# POST-MEDIEVAL AND MODERN COPPER SMELTING

## TECHNOLOGY REPORT

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**ARCHAEOLOGICAL SCIENCE**

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SUMMARY
This report investigates a range of copper smelting remains which are derived from known technologies in use during the Post-Medieval and Modern periods. The material was investigated in an attempt to establish criteria for the identification of similar remains from the archaeological record.

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# INTRODUCTION

This report investigates a collection of material derived from a number of copper smelting technologies used during the post-medieval and modern periods. The material is thought to have been collected by John Smythe (1874–1958) sometime in the 1930s although exact locations are unknown. The surviving collection consists of 20 samples, each of which represents a different stage in the copper smelting process though the numbering of the samples suggests that there were originally a further 24 samples. Some details of the collection were recorded by Smythe including the quantity of copper contained in each sample (Appendix 1).

The aim of this study is to conduct further analyses (primarily SEM-EDS) on these specimens in an attempt to characterise the various processes involved. The information gained will be used to establish criteria for more accurate identification of copper smelting remains recovered from archaeological sites, and in particular the processes from which they are derived.

In the past the archaeology of the British copper industry has received relatively little attention when compared to other extractive metal industries (Cranstone 2001). Increasingly industrial sites are being revealed as a result of urban development and therefore it is important to have a greater awareness of the types of material which are likely to be uncovered on such sites (Dungworth and Paynter 2006). This study will improve our ability to identify and understand excavated material derived from copper smelting.

# COPPER PRODUCTION IN POST-MEDIEVAL AND MODERN BRITAIN

The British copper smelting industry has had an erratic history, with periods of development and growth followed by several decades when the copper industry declined to a point of virtual non-existence. The latter part of the period saw the re-emergence of the industry on a large scale and British smelters, particularly those in Wales, were considered the most knowledgeable and skilled in the world.

In the mid 16th century the British copper smelting industry was developed largely by German workers who were employed by the Company of the Mines Royal. On the 19th September 1567 the German smelters were finally successful in producing copper on a commercial scale and so the British copper smelting industry began (Donald 1955, 146). The German smelters were responsible for setting up a smelter at Keswick employing similar techniques to those described by Agricola (Hoover and Hoover 1950). In *De Re Metallica*, Agricola gives a detailed account of the smelting of copper-bearing schist from the Mansfeld region in Germany. The technique involved a series of roasting and smelting processes conducted in shaft furnaces fuelled by charcoal. Seven principal operations were involved (see below for details) ore roasting, smelting of roasted ore, roasting of

low grade matte, concentration smelting to obtain rich matte, dead roasting of rich matte which was then smelted to recover black copper which could be further refined to produce usable copper (Hoover and Hoover 1950; Kirnbauer 1966; Tylecote 1992). These operations were time-consuming and the transformation of ore to usable copper took somewhere in the region of 22 weeks. In its 17 years of operation (1567–1584) the Keswick smelter produced approximately 500 tonnes of copper. After 1584 Cornish copper ores were also smelted at Neath in South Wales and it was here that the Welsh tradition began.

Between 1640 and 1680 the copper-smelting industry appears to have been at an all time low. Hammersley (1977, 23) estimates that as little as 40 tons of copper were smelted in Britain during this time. There is still little agreement about why exactly the industry went into such decline. One suggestion is that the monopoly held by the Society of Mines Royal was to blame, the proof being that the industry picked up once again when this monopoly was destroyed and private enterprise was encouraged (Hamilton 1967). Other possible reasons are the high cost of fuel which made it expensive to produce when compared with the relatively low cost of importing finished copper from Europe (Jenkins 1943–45) however it is possible that the demand for copper simply was not high enough to warrant large scale production (Hammersley 1977).

The end of the 17th century brought with it a revival of copper smelting in Britain. This revival coincided with an Act of Parliament in 1688 which decreed that mines containing copper, tin, iron and lead were no longer considered Royal even if they contained gold and/or silver. One of the first people credited with the re-establishment of the copper industry was Sir Clement Clarke who founded a small copper smelting enterprise in London. Later, in 1691 Sir Joseph Herne and five others petitioned for a grant to form The Company of Copper Miners, and various records from the period show that copper mining and smelting activities were on the increase once again (Jenkins 1943–45, 78; Tylecote 1992, 110).

The 18th century saw the foundation of a cartel of smelters called known as 'The Old Company' or 'Associated Smelters' which dominated the industry until the 1780s. At the same time, there was a great expansion of mining in Cornwall and the development of smelting at Swansea and a number of other lesser centres (Hamilton 1967). In the second half of the 18th century the dominance of the 'Associated Smelters' was broken by one Thomas Williams of Llanidan (commonly known as The Copper King) who made an agreement with the Cornish Metal Company to purchase their ores. Williams, who was based at the world's largest copper mine at Parys Mountain in Anglesey, became the most dominant force in the British copper industry until the very end of the century (Hughes 2000; Harris 2003).

At the beginning of the 19th century world copper production was estimated at about 9000 tonnes per year, three quarters of which was smelted in South Wales; by the middle of the century this total had increased to approximately 55,000 tons, and by 1900 this

figure had reached 525,000 tons. The Welsh smelters remained the dominant players in the industry until the latter half of the 20th century (Singer *et al* 1958, 76).

Surprisingly little detail is known about the techniques used to smelt copper. One reason for our lack of knowledge was technological secrecy among industrial competitors. Such secrecy is well illustrated in statements such as this one by J M Douglas in his survey of copper smelting practice in 1899, 'the ridiculous secrecy maintained at so many of the metallurgical works, especially in Europe, benefits no one.' He goes further to say, 'It stands to reason that there must be in art as well as in science, a give and take rule, and those who contribute nothing to the information of the world or their co-workers are not those who are generally most progressive in their own practice.' (Douglas 1899–1900).

## COPPER SMELTING TECHNOLOGY

Copper occurs predominately as sulphide minerals such as chalcopyrite ($CuFeS_2$), bornite ($Cu_5FeS_4$) and chalcocite ($Cu_2S$), although it does occur much less frequently in oxide form (Biswas and Davenport 1976, Atkinson 1987). Metallic copper cannot be produced directly from sulphide ores but instead they must undergo a number of intermediate processes to produce 'matte', a liquid sulphide material which contains all the copper from the ore (copper has an extremely high affinity for sulphur). Matte smelting also produces a liquid slag phase which contains the gangue materials and other metal oxides. Matte is predominately composed of copper and iron sulphides and must undergo a series of oxidation processes to refine it to blister copper which is further refined to usable copper.

Matte smelting is accomplished by melting the furnace charge at temperatures in the region of 1200˚C. The copper, sulphur, iron and precious metals combine to form matte, while the silica ($SiO_2$), alumina ($Al_2O_3$), iron oxides (FeO), lime (CaO) and other minor oxides present in the ores form molten slag. Matte has a high density and low viscosity and will settle below the slag in the furnace so the slag is easily separated and tapped off (Biswas and Davenport 1976).

The principal constituents of a smelting charge are sulphides and oxides of iron and copper along with other oxides such as alumina, lime, magnesia (MgO) and silica. The chemistry of the smelt is largely dictated by the iron, copper, sulphur and oxygen which control matte and slag formation. When melted, the sulphur-bearing charge forms matte which consists principally of iron sulphide (FeS) and copper sulphide ($CuS/Cu_2S$) along with small amounts of other sulphides, e.g. cobalt (CoS), nickel (NiS), lead (PbS) and zinc (ZnS), as well as any precious metals present. Matte can also contain up to 3% dissolved oxygen (Bor and Tarassoff 1971).

The silica content of the smelt is very important as if silica is absent the sulphide-oxide system forms a single phase so there is no slag/matte separation. The higher the silica

content the greater the separation between the two phases so it will be added as a flux if not already present as a gangue material. Yazawa and Kameda (1953, referenced in Asaki *et al* 2007) showed that matte/slag separation will occur when silica is present in quantities of more than 5%. The higher the silica content the greater the separation between the two phases.

A number of different copper smelting techniques have been used at different times and places throughout Europe. This main focus of this report are those technologies which are represented by the material under study (Table 1), however other key technologies used during the period are also discussed.

## Forced-draught shaft furnace

Some of the earliest furnaces used to smelt copper in Britain were forced-draught shaft furnaces, similar to those described by Agricola (Hoover and Hoover 1950, 357, 359) which saw widespread use throughout Europe. In this type of furnace the metal ore and fuel were mixed together and charged from the top. Externally they were square and measured approximately 0.6 metres wide and 1.8 metres high. They were generally built in banks of six against a stone wall, behind which were water powered bellows that supplied air to the furnaces. The fuel used was coal, except for the final stage where it was necessary to use charcoal to eliminate the sulphur which was introduced as a contaminant due to mixing the copper ore with coal. These furnaces were the most common type used at Keswick and Aberdulais (Hughes 2000; Tylecote 1992), however were gradually superseded by the reverberatory furnace in the late 17th century.

## Reverberatory furnace

The use of a reverberatory furnace for copper smelting began in the 1680s and constituted a major advance over previous copper smelting techniques. The reverberatory furnace differed from previous types in that the fuel and charge were contained separately and thus smelting could be conducted using coal without furnace reactions being contaminated by sulphur from the fuel. Reverberatory furnaces were long, low structures with a fire box at one end and a domed roof which deflected the heat down onto the furnace charge (Jenkins 1933–34; Hughes 2000).

Reverberatory furnaces could be used for roasting, melting and refining. In 1698 a Swedish mining engineer, Thomas Cletscher, visited a copper smelting works near Bristol and reported that there were three melting houses each containing three furnaces which were used for roasting, melting and refining. He described the melting furnaces as being built with 'ordinary brick with a lining of fire brick from Windsor, and bound with iron bars'. The refining furnaces were similar in construction but smaller; he gives no description of the roasting furnaces (Jenkins 1933–34, 73).

A Swedish industrialist who travelled around English and Wales between 1753 and 1755, gives similar accounts of reverberatory furnaces in Warmley and Crew's Hole near Bristol and Camborne in Cornwall (Berg and Berg 2001).

The atmosphere created within the furnace is practically neutral and it acts predominately as a melting furnace. For successful working the furnace must reach high temperatures (1400–1600˚C) quickly to allow for the thorough fusion and subsequent separation of materials. In order to achieve these high temperatures large quantities of coal must be burned at a rapid rate (Biswas and Davenport 1976). This furnace type was particularly well suited to many parts of Britain, and in particular Wales, where large quantities of coal were readily available. By the early 1700s the reverberatory furnace had largely replaced the shaft furnace for copper smelting in Britain.

## The Welsh Process

Although the Welsh process is not represented in the surviving part of Smythe's collection, it played an extremely important part in the history of British copper smelting and therefore cannot be overlooked. The process was introduced sometime around 1700 and in its early stages consisted of ten separate operations conducted in reverberatory furnaces (Hopkins 1971). The process was gradually refined by smelters at Swansea until the number of operations involved was reduced to six or seven (Vivian 1823; Tylecote 1992, 149; Percy 1881). The main difference from previous techniques was the use of a roast reaction or double decomposition process which made use of sulphur as a reductant. This was done either by using oxide ores or pre-roasted sulphide ores and utilising the double decomposition reaction which involved cycles of roasting (calcination) and melting (fusion).

$$Cu_2O + FeS = Cu_2S + FeO$$
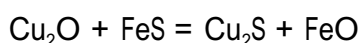
One of the earliest surviving written accounts of the process is given by John Henry Vivian, owner of the Hafod copper works near Swansea, in which he describes in some detail the operations involved. The coarse metal which Vivian refers to is matte which is also sometimes described as 'regulus' (Percy 1881).

The operations basically consist of alternate calcinations (roasting) and fusions (melting) which result in a separation of the metal from waste materials which are skimmed off as slag (Vivian 1823). We can see that the copper content of matte increases as the stages progress.

Process 1: The calcination of the ore

The ore was roasted for a period of 12 to 24 hours after which it was raked into holes at the side of the roasting bed and cooled with water. If the process had been successful, the ore was black and powdery due to the oxidation of some of the iron.


Process 2: The fusion of the calcined ore

The calcined ore is placed in a hopper bin at the top of the furnace and passed into the furnace as required. The principle objective of this process is to heat the substances until they fuse and separate waste slag from metal-bearing material (matte). Some slags from this and later processes were often added to the charge to recover the metal they contained. When the charge was melted the door of the furnace was opened and the liquid mass stirred to allow the complete separation of the matte from the slag. The slag, which would be lighter than the matte, floated to the surface from where it could be skimmed off. This process was repeated several times until a sufficient quantity of matte had collected. It was then tapped from the furnace and granulated by running it into water. The slag was examined and any copper rich material re-smelted; slag which was free from metal (clean slag) was disposed off. The granulated matte contained approximately one third copper, its chief components were sulphur, copper and iron.


Process 3: Calcination of the coarse metal (matte), the product of the first fusion

This process was conducted in a similar fashion to ore calcination. The granulated matte was calcined for 24 hours, being stirred frequently, and the temperature was raised gradually towards the end. At this point one of the chief objectives was to oxidise the iron content.


Process 4: Fusion of the coarse metal after it has undergone calcination

This process was performed in furnaces similar to those in which the ore was melted. Calcined matte (the product of Process 3) was melted along with slags rich in copper oxide (Processes 5 and 6). The copper oxide in the slags and calcined matte was reduced by sulphur which combined with oxygen, and passed off as sulphurous acid gas, while the reduced metal combined with the matte. The coarse metal (matte) was once again tapped into water and in the granulated state was called fine metal, and in solid form blue metal due to the colour of its surface. The process resulted in copper which is approximately 60% pure. The slag was again examined and recycled if it contained sufficient copper.

Process 5: Calcination of the fine metal

This process was performed in the same way as the calcination of coarse metal (see Process 3), oxidising much of the remaining iron.

Process 6: Fusion of the calcined fine metal

This was performed in the same manner as the melting of the coarse metal (Process 4) and resulted in a coarse copper which was 80–90% pure.

Process 7: Roasting

Pigs of coarse copper were placed into a furnace and exposed to the action of air, which was drawn through the furnace at high temperatures. Any volatile substances were expelled from the copper and any iron or other metals combined with the copper were oxidized. Towards the end of the operation the temperature was raised until the metal was fused and tapped into sand beds to form pigs, which were covered with black blisters, hence the name — blister copper.

Process 8: Refining or toughening

The pigs of metal from the roasters were placed in the furnace and in the first instance heated to a moderate temperature in order to complete the roasting or oxidizing process if necessary. When the charge was melted the slags were skimmed off leaving refined copper. The refined copper was then toughened by throwing charcoal or anthracite on the surface, which reduced any copper oxide present, and the molten metal was stirred or poled using green wood to enhance the reducing atmosphere (Vivian 1823; Percy 1881; Derry and Williams 1960).

Blast furnace smelting

Blast furnaces are large vertical structures wherein copper ore is mixed with fuel (and a flux of limestone or sand – depending on the nature of the copper ore) and blown with a powered air blast (Hughes 2000). Smelting in a blast furnace was cheap, efficient and flexible, in particular because its atmosphere could be controlled, and therefore was used to melt, oxidise or reduce. The mixed ore and fuel were charged at the top of the furnace and slag and matte were tapped at the bottom. Furnaces of this type were introduced in the Hafod copper works around 1859 (Percy 1881). The technology works on the principle that oxygen is added to the charge to eliminate the sulphur and iron content and to concentrate the copper. Oxygen can be added in one of three ways

a) prior to actual smelting by roasting
b) during the smelting process either by
- adding oxidised materials to the charge
- using the air blast of the furnace to oxidise the iron and sulphur while at the same time using their combustible qualities as fuel (pyrite smelting).

Distinction must be made between the smaller shaft furnaces which are described by Agricola which are often referred to as 'blast furnaces' by some authors (eg Tylecote 1986; 1992).

## Pyrite smelting

The notion of pyrite smelting was introduced to the copper industry in the late 1800s and was one of the most important developments of blast furnace technology. It was successfully demonstrated that the heat generated by the oxidation of sulphur contained in pyrite copper ores was strong enough to make their smelting a self-supporting operation (it was an exothermic reaction). It was essential that the charge contained the correct proportions of sulphur, iron and silica, and coke fuel was used to initiate the reaction. The process had several advantages, one of the most important of which was that less carbonaceous fuel was needed providing that the furnace conditions were sufficiently oxidising for the necessary reactions to take place. Three key factors are essential for successful smelting:

- a sufficient amount of iron sulphide in the charge to generate the required heat
- sufficient amounts of air for the rapid oxidation of the sulphur and iron
- sufficient quantities of flux (free silica) to combine with the iron to form slag.

There are two types of pyrite smelting. In the first the operation is sustained solely by the combustion of sulphur from the ore without the assistance of either fuel or a hot blast, and in the second the process is accelerated by fuel or hot blast or both (Levy 1912).

The extent to which pyrite smelting can be conducted depends largely on the nature of the charge, particularly on the relative proportions of copper, iron and sulphur in the ore and on the composition and quality of the gangue material.

## The Bessemer process

The Bessemer process was originally patented (1855) as a method of converting molten pig iron to steel by blowing air through the molten iron. In the copper industry the process is used to convert liquid matte to metal (blister copper). It was first successfully applied to the copper industry on a commercial scale in the early 1880s (Levy 1912).

The process involves the rapid oxidation of iron and sulphur under controlled conditions at temperatures in the region of 1150–1250˚C. Silica is added as a flux and reacts with the iron oxide to form slag while the sulphur dioxide evaporates from the system, or in some cases is collected for the manufacture of sulphuric acid. The heat derived from the combination of oxygen with iron and sulphur and the reaction between the iron oxide and silica produces adequate heat to make it an exothermic process and thus independent of external heat sources (Biswas and Davenport 1976).

During the Bessemerisation of mattes the quantity of slag produced is almost equal in weight to the original amount of matte, while the resulting blister copper is less than half the original weight of matte (Peters 1887; Levy 1912; Biswas and Davenport 1976). The duration of the process depends on the grade of matte, the higher the grade (i.e. the greater the proportion of copper) the quicker the process. Use of the Bessemer process dramatically decreased the amount of time required to produce copper, what used to take four or five days could be achieved in a matter of hours (Lynch 2002).

## Refining

Refining of blister copper to usable copper is the last stage in the copper smelting process. Smythe refers to refining without providing any specific detail of the process. It is likely that most refining techniques are similar to those described by Vivian (1823) which involved the re-melting of blister copper under oxidising conditions, while blowing a blast of air over the metal surface. This would eliminate any residual sulphur and iron resulting in a better quality metal (Mei and Rehren 2005).

## SMYTHE'S SAMPLES AND THEIR EXAMINATION

Samples from four different technologies were represented in the collection: blast furnace smelting, the Bessemer process, pyrite smelting and refining – all of which have been described above. Slag and matte are the most common materials from each of these processes and Smythe collected both materials from different stages of each process.

Photographs of the specimens before sampling are included in Appendix 4. After visual examination samples were cut from Smythe's specimens and were mounted in epoxy resin and ground and polished to a 1micron finish. They were examined using a reflected light microscope followed by a scanning electron microscope (SEM) (FEI Inspect F). Most specimens were inhomogeneous with different phases present in different areas. Chemical compositions of bulk areas and individual phases were determined using an energy dispersive spectrometer (EDS) (Oxford Instruments INCA X-act) attached to the electron microscope. The instrument was operated at 25kV. Detection limits vary and a full list is presented in Appendix 2.

Table 1: Samples collected by Smythe

| Sample | Smythe's Description | Process | Material |
|--------|---------------------|---------|----------|
| 25 | First matte | Blast furnace smelting | Matte |
| 26 | Rich slag | Blast furnace smelting | Slag |
| 27 | Clean slag | Blast furnace smelting | Slag |
| 28 | Lining of blast furnace | Blast furnace smelting | Matte |
| 29 | Bessemer copper | Bessemer process | Copper |
| 30 | Rich matte | Bessemer process | Matte |
| 31 | Matte | Bessemer process | Matte |
| 33 | Slag from copper | Bessemer process | Slag |
| 34 | Slag from rich matte | Bessemer process | Slag |
| 35 | Slag from settlers | Bessemer process | Slag |
| 36 | Poor slag | Bessemer process | Slag |
| 36a | Dust from Bessemer process | Bessemer process | Copper oxide dust |
| 37 | Matte | Pyrite smelting | Matte |
| 38 | Slag | Pyrite smelting | Slag |
| 39 | Slag, re-smelted with the addition of matte | Pyrite smelting | Slag |
| 40 | Slag from fore-hearth | Pyrite smelting | Slag |
| 41 | Dust from the furnace | Pyrite smelting | Dust |
| 42 | Slag from early stages of refining | Refining | Slag |
| 43 | Slag from end of refining process | Refining | Slag |
| 44 | Dust from the dust chamber | Refining | Dust |
| 45 | Bar copper | Refining | Copper |

Bulk chemical analyses were conducted to determine the overall composition of the samples. Where possible, the mean composition of four bulk areas, each measuring approximately 3mm wide were calculated and reported here. Analytical results for these bulk areas are given stoichiometrically as oxides, normalised to 100% so that they are comparable and are expressed in weight %. The compositions of individual phases are reported as elements rather than oxides due to the matte content of the slag, the composition of which is predominately sulphide and therefore cannot be calculated stoichiometrically as oxides.

Many of the phases identified do not correspond precisely with theoretical composition of compounds (a list of which are given in Appendix 3). In many cases this is due to the presence or substitution of other minor elements which distort 'pure' compositions. For this reason, many phases are labelled as 'olivine', 'spinel', 'CuFeS' etc. where we can say that a certain phase belongs to the olivine family, for example, but where precise nomenclature is difficult. In other cases phases are not attributable to any particular group of minerals.

# RESULTS FOR THE SLAG SAMPLES

## Blast furnace smelting

The two samples of blast furnace slag were macroscopically different; sample 26 (rich slag) was extremely porous, physically heterogeneous and contained several fuel inclusions. Sample 27 (clean slag) on the other hand was much less porous and had a platey appearance with several glassy areas. Bulk area analyses of these specimens (Table 2) revealed relatively minor differences. The rich slag contained slightly higher quantities of alumina and iron oxide while the clean slag contained slightly more silica and lime. Of note is the fact that the clean slag contains almost equal amounts of silica and iron oxide. Significant amounts of lime are present in both specimens and this may indicate that it was added to the charge as a flux.

*Table 2. Mean bulk compositions of areas in blast furnaces slags*

|  | Sample 26 rich slag | Sample 27 clean slag |
|---|---|---|
| MgO | 1.5 | 1.7 |
| $Al_2O_3$ | 7.3 | 6.4 |
| $SiO_2$ | 34.3 | 37.1 |
| $SO_2$ | 1.8 | 1.4 |
| $K_2O$ | 0.6 | 0.5 |
| CaO | 11.5 | 14.6 |
| $TiO_2$ | 0.3 | 0.4 |
| MnO | 0.4 | 0.4 |
| FeO | 41.9 | 37.2 |
| CuO | 0.4 | 0.3 |
| ZnO | 0.3 | 0.3 |

Both specimens contain dendrites of olivine with an approximately fayalitic composition ($Fe_2SiO_4$) dispersed in a glassy matrix (Fig 1 a, c)(Table 3). In both cases some of the iron has been substituted by magnesium and lime. The dendrites are finer and more elongated in the clean slag (sample 27, Fig 1c). Both specimens also contain separate phases of copper-iron-sulphide ('CuFeS') and iron sulphide, (possibly troilite — see Appendix 3), with a small amount of copper substituting for the iron; however these areas are more numerous in the rich slag which also contains un-reacted silica (Fig 1b). The copper-iron-sulphide phases contain just under 3% oxygen which is just within the limits suggested by Bor and Tarassoff (1971). The matrices are rich in silica and lime and to a lesser extent alumina. In terms of distinguishing between the two specimens there is little difference in bulk chemistry, however the microstructure of sample 26 has a higher proportion of sulphide material (copper iron sulphide (matte) and iron sulphide; Fig 1d) as well as un-reacted silica.
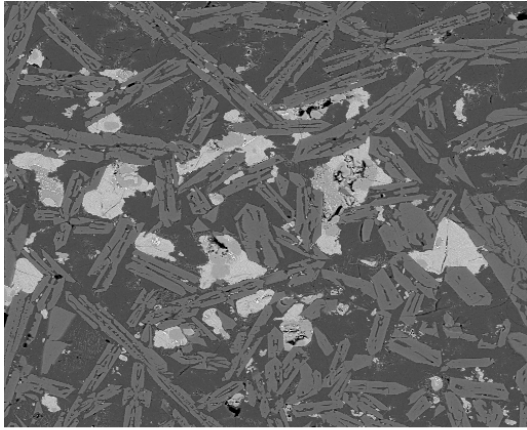
(a) dendrites of fayalite (mid grey) and droplets of matte (light grey) in a glassy matrix (darker grey)
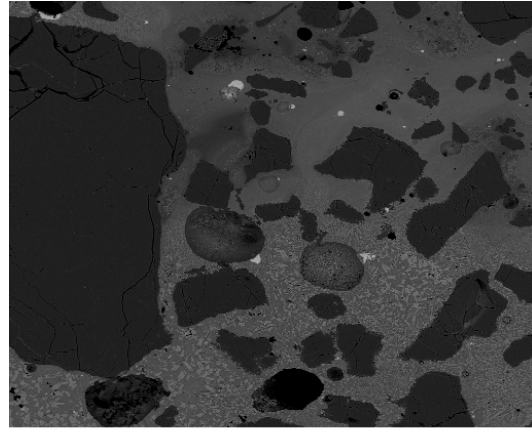


(b) area showing angular grains of un-reacted silica (dark areas)
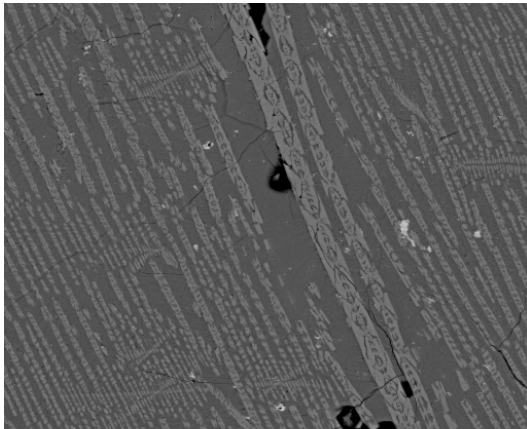


(c) slag matrix with elongated dendrites of fayalite (mid grey)
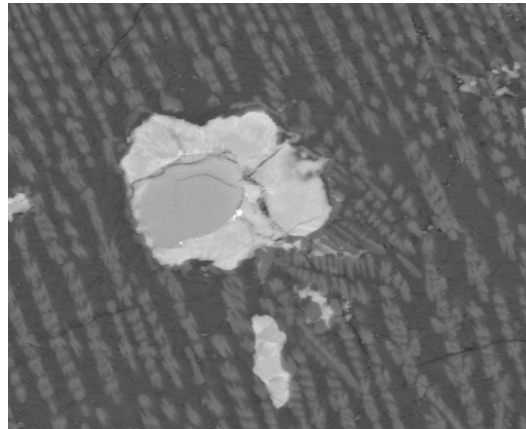


(d) matte droplet containing copper-iron-sulphide (light grey) and iron sulphide (mid grey).

Figure 1. Backscatter electron (BSE) micrographs showing the range of phases present in two samples of blast furnace slag, a – b are sample 26 and c – d are sample 27.

*Table 3. Composition of individual phases contained in the blast furnace slags (wt%)*

|  | Sample 26 | | | | Sample 27 | | | |
|  | 'Olivine' | 'FeS' | 'CuFeS' | Matrix | 'Olivine' | 'FeS' | 'CuFeS' | Matrix |
|---|---|---|---|---|---|---|---|---|
| O | 33.1 | <0.5 | 2.8 | 40.9 | 35.8 | <0.5 | 2.6 | 40.4 |
| Mg | 1.7 | <0.2 | <0.2 | 0.3 | 2.6 | <0.2 | <0.2 | 0.6 |
| Al | <0.2 | <0.2 | <0.2 | 5.7 | 0.9 | <0.2 | <0.2 | 4.1 |
| Si | 13.2 | <0.2 | 0.3 | 18.1 | 14.3 | 0.2 | 0.7 | 18.4 |
| S | <0.1 | 35.5 | 24.1 | <0.1 | <0.1 | 35.5 | 25.1 | 0.3 |
| K | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | <0.1 | <0.1 | 0.2 |
| Ca | 2.5 | <0.1 | <0.1 | 14.9 | 3.9 | 0.3 | 0.6 | 13.7 |
| Ti | <0.1 | <0.1 | <0.1 | 0.3 | <0.1 | <0.1 | <0.1 | 0.3 |
| Mn | 0.5 | <0.1 | <0.1 | 0.2 | 0.5 | <0.1 | <0.1 | 0.2 |
| Fe | 48.8 | 62.8 | 15.6 | 19.7 | 41.9 | 61.9 | 17.9 | 21.6 |
| Ni | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.3 | <0.2 | <0.2 |
| Cu | 0.2 | 1.7 | 57.3 | <0.2 | <0.1 | 1.9 | 53 | <0.2 |
| Zn | <0.2 | <0.2 | <0.2 | <0.2 | 0.2 | <0.2 | <0.2 | <0.2 |

## Pyrite smelting

Three different slag samples (samples 38, 39 and 40) were derived from pyrite smelting. The first, sample 38 was described by Smythe as slag from pyrite smelting, sample 39 as slag with added matte (it is unclear exactly what this means), and sample 40 as slag from the fore hearth.

*Table 4. Mean compositions of bulk areas of slag from pyrite smelting*

|  | sample 38 slag | sample 39 with matte | sample 40 fore hearth |
|---|---|---|---|
| $Na_2O$ | 0.4 | 0.6 | 0.4 |
| MgO | 1.0 | 1.8 | 1.2 |
| $Al_2O_3$ | 4.3 | 8.0 | 5.7 |
| $SiO_2$ | 31.7 | 40.0 | 32.4 |
| $SO_3$ | 4.2 | 1.1 | 5.5 |
| $K_2O$ | 0.4 | 0.6 | 0.5 |
| CaO | 5.1 | 13.2 | 5.4 |
| $TiO_2$ | <0.1 | 0.5 | <0.1 |
| MnO | <0.1 | 0.4 | <0.1 |
| FeO | 49.3 | 34.0 | 44.5 |
| CuO | 0.4 | 0.4 | 0.9 |
| ZnO | 0.5 | <0.2 | 0.4 |
| BaO | 3.2 | <0.1 | 3.6 |

In terms of bulk chemistry, sample 39 stands out in the group as having the lowest quantities of iron oxide and sulphur, while levels of lime and to a lesser extent silica and alumina are higher than in the other samples (Table 4). What is striking here is that as

sample 39 is described as Smythe as having added matte, one might expect it to contain higher amounts of sulphur, iron and copper, however the opposite is true and it contains the lowest quantities of each oxide.

Also of note is that both samples 38 and 40 both contain around 3% barium oxide which is likely to be a component of the gangue material of the ore.

The microstructure of sample 38 is extremely fine (Fig 2a) and in most cases too fine for individual phase analyses. The specimen contains visible droplets of copper-iron-sulphide and iron sulphide (Fig 2b). The iron sulphide has a composition close to troilite while the copper-iron-sulphide is probably a mixture of two different phases.
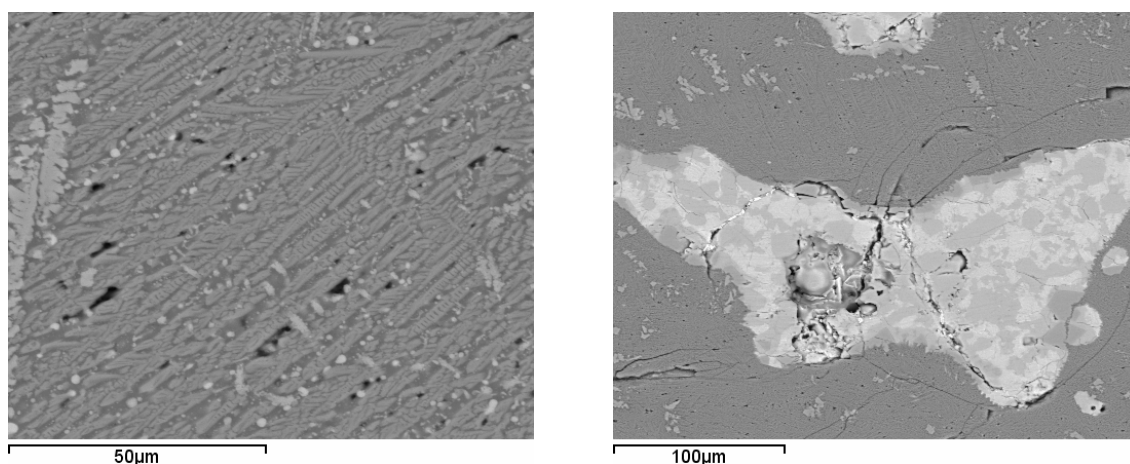


Figure 2. BSE images of sample 38, slag from pyrite smelting. (a, left) fine dendritic structure. (b, right) droplet of mixed copper-iron-sulphide (light grey) and iron sulphide (mid grey).

Table 5. Composition of phases identified in sample 38 – slag from pyrite smelting.

|     | 'FeS' | 'CuFeS' |
| --- | --- | --- |
| O | <0.5 | <0.5 |
| Na | <0.2 | <0.2 |
| Mg | <0.2 | <0.2 |
| Al | <0.2 | <0.2 |
| Si | 0.2 | <0.2 |
| S | 36.6 | 27.6 |
| K | <0.1 | <0.1 |
| Ca | <0.1 | <0.1 |
| Ti | <0.1 | <0.1 |
| Fe | 63.2 | 20.6 |
| Cu | <0.2 | 51.8 |
| Zn | <0.2 | <0.2 |
| Ba | <0.1 | <0.1 |

Sample 39 contains areas of copper-iron-sulphide (Fig 3a) with a range of compositions (Table 6). It also contains iron silicate of varying compositions some of which have high lime and alumina. There are several areas of un-reacted silica (Fig 3b), the oxygen content of which is lower than one would expect which may suggest that oxygen is being under estimated. The matrix is rich lime and alumina and also contains minor amounts of other elements.
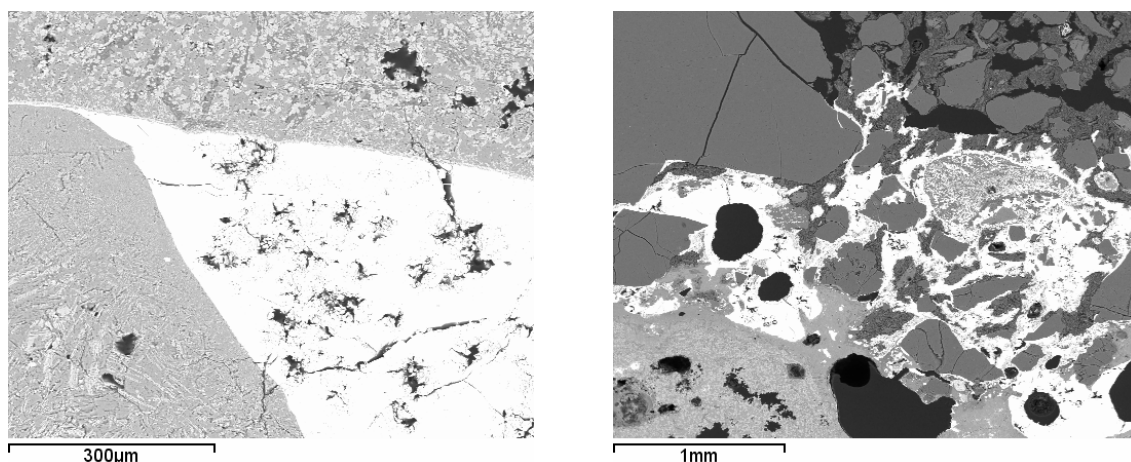


Figure 3. BSE images of sample 39. (a, left) very fine dendritic olivine structures surrounding large area of copper-iron-sulphide (white). (b, right) showing silica (dark grey), iron sulphide (mid-grey), iron silicates (light grey), copper-iron-sulphide (white), the darkest sub-circular areas are voids.

Table 6. Composition of phases identified in sample 39

|    | Olivine | 'FeSi' | 'CuFeS' | 'CuFeS' | Silica | Matrix |
|----|---------|--------|---------|---------|--------|--------|
| O  | 35.5    | 28.3   | 4.6     | 3.1     | 49.3   | 42.3   |
| Na | 0.4     | <0.2   | <0.2    | <0.2    | <0.2   | 0.7    |
| Mg | 1.1     | 3.7    | <0.2    | <0.2    | <0.2   | <0.2   |
| Al | 4.2     | <0.2   | <0.2    | <0.2    | <0.2   | 18.1   |
| Si | 20.1    | 15.1   | <0.2    | <0.2    | 50.7   | 23.0   |
| S  | 0.4     | <0.1   | 22.7    | 24.1    | <0.1   | <0.1   |
| K  | 0.6     | <0.1   | <0.1    | <0.1    | <0.1   | 0.6    |
| Ca | 10.1    | 1.4    | <0.1    | <0.1    | <0.1   | 13.7   |
| Ti | 0.3     | <0.1   | <0.1    | <0.1    | <0.1   | <0.1   |
| Mn | 0.3     | 0.6    | <0.1    | <0.1    | <0.1   | <0.1   |
| Fe | 27.2    | 51.0   | 20.0    | 16.0    | <0.1   | 1.7    |
| Cu | <0.2    | <0.2   | 52.8    | 56.9    | <0.2   | <0.2   |
| Zn | <0.2    | <0.2   | <0.2    | <0.2    | <0.2   | <0.2   |

Sample 40 is composed of olivine, spinel and iron sulphide dispersed in a glassy matrix. The olivine contains significant quantities of magnesium (Table 7) and is likely to be fayalite with magnesium substituting for some of the iron. The oxygen content of the spinel is low and in this respect resembles wüstite, however its crystal structure resembles magnetite (Fig 4). It is possible that the oxygen content is being underestimated. The iron

sulphide has a similar composition to troilite with a small amount of copper. The matrix is composed of similar amounts of iron and silica (22–25%) with medium levels of lime and approximately 5% alumina and barium. No copper-iron-sulphide (matte) is visible in the sample.



300μm
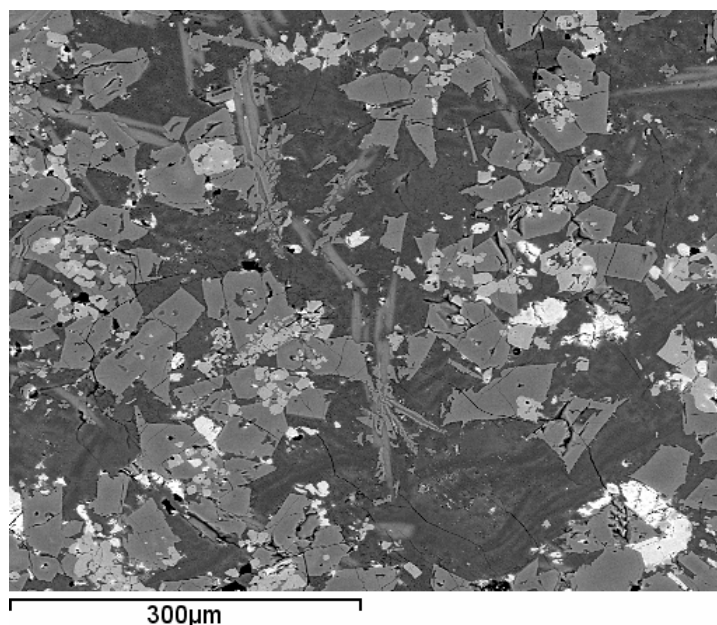
*Figure 4. BSE image of sample 40 showing iron sulphide (mid-grey), olivine (dark grey), spinel (white) in a glassy matrix (dark background)*

*Table 7. Composition of phases in sample 40*

|      | Spinel | Olivine | FeS   | Matrix |
|------|--------|---------|-------|--------|
| O    | 22.8   | 27.4    | <0.5  | 32.9   |
| Na   | <0.2   | <0.2    | <0.2  | 0.3    |
| Mg   | <0.2   | 4.3     | <0.2  | <0.2   |
| Al   | 2.9    | <0.2    | <0.2  | 4.9    |
| Si   | 0.8    | 15.4    | <0.2  | 22.1   |
| S    | <0.1   | <0.1    | 36.1  | 0.2    |
| K    | <0.1   | <0.1    | <0.1  | 0.6    |
| Ca   | 0.3    | 0.5     | <0.1  | 7.2    |
| Ti   | 0.8    | <0.1    | <0.1  | <0.1   |
| Fe   | 72.1   | 52.1    | 62.1  | 24.7   |
| Cu   | <0.2   | <0.2    | 1.8   | <0.2   |
| Zn   | 0.4    | 0.3     | <0.2  | 0.4    |
| Ba   | <0.1   | <0.1    | <0.1  | 6.8    |

## Bessemer process

Four samples of slag, each derived from a different stage of the Bessemer process, were examined. They are described by Smythe as slag from copper (sample 33), slag from rich matte (sample 34), slag from settlers (sample 35) and poor slag (sample 36). Visually samples 33, 34 and 36 are fairly similar and can be described as dense slags, dark grey in colour with a sub-metallic lustre while sample 35 has a high degree of porosity, is green in colour and has a dull lustre. They are broadly characterised by high silica contents and very high levels of iron oxide, as well as alumina in the range of 3–3.5% (Table 8).

*Table 8. Mean compositions of bulk areas of Bessemer slags*

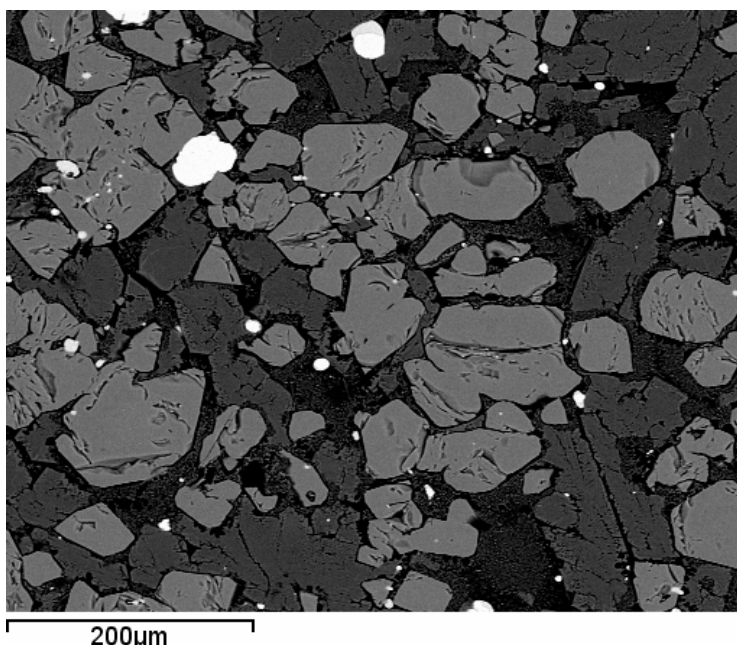|  | Sample 33 (copper) | sample 34 (rich matte) | sample 35 (Settlers) | sample 36 (poor slag) |
|---|---|---|---|---|
| MgO | <0.2 | 0.4 | 0.3 | <0.2 |
| $Al_2O_3$ | 2.6 | 3.5 | 2.6 | 3.5 |
| $SiO_2$ | 25.6 | 36.5 | 37.7 | 32.0 |
| $SO_3$ | 0.6 | 2.0 | 1.1 | 2.3 |
| $K_2O$ | 0.2 | 0.3 | 0.3 | 0.3 |
| CaO | <0.1 | <0.1 | 1.9 | 0.2 |
| MnO | <0.2 | <0.2 | 0.2 | <0.2 |
| $TiO_2$ | 0.2 | 0.4 | <0.1 | 0.3 |
| CrO | <0.1 | 0.9 | <0.1 | <0.1 |
| FeO | 67.5 | 51.5 | 55.0 | 60.9 |
| CuO | 4.0 | 5.3 | 1.1 | 0.6 |



200µm

*Figure 5. BSE image of sample 33 containing iron silicate (dark grey), spinel (mid grey) and droplets of copper (white) in a glassy matrix (darkest).*

*Table 9. Composition of the phases identified in sample 33*

|      | Spinel | FeSi  | Copper | Matrix 1 | Matrix 2 |
|------|--------|-------|--------|----------|----------|
| O    | 29.0   | 36.2  | 1.0    | 47.3     | 41.8     |
| Al   | 1.0    | 0.5   | <0.2   | 8.0      | 2.6      |
| Si   | 0.3    | 17.2  | <0.2   | 26.0     | 21.5     |
| S    | <0.1   | <0.1  | 0.2    | <0.1     | <0.1     |
| K    | <0.1   | 0.3   | <0.1   | 0.6      | 0.4      |
| Ca   | <0.1   | <0.1  | <0.1   | 1.3      | 0.3      |
| Ti   | <0.1   | <0.1  | <0.1   | 0.2      | <0.1     |
| Mn   | <0.1   | 0.2   | <0.1   | <0.1     | <0.1     |
| Fe   | 69.8   | 45.7  | 2.7    | 16.4     | 33.1     |
| Cu   | <0.2   | <0.2  | 96.1   | 0.4      | 0.3      |

Other minor oxides ($K_2O$, $TiO_2$, ZnO) are present in quantities below 1% and as a result cannot be used to characterise samples in terms of their bulk chemistry.

Three of the samples (samples 33, 34 and 35) contain quantities of copper ranging from 1–5% while sample 36 (poor slag) contains less than 1% copper along with the highest quantity of sulphur (Table 8).

Sample 33 consists of iron silicate, the composition of which lies somewhere between the olivine fayalite ($Fe_2SiO_4$) and pyroxene ferrosilite ($Fe_2Si_2O_6$) (see Appendix 2). The spinel composition approximates to magnetite ($Fe_3O_4$) however the iron content is slightly lower. The glassy matrix contains some areas with high iron and relatively low alumina while the opposite is true in other areas (Table 9). The specimen also contains a number of copper droplets which contain a small quantity of iron as well as other minor elements. The specimen contains no visible copper-iron-sulphide (matte) inclusions (Fig 5).

Sample 34 is made up of olivine and spinel as well as silica and copper sulphide inclusions in a complex matrix (Fig 6 and Table 10). The composition of the copper sulphide corresponds well with chalcocite ($Cu_2S$). The glassy matrix contains a number of phases which are too small for individual analysis and therefore the average analysis cannot be interpreted. Unlike sample 33, this sample contains no copper droplets but does contain matte (copper sulphide). Within the spinel phase, which is mainly magnetite, some of the iron is substituted by a number of minor elements including chromium which is also detected in the bulk analysis (Tables 8 and 10). The chromium is likely to reflect the type of ore being smelted, however further discussion of the ore type is beyond the scope of this report.
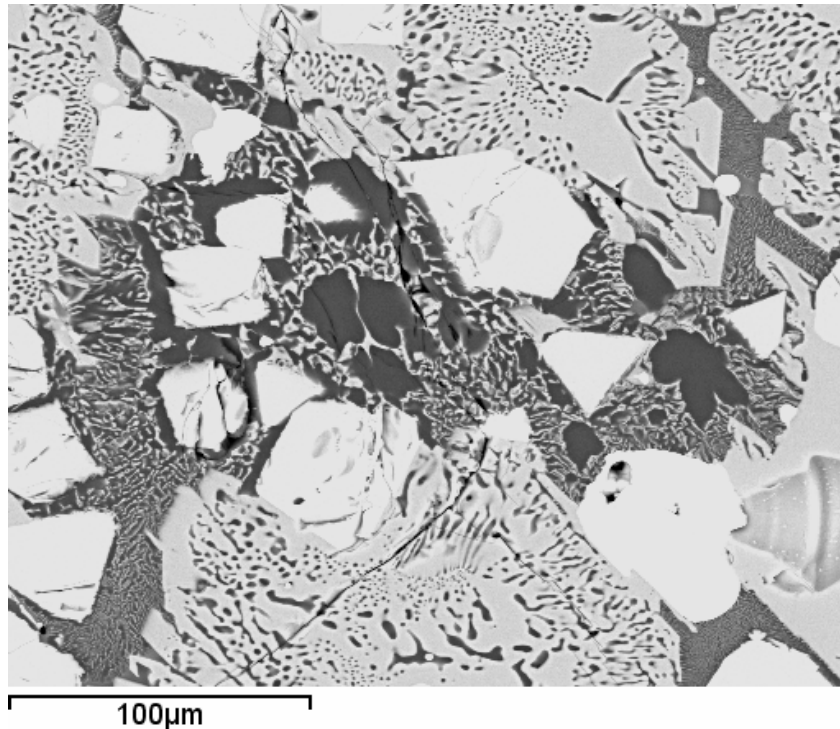
*Figure 6. BSE image of sample 34 – showing fayalite (mid-grey), magnetite (light-grey), copper sulphide (brightest phase) and silica (darkest phase) in a multi-phase matrix.*

*Table 10. Composition of the phases contained in sample 34*

|     | Spinel | Olivine | Silica | Cu$_2$S | Matrix |
|-----|--------|---------|--------|---------|--------|
| O   | 28.4   | 33.2    | 53.3   | 1.6     | 45.8   |
| Na  | <0.2   | <0.2    | <0.2   | <0.2    | 0.3    |
| Al  | 1.2    | 0.3     | <0.2   | <0.2    | 8.0    |
| Si  | 0.4    | 14.5    | 46.1   | <0.2    | 27.2   |
| S   | <0.1   | <0.1    | <0.1   | 20.1    | <0.1   |
| K   | <0.1   | 0.2     | <0.1   | <0.1    | 1.2    |
| Ca  | <0.1   | <0.1    | <0.1   | <0.1    | 0.3    |
| Ti  | 0.7    | <0.1    | <0.1   | <0.1    | 0.2    |
| Cr  | 0.9    | <0.1    | <0.1   | <0.1    | <0.1   |
| Fe  | 68.5   | 51.9    | 0.6    | 0.7     | 16.9   |
| Cu  | <0.2   | <0.2    | <0.2   | 77.7    | <0.2   |
| Zn  | <0.2   | <0.2    | <0.2   | <0.2    | 0.2    |

The slag from settlers (sample 35) is composed of dendrites of fayalite (iron silicate 1) and other iron silicates which vary in composition as proportions of silica and iron fluctuate (Table 11: iron silicates 1, 2, 3). These are set within a complex matrix containing lime and alumina in quantities ranging from 3–4% and containing minute crystal structures which are likely to be fayalite, however these are too small for analysis. The specimen contains several droplets of matte with mid-range copper contents (48–58%).
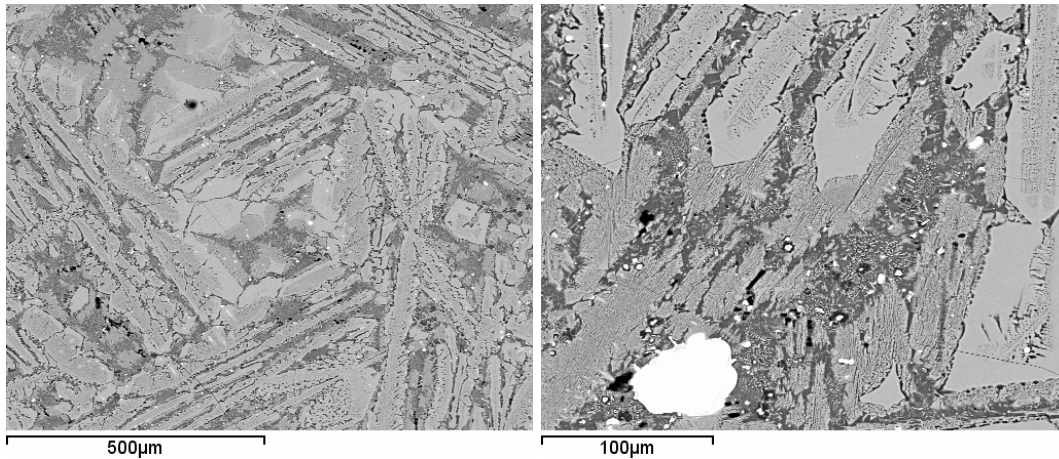
*Figure 7. BSE images of sample 35 – showing fayalite (light grey and mid-grey) and copper-iron-sulphide (white) in a glassy matrix (darker grey).*

*Table 11. Composition of the phases contained in sample 35*

|     | 'iron silicate 1' | 'iron silicate 2' | 'iron silicate 3' | 'CuFeS' | 'CuFeS' | Matrix |
|-----|-------|-------|-------|-------|-------|-------|
| O   | 31.8  | 34.6  | 46.3  | 4.7   | 2.5   | 40.7  |
| Na  | <0.2  | <0.2  | 0.4   | <0.2  | <0.2  | 0.3   |
| Mg  | 0.5   | 0.3   | <0.2  | <0.2  | <0.2  | <0.2  |
| Al  | <0.2  | 0.4   | 1.9   | <0.2  | <0.2  | 3.2   |
| Si  | 13.6  | 17.1  | 30.5  | 0.8   | 0.2   | 21.3  |
| S   | <0.1  | <0.1  | <0.1  | 24.7  | 24.9  | 0.4   |
| K   | <0.1  | 0.2   | 0.9   | <0.1  | <0.1  | 0.5   |
| Ca  | <0.1  | 0.2   | 1.3   | <0.1  | <0.1  | 4.0   |
| Ti  | <0.1  | <0.1  | <0.1  | <0.1  | <0.1  | 0.5   |
| Mn  | 0.2   | 0.2   | <0.1  | <0.1  | <0.1  | <0.1  |
| Fe  | 53.9  | 47.1  | 18.7  | 21.8  | 13.9  | 29.0  |
| Cu  | <0.2  | <0.2  | <0.2  | 48.0  | 58.6  | 0.2   |

Sample 36, described by Smythe as poor slag, is primarily composed of iron oxide, silica and alumina (Table 8). Its microstructure is composed of long dendrites of olivine, basically fayalite, interspersed with the spinel phase, a low-iron magnetite, and iron sulphide (possibly troilite) (Fig 8). Minute droplets of copper-iron-sulphide (Table 12) are dispersed throughout the sample. The matrix is composed of iron oxide and silica with approximately 8% alumina.
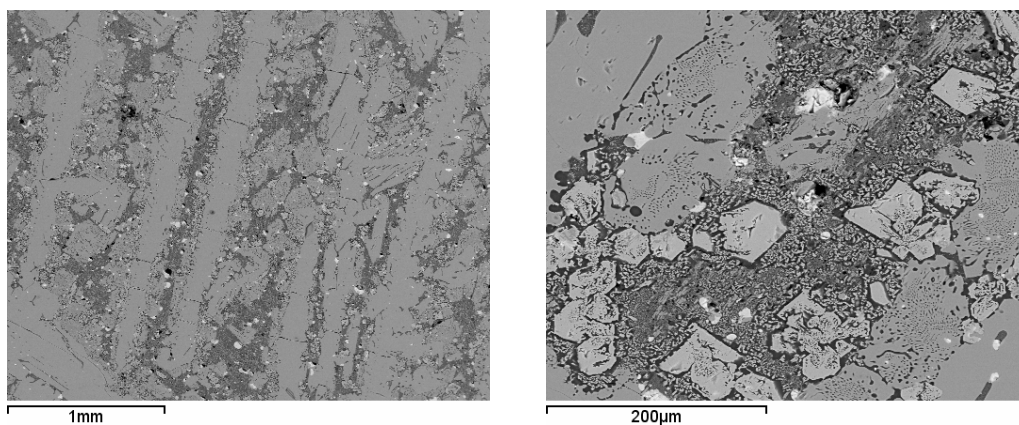
*Figure 8. BSE images of sample 36 showing (a, left) dendrites of fayalite (mid grey), (b, right) magnetite (angular - light grey), and iron sulphide (dark grey).*

*Table 12. Composition of the phases contained in specimen sample 36*

|    | Olivine | Spinel | CuFeS | FeS | Matrix |
|----|---------|--------|-------|-----|--------|
| O  | 31.9    | 28.9   | 3.6   | <0.5 | 42.4  |
| Na | <0.2    | <0.2   | <0.2  | <0.2 | <0.2  |
| Al | <0.2    | 1.9    | <0.2  | <0.2 | 8.1   |
| Si | 13      | 0.9    | 0.2   | 0.2  | 22.9  |
| S  | <0.1    | <0.1   | 28.3  | 36.3 | 0.5   |
| K  | <0.1    | <0.1   | <0.1  | <0.1 | 0.5   |
| Ca | <0.1    | <0.1   | <0.1  | <0.1 | 0.5   |
| Ti | <0.1    | 1.2    | <0.1  | <0.1 | 0.5   |
| Fe | 54.3    | 67.1   | 30.5  | 61.9 | 24.1  |
| Co | 0.8     | <0.2   | <0.2  | <0.2 | <0.2  |
| Cu | <0.2    | <0.2   | 37.5  | <0.2 | 0.2   |
| Zn | <0.2    | <0.2   | <0.2  | <0.2 | 0.3   |

Refining

The refining process is represented by two samples. The sample from the early stage (sample 42) is characterised by high iron oxide and low copper while the opposite is true for the slag from the end of refining (sample 43) (Table 13). In terms of other oxides, alumina and silica are notably higher in the slag from the later refining stage, while minor amounts of cobalt appear in the slag from the early stages of refining.

Table 13. Mean bulk compositions of two specimens of refining slag.

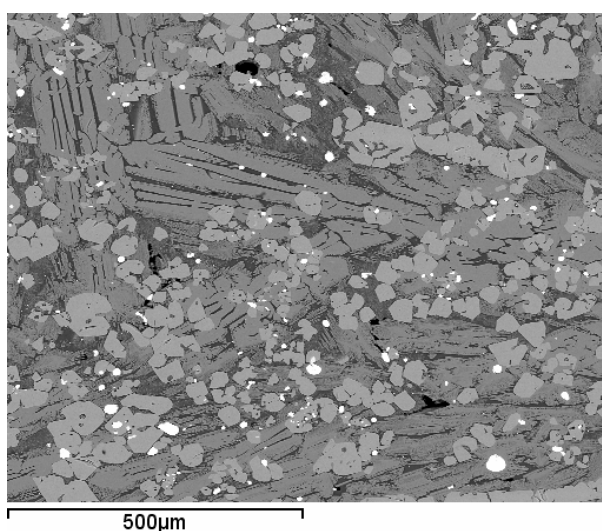|  | Sample 42 | Sample 43 |
|---|---|---|
| MgO | <0.2 | 0.6 |
| $Al_2O_3$ | 2.8 | 4.7 |
| $SiO_2$ | 28.3 | 37.2 |
| $K_2O$ | 0.3 | 0.3 |
| CaO | 1.0 | 1.7 |
| $TiO_2$ | <0.1 | 0.3 |
| FeO | 62.1 | 2.7 |
| CoO | 2.6 | <0.2 |
| NiO | <0.2 | 0.5 |
| CuO | 2.8 | 52.7 |
| ZnO | <0.1 | <0.2 |



Figure 9a. BSE image of sample 42 – slag from the early stages of refining showing olivine (mid grey), spinel (light grey) and minute droplets of copper (white).
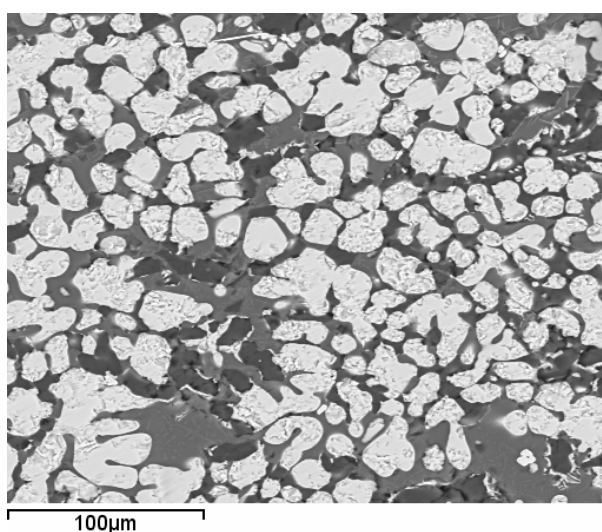


Figure 9b. BSE image of sample 43 – slag from the end of the refining process showing dendrites of copper (light grey), copper/iron phases (mid grey) and silica (dark grey).

Sample 42 is composed of olivine (fayalite) and spinel (magnetite) with tiny droplets of copper dispersed in a glassy matrix (Fig 9a). In the later stages of refining there are no longer olivine and spinel phases and instead the microstructure is dominated by copper dendrites along with some copper/iron and some silica which is likely to have been added as a flux (Fig 9b). Sulphur was not detected in either sample.

*Table 14. Composition of phases present in samples 42 and 43*

| | Sample 42 | | | | Sample 43 | | | |
|---|---|---|---|---|---|---|---|---|
| | Olivine | Spinel | Copper | Matrix | Copper | Copper/iron | Silica | Matrix |
| O | 27.2 | 24.4 | 0.8 | 36.7 | 8.9 | 9.5 | 47.5 | 43.6 |
| Na | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| Mg | 0.4 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.8 |
| Al | <0.2 | 1.2 | nd | 2.9 | nd | 1.5 | 0.7 | 4.9 |
| Si | 14.3 | 0.4 | nd | 22.7 | nd | 4.1 | 49.6 | 25.1 |
| K | <0.1 | <0.1 | <0.1 | 0.9 | <0.1 | <0.1 | <0.1 | 0.8 |
| Ca | <0.1 | <0.1 | <0.1 | 1.6 | <0.1 | 0.4 | 0.1 | 4.3 |
| Ti | <0.1 | 0.3 | <0.1 | 0.2 | <0.1 | 3.2 | <0.1 | 0.5 |
| Cr | <0.1 | 0.3 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Mn | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 |
| Fe | 54.4 | 70.8 | 1.4 | 35.0 | <0.1 | 30.5 | <0.1 | 5.1 |
| Co | 3.8 | 2.3 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| Ni | <0.2 | 0.3 | 0.4 | <0.2 | <0.2 | 3.5 | <0.2 | 0.8 |
| Cu | <0.2 | <0.2 | 97.4 | <0.2 | 91.1 | 47.4 | 2.1 | 14.0 |
| Zn | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |

## RESULTS FOR THE MATTE

Four samples of matte were collected by Smythe, one derived from blast furnace smelting (sample 25 – first matte), two from the Bessemer process (sample 30 – rich matte and sample 31– matte) and one from pyrite smelting (sample 37 – matte). The sample described by Smythe as furnace lining is also included here as it was chemically similar to the matte samples.

Macroscopically all four samples appear different. Sample 25 is a very dense material with a metallic lustre and a number of small copper droplets visible throughout the section. Sample 30 is also extremely dense with a metallic lustre. Sample 31 is similar externally to sample 30 however tiny ribbons of copper are clearly visible in section. Sample 37 is quite different, having a lower density than the others and a high degree of fine porosity. Samples were analysed using a similar approach to the slag, however all elements are reported in weight percentage not as oxides, and are normalised to 100%.

Bulk chemical analyses show significant differences between specimens (Table 15). The two samples from the Bessemer process are characterised by their high copper contents (69–78%) and very low iron contents (0.4–7%). The blast furnace matte contains almost twice as much copper as iron, while the matte from pyrite smelting contains the highest quantity of iron and the least amount of copper (1:3.5 Cu:Fe). All samples contain in the

region of 20% sulphur. In terms of their microstructure the matte samples vary greatly and they reflect the complexity of the smelting processes.

*Table 15. Mean bulk compositions of the matte samples.*

|  | sample 25 (Blast Furnace) | sample 30 (Bessemer) | sample 31 (Bessemer) | sample 37 (Pyrite) | sample 28 (furnace lining) |
|---|---|---|---|---|---|
| O | 5.6 | 1.4 | 2.4 | 12.6 | 4.4 |
| Si | 0.2 | <0.2 | <0.2 | 0.9 | 0.4 |
| S | 21.6 | 19.6 | 21.3 | 22.1 | 13.2 |
| Ca | <.01 | <.01 | <.01 | <.01 | 0.3 |
| Fe | 24.7 | 0.4 | 7.0 | 49.9 | 57.6 |
| Co | <0.2 | <0.2 | <0.2 | <0.2 | 1.9 |
| Ni | <0.2 | <0.2 | <0.2 | <0.2 | 0.3 |
| Cu | 47.9 | 78.6 | 69.2 | 13.8 | 25.3 |
| Zn | <0.2 | <0.2 | <0.2 | 0.7 | <0.2 |
| As | <0.4 | <0.4 | <0.4 | <0.4 | 0.6 |
| Ag | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |

## Sample 25 – First matte

Sample 25 is described by Smythe as first matte smelting and contains five phases (Table 16). The main matrix is copper-iron-sulphide, the composition of which varies slightly from area to area (Table 16). In some cases it has a composition close to the naturally occurring mineral bornite ($Cu_5FeS_4$) (see Appendix 3). Iron oxide is present in the form of wüstite. Impure iron phases contain significant quantities of cobalt, nickel, copper and arsenic. These iron-rich phases indicate that the reducing conditions within the furnace were strong enough to produce metallic iron.
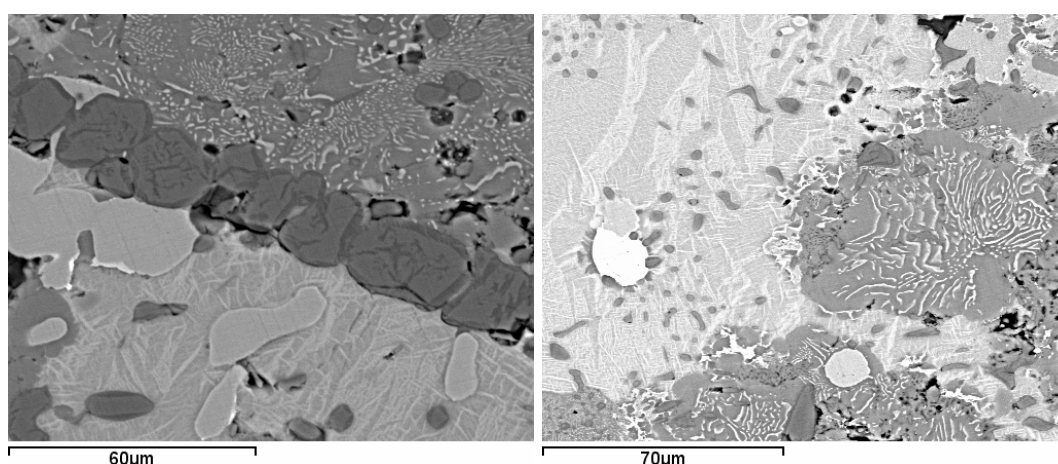


60μm            70μm

*Figure 10. BSE images of various phases contained in sample 25. The structure varies considerably across the sample and is therefore shown in two separate images. The image on the left shows a band of iron oxide (darkest phase) and iron sulphide (mid grey), the image on the right shows predominately copper-iron-sulphide (light grey) and copper (white).*

*Table 16. Compositions of phases present in sample 25*

|  | 'CuFeS' | 'CuFeS' | Wüstite | 'FeS' | 'FeS' | Iron | Copper |
|---|---|---|---|---|---|---|---|
| O | 1.8 | nd | 22.1 | <0.5 | <0.5 | <0.5 | 0.7 |
| Si | <0.2 | 0.2 | <0.2 | 0.2 | <0.2 | <0.2 | <0.2 |
| S | 23.2 | 25.9 | <0.1 | 27.4 | 28.8 | <0.1 | <0.1 |
| Mn | <0.1 | <0.1 | 0.2 | <0.1 | <0.1 | <0.1 | <0.1 |
| Fe | 10.9 | 15.6 | 77.8 | 70.6 | 70.2 | 89.5 | 3.0 |
| Co | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 6.2 | <0.2 |
| Ni | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.6 | <0.2 |
| Cu | 64.1 | 58.4 | <0.2 | 1.9 | 1.0 | 1.7 | 96.3 |
| As | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | 2.1 | <0.4 |

## Sample 30 – Rich matte

Smythe referred to sample 30 as a rich matte due to its high copper content which he estimated at approximately 80%. This correlates well with the results of bulk analyses conducted here which show over 78% copper (Table 15). The specimen is primarily composed of copper sulphide which has a composition similar to chalcocite ($Cu_2S$) (Table 17). It also contains iron oxide (phase A) which in some cases contains low quantities of copper (5%) and nickel (<1%). There are several bright phases (such as the one visible in Figure 11) which are rich in silver (60–90%) and contain a little gold (Table 17 phases D, E and F). This silver-rich material has accumulated at the grain boundaries as it has a lower melting point (copper sulphide 1136˚C, silver 961˚C, copper 1083˚ C) than the copper sulphide and so is the last phase to solidify from the melt. The deposits have become elongated as the surrounding crystal structures grew into the melt (Fig 11).
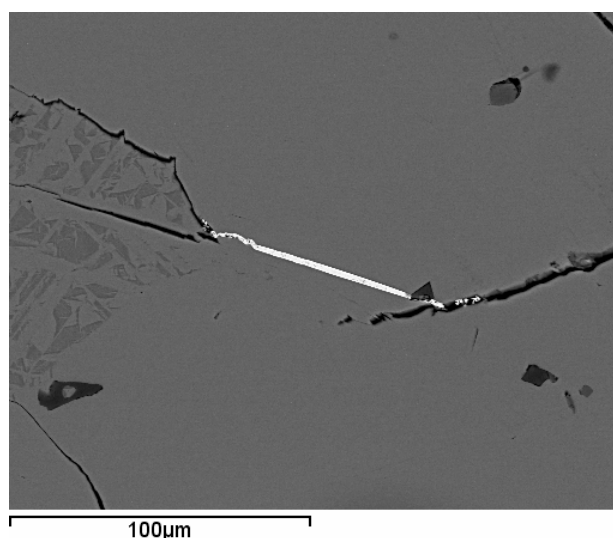


*Figure 11. BSE image of sample 30. The main matrix is primarily copper sulphide (mid grey) with occasional iron oxide inclusions (dark grey). The long bright phase is silver containing a small quantity of copper.*

*Table 17. Composition of phases in sample 30.*

| Phase | 'FeO' A | $Cu_2S$ B | 'CuFeS' C | Ag/Cu D | Ag/Cu E | Ag/Cu F |
|---|---|---|---|---|---|---|
| O | 28.5 | 1.0 | <0.5 | 2.1 | <0.5 | 2.2 |
| Mg | <0.2 | <0.2 | <0.2 | <0.2 | 0.4 | 0.3 |
| Si | 0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| S | 0.5 | 20.1 | 24.0 | 5.1 | 0.7 | 0.9 |
| Fe | 65.6 | 0.4 | 7.5 | <0.1 | <0.1 | <0.1 |
| Co | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.5 |
| Ni | 0.5 | <0.2 | <0.2 | 1.7 | <0.2 | <0.2 |
| Cu | 4.8 | 78.5 | 68.6 | 24.3 | 5.9 | 7.0 |
| Ag | <0.2 | <0.2 | <0.2 | 64.3 | 93.0 | 89.1 |
| Au | <0.4 | <0.4 | <0.4 | 2.4 | <0.4 | <0.4 |

## Sample 31 – Matte from Bessemer process

Sample 31 has an extremely fine microstructure, however at high magnification one can see that it is mainly composed of copper sulphide (as $Cu_2S$) and copper-iron-sulphide (with a relatively high amount of oxygen) with long metallic 'ribbons' appearing throughout the sample (Fig 12a). Some of these 'ribbons' are relatively pure copper while others also contain silver (up to 1:1 Ag:Cu; Table 18).
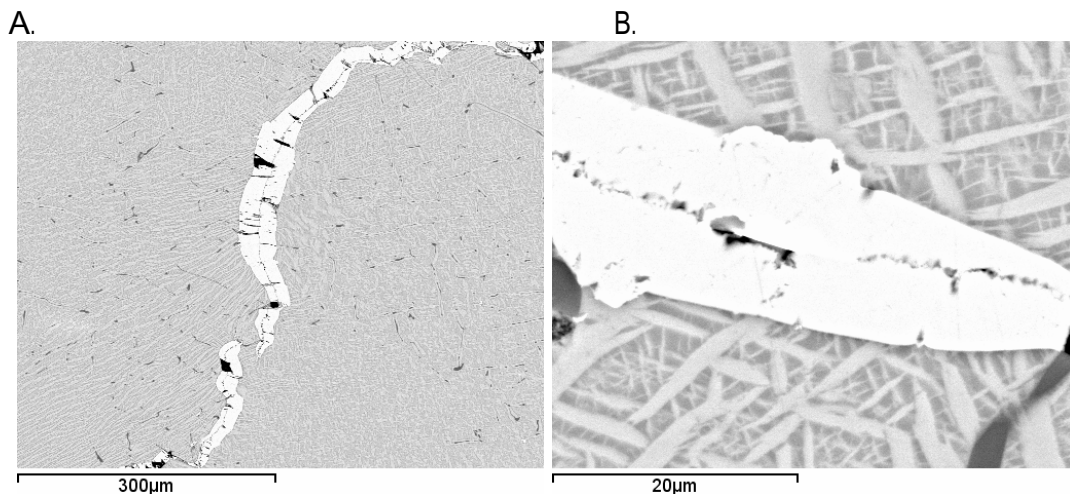
A.    B.



300μm    20μm

*Figure 12A – sample 31 showing a fine structure of copper sulphide (light-grey) and copper-iron-sulphide (mid-grey) with a thin film of copper-silver metal (white)*
*Figure 12B – the same as above at higher magnification showing the copper sulphide crystals and copper-iron-sulphide matrix.*

*Table 18. Composition of phases in sample 31*

|     | Cu₂S | 'CuFeS' | Copper | Ag/Cu |
|-----|------|---------|--------|-------|
| O   | 1.5  | 15.0    | 0.9    | 2.1   |
| Mg  | <0.2 | <0.2    | <0.2   | 0.3   |
| S   | 20.0 | 7.1     | 0.6    | <0.1  |
| Fe  | 2.5  | 48.8    | 0.6    | 0.8   |
| Co  | <0.2 | <0.2    | <0.2   | 0.4   |
| Ni  | <0.2 | <0.2    | <0.2   | 1.1   |
| Cu  | 76.1 | 29.0    | 97.9   | 49.9  |
| Ag  | <0.2 | <0.2    | <0.2   | 45.5  |

## Sample 37 – Matte (pyrite smelting)

The main matrix of sample 37 is composed of copper-iron-sulphide with a broad range of compositions (Table 19). The sample contains an appreciable quantity of iron in the form of silicates (olivine, fayalite), sulphides (troilite) and oxides – magnetite and wüstite, which are recognisable by their chemistry rather than their structure (Fig 13).
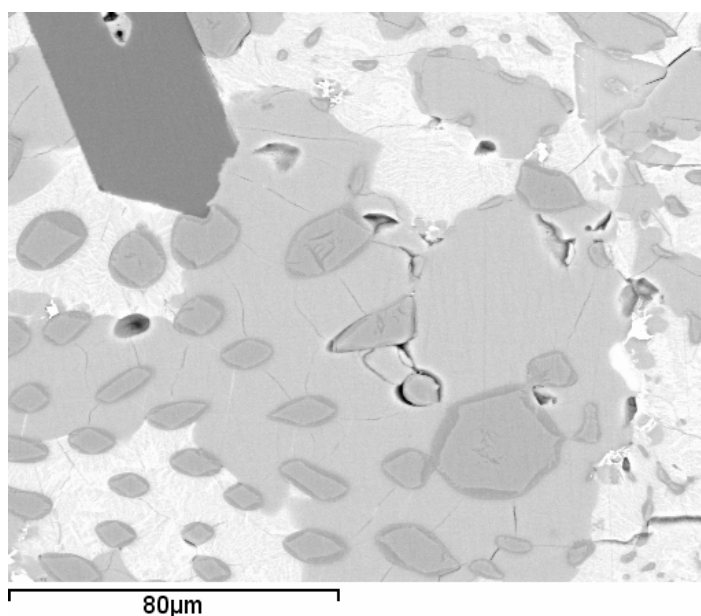


*Figure 13. BSE image of sample 37. The main matrix is copper-iron-sulphide (very light grey), iron sulphide (mid grey) iron silicates (light grey) and iron oxides (dark grey).*

*Table 19: Composition of phases in sample 37*

|     | Fayalite | Magnetite | Wüstite | 'FeS' | 'CuFeS' | 'CuFeS' |
|-----|----------|-----------|---------|-------|---------|---------|
| O   | 30.5     | 26.4      | 21.9    | <0.5  | 2.3     | 1.2     |
| Mg  | 0.2      | <0.1      | <0.1    | <0.1  | <0.1    | <0.1    |
| Al  | <0.2     | 1.6       | <0.2    | <0.2  | <0.2    | <0.2    |
| Si  | 13.0     | 0.3       | <0.2    | 0.1   | <0.2    | <0.2    |
| S   | <0.1     | <0.1      | <0.1    | 35.0  | 23.6    | 2.5     |
| Ca  | 0.8      | <0.1      | <0.1    | <0.1  | <0.1    | <0.1    |
| Ti  | <0.1     | 1.5       | <0.1    | <0.1  | <0.1    | <0.1    |
| Cr  | <0.1     | 0.5       | <0.1    | <0.1  | <0.1    | <0.1    |
| Mn  | <0.1     | <0.1      | <0.1    | <0.1  | <0.1    | <0.1    |
| Fe  | 54.9     | 69.4      | 78.1    | 63.3  | 16.9    | 7.6     |
| Cu  | 0.3      | <0.2      | <0.2    | 1.6   | 57.2    | 88.8    |
| Zn  | 0.4      | 0.4       | <0.2    | <0.2  | <0.2    | <0.2    |

## Sample 28 – Blast furnace lining

Sample 28 is described in Smythe's notes as blast furnace lining. It is a dense material with a metallic lustre which corroded quickly when sectioned and exposed to air. Despite its label its composition shows it is unlikely to be part of the actual furnace structure but rather a layer on the surface of the furnace lining which accumulated during the smelting process. It has a similar bulk composition to matte although the sulphur content is slightly less than the samples described as matte and it contains a range of other metals (Co, Ni, As) (Table 15). It is in essence matte which has adhered to the furnace wall.
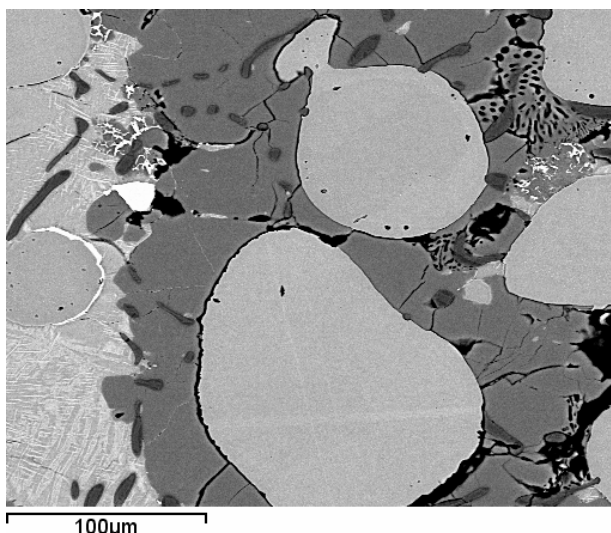


100µm

*Figure 14. BSE images of sample 28 containing impure iron (mid grey), iron oxide (darkest phase), iron sulphide (dark grey), copper (white) and copper-iron-sulphide (mottled grey).*

In terms of its microstructure it has similar phases to the other matte samples, being composed primarily of copper-iron-sulphide, iron sulphide with just over 2% copper, iron

oxide and an impure iron phase containing copper, cobalt, arsenic and nickel (Fig 14, Table 20).

*Table 20. Composition of various phases of the blast furnace lining (sample 28).*

|     | 'CuFeS' | 'CuFeS' | 'FeS' | Iron | FeO | Cu |
|-----|---------|---------|-------|------|-----|-----|
| O   | 1.6     | 1.8     | <0.5  | <0.5 | 20.7 | 0.7 |
| S   | 23.7    | 23.1    | 35.2  | <0.1 | 0.3  | <0.1 |
| Mn  | <0.1    | <0.1    | <0.1  | <0.1 | 0.3  | <0.1 |
| Fe  | 10.5    | 10.6    | 62.4  | 91.9 | 76.7 | 2.9 |
| Co  | <0.2    | <0.2    | <0.2  | 3.8  | <0.2 | <0.2 |
| Ni  | <0.2    | <0.2    | <0.2  | 0.6  | <0.2 | <0.2 |
| Cu  | 64.2    | 64.5    | 2.3   | 2.6  | 2.0  | 96.4 |
| As  | <0.4    | <0.4    | <0.4  | 1.2  | <0.4 | <0.4 |

## EXAMINATION OF OTHER MATERIALS

As well as matte and slag there were a number of other materials associated with copper smelting in Smythe's collection.

### Dust

Three dust samples produced by three different processes were collected by Smythe. Two of the samples (samples 36a and 44) are dark grey to black in colour, and one is a reddish brown (sample 41). Sample 41 is more friable than the other two and more instantly recognisable as dust, the other two could be easily misinterpreted as they are tightly compacted and at first glance do not resemble what one might think of as dust.
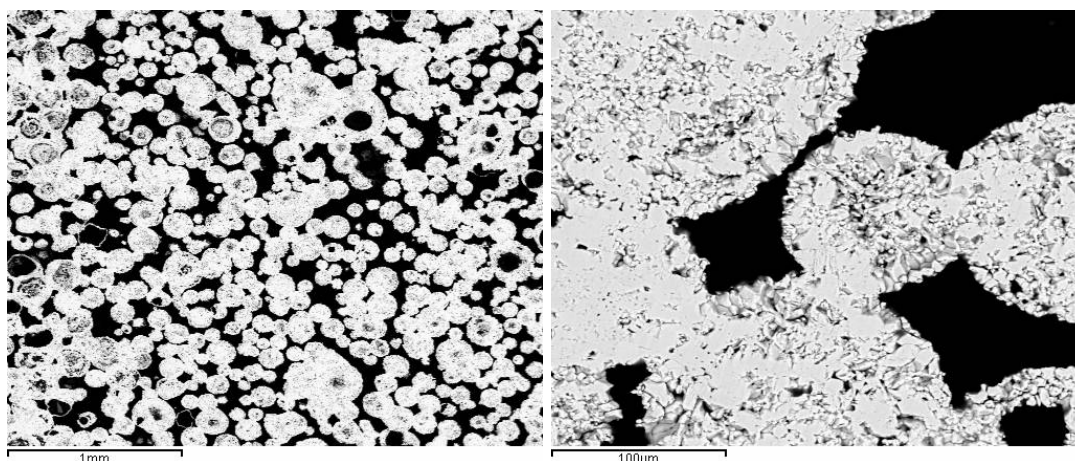


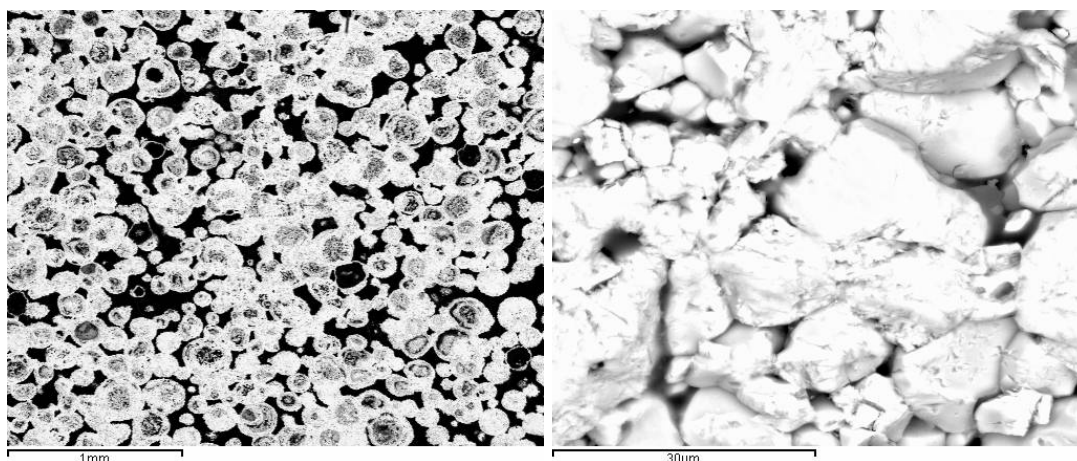*Figure15. BSE image of dust from the Bessemer process (36a).*

*Figure 16. BSE image of sample 44 – dust from dust chamber (refining)*

*Table 21: Composition of dust from the Bessemer and refining processes*

|    | Sample 36a | Sample 44 |
| --- | --- | --- |
| O  | 18.4 | 15.7 |
| Cl | nd | 0.3 |
| Cu | 81.6 | 84.2 |

Analyses show that the dust from the Bessemer (sample 36a) and refining (sample 44) processes are copper oxide (CuO – possible tenorite) (Table 21). The backscatter images of both samples appear very similar and show rounded particles generally in the range of 100 to 500 μm (Figs 15 and 16) which comprise large number of angular crystals, suggesting the dust is an agglomeration of crystals that grew as CuO condensed from the vapour phase.
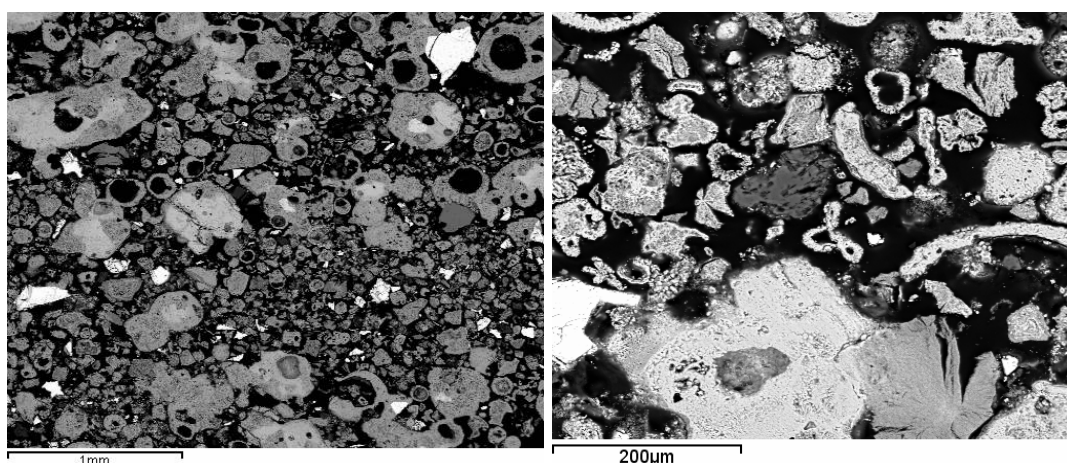


*Figure 17. BSE image of sample 41 'dust from a furnace' after pyrite smelting.*

Table 22. Mean composition of bulk areas of dust from pyrite smelting.

| O | Al | Si | S | Cl | Ca | Fe | Cu | Zn | Ba |
|------|------|------|------|------|------|------|------|------|------|
| 25.4 | 0.4 | 1.8 | 5.0 | 0.4 | 0.2 | 59.2 | 5.1 | 0.6 | 2.0 |

The dust from pyrite smelting (sample 41) has a more complex chemistry than the previous dust samples. It has a high iron content along with smaller amounts of sulphur and copper (c. 5% each). Its bulk chemistry does not correspond particularly well with either the slag or matte samples from pyrite smelting, apart from the barium content which is present in similar amounts in all three materials. This dust sample differs from the other dusts in the heterogeneous nature of its grains and in the grain sizes which are much more variable, ranging from <50 to 1000 μm (Fig 17).

## Copper

Both the copper samples contain inclusions of copper oxide in the form of $Cu_2O$. Sample 29 also contains a small quantity of sulphur which is present as $Cu_2S$. The samples appear to represent two different stages of refining. The sulphur content of sample 29 suggests that it is in need of further refining to remove all of the sulphur. Sample 45 on the other hand appears to have been over refined and would require poling or a similar technique to remove the oxygen if it were to be used in a way that required a higher purity.

Table 23. Mean bulk compositions of copper samples

|    | Sample 29 | Sample 45 |
|----|-----------|-----------|
| O  | 1.1 | 4.9 |
| S  | 1.0 | <0.1 |
| Cu | 97.8 | 96.7 |

# DISCUSSION AND CONCLUSIONS

The samples analysed are derived from different copper smelting processes, each of which involved a number of stages, however it is important to note that not all of these stages are represented Smythe's collection (Table 1).

## Blast furnace smelting

The first group of materials were produced by blast furnace smelting and consist of slag, matte, and so-called blast furnace lining which is actually matte (Tables 15 and 20). When examined in the hand, the slag samples have much higher degree of porosity and are much lighter than the matte. The matte may also be distinguished by the presence of

minute droplets of copper which are visible in newly cut sections. Smythe described sample 25 as 'first matte containing 20–25% copper', however bulk analyses conducted here show a much higher concentration of copper (48%). The reason for this discrepancy is currently unknown and should be investigated further.

The slag samples were described by Smythe as rich slag (sample 26) and clean slag (sample 27). There is little difference between these two samples in terms of their bulk chemistry, however they are distinguishable by their microstructures. The rich slag (sample 26) contains a number of areas with un-reacted silica as well as a much higher proportion of matte inclusions than the clean slag. In both cases the composition of the matte inclusions are relatively similar with copper contents around 55%. The blast furnace slags stand out from the other types of slag in terms of their bulk chemistry with higher levels of lime, alumina and magnesia which may be the result of the addition of a flux (perhaps limestone) during smelting (Fig 18).
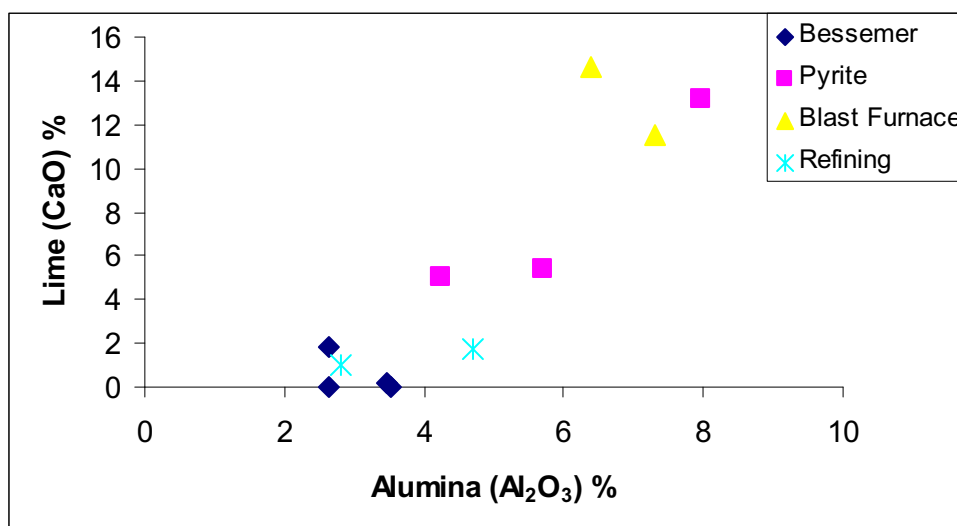


*Figure 18. Lime and alumina contents slag samples.*

Pyrite smelting

Pyrite smelting is represented by samples of slag, matte and dust. Samples 38 (slag) and 40 (slag from fore hearth) have similar bulk compositions (Table 4) while sample 39 (slag with added matte) has significantly higher quantities of lime and lower iron oxide.

Two of the slag samples contain droplets of matte with copper contents of 50–60%. Therefore, we can suggest that these are derived from a mid-way production stage. The sample from the fore-hearth is more difficult to characterise as it contains no matte. It does however contain iron sulphide which may suggest that it is derived from an early stage of the process. This suggestion is made on the basis that the purpose of the smelt is to eliminate iron and sulphur, and therefore the presence of iron sulphide in the slag

suggests that it was separated from material rich in iron and sulphur and therefore at an early stage of the smelting process.

## Bessemer process

The samples derived from the Bessemer process included slag, matte, dust and copper.

Analyses of bulk areas of the slag samples show that they all contain high quantities of silica (25–38%) and iron oxide (51–67%) (Fig 19). The $SiO_2$ is similar to other slags but the iron oxide is higher than most of the other slags. The copper quantities vary considerably from 0.5% CuO in the poor slag (sample 36) to 5% CuO in the slag from rich matte (sample 34) (Table 8). All samples contain olivine structures which have approximately the composition of fayalite but in which some of the iron has been substituted by other elements. Three of the samples (33, 34, 36) contain magnetite, however the presence or absence of this spinel does not appear to be a useful criterion for characterisation. A much more useful method of distinguishing between samples and the production stages from which they are derived is by the composition of matte inclusions, where they are present. Three of the Bessemer slags contain matte either as copper-iron-sulphide or copper sulphide. In the poor slag (sample 36) the matte contains 30–37% copper which may be classified as a low quantity. The matte contained in the 'slag from settlers' contains between 48–58% copper and therefore can be classified as mid-range. The 'slag from rich matte' (sample 34) contains large amounts of copper sulphide with a high proportion of copper (78%), while the 'slag from copper' (sample 33) contains no matte, but does have copper droplets dispersed throughout it which are almost pure (96%).
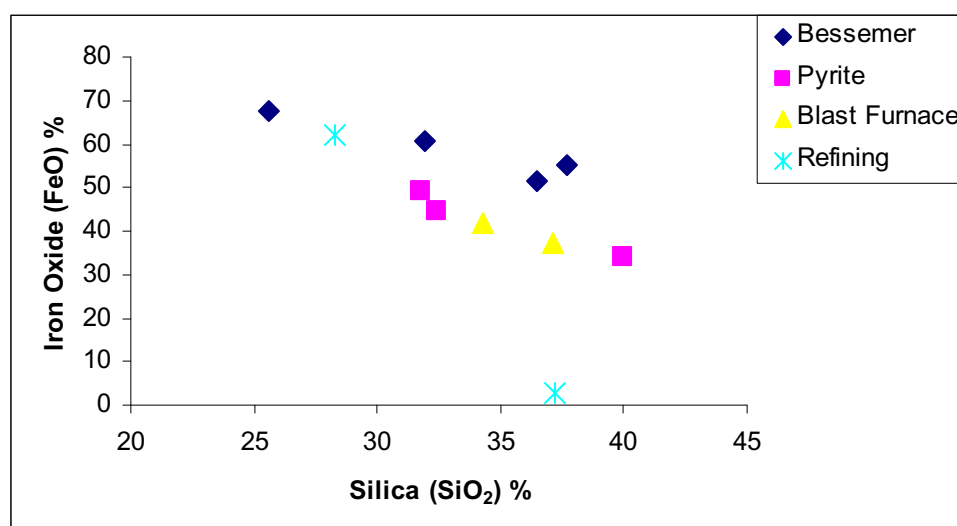


*Figure 19. Iron oxide and silica contents of slag samples.*

The major difference between the Bessemer slags and other slag types is the presence of consistently higher levels of iron oxide. We can therefore begin by suggesting this as one possible criterion for the identification of the use of the Bessemer process. Caution must be exercised however as other technologies which are not discussed here may produce waste materials with similar compositions to Bessemer slags. The results have shown that it is possible to broadly determine the smelting stage in terms of being early, middle or late by looking at the proportion of copper in the droplets of matte trapped in the slag; the lower the copper content, the earlier the stage of smelting. This characterisation corresponds well with Vivian's (1823) description of the materials produced at various stages of the Welsh process. He states that the second stage of smelting produces a material with approximately one third copper. Stage four results in a material with 60% copper and stage six produces copper which is 80–90% pure.

Refining

The material derived from refining consists of slag, dust and bar copper. We know from Smythe's descriptions that the slag samples come from two different phases of the refining process, early and late. The two samples could be described as being exactly opposite to each other, particularly in terms of their iron and copper contents. As one would expect, as refining progresses the copper content is enriched, and this is evident in both the bulk chemistry and microstructure of the slag from the 'end of refining' (sample 43) which contains 53% copper in its bulk composition and a high quantity of copper droplets visible under magnification (Fig 9B). It is therefore possible to say that slag from the later stages of refining can be distinguished by high quantities of copper in its bulk composition.

## SUMMARY

Slag as a waste material is ubiquitous in the archaeological record and therefore likely to be the most common remains of copper smelting. Some stages of the smelting process rely on slag from later stages being re-smelted, and therefore these are less likely to be represented in any assemblage.

Matte on the other hand is less likely to be found archaeologically as it is a valuable intermediate material which will undergo further processing to enrich its copper content. It may however be found as inclusions in the slag.

If matte is found, it may be possible to characterise the stage of smelting from which it derives using similar methods to those suggested above for slag. The aim of smelting is to enrich the copper and therefore we can say that the higher the quantity of copper contained in a sample the later the stage of smelting it represents. Rich mattes such as sample 30 may also contain quantities of precious metals (Table 17) which like the copper, will also become enriched as smelting progresses.

Samples of matte may also be distinguished by the quantities of iron they contain. It has been shown above (Table 16) that matte from the early stages of smelting (sample 25 – first matte smelting) contains iron as oxides, sulphides and even what appears to be metallic iron. Matte from later stages (e.g. sample 30 – rich matte) (Table 17) contains only a small amount of iron oxide and no iron sulphide.

The aim of this report was to investigate the possibilities for establishing criteria for the identification of a range of copper smelting remains derived from the use of different technologies.

During the course of this investigation it has become evident that distinguishing a precise technology by looking at either slag or matte is extremely difficult. We may however begin to make some inferences such as the presence of high quantities of lime being indicative of the addition of a flux and therefore of blast furnace smelting, and high levels of iron oxide suggesting a highly efficient method such as the Bessemer process. However it is possible to broadly determine the stage from which both slag and matte derive. This can be done with reference to the quantity of copper in droplets of matte contained in the slag, and by the overall quantity of copper and iron contained in matte samples.

At this point three different ranges of copper content are suggested as indicating three broad stages of smelting: the first at approximately 30% corresponds to an early stage of smelting; a mid-way stage between 40–60%; and a late stage between 70–90%. It is hoped that these can be further refined in the future.


## RECOMMENDATIONS FOR FURTHER WORK

If and when possible, further analyses of samples from known processes should be conducted in order to refine the results presented here. Of particular interest would be samples known to derive from the Welsh Process, no remains of which were included in this study. Furthermore, the criteria suggested here should be tested on known samples in order to check their reliability.

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Specimens illustrating the
Smelting of Copper

Blast Furnace Smelting

| | No. | |
|---|---|---|
| | 25. | First matte containing 30-35 p.c. of copper |
| NFSCo/6 | 26. | Rich slag (Cu = 3-5 p.c) To be re-smelted |
| NFSCo/7 | 27. | Clean slag (Cu = 0.2-0.25 p.c.) |
| | 28 | Lining of the blast furnace, containing 10-15 p.c. copper |
| NFSCo/8 | 28a. | Granulated slag (No. 27. |

Bessemer Method

| | No. | |
|---|---|---|
| | 29. | Bessemer Copper (cuivre noire), containing 96-99 p.c. copper. |
| | 30. | Red matte (Cu = 80 p.c.) |
| | 31. | Matte (Cu = 65 p.c.) |
| | 32. | Matte (Cu = 55 p.c.) (missing) |
| NFSCo/9 | 33. | Slag from the copper (Cu = 3-4 p.c.), to be re-treated |
| NFSCo/10 | 34. | Slag from rich matte (Cu = 2.5-3.5 p.c.) |
| NFSCo/11 | 35. | Slag from settlers (Cu = 5-10 p.c.) |
| NFSCo/12 | 36. | Poor slag (Cu = 0.5 p.c |
| | 36a. | Dust from the Bessemer process. 36(b)? |

Pyrite Smelting

| | No. | |
|---|---|---|
| | 37. | Matte (Cu = 14-15 p.c.) |
| NFSCo/13 | 38. | Slag (Cu = 0.2-0.25 p.c.) |
| NFSCo/14 | 39. | Slag, re-smelted with addition of matte (Cu = 4-5 p.c.) |
| NFSCo/15 | 40. | Slag from fore-hearth, to be resmelted. |
| | 41. | Dust from the furnace (Cu = 4-5 p.c.) |

Refining

| | No. | |
|---|---|---|
| NFSCo/16 | 42. | Slag from early stages of refining (Cu = 10-20 p.c.) |
| NFSCo/17 | 43. | Slag from end of refining process (Cu = 40-50 p.c) |
| | 44. | Dust from the dust chamber (Cu = 50-60 p.c.) |
| | 45. | Bar copper |

## APPENDIX 2 – DETECTION LIMITS (WT%)

| | |
|---|---|
| O | 0.5 |
| Na | 0.2 |
| Mg | 0.2 |
| Al | 0.2 |
| Si | 0.2 |
| P | 0.2 |
| S | 0.1 |
| K | 0.1 |
| Ca | 0.1 |
| Ti | 0.1 |
| Cr | 0.1 |
| Mn | 0.1 |
| Fe | 0.1 |
| Co | *0.2 |
| Ni | 0.1 |
| Cu | 0.1-0.2 |
| Zn | **0.2 |
| As | 0.4 |
| Ag | 0.2 |
| Ba | 0.1 |
| Au | 0.2 |
| Pb | 0.4 |

[* 0.1 in Fe poor (<50%)]
[** 0.1 in Cu poor (<50%)]

## APPENDIX 3 – COMPOSITIONS OF PURE COMPOUNDS (WT%)

| | | O | Ca | Si | S | Fe | Cu |
|---|---|---|---|---|---|---|---|
| Silica | $SiO_2$ | 53.24 | | 46.75 | | | |
| Fayalite | $Fe_2SiO_4$ | 31.39 | | 13.77 | | 54.82 | |
| Ferrosilite | $Fe_2Si_2O_6$ | 36.37 | | 21.29 | | 42.33 | |
| Hedenbergite | $FeCaSi_2O_6$ | 38.68 | 16.15 | 22.64 | | 22.51 | |
| Pyrrhotite | $Fe_7S_8$ | | | | 39.62 | 60.37 | |
| Troilite | $FeS$ | | | | 36.47 | 63.52 | |
| Pyrite | $FeS_2$ | | | | 50.06 | 49.93 | |
| Covellite | $CuS$ | | | | 33.53 | | 66.46 |
| Chalcocite | $Cu_2S$ | | | | 20.87 | | 79.12 |
| Chalcopyrite | $CuFeS_2$ | | | | 31.92 | 31.84 | 36.2 |
| Bornite | $Cu_5FeS_4$ | | | | 25.55 | 11.12 | 63.31 |
| Wüstite | $FeO$ | 22.22 | | | | 77.78 | |
| Hematite | $Fe_2O_3$ | 30.04 | | | | 69.95 | |
| Magnetite | $Fe_3O_4$ | 27.63 | | | | 72.36 | |
| Cubanite | $CuFe_2S_3$ | | | | 35.44 | 41.15 | 23.41 |
| Idaite | $Cu_5FeS_6$ | | | | 33.99 | 9.87 | 56.14 |
| Tenorite | $CuO$ | 20.15 | | | | | 79.85 |

Olivines are silicate minerals of general form $M_2SiO_4$ where M = Fe, Mg, Ca

Spinels are oxide minerals of the general form
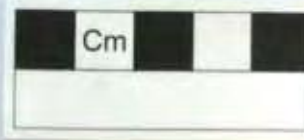
$M^{2+}O. M_2^{3+}O_3$ where

$M^{2+}$ = Fe, Mg, Zn, Mn
$M^{3+}$ = Fe, Al, Cr, Mn

# APPENDIX 4 – SAMPLE PHOTOS
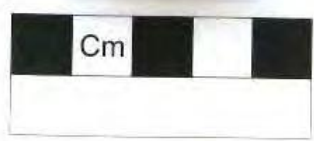


Sample 25 – first matte



Sample 26 – rich slag



Sample 27 – clean slag



Sample 28 – lining of blast furnace

Sample 29 – Bessemer copper



Sample 30 – rich matte



Sample 31 – matte



Sample 33 – slag from the copper

Sample 34 – slag from rich matte



Slag 35 – slag from settlers



Slag 36 – poor slag



Slag 36a – dust from the Bessemer process

Sample 37 – matte

Sample 38 – slag

Sample 39 – slag, re-smelted with the
addition of matte

Sample 40 – slag from the fore hearth

Sample 41 – dust from the furnace



Sample 42 - slag from early stages of refining



Sample 43 - slag from end of refining



Sample 44 – dust from the dust chambers

Sample 45 – bar copper

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