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# DOWNSIDE MILL, COBHAM, SURREY ANALYSIS OF THE METALWORKING REMAINS

# TECHNOLOGY REPORT

Matt Phelps, Sarah Paynter and David Dungworth







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#### SUMMARY

Downside Mill was an iron and copper working mill site owned by Alexander Raby, which operated from the late 18th to the early 19th century. Excavations by Surrey Archaeological Society recovered a large and varied range of metalworking debris. Some of this was analysed using a combination of XRF, SEM-EDS, XRD and optical microscopy to identify the metalworking processes used on the site. The majority of the waste was from dry puddling, a method for converting cast iron into malleable wrought iron. There was also waste from iron smithing, copper alloy casting and iron casting. Both coke and charcoal were used at the site.

#### ACKNOWLEDGEMENTS

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#### ARCHIVE LOCATION

The material will be archived with Elmbridge Museum, Church Street, Weybridge, Surrey.

DATE OF RESEARCH

#### CONTACT DETAILS

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# INTRODUCTION

Downside Mill is a late 18th- to early 19th-century mill and industrial complex approximately 2.6km to the south-east of Cobham, Surrey. The site was owned by the industrialist Alexander Raby (Taylor 2000) and was operated as a metalworking site for almost 40 years at a time of rapid development in metalworking technologies. This period saw the increasing replacement of charcoal with mineral fuel (coal) and the development of new processes for the conversion of cast iron into malleable or wrought iron. The progression of metalworking technologies is only partially recorded in patents and other contemporary documents; there is very little information available which would allow the archaeological recognition of these processes through material remains (structures or residues).

This report details the analysis of metalworking waste using a range of scientific methods, including optical microscopy, SEM-EDS, XRF and XRD. Metalworking debris from this period has been little studied (Morton and Wingrove 1969b; 1970; Killick and Gordon 1987; Gordon 1997). The analysis of the varied materials from Downside Mill will enhance our knowledge of late 18th-century metalworking.

# METALLURGY IN THE LATER 18TH CENTURY

The 18th century was a period of rapid industrial change in metallurgy, especially the iron industry. The capacity of the industry expanded to meet increased demand for both cast and wrought iron. The most significant restriction on the iron industry was the traditional use of charcoal as a fuel. By the 19th century coal had (except for a few niche applications) replaced charcoal for the production of both cast and wrought iron. These mineral fuel technologies are largely known only from documentary sources and their identification through archaeological residues is a research priority (Bayley *et a*/2008).

### Post-medieval iron production

Prior to the 16th century iron manufacture in Britain used the bloomery process (Tylecote 1986, 128–130). Iron was smelted from iron ore but at a low enough temperature that the iron did not melt; instead a spongy mass or bloom formed near the base of the furnace. The bloom was converted into bars by forging which removed some of the excess slag trapped within the bloom. The bloomery process required large quantities of charcoal for smelting; coal could not be used instead because the sulphur in the coal would have entered the bloom and made it brittle. The bloomery process was not very efficient as a significant proportion of iron was lost as fayalite in the production of the slag. Yields from the best ores rarely exceeded 55%, and most yields were much less (Tylecote 1986, 213). The process could not be run continuously as the iron bloom had to be manually removed from the base of the furnace after smelting. The diameter of the

furnace and the size of the furnace opening gave an upper limit on the size of the bloom and thus how much metal could be produced.

The bloomery process was superseded by the blast furnace which was introduced to Britain towards the end of the 15th century (Tylecote 1986, 213). The blast furnace produced a molten iron-carbon alloy (cast iron) and so allowed continuous smelting over months at a time. Cast iron is a brittle material not suitable as stock for a blacksmith and so most cast iron had to be converted into malleable (low-carbon) iron (see below). Early blast furnaces used charcoal but the rising price of charcoal encouraged the search for alternative fuel sources, in particular coal (Hayman 2005, 42). Most coal was high in sulphur (Tylecote, 1986, 224) and this affected the working properties of the iron, making it brittle when heated and unworkable (den Outen 1981, 77). Darby developed the use of coke (roasted coal) for the blast furnace in Coalbrookdale in the early 18th century (Crossley 1990, 166; Hayman 2005, 43). By the end of the century coke-fuelled blast furnaces had become widespread. The increased physical strength of coke allowed higher stacking of the fuel so furnaces could be built larger, for example the furnace at Bleanavon was 19m high (Crossley 1990, 166). Blast furnaces were operated at higher temperatures than bloomery furnaces which resulted in slag with a much lower iron content. This meant that poorer ores could be used, including older bloomery smelting slags.

### Cast iron conversion processes

The blast furnace largely replaced the bloomery process because it could produce much larger quantities of metal using less fuel. The resulting metal was brittle, however, while almost all demand was for a malleable form of iron which could be forged. The conversion of cast iron to malleable iron required the removal of most of the carbon (and other elements including silicon, manganese and phosphorus).

The earliest cast iron conversion process employed in Britain was the so-called Walloon process which used a two-hearth system — a finery and a chafery (Morton and Wingrove 1970; den Outen 1981). In the finery hearth, cast iron was melted in a sufficiently oxidising atmosphere to remove the carbon as carbon dioxide gas and various impurities (especially silicon) as slag (Figure 1). The process can be thought of as containing two steps: *refining* during in which primarily silicon, manganese and other elements are oxidised and removed from the metal as slag, and *fining* during which the carbon is removed (Morton and Mutton 1967, 722). These two processes are likely to have occurred within the same hearth when converting cast iron that had been produced in charcoal blast furnaces (Morton and Wingrove 1970, 26); not least because the silicon, phosphorus and manganese content of charcoal cast iron was rather low. Some later cast iron conversion processes; however, appear to have made use of separate hearths or furnaces for refining and fining (see below).



Figure 1. Diagram of the oxidation of cast iron in a finery furnace. Pig iron is melted and the droplets fall through an oxidising zone removing carbon before falling into the slag and solidifying (from Tylecote 1986, 219)

Within the finery hearth, the cast iron was melted and carbon was removed from the metal. The cast iron would have a melting temperature of around 1200°C but this would rise to around 1450°C as the carbon reached negligible levels and so the metal would solidify. The solid iron would form into a pasty mass or ball (sometimes known as a bloom) near the base of the hearth and was protected from further oxidation by a slag bath. To help slag creation, other additives such as hammerscale, clay, sand or ore could be added by the finer (Morton and Wingrove 1970).

Further heating and reheating of the ball, necessary to allow the forging of the metal into bars, was usually carried out in a separate hearth (the chafery). The finery/chafery process appears to have made use of water power for both bellows and hammers from the outset. It is known that slag was produced in the chafery hearth and that at least some of this comprised large masses of slag known variously as hambones or mossers (Morton and Wingrove 1970, 28).

The finery/chafery process was the primary method for converting brittle cast iron into malleable wrought iron from the 16th century to the end of the 18th century in Britain. The finery could only be operated using charcoal although the chafery could make use of coal. The later 18th century saw various attempts to develop conversion methods which would allow greater use of coal and less reliance on charcoal. In the 1770s 'potting and stamping' was patented as an alternative conversion method (Hayman 2005, 43–44). The pig iron was melted in an oxidising atmosphere, allowed to cool, and broken up (stamping). The metal was then heated in crucibles (potting) in a reverberatory furnace. The reverberatory furnace allowed the use of coal as the fuel and the charge were kept separate.



Figure 2: Reverberatory puddling furnace from Ebbw Vale from the mid 19th century (from Percy 1864, 648)

The conversion method that finally came to dominate the iron industry was puddling (Hyde 1983; Morton and Mutton 1967; Mott and Singer 1983). This was patented in 1783–84 by Henry Cort and became widely used in the 19th century. Cort's process (often later known as 'dry puddling') consisted of melting pig iron in a coal-fired reverberatory furnace (Figure 2); the oxidising atmosphere of the furnace removed carbon and other impurities from the molten iron until it gathered into a pasty ball also sometimes known as a bloom. This ball was removed and hammered to expel trapped slag. Cort's process also importantly used rollers, initially water-powered, but steampowered in the 19th century, to thoroughly homogenise the metal. The 'running out' furnace was used to refine cast iron produced by coke-fuelled blast furnaces, to remove silicon and other metals (Killick and Gordon 1987). Puddling was much more cost effective than charcoal-fired finery furnaces and removed the reliance on charcoal. Later in the 19th century dry puddling was replaced by wet puddling invented by Hall in 1832 (Photos-Jones *et al* 2008, 159).

### Previous investigations of contemporary metalworking debris

While the nature of bloomery smelting slags has been the focus of study for the last half a century (eg Morton and Wingrove 1969a; 1972; Paynter 2006; Paynter 2007) much less attention has been devoted to post-medieval metalworking debris. Tylecote (1986) and

Rostoker and Dvorak (1990) draw on a range of sources giving analyses for blast furnace, finery and chafery slag, cast and wrought iron, and a range of fuels. Principal sources of information on puddling, chafery and finery slags are Morton and Wingrove (1969b, 1970), Killick and Gordon (1987) and Gordon (1997). Starley (1999) provides analyses of slag inclusions in wrought iron of late 18th- and 19th-century manufacture.

The conversion of cast iron to malleable iron required the removal of silicon and other impurities which would react with some of the iron to form a fayalitic slag (Morton and Wingrove 1969b; Killick and Gordon 1987). This slag is difficult to distinguish from fayalitic slags produced by other processes. Much of the research into post-medieval iron slags has attempted to identify criteria for distinguishing between the various cast iron conversion processes (finery/chafery and the types of puddling) and processes used to manufacture the iron (bloomery or blast furnace).

The finery process led to the removal of silicon, phosphorus and manganese, depending on the nature of the cast iron, and these would have combined with some of the iron to form a fayalitic slag. However the iron was in contact with the charcoal fuel and so a reducing atmosphere was maintained in areas of the hearth. The resulting slags contain fayalite and also wüstite (FeO). The ash from the charcoal could contribute to the formation of the slag but the sulphur content should be low. Later accounts suggest a range of materials was added to help form the slag bath, including iron ore, hammerscale, and even sand or clay (Morton and Wingrove 1970).

Morton and Wingrove concluded that chafery slags could best be identified by their visual appearance rather than by analysis and microstructure (Morton and Wingrove 1970, 28). Their analyses indicated that coal-fuelled chafery hearths resulted in slag that often contained high concentrations of sulphur (0.5–5wt%), presumably due to the use of coal fuel (Morton and Wingrove 1970, Table V).

Killick and Gordon (1987, 35) have argued that puddling slags can be distinguished from other fayalitic slags by their lower alkali (sodium and potassium) content as the metal and slag in the puddling process was never in physical contact with the fuel, unlike the situation in the bloomery and finery processes. They illustrate examples of puddling slag microstructures with samples from Fontley and Roxbury, which show that the principle phases in these slags are fayalite, magnetite, silica and iron sulphides. Killick and Gordon (1987) noted that the correct identification of many phases, not least the iron oxides (wüstite, magnetite, etc) and silica polymorphs (quartz, tridymite and cristobalite), was problematic and recommended the use of XRD analysis. They noted the absence of wüstite and stressed that the free iron oxide was exclusively present as magnetite (Killick and Gordon 1987, 34). They suggested that the presence of magnetite (rather than wüstite), iron sulphides and the low proportion of alkalis were all characteristic of puddling slags (cf Mackenzie in Proctor 2011).

Gordon (1997) analysed slag from bloomery, finery and puddling sites in the USA. He reiterated that that these could be best distinguished by the nature of the minerals

present rather than by bulk composition. Puddling slags were characterised by iron sulphide and magnetite, bloomery slags by their exotic phases: leucite (KAISi<sub>2</sub>O<sub>6</sub>), hercynite (FeAI<sub>2</sub>O<sub>4</sub>), monticellite-kirschsteinite (Ca(Mg,Fe)SiO<sub>4</sub>), and finery slags by their high wüstite (FeO), fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and lack of exotic phases (Gordon 1997).

Rostoker and Dvorak (1990) have proposed that chemical analysis can be used to distinguish between bloomery, finery and puddling slags. They used published chemical data on slags and carried out a multivariate analysis (using Weibull distribution functions) which they claimed would allow the different processes to be distinguished (in at least some cases). This approach has not proved to be popular among archaeometallurgists.

Starley (1999) undertook the analysis of slag inclusions within a range of architectural iron samples with a view to determining their technological origin (finery or puddling). He showed that the use 'of the sulphur or alkali content of their inclusions should be viewed with some caution'. Dillmann and L'Héritier (2007) carried out a similar study of French architectural iron and analysed a large number of slag inclusions. They confirmed that slag inclusions associated with either process could have varied chemical compositions and that there was a good deal of overlap. They used a simple multivariate analysis (a plot of  $P_2O_5$  against (MgO +  $Al_2O_3$  + $K_2O$ )/FeO to minimise this overlap and used this to investigate the adoption of the indirect method (blast furnace and finery forge) in France.

# DOWNSIDE MILL

Downside Mill was a large but relatively short-lived industrial site owned by Alexander Raby (Crocker 2000; Potter 2000; Taylor 2000). It was sited on the River Mole and this location had been subject to a succession of mills over the years. The first was a corn mill recorded in 1331, and this use continued until 1728 when the corn mill was replaced with a paper mill. In 1770 the mill and land was acquired by Alexander Raby (Taylor 2000). Raby was a local industrialist who already ran a bronze casting and iron cannon business in the Weald inherited from this father. He converted the paper mill for metalworking and greatly expanded the site. A labelled map from 1798 shows the extent of the site (Figure 3). The site was finally sold in 1806 when the Mill was no longer found to be profitable. Alexander Raby relocated his metalworking business to South Wales. In 1809/10 Downside Mill was sold again. By 1814 the metalworking structures were dismantled and the mill used for flock manufacture and as a timber saw mill. In 1925 the final mill closed and the site used for storage. In 1990 the mill was converted into office accommodation and the remains of the waterwheel conserved (Crocker 2000, 27). Some of the original buildings from the Raby period survive at the site, although all that survives of the copper mill is the sluice.

Downside Mill is one of several post-medieval water-powered metalworking sites on the lower Thames and its tributaries. In most cases these mills were associated primarily with the working of non-ferrous metals (copper and brass). The earliest conversions to non-

ferrous metalworking appear to have been in the 16th century and most of these sites ceased to work metals by the early 19th century. In the northern Surrey area, documentary references and slag finds have indicated five other metalworking mills (Potter 2000, Table 1). There were iron-working mills at Esher and Coxes Lock and iron and copper were worked at Byfleet, Weybridge and Ember. Ironworking requires a greater force of water and these mills tended to be on sites of particularly steep river gradients (Potter 2000, 11). The location near to the London markets added to the suitability of these mill sites at that time, although the benefits of this location began to drop off into the 19th century as the need to be located near fuel and raw materials became of primary concern.

### Cartographic evidence for metalworking at Downside Mill

A contemporary site plan believed to have been drawn in 1798 (Figure 3) indicates a range of metalworking activities took place at Downside Mill including the casting, fining, shaping and fabrication of copper alloy and iron. The main activities, being housed in the two largest buildings, were the copper foundry (23) and the iron foundry (18) and forge (17). The iron foundry would have been used for the melting of cast iron for casting objects. This would probably have been carried out either in a cupola furnace (using coke) or a reverberatory furnace fuelled with coal. The presence of the coke house (26) could suggest that the cast iron was melted in a cupola furnace. The copper foundry, likewise, was for the casting of copper alloy objects into moulds, most likely heated in a reverberatory furnace.

A forge is identified on the plan (17) and this is likely to have been for the conversion of pig iron to wrought iron. From the introduction of the blast furnace at the end of the 15th century to the turn of the 19th century, most wrought iron was produced from pig iron using a charcoal-fuelled finery forge and a chafery hearth. Both hearths were air blown and used a hammer powered by a waterwheel for consolidating the iron (16). In the late 18th century the range of processes used to convert pig iron into wrought iron increased but there is no documentary evidence to suggest that any of these processes were employed at Downside Mill.

Additional metalworking apparatus include water-powered helve and tilt hammers (11; 16) for the smithing and shaping of the wrought iron produced in the forge. The mill (22) could be used for rolling the different metal bars into sheets and the cutting house (14) for removing uneven edges or for cutting the sheets or bars. A smith shop (30) is also present as would be expected of an industrial complex. Smithing on site would be needed to repair parts or tools. The cylinder race (10) possibly indicates the use of cylinders to pump air for the forge and foundry as opposed to bellows which were becoming obsolete.



Figure 3: A redrawn and relabelled plan of Downside Mill from the original thought to have been made in 1798 (Crocker 2000).

I = Floodgates; 2 = Flood Gate House; 3 = Standen's House; 4 = Garden; 5 = Dog Kennell Field;
6 = Dog Kennell; 7 = Flash Race; 8 = Forge & Tilt Race; 9 = Brick & Lime House; 10 = Cylinder Race;
11 = Helve House; 12 = Smoak House; 13 = Women's Shop; 14 = Cutting House; 15 = Break House;
16 = Tilt; 17 = Forge; 18 = Iron Foundry; 19 = Mill Head; 20 = Bridge; 21 = Mill Garden; 22 = Mill;
23 = Copper Foundry; 24 = Triangles; 25 = Coak House; 26 = Coak Penn; 27 = Charcoal Penn;
28 = Charcoal Penn; 29 = Coal Penn; 30 = Smith's Shop; 31 = Counting House & Assay House;
32 = Ware House; 33 = Bridge; 34 = Dung Yard; 35 = Gibb's House; 36 = Sty; 37 = New Stables & Coach House; 38 = March Meadow; 39 = Carpenter's Shop; 4 0= Road to Cobham; 41 = Kitching Garden; 42 = Sty; 43 = Old Stables and Coach House; 44 = Botany Garden; 45 = Dairy; 46 = Laundry, Washouse, Coal House & Stable; 47 = Cellars; 48 = Scullery and Pantry; 49 = Dwelling House; 50 = Cold Bath; 51 = Pleasure Ground; 52 = Road to Down Farm (Labels and caption taken from Crocker 2000, 24)

A further process that may have taken place at Downside is tin plating. The process of applying molten tin to sheet iron to stop corrosion of the iron was introduced to England in the early 18th century. A tin-plate works is not indicated on the plan (Figure 1) but it can be inferred from new workers housing built in 1803–4 which included a group of houses called 'Tinman's row' (Taylor 2000, 19). Another possible indication is the Woman's shop (13). Before tin plating the iron sheet or bars had to be cleaned, and this was normally done by women (Crocker 2000, 24). Other processes involved in tin plating were iron rolling and cutting, both of which were available at Downside Mill.

At Downside Mill the presence of charcoal penns (27, 28), coal penn (29), coak (ie coke) house (25) and coak penn (26) indicate the use of all three fuels on site and also the preparation of coke. Other notable buildings include the assay house (31).

# Excavation

The excavation, comprising two trenches, was carried out at Downside Mill, near Cobham as a training exercise by Surrey Archaeological Society in early August 2008. The first trench was 15.0 by 11.8m and was sited over the expected location of the copper mill. Demolition rubble and large quantities of industrial residues were found as well as sections of the north and south mill race. Possible locations were identified for the south water wheel and the gear mechanism plus a large iron lump (termed 'stanchion base') that was possibly used as a support for a large post or a piece of heavy machinery. The second trench was much smaller (2.85 by 1.00m) and was placed on the expected location of Alexander Raby's house but recovered very few finds.

# **PROJECT AIMS**

The main aim of this research was to identify the activities taking place at Downside Mill and to provide detailed descriptions of the type of waste from each process. Analysis and understanding of metalworking remains is an important tool in industrial archaeology. The progression of metalworking methods during the Industrial Revolution are recorded in numerous patents and other historical documents, but there is little information about how these new tools and processes were implemented, and even fewer analyses of the associated metalworking remains (Bayley *et al* 2008, 68–69). In some cases industrial espionage (and the fear of such espionage) led to the deliberate concealment of crucial technological developments. The analysis of materials from Downside Mill will contribute to an improved ability to recognise similar processes at other sites.

The aims are:

- Confirm which metalworking processes were taking place on site, based on the archaeological evidence, compared to those indicated in the map (Figure 1). Specifically:
  - a. Which conversion process was being used to convert cast iron to wrought iron: finery/chafery or puddling?
  - b. Is there evidence for a tinplate works on site?
  - c. What copper alloy was being produced and was there a standardised copper alloy composition?
  - d. Is there any evidence of assaying on site?
- 2. Establish the conditions and fuel used for each process coal, coke or charcoal?
- 3. Provide a detailed description, in terms of appearance, composition and microstructure for each type of metalworking waste with the aim of making similar material easier to identify in the future.

# MATERIAL

50kg of industrial residues were collected by Surrey Archaeological Society. All of the material was examined visually, weighed, described and photographed. The materials are identified by their context and bag number; most contexts providing several different bags of material. Where a single bag contained more than one type of material this is indicated by a suffix, eg #27-1 and #27-2. The bag numbers therefore served as unique sample identification numbers.

Standard practice is to first categorise material on the basis of colour, texture and morphology (Bayley *et al* 2001) (see Table 1 and Appendix 1). However the number of processes taking place at Downside Mill, and the relative scarcity of material with which to compare, made distinguishing some of the waste products from each other very difficult. In particular there were a number of processes taking place that generated fayalitic slags. The analytical results have therefore been used to confirm the morphological distinctions between different groups of slag in Table 1; the analyses themselves are discussed more fully in the following section.

### Flowed fayalitic slag

The single most abundant material (~25kg) was **flowed fayalitic slag**. It had flow features but had not wetted the surface that it had run over. It tended to have a ropey upper surface (Figures 4 and 5) and an undulating base with impressions of the surface on which it solidified (Figure 6). This slag derives from the dry puddling iron conversion process, which is discussed later.



Figure 4: Top view of flowed fayalitic slag from dry puddling (#11)

[]	Flowed	Hearth lining	Dense fayalitic	Fe and Fe conc.	Bubbly	Mould	Cu	Glassy Cu	Fuel Undia	g	Misc. Al	
	fayalitic slag		slag		fayalitic slag		alloy	slag		slag		
	415				830		488	150	74			1957
2				105					33			138
36	037	6823	1687	3732					653			18449
4				19	326						3 (alum'm)	348
6	315								33			348
8   3	3	254		754	308		94		157			1702
9 26				64					I			91
20	17953			56	88	187						18284
22 9				19			265		74		602 (vessel)	969
23 53		6261		632		126			447			7519
24				21								21
26							4					4
35		70				15			28			113
All	24941	13408	1689	5402	1552	328	851	150	91010	7 60	5	49943

#### Table 1: Summary of materials by context (weight in g)



Figure 5: Side view of flowed fayalitic slag from dry puddling (#11)



Figure 6: Underside view of flowed fayalitic slag from an iron conversion process (#11)

Amongst this slag were some fragments that did not have typical flowed surfaces. These samples are thought to derive from the early or preparatory stages of puddling, the details of which are discussed later. These atypical samples were #18 (Figures 7 and 8), which had a flat base and side with a convex surface, and #50 (Figures 9 and 10), which was in the form of a dense pool of slag but without a flowed surface.



Figure 7: Plan view of sample #18, which probably derives from refining



Figure 8: Side (bottom) view of sample #18, which probably derives from refining



Figure 9: Side view of sample #50, which probably derives from refining



Figure 10: Plan view of sample #50, which probably derives from refining

# Hearth lining

Substantial quantities (~13kg) of **hearth lining** were identified. This largely comprised sandy ceramic bricks typically 50 by 100mm, fired to a grey or purple colour and sometimes permeated by fayalitic slag on the inside. The outer layers were orange and oxidised fired (Figures 11 and 12).



Figure 11: Upper surface of a large mass of puddling slag adhered to the hearth lining (sample #67)



Figure 12: Lower surface of sample #67 showing that the hearth lining made up of small individual bricks (grading from orange oxidised-fired to purple then grey towards the inside surface of the hearth)

The association with the slag indicates that this material is the lining of the hearth used for the puddling iron conversion process at the site. In most cases the lining material lacked any curvature, suggesting that it derived from a rectangular structure.

### Dense fayalitic slag

A very small proportion of the fayalitic slag did not have flowed surfaces. This dense slag has probably derived from a foundry process and is discussed further later. The only substantial sample was #10, a 1.7kg lump lacking the distinctive flow patterns of the puddling slag. It had a rusty appearance, bowl-shape, fairly low porosity and was covered by concreted smithing waste including hammerscale (Figure 13).



Figure 13: Plan view of sample #10, a large mass of dense fayalitic slag with adhering hammerscale and concretions.

### Iron and iron-rich concretions

5.4kg of the material submitted for examination consisted of corroded iron metal often with a mixture of concreted material (Figure 14) including slag, sand, stone, charcoal, coke/coal and hammerscale, labelled **Fe and Fe conc** in Table 1. Hammerscale is a microslag formed during smithing and comprises small spheres and flakes, largely made up of iron oxides (Bayley *et al* 2001). Some of the metal fragments were pieces of objects.



Figure 14: Iron concretions, including sample #66 (top right).

# Bubbly fayalitic slag



Figure 15: Bubbly fayalitic slag sample #43

1.5kg of **bubbly fayalitic slag** (Table 1) was recovered. This slag varied widely in appearance. Most of it was iron-rich, amorphous and bubbly with some evidence of flow on the surface (Figure 15). Some fragments were also heavily stained green due to copper corrosion products and had pieces of orange-fired ceramic incorporated (Figure 16). Several pieces of bubbly slag had adhering hammerscale and contained within them broken pieces of more dense fayalitic slag.



Figure 16: Bubbly fayalitic slag with green staining from copper corrosion products and adhering orange-fired fragments of ceramic (sample #6)

### Mould

A very small amount (~0.3kg) of heated sandy ceramic was recovered from three contexts. This material was fine-grained, with smooth, reduce-fired interior surfaces, and was tentatively identified as fragments of mould from metal casting. There were slight colour variations possibly indicating heating or heat damage to the surface. The top surfaces were completely flat but the outer surfaces were often missing. The only complete section was 30mm thick (Figure 17).



Figure 17: A plan view of a fragment of mould sample #47, with the internal surface to the top and external surface to the bottom and a raised ridge of residue along the rim.

### Copper alloys

The assemblage included several fragments of copper (Cu) alloy including pieces of finished artefacts and amorphous lumps. A hemisphere of metallic copper alloy was identified as the possible fill of a ladle (Figure 18).



Figure 18: Copper alloy lump, left, and right, sample #5, a hemispherical mass of leaded bronze

### Glassy copper slag



*Figure 19: Glassy copper slag (sample #2 is top left)* 

150g of this material were recovered from context [1]. The analytical results, discussed later, suggest that this slag was probably produced in a copper foundry, using a reverberatory furnace for heating and casting copper alloys (Figure 19).

### Undiagnostic slag

Some of the material was described as undiagnostic as it could not be allocated to the categories described previously.

### Miscellaneous material

Some of the material submitted for examination did not fit into the previously described categories (Table 1). This included fragments of one or more white ceramic vessels containing a dark grey charge (Figures 20, 21 and 22), as well as a dark grey rectangular plate (Figure 23). The best preserved ceramic vessel (Figure 20) is cylindrical, 62mm in diameter and surviving to a height of 150mm with thin walls (3mm) and a flat base. The fabric is fine-grained and refractory but there was no evidence of heating. A maker's stamp 'Bailey & Co London' near the base (Figure 21) indicates that it was made at the Fulham pottery between 1864 and 1888 (Green 1999, Figure 130k). The contents (Figure 22) comprised small fragments of a dark grey material exhibiting numerous lustrous fracture surfaces. Samples of the vessel, its contents and the rectangular plate (Figure 23) were taken for scientific analysis (Table 2).



Figure 20: Ceramic vessel sample #52



Figure 21: Close up of the stamp on sample #52



Figure 22: Contents of the ceramic vessel sample #52



Figure 23: Rectangular artefact (#55)

A single small fragment of aluminium (AI) was recovered from context [4]. Aluminium was extremely scarce before the 20th century and its presence in this context suggests that this deposit formed after the 19th century (and probably after the middle of the 20th century).

# METHODOLOGY

Twenty-six samples were selected for scientific analysis (Table 2).

Sample [	Descriptio n
#10-1	Large mass of dense fayalitic slag
#	Flowed fayalitic slag
#15	Flowed fayalitic slag
#18	Fayalitic slag with atypical curved surface
#21-1	Fayalitic slag adhering to hearth lining
#37	Flowed fayalitic slag
#43-I	Small flow of fayalitic slag
#50	Mass of dense fayalitic slag
#21-2 H	earth lining
#67-I	Hearth lining – top
#67-2	Hearth lining – bottom
#70 Hea	urth lining
#27-I	Hearth wall/ceiling – inside
#27-2	Hearth wall/ceiling – outside
#10-2	Flake and spheroidal hammerscale from iron concretion
#14	Amorphous iron lump (cast iron)
#26	Flake and spheroidal hammerscale from iron concretion
#39 Iro	n concretion
#66	Iron concretion (iron lump)
#68 lr	on object
#6	Bubbly fayalitic slag (green stained)
#8	Small flows of fayalitic slag
#25 Bub	bly slag
#43-2	Bubbly fayalitic slag
#2	Glassy copper alloy slag
#5	Copper alloy casting waste
#58	Copper alloy casting waste
#34	Copper alloy rod
#59	L-shaped worked copper alloy
#53	Contents of #52/#54
#54 Cer	ami c vessel

Table 2: List of analysed samples

The range of analytical techniques used were EDXRF, microhardness testing, XRD and SEM-EDS.

EDXRF (energy dispersive x-ray fluorescence) spectroscopy was used for surface analysis on unprepared samples and gave qualitative compositional results. An Eagle II EDXRF was used under vacuum and calibrated using a copper aluminium standard. The voltage was 40kV with a current of between 400–500mA and a deadtime of between 20–30%.

For mineralogical investigation of selected samples a Bruker D8 Advance X-ray diffractometer (XRD) with a Lynxeye detector was used. Small samples were removed

and crushed to a powder. The analytical parameters were 40kV and 40mA, counting at 0.2 second intervals for approximately 30minutes.

To examine and analyse samples with the SEM, they were cross-sectioned using a cutting disk or circular saw. The samples were then embedded in low-viscosity epoxy resin and ground and polished down to a 1-micron finish (Vander Voort 1999). The iron samples were etched using 2.5% nital for approximately 10 seconds to reveal the metal microstructure (cf Scott 1991). Microhardness testing was also performed using 500g weights for 15 seconds on 2 sites and an average taken.

The bulk of the compositional analysis was performed using an FEI Inspect F Scanning Electron Microscope (SEM) and an EDS (energy dispersive spectrometer) detector. The results were quantified using Oxford Instruments INCA software and the equipment was calibrated against a cobalt standard at the beginning of each session. Working parameters were set to 100 seconds live time, 25kV and a 5.0 spot size with a working distance of 10mm. A number of reference materials were analysed to check the accuracy and precision of the results; W25R was used for the slag standard (Kresten and Hjarthner-Holdar 2001), B10 and B22 for copper alloys and MBH Cast Iron Reference C1 for the iron (see Appendix 2).

The SEM was used to obtain information on the microstructure of each sample followed by bulk compositional analysis and individual analysis of phases and inclusions where appropriate. For the bulk composition, area analysis of between 2.6 by 3mm to 0.8 by 1mm (equivalent to 100x to 300x magnification) was performed on 3–8 areas depending on the homogeneity of the sample. In samples where more than one material is present (slag and clay) separate bulk analysis was carried out on the separate areas. Care was taken to avoid areas of corrosion and to use representative areas. Phases and inclusions were analysed separately using spot analysis (approximately 10micron spots). Depending on the number and compositional variation of the phases and inclusions between 1–6 analyses were taken. The elements analysed for were Na, Mg, Si, P, S, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sn, Ba, Cl, Pb, Bi and Sb, although not all elements were detected and only the relevant elements are reported.

# RESULTS

### Flowed fayalitic slags

These flowed fayalitic slags made up the vast majority of the assemblage from Downside Mill. This slag (Figure 24) is dominated by fayalite, the margins of which often display finely dispersed inclusions of a silica phase (Figure 25). The very low concentrations of minor oxides, such as the alkalis, in these samples (Table 3) distinguish them from bloomery smelting slags (Paynter 2006; cf Killick and Gordon 1987). The presence of magnetite suggests an oxidising process such as iron conversion (Table 4). The low levels of sulphur and alumina in most of the samples are indicative of a reverberatory furnace. These slags are therefore likely to be waste from dry puddling and are very similar in terms of their composition and microstructure to slag from known puddling sites.



Figure 24: SEM image (back-scattered electron) of sample #11 dominated by large fayalite crystals (grey) with occasional dendrites of magnetite (white)

Table 3: Chemical composition of the platy flowed slag samples from dry puddling (wt% normalised to 100%)

Sample Na	<sub>2</sub> O M	gO	Al <sub>2</sub> O <sub>3</sub> Si	O <sub>2</sub>	$P_2O_5$	SO3	K₂O	CaO	TiO₂ MnC	)	FeO
#II 0.	2	<0.1	1.4	27.1	0.7	1.0	0.4	0.4	<0.1 <0	.1	68.7
#I5 <0.		<0.1	1.3	31.1	0.3	< 0.3	0.3	0.1	<0.1 <0	.1	66.2
#21-1 0.		<0.1	2.5	29.9	< 0.3	< 0.3	0.3	0.5	0.1 <0.	Ι	65.7
#37 0.	2	<0.1	1.4	29.5	0.5	0.4	0.4	0.2	<0.1 <0	.1	67.3

Table 4: Mineral composition of the platy flowed slag samples from dry puddling (XRD analyses)

Sample M	ineral phases
#11 Fayalite	$(Fe_2SiO_4)$ , Magnetite $(Fe_3O_4)$
#15 Fayalite	(Fe <sub>2</sub> SiO <sub>4</sub> ), Magnetite (Fe <sub>3</sub> O <sub>4</sub> )
#21-1 Magnet	ite (Fe <sub>3</sub> O <sub>4</sub> ), Fayalite (Fe <sub>2</sub> SiO <sub>4</sub> ), Tridymite (SiO <sub>2</sub> ), Cristobalite (SiO <sub>2</sub> )
#37 Fayalite	$(Fe_2SiO_4)$ , Magnetite $(Fe_3O_4)$



Figure 25: SEM image (back-scattered electron) of sample #11 at higher magnification, showing fayalite (grey), with fine silica phase (dark grey) in the fayalite towards the edges, in a matrix of magnetite (light grey and angular), iron sulphide (white spheres), leucite (dark grey) and glass (mid-grey)

Sample #21-1 comprises slag adhering to one of the pieces of hearth lining (sample #21-2). The overall chemical composition of this sample is very similar to samples #11, #15 and #37 but the microstructure contains considerably more magnetite and silica polymorphs (Figure 26; Table 4), representing an earlier stage in the process of puddling slag formation. The quartz derives from the quartz-rich hearth lining, which is described further below. The size, shape and distribution of the silica polymorphs indicate that these have crystallised from a melt (Baldwin 1954). Photos-Jones *et al* (2008, 171–173) note the presence of both silica polymorphs and iron oxide in material from Monklands that was interpreted as 'fettling', that is the lining of a puddling furnace. Very similar microstructures are illustrated by Killick and Gordon for the 19th-century puddling slag from Roxbury (Killick and Gordon 1987).



Figure 26: SEM image (back-scattered electron) of sample #21-1 showing magnetite (white), fayalite with inclusions of silicate phase (mid-grey with dark grey pattern), silica polymorphs, probably tridymite (dark grey), a matrix of eutectic glass and fayalite (mid-grey) and voids (black)

# Possible refining slags

A small subset of samples had atypical shapes (samples #18 and 50) and slight compositional differences from the flowed fayalitic slag in that they contained higher levels of manganese and slightly elevated levels of phosphorus and sulphur (Table 5). Similar phases were present in these slags as to the puddling slags however (Figure 27, Table 6), suggesting that they were also waste from an oxidising process in a reverberatory furnace.



Figure 27: SEM image (back-scattered electron) of sample #18 showing fayalite containing inclusions of a silicate phase (mid-grey with dark grey patterning), magnetite (angular light grey crystals), iron sulphide (white spheres), silica polymorphs (black angular tridymite and possible spherulitic cristobalite) and a glass matrix

*Table 5: Chemical composition of the manganese-rich slag samples (wt% normalised to 100%)* 

Sample Na	<sub>2</sub> O M	gO	Al <sub>2</sub> O <sub>3</sub> Si	O <sub>2</sub>	$P_2O_5$	SO3	K₂O	CaO	TiO₂	V <sub>2</sub> O <sub>5</sub> M	nO	FeO
#180.		<0.1	1.7	40.9	0.9	0.4	0.3	0.3	0.6 0.	2	5.4	48.7
#50 <0.	l	<0.1	1.9	42.5	0.7	0.4	0.6	0.3	0.4 <0	. I	3.3	50.0

Table 6: Mineral	composition	of the manganese-m	ich slag samples	(XRD analyses)
------------------	-------------	--------------------	------------------	----------------

Sample M	ineral phases
#18 Fayalite	$(Fe_2SiO_4)$ , Magnetite $(Fe_3O_4)$ , Quartz $(SiO_2)$
#50 Fayalite	$(Fe_2SiO_4)$ , Magnetite $(Fe_3O_4)$ , Cristobalite $(SiO_2)$

The high concentrations of magnetite in these slags strongly suggest that these are also a waste product from an iron refining process however they contain more silica and manganese than the typical puddling slag. There are a number of possible explanations for this, such as the refining of pig iron from different sources perhaps richer in manganese. Alternatively, the more manganese-rich slag may have been generated at an earlier stage in the refining process, for example when the silicon, phosphorus and manganese content of the iron was reduced, while the fayalitic flowed slag is waste from later in the process as the carbon content was reduced.

A final possibility is that this slag derives from a refining process used to prepare the metal for puddling. Cort's puddling process reportedly worked best with white cast iron rather than the more commonly available grey, but if the grey cast iron was first refined to reduce the silicon content then the resulting 'finers metal' was suitable for puddling. By the beginning of the 19th century a reverbatory 'refinery' or 'running out fire' was being used for this purpose, from which the molten refined metal was run out into a trough, where the slag floated on top and was removed by lowering a dam. This process, using a reverbatory furnace and an oxidising atmosphere, might be anticipated to result in slag with a microstructure and composition of the type observed in slag samples #18 and #50. It may also explain the atypical morphology of these samples, particularly fragment #18, which appears to have cooled in contact with iron surfaces. However a larger number of samples are required to investigate this fully.

### Dense fayalitic slag

Dense fayalitic slag samples #10-1 and #43 are distinguished from the other slags by both their microstructures and chemical compositions. There is abundant fayalite but this tends to be present as long thin laths (Figure 28) indicating relatively fast cooling. Spinels and iron sulphide are also present due to the high alumina and sulphur contents respectively (Table 8).

The high concentrations of sulphur, as well as alumina and other elevated elements (Table 7), indicate that the slag was formed by a process in which iron came into contact with a mineral fuel, such as bituminous coal. (The use of lignite would result in a more lime-rich slag). This eliminates reverberatory furnaces, in which the fuel and metal are kept separate. No magnetite was identified in these samples, discounting oxidising refining processes. This slag is most likely to be waste from a foundry at Downside Mill. The high iron content suggests that it is probably from an iron foundry, such as a cupola furnace for melting pig iron. The slag formed during the process floated on the top of the liquid metal and was tapped off.

Table 7: Chemical composition of the dense fayalitic slag (wt% normalised to 100%)

		/					01			/		
Sample Na	₂O M	gO	Al₂O₃ Si	O <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO	TiO₂	V <sub>2</sub> O <sub>5</sub> M	1nO	FeO
#10-1 0.	3	0.6	11.8	32.9	1.3	3.1	1.2	3.5	0.5 <0	). I	0.8	43.9
#43-1 0.	2	0.6	9.7	25.5	1.0	2.9	0.6	2.2	0.5 <0	. I	0.4	56.5

Tabla Q.	Minoral	composition	of the	(YPD analycoc)	)
TADIE O.	i'iiiiei ai	Composition	01 lite	(AND analyses)	/

Sample M in	eral phases
#10-1 Fayalite	(Fe <sub>2</sub> SiO <sub>4</sub> ), Hercynite (Fe <sub>1.1</sub> AI <sub>1.9</sub> O <sub>4</sub> ), Iron sulphide (FeS)
#43-1 Fayalite	(Fe <sub>2</sub> SiO <sub>4</sub> ), Spinel (Mg <sub>0.3</sub> Fe <sub>0.7</sub> Al <sub>2</sub> O <sub>4</sub> )



Figure 28: SEM image (back-scattered electron) of sample #43 showing fayalite laths and occasional spinels (top of image)

# Hearth lining

Several fragments of hearth lining were sampled. The surface of the hearth lining varied considerably. In some cases the adhering slag was so thick (>25mm) that it was sampled separately (e.g. #21-1), while in other cases (e.g. #70) this layer was less than 1mm thick. These differences may reflect the different parts of the hearth: those parts with thick

layers of adhering slag may come from furnace floor or the lower portions of the walls while those with thin layers may come from the roof or upper portions of the walls.

The puddling hearth was lined with a quartz-rich material. Two samples (#27 and #67) give some indication of the chemical composition of the ceramic as manufactured and contain 90wt% silica (Table 10). This material would be sufficiently refractory to withstand prolonged exposure to high temperatures. The hearth lining fragments had similar microstructures (Figure 29) consisting of abundant silica polymorphs (XRD analysis indicated the presence of quartz, tridymite and cristobalite) and a vitrified matrix. These microstructures have developed through the reaction of the lining with iron-rich slag and prolonged exposure to heat. The elevated concentrations of manganese in #70 and iron in #21-2 are due to the lining being permeated by slag. The range of phases present (in particular the silica polymorphs) suggests the furnace would have operated at temperatures in excess of 1300°C.



Figure 29: SEM image (back-scattered electron detector) of hearth lining (#27) showing dissolving quartz grains (grey, rounded and cracked grains) and silica polymorphs (small grey crystals) in a glassy matrix (light grey) with some porosity (black)

Table 10: Chemical composition of the hearth lining

Sample Na	<sub>2</sub> O M	gO	Al <sub>2</sub> O <sub>3</sub> Si	O <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO	TiO <sub>2</sub>	MnO FeO
#21-2 0.		0.1	2.4 79	.8	<0.3	<0.3	0.3	0.6	0.2	<0.11 6.5
#27 0.	3	0.4	5.3 88	.9	< 0.3	< 0.3	1.0	0.4	0.5	<0.12.8
#67 <0.	I	0.4	5.0 89	.9	< 0.3	<0.3	0.9	0.4	0.4	<0.12.3
#70 <0.	Ι	0.2	4.181	.9	<0.3	< 0.3	1.0	0.7	0.3	1.1 10 .1

#### Iron concretions



Figure 30: SEM image (back-scattered electron) of sample #66 showing iron oxide-rich hammerscale (white rectangular masses), quartz grains (dark grey and the black inclusions mineral fuel (black) in a light grey matrix made up of corrosion products.

The examination of three iron concretions (#10-2, #26 and #66) showed these to contain numerous fragments of hammerscale (Figure 30). The hammerscale mostly comprised small flakes, however, spheroidal hammerscale and some larger (but <5mm) miscellaneous lumps of slag were also present. These iron concretions are largely smithing waste (Bayley *et al* 2001), made up of hammerscale which was incorporated into floor deposits during ironworking. This material could have formed during a variety of operations when iron was heated and then worked. However, the elevated levels of

phosphorus, sulphur and manganese (Table 11) in much of the hammerscale suggests that it was produced during foundry casting or puddling, for example as foundry spatter or as scale generated during the forging of the ball or bloom of iron produced in the puddling hearth. In sample #10, the scale is concreted around a mass of foundry slag, which supports this conclusion.

TIAITIITIET.	scarc)											
Sample Ty	pe	Na <sub>2</sub> O	MgO A	$I_2O_3$	SiO2	P₂O₅	SO₃	K₂O	CaO TiO	2 N	1nO	FeO
10-2 HS		<0.1	0.1 0.		1.3	<0.3	<0.3	<0.1	<0.1 <0	.1	<0.1	98.5
10-2 HS		<0.1	<0.1 0.3		2.3	0.8	0.3	<0.1	0.1 <0.	Ι	0.2	95.7
10-2 HS		<0.1	<0.1 <0.	l	2.3	< 0.3	<0.3	<0.1	<0.1 <0	.1	<0.1	97.4
10-2 HS		<0.1	<0.1 1.1		1.4	<0.3	< 0.3	<0.1	0.4 <0.	Ι	0.2	96.8
10-2 HS		<0.1	<0.10.1		1.0	0.4	<0.3	<0.1	<0.1 <0	.1	<0.1	98.I
10-2 HS		<0.1	<0.10.1		4.4	0.5	<0.3	<0.1	<0.1 <0	.1	<0.1	94.7
10-2 HS		<0.1	<0.1 0.2		5.1	< 0.3	<0.3	<0.1	<0.1 <0	.1	<0.1	94.4
10-2 S	S	0.2	<0.1 0.4		5.5	0.8	0.8	<0.1	0.1 <0.	Ι	0.1	92.0
10-2 S	S	<0.1	0.1 0.	3	4.5	3.2	0.6	<0.1	0.2 <0.	Ι	0.6	90.6
10-2 M	isc	<0.1	<0.1 1.2		25.6	0.5	0.3	0.3	0.2 <0.	Ι	0.1	71.5
10-2 M	isc	0.2	0.3 0.	5	13.0	6.I	0.4	0.3	1.7 0.	Ι	2.2	75.3
10-2 M	isc	0.2	0.2 0.	3	6.8	3.7	0.6	0.1	0.5 <0.	Ι	1.3	86.4
26 HS		<0.1	<0.10.1		0.4	0.4	0.4	<0.1	<0.1 <0	.1	<0.1	99.5
26 HS		0.1	0.2 0.	6	4.4	1.3	0.6	<0.1	0.1 0.	Ι	0.6	92.0
26 HS		<0.1	0.1 0.	3	0.3	< 0.3	<0.3	<0.1	<0.1 <0	.1	<0.1	99.0
26 HS		0.2	<0.1 1.1		2.7	0.3	< 0.3	<0.1	0.6 <0.	Ι	<0,1	95.I
26 HS		<0.1	<0.1 <0.	l	1.3	1.0	1.1	<0.1	0.2 <0.	Ι	<0.1	96.I
26 HS		0.2	<0.1 0.2		5.5	4.4	2.0	<0.1	0.3 <0.	Ι	0.6	87.0
66 S	S	<0.1	<0.1 0.3		10.7	0.3	< 0.3	<0.1	<0.1 <0	.1	<0.1	88. I
66 HS		<0.1	<0.10.1		1.2	< 0.3	0.6	<0.1	<0.1 <0	.1	<0.1	97.8
66 HS		<0.1	<0.1 0.2		1.6	< 0.3	0.4	<0.1	<0.1 <0	.1	<0.1	97.7
66 HS		<0.1	<0,   <0,	l	0.6	< 0.3	< 0.3	<0.1	0.1 <0.	Ι	<0,1	99.1
66 HS		<0.1	<0,   <0,	l	1.5	< 0.3	< 0.3	<0.1	<0.1 <0	.1	<0.1	98.1
66 HS		<0.1	<0,   <0,	l	0.9	< 0.3	< 0.3	<0.1	<0.1 <0	.1	<0.1	99.0
66 HS		<0.1	0.2 0.	2	0.8	<0.3	0.5	<0.1	<0.1 <0	.1	<0.1	98.4
66 HS		<0.1	<0.1 <0.	I	0.8	0.3	0.3	<0.1	<0.  <0	.1	<0.1	98.6

Table 11: Chemical composition of hammerscale and related material from iron concretions (HS = hammerscale, SS = spheroidal hammerscale, Misc = miscellaneous hammerscale)

### Bubbly slag and slag runs

The samples of bubbly slag were heterogeneous, often with pieces of ceramic or fragments of denser slag incorporated. Slag sample (#6) was green-stained indicating the presence of copper but also contained several fragments of denser slag. Analysis showed that these denser flows within sample #6 were dominated by laths of anorthite with occasional metallic copper droplets (Figure 35). The slag also contained a platy mineral fragment, probably derived from the use of mineral fuel. Some iron oxide scale was dissolving in the slag. Another region was made up of copper iron sulphide, which had been in contact with the slag whilst hot. The sample also included quartz-rich ceramic,

hammerscale and charcoal, which were adhered by copper and iron corrosion products (Table 15).



*Figure 35: SEM image (back-scattered electron detector) of bubbly slag with green staining (#6)* 

Table 15: Chemical co	mposition	of the slag runs	s (#8) and bub	bly slag (#6	and #25)
			(		

Sample Na	20 N	1 gO	Al <sub>2</sub> O <sub>3</sub> Si	O <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO	TiO <sub>2</sub>	MnO FeO	CuO	SnO <sub>2</sub>
#8 <0.1		<0.1	0.2 8.	7	0.6	<0.3	<0.1	0.1	<0.1	<0.190.1	<0.1	<0.5
#6 0.	3	1.1	22.14	1.6	<0.3	0.4	1.8	14.2	0.7	<0.1 16 .6	0.5	<0.5
#25 0.	3	<0.1	0.2 9.	4	1.1	0.2	<0.1	0.6	<0.1	1.8 86 .3	<0.1	<0.5

Table 16: Mineral composition of the slag runs (#8) and bubbly slag (#6 and #25) (XRD analyses)

Sample M	ineral phases
#8	Wustite (FeO), Fayalite ( $Fe_2SiO_4$ ), Magnetite ( $Fe_3O_4$ )
#25	Wustite (FeO), Fayalite ( $Fe_2SiO_4$ )
#43-2	Wustite (FeO), Fayalite (Fe <sub>2</sub> SiO <sub>4</sub> ), Quartz (SiO <sub>2</sub> )

Sample #25 had no visible traces of copper alloy on its outside surfaces but examination at high magnifications revealed tiny metallic inclusions rich in tin and iron, with low levels of copper. These did not appear to be post-depositional contamination. The microstructure was again dominated by wustite (Figure 36) with some fayalite.



Figure 36: SEM image (back-scattered electron detector) of bubbly slag (#25) showing wustite (light grey), fayalite (dark grey) and metallic tin / iron inclusions (white)

The small runs of slag (sample #8) were also very iron-rich with a microstructure dominated by wüstite (Figure 37). These small runs are likely to be spatter from ironworking activity.

The detection of wüstite in this selection of samples and the dissolving iron oxide scale in sample #6 are all suggestive of smithing activity. Morton and Wingrove (1970) describe chafery smithing slags as being poured 'wild and gassy', which is consistent with the evidence of flow and porosity of samples #6, 25 and 43-2. Chaferys used mineral fuel and were reheating hearths for consolidating iron once it had been refined. It is likely that a combination of finery and chafery were used to convert pig iron to malleable iron when

Raby initially started working iron in the 'ovoid mill' at Downside (23 on Figure 3). The copper foundry was a later addition in that structure however a large chafery-type smithing hearth may still have been required at the site. The presence of copper and tin in some of the slag suggests that it was contaminated by copper foundry waste whilst the slag was hot and that the chafery-type hearth was located near to the copper foundry and perhaps used for copper working on occasion as well. An additional route for contamination may be the use of metalworking waste to construct the muffle on chafery hearths, as described by Morton and Wingrove (1970), which would exacerbate the mixing of different types of waste. With so few samples of this type in the assemblage however, this identification remains speculative.



Figure 37: SEM image (back-scattered electron) of sample #8, showing a microstructure dominated by wüstite (light grey) with some fayalite (mid-grey)

This study has established that at some point puddling superseded the finery and chafery hearth technology for iron refining at Downside Mill, but the puddling hearth was probably constructed in the new mill further upstream.

### Mould

XRF analysis of the mould fragments detected traces of copper but these fragments were recovered from the wheel pit associated with the copper mill and this is likely to be postburial contamination. Other fragments were coated with iron oxides, which may also be a post-burial effect. However one fragment had a line of thicker residue around the rim, which proved to be made up of iron oxides, suggesting that the mould fragments were used in iron casting, rather than copper casting.

### Metals

#### Iron alloys

Three samples of iron were examined to determine their microstructure. One of these (#68) is a plain iron with little or no carbon but abundant slag inclusions (Figure 38). This microstructure is typical of wrought iron produced either in the finery/chafery furnace or a puddling furnace.



Figure 38: Optical microscope image of plain iron #68, showing grains of ferrite and slag inclusions



*Figure 39: Optical microscope image of sample #14, showing pearlite, grain-boundary cementite and corrosion* 

The other two samples (#14 and #66) both have a microstructure which is dominated by pearlite with cementite (Figure 39). This microstructure is typical of hypereutectoid steels (ie those with more than 0.8% carbon) but overlaps with some low-carbon cast irons. The chemical analysis of these samples shows that one contains more silicon and manganese, and the other more sulphur, than would be usual for steels of the late 18th century or early 19th century (Table 12). The chemical composition is consistent with the samples being white cast iron; that is cast iron in which all of the carbon is present as cementite rather than pearlite. The presence of white (rather than grey) cast iron at Downside may indicate that the cast iron was routinely refined, that is melted to remove the silicon, prior to conversion to wrought iron in the finery.

. ao.o	00					1
Sample C		Si	Р	S	Mn	
#I4 ~I.	5	0.5	0.3	<0.1	0.2	
#66 ~l.	4	0.1	0.2	0.6	<0.1	
#68 <0.		0.2	0.2	<0.1	<0.1	

Table 12: Chemical composition of the iron samples

# Copper alloys

The four samples of copper alloy analysed included two finished objects (#34 and #59) and two examples of casting waste (#5 and #58). The chemical composition of the samples shows the use of a variety of alloys including impure copper, gunmetal and brass (Table 13). The two impure copper samples share the same composition which includes minor amounts of arsenic. This composition appears to be typical for the late 18th century and early 19th century (Peter Northover personal communication). The zinc content of the brass sample is towards the upper limit that could be achieved using the cementation process (Dungworth and Wilkes 2010).

Sample S		Fe	Ni Cu		Zn	As	Sn	Pb			
#5 0.		0.2	0.1 77	.9	6.8	0.2	10.6	1.9			
#34 <0.I		<0.1	<0.19	7.3	<0.1	0.6	<0.3	<0.3			
#58 <0.I		<0.1	<0.19	7.2	<0.1	0.6	<0.3	<0.3			
#59 <0.	Ι	0.4	0.2 65	.5	30.6	0.3	0.5	0.8			

Table 13: Results as elemental wt% normalised to 100%.

### Glassy copper slag

The red glassy copper slag (#2) from Downside Mill is most likely to be foundry slag, from the melting and casting of copper alloys, such as bronze, in a reverberatory furnace. There was no clear archaeological or documentary evidence for copper smelting at Downside Mill. The copper slag comprised copper- and tin-rich droplets under 10 microns in size, in a glassy matrix (Figure 40, Table 14).

Table 14: Composition of glassy copper slag determined by SEM-EDS, results as compound wt% normalised to 100%

Sample Na	<sub>2</sub> O M	gO	Al₂O₃ Si	O <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO	TiO <sub>2</sub>	FeO CuO		SnO₂
#2 <0.1		0.5	5.7 56	.3	<0.3	<0.3	0.8	20.2	0.3	10.6 2.	1	2.6



Figure 40: SEM image (back-scattered electron detector) of glassy copper slag (#2) showing the metal-rich droplets (white) in a glassy matrix (grey) with occasional voids (black)

### Ceramic vessel

The ceramic vessel (#54) and its contents (#52-1 and #52-2) were analysed to identify the contents and the possible process(es) being carried out. However the maker's mark demonstrates that the vessel was produced at least half a century after the metallurgical phase at Downside Mill ended. The vessel, including its contents and any inferred process, cannot therefore be linked to the metallurgical activities of Alexander Raby.

The chemical composition of the ceramic vessel (sample #54) suggests that this was made from carefully selected raw materials to ensure that it was highly refractory: it contains low levels of alkalis and very low levels of iron (Table 17, cf Percy 1861, 214–215). The high ratio of aluminium to silicon (1:3) is appropriate for porcelain. The

dominant minerals detected in the ceramic vessel were quartz  $(SiO_2)$  and mullite, ideal for refractory applications (Martinón-Torres *et al* 2006), however high-temperature silica polymorphs, such as tridymite and cristobalite, were absent (Eramo 2005). This suggests that the vessel did not experience high temperatures for prolonged periods.

Table 17: Chemical composition of the vessel (#54) and its contents (#52-2) (average of 3 SEM-EDS analyses, normalised wt%)

					/								
Sample Na	20 M	lgO	Al2O3 Si	O2	P2O5 S	О 3	K₂O C	aO	TiO₂ N	1nO	FeO	ZnO	BaO
#52-2 0.	2	<0.1	3.0	1.2	0.5	<0.3	2.3	0.1	<0.1	78.0 0.	8	0.4	12.9
#54 I.	0	0.3	23.2	69.2	0.2	0.5	2.6	0.6	1.2	<0.1 0.	8	<0.1	< 0.3

Table 18: Mineral composition of the contents of the ceramic vessel (XRD)

Sample	Mineral phases detected
#52-1 PI	umbago (C)
#52-2 Pyro	lusite (MnO <sub>2</sub> ), Barium manganese oxide (BaMn <sub>8</sub> O <sub>16</sub> ), Quartz (SiO <sub>2</sub> )



Figure 41: SEM image (secondary electron) of plumbago (sample #52-1)

The contents of the vessel (sample #52) are made up of two different materials. Both are dark grey with lustrous fracture surfaces but one is softer and has a lower density than the other. The soft, low density material was designated #52-1 and the harder, higher density material #52-2. The XRD spectrum for sample #52-1 produced three very broad peaks corresponding to the main peaks for plumbago/graphite (C):  $2\theta = 26.5^{\circ}$ , 44.7° and 54.5°. The severe XRD peak broadening is likely to result from stacking faults typical of materials like graphite (Dittrich and Wohlfahrt-Mehrens 2001). The SEM examination of sample #52-1 showed 'artichoke-like globular structures' (Jaszczak 1995) typical of lump graphite of hydrothermal origin (Figure 41). The SEM-EDS analysis of #52-1 identified carbon with only traces of other elements (iron, sulphur, silicon and oxygen).



Figure 42: SEM image (back-scattered electron) of manganese mineral (sample #52-2).

XRD analysis confirmed that the other material in the vessel (#52-2, Figure 42) was a manganese ore (pyrolusite). The presence of a barium-bearing manganese mineral suggests that this ore may have originally been a psilomelane, a poorly defined mixture of manganese minerals of fairly wide occurrence (eg Cornwall, the Mendips, and the Lake District). If heated together to in excess of 1400°C the graphite would be capable of

reducing the manganese oxide into metallic manganese; this was the method employed by Grahn in 1774 for the isolation of the metal. However in this case, the crucible and its contents appear to have discarded without being heated. Further than this, it has not been possible to identify the origins of the vessel, but it post-dates Raby's metalworking ventures.

# Electrode

The rectangular artefacts (Figure 23) was analysed using EDXRF. This yielded very minor peaks for a range of minor elements (eg Si, Al, S, and Fe). The EDXRF Compton Scattering peak was very strong suggesting that the artefact is made from a material with a very low average atomic number. XRD analysis produced a spectrum with very no apparent peaks. It is most likely that this artefact is made of graphite. It is proposed that this artefact is an electrode.

# DISCUSSION

Documentary evidence shows that Downside Mill operated as a forge where cast iron was converted into malleable wrought iron. The limited duration of metallurgical activity (possibly as early as 1770 to 1810 at the latest) allows much of the recovered waste to be linked to the use of the mill during this period. The changes in iron manufacturing technology seen in the post-medieval period (bloomery to finery and then to puddling) constitute a technological revolution which had a profound impact on almost all other areas of industry and commerce. Evidence that helps better our understanding of this important period is of national importance.

The process developed by Cort, known as dry puddling, used a silica-rich furnace lining. The later wet puddling process used an iron-rich furnace lining. The nature of the furnace lining would have had a significant effect on the nature and quantity of the slag produced. It is also clear that the nature of the slag produced would vary depending on the type of pig iron employed. The composition of puddling slag may have varied between the beginning and the end of the process. The exact effect of all of these variables on the resulting slag is poorly understood.

# Puddling at Downside Mill

The most abundant debris from Downside Mill is a platy flowed fayalitic slag, which analysis has demonstrated was produced in a reverberatory furnace, lined with quartz-rich bricks, using an oxidising atmosphere, evidence that the dry puddling process was being used at Downside Mill at the end of the 18th or beginning of the 19th century. This is a fascinating result because the metalworking at Downside Mill coincides roughly with the period when puddling was invented by Henry Cort, and relatively little is known about how the technology spread. The puddling process was patented for fourteen years by Cort in 1783–4. Although Cort went bankrupt in 1789, the Crown confiscated his patent rights, which only expired in 1798 (Hayman 2005; Singer 1983). A license was taken to use the process by Crawshay in 1787 and he was successfully using puddling at Cyfarthfa in 1789. Documentary evidence suggests that in 1791 Crawshay developed the use of the running-out furnace to convert grey cast iron into white cast iron before it was charged into the puddling furnace. The first puddling furnaces in Shropshire are recorded in 1794 with the rapid adoption of puddling in South Staffordshire around 1800.

There are hints in contemporary accounts about connections between Raby and Cort. The Weale manuscript contains a transcript of a letter of 20th June 1812 from Alexander Raby to Henry Cort's son (Coningsby) which includes 'I was in the habit of intimacy with your father several years before he began his Puddling System' (Eric Alexander personal communication). Earlier in the 18th century, there is also reference to the purchase of barrel hoops by the Victualling Board who were supplied by a group of mill proprietors in the vicinity of London. These mill owners 'combined together at the time of tendering for the contracts, and a certain proportion of the whole quantity required being allotted to each contributor according to their private agreement'. This group may have included Raby and Cort and suggests closer collaboration, and perhaps sharing of technology, between the ironworkers in the area.

### Distribution of material

The vast majority of the waste recovered was from contexts [3] and [20], making up 37wt% each of the assemblage, and context [23] with 15wt% of the assemblage. Context [3] was a demolition layer in the southern part of the site of the original mill (the features labelled 22 and 23 in Figure 3) and context [23] was the fill of the southern mill-race. Context [20] was the fill of the wheel pit in the northern part of the site. All of these deposits are dumps of material and are largely made up of waste from dry puddling, including flowed fayalitic slag and hearth lining. Context [3], a widespread demolition layer in the area of the mill, also contains a large proportion of iron fragments and concretions and what has been interpreted as iron foundry slag. The large amounts of puddling waste recovered from this trench do not necessarily indicate that the activity took place at this mill; more probably puddling took place in the mill upstream added later. However the process may have generated a larger volume of waste than the others at the site, which then dominated the fill of the wheel pits when they ceased to be used.

The copper alloy fragments and glassy copper slag, from copper alloy casting, and the bubbly slag, which may derive from smithing, are from contexts [1] (the top soil), [4], [8] and [22] (probable later demolition layers and made ground). Context [22] contained the ceramic vessel and electrode, known to be of a later date and unconnected with Raby's use of the site.

# Slag microstructure

Many of the puddling slag samples had distinctive microstructures, where a finely dispersed silica-rich phase was present throughout the fayalite crystals or towards the edges of the crystals (Figure 43).



Figure 43: Back-scattered electron image showing the finely dispersed silicate phase (dark grey) dominated by potassium, aluminium and silicon oxides, in the fayalite (light grey) in sample #18

This microstructure was particularly common in samples that were richer in silica, for example samples from the interface between puddling slag and hearth lining (#21) or the samples interpreted as refining slags (#18 and #50) (Figure 43). Analysis of this phase was difficult, due to the small size of the features, but elevated levels of potassium, aluminium and silicon were noted relative to the fayalite, sometimes approaching the composition of leucite (KAISi<sub>2</sub>O<sub>6</sub>) even though there are only low levels of potassium and aluminium oxides in these slags. Immiscible silicate liquids form over quite a large range of silica-rich compositions in the system FeO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O-FeO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, etc. One explanation

for the microstructure observed in these slags is that two immiscible liquids formed at high temperatures. On cooling fayalite crystals precipitated from the liquid but tridymite did not and a silicate-rich phase persisted. The formation of immiscible silicate liquids would therefore result in the distinctive microstructures observed.

### Distinguishing waste from iron conversion processes

This study has once again demonstrated the difficulty of distinguishing waste from different processes at post-medieval industrial sites. Such sites are often large and complex, with multiple processes taking place in different areas and developing rapidly over time. Unlike earlier sites, where it is often possible to identify processes from the visual examination of the waste, scientific analysis is essential in order to attempt the categorisation of waste from later industrial complexes.

With iron conversion processes, the phases present in the slag are particularly diagnostic. X-ray diffraction analysis provides a rapid and relatively cheap way of identifying these phases. Typical XRD patterns for the different types of waste identified in this study are shown below for comparison (Figures 44–46).



Figure 44: XRD analysis of slag from dry puddling (sample #15): red lines indicate fayalite, blue lines indicate magnetite, green lines indicate quartz and turquoise lines indicate haematite



Figure 45: XRD pattern of slag probably from an iron foundry (sample #10); red lines indicate fayalite, green lines indicate iron sulphide and blue lines indicate spinel



Figure 46: XRD analysis of slag probably from smithing (sample #43b); blue lines indicate fayalite, green lines indicate magnetite, pink lines indicate wustite, red lines indicate quartz and grey lines indicate haematite

# CONCLUSIONS

The examination of the slag and other industrial residues from Downside Mill provides evidence that dry puddling was being used there at the end of the 18th century to convert cast iron into malleable iron. The most abundant type of waste at the site, a flowed fayalitic slag, derives from this process. These slags contain magnetite rather than the wüstite typical of bloomery smelting slags and smithing slags. Two slag fragments contained more manganese and silica, and lacked the distinctive flowed morphology of the majority of slag. These were tentatively identified as waste from a 'running out' refining hearth, used to refine cast iron prior to puddling. Evidence of the use of these processes at Cobham Mill at the end of the 18th century is significant since little is known about how quickly or widely dry puddling was adopted following Cort's patents in 1783 and 1784. Slag from an iron foundry, using a cupola furnace, was also recovered. All of these processes; iron casting, refining and puddling, probably took place in the upstream mill (labelled 17 and 18 in Figure 3) but the waste was dumped into the wheel pits of the 'ovoid mill' (23 in Figure 3).

A small amount of slag from copper alloy casting was found. Some frothy wüstite-rich slag, possibly from a large chafery-type smithing hearth, was also identified and in several instances this was mixed with waste from copper alloy casting, suggesting that some smithing activity took place near to the copper foundry in the 'ovoid mill' (23 in Figure 3).

Some of the material, including the ceramic vessel, the electrode and the aluminium fragment, post-date the metalworking activity at the site.

Each type of waste was extremely difficult to attribute to particular processes without using analytical equipment. XRD (X-ray diffraction) is recommended as the best initial technique to employ at sites of this kind, since the presence of particular phases is diagnostic of waste from different processes, and XRD analysis is cheap and fairly accessible.

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# APPENDIX 1: CATALOGUE OF ALL MATERIAL EXAMINED

[] Bag	Wt (g)	Туре	Interpretation	Description
	8	Copper glassy slag	Cu alloy casting	Very glassy slag. Banded in black and red layers.
12	125	Copper glassy slag	Cu alloy casting	Very dark, black glassy slag with some reddish colouration.
3	88	Flowed fayalitic slag	Puddling	All have flow textures.
4	17	Copper slag	Cu alloy casting	Irregular lumps of slag, green colouration from copper corrosion.
5	488	Copper alloy	Cu alloy casting	Hemisphere of copper alloy from a crucible or ladle + irregular copper alloy lump.
16	830	Copper slag	Cu alloy casting	Slag lumps. Some green corrosion products.
7	401	Flowed fayalitic slag	Puddling	Some with flow features very vitrified fayalitic slag lump.
2 30	68 I	ro n concretion		
231	33	Fuel and other vitrified		Cinder: very light and porous
		materials		
2 32	37	Iron concretion		Dense, orange and corroded
38	37	Small slag runs	Smithing	Small dribbles of slag. One side is flat.
39	170	Fuel and other vitrified	Coal.	
		materials		
3 10	1687	Dense fayalitic slag with	Iron foundry	Pool of slag with concreted hammerscale.
		iron concretion		
3	1776	Flowed fayalitic slag	Puddling	30mm thick plate of slag. Flat and smooth at base with a few undulations, ropey texture on surface,
				like tap slag. Very dense. More than one flow
3 1 2	1931	Hearth lining		Vitrified furnace lining. Approx 60mm thick. Underside very sandy and dark grey ceramic. One side is
				vitrified.
3   3	2280	Flowed fayalitic slag	Puddling	Very dense slag. Smooth underside, 35–40mm thick. Some ropey flow textures at topside.
3 1 4	3093	Iron concretion		Large very dense mass containing iron.
3 15	727	Flowed fayalitic slag	Puddling	Irregular underside but topside with ropey flow features. Tap slag. Very dense. 40–50mm thick.
3 16	483	Clinkery fayalitic slag	Iron foundry	Low density clinkery slag with coal inclusions. Very porous.
3 17	4	r on concretion		
3 18	102	Atypical fayalitic slag	Puddling / Running	No flow features but one surface flat, the opposite surface curved.
			out	
3 19	348	Hearth lining		Red ceramic furnace lining with adhering slag. 60mm thick.
3 20	64	Flowed fayalitic slag	Puddling	Dense slag flow, smooth top side, underside with undulations.
321	2298	Hearth lining		25-30mm of red ceramic floor/wall. 35mm thickness of slag adhering.

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[] Bag	Wt (g)	Туре	Interpretation	Description
3 22	30	Flowed fayalitic slag	Puddling	Dense piece of dark black slag
3 23	204	Flowed fayalitic slag	Puddling	Less dense undiagnostic slag. Some flow textures
3 24	550	Hearth lining		Vitrified furnace lining, some red clay/brick visible, maybe some slag on inside surface.
3 25	817	Bubbly fayalitic slag	Smithing	Some flow on top surface. Very porous
3 26	498	Iron concretion		Some possible hammer scale embedded in plano-convex shaped iron concretion.
3 27	1213	Hearth lining		Vitrified furnace floor, slightly curved. Underside has a red brick, 30mm thick
4 28	326	Bubbly fayalitic slag	Smithing	Porous ironworking slag
4 29	19	Iron		Corroded pieces of iron from an iron object. Maybe a large nail?
4 29-2	3	Other metal		Possibly aluminium sheet – intrusive
6 33	348	Flowed fayalitic slag	Puddling	Black dense
8 34	19	Copper alloy		Copper rod, green corrosion, 110mm long, 50mm wide.
8 35	75	Copper alloy	Cu alloy casting	Copper alloy dross, corroded copper metal.
8 36	56	Fuel and other vitrified materials		Clinker: dark, brittle, low density, porous.
8 37	115	Flowed fayalitic slag	Puddling	Flowed plate, grey slag. Very dense.
8 38	20	Flowed fayalitic slag	Puddling	Flowed fayalitic slag with flow features,
8 39	544 I	r on concretion		
8 40	101	Fuel and other vitrified materials		
841	210	Iron concretion		Conglomerate of material including corroded iron and some hammerscale
8 42	254	Hearth lining		Furnace hearth lining, 60mm thick. Not very vitrified, greyish glaze on inside surface approx 1mm thick.
8 43a	2	Fayalitic runs	Iron foundry	Small run of fayalitic slag.
8 43b	308	Bubbly fayalitic slag	Smithing	Porous fayalitic slag, some charcoal inclusions.
9 44	26	Flowed fayalitic slag	Puddling	
9 45	64	Iron concretion		Corroded conglomerate with some possible hammerscale embedded.
9 46		Fuel and other vitrified materials		Small burnt fragment of wood
20 47	187	Mould	Iron casting	Clay/loam mould fragments, hardened but not fully fired, grey fabric. One does show increased
			-	heating to the inside surface compared to the outside
20 48	56	Iron		Fragment of circular iron artefact with a raised rim. Very corroded.

[] Bag	Wt (g) Type	Interpretation	Description
20 49	88 Copper related slag	Iron casting	Copper alloy 'dross': slightly porous irregular slag like stony material with green corrosion
20 50	444 Atypical fayalitic slag	Puddling / running	Dense slag plate, smooth sides, 30mm thick
		out	
20 5 1	1797 Flowed fayalitic slag	Puddling	Tap slag, one piece with ropey texture.
20 61	15712 Flowed fayalitic slag	Puddling	
22 52	160 Cerami c vessel		
22 53	254 Cerami c vessel		
22 54	116 Cerami c vessel		
22 55	72 Graphite electrode?		Rectangular plate 155 $ imes$ 38 $ imes$ 8mm. 2 oval holes, 4mm across, and a v shaped notch at one end.
22 56	74 Fuel		Coal
22 57	19 Iro n concretion		Corroded mass with embedded coal.
22 58	252 Copper alloy	Cu alloy casting	
22 59	13 Copper alloy	Cu alloy casting	L-shaped strip of Cu alloy 80mm long, 5mm wide, 1mm thick.
22 60	9 Runs of fayalitic slag	Smithing?	Slag runs
23 62	126 M ould	Iron casting	
23 63	426 Fuel and other vitrified materials		
23 64	21 Fuel and other vitrified materials	Clinker	
23 65	53 Flowed fayalitic slag	Puddling	Flowed slag.
23 66	632 Iron concretion		Orange, corroded conglomerate with attached hammerscale.
23 67	6261 Hearth lining		Large fragment (330 $\times$ 220 $\times$ 100mm) of hearth/furnace lining. Vitrified surface. Back closely fitting, oxidised-fired brick (end on 55 $\times$ 100mm).
24 68	21 Iron		Iron object 70mm long, 10–20mm wide and 5mm deep.
26 69	4 Coppe r alloy		,
35 70	70 Hearth lining		Vitrified furnace lining
35 71	I5 M ould		-

# APPENDIX 2: SEM-EDS ANALYTICAL DATA

SEM-EDS analysis of reference materials compared to known values, calculated as wt% oxides. All results are normalised to 100%

W25R Na	<sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	$P_2O_5$	K₂O	CaO	TiO₂	MnO	FeO			
Average of 3	1.4	0.4	8.4	23.6	0.2	1.2	1.6	0.3	3.3	59.5			
Known O.	61	0.38	7.14	24.7	0.26	1.02	1.42	0.32	3.01	57.1			
Relative % diff	128	2.63	17.9	4.3	7.7	14.7	10.6	6.25	11.0	4.2			
CIK Cast Iron	Si	Р	S	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu		
Average of 3	1.2	bd	0.1	bd	0.1	0.2	0.3	1.4	95.9	0.6	0.2		
Known I.	14	0.11	0.08	0.01	0.07	0.13	0.28	1.22		0.59	0.23		
Relative % diff	2.63		12.5		28.6	30.8	3.57	13.9		1.69	13		
BIO AI		Si	Р	S	Mn	Fe	Ni	Cu	Zn	As	Sn	Sb	Pb
Average of 3	0.3	0.2	bd	bd		0.2	1.1	83.8	2.5	0.0	8.4	1.3	2.8
Known O.	22		0.01	0.05		0.17	1.01	83.6	2.77	0.01	7	1.14	4.07
Relative % diff	31.8					17.6	10.9	0.25	9.03	433	20.6	12.3	31
B22 AI		Si	Р	S	Mn	Fe	Ni	Cu	Zn	As	Sn	Sb	Pb
Average of 3	0.4	0.3	0.2	0.1	0.2	0.1	0.2	83.6	4,	0.1	0.4	0.1	0.4
Known O.	21	0.15	0.14	0.14	0.15	0.1	0.18	83.4	14.6	0.14	0.19	0.14	0.15
Relative % diff	88.4	127	35.7	3.7	36.1	12.2	11.7	0.25	3.29	55.9	131	26.5	188

Sample Na	20 M	gO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO₃	K₂O CaO		TiO <sub>2</sub>	MnO	FeO
	0.2 0.	21.	2	30.7	0.4	<0.3	0.3 0.	2	<0.1	<0.1	66.6
	0.2 <0.	I	1.2	30.7	0.3	0.4	0.4 0.	2	<0.1	<0.1	66.5
	<0.1 <0.1		1.3	30.6	0.3	< 0.3	0.3 <0.	I	<0.1	<0.1	66.8
	0.2 0.	21.	3	30.8	0.3	< 0.3	0.3 0.	I	<0.1	<0.1	66.0
15	<0.1 <0.1		1.4	31.3	< 0.3	< 0.3	0.3 0.	I	<0.1	<0.1	66.0
15	<0.1 <0.1		1.1	30.3	< 0.3	< 0.3	0.3 0.	2	<0.1	<0.1	67.2
	<0.1 <0.1		1.1	30.5	< 0.3	< 0.3	0.3 0.	Ι	<0.1	<0.1	67.5
	0.2 0.	ΙΙ.		30.3	< 0.3	< 0.3	0.3 <0.	I	<0.1	<0.1	67.1
	<0.1 <0.1		1.3	32.9	0.3	< 0.3	0.3 0.	2	<0.1	<0.1	64.8
	<0.1 <0.1		1.3	32.0	0.4	< 0.3	0.4 0.	Ι	<0.1	<0.1	65.I
	0.1 0.	22.	7	39.6	0.3	<0.3	0.5 1.	2	<0.1	0.1	55.0
	0.1	<0.1	2.0	44.5	<0.3	<0.3	0.3 0.	4	<0.1	<0.1	51.9
	0.1	<0.1	2.9	23.9	<0.3	<0.3	0.3 0.	6	0.2	<0.1	71.4
21	0.1	<0.1	3.5	24.0	<0.3	<0.3	0.3 0.	6	0.3	<0.1	70.0
	0.4 0.	23.	0	20.4	<0.3	<0.3	0.3 0.	5	0.2	<0.1	74.4
	<0.1 0.	2 2.	8	22.9	0.3	<0.3	0.3 0.	5	0.1	<0.1	72.3
	0.2 0.	ΙΙ.	7	29.6	< 0.3	<0.3	0.2 0.	3	0.1	<0.1	67.3
	0.1 0.	21.	4	29.4	0.4	0.5	0.4 0.	3	<0.1	<0.1	67.3
27	0.2 <0.	I	1.6	30.7	0.5	0.5	0.5 0.	3	<0.1	<0.1	65.7
37	0.2 <0.	I	1.3	28.8	0.5	0.4	0.4 0.	I	<0.1	<0.1	68.2
	0.3 <0.	I	1.1	29.4	0.4	0.2	0.3 0.	Ι	<0.1	<0.1	68.2
	0.2 <0.	I	1.3	27.6	0.6	0.8	0.4 0.	4	<0.1	<0.1	68.5
	0.3 <0.	I	1.5	28.0	0.7	0.8	0.4 0.	4	<0.1	<0.1	68.0
11	0.1 0.	.	3	25.7	0.7	1.0	0.4 0.	3	<0.1	<0.1	69.9
	0.3 0.	Η.	3	27.2	0.6	1.1	0.4 0.	3	<0.1	<0.1	68.9
	0.3 <0.	I	1.7	27.5	0.7	1.5	0.5 0.	4	<0.1	<0.1	67.6

Flowed fayalitic slags from dry puddling (normalised wt% oxides)

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Sample Na	₂O M	gO	$Al_2O_3$	SiO2	$P_2O_5$	SO₃	K <sub>2</sub> O CaO		TiO₂	MnO	FeO
	0.2 <0.		1.6	42.2	0.9	0.5	0.3 0.	3	0.5	5.2	47.6
	<0.1 0.	Ι2.	0	46.0	1.0	0.6	0.4 0.	3	0.6	5.0	43.4
18	<0.1 0.	Η.	5	39.0	0.9	0.4	0.3 0.	3	0.7	5.6	50.7
	0.2 <0.		1.5	38.6	0.9	0.3	0.3 0.	3	0.7	5.5	51.0
	<0.1 0.	.	6	38.9	0.1	0.3	0.3 0.	3	0.6	5.7	50.9
	0.2 <0.	I	1.9	41.1	0.7	0.3	0.6 0.	2	0.4	3.3	51.4
50	<0.1 <0.1		1.8	43.0	0.7	0.4	0.6 0.	2	0.4	3.3	49.5
30	0.1 <0.		1.9	42.9	0.7	0.4	0.6 0.	3	0.4	3.4	49.2
	<0.1 0.	21.	9	42.8	0.8	< 0.3	0.6 0.	3	0.4	3.2	49.5

Atypical fayalitic slags probably from a running out furnace (normalised wt% oxides)

Dense fayalitic slags, probably from an iron foundry (normalised wt% oxides)

Sample Na	<sub>2</sub> O M	gO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO₃	K <sub>2</sub> O CaO		TiO <sub>2</sub>	MnO	FeO
	0.2 0.	5	11.9	32.5	1.3	3.3	1.3 3.	5	0.5	0.8	44.3
	0.2 0.	7	12.5	33.4	1.4	3.1	1.2 3.	6	0.5	0.8	42.6
10	0.3 0.	7	12.2	33.6	1.3	2.9	1.2 3.	6	0.5	0.9	43.0
10	0.5 0.	7	12.1	33.8	1.2	2.9	1.2 3.	6	0.5	0.9	42.7
	0.4 0.	7	11.7	33.5	1.1	2.9	1.2 3.	4	0.5	0.9	43.7
	0.4 0.	5	10.8	30.8	1.3	3.5	1.1 3.	Ι	0.5	0.8	47.3
	0.1 0.	6 9.	6	24.3	0.8	3.1	0.6 2.	4	0.5	0.4	57.5
	0.2 0.	7	10.3	28.2	1.2	1.9	0.4 1.	5	0.6	0.4	54.7
43-1	0.3 0.	6	10.2	26.8	0.9	2.9	0.6 2.	2	0.5	0.4	54.7
	0.2 0.	69.	2	24.2	0.9	3.2	0.8 2.	4	0.4	0.4	57.8
	0.3 0.	79.	4	24.0	0.9	3.4	0.6 2.	4	0.3	0.3	57.8

Hearth linings, from dry puddling (normalised wt% oxides)

Sample Na	₂O M	gO	$Al_2O_3$	SiO <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO TiO	2	MnO	FeO
	0.1 0.	2	4.5	89.6	< 0.3	< 0.3	0.7	0.5 0.	4	<0,1	3.8
	0.1 0.	2	4.9	87.1	< 0.3	< 0.3	0.9	0.5 0.	3	<0.1	5.6
	<0.1	0.3 5.	3	85.7	< 0.3	< 0.3	0.9	0.5 0.	5	<0,1	6.8
	<0.1	0.3 5.	2	89.4	< 0.3	< 0.3	0.1	0.4 0.	5	<0,1	2.5
67	<0.1	0.4 4.	9	89.7	< 0.3	< 0.3	1.0	0.4 0.	2	<0,1	2.8
	<0.1	0.4 4.	9	89.0	< 0.3	< 0.3	0.9	0.3 0.	5	<0.1	2.7
	<0.1 0.	3	4.7	90.4	< 0.3	< 0.3	0.8	0.4 0.	4	<0.1	2.2
	0.1 0.	4	4.5	90.3	< 0.3	< 0.3	0.8	0.4 0.	4	<0.1	2.3
	<0.1	0.4 6.	2	89.3	<0.3	<0.3	0.8	0.5 0.	5	<0.1	1.9
	<0.1	0.1 5.	7	57.9	< 0.3	0.6	0.6	1.0 0.	4	2.2	31.6
	0.1 0.	2	5.7	60.2	< 0.3	0.6	0.6	0.9 0.	4	1.9	28.8
	0.1 0.	I	4.0	74.9	< 0.3	0.6	0.5	0.5 0.	4	1.7	16.8
	<0.1 <0.1		4.1	74.8	< 0.3	0.5	0.5	0.6 0.	5	2.5	16.6
	0.2 0.	2	3.3	78.2	< 0.3	0.5	0.6	0.5 0.	3	2.2	14.2
	0.1 <0.	I	2.7	82.0	< 0.3	0.3	0.4	0.5 0.	3	1.9	11.7
	<0.1 0.	2	2.7	82.3	< 0.3	< 0.3	0.5	0.6 0.	3	1.8	10.9
70	0.1 0.	I	3.1	81.7	< 0.3	0.3	0.5	0.7 0.	4	1.7	11.4
	<0.1 0.	I	4.0	80.1	< 0.3	0.3	0.7	0.8 0.	4	1.5	12.2
	0.1 0.	2	5.2	83.3	< 0.3	< 0.3	1.5	0.7 0.	2	0.7	7.7
	<0.1	0.2 5.	2	82.0	< 0.3	< 0.3	1.5	0.8 0.	4	0.8	8.6
	<0.1	0.2 5.	0	80.8	< 0.3	< 0.3	1.3	0.8 0.	3	1.0	10.4
	0.1 0.	2	4.6	80.4	< 0.3	< 0.3	1.1	0.9 0.	3	0.9	0.11
	0.3 0.	2	4.0	81.7	< 0.3	< 0.3	0.9	0.7 0.	3	0.8	10.3
	<0.1 0.	2	3.3	85.I	<0.3	<0.3	0.8	0.6 0.	2	0.7	8.7
210.	I	0.1	2.4	79.8	<0.3	<0.3	0.3	0.6 0.	2	<0.1	16.5

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Sample Na	20 M	gO	$Al_2O_3$	SiO2	$P_2O_5$	SO3	K₂O CaO		TiO₂	MnO	FeO	CuO
	<0.1 <0.1		0.2	8.8	0.6	< 0.3	<0.1 0.1		<0,1	<0.1	90.1	<0,1
0	<0.1 <0.1		0.2	9.3	0.6	< 0.3	<0.1 0.1		<0.1	<0.1	89.4	<0.1
0	0.1 <0.		0.2	8.3	0.6	< 0.3	<0.1 0.1		<0.1	<0.1	90.4	<0.1
	0.2 <0.	I	0.2	8.4	0.6	<0.3	<0.1 0.1		<0.1	<0.1	90.3	<0.1
	040	3.0	6	10.6	2.1	<0.3	0.2.2	0	<0.1	1.7	81.9	<0.1
25	<0.1 0.	4 0.	3	8.7	1.5	< 0.3	<0.1 0.6	Ū	<0.1	1.5	86.7	<0.1
	0.1 <0.	Ι	0.3	9.1	1.6	<0.3	0.2 0.	8	<0.1	1.6	86.1	<0.1
	0.3 1.	5	21.8	43.9	<0.3	0.5	1.9 15	.2	0.8	0.2	13.1	0.2
6 (slag)	0.3 0.	9	22.0	40.8	< 0.3	0.3	1.6 14	.8	0.7	0.2	17.4	0.5
	0.2 0.	9	22.4	40.0	< 0.3	<0.3	1.8 12	.7	0.7	<0.1	19.3	0.8
6 (au'z-	0.1 0.	2.	2	45.0	0.4	0.5	0.4 0.	2	0.1	<0.1	48.2	2.2
area)	<0.1 0.	3 3.		57.9	0.3	0.4	0.5 1.	5	0.2	<0.1	34.5	0.8

Bubbly slag (#25 and #6) and slag runs (#8), probably from iron smithing, in #6 contaminated by copper casting waste (normalised wt% oxides)

Sample	Fe Ni		Cu	Zn	As	Sn	Pb
5	0.2 <0.		79.5	6.6	0.4	.	2.2
J	0.2 0.	I	79.5	7.2	0.2	10.8	1.9
	<0.1 <0.1		99.5	<0.1	0.5	<0.3	< 0.3
34	<0.1 <0.1		99.2	<0.1	0.5	<0.3	< 0.3
	<0.1 <0.1		99.3	<0.1	0.7	<0.3	< 0.3
	<0.1	<0.1	99.2	<0.1	0.8	<0.3	< 0.3
EO	<0.1	<0.1	99.6	<0.1	0.4	<0.3	< 0.3
20	<0.1	0.1 99	.3	<0.1	0.6	<0.3	< 0.3
	<0.1 <0.1		99.4	<0.1	0.6	<0.3	< 0.3
59	0.4 0.	2	66.5	31.0	0.2	0.5	1.1
57	0.5 0.	2	66.7	31.2	0.3	0.5	0.7
	0.4 0.	2	66.5	31.1	0.4	0.5	0.7

Copper alloys (normalised element %)

Sample	Si P		S	Mn	Fe
	0.3 <0.	2 <0.	3	0.3	99.6
14	0.3 0.	2	< 0.3	0.3	99.5
	0.3 0.	2	<0.3	0.3	99.5
( (	<0.1 <0.2		0.4	<0.1	99.4
66	0.2 0.	2 0.	6	0.2	99.1
	0.3 <0.	2 <0.	3	<0.1	99.6
68	0.3 0.	2	< 0.3	<0.1	99.4
	0.3 0.	2	< 0.3	<0.1	99.4

Iron alloys (normalised element wt%, not including carbon)

Copper slag (#2) (normalised wt% oxides)

Na <sub>2</sub> O	MgO A	l₂O₃ Si	O <sub>2</sub>	$P_2O_5$	SO₃	K₂O	CaO	TiO <sub>2</sub> MnO		FeO	CuO	SnO₂	PbO
<0.1	0.6 5.	6	55.2	< 0.3	<0.3	0.8	19.7	0.3 < 0.		10.5	4.2	2.7	0.2
<0.1	0.5 5.	7	55.4	< 0.3	< 0.3	0.8	19.7	0.2 <0.	1	10.3	4.0	2.5	<0.2
0.2	0.6 5.	6	54.8	< 0.3	< 0.3	0.8	19.6	0.3 < 0.		10.5	4.2	2.7	<0.2
0.1	0.5 5.	6	55.0	< 0.3	<0.3	0.8	19.8	0.3 <0.	I	10.5	4.2	2.6	0.3

Ceramic vessel (#54) (normalised wt% oxides)

Na <sub>2</sub> O	MgO A	$I_2O_3$ Si	O <sub>2</sub>	$P_2O_5$	SO₃	CI	K₂O	CaO TiO	2	MnO	FeO
1.3	0.3 23	.1	68.5	0.2	0.8	<0.1	2.6	0.6 1.	3	<0.1	0.9
1.4	0.2 23	.4	68.6	0.2	0.7	0.1	2.6	0.6 1.	3	<0,1	0.8
0.1	0.4 23	.8	68.5	0.2	0.4	<0.1	2.7	0.7 I.	2	<0,1	0.8
0.4	0.3 22	.4	71.1	0.2	0.2	0.1	2.5	0.4 I.	2	<0.1	0.8

Contents of ceramic vessel (#53) (normalised wt% oxides)

Na <sub>2</sub> O	MgO A	l₂O₃ Si	O <sub>2</sub>	$P_2O_5$	SO3	K₂O	CaO	TiO₂	MnO	FeO	ZnO	BaO
0.2	<0.12.	2	0.1	0.5	<0.3	1.4	0.1	<0.1	79.6	0.4	0.2	15.1
0.3	0.1 4.	2	3.2	0.6	<0.3	2.3	0.1	1.0	73.2	1.3	0.4	12.8
0.1	<0.1 2.	7	0.3	0.5	< 0.3	3.1	0.1	<0.1	81.2	0.5	0.5	10.8



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