the structure crystallized first and the fayalite then nucleated on the dendrites. Such textures would not be predicted from the phase diagrams, which indicate that under equilibrium conditions there should generally be precipitation of a primary phase (usually fayalite for the slags of this study) followed by a co-precipitation of two phases (usually fayalite + wüstite or fayalite + hercynite in this case) then complete solidification of a ternary eutectic. None of the investigated slags display textures which could be interpreted as following such a simple crystallization path. Whilst the slag composition (i.e. the content of minor elements in particular) may have some effect on the overall structure, it seems more likely that it is the rapid rate of crystallization, shifting the system away from equilibrium, that is the major control. It is possible that the species of nuclei present in the liquid also have an

effect on structure. It has been argued above that the relatively large size of the fayalite laths suggests that nucleation centres for this mineral were few in number, whereas in those slags in particular which contain abundant, short, randomly oriented, dendrites there must, in contrast, have been numerous nucleation ~~centres~~ for wüstite (c.f. Fig. 4.26). Reimann and Sperl[78] in their discussion of slag structures remark on the fact that the cross-cutting of fayalite by wüstite dendrites cannot be interpreted in terms of the phase diagram for the $CaO-FeO-SiO_2$ system and they suggest that a finely divided crystalline phase (probably another silicate) observed in the matrix probably plays an important role in the crystallization. Their idea must be erroneous, as the finely-divided phase could only have crystallized at a late stage and so cannot have influenced the overall structure. In the cases where wüstite is confined to the glass phase, fayalite crystallization has clearly preceeded the precipitation of wüstite and these slags have presumably followed a more 'normal' crystallization path.

4.4.3 Magnetite

Where magnetite occurs with wüstite, it can be distinguished from the latter by its slightly higher reflectivity (wüstite reflectivity 19%, magnetite reflectivity 21%) and by its tendency to form euhedral cubic crystals or short angular dendrites. When only one iron oxide is present, shape is the only real clue to identity, although Finlow-Bates[108] suggests that with increasing content of Fe^{3+} in the wüstite lattice, its crystal habit should change from rounded to angular. No information is given as to the proportion of Fe^{3+} required before this happens and no further discussion of this point

has been found in the literature.

Magnetite occurs in several slags, but in general only as small euhedral crystals or angular dendrites immediately beneath the layer of densely-packed wüstite globules marking a chilled surface (Fig. 4.28a). Often, the wüstite layer is also partly converted to magnetite (Fig. 4.28b). In these cases, the magnetite has evidently been produced by superficial oxidation after it left the furnace. As might be expected, all slags containing such magnetite are clearly tap slags, though there are two exceptions (GO 792017, which may represent a break-out of slag from a fissure in the furnace wall and WK-AV which may have been raked out of the furnace; for further details, see Chapter 2).

In one slag (WK K(4), a furnace slag from Wakerley, Northants) there is evidence for more extensive oxidation. Wüstite dendrites, the lobes of which are unusually irregular in outline, show networks of a lighter phase running through them. Rounded patches of this same phase, confirmed as magnetite by Kevex analysis, occur on the edges of the lobes and occasionally coalesce to form a rim (see Fig. 4.29). The relationship of the two oxides suggests that furnace conditions became more oxidising at a late stage during crystallization. The magnetite network indicates that the wüstite dendrites themselves have been partially oxidised, but it is unclear whether the rounded patches also represent oxidised wüstite or whether magnetite was being precipitated directly from the liquid and was nucleating on the wüstite. No crystals of magnetite are visible in the glass. Similarly, in the Populonia slag formed by Reimann and Sperl[78] and Sperl,[6] where the dendrites consist of thick magnetite rims around wüstite

cores it is not possible to determine how much of the magnetite has been formed by oxidation of wüstite and how much, if any, by direct precipitation.

Magnetite occurs as a primary phase, in the form of small, euhedral, often skeletal, crystals and angular dendrites (see Fig. 4.30) in the slags from the furnace reconstructions. These attempts to reproduce early ironmaking methods were unsuccessful in that little iron was extracted and the slag mineralogy suggests that conditions were insufficiently reducing. This is one example where the mineralogy of a slag directly reflects the processes involved in its formation.

Only one of the archaeological slags examined (NOR 1) contains primary magnetite. No wüstite is present and the magnetite occurs as tiny euhedral crystals within the glass phase. The upper surface of this particular sample has the appearance of ropy lava and a cross-section shows it to be made up of several separate 'flows'. This slag is clearly not a forging slag and, whether tapped or raked, by analogy with the slags from furnace reconstructions, its mineralogy presumably indicates that conditions were insufficiently reducing for efficient working. It is highly unlikely that such extensive re-oxidation could have occurred outside the furnace.

4.4.4 Hercynite

Large (up to 0.25 mm across), euhedral hercynite crystals occur in only two slags, Brigstock (No. 33) and WAK 48A (No. 9), and these two are also the only slags to plot in the hercynite primary phase field of the $FeO-SiO_2-Al_2O_3$ ternary diagram (only WAK 48A plots in

the hercynite field of the anorthite-FeO-SiO$_2$ diagram). In all other

slags, the hercynite occurs mostly as an angular intergowth with

fayalite, although additional small scattered euhedral crystals are

present in a number of samples. The textures displayed by hercynite

appear to conform closely with what might be predicted on the basis of

the phase diagrams. The Stamford slag ST 700130 (No. 35) is a very

good illustration of this. The bulk composition plots in the fayalite

primary phase field of the FeO-Al$_2$O$_3$-SiO$_2$ ternary and on cooling under

equilibrium conditions should crystallize fayalite, then fayalite +

hercynite as the liquid composition moves along the cotectic, finally

solidifying at the ternary eutectic to a mixture of fayalite + hercynite

+ wüstite. It can be seen from Fig. 4.31 that the fayalite is in the

form of sub-parallel skeletal laths from which there are lobe-like

projections, consisting of fine intergrowths of fayalite + hercynite.

Hercynite also fills some of the holes in the fayalite 'skeletons'.

As discussed above, wüstite does not conform to the predictions made

from phase diagrams. Ignoring the behaviour of wüstite for the present,

the structure described could quite simply be interpreted as

crystallization of primary fayalite, followed by cotectic intergrowths

of fayalite + hercynite, then final solidification of the remaining

liquid to a glass before the eutectic is reached.

The picture is unfortunately not as simple as it might appear.

Firstly, there may be a base level of alumina in the bulk composition

below which hercynite does not appear in the structure. For example

no hercynite was observed in slags NOR and GH2, which have Al$_2$O$_3$ contents

of 1.74 and 2.95 wt % respectively, whereas in GH 1, which contains

Al$_2$O$_3$ 3.32 wt %, rare isolated patches of hercynite + fayalite inter-

growth occur, except in the area adjacent to a fragment of furnace

lining (partial slagging of which might give a local increase in Al_2O_3 and SiO_2), where the intergrowth is more abundant and there are some scattered tiny euhedral hercynite crystals in addition. There is also no obvious relationship between the proportion of Al_2O_3 in the bulk composition and the amount of hercynite observed in the structure. Slag from Wakerley Great Wood (WGW, No. 10) contains Al_2O_3 7.50% yet only 2-3% hercynite is visible, while RR 1 (No. 15) and RR 2 (No. 15) contain Al_2O_3 7.15 and 7.28 wt % respectively yet there is no hercynite present, only a very small proportion of an iron-rich spinel (with approximately 12% Al_2O_3). In contrast ST 630532 (No. 36) has Al_2O_3 6.20 wt % in its bulk composition and contains 10-15% of hercynite. Assuming that no serious errors have been made in visually estimating the proportion of hercynite, other reasons for the discrepancy between the percentage of Al_2O_3 in the bulk composition and the amount of hercynite observed must be explored. One possible explanation is that cooling rate strongly influences whether or not hercynite is formed. It might be expected that slowly cooled slags would show more hercynite in the structure than rapidly cooled ones, yet both WGW and ST 630532 are tap slags and both presumably cooled quickly, so that cooling rate alone is not the deciding factor. The amount of glass depends on cooling rate, but probably also on the proportion of network-forming oxides in the bulk composition (principally SiO_2, but also P_2O_5) and it seems reasonable to assume that there would be less hercynite in those slags with a high glass content, since the more glass there is, the more Al_2O_3 and FeO could be dissolved in it. However, there is no apparent relationship, inverse or otherwise, between the proportions of hercynite and glass in the slags, WGW for instance contains 2-3%

hercynite and approximately 2% glass while ST 630532 contains 10-15%
hercynite and 7% glass. Little or no hercynite was observed in the
slags from furnace reconstructions (the maximum amount, estimated
as 0.5%, occurs in GHR 10), yet relative to other slags they contain
high proportions of Al_2O_3 (5.15-7.28 wt %). These slags all contain
primary magnetite and must have formed under slightly oxidising
conditions. This suggests that oxygen pressure perhaps influences
the formation of hercynite. If this is so, then those slags which
contain a relatively high proportion of Al_2O_3 yet shows little or no
hercynite in the structure perhaps formed under higher Po_2 conditions
than others with similar Al_2O_3 contents but showing a greater
proportion of hercynite. Supporting evidence is provided by the
spinels commonly observed adjacent to cooling surfaces. These spinels
are initially close to hercynite in composition, but outer zones show
a progressive enrichment in iron. Since the longer the liquid slag
is exposed to air the more oxidised it becomes, the composition of the
spinel appears to be directly related to the degree of oxidation of
the slag. The proportion of hercynite in the structure (that is in
the main body of the slag, away from chilled surfaces) relative to the
percentage of Al_2O_3 in the bulk composition may therefore be an
indication of Po_2 in the furnace. Morton and Wingrove[5] note that
hercynite crystals appear to be concentrated around the edges of gas
holes in the general structure and this provides extra evidence
that the influence of the gas phase is important in determining
whether or not hercynite appears.

4.4.5 Leucite

The textures shown by leucite have proved particularly
problematical to interpret. In some slags, a fayalite-leucite

intergrowth fills the intestices between fayalite crystals (e.g. in RAM 5, see Fig. 4.32) and this could be interpreted as a cotectic intergrowth of leucite plus fayalite (c.f. leucite-fayalite-silica system, Fig. 4.8). However, in most slags (and other parts of RAM 5 also) leucite occurs as rounded patches, either within the glass or between fayalite crystals (see Fig. 4.33). In the latter case, it is evident that the shape of the leucite has not been determined by the fayalite (i.e. the fayalite crystals do not retain their straight edges), which suggests that the shapes of both are to some extent mutually dependent and the two phases must be crystallizing together. Perhaps this also represents cotectic crystallization. In contrast, the rounded patches of leucite within the glass are suggestive of globules of one liquid in another. In addition, in some slags there is a transition from 'normal' glass, through a fine net-like structure in which leucite can be discerned, to large patches of leucite (see Fig. 4.34). This too gives the impression of two liquids separating out, although it should be noted that investigations of liquid immiscibility have shown droplet sizes of the order of a few microns in diameter, whereas the scale of these slag textures is at least one order of magnitude greater. The presence of an immiscibility gap in the leucite-fayalite-silica and related systems has already been discussed. As far as the former system is concerned, the compositions of the conjugate liquids are not close to the supposed leucite (plus some wüstite) and associated glass in the investigated slags (see Appendix B for analyses). For instance, the compositions of the liquids at each end of the conjugation line AA^1 on Fig. 4.8 are as follows:

Liquid at A, FeO 51%, SiO_2 45%, K_2O 2%, Al_2O_3 2%;

Liquid at A^1, FeO 9%, SiO_2 75%, K_2O 7%, Al_2O_3 8%. For this reason

it seems unlikely that the observed textures represent separation of the remaining liquid into two phases, one of which is very close to leucite in composition (although the presence of a 'leucite glass' does provide an alternative explanation to masking by the high level of background radiation for the non-appearance of leucite peaks on XRD traces). Natural crystals of leucite tend to appear rounded, with no distinct crystal form and this perhaps accounts for the apparent lack of crystallinity shown by leucite in most slags. Primary crystals of leucite occur in slag RR2 (Fig. 4.35a), their rather rounded shape and concentric zones of inclusions being typical of naturally-occurring crystals (Fig. 4.35b); a few even show evidence of the characteristic twinning pattern.

(Fig. 4.36a)

Finally, it is important to note that leucite commonly rims pores ⟨ and in RR1 and RR2 also forms arc-like shapes ⟨ which perhaps mark (Fig. 4.36b) the position of former gas bubbles. In addition, in some slags containing very small proportions of leucite, this phase occurs only near chilled _ surfaces, where it is usually interstitial, but may form dendrites (c.f. Fig. 4.28 of this work and Fig. 9 of Morton and Wingrove [5], suggesting earlier crystallization. This evidence indicates that the gas phase has some influence on the presence of leucite, but the relationship is unclear.

4.4.6 Glass

The glass phase of the slags studied almost always appears speckled in reflected light. This appearance is probably due to internal reflections, but it is uncertain whether these are caused by devitrification crystallites, domain-type structures or microporosity resulting from corrosion. There is no clear evidence for devitrification

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in the form of either patches of 'cloudiness' or feathery dendrites, whereas many slags do show signs of weathering, so that the third possibility is perhaps more likely. In thin section, weathered glass is generally brown and semi-opaque, but when fresh it is transparent and either yellow or pale green in colour (presumably depending on whether the contained iron is in the di- or trivalent state). The glass commonly contains tiny crystals which represent the last stages of crystallization before final solidification. In many slags these crystallites are too small to identify, even with the aid of the Scanning Electron Microscope, but in others 'olivines' ranging from fayalite to kirschstenite, spinels ranging from hercynite to magnetite, wüstite and an unidentified phase containing CaO, Al_2O_3, FeO, SiO_2 and TiO_2 have been identified. Anorthite has not been observed amongst these late-stage crystals, and although Rogers[109] found anorthite formed as a devitrification product of some glasses in the $CaO-MgO-Al_2O_3-SiO_2$ system, this mechanism seems unlikely to be significant for the glass phase of slags. Firstly, there is no clear evidence for devitrification in the slags investigated. Secondly, the number of nuclei formed is highly sensitive to temperature and it would be fortuitous if the slags had maintained a suitable temperature for a sufficient length of time. Thirdly, there is no evidence of the effect that other oxides might have, either on the devitrification process or on the likely products, although it is known that more complex glasses devitrify less readily than glass with fewer components because more complicated atomic adjustments or migrations must be made in order to form the primary devitrification product.

4.4.7 Special textures

(i) Chilled surfaces

A fuller description of the chilled surfaces, already alluded to
several times, rightly belongs to this subsection on slag textures.
Such a surface is marked by a layer of densely-patched wüstite globules,
sometimes partially oxidised to magnetite (see Fig. 4.28b). Long,
fine fayalite laths radiate down from the wüstite layer, the olivine
evidently having nucleated at relatively few centres at the surface.
Occasionally, when sufficient cooling has occurred prior to the next
influx of molten slag, shorter fayalite laths also radiate up from the
base of the later flow, so that the olivine is oriented roughly
perpendicular to the chilled surface both above and below (see Fig.
4.37). Euhedral spinels are often found associated with the chilled
surface, these commonly being more iron-rich than the spinels in the
main body of the slag and sometimes showing signs of compositional
zoning (recognisable in polished section by concentric colour banding).
Magnetite (also a spinel group mineral) is also commonly present,
taking the form of tiny angular dendrites or euhedral, often skeletal,
crystals. These commonly give way over a distance of a few tenths
of a millimetre to rounded dendrites, presumably of wüstite, indicating
that oxidation of the slag is superficial. In some tap slags, leucite
may be absent except in the area immediately beneath a chilled surface.
Finally, slags typically show extra porosity along the line of the
chilled surface. Apart from the upper surfaces of tap slags, some or
all of the features associated with chilled surfaces may be found
within the main body of the slag where they delimit previous flows.
In some cases, the wüstite layer peters out and the fayalite structure
is disturbed, indicating that another influx of molten slag arrived

before the previous one had crystallized completely. Although not confined exclusively to indisputable tap slags, chilled surfaces do indicate rapid cooling at a free liquid surface. If there are signs of superficial oxidation in addition (i.e. magnetite is present), then the interpretation of a slag fragment containing such features as tap slag is more than likely to be correct.

(ii) Phenocrysts and xenocrysts

Isolated large crystals not conforming to the main slag structure are rarely seen. However, in WK K(4)2, there are a few fragments of skeletal fayalite much larger than the rest which appear partly resorbed (see Fig. 4.38). These probably represent crystals from a partly crystallized portion of the slag which were broken and swept away by a still liquid portion flowing past (i.e. they are phenocrysts). No obviously 'foreign' crystals (xenocrysts) of any of the phases, which might provide evidence for recycling of slag, have been recognised.

(iii) Inclusions in minerals

Concentric zones of inclusions in minerals of igneous or metamorphic rocks usually indicate changes of physical or chemical conditions during crystallization such that precipitation of the host phase was temporarily interrupted and another phase formed instead. In slag GO3, a euhedral fayalite crystal shows concentric zones of hercynite inclusions, with some accompanying wüstite in the outermost zones (see Fig. 4.39). This well-ordered texture does not resemble the fayalite-hercynite cotectic intergrowth in the bottom left of the photograph and probably indicates fluctuating conditions during crystallization.

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4.4.8 Relationship between slag texture and iron making technique

Iron smelting slags exhibit a variety of textures, as the figures to this chapter illustrate, but although slags of different periods produced in a variety of furnace types (see Chapter 2) have been examined, no consistent patterns have been found that would allow slag texture to be related to production technique. The features referred to as 'chilled surfaces' (see previous subsection) are an exception, since although not exclusively confined to indisputable tap slags, they do indicate very rapid cooling at a free liquid surface. If a slag shows evidence of superficial oxidation as well as chilling, then its interpretation as tapped or possibly raked slag can be quite confident. There is also a tendency for tap slags to contain individual laths of fayalite suspended in glass or at least separated by glass, leucite or perhaps a leucite/fayalite intergrowth, whilst the more slowly cooled furnace slags display more massive olivine, but this is not always the case. For instance, in hand specimen the Roman period slags BCR 3 and WGW have ropy upper surfaces whilst their lower surfaces show the form of the slag channel or tapping pit, yet both contain massive fayalite. Similarly, in the saxo-norman tap slag ST 630532 individual fayalite laths are barely distinguishable in polished section. In contrast, a sample taken from a large saxon period furnace bottom (RAM) contained individual laths of fayalite randomly oriented and suspended in glass. Similar textures are seen in furnace bottoms from reconstructions of both tapping and non-tapping furnaces (e.g. GHR4, GHR10 and RR1). Wüstite, like fayalite, is also variable in its form and although there is a tendency for wüstite to occur as long fine dendrites in slags where individual fayalite laths are distinguishable, some samples (e.g. WAK, WAK48A and WK/AV) show

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long fine wüstite dendrites and massive fayalite whilst others
(e.g. GH 653 and RAM) contain short thick dendrites and single
rounded grains of wüstite yet the fayalite laths are easily distinguishable
and are separated by relatively large amounts of glass. 'Therefore,
although the form of fayalite and to a lesser extent wüstite, as
observed in polished section, is partly determined by cooling rate it
is not sufficiently reliable even to allow differentiation of furnace
slag and tap slag. The form and distribution of the minor minerals
and glass are similarly unhelpful.

4.5 Summary

Morton and Wingrove[5] found that the presence of spinel in
medieval slags from lean Carboniferous ores distinguishes then from
slags of the same age produced from the rich hematite ores of the Lake
District. The range of ores employed in this study do not show the
great compositional contrast of those chosen by Morton and Wingrove,
but are considered typical of the ores available to the early iron-
workers. Within this more realistic suite the resultant slags
contain no minerals by which the particular parent ore can be
distinguished. There is also no clear relationship between the relative
proportions of the various minerals and the compositions of the ores.
This is partly because the actual slag composition does not necessarily
directly reflect ore composition (see Chapter 5) and partly because
differing conditions before or during solidification influence the
mineralogy. The latter factor in some cases determines whether or
not phases appear and in other cases apparently affects the relative
proportions of the minerals, sometimes also controlling their
compositions. Despite the influence of conditions, the mineralogical

composition of slags appears to be unaffected by the furnace type
or the period in which they were produced.

The application of published phase diagrams, particularly those
for the systems $FeO-Al_2O_3-SiO_2$ and $FeO-anorthite-SiO_2$, to the bulk
compositions of slags enables their gross mineralogical compositions
to be predicted, despite the limitations of this technique (see
subsection 4.2.3). The detailed mineralogy however cannot be predicted
because the composition of the remaining liquid changes significantly
during crystallization of the major phases and therefore the phase
diagrams relevant to the bulk composition no longer apply. The late
liquids mostly contain significant concentrations of oxides such as
K_2O and P_2O_5 in addition to FeO, SiO_2, Al_2O_3 and CaO and this results
in late-stage crystallization of minor phases such as leucite, a
calcium-phosphorus mineral and complex silicates. Further difficulties
in relating detailed mineralogy to phase diagrams are caused by the
fact that systems comprising such complex mixtures of oxides, not
normally encountered in industrial processes (e.g. in the ceramics
or iron and steel industries) and not generally applicable in geology,
have not been investigated.

Variations in the compositions of the different minerals of slags
in general fall within the ranges shown by natural minerals. In some
cases, however, substitution has not occurred as might have been
expected on the basis of synthetic systems or by comparison with
natural minerals. There is no obvious relationship between
compositions of the minerals and those of the ores.

The textures shown by the minerals of slags do not conform
closely to what might be expected on the basis of crystallization

paths predicted from phase diagrams for the systems $FeO-Al_2O_3-SiO_2$ and $FeO-anorthite-SiO_2$. The variance can usually be ascribed to the non-establishment of equilibrium conditions during the rapid crystallization. In some cases, other factors such as oxygen pressure and species of nuclei in the liquid appear to have influenced slag structure. The form of the fayalite is related to the degree of super-heating and undercooling of the liquid as well as to the cooling rate itself. For this reason, the form of the fayalite is unreliable as a means of differentiating rapidly cooled tap slag from more slowly-cooled furnace slag, although there is a trend from individual laths separated by glass in the former to massive olivine in the latter. The form of the other minerals is similarly inconsistent and despite the wide variety of textures observed in the investigated slags, no clear relationships between slag texture and furnace type or period have been found. The only exception is that the presence of chilled surfaces (recognisable by certain mineralogical and textural features, see subsection 4.4.7) is a good indication that the slag was tapped or possibly raked out of the furnace.

CHAPTER 5

ORE PROVENANCING

5.1   Introduction

One aspect of the study of bloomery slags is the relationship
between their chemical compositions and the chemical composition of
the ores they were produced from. Particularly interesting is the
possibility of using slag composition to determine the provenance of
the ore. On most ancient ironworking si tes slag is plentiful, but
ore fragments are generally either rare or absent. In such cases some
means of provenancing the ore would be very valuable to the
archaeologist, since apart from telling him what the iron was made
from, it might also provide clues about the organization behind the
ironmaking.

Morton and Wingrove,[5] in their paper on medieval bloomery slags,
accused previous writers of failing to give sufficient attention to
the relationship between ore and slag and they cited cases where
fragments of ironstone found in excavations were apparently
unrepresentative of the ore used. Morton and Wingrove formulated a
method for calculating the composition of a possible slag, which
might be formed from smelting a particular excavated ironstone, given
the composition of that ironstone and the associated excavated
slag. They showed that a comparison of the calculated slag with that
actually excavated could be informative. In order to calculate the
composition of the possible slag, these authors first made the assumption
that it would have the same FeO content (all iron oxide is calculated
as FeO) as the excavated slags, i.e. they have apparently assumed

similar operating conditions (temperature, Po_2, etc.). The proportion
of FeO in the possible slag (x wt %) was therefore established by
averaging the FeO contents of the excavated slags. Then, assuming
insignificant partitioning of elements between slag and metal (the
generally high purity of bloomery iron, as seen in the literature,[73,110]
suggests this is valid), all the oxides of the ironstone, with the
exception of the iron oxides, were recalculated to total (100-x) wt %.
This method should be used with caution, as operating conditions may
have varied from smelt to smelt, giving rise to slags containing
different proportions of FeO. In addition, the amount of slag
produced per unit mass of iron is unknown. Providing the analysed
slag samples are representative, such calculations could nevertheless
provide a convenient way of checking whether ironstone fragments
found at a primitive ironworking site are similarly representative
of the 'average' ore charged. If, however, there is not a close
correspondence between actual and calculated slag analyses, this
should be interpreted with caution and it should first be ascertained
that the slags analysed are typical and that the ore source is
relatively homogeneous before speculating about the ironworking
practice, e.g. whether ores were sorted or mixed or whether flux
was added.

In cases where no ore is discovered in the excavation, several
possible sources may have to be considered, but providing there are
large enough compositional differences between the different ironstones,
Morton and Wingrove's method might still be used to determine the
most likely possibility. However, when the various ore sources show
less distinct differences, a much more detailed comparison of ores
and slags is necessary. For instance, Todd[14] found during the course

of her work that only limited conclusions could be drawn from a simple comparison of ore and slag analyses. In order to test the feasibility of provenancing bloomery iron on the basis of the composition of slag inclusions, she analysed ore, slag and slag inclusions in metal artifacts from a contemporary bloomery in Ethiopia. Visual comparison of the analyses of slag inclusions and slag formed during laboratory reduction of two ore samples, one containing MnO 3.70 wt % and the other containing a very small amount showed only that the inclusion phases are consistent with the ores of the region. Todd concluded from the relatively low MnO content ($\leqslant$ 2.2 wt %) of the inclusions that the iron was probably produced from a low manganese ore. She did not attempt to relate the compositions of the ores to ore type (both limonite and magnetite ores were smelted), neither did she try to correlate other oxides of the ores and slags despite the wide variation shown by some, for instance, in the six ore analyses Al_2O_3 varied from 1.29 to 18.31 wt %, P_2O_5 from a 'trace' to 2.05 wt % and TiO_2 from ?0 to 2.5 wt %. These results and those of a similar study she made on Roman material from Longthorpe, Northamptonshire, led Todd to conclude that:

> "There is no complete correlation possible between the
> composition of the roasted ore, the furnace slag and
> the individual phases present in the slag."

To return to the work of Morton and Wingrove,[5] in addition to comparing actual and calculated slag analyses, these authors plotted the compositions of their slags on the anorthite-SiO_2-FeO ternary diagram and found that the medieval slags produced from hematite ore fell in a different region from those produced from the largely sideritic Carboniferous ores. They ascribe this to the fact that the

latter ores have a higher gangue content than the former. Although

the authors do not make the point themselves, they have actually

demonstrated that the ratios of certain elements (or their oxides)

in the slags reflect the ratios in the ores; the medieval slags plot

in different places not simply because of the different amounts of

gangue in the two ore types but because those ore types are characterized

by different proportions of silica, alumina and lime. Owing to the

extraction of iron, the absolute values of these oxides (and many others)

vary from ore to slag, but providing partitioning of elements between

metal and slag is insignificant, the oxide ratios should remain the same.

This then potentially provides the means for accurate provenancing of

material, although a number of problems are encountered and these are

discussed later.

Morton and Wingrove[5] and Todd[14] were only concerned with comparing

the minor elements of ores and slags. Todd in fact argued that it is

unnecessary to resort to trace element analysis (trace elements are

usually defined as those occurring in amounts ≤ 0.01 wt %), which is

beset by such problems as the difficulties inherent in determining very

low concentrations of elements and the possibilities of inhomogeneity

in the ore and heterogeneity in the sample. Riley[111] has also cast

doubt on the value of trace element analysis. He analysed an

Early Iron Age iron 'currency' bar from Gretton, Northamptonshire,

and compared the results with analyses of the local Northampton Sand

Ironstone. He concluded that the composition of the metal is consistent

with the local ores (although he apparently did not take into account

the stratigraphically younger Ironstone Junction-Band, also locally

available and exploited during the Roman period and earlier) but

noted that the trace element content of the Northampton Sand Ironstone

is variable and it is, therefore, not really possible to relate trace elements in metal or slag inclusions to source. This seems to support Todd's argument. However, in other fields of archaeology, the pattern of trace elements in artifacts has been used with varying degrees of success as a means of determining their provenance. This approach was first used on items made of the glassy volcanic rock, obsidian,[112] where clear results might be expected in view of the relative homogeneity of the sources and the fact that making the articles involved only the mechanical process of shaping. Since then, trace element patterns have been used in attempts to provenance articles of native and smelted copper,[113,114] clay[115] and bronze.[116] In addition, Haldane[22] and Hedges and Salter[23] have applied the method to iron artifacts.

Haldane,[22] in his study of pre-Roman ironwork from Somerset, discussed in detail some of the problems inherent in this kind of study, the most important of which are inhomogeneity of the ore body, heterogeneity in the artifacts and lack of knowledge about the variation in composition (particularly with respect to trace elements) caused by differences in the extraction technique. Difficulties in sampling the material and the commonly small number of analyses available for comparison cause further problems. The author took particular care to obtain representative and uncontaminated samples and analysed for twelve elements using spectrophotometric and colorimetric techniques. The twelve elements were selected from all those reported to be present in the hematite ores of south-west England[68] because they showed a wide range of variation in the possible ore sources and also should not be severely affected by the smelting process. Since some of these elements might be expected to occur in the metal

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while the rest remain in the slag, both metal and slag inclusions were analysed together to obtain a bulk composition. This is a good idea in principle since it also avoids any partitioning effects, but Haldane made no attempt to ascertain whether the distribution of slag inclusions was the same in all the artifacts. Variation in the number of inclusions per unit volume from one article to another could severely affect the ratio of those elements which should be found in the iron (e.g. cobalt, lead, copper, nickel) to those which should remain in the slag (e.g. calcium, magnesium, titanium, vanadium). It is possible that even items made from the same bloom, by smiths with varying degrees of skill, could have different proportions of inclusions per unit volume and would show different patterns of trace elements in their bulk analyses.

Little information could be gleaned about the relationships between elements from the raw results and Haldane, therefore, decided on a statistical treatment. He first assigned the results to logarithmic ranges subdivided into (i) less than the detection limit, (ii) the detection limit to ten times this value, and (iii) greater than ten times the detection limit. This method has the advantage of 'smoothing out' some of the minor fluctuations, but it is possible that by having only three categories some sensitivity is lost. The categories were coded and a similarity matrix constructed by comparing each sample (i.e. according to its category code) with every other, the value of the similarity being obtained as a percentage figure. The individual samples were then grouped into clusters with similar compositions by performing a complete linkage cluster analysis on the similarity matrix. At a 60% level of similarity, four groups were formed, which the author considered to be significant with respect

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to provenance, although owing to the scarcity of local ore analyses he made no attempt to suggest likely sources for these groups.

Hedges and Salter,[23] using an electron-probe micro-analyser, analysed slag inclusions in three geographically well-separated hoards of Iron Age iron 'currency bars'. A graph representing the data on a logarithmic scale (Fig. 5.1a) showed that many of the seventeen elements (major, minor and trace) analysed for occur in a wide range of concentrations, the values for any one hoard commonly varying by a factor of ten and sometimes by a factor of one hundred. In addition, for many elements the variation tended to be similar in all three hards making visual distinction difficult. The authors therefore applied a statistical method, linear discriminant analysis, to the values for all seventeen elements. A graphical representation of the results (Fig. 5.1b) showed that the inclusions plot in three distinct groups, hence a relationship between the ores and slag inclusions is probable. No flux appeared to have been used and the authors also argued that contamination of slag by fuel ash was low (this is debatable, see section 5.6) and any additions arising from slagging of furnace walls was unlikely to have significantly affected the slag inclusions within the bloom. Despite this, the authors go on to state that owing to the contribution from material added during smelting and the effects of partitioning and redistribution of elements between slag and metal during processing:

> "... an obvious relationship with the composition of
> the original ores cannot be expected."

This seems unduly pessimistic, since they could either have analysed both the metal and the slag inclusions or they could have simply excluded those elements which are mainly reduced into the metal; in

addition those elements occurring in large amounts in the fuel ash could also have been excluded from the comparison. However, Hedges and Salter concluded that the average analysis of a hoard having four or five members should be sufficiently distinctive to enable the ore source to be identified, although they make no attempt to do so for the three hoards investigated because of the lack of sufficiently detailed ore analyses.

The distribution patterns of two or three elements can easily be assessed by plotting the values on a composition diagram with two orthogonal axes or on a triangular diagram, but as the work of Haldane[22] and Hedges and Salter[23] shows, when the relationships of a large number of elements or oxides are being evaluated, some statistical treatment is necessary. Multivariate statistical analysis usually requires long and complicated procedures, but fortunately computer programes are available today to handle the large amount of data. Various techniques for determining significant groupings from sets of analytical data have recently been applied to archaeological problems. Cluster analysis, for which a variety of methods are available, seems to be the most widely used technique, and has successfully been used to group items on the basis of their chemical analyses e.g. bronzes,[116] ceramics,[116] glasses[116,117] and coins.[118] It has also been applied in provenance studies of pottery.[115,119] Another method, principal components analysis, has been used in an attempt to classify glasses on the basis of composition[120] and has been used with reasonable success in a provenance study of Middle Eastern copper artifacts.[114]

The few attempts to provenance iron artifacts using the composition of either the metal itself or the slag inclusions have been inconclusive, largely because no real attempts were made to relate the results to the

possible ore sources. In the present study, the aim of which is to use
slag composition to locate the source of the iron ore, the local
geology of the archaeological sites was also investigated and likely
· ores sampled. In this chapter, the choice of oxides for provenancing
is considered in the light of published information on the composition
of ironstones and the previous attempts to provenance iron. The
sampling methods for both ironstones and slags and the analytical
techniques are described. The value of simple oxide ratios in
provenancing is investigated by the use of two- and three-component
plots. A number of methods for multivariate statistical analysis
and their application to the data of this study are described and
the results discussed, taking into account the limitations of the
different methods. Finally, an attempt is made to evaluate the factors
which affect _any_ provenance study, and the provenancing of iron ore
on the basis of slag composition in particular.

5.2 Choice of oxides for analysis

As discussed in the introduction to this section, Riley[111] and
Todd[14] doubted the value of trace element analysis, although Haldane[22]
and Hedges and Salter[23] based their statistical work on trace element
compositions (the latter two authors also used major and minor
elements). Few published analyses of ironstones include trace-element
contents, but where information is available (e.g. in Riley,[111] Groves,[68]
Rose and Dunham,[121] Worssam and Gibson-Hill[43]), it appears that a
wide variation of trace elements can be found; it is not uncommon
for an element to vary by a factor of ten in different samples from·
the same source. In addition, Hedges and Salter[23] found similarly
wide variation in slag inclusions within Iron Age 'currency bars'.
In view of this variation, combined with the problems of obtaining

representative samples of ore and slag, the difficulties in making accurate analyses at such low concentrations and the lack of information about the behaviour of many trace elements under the assumed furnace conditions, it was decided to analyse the material under investigation for major and minor elements (i.e. those present in concentrations > 0.01 wt %) only. It was also considered that if a method of provenancing ores is to be widely applicable, it should be relatively straightforward, should not require any particularly sophisticated equipment and should preferably permit the use of already published data for comparison. These factors also argue against the use of trace-elements for provenancing. A survey of published analyses of slags and ironstones suggested that FeO and/or Fe_2O_3, SiO_2, Al_2O_3, CaO, MnO, MgO, TiO_2, P_2O_5 and K_2O should be determined. V_2O_5 was also included in the analysis because although it is apparently present in very low concentrations (generally <0.05 wt %) in most ironstones, it is generally higher (around 0.1 wt %) in the Northampton Sand Ironstone and so might be diagnostic. It was felt that this range of oxides would enable useful comparisons to be made of the bulk composition and the mineralogy of slags (see Chapter 4, section 4.3) and would also provide a set of data which could be used in provenancing.

It was recognised as early as 1884[122] that charcoal, used as fuel, was the source of phosphorus contamination in pig iron. In the bloomery process this element is partitioned between the slag and the metal and it must therefore be assumed that the amount of phosphorus in the slag is not a direct reflection of the phosphorus content of the ore. It has also been suggested,[14] that lime and alkalis in the charcoal ash are absorbed into the slag. The problem of contamination by the

fuel ash is discussed in more detail in subsection 5.6, but clearly phosphorus, lime and alkalis are unreliable as indicators of ore source.

Oxides which are to be used in provenancing must also remain unaffected by the bloomery process. That is to say, within the range of operating conditions of the bloomery furnace there must be insignificant partitioning between slag and metal, no boiling or subliming and no reactions resulting in a gaseous phase which could be lost. The free energy diagram shows that of the elements considered, potassium boils at temperatures greater than $750^{\circ}C$, whilst P_2O_5 sublimes at temperatures around $360^{\circ}C$. With the exception of iron of course, all other oxides should concentrate in the slag.

Finally, although there is no real evidence of lime being used as a flux in the bloomery process, there have been suggestions[6,85] that silica may have been added in some form, since this was known as a flux in copper smelting. Sperl[6] reports quartz from a number of slags, notably in a furnace slag from an ironworking site at Nebersdorf in Austria, which lends support to this idea, although the quartz could equally be from the gangue. For this reason, the proportion of SiO_2 relative to other oxides might also prove to be unreliable for use in provenancing ores. It was therefore considered that the provenance studies should concentrate on Al_2O_3, MnO, MgO, TiO_2 and V_2O_5. For the reasons already discussed in section 5.1, the ratios of these oxides with one another were expected to be most useful as these would allow direct comparison of ores and slags.

5.3 Sampling techniques and analytical methods

Since the present work involves comparison of ore and slag
compositions, it was important that the samples analysed were as
representative and as free from contamination as possible. Where a
reasonable volume of slag was available, the sample was selected by
taking approximately one third of the pieces at random or by taking
half of each fragment, depending on the size and apparent homogeneity of
the slag lumps. The selected pieces were then crushed in a jaw crusher
and after coning and quatering, a 60-100 cm^3 portion of each sample
was ground in a TEMA mill. In many cases, however, only one or two
fragments of slag from a particular context were extant and it was
impossible to be certain that a representative sample had been obtained.
In these circumstances, one of the following had to be chosen:
(i) one representative piece, (ii) half the fragment, (iii) a thick
slice from the centre of the slag lump. Such small samples were
usually crushed by hand with a pestle and mortar and subsequently
ground in a small ball mill. In all cases, every precaution was taken
to ensure that loose earth and any furnace lining, cinder, or partially
reduced ore adhering to the slag were removed prior to crushing,
then before grinding, the fragments were sorted and any which contained
'foreign' material were rejected.

Similar safeguards were used to obtain representative ore
samples. Whenever possible, at least fifteen fragments of ironstone
were collected from along the whole length of the exposure (e.g. a
quarry face). In the laboratory, the fragments were broken in half,
the halves crushed and a portion ground using the same procedure as for
the slags. As a test of variability, four samples of Ironstone

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Junction-Band were collected at roughly 60 m intervals from Ketton Quarry, Northants, and a further four samples were obtained from field brash along the line of the outcrop at Wakerley Great Wood. Similarly, six samples of Northampton Sand Ironstone, showing a variety of facies and weathering characteristics, were collected from Brookfield Cottage Pit, Northants (see Chapter 4 for geological details). All fourteen samples of the two lithologies were analysed individually. In general, the quantities of ore obtained from archaeological excavations are small and the same approach was used as for small quantities of slag.

Once the slags and ironstones had been powdered, 5-10 g samples for chemical analysis were obtained by means of coning and quartering. These same powder samples were also used for the X-ray diffraction analyses (see Chapter 4).

To avoid cross-contamination, between every sample the mills used in grinding were washed, dried with compressed air, a charge of quartzite (i.e. almost pure silica) ground in them and the washing process repeated. The only possible contaminants are then silica and the coating material of the mill components. With regard to silica, there is a relatively high proportion of this oxide in the slags and most ironstones so that the total amount would not be significantly altered. In the case of the mills, those in the Department of Geological Sciences are tungsten coated, while the TEMA mill at the British Steel Corporation's Sheffield laboratories, in which the remaining eight samples were ground, is nickel coated; neither of these elements were analysed for. The jaw crusher was also cleaned between each sample by crushing a charge of quartzite, brushing with a wire brush and removing the dust with an air line.

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Seven ironstone samples (WAK 01, WAK 03, WAK 04, WAK 05, WAK 06, GO1 and GO2) were initially analysed for Fe, Si, Al, Ca, Mn, Mg, V and K using atomic absorption spectrophotometry. The determination of phosphorus was not feasible using this method. Lithium metaborate fusions were used to get the material into solution, after the method of Dharma Rao.[123] This particular method was chosen because it involved less dilution of the sample than the more usual one for silicate rocks detailed by Omang[124] and Ingamells.[125] In brief, ~ 0.2 g of sample were fused with 1.0 g lithium metaborate in a graphite crucible at 900°C for fifteen minutes. The melt was then tipped into 50 ml of 10% HCl and stirred with a magnetic stirrer until dissolved. The resultant solution was used directly for the determination of titanium and vanadium. For the remaining elements, 25 ml of the solution was diluted to 250 ml with distilled water. In general, it was found that a small amount of magnetite formed, which did not dissolve in the acid. The formation of magnetite with WAK 05 was so extensive, however, that the above technique could not be used. In this case, 0.1 g of the sample was digested in 1 ml of Aqua Regia (made up as one volume of concentrated HNO_3 to three volumes of concentrated HCl) and 6 ml of HF, following the method developed by Rantala and Loring.[126] The solution was then diluted to 100 ml with distilled water containing 5.6 g H_3BO_3.

To check the accuracy of the methods used, a U.S. Geological Survey standard rock (AGV-1), corresponding as closely as possible to the expected compositions of the slags, was prepared and analysed at the same time as the samples. The accuracy was found to be reasonable for all elements except iron. In this case, the loss of iron by magnetite formation and the very large amount of dilution

necessary had apparently caused the loss of accuracy.

The instrument used was a Perkin-Elmer Model 460, which is fitted with a digital readout giving ppm readings directly. The average of three or more such readings was converted to weight percent oxide by a simple calculation. The so-called 'Perkin-Elmer Cookbook' was consulted for details of the analytical method, the theory of which is well-documented in the literature (see for instance Slavin[127]). The work of several authors[128,129,130,131] on problems of interference encountered in the determination of particular elements was also taken into account.

The opportunity to use the X-ray fluorescence equipment at the British Steel Corporation's Sheffield laboratories arose and on the first visit 34 samples were analysed for Fe, Si, Al, Ca, Mn, Mg, Ti, V, P and K. These included the seven ironstones already analaysed using atomic absorption spectrophotometry in order to check the reproducibility of the results. The accuracy was found to be very good for all elements including iron and phosphorus, although some instability on the channel set for magnesium meant that this element had to be re-determined using atomic absorption spectrophotometry. The speed and accuracy of the X-ray fluorescence technique makes it highly suited to the bulk analysis of both slags and ores and all further samples were analysed using the British Steel Corporation's equipment (no problems in the determination of magnesium were encountered on subsequent visits). The results of the analyses are given in Appendix C.

Each sample was fused with lithium metaborate and 'cast into the form of a glass disc for insertion into the instrument, an Applied

Research Laboratories Model ARL 72 000. The method used was the standard one practised by the analysts at the British Steel Corporation, i.e. 0.5 g sample and 0.9 g lanthanum oxide were fused with 8.5 g lithium metaborate in a platinum crucible at $1200^{\circ}C$ for ten minutes. A few crystals of sodium oxide were added to the fusion to increase surface tension and so prevent the wetting of the crucible which might lead to sample loss. After heating for a further minute, the fusion was quickly poured into a red-hot platinum mould and allowed to cool. Six standards were similarly made up, using mixtures of spectrographically pure oxides, to cover the expected range of variation for each of the elements analysed for.

It has been found (see for instance Norrish and Chappell[132]) that for silicates, fusion into a borate glass, with the addition of lanthanum to further suppress matrix effects, largely overcomes the problems caused by variations in absorption coefficients, enabling a linear calibration curve to be plotted (if the mass absorption coefficient is constant, then there is a simple linear relationship between fluorescent intensity and concentration). The curves were plotted using the six standards and the concentrations of the elements in each sample were then determined by reading off against the measured fluorescent intensities.

The instrument was operated at 45 kV, 35 mA and a 30 second integration time was used. For greater precision, the fluorescent intensities were measured two or three times and the results averaged. To check the accuracy of the method, eight discs of the British Steel Corporation's standard ores, of known composition, were made up and run with the samples. The correspondence was found to be very good. As a further check on the calibration graphs in particular, the samples

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and the eight test discs were re-run, calibrating against the British Steel Corporation's own set of nineteen standards, which covered most of the ranges in variation of the elements. The on-line mini-computer gave the concentrations directly. Again the correspondence was good.

The analyses have been completed by determining the loss on ignition for the ores (and as a check, for some of the slags too). Mr K. Smith has also determined the proportions of Fe^{2+} and Fe^{3+} for most of the slags, using standard wet chemical methods.

5.4 Two and three component plots

Sperl[85] noted that the ancient slags he was investigating seemed to be characterized by their manganese and phosphorus contents. He argued that since neither of these elements were reduced into the metal in the early ironsmelting process, they will usually be present in the slags in the same relative proportions as were in the ores. A plot of weight per cent MnO against weight per cent P_2O_5 for slags from six different sites showed three distinct groups, which Sperl was able to relate to ore type. However, the generalizations made about the compositions of the different varieties of ore are very broad and should be approached with caution. Despite the possibilities of addition of P_2O_5 from charcoal ash and in some cases from clay or perhaps even bone, Sperl[6,85] nevertheless considered the MnO and P_2O_5 contents of slags (particularly slag inclusions) to be of use in provenancing.

It has already been argued (see subsections 5.1 and 5.2) that probably the most useful criteria for provenancing iron ores on the basis of slag composition are the ratios of Al_2O_3, MnO, MgO, TiO_2 and

V_2O_5 with one another. The usefulness of these ratios is best
illustrated by plotting the compositions of the material under
investigation on two component plots, or scattergrams, representing
the ten possible combinations of the five oxides above. The resultant
diagrams are presented in Figures 5.2 to 5.11. It can be seen that
for each ore source, the ores and slags tend to plot in elongated
groups radiating out from the origin, although for various oxide
pairs some of the sources show rather scattered distributions. For
comparison, the MnO contents of the samples have also been plotted
against their P_2O_5 contents (Fig. 5.12). The distribution of the
points is similar to the other oxide pairs and for the ores alone,
the groups are clearly distinguishable. The slags show a slightly
more random pattern, although their scatter is not as bad as might
be expected when the probable contribution of P_2O_5 from charcoal ash
is considered. It appears that, as Sperl[85] has suggested, the
proportion of MnO relative to P_2O_5 may be of value in provenancing.

Returning to the ten oxide pairs under consideration, the
scattergrams show that the Northampton Sand Ironstone and Wealden
groups are clearly differentiated whichever pair is chosen. The
Ironstone Junction-Band group is also easily distinguishable, except
on the plots of Al_2O_3 versus V_2O_5, TiO_2 versus V_2O_5, Al_2O_3 versus
TiO_2 and MnO versus TiO_2; this appears to be directly related to the
large variation shown by V_2O_5 and TiO_2 in this ironstone. The
smaller groups, for instance those representing material from
Ramsbury or the Berkhamsted area, are however not easily separable
from the major groups. Whilst it is unlikely that such a large
number of potential sources would have to be considered and the
resultant scattergrams would presumably be simpler, it does appear

that no particular oxide pair (including MnO versus P_2O_5) is generally applicable to all provenancing problems.

Morton and Wingrove[5] found that medieval slags produced from hematite and from Carboniferous siderite were distinguishable when plotted on the ternary Anorthite-SiO_2-FeO. The slags and ironstones under investigation have also been plotted on this ternary, as well as on the FeO-SiO_2-Al_2O_3 and CaO-FeO-SiO_2 diagrams, in the latter case using the method of Reimann and Sperl[79] (see Figures 3.4, 3.6 and 3.7). No clear groups can be differentiated, apart from a recent group (i.e. slags from present day reconstructions of early furnaces) and an archaeological group, hence these particular three component plots are of little use for provenancing. However, the extraction technique affects the relative proportions of CaO, Al_2O_3, SiO_2 and FeO and it is therefore probable that the differences between ores, if these are characterized by only slightly different relative amounts of the four oxides above, might be masked by variations in the smelting technique. This point is discussed further in subsection 5.6. Other three compoment plots, using combinations of Al_2O_3, MnO, MgO, TiO_2 and V_2O_5, might show more distinct groupings. However, it appears from the two component plots that all of those five oxides are of value in distinguishing ore sources and the best results would probably be obtained by using a combination of all of them. The pattern of the ten ratios of these five oxides should give a more specific characterization of the ore source and would allow direct comparison of ores and slags. Statistical techniques which enable several variables to be considered simultaneously are described in the following subsection and their application to the problem of provenancing is discussed.

5.5 Multivariate statistical analysis

Multivariate statistical analysis provides the means for recognising patterns in data which may consist of a large number of variables, the relationships between which are difficult to determine simply by observing the raw numbers. Computer programs are available to carry out the often complicated procedures.

5.5.1 Principal component analysis

The technique of principal component analysis is designed to reduce a large number of variables to a smaller number, the principal components. These principal components combine the original variables in such a way as to account for as much variance as possible in the first component and as much as possible of the remaining variance in the second and so on. Plots, usually of the first principal component versus the second, may reveal a distribution pattern of the data points which could not have been recognized from a simple comparison of all the variables for all the samples. As only ten variables (i.e. the ratios of the weight percentages of Al_2O_3, MnO, MgO, TiO_2 and V_2O_5 with one another) were being considered in the present investigation, a reduction in their number seemed unnecessary and although this method has been used with some success in a provenance study of copper artifacts[114] it was decided not to apply it to the data of this study.

5.5.2 Cluster analysis

The technique known as cluster analysis allows the classification of objects on the basis of a number of variables considered simultaneously. Widely used in the fields of psychology, sociology and

biometry, this method has recently been applied in other disciplines and is currently enjoying some popularity amongst archaeologists. Much of the archaeological work published so far as been directed towards grouping objects on the basis of their chemical compositions. In many cases the identification of groups, considered to be 'significant' in an archaeological sense, has been the sole aim of the work, but some authors have attempted to apply the groupings to specific problems. Cox and Pollard,[117] for instance, in their work on medieval window glass, used cluster analysis to group some 250 samples on the basis of their chemical composition (eleven oxides were measured). The resulting groups were found to be reasonably consistent with the colour, age and weathering properties of the glass and the authors were able to draw some conclusions about the effect of composition on glass durability. In another study, Pollard et al[115] clustered the chemical analyses of 'Rhenish' potsherds excavated in Britain and found that the two major groups formed coincided with the division made on the basis of shape and ornament. In a second run, the analyses of typologically similar potsherds (terra sigillata) from known production centres were added to the data. Distinct clusters were formed in which many of the 'Rhenish' ware samples were grouped with terra sigillata sherds from either Trier or Lezoux. The authors therefore concluded that Rhenish ware and terra sigillata were made from the same clay sources (and hence production centres) and that Trier and Lezoux were the two main centres supplying Britain.

The use of cluster analysis in other areas of archaeology, particularly in the provenance study of Pollard et al and in the work of Haldane (see subsection 5.1), suggested that this technique might be applicable to the present problem. In addition, Sokal and Sneath[133]

argued that clumped distributions are required for the formation of significant clusters; application of the method to a random distribution would still produce clusters although they would be purely arbitrary. The oxide versus oxide plots (Figs. 5.2 to 5.12) show 'clumped' distributions in many cases which suggests that the data is suitable for this type of statistical analysis. It was hoped that the 'ores' (whether probable or possible) from different sources would fall into distinct groups along with their resultant slags, or that at least ironstones and slags from different geographical areas would be differentiated. The validity of the grouping could be tested since at some sites both ore and slag were excavated and if these were correctly assigned to the same source (i.e. cluster) then it could be reasonably assumed that other slags or indeterminate ironstone fragments from the same broad geographical area would also fall into the correct cluster. It was hoped that if one ore source showed a greater compositional range than another, then its cluster would simply be less dense, although no less distinct, than one showing a smaller degree of variation.

In the clustering process, each individual is initially regarded as a cluster and then according to the method used, the two most similar clusters are fused. The fusion process takes place N-1 times, where N is the number of individuals and the final result is therefore one large cluster encompassing all of them. In effect, the two individuals most closely related are grouped together to form one cluster, then as the criteria of admission are gradually lowered (i.e. as a progressively lower similarity coefficient is required to gain admission), further individuals may join that group. Other clusters form when individuals are more closely related to each other

than to the group of individuals forming a cluster already present.
As the fusion continues, the clusters are joined together, forming a
progressively smaller number of composite groups, thus producing a
hierarchical structure with individuals at the base and a single
cluster at the top.

The cluster analyses were performed using the CLUSTAN 1A package
(based on that of Wishart[134]) as implemented at the University of
Aston. The similarity matrix can be computed using a variety of
similarity coefficients, from raw or standardised data or factor
scores (i.e. the results of a principal components analysis, which may
be carried out initially using the same program) and there are eight
hierarchical fusion methods available to produce the clusters.

Only five oxides (Al_2O_3, MnO, MgO, TiO_2 and V_2O_5) were considered
for the reasons discussed in subsection 5.2. In order to be able to
compare slag and ore analyses directly, the assumption was used that
the ratios of these oxides with one another should be unaffected by
the extraction process (see subsection 5.1). The ten ratios of the
above oxides with one another were therefore used as the variables.
It was further assumed that the ratios would show clumped distributions
similar to those of the raw oxides.

It was considered unnecessary to perform a principal components
analysis on the data prior to clustering in view of the small number
of variables. The data was standardised since if this is not done,
the similarity coefficients will be biased towards those variables
which have large variances;[134] it is essential when the data contains
both large and small numbers.[117]

The similarity coefficient chosen was the squared Euclidean distance and although it might be expected that different clusters might be formed from different similarity matrices, it can be shown that for the clustering methods applied, many similarity coefficients produce the same classifications as are obtained when distances are used. It should be noted that the Euclidean distance is actually a measure of dissimilarity and the first fusion therefore involves the two individuals with the lowest coefficient.

Of the available clustering methods, Wishart[134] favours Ward's method, but states that Average Linkage (i.e. Group Average of CLUSTAN 1A at Aston University) is also "reasonably well-behaved". However Ward's method does not always work as Sneath[135] and Wishart[136] point out. Sneath,[135] using the cophenetic correlation technique (this is the best-known means of testing a cluster method, although it may not necessarily be the ideal criterion), found that the Unweighted Pair Group Method (i.e. Group Average) is the best. It was therefore decided to apply both Ward's method and the Group Average method to the data in this study. Both are 'minimum-variance' methods, that is the overall variable distribution within each group is minimized, so that the clusters found are tight spherical ones. One further method, the Nearest Neighbour (Single Linkage) method was also used as this finds 'natural' classes for which some internal variation is allowed, i.e. it can pick out straggly clusters which would probably be subdivided rather arbitrarily by the other two procedures. However, the virtue of being able to pick out such non-spherical clusters may become a vice when the fusion continues to such an extent that extremely long and complicated clusters are produced, the individuals at each end of which may show little similarity to one another. This

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effect is known as 'chaining'. In all three cases, dendrograms were plotted to illustrate the results of the clustering (Figs. 5.13 to 5.15).

It can be seen from the dendrograms that the Nearest Neighbour method has produced no useful clusters and judging from the shape of the dendrogram and the similarity levels at which fusions took place, it appears that chaining has been severe. Although the Group Average method tends to find spherical clusters, the shape of the dendrogram is very similar to that for the Nearest Neighbour method and most clusters are joined together at an early stage. This indicates that whatever the shape of these clusters, they are not sufficiently different to remain as separate entities at lower levels of similarity and hence they are unlikely to be of much use in differentiating materials from different sources. The dendrogram illustrating the clusters produced by Ward's method shows that these groups tend to remain distinct for much longer and even at a low level of similarity (up to a 'dissimilarity' coefficient of 2.8), the Northampton Sand Ironstone and the slags produced from it appear in a separate cluster from other Northamptonshire ores. However, of the three other major groups appearing at this level, one consists of most of the material from the Weald while the other two groups are poorly resolved, both containing high proportions of ironstone from the Ironstone Junction-Band as well as material from other areas.

Of the three clustering methods applied, Ward's method gives by far the best results, although small groups such as the Ramsbury material or the Berkhamsted area slags have not been picked out despite their apparent compositional distinctness. It therefore appears that this particular statistical approach is of limited value in provenancing

ores on the basis of the composition of the resultant slags.

The reasons for the poor performance of cluster analysis probably
lie partly in the technique itself and partly in the data. If the
statistical technique is first considered, perhaps the greatest
disadvantage is that these hierarchic methods form non-overlapping
clusters. End members of one range of ore compositions (or ratios)
characterising one source may therefore be placed in the 'wrong'
cluster because they overlap with members from another range
characterising a different source. There is also the problem of
cluster shape and density. The minimum-variance methods will not find
elongate clusters and will tend to subdivide them into more closely
spherical groups, yet the Nearest Neighbour method, which can do so,
has in this case completely failed to pick out any significant
clusters. As mentioned previously, the major disadvantage of the latter
method is the problem of chaining. If, for instance, there are one
or two points falling between two otherwise distinct 'clouds' of
data points, then this method would tend to find only one large group.
Obviously in the case of these ore and slag analyses there are sufficient
points between the main 'clouds' to prevent the finding of any
significant clusters. Since these particular analyses were carried
out using ten variables, the clusters are located in ten-dimensional
space and there is no easy method for determining how the samples
are distributed, i.e. what shape the clusters ought to be and whether
there are points in the space between them.

The minimum-variance methods may also easily subdivide a cluster
which happens to be less dense than the others. Hence such a method
should find clusters for those ores and slags showing only a small
degree of variation, but may subdivide a group of samples from a more

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variable source in an app arently arbitrary manner.

Wishart[136] points out other limitations of minimum-variance methods which are related to the distribution of the data points. For instance, he argues that the clusters produced are modified by changes in the character set and are transformation-dependent. To illustrate this, he shows that in some cases the use of ratios or standardised variables alters the shape of the distributions (relative to the distributions of the raw data) to such an extent that different clusters are found. In addition, the clusters produced by minimum-variance methods may be destroyed by the introduction of non-relevant characters (variables). In the present study, it appears that the variation of MgO is such that it is perhaps of doubtful value for differentiating ore sources (see Fig. 5.3 for instance). The ratios involving MgO may therefore be non-relevant characters in the above sense (compare Table 5.1).

The data itself is probably in part responsible for the poor clustering. As discussed above, the minumum-variance methods by their very nature will not find groups which show more than a small amount of internal variation. However, if the original ore sources are of very variable composition, it would be unreasonable to expect any clustering methods to produce accurate groupings of ores, let alone ores and slags. Table 5.1 lists the means, standard deviations and coefficients of variation of all ten oxide ratios calculated for the three major ore sources, i.e. the Ironstone Junction-Band, the Northampton Sand Ironstone and the Wadhurst Clay Ironstone. It appears that the Ironstone Junction-Band is of very variable composition and for many ratios its range encompasses that of the Northampton Sand Ironstone, so it is not surprising that these two groups were fused at an early stage in the clustering procedure.

In contrast with the Ironstone Junction-Band, which was sampled at ten different localities, eight of the nine Northampton Sand Ironstone samples were collected from a single quarry, as were five of the six Wadhurst Clay Ironstone samples and the relative homogeneity of these latter two ores is perhaps apparent rather than real. To test this, the means and standard deviations were recalculated to include six published analyses of Northampton Sand Ironstone[111] from two further localities (see Appendix C, Table C.6) and four published analyses of Wadhurst Clay Ironstone[43] from a further four localities (see Appendix C, Table C.11). A comparison of columns 2 and 3 and columns 4 and 5 of Table 5.1 reveals that the inclusion of data from other localities greatly increases the variation of those ratios which do not involve MgO. The ratios of MgO with other oxides are already very variable and the additional data therefore has little effect. It is possible that ironstones of different origin might display different degrees of compositional variation, but the number of samples analysed is too small to be able to detect such trends.

It has to be concluded that cluster analysis is not a suitable method for determining ore source from slag composition. The failure of this technique appears to be partly due to the limitations of the method itself and partly due to the variable compositions of the ore sources. The ironstones and the slags produced from them (where this was known) did not fall into groups which were sufficiently distinct to allow the assignments of unknowns to be accepted with any confidence. Some significant groups however were distinguished, for instance that formed by the Northampton Sand Ironstone with slags and ore fragments excavated at Stamford and South Witham, or that comprised of Wadhurst Clay Ironstone, slag produced from this ore

in furnace reconstructions and slag from the Gardon Hill and Millbrook
sites. This is encouraging as it lends support to the idea that
oxide ratios in slags are the same as those in the original ores and
that the pattern of these ratios can be used to differentiate ore
sources.

5.5.3 Discriminant Analysis

In general, the problem facing the archaeologist will not be one
of locating which of the many British ironstones a particular slag
was derived from, but will be more a matter of deciding which of
several local sources was the one used. Another method of multi-
variate statistical analysis, discriminant analysis, can be used to
help solve such problems. The basis of this method is that the user
defines a number of groups into which a set of observations (each
consisting of several variables) is to be divided. Each group must
consist of two or more observations. The probability of each observation
being in the group it was allocated to can be computed and a number of
other tests to determine the statistical significance of the groupings
can also be performed (see below). An identification routine can then
be used to assign another set of observations (the unknowns) to these
groups such that the probability of assigning an observation to the
wrong group is as small as possible.

The mathematics of this procedure are fully explained in the
literature (e.g. Cooley and Lohnes[137]), but it can be more easily
illustrated in geometrical terms. Figure 5.16 shows the distributions
of two sets of observations, A and B, of two variables X and Y.
Each ellipse is the locus of points of equal density for a particular
group. These ellipses are also known as centours, from centile contours

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and as drawn in Figure 5.16, the outer centours for groups A and B might, for instance, define the regions within which 95% of each group lies and the inner centours might define the regions within which 50% of each group lies. The two points at which corresponding centours intersect define a straight line, I. If the distributions of the points are projected onto a second line, II, perpendicular to I, the overlap between the two groups is smaller than it would be for projections onto any other possible line. The discriminant function therefore transforms each observation (x,y) into a discriminant score which is the location of the observation on line II. The point where line I intersects line II divides the latter into two regions such that if the projection of a point fell in one region it would probably belong to group A, while if it fell in the other it would probably belong to group B.

In a preliminary run to test the performance of this method two groups were defined, a Northamptonshire group and a Wealden group, using all the analyses of slags and ironstone. The ten oxide ratios used for the cluster analysis (see subsection 5.5.1) were also used as the variables in this analysis. The probability of an individual sample being assigned to each of the two groups, if its origin were not already known, was then computed for all samples. No unknowns were put in for identification.

The groups as defined were found to be distinct and two tests of the 'realness' of the differences between the two groups showed good results. The first, Wilks' Lambda criterion, is given by $\Lambda = \frac{W}{T}$, where W is the within groups deviation matrix and T is the total deviation matrix (for further explanation, see Cooley and Lohnes[133]. This is a test of the null hypothesis that the centroid

for each group is equal to the overall centroid for the whole population, i.e. that there is no real difference between the groups. The term centroid is most easily illustrated using a geometrical approach: if each sample is regarded as a vector (i.e. possessing magnitude and direction) then the centroid would be the resultant vector. As Λ decreases, the null hypothesis can be rejected with increasing confidence. Rao's F approximation also tests the significance of the difference between population centroids. This is an approximation to the variance ratio, F, which is a standard test of variance. The observed value for F and the degrees of freedom are given on the output so that published tables for F can be used in the normal way.

For this particular run, F is 9.6278 with 10 and 61 degrees of freedom. Entering the tables for a 1% level of significance with these degrees of freedom, a value for F of 2.63 is obtained and since the observed F is much greater, this suggests that the difference between the group centroids is highly significant. Wilks' Lambda is 0.3878. Knowing the true origins of the samples, it is clear that only four out of a total of 72 would have been misplaced, one sample from the Northants group being given a probability of 0.55 of belonging to the Wealden group and three samples from the Wealden group being given probabilities of 0.71, 0.97 and 0.97 of belonging to the Northants group.

For the example chosen, the use of discriminant analysis has enabled slags and ores from the different geographical areas to be clearly differentiated. A more severe test of this method, and a more realistic one in terms of application to archaeometallurgical

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problems, would be to see whether it can be used to differentiate ore types within a geographical area. The Northants area was chosen for this test since there are two ironstones known to have been used as ore (the Ironstone Junction-Band and the Northampton Sand Ironstone) and one further possible source (limonitic nodules within the Boulder Clay) and slag analyses from seven localities have been obtained. Three ironstone groups were first defined using only samples obtained at outcrop, the Northampton Sand Ironstone data being augmented by six analyses from the literature.[111] As in the previous run, ten oxide ratios were used as the variables.

The results show that the F ratio is 5.1843 with 20 and 54 degrees of freedom. At the 1% significance level, a value for F of ∼2.1 is obtained, which is much lower than the observed F and therefore indicates a highly significant difference between the group centroids. This is supported by the low value of Wilks' Lambda criterion (0.1173). Only two of the 39 samples, one from the Ironstone Junction-Band and one from the Boulder Clay nodule group would have been wrongly assigned if their origins had not been known. Their probabilities of belonging to the Ironstone Junction-Band, Northampton Sand Ironstone and Boulder Clay nodule groups were given as 0.188, 0.444, 0.368 and 0.027, 0.587 and 0.387 respectively.

An identification routine was then used to determine which of these three ironstone groups the excavated slags and ore fragments belong to. The results are shown in Table 5.2. The assignment of the five excavated ore samples correspond to the visual identifications (although these were somewhat tentative in the case of the two roasted samples from Wakerley), with the exception of the roasted ore

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sample from Stamford, which appears to consist of fragments of

Northampton Sand Ironstone but has a probability of 0.601 of

belonging to the Ironstone Junction-Band. The raw ore from Stamford

fell into the Northampton Sand Ironstone group as did one of the Stamford

slags, although the other Stamford slag had a very low probability of

belonging to this group (0.086, as opposed to 0.517 for the Boulder

Clay nodule group and 0.397 for the Ironstone Junction-Band group).

It appears that the Stamford ironworkers were exploiting a source of

Northampton Sand Ironstone which was outside the range of variation

shown by the samples collected recently from quarries. This may be

because the source was a weathered outcrop rather than a fresh quarry

face. The excavated ore fragments from both Wakerley and Great Oakley

were identified as Ironstone Junction-Band and the slags from these two

sites also fall into this group. The slag from Bulwick also has a

very high probability of belonging to the Ironstone Junction-Band

and this assignment is supported by the discovery of quarry pits close

to the furnace which were apparently dug to exploit this ironstone.

The South Witham slag was identified as a member of the Northampton

Sand Ironstone group and the find of a small fragment of oolitic

ironstone, most probably from the Northampton Sand Formation, on the

site helps to confirm this. No ore was found on site with the

Blind Eye Quarry slags, but these were unequivocally identified as

Ironstone Junction-Band group members, while the single lump of ore

found on the site of a Roman temple at Brigstock is apparently derived

from the Northampton Sand Ironstone (probability is 0.957). With

the exception of one of the Stamford slags, which seems to have been

misidentified, none of the unknowns were assigned to the Boulder Clay

nodule group and this suggests that the nodules were not exploited as

a major ore source at any of the sites investigated.

The distinctness of the three ironstone groupings, the generally high probabilities with which the excavated slags and ores are assigned to these groups and the good agreement of these assignations with the available outside evidence shows that discriminant analysis has performed extremely well in this case. This suggests that, with the use of oxide ratios as variables, discriminant analysis could prove to be an extremely useful tool in the provenancing of ores from slags and in the identification of excavated ore fragments.

The one constraint is that each potential ore source must be represented by at least two analyses and this has hampered efforts to apply discriminant analysis to the Weald. Six analyses of Wadhurst Clay Ironstone and one of a limonitic fragment from the Millbrook site have been made during the course of this study. In addition, four further analyses of Wadhurst Clay Ironstone and five analyses of other Wealden ironstones have been published,[43] although V_2O_5 was not determined for most of them. The latter five ironstones have such a wide range of compositions that it is impossible to define a Wadhurst Clay Ironstone group and a non-Wadhurst Clay Ironstone group. It was therefore decided that a second group should be defined using two silty siderite mudstone analyses, one from the Ashdown Beds and the other from the Upper Tunbridge Wells Sand. The results of the discriminant analysis (this time using only six oxide ratios since those involving V_2O_5 had to be omitted) show that this grouping is however not a particularly useful one. The F-ratio is 0.8085 with 6 and 5 degrees of freedom and there is therefore no significant difference between the centroids of the groups. Wilks' Lambda criterion was in

this case 0.5076. The failure of discriminant analysis in this case is due to lack of data and for this reason it is not a fair test of the method.

The results of the present work suggest that providing sufficient representative analyses of the local ironstones are available, discriminant analysis can be used to determine which ore is most likely to have been exploited on the basis of slag composition. However, it can be predicted that there will be some limitations to the use of this method. If, say, two ores were mixed in the proportions of seven parts of A to three parts of B, then this would be reflected in the probabilities of a resultant slag belonging to Group A or Group B. For the sake of the argument, the probability of the slag belonging to Group A might be 0.55 and the probability of belonging to Group B 0.45, but such probabilities could just as easily arise if the ores were not mixed and the composition of the slag happened to fall in the area of overlap of the two groups, just to one side of the dividing line (compare Fig. 5.16). Similar probabilities for membership of the two groups must obviously be interpreted with care. If only a few samples from a batch show similar probabilities, then this is most likely to be a result of their position in the distribution. If however all the slags show similar probabilities of belonging to either group, it might then be reasonable to speculate whether ores were mixed.

If the slag were actually derived from a source other than those considered, the probabilities would again be affected, although not in any systematic way, since the sum of the probabilities of belonging to the groups considered will still be made equal to one. However, if the provenance of a particular sample were in doubt, a test of

variance for each oxide could be made between that sample and the group it had been assigned to. This should be able to detect any major differences between the unknown and the 'typical' members of the group. The use of flux is likely to have a similarly unsystematic effect on the probabilities. Therefore if mixing of ores had been standard practice at a particular site, this would be reflected in the results of a discriminant analysis, but the method is unlikely to detect occasional mixing of ores, addition of flux or the use of an ore other than those considered. Despite these limitations, it is considered that discriminant analysis could be a good means of provenancing ores for early (perhaps up to early medieval) ironworking slags.

5.5.3 Multiple Regression Analysis

In some cases the archaeologist might find it more useful to be able to predict probable ore composition from the slag composition. A further multivariate statistical technique, multiple regression analysis can be applied to data to obtain a predictive formula based on chosen variables. In simple regression analysis, if a variable y is to be predicted from a variable x, a linear correlation between the two being assumed, the regression line itself is found by the least squares method, that is the sum of the squares of the differences between observed and predicted values for y (the error sum of squares) is minimized. The equation of the line is of the form $y = mx + c$ and the slope of the line (m) is the regression coefficient of y on x. In the case of multiple regression it is assumed that a particular variable can be approximated by a linear function of several independent variables and the regression 'line' is calculated in a similar way to that for simple regression. The equation is of the form

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$y = m_1x_1 + m_2x_2 + \ldots m_{p-1}x_{p-1} + c$, where m_1, m_2 $\ldots$ m_{p-1} are the standard partial regression coefficient, c is a constant (this is the intercept term as in the simple case) and p is the total number of variables (i.e. there is one dependent variable, y, and p-1 independent variables x_1, x_2 etc.). The output of the program gives the partial regression coefficients, the intercept term, the multiple correlation coefficient and the residual error. The multiple correlation coefficient is the product-moment correlation between the actual variable y and its predicted value. The square of this multiple correlation coefficient gives the fraction of the error sum of squares that has been accounted for by the linear regression and is a measure of the overall effectiveness of the multiple regression. The residual error is given by $(E.S.S./df)^{\frac{1}{2}}$, where E.S.S. is the error sum of squares and df is the number of degrees of freedom. The residual error allows confidence limits to be calculated, these being given by residual error x t, where t is the value of student's t (obtained from published tables) for the relevant number of degrees of freedom at the required level of significance.

The aim of the present study is to obtain a series of equations by which each oxide in the ore can be predicted from the oxides in the slag. Nine pairs of slags and ores, representing all cases where the slags could reasonably be assumed to have been derived from their associated ores, were used to produce the equations. Three pairs were from recent furnace reconstructions where samples of both ore and slag were available, five pairs were from sites where both slag and ironstone fragments were excavated (Wakerley, Great Oakley, Stamford, Ramsbury and Garden Hill) and in addition the Bulwick slag was paired with a bulk sample of Ironstone Junction-Band collected

very close to the furnace site (see Chapter 2). Where more than one analysis of slag or ironstone was available, an average analysis was calculated, except in the case of Garden Hill where two of the three ore samples were rejected as being unrepresentative (these were fragments of boxwall from boxstone-weathered ironstone, whereas the other sample consisted of both box and core). Some of the excavated ores had been roasted and since in this case the actual weight percentages rather than ratios were being used, it was necessary to 'standardise' the ores by subtracting the loss on ignition from each and recalculating the oxides to 100%, thus in effect roasting them all.

As in the previous two analytical methods, it was assumed that contributions from the charcoal ash might have affected the proportions of CaO, K_2O and P_2O_5 in the slag and no attempt was made to predict the amounts of these oxides in the ore. It was further assumed that the final proportions of Al_2O_3, MnO, MgO, TiO_2 and V_2O_5 in the slag would not be seriously affected by the quantities of CaO, K_2O and P_2O_5 either in the slag or in the original ore and these latter three oxides were therefore omitted from the calculations. From a metallurgical point of view, it is likely that the amounts of 'Fe_2O_3' (i.e. total iron calculated as Fe_2O_3 to permit direct comparison with ore), SiO_2, Al_2O_3, MnO, MgO, TiO_2 and V_2O_5 in the slag would be at least in part determined by the quantities of the latter five oxides in the ore. It therefore seems fair to try to predict the content of Al_2O_3, MnO, MgO, TiO_2 and V_2O_5 in the ore on the basis of the seven oxides in the slag listed above.

Using the multiple regression analysis program, an equation was

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obtained in terms of the seven slag oxides (the independent variables) for each of the five ore oxides (the dependent variables). Initially a 10% level of significance was specified, that is only those independent variables which were significant at the 10% level were included in the regression equation. The following set of equations was obtained:

(1) wt % Al_2O_3 in roasted ore = 9.139 − 0.159 SFe_2O_3 + 0.635 $SSiO_2$ − 8.485 SAl_2O_3 + 14.017 SMnO − 10.397 SMgO + 14.927 $STiO_2$ + 365.235 SV_2O_5

   multiple correlation coefficient = 1.000

      confidence limits   ± 0.928

(2) wt % MnO in roasted ore = − 0.211 + 1.179 SMnO

   multiple correlation coefficient = 0.881

      confidence limits   ± 1.433

(3) wt % MnO in roasted ore = − 0.331 + 1.335 SMgO

   multiple correlation coefficient = 0.902

      confidence limits   ± 1.123

(4) wt % TiO_2 in roasted ore = − 0.102 + 0.842 $STiO_2$

   multiple correlation coefficient = 0.852

      confidence limits   ± 0.199

(5) wt % V_2O_5 in roasted ore = 0.550 − 0.005 SFe_2O_3 − 0.057 SAl_2O_3 + 0.056 SMnO − 0.043 SMgO + 2.605 SV_2O_5

   multiple correlation coefficient = 0.993

      confidence limits   ± 0.013

where SFe_2O_3 = wt % Fe_2O_3 in slag (all Fe calculated as Fe_2O_3), $SSiO_2$ = wt % SiO_2 in slag, etc.

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With the exception of the equation for ore TiO_2, the multiple correlation coefficients are very high, which suggests that the results of the regression analysis are reasonably good. This is reflected in the closeness of fit of the lines in the graphs of observed value of the dependent variable against predicted value (Figs. 5.17 to 5.21). The plots of the dependent variables, y against each of the relevant independent variables (x_1, x_2, etc.), all the other independent variables being held at their average values, shows how well the regression lines fit the data (Figs. 5.22 to 5.36). Although the regression lines are a good fit, the variation of the data means that the confidence limits are wide however and the amounts of the five oxides in the ore cannot be predicted with any real accuracy.

The potential value of these equations can be best assessed by applying them to real problems. As discussed in Chapter 2, although a number of furnaces have been found in the Bulbourne valley, there is no clear evidence to indicate what type of ironstone was smelted. Two possible sources are considered, marcasite nodules from the Chalk or Boulder Clay and boxstones, etc. from the ferruginous sandstones of the Lower Greensand. As can be seen from Table 5.3, because of the wide confidence limits the ore predicted from the bulk analysis of slags from the Bulbourne valley using the regression equations corresponds just as well to both ore types. Similarly, in the case of Caerwent (see Table 5.3) all that can be said is that the predicted ore composition is consistent with the compositions of hematite from both the Forest of Dean and the Bristol District. More encouraging results were obtained for the Blind Eye Quarry slags. Discriminant analysis (see subsection 5.5.2) indicated that there was a very high probability that these two slags were produced from the Ironstone

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Junction-Band and the ore composition as predicted from the regression equations is closely comparable to samples of Ironstone Junction-Band obtained at Clipsham New Quarry, less than 2 km away. Unfortunately however, the nearest locality for which analyses of Northampton Sand Ironstone are available is Stamford (8 km away) and these particular samples appear to be unrepresentative of that ironstone as quarried recently (see subsection 5.5.2). The Northampton Sand Ironstone obtained in or near Stamford in the early medieval period is also closely comparable to the ore predicted from the Blind Eye Quarry slags and no firm conclusions can therefore be drawn.

It is possible that the slags from Berkhamsted and Caerwent were produced from ironstones other than those considered and this would account for the disappointing results. However, it must be concluded that the set of regression equations which have been obtained cannot be used to predict ore compositions with sufficient accuracy to be of much use in the provenancing of ores.

Assuming that the nine slag-ore pairs used to produce the regression equations are representative of excavated material, then the equations are unlikely to be improved by the use of further pairs of analyses. The main problem is one of obtaining samples of ore which are truly representative of that from which the slags were produced. The composition of the few fragments of ironstone which may sometimes be found on an ironworking site may not correspond closely to the 'average' ore charged if the source is heterogenous. The fragments may even have been discarded by the ironworkers. In addition, an archaeologist may inadvertently choose an unrepresentative selection of supposed ore fragments for preservation (as an extreme example, at one of the sites investigated, the ore sample turned out to be two

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iron-oxide coated flint pebbles). It might be possible to use only material from furnace reconstructions to produce the regression equations, but in this case although the ores are known, the slags may differ from archaeological slags derived from the same ore source; too little is known about the effect of different process-steps on the slag composition.

5.6 Factors affecting provenance studies

The present investigation has highlighted the difficulties involved in provenancing iron ores on the basis of slag composition. Some of these difficulties are encountered in any provenance study and include large-scale heterogeneity of the source, smaller-scale heterogeneity of the material under examination and the difficulty of reliably obtaining representative and uncontaminated samples for analysis. Other complications arise from the smelting process itself and from geographical and temporal variations in technique.

For the ore sources studied, careful sampling (see section 5.3) ensured that an 'average' composition for the ironstone at a particular locality was obtained whenever possible. However, 'internal' or intrinsic variability is considerable and to gain an impression of this, consider the analyses of eight Ironstone Junction-Band samples (K1-K4, from Ketton Quarry and WAK 03-06, from Wakerley Great Wood) and of six samples from the genetically different Northampton Sand Ironstone (BC6-BC11, from Brookfield Cottage Pit). The latter six samples were chosen to represent a variety of lithofacies and differing weathering characteristics. The full analyses are given in Appendix C and details of the means and standard deviations are presented in Table 5.4 The Ironstone Junction-Band shows a wide range

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of compositions at every locality. For instance, at Ketton Quarry the mean TiO_2 content was 0.13 wt % with a standard deviation of 0.08 whilst at Wakerley Great Wood $\bar{x}$ = 0.39 and σ = 0.22. Similarly for Al_2O_3, at Ketton $\bar{x}$ = 3.01 and σ = 3.13 whilst at Wakerley Great Wood $\bar{x}$ = 4.14 and σ = 1.80 and for MnO $\bar{x}$ = 0.38 and σ = 0.27 for the former locality and $\bar{x}$ = 0.29 and σ = 0.25 for the latter. There is however no evidence for lateral variation along the outcrop and taking all ten Ironstone Junction-Band localities into account, the means for TiO_2, Al_2O_3 and MnO are 0.27, 3.28 and 0.55 with standard deviations of 0.06, 1.95 and 0.44 respectively. The Northampton Sand Ironstone displays similar characteristics.

Variation in weathering intensity may also give rise to compositional variability. For example, fragments of Northampton Sand Ironstone excavated at Stamford are atypical of recently quarried material in having particularly low CaO and MgO contents. Comparing their compositions with the boxstone weathered Northampton Sand Ironstone from Brookfield Cottage Pit (BC6 and BC8), the fragments most closely correspond to the walls of the boxes rather than the unweathered or rather less weathered box cores (see Table 5.5; geological details are given in Chapter 2). It should be mentioned that the overburden at Brookfield Cottage Pit consists of some 6.5 m of solid strata and a variable thickness of Boulder Clay. Since weathering intensity is broadly related to thickness of cover, the Stamford samples are consistent with their having been obtained from shallow diggings at outcrop. Similar weathering effects are shown by the Wadhurst Clay Ironstone. Shallow diggings at outcrop are of course likely to have been the main method of obtaining ore in early and pre-medieval times.

In contrast with provenance studies of artifacts, where there are often restrictions on the quantity of material removed and on the positions from which samples can be taken, lumps of slag very rarely needed to be preserved in their original form, hence the problem of heterogeneity in the slag was overcome to some extent by extensive and careful sampling. No detailed work on the compositional variation shown by slag from a particular smelt has yet been published, but Straube[1] made five separate analyses of the slag produced during ore smelt in the larger of his two shaft furnace reconstructions. Although the iron oxide and silica contents were similar for each analysis, the minor elements showed a surprising variation (e.g. Al_2O_3 3.33 - 9.67 wt %, MnO 1.55 - 4.70 %, MgO 1.40 - 2.00 %). Straube used a fairly high fuel to ore ratio (1.3:1 during the course of the smelt) in an attempt to produce steel directly and the resultant relatively low iron slag would have been more viscous than the archaeological slags of this study, which are iron rich (Straube's slags averaged 41 wt % FeO, whilst the slags of this study contain more than 60%). Certainly, no tappable slag formed in Straube's experiments, though the furnace had been provided with a tapping arch. The high viscosity of the experimental slag, and the variation in furnace conditions which must have occurred when blocking of the tuyere by slag twice necessitated a change in the direction of the blast, accounts for the presumably unusual heterogeneity. It is thought therefore that the higher degree of operating skill possessed by the early ironworkers and the generally high loss of iron to the slags giving lower viscosities would have resulted in more homogeneous products.

One major complication in the provenancing of iron ores on the basis of slag composition is the absorption into the slag during

its formation of materials other than the gangue component of the ore. These contaminants may include fluxes, fuel ash and the material with which the furnace is constructed or lined.

Limestone and quartz are the materials most likely to have been used as flux. However, apart from a small quantity of high lime slag found on a Romano-British ironworking site,[138] which is assumed to be the result of an accidental addition of limestone to the charge, the proportion of CaO in ancient slags is low and it is generally accepted that limestone was not used as a flux until the medieval period. An early example of the intentional addition of limestone was reported by Morton and Wingrove from a bloomery site at Bourne Pool,[5] dated to the last quarter of the fifteenth century, whilst the earliest documentary evidence appears in the work of Agricola[139] (published in 1556). Sperl[85] argued that since quartz had been used in the smelting of copper during the Bronze Age, it may also have been used as a flux in iron smelting and he reported a number of slags containing quartz from sites in Austria and Italy.[6] It is possible, however, that this quartz represents a portion of the gangue rather than material added as flux. Less likely fluxes are bones (basically calcium phosphate) and gabbro, an igneous rock rich in iron, magnesium and calcium. Sperl[6] speculated that bones may have been charged in bloomery furnaces, either as flux or as part of some magic ritual, although no evidence is presented to support this suggestion. Gabbro was used as flux in an early (mid seventeenth century) blast furnace in America run by well-known English ironmasters,[140] but there is at present no evidence for its use in Britain in either blast furnaces or bloomeries. Clearly, the possibility of such materials being added should be borne in mind when conducting provenance studies involving

iron slag. However, the compositions of the slags investigated give no cause to suspect that <u>any</u> flux was added. Furthermore, the use of oxides such as CaO, SiO_2 and P_2O_5 is avoided in the provenancing methods suggested in this work so that the addition of any of the above materials should not actually affect the results.

Todd[14] (see also Todd and Charles[15]) observed that the ironworkers of the Dimi tribe in Ethiopia charged some slag from previous reductions along with the ore. The pieces selected for addition were of higher density than the rest of the slag and were presumably richer in iron; they probably acted as flux by absorbing some of the gangue components from the ore and so would have improved yield, since a smaller proportion of the iron in the ore would have been required to form a fluid slag. A report on ironworking in Nigeria in the early part of this century[10] also emphasized that the native iron smelters considered the recycling of slag to be of prime importance. Again, the slag selected for charging was more iron-rich than the remainder. Of particular interest in this context is the evidence presented by Tylecote[141] for the utilization of old slag in the early fifteenth century bloomery of Byrkeknott. Tylecote quotes an account roll of Bishop Langley, detailing the building and running of this bloomery, in which reference is made to twelve cartloads of cinders brought from the field of Hopyland and used to modify the iron produced in the new furnace. There was no suggestion of any experimentation and it is possible that the recycling of slag was common practice at the time. By the mid seventeenth century large quantities of Roman slag were being taken · from Worcester to be used as part of the charge of blast furnaces[142] (although in this case the added slag may have been an extra source of iron as well as a flux). Further reports of the recyclying of slag

in the bloomery process date from the mid eighteenth century, when Percy [11] recorded that in the Catalan 'forge' the first slags to be tapped were frequently iron-rich, in which case they were put back into the furnace. In addition, the 'ash' charged in the bloomery at Nornäs, Sweden in 1851[143] may have been cinder or slag from previous smelts. The fluxing properties of the heavier (i.e. more iron-rich) slags could have been discovered at an early date and although not widely documented the addition of such slags to the charge may have been commonly practised. Clearly, the recycling of old slag would influence the composition of the new slag. Where ore from the same source was used to produce both old and new slags, and this would surely have been the usual case, anomalously high values for the minor oxides would result. However, the ratios of the minor oxides with one another should not be affected and attempts to provenance ores using these ratios should therefore still be successful. If, in contrast, the old slag had been produced from a different ore from the one it was being charged with, as was the case when Roman slags from Worcester were charged with Forest of Dean ironstone[142] and as appears to have happened at Byrkeknott, this would cause complications in a provenance study.

In the absence of materials added as flux, the most important contaminant of bloomery slags is the ash from the charcoal. Percy, in the first volume of his extensive work on metallurgy[144] reported in detail the contemporary research on charcoal and wood ash. From the figures quoted, the average ash content of charcoal appears to be approximately 3 wt % and this is supported by a more recent analysis,[109] when the ash content of beech charcoal was determined as 2.62 wt %. However, the proportion of ash does depend on the method of charcoal

burning, the wood type and even on the part of the tree (for instance, the bark of the wild cherry was found to contain 10.37 wt % of ash whilst the wood contained only 0.28 %).[144] A greater degree of slag contamination might therefore be expected if the whole tree was used (as observed by Todd in Ethiopia, for instance)[14,15] than if the trunk only was made into charcoal. It should be mentioned that although coppicing and pollarding have been practised since the neolithic period,[145,146] it seems unlikely that in pre-Medieval times at least, such wood was burnt for charcoal when it was so much in demand for construction work. ·

The composition of charcoal ash varies widely and depends on where the tree grew, since the composition of the soil exerts a strong influence on the mineral oxide content of the wood. Other factors such as the part of the tree, its age and the time of year it was felled also affect the composition of the wood (see for instance the report on investigations made in Sweden in JISI, 1889[147]). Ash analyses quoted by Percy,[144] recalculated as simple oxides, are given in Table 5.6 and the analysis of beech charcoal ash from Tylecote[110] is reproduced for comparison. The main constituents of the ash are K_2O, Na_2O and CaO, with varying amounts of MnO and MgO which occasionally exceed 10 wt %. P_2O_5 and SiO_2 form a variable though generally small (< 5%) proportion of the total.

The significance of the charcoal ash as a slag contaminant depends on the fuel to ore ratio and also on the quality of the ore, since this influences the amount of slag produced. Consider Tylecote et al's[7] figures for the products per unit weight of ore for their experimental shaft furnaces: assuming an ash content of 3 wt % for the charcoal, it

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can be calculated that the ash forms from 1.1 to 20% of the slag

weight, depending on the fuel to ore ratio (see Table 5.7a). Taking

smelts 17, 19 and 20 of these authors, which yielded slags with the

highest FeO contents (46.0, 50.0 and 56.3 wt % respectively), the

average amount of slag produced per unit weight of ore was 0.6.

Provided ores of similar quality were smelted and slags of similar

FeO contents produced, this figure can be used as an estimate of the

amount of slag yielded by other furnaces. Table 5.7a includes

calculations, made using this estimate, of the proportion of fuel ash

in slags from shaft furnaces in Ethiopia[14] and India[11] and from the

Catalan process.[11] The calculations show that for a typical bloomery

furnace under 'normal' operation, the ash from the charcoal used in

smelting constitutes up to 7% of the total slag produced.

It should be noted that additional charcoal may have been used

in preheating the furnace. Reports of present-day bloomeries

indicate that each smelt is begun in a cold furnace, hence a considerable

amount of fuel is required for preheating, and this was probably also

common practice in the past. Tylecote et al.[7] used an average of 72%

of the total charcoal consumption in preheating their experimental

furnaces, whilst Straube[1] used 73% and 65% in preheating his large

and small furnaces respectively, although Todd[14,15] found that the more

skilled ironworkers of the Dimi tribe were more economical, using only

27%. Assuming that most of the ash remained in the furnace, this too

could have been absorbed into the slag and should be taken into account.

Table 5.7b shows the percentage of ash in the slags produced by

Tylecote et al.[7] when the calculations are based on the total

charcoal consumption. Comparison of Tables 5.7a and b shows that fuel

ash could easily constitute 5-10% of ancient slags and it is therefore

a significant contaminant.

The provenancing methods suggested take into account the possibility of contamination by fuel ash and therefore avoid the use of the ash's major constituents, i.e. alkalis and lime, as well as P_2O_5 and SiO_2. Misleading results may be obtained if the soils on which the trees grew were particulary rich in oxides such as MgO or MnO. However, very high concentrations of such oxides, sufficient to affect a provenance study, are probably unusual. It should be noted that although commonly present in large amounts in wood ash (see Table 5.6), Na_2O was rarely detected in the slags of this study. and it is probable that this volatile oxide was lost either during the charcoal burning or the smelting or may even have been leached from the glass phase of the slags.

The clay of the furnace walls or lining constitues another potential source of slag contamination. There appears to be no consensus as to the significance of the erosion of the furnace structure and this is probably because the degree of wear depends on furnace design and operating technique.

Some appreciation of this problem can be gained from the operation of furnace reconstructions. For instance, Adams[148]observed that the fronts of his experimental furnaces (i.e. the area around the tuyere) suffered the most wear and generally had to be rebuilt before the next smelt. He also noted that no iron was produced on those few occasions when the amount of damage had been relatively slight and. rebuilding had been considered unnecessary. This led him to suggest that the furnace walls had some effect in fluxing the embryonic bloom, but unfortunately six experimental smelts designed to test the

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dependence of this process on the composition of the furnace walls were unsuccessful, as each time the atmosphere was insufficiently reducing. No conclusions could therefore be drawn about the significance of the composition of the construction/lining material. Tylecote et al.[7] also reported slagging of the furnace wall around the tuyere of their experimental shaft furnace. Similarly Straube,[1] whose shaft furnace reconstructions were built out of unfired clay bricks cemented together and lined on the inside with clay, found that during the smelt the bricks suffered little damage, except round the tuyere where severe erosion had occurred. In this context, the work of Merkel[149] on reconstructions of Bronze Age copper-smelting furnaces should be mentioned. Using a small shaft 70 cm high and 30 cm diameter constructed of firebricks, Merkel observed severe erosion, particularly at the tuyere level and he estimated that 1 kg of firebrick was lost per smelt. Approximately 20 kg of slag were tapped for each smelt, hence the firebrick components constitute up to 5% of the slag. The same degree of wear was found when the furnace was constructed of clay.

Little information is available about the wear of bloomeries in operation today or in the more recent past. Percy,[11] in his description of the simple slag-tapping clay shaft furnace used in the more remote parts of India in the nineteenth century, reported that in use the lower part wore rapidly away and needed to be constantly repaired with a lining of fresh clay. He also observed the working of the Catalan furnace and noted that one of the walls was purposely constructed of a material which allowed it to become hollowed out during working. This strongly suggests that the fabric of the wall provided an additional source of flux. In contrast,

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Todd[14] (see also Todd and Charles[15]) observed that there was no significant damage to the clay walls of shaft furnaces in use in present-day Ethiopia.

Since preservation is usually poor, it is difficult to assess the extent of wear suffered by ancient furnaces and it is therefore particularly difficult to evaluate the significance of the clay as a slag contaminant. Sperl,[6] in his discussion of the change in composition of the slag during the reduction process stated that the furnace lining is frequently absorbed into the slag in some proportion, thus altering its composition. Furthermore, Norwich[150] concluded that the use of calcareous clay to build the Roman period furnaces at Sacrewell in Northamptonshire, when more suitable clay was available locally, was deliberate and that the clay acted as flux. However, from the available evidence it appears that the furnace walls or linings were often only seriously affected around the tuyeres and this suggests that contamination of the slag would have been localized, since large-scale diffusion is unlikely to have taken place in a matter of hours if the temperatures were near the freezing point of the slag and mechanical mixing would have been limited. Nevertheless in view of Merkel's[149] experiments and Percy's[11] observations on the operation of the Catalan furnace, it appears that under certain conditions relatively large amounts of refractory could have been absorbed into the slag and probably would have significantly altered its composition.

Consider the effect of absorption of clay from the furnace walls into the slag. Clays are hydrous silicates, principally of aluminium or magnesium, with additional cations (particularly alkalis or alkaline

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earths) held between the structural layers. Fireclays however are largely hydrous alumino-silicates, their interlayer cations having been leached by percolating rainwater in the lower soil levels. Early ironworkers were presumably aware that some clays had better refractory properties than others and the clays selected for furnace construction are therefore likely to consist principally of Al_2O_3 and SiO_2. During the course of this study a few samples of slag with pieces of furnace lining/wall attached have been examined. There are usually signs of slag penetration along cracks in the clay and in general a change in the mineralogical composition and structure of the slag in the few millimetres immediately adjacent to the clay is evidence of localized contamination. For example, slag GH1 (from Garden Hill) has a typical mineralogy of wüstite, fayalite and a small amount of glass, with rare isolated patches of hercynite/fayalite intergrowth, but in the vicinity of the attached clay, wüstite is absent, patches of hercynite/fayalite intergrowth are more common and there are also euhedral hercynite crystals present, and the proportion of the glass is increased. This indicates that some of the silica and alumina from the clay has combined with FeO to form extra fayalite and hercynite whilst the remainder has contributed to the glass. Supporting evidence is provided by electron microprobe analyses of the glass adjacent to the clay which show that it has slightly less FeO and more SiO_2 and Al_2O_3 than that in the main body of the slag.

The possibility of contamination of slag resulting from erosion of the furnace walls must be considered when provenancing ores on the basis of slag compostiion, although in many cases such contamination was probably localized and on a small scale. Absorption of clay into the slag would most seriously affect the proportions of Al_2O_3 and SiO_2

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and since the former is used in the suggested provenancing methods, it could give rise to misleading results. This is likely to be more of a problem when furnace slags rather than tap slags are being investigated since the former would have had a much longer contact time with the clay.

The effects of variations in technique on slag composition are not well-known, although attempts have been made in this study to evaluate the effect of variations in fuel consumption and in the conditions governing the degree of wear of the furnace walls or linings. Differences in operating temperatures would have altered the degree of partitioning of elements between slag and metal, but in the bloomery furnace such differences would have been relatively small and should not have any serious effect on slag composition. Small changes in operating methods should not have significantly altered the minor element composition of slags and so should not complicate provenance studies. However, there are some possible procedural differences which might cause problems and which would be difficult to detect. Different strategies for collecting the ore could have given rise to variations in slag composition. For instance, if the ore was collected in small batches, sufficient for only one or two smelts, heterogeneity in the source could lead to some variation in slag composition from smelt to smelt. If in contrast, the work was seasonal and enough ore for the season's campaign was collected and stored in one place, some mixing would have occurred. Roasting and screening of the ore prior to smelting would also have helped to improve its overall homogeneity. Cleere[16,151] presents good evidence for seasonal working at Roman sites in the Weald, operated on a relatively large scale by the Classis Britannica, but similar evidence

from sites in other areas or of other periods is lacking and one can only speculate about how the ironworking was organized. Mixing of ores from different sources might also give misleading results in a provenance study and would be difficult to detect (see for instance subsection 5.5.2).

CHAPTER 6

CONCLUSIONS

Despite the poor preservation of the majority of furnaces on the investigated sites, a great variety of designs and construction methods is apparent. These differences may be due to local evolution of 'imported' designs, variations in quality of local refractories, differences in the nature of the substrate, or genuine technological improvements. Well designed and built slag-tapping shaft furnaces associated with Belgic pottery at Berkhamsted provide evidence in support of that from the Weald [115] that these furnaces were not necessarily introduced by the Romans. The form of some furnaces, e.g. at Wakerley, suggests that the slag was raked out and this is supported by the mineralogical textures of the slags. The raking out of slags, which may have been commonly practised, could have been an intermediate stage in the evolution of tapping from non-tapping furnaces.

The production of iron was widespread in the Iron Age and Romano-British period, not being confined to areas with major ore deposits. Little is known about the prospecting methods employed by the early ironworkers, but a study of the Northamptonshire area suggests that local geomorphology may have been important in the locating of the ores, whilst the ironstone's colour and ease of collection may also have influenced the choice of the early ironworkers.

Recent research on the reduction of iron ores supports Percy's [11] conclusions on the reduction mechanism in the Catalan furnace and although in this case the formation of the bloom and the descent of the ore were controlled, the process must have been closely similar to that in earlier bloomeries. The timing of the formation and separation of slag are

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seen to be crucial for the efficient reduction of the ore and the importance of ore quality is emphasized. Carburisation and subsequent decarburisation of the iron appears to have been a normal part of the bloomery process, the final carbon content of the bloom depending not only on the degree of oxidation in the tuyere zone but also on conditions at the bottom of the furnace.

The investigated bloomery slags have been found to consist principally of fayalite, wüstite and glass. Hercynite and leucite are commonly present, but tend to occur as fine intergrowths. It is therefore possible that the latter minerals were present in slags examined by other workers, but were overlooked. The occurrence of magnetite is generally due to superficial oxidation of the rapidly solidifying slags. Other minor phases have been identified, but no anorthite has been observed and it is considered that this mineral is rare in bloomery slags.

Morton and Wingrove's work on the constitution of medieval bloomery slags[5] has led to the expectation that different ore types might give rise to slags with differing mineralogies. In the present study, slags ranging in age from Early Iron Age to early medieval, produced from a variety of ironstones, have been investigated. There are no great compositional contrasts between the ironstones, as there were between those chosen by Morton and Wingrove, but they are considered typical of the ores available to the early ironworkers. The slags produced from them do not contain any minerals which are characteristic of any of the parent ores, not is there any clear relationship between ore composition and the relative proportions of the slags' constituent phases. It is clear that slag mineralogy can be used to differentiate ore sources only when the ores have markedly

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different contents of certain oxides (that is, oxides such as Al_2O_3 which can influence mineralogy, rather than MgO or MnO which would simply alter the compositions of the major phases; see Chapter 4 section 4.3). Furthermore, the various ore types (e.g. siderites, hematites, etc.) do not necessarily have characteristic compositions and slag mineralogy therefore cannot even be used to determine which ore type was smelted.

Morton and Wingrove[5] found that the medieval slags they investigated generally contained less wüstite than those dating from the Roman period and they inferred that this reflected an improvement in iron-making technique with time. The wüstite contents of the slags in the present study however showed no clear trends and the mineralogical composition in general appears unaffected by either furnace type or the period in which they were produced. The mineralogical composition of bloomery slags cannot therefore be related to technique.

The chemical composition of slags is the principal control on mineralogy and the approximate proportions of the major phases can be predicted by plotting the three or four main components on relatively simple phase diagrams. The presence of minor oxides, making the system far more complex than those represented by the phase diagrams, and non-equilibrium conditions during crystallization are responsible for the discrepancies between predicted and observed amounts of the major phases. The late stage crystallization of minor phases such as leucite, a calcium phosphate mineral and complex silicates can be explained in terms of the change in liquid composition as crystallization proceeds. The type and extent of substitution in the major phases therefore influences the variety and amounts of minor phases which appear.

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The mineralogical textures cannot easily be explained with reference to crystallization paths predicted from the relevant phase diagrams. Many of the textural features are in fact related to the non-equilibrium conditions during cooling, but the gas phase also exerts an influence and the species of nuclei present in the liquid may also be important. Very rapid cooling at a free liquid surface gives rise to a distinctive texture (referred to as a 'chilled surface') and may also locally affect mineralogy, particularly when superficial oxidation occurs in addition. The presence of such chilled surfaces is a good indication that the slag was tapped or possibly raked out of the furnace. Although some textural trends are discernible, no textures apart from the chilled surface which can be related to a specific process-step, technique or furnace type have been distinguished.

Slags ranging in age from Early Iron Age to early medieval, produced in a variety of furnaces and from several different ores have been examined and it must be concluded that although the mineralogical compositions and textures of early bloomery slags can be informative, the lack of consistent trends means that they cannot be used to provide reliable information of wider value to the archaeologist, that is on the ores, furnace type, production technique or age. However as further research produces a better understanding of furnace types and production techniques, perhaps the apparent inconsistencies will be explained.

The relationship between the compositions of ore and slag has been investigated to assess the possibility of identifying ore on the basis of slag chemistry. Unlike copper or tin ores, for which trace element 'fingerprinting' has proved successful, there are large numbers of iron ore deposits and a wide range of different ironstones, making the determination of characteristic trace element patterns for

each very difficult. For this reason and because of the lack of
published data for comparison, uncertainty about the behaviour of
many trace elements under the conditions prevailing in a bloomery
furnace, the possibility that contributions to the slag (e.g. from
fuel ash or clay) might seriously affect the trace element pattern and
the difficulties inherent in determining low concentrations of elements,
trace elements are considered unsuitable for the provenancing of iron
ores. The five minor oxides, Al_2O_3, MnO, MgO, TiO_2 and V_2O_5 are
considered to be more useful because they show a good range of
variation in the different ironstones, should pass directly into
the slag under normal bloomery conditions regardless of minor differences
in operating technique and are not usually present in significant amounts
in charcoal ash.

Two-component plots using different combinations of these oxides
(Figs 5.2-5.12) show a reasonable separation of the Wealden and
Northamptonshire ironstones and slags, although the smaller groups
(e.g. Ramsbury and the Bulbourne Valley) are not so clearly differentiated.
No particular oxide pair is ideal for the purposes of provenancing and
it has been found that the best characterization of ore sources can
be obtained by considering simultaneously the ten ratios of these
five oxides with one another. The use of ratios allows direct
comparison of raw ore, roasted ore and slag as it overcomes the problem
of changing absolute values during roasting and smelting. Multivariate
statistical analysis provides the means for working with such data and
three diffferent techniques have been applied. Cluster analysis,
although used with some success in other branches of archaeology,
does not give sufficiently clear groupings to be of use in provenancing
iron ores. Discriminant analysis however clearly separated Wealden
and Northamptonshire ores and slags, but more importantly it also

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correctly allocated slags from Northamptonshire to each of three
possible sources (Chapter 5, subsection 5.5.2 and Table 5.2). It
has not proved possible to further test this analytical technique
by applying it to other areas as each ore type must be defined on the
basis of at least two samples and in many cases only one was available.
Despite this limitation and the limitations inherent in the technique
(Chapter 5, sections 5.5 and 5.6) discriminant analysis is considered
to be potentially a very useful method of provenancing iron ores and
is probably more widely applicable. Multiple regression analysis was
applied to the data to obtain a set of equations by which the content
of the above five minor oxides in the ore could be predicted from the
slag composition. The multiple correlation coefficients were high,
but the confidence limits were rather wide, hence any predicted oxide
content for an ore would cover a wide range of possible values
(Chapter 5, subsection 5.5.3). The set of equations obtained is
therefore of little use for the determination of ore source on the
basis of slag composition.

A number of factors may affect such provenance studies and these
should always be borne in mind. Slag composition is determined by
ore composition, but may be modified to a varying extent by
contributions from fuel ash, fluxes (if used) and the clay of the
furnace walls or lining. It is considered however that the variation
in slag composition caused by such contaminants would significantly
affect the results of a provenance study only on rare occasions,
providing the pattern of the ratios of Al_2O_3, MnO, MgO, TiO_2 and
V_2O_5 with one another was used as the criterion for comparison of ore
and slag. Slag composition is also influenced by the operating
conditions of the furnace, but the variation in conditions within the

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range conducive to successful smelting is unlikely to have altered slag composition to such an extent that it would complicate the provenancing of ore if based on the pattern of minor oxide ratios. The available information on the variation in composition of slag from a particular smelt is limited. It is expected that tap slags would be more homogeneous than furnace slags, but careful and extensive sampling should however overcome some of the problems of heterogeneity. It is considered that weathering of slags would not significantly affect a provenance study based on the ratios of the five oxides cited above. A close examination of the Northampton Sand Ironstone and the Ironstone Junction-Band has indicated that these two lithologies may show a wide range of compositions at any locality. There appears however to be little further variation along the outcrops so that a bulk sample obtained at one locality should generally be representative of that particular ironstone. It is likely that most other ironstones would show a similar pattern of variation and it is therefore considered that problems caused by heterogeneity in the ore source can be largely overcome by careful sampling. The degree of weathering suffered by an ironstone affects its composition and allowance should be made when comparing ores excavated at archaeological sites with material obtained from recent quarries, where the overburden may be very thick and relatively impermeable. It is likely that sideritic ores would be more severely affected by weathering than chamositic, limonitic or haematitic varieties. Finally, the way in which the ironworking operation is carried out, particularly with regard to the collection of ores, may also cause variations in slag composition which could cause complications in a provenance study; the mixing of ores for instance may be very difficult to detect.

CHAPTER 7

SUGGESTIONS FOR FURTHER WORK

It is generally accepted that, because of its control over the
separation of slag and metal, slag viscosity was an important factor
in early metallurgical processes. Bachmann[64] has developed a formula
relating viscosity to temperature and the viscosity coefficient, K, the
latter being determined from the slag's chemical composition using the
equation:

$$K = \frac{RO + R_2O}{SiO_2 + Al_2O_3} \text{ , where the oxides are in}$$

weight percentages. The relationship does not however hold for slags
containing oxide minerals such as spinels, because the equation used
to calculate the viscosity coefficients is apparently only valid for
basic oxides in combination as silicates or aluminosilicates. In view
of the importance in the bloomery process of obtaining a low melting
point, low viscosity slag, further work in this field would be of
value. The influence of the minor oxides on melting point and viscosity
could be established and the range of compositions and temperatures
giving easily tappable slags more clearly defined. It might then be
possible to find out whether ore composition had any significant
influence on viscosity and whether this in turn influenced furnace type
(i.e. tapping or non-tapping) or whether it was simply the ability to
achieve higher temperatures in some furnaces which allowed the tapping
of slags. The melting/solidifying ranges of slags of different
compositions could also be investigated as this might have some
bearing on the possibility of raking slags out of furnaces.

Experimental work on the effect of cooling rate and degree of undercooling on slag petrography would be of use in comparison with archaeological slags.

The apparently frequent experiments using bloomery furnace reconstructions provide an opportunity to determine the compositional variation of slag from a single smelt in a particular furnace type. It would obviously be of use to have an idea of the heterogeneity of the slag, particularly when using slag composition to provenance ores. Tylecote et al.[7] have published some information on the compositions of slags produced under different operating conditions in their shaft furnace reconstruction, but a more detailed investigation of the variation in chemical and mineralogical composition caused by changing techniques would be useful.

P_2O_5 was rejected for the purposes of provenancing ores on the basis of slag composition because it was considered that the charcoal ash might have contributed large amounts of this oxide to the slag. However, comparison of published analyses of wood and charcoal ash with the compositions of the ironstones studied suggests that in the Northamptonshire area at least the differences in P_2O_5 content of the potential ore sources would probably not have been masked by contributions from the fuel ash. It would perhaps be worth testing whether in some cases P_2O_5 might usefully be included as a discriminating oxide. The discriminant analysis technique described in Chapter 5 might be extended to the provenancing of ores of metals other than iron, in which case it might be desirable to use other minor oxides in addition to the five suggested. The technique could also be tested for use with the iron slags where limestone flux had been used, although its success would obviously depend on the limestone's

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composition, a high MgO content for instance would cause complications.

The choice of 'clays' used in furnace construction is an
interesting problem. The Memoirs of the Geological Survey and Soil
Survey provide useful background data and the comparison of furnace
remains with locally available materials should indicate how discerning
the early ironworkers were and might also suggest what criteria were
used to select suitable refractories.

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