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Archaeometallurgical residues from
the M74 Completion, Glasgow

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Archaeometallurgical residues and associated materials from the M74 Completion, Glasgow

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Abstract

The archaeometallurgical materials sampled from the three sites of the Govan Ironworks Foundry (WP5), The Caledonia Foundry/Scotland Street Engine Works (WP3-LP4) and the Dundas Street Foundry (WP3-LP3) provide an insight into both the ferrous and non-ferrous foundry industries, together with their supporting activities.

Materials sampled include slags from within the flues of a brass foundry, slags from cupola and reverberatory furnaces for melting iron, slags from blast furnaces for smelting iron, possible slags from puddling furnaces for converting pig iron to wrought iron, hammerscale from the forging of hot iron, microscopic spatter from the iron foundry, together with samples containing the ferrous and non-ferrous materials themselves. Many of the materials are representatives of classes of residues that have rarely, if ever, been examined analytically before. Some identifications of material must remain tentative, therefore.

For the Dundas Street Foundry (WP3-LP3), only highly zinc-rich slags, probably formed within the flues of the foundry, were recovered. Such materials have not been described from archaeological sites before, but provide little evidence for the processes and materials employed.

The activities of the Newton, Bennie & Co. Caledonia Foundry (northern part of WP3-LP4, Phase 2, c.1835 - c.1867) are evidenced by significant deposits of slag from cupola furnaces. These show castings were produced in mainly high phosphorus grey cast iron and that the cupola charges did not generally include flux. Both these features suggest that castings may have been typically small and possibly intricate. Backfill of pits in the floor of the moulding shop contained residues from smithing, but it is unclear if this indicates an activity of the original Caledonia Foundry, or activity in the former moulding shop after foundry work was abandoned in 1867, or indeed whether waste from other areas of the Scotland Street Works was imported for levelling purposes during the structural alterations between Phases 2 and 3 with the rebuild associated with the incorporation of this area into the Engine Works.

The contemporary early phase of the McOnie Engine Works (southern part of WP3-LP4, Phase 2, c.1841-c.1879) was not particularly well seen in the excavations and few metallurgical residues were recovered.

With the expansion of the McOnie Scotland Street Engine Works (WP3-LP4, Phase 3, c.1879-c.1930) the focus of activity on the site switched to finishing processes, such as turning and grinding, with evidence mainly in the form of swarf. A small foundry facility for the production of gunmetal castings was built at the northern end of the works. It is likely that many of the residues examined from this works relate to the final years of operation of the works.

At the Govan Ironworks Foundry (WP5), probably the most volumetrically significant residue assemblage is the large quantity of waste from other parts of the ironworks (particularly the blast furnaces) employed to level the site prior to construction of the foundry in the 1840s. The blast furnace slags of significance for they date from the earliest years of the adoption of hot blast techniques. Although truncation had removed most floor levels, some residues from site usage occurred in the moulding shop (both cupola and reverberatory furnace slag together with microresidues), the boiler shop and smithy (smithing slags and microresidues), the turning shop (turning and grinding wastes) and 'structure 14' (thick hammerscale).

Contents

Abstract	1
Methods	3
Results	
<i>Description of analysed samples</i>	
WP3-LP3: Dundas Street Foundry	4
WP3-LP4: Caledonia Foundry/ Scotland St. Engine Works	4
WP5: Govan Ironworks Foundry	8
<i>Description of the residue classes</i>	
Iron	16
Iron-rich slag	16
<i>Slag from reverberatory furnace leak</i>	16
<i>Dense granular iron oxide slag</i>	16
<i>Flowed-lobed dense slags</i>	17
Iron-poor slags	17
<i>Caledonia Foundry</i>	17
<i>Govan Ironworks Foundry</i>	18
Clinker and smithing slag	19
Microresidues	19
<i>Spheroidal particles</i>	20
<i>Tabular particles</i>	20
Grinding and turning waste	21
Brass Foundry Slags	22
Copper alloys	22
Discussion by site	
WP3-LP3: Dundas Street Brass	22
WP3-LP4: Caledonia Foundry/ Scotland St. Engine Works	22
WP5: Govan Ironworks Foundry	22
References	24
Figure Captions	25
Tables	
Table 1: Samples investigated from WP3	28
Table 2: Samples Investigated from WP5	29
Figures	30

Appendices

Appendix A: Backscattered Electron Photomicrographs and EDS microanalyses

Key to Plates A1-A92	A1
Plates A1-A92	A11
Table A1. EDS analyses from WP3-LP3	A103
Table A2. EDS analyses from WP3-LP3	A106
Table A3. EDS analyses from WP3-LP3	A122

Appendix B: Whole sample chemical analyses

Table B1: WP3, major elements by XRF	B2
Table B2: WP5, major elements by XRF	B3
Table B3: WP3, major elements by ICP-MS	B4
Table B4: WP5, major elements by ICP-MS	B5
Table B5: WP3, trace elements, by ICP-MS	B6
Table B6: WP5, trace elements by ICP-MS	B7
Table B7: table B5 continued	B8
Table B8: table B6 continued	B9

Appendix C: Optical Metallography

Key to Archive Plates C1-C7	C1
Plates C1-C7	C2

Methods

All materials were examined visually with a low powered binocular microscope as part of the evaluations (Young 2008a, b and c). The evaluations identified the assemblages as containing materials associated with brass production or casting (WP3-LP3), non-ferrous casting (WP3-LP4), ferrous casting (WP3-LP4 and WP5), finishing of castings (WP5), machining (WP3-LP4) and ferrous forging (WP3-LP4 and WP5). In addition, materials included within the initial make-up deposits from WP5 provided apparent evidence for both primary iron smelting and iron refining (puddling); processes undertaken elsewhere at the Govan Ironworks, outside the excavated foundry. During analysis evidence was also found for non-ferrous casting and finishing at WP5.

From the materials examined for the evaluation reports, a selection of samples was taken forward for detailed analysis, including 6 samples from WP3-LP3, 28 samples from WP3-LP4 and 38 samples from WP5. The codes for specimens analysed were prefixed LP3 (for material from WP3-LP3), LP4 (for material from WP3-LP4) and GOV (for material from WP5). As results developed during the course of the project, so slight alterations were made to the priorities, and the investigation of some material types was pursued in more detail at the expense of that of others. Not all of the samples taken for analysis were thus actually analysed in full, whereas others were subdivided to allow more detailed investigation of various fractions or components (Tables 1-3). These 72 samples have generated 33 whole-sample chemical analyses, 1037 backscattered electron photomicrographs and 2228 energy-dispersive X-Ray microanalyses. These data are provided in full as an archive appendix to this report and in summary within the report.

The evaluation reports contained full details of samples of metallurgical interest and their stratigraphic provenance. The tables contained in those reports remain the primary source for the broader distribution of archaeometallurgical residues across the sites, and that detail is not repeated in this report. Detailed descriptions and interpretations of some of the materials will, however, be replaced by information in this report, following the detailed analysis.

Electron microscopy was undertaken on the LEO S360 analytical electron microscope in the School of Earth, Ocean and Planetary Sciences, Cardiff University. Microanalysis was undertaken using the system's Oxford Instruments INCA ENERGY energy-dispersive x-ray analysis system (EDX). All petrographic images presented in this report are backscattered electron photomicrographs. The polished blocks for investigation on the SEM were prepared in the Earth Science Department, The Open University. Chemical analysis was undertaken using two techniques. The major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P) were determined by X-Ray Fluorescence using fused beads, variously on the Open University Earth Science Department's Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) system (for samples from WP5) or on a similar instrument in the department of Geology, Leicester University (for samples from WP3; this also generated analyses for S, V, Cr, Sr, Zr, Ba, Ni, Cu, Zn, Pb and Hf). Whole-specimen chemical analysis for minor and trace elements was undertaken using samples in solution on the ThermoElemental X-series Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth, Ocean and Planetary Sciences, Cardiff University.

A limited programme of optical inspection of polished and etched metallographic samples of ferrous metals was undertaken by Eleanor Blakelock.

The convention adopted in this report is to describe crystalline phases by their mineral names, as is normally done in archaeometallurgy, despite those names being strictly defined only for the natural occurrences of those phases. Olivine bearing Fe, Mg, Ca and Mn is described in terms of an olivine on the forsterite-fayalite join (using the notation for instance of Fa95Fo5 for an olivine that is 95% fayalite and 5% forsterite; where $Fe/(Fe+Mg) = 0.95$) plus figures for the overall percentage replacement by calcium and manganese.

This project was undertaken for HAPCA, a consortium of Headland Archaeology and Pre-construct Archaeology.

Results

Description of analysed samples

WP3-LP3: Dundas Street Brass Foundry

LP3-01: (S5001) the slag has an initial phase of globular or tabular zincite (mostly less than 20µm) overgrown by willemite in a somewhat irregularly massive form. The matrix is a glass with a high calcium content and low levels of copper, iron and titanium. The matrix also bears euhedral grains of gahnitic spinel with franklinite rims. In the matrix the spinel is overgrown by hollow needles of willemite, but the massive willemite appears to overgrow, or be marginally intergrown with, gahnite. [Figure 20 a, Plate A1 a,b]

LP3-02: (S5001) the slag bears irregularly shaped equant grains of willemite (up to 150µm) and aggregates of equant willemite, bearing blebs and plates of zincite and small gahnite crystals, forming irregular masses of up to 1mm. Equant gahnite grains with franklinite rims up to 50µm occur widely in the glassy matrix and are followed by elongate prisms of willemite, often hollow, of up to 300µm in length. [Figure 20 c-d, Plate A1 c-e]

LP3-03: (S5010) this slag has an unusual finely crystalline texture with small (5µm) equant euhedral grains of spinels (with a composition ranging from aluminium-rich magnetite to magnesium-rich hercynite), forming irregular aggregates or as components of complex skeletal structures up to 150µm in length and 20µm across, with rarer discrete skeletal hercynite of up to 40µm. The compound structures can locally be seen to be long square cross-sectioned prisms. It seems likely that these structures are a reaction product after an uncertain primary mineral.

The groundmass to this unusual hercynite is finely crystalline (5-15µm) anorthite, of mainly rather equant habit, set in glass. The slag contains a moderate number of scattered vesicles of up to 100µm diameter as well as much larger vesicles. The large vesicles may show complex spinel-dominated rims. [Plate A1 f-h, Plate A2 a-c]

LP3-04: (S5010) this is a coarse-grained slag formed of large melilite crystals (laths?) of up to at least 500µm in length in a matrix either of glass, or of glass bearing Al-diopside dendrites. [figure 20 b, Plate A2 d-g]

LP3-05: (S5005) sand: chemical analysis only, no microscopy.

LP3-06: (S5006) sand: chemical analysis only, no microscopy.

WP3-LP4: Caledonia Foundry/Scotland St. Works

LP4-01: (C60422, S6002) a small prill of leaded gunmetal. The composition is approximately 79% Cu, 4.8% Zn, 11.7% Sn, and 3.4% Pb. The microstructure is coarsely dendritic, with a coarse-grained lead segregation. [Figure 21 a, Plate A3 a-e]

LP4-02: (C60422, S6002) a small prill of leaded gunmetal. The composition is approximately 82% Cu, 4.6% Zn, 10.4% Sn, and 2.6% Pb. The microstructure is coarsely dendritic, with a coarse-grained lead segregation. [Plate A3 f-g]

LP4-03: (C60422, S6002) a prill of leaded gunmetal. The composition is approximately 73% Cu, 4.2% Zn, 11.7% Sn, and 2.5% Pb, together with 6.5% of silica and alumina, possibly present as fuel ash (clinker) inclusions. The microstructure is coarsely dendritic, with a coarse-grained lead segregation. [Plate A3 h, Plate A4 a]

LP4-04: (C60422, S6002) a larger flow of leaded gunmetal. The composition is approximately 78% Cu, 4.4% Zn, 10.0% Sn, 0.4% Sb and 2.9% Pb. The microstructure is coarsely dendritic, with a much lower proportion of interdendritic material than the previous examples and with a coarse-grained lead segregation occupying much of the interdendritic area. [Plate A4 d]

LP4-05: (C60594, S6040) a grey cast iron particle taken from a large cupola slag block. Bulk EDS analysis gives a low total, with 84.0% Fe, 0.5%Mn, 1.3%P, 0.15%S and 0.9%Si. The iron bears large (up to 0.5mm) graphite flakes and smaller blebs, with a texture of rounded cells (containing at least some pearlite) surround by a steadite eutectic. [Figure 1 a-b, Plate A4 e-h, Plate A5 a]

LP4-06: (C60594, S6040) The sample (taken from a large cupola slag block) includes a 3mm diameter grey cast iron particle. Bulk EDS analysis gives a low total, with 81.0% Fe, 0.2%Mn, 0.9%P, 0.20%S and 1.0%Si. Inclusions of iron-manganese sulphide contain detectable levels of titanium (0.3%) chromium (0.2%) and vanadium (0.3%). The microstructure of this iron droplet is very similar to that of LP4-05, and suggests a carbon content of 2-3%. Away from the graphite flakes, the microstructure is dominantly pearlite+steadite, but it is unclear whether this local heterogeneity is significant

A much smaller grey cast iron droplet gave a broadly similar EDS analysis.

The grey iron particles are in a glassy slag which bears abundant quartz grains. Analyses give low totals (because of the carbon and porosity) but indicate 20% Si, 8% Al, 0.5%Mg, 0.8% K, 2.0% Ca, 6.0% Mn and 7.5% Fe (un-normalised wt%). [Figure 1 c-e, Plate A5 b-h, Plate C1]

LP4-07: (C60598, S6042) This sample contains a high-Si (approximately 3%) grey cast iron particle with 0.22% P and 0.48%Mn, set in a glassy slag with abundant tiny iron droplets and elongate crystals of

mullite. The iron shows a bimodal size distribution of the graphite, with both long coarse flakes and delicate clumps of fine dendritic growths; there is some steadite. The carbon content was estimated at 4%. [Figure 1f, Plate A6 a-f, Plate C2]

The subsample for chemical analysis was typical slag (without the large iron droplets).

LP4-08: (C60598, S6042) The sample is a grey glassy slag with abundant (and rather large) mullite needles and iron droplets. The iron shows a very variable Si content, with grains of high Si iron (3-10%) and one grain of ferrosilicon (up to 29% Si) 600µm in diameter. [Figure 4 g, Plate A6 g-h, Plate A7 a-b]

LP4-09: (C60599, S6043) Sample has iron bleb approximately 5mm across. The droplet is of grey cast iron with a high silicon content of 3.2%, 0.8% P and 0.3% Mn. The associated slag is glassy with long needles of mullite. [Plate A7 c-e]

LP4-10: (C60599, S6043) This isolated iron bleb, from the same samples as LP4-09, was heavily altered precluding meaningful analysis. However, the prominent development of steadite showed that it had been a high-P iron. [Figure 1h, Plate A7 f-h, Plate A8 a]

LP4-11: (C60262, S6015) dark brown glassy slag from large coke rich flow puddle. A small bleb shows the development of steadite, as well of iron sulphide inclusions. This iron has silicon below detection limits.

A second smaller bleb shows similar properties with high P (2.4%), low Si (below detection) and blebs of iron sulphide.

The slag containing the blebs is a simple glass, with 8-9% Mn, 26% Si, 7% Al, 2.3% Ca, 1.3% Ti, 0.5%Mg and 0.3% Na. The contrast between the high manganese content of the slag and the content below the EDS detection limits in the iron blebs (where even the iron sulphide inclusions contained less than 0.5% Mn) is remarkable. [Plate A8 b-d]

LP4-12: (C60262, S6015) The sample included a large grey cast iron droplet, which had a high silicon content (3.1%), 0.8% P, 0.3% S and 0.3% Mn. Some tiny droplets in the glassy matrix were of iron bearing up to 2% nickel and also with low amounts of copper (0.3%).

The slag was dominantly glass with elongate mullite crystals. In hand specimen it was a coke-rich white stony flow with a clinkery surface. The glass was aluminous (16% Al, 26% Si) with an elevated potassium content (1.4 -1.6%), but with only a low calcium content (0.9 - 1.4%). [Plate A8 e-h, Plate A9 a-b]

LP4-13: (C60537, S6021) A dark brown glassy slag, with a grey cast iron bleb, which had a bulk composition with 1.2-1.6% Si, 0.7-1.2% P, 0.2% S and 0.3% Mn. Some areas of the iron droplets gave EDS analyses with low, but just detectable, contents of nickel and copper. The grey cast iron is rich in cementite, with small quantities of pearlite and steadite. The carbon content was estimated at 3-4%.

The slag was a simple glass, with up to 8% calcium, 3.8% manganese, 1.4% magnesium, 7.3% aluminium, 23% silicon, 0.8% potassium, 0.9% titanium and 7.2% iron. [Plate A9 c-e, Plate C3]

LP4-14: (C60263, S6016) Sample from a pale, stony, slag ball surrounded by clinkery slag showed a variably vesicular glass with mullite needles of up to 1.5mm. Adjacent to larger vesicles were zones of dendrites of manganese- and aluminium-rich magnetite. In these areas the manganese content of the glass was also elevated (2.7%) as was the calcium content (2.5%). In the mullite-rich areas both the manganese and calcium contents of the glass were low (at 0.3 and 0.8% respectively). [Figure 4 h, Plate A9 f-h]

LP4-15: (C60573, S6035) This sample was of fine particles from the same deposit as LP4-16 and -17. The particles were mainly highly corroded fragments of grey cast iron with varying amounts of steadite, bound by secondary iron oxides.

There were a few small (<100µm) grains of leaded gunmetal (one of which gave a bulk composition by EDS of 79% Cu, 3.6% Zn, 4.6% Sn and 7.5% Pb. [Plate A10 a-h])

LP4-16: (C60573, S6035) This sample was of aggregated material from the same deposit as LP4-15 and -17. The particles were mainly highly corroded fragments of cast iron, bound by secondary iron oxides.

The particle of cast iron analysed in detail showed a very high Mn content (in the range of 0.7-1.0%) and manganese sulphides were abundant. The silicon content was between 0.4 and 0.7%. [Plate A11 a-g]

LP4-17: (C60573, S6035) A sample of large particles isolated from the same deposit as LP4-15 and -16. The material was very weathered but showed iron of a broadly similar composition to that in LP4-16. [Plate A11 h, Plate A12 a]

LP4-18: (C60344, S6006; fill of pit 60419 in casting floor) This sample was taken from a clinker-like slag with a morphology suggesting that it was a smithing slag. Although apparently glassy, much of the matrix included microcrystalline spinels and feldspars. Spinel, both Al-rich magnetite and Fe-rich hercynite occurred as phenocrysts within this groundmass. Voids in the slag were commonly filled by secondary iron oxides.

Bulk chemical analysis showed that the iron content was very modest (19.0wt% calculated as Fe₂O₃) indicating that this might be a simple clinker. [Figure 4 f, Plate A12 b-f]

LP4-19: (C60344, S6006; fill of pit 60419 in casting floor) this sample was not examined in detail. Its bulk chemical composition was almost identical to that of LP4-18, except for cobalt and nickel, both of which were elevated by a factor of two in this sample.

LP4-20: (C60592, S6037) medium swarf (6 pieces) from Structure 19 showed highly deformed iron of similar appearance to samples LP4-17. The

microstructure comprises pearlite and cementite in coarse bands. Analysis showed 0.3% Si and about 0.6% Mn. [Plate A12 g-h, Plate A13 a-d]

LP4-21: (C60592, S6044) medium-small swarf (6 pieces) from Structure 19 showed highly deformed microstructures. The microstructure comprises pearlite and cementite in coarse bands. Analyses suggested 0.3-0.45% Si and 0.6-1.0% Mn. [Plate A13 e-h, Plate A14 a, Plate C4]

LP4-22: (C60993, S6087) very large swarf fragments from Structure 2 showed, as expected, high degrees of deformation. The iron showed about 0.5% Mn, present largely as sulphides. The texture was of cementite plus pearlite, lacking the banded structure seen in LP4-20 and -21. One area showed a casting line with inclusions. The inclusions did not produce high quality analyses, but were of oldhamite (calcium sulphide) with an appreciable sodium content.

Analyses of the bulk iron showed 0.5-0.6% Mn with other elements below detection. [Plate A14 b-f, Plate C5]

LP4-23: (C60344, S6006; fill of pit 60419 in casting floor) This sample was a mount of particles provisionally identified as being clinker. It was from the same context (60344) as LP4-18, LP4-19, LP-24 and LP4-25. 5 particles were examined:

P1: (SOI 3, 4) 2300µm spheroidal bleb of glass, containing mullite. Low iron (8 wt% Fe), with 23 wt% Si, 20wt% Al, 2wt% Ca and 0.6wt% K. [Plate A14 g-h]

P2: (SOI 5, 6, 7) 7mm x 1.8mm, elongate piece of fuel residue with melt on one surface. Slag contains spinels (including pleonaste and Al-magnetite) in glass. [Plate A15 a-c]

P3: (SOI 8, 9) 7mm x 5mm, fragment of curved slag with higher iron content (40-52% Fe) than the other particles. Also more siliceous (Si at 8-10% and Al at 4-5%). Calcium and potassium both low at around 0.6%. [Plate A15 d-e]

P4: (SOI 10, 11) Two fused hollow blebs, each c. 2500µm diameter, of melt with a low iron content (13% Fe). Mineral assemblage includes corundum, mullite and Al-magnetite. Calcium and potassium both moderate at around 1.9-2.0%. [Plate A15 f-g]

P5: (SOI 12, 13, 14) Irregularly-shaped particle, 6mm x 3mm, with very similar chemical composition to P4. Minerals include mullite and Al-magnetite in glass. [Plate A15 h, Plate A16 a-b]

LP4-24: (C60344, S6006; fill of pit 60419 in casting floor) This sample was a mount of particles provisionally identified as being flake hammerscale. It was from the same context (60344) as LP4-18, LP4-19, LP-23 and LP4-25. 15 particles were examined:

P1: (SOI 2, 3) very irregular largely melted flake hammerscale, to 250µm, slaggy and void-rich. [Plate A16 d-e]

P2: (SOI 4, 5) thin simple flake hammerscale, to 80µm, wustite with magnetite plates. [Plate A16 f-g]

P3: (SOI 6, 7) complex degraded plate-rich flake hammerscale, c. 400µm thick, void-rich. [Plate A16 h, Plate A17 a]

P4: (SOI 8, 9) Very irregular flake hammerscale, similar to particle 1, c. 250µm thick. [Plate A17 b-c]

P5: (SOI 10, 11, 12) Flake hammerscale with rounded wustite, slag-rich, no plates. [Plate A17 d-e]

P6: (SOI 13) Conventional oxide flake hammerscale, to about 150µm. [Plate A17 f]

P7: (SOI 14, 15) irregular flake hammerscale, to 200µm, plate rich outer, slaggy inner. [Plate A17 g-h]

P8: (SOI 16, 17) conventional flake hammerscale, if somewhat irregular, to 250µm. [Plate A18 a-b]

P9: (SOI 18-24) very irregular flake hammerscale, densest in core, slaggy inner part, many plates and voids, to 350µm. [Plate A18 c-h, Plate A19 a]

P10: (SOI 25-28) very irregular flake hammerscale to 200µm, similar to particle 9, densest in core, slaggy void-rich inner layer. [Figure 18 h, Plate A19 b-e]

P11: (SOI 29, 30) Conventional flake hammerscale in outer part of thickness, slaggy and plate-rich internal layer, to 100µm. [Plate A19 f-g]

P12: (SOI 31, 32) As particle 11, but rather more melted and slaggy. [Plate A19 h, Plate A20 a]

P13: (SOI 33-38) flake hammerscale to 400µm, very irregular piece with iron poor spinels on outside. Away from this the flake hammerscale is much more conventional and about 250µm thick. [Plate A20 b-g]

P14: (SOI 39-42) Plate-rich outer layer, pseudodendritic wustite inner layer. Outer layer is clearly relict, whereas inner has melted, to 1000µm. [Plate A20 h, Plate A21 a -c]

P15: (SOI 43-45) Mainly quite conventional flake hammerscale, but deformed over large rounded bubbles. [Plate A21 d-f]

LP4-25: (C60344, S6006) This sample was a mount of particles provisionally identified as being spheroidal hammerscale. It was from the same context (60344) as LP4-18, LP4-19, LP-23 and LP4-24. 22 particles were examined:

P1: (SOI 3, 14, 15) 1400µm. Clinker droplet with attached oxide scale. Mullite and spinels in glass. Solid droplet with multiple vesicles. [Figure 17 e, Plate A22 a, Plate A23 d-e]

P2: (SOI 4, 16, 17) 700 µm. Spheroidal droplet dominated by fayalite, with some quartz relicts. Solid droplet with rare vesicles. [Plate A22 b, Plate A23 f-g]

P3: (SOI 4, 18, 20, 21) 1200 µm. Material shows large primary hercynite, which have reacted to give magnetite + corundum. Subsequent fine groundmass includes spinels and probably Fe-gehlenite in glass. Slightly irregular spheroidal droplet with convoluted central void. [Figure 17 f, Plate A22 b, Plate A23 h, Plate A24 a-b]

P4: (SOI 4, 22) 1500 µm. Slag-textured spheroidal hammer scale, with magnetite-rich rim and adhering flake hammer scale. Has a large central void, plus other vesicles. [Plate A22 b-c, Plate A24 c]

P5: (SOI 5, 23, 24) 2500 µm. Clinker droplet, with mullite, and locally magnetite, in glass. Bears variable sulphidised droplets of iron with high nickel. Contains relict quartz grain. Solid droplet with multiple vesicles, particularly near margin. . [Plate A22 c, Plate A24 d-e]

P6: (SOI 6) 800 µm. Fragment of quartz-rich 'smithing floor'. [Plate A22 d]

P7: (SOI 6, 25) 3000 µm. Clinker droplet with Al-magnetite and mullite in glass. Irregular rounded droplet with large central cavity and other vesicles. [Plate A22 d, Plate A24 f]

P8: (SOI 6, 26) 800 µm. Small spheroidal hammer scale particle with wustite and fayalite in interior and magnetite-rich crust. Dense spheroidal droplet with sparse vesicles. [Plate A22 d, Plate A24 g]

P9: (SOI 6, 27, 29) 1600 µm. Spheroidal hammer scale particle with wustite and fayalite in interior and magnetite-rich crust. Dense spherical droplet with multiple vesicles. Contains relict quartz particles. [Plate A22 d, Plate A24 h, Plate A25 a]

P10: (SOI 7, 30, 31) 1000 µm. Spheroidal hammer scale with some primary magnetite, but dominated by wustite pseudodendrites with a little fayalite. Dense spherical droplet with multiple vesicles. [Plate A22 e, Plate A25 b-c]

P11: (SOI 7) 1400 µm. Spheroidal hammer scale with some primary magnetite, but dominated by wustite pseudodendrites with a little fayalite. Dense rounded droplet with multiple vesicles. [Plate A22 d]

P12: (SOI 7, 32) 400 µm. Spheroidal hammer scale, rich in magnetite including dendrites and plates in glass. Dense spherical droplet with multiple vesicles. [Plate A22 e, Plate A25 d]

P13: (SOI 8, 33) 1600 µm. Clinker droplet, with mullite in glass. Also has variably sulphidised iron with phosphorus and nickel. Solid droplet with central void and multiple vesicles, particularly near margin. [Plate A22 f, Plate A25 e]

P14: (SOI 9, 34) 1400 µm. Slag-textured spheroidal hammer scale with magnetite rim, but with wustite dendrites and fayalite internally. Spheroidal droplet with very large multicuspate central cavity and minor vesicles in slag. [Plate A22 g, Plate A25 f]

P15: (SOI 10, 35, 36) 1100 µm. Spheroidal hammer scale with magnetite crust, but dominantly wustite pseudodendrites internally. Slightly irregular grain (burst on contact?), solid with sparse vesicles. [Plate A22 h, Plate A25 g-h]

P16: (SOI 10, 37, 38) 1100 µm. Spheroidal hammer scale. Some wustite and altered glass, but dominated by Al-magnetite, including some plates. Irregular grain with horseshoe-shaped section caused by breakage into central void. Slag bears minor additional vesicles. [Plate A22 h, Plate A23 b, Plate A26 a-b]

P17: (SOI 10, 11, 39, 40) 1500 µm. Primary hercynite, locally cored on corundum, in glass. Some iron blebs with elevated copper and nickel where sulphidised on margins. Slightly irregular spheroidal droplet with convoluted central void and other vesicles. [Plate A22 h, Plate A23 a, Plate A26 c-d]

P18: (SOI 10, 12, 41) 800 µm. Spheroidal hammer scale, with magnetite, mainly euhedral, in glass. Thin-shelled grain with very large central multicuspate cavity. [Plate A22 h, Plate A23 b, Plate A26 e]

P19: (SOI 10, 12, 42) 1000 µm. Slag-textured spheroidal hammer scale, with magnetite rim and finely dendritic wustite in interior. Solid grain with sparse vesicles mainly near the margin. [Plate A22 h, Plate A23 b, Plate A26 f]

P20: (SOI 12, 43) 500 µm. Spheroidal hammer scale with magnetite dendrites in glass. Spheroidal grain with large central cavity and minor vesicles in shell. [Plate A23 b, Plate A26 g]

P21: not examined

P22: (SOI 13, 44, 45) 1600 µm. Spheroidal hammer scale with magnetite crust passing inwards to wustite pseudodendrites and fayalite. Slightly irregular spheroidal grain with multiple scattered vesicles. [Plate A23 c, Plate A26 h, Plate A27 a]

LP4-26: (C60912, S6073) Sample taken as being "fresh sand". Mainly quartz in grains of silt up to 300µm. Some iron oxides. Not examined in detail. [Plate A27 b]

LP4-27: (C60664, S6027) Sample taken as being "fresh sand". In fact largely comprises comminuted fragments of corroded grey cast iron, some with relict steadite. Interpreted as grinding swarf. Includes some fine-medium quartz (rarely up to 800µm). Not examined in detail. [Plate A27 c-h]

LP4-28: (C60454, S6018) Sample taken as being "used sand". Bears quartz and potassium feldspar up to 500µm and coal grains of up to 800 µm. Some iron oxide grains. Not examined in detail. [Plate A28 a]

WP5: Govan Ironworks Foundry

GOV1: (C22061, S2053; make-up from yard surface) Sample from a thin flow of dark glassy slag with a convoluted surface. This sample contains somewhat feathery crystals of anorthite (up to about 100µm), together with blebs of Fe-Mn sulphide (<5 µm), in a glass. The sulphide occurs as very small blebs dispersed in the glass and much larger ones clustered on the outside of the anorthite. Some sulphide inclusions also occur within the anorthite. No detailed microanalytical data are available. [Figure 4 b, Plate A29 a-b]

GOV2: (C22061, S2053; make-up from yard surface) Sample from a thin flow of dark glassy slag with a convoluted surface grading into a honeycomb-like texture. No microscopy was undertaken.

GOV3: (C22061, S2053; make-up from yard surface) A porcellaneous slag grading to blue glass. Microscopically this sample grades from a glass bearing fine dendritic oldhamite? (CaS), through to a more fully crystalline texture with melilite dendrites. No detailed microanalytical data are available. [Figure 4 a, Plate A29 c-f]

GOV4: (C22061, S2053; make-up from yard surface) A stony slag with marginal blue glass, which has a dimpled base with coke. In the microscope, this sample has complex intergrowths of melilite and oldhamite, as well as discrete primary dendritic oldhamite. Much of the oldhamite has been dissolved leaving cavities in the sample. [Figure 4 c, Plate A29 g-h, Plate A30 a-e]

GOV5: (C23119, S2124; coarse make-up) A stony slag, vesicular and dense as GOV4, but with very little surviving oldhamite. [Figure 4 d, Plate A30 g-h]

GOV6: (C23119, S2124; coarse make-up) A stony, vesicular slag with a lobed top very similar to GOV5. Once again, the location of former oldhamite is represented by porosity. [Plate A31 a-d]

GOV7: (C22286, S2047; surface in moulding shop) A blue-green glass in thick contorted flow. In the microscope this was a glassy slag, bearing small blebs of iron (which have high Si and Mn). [Plate A31 e-g]

GOV8: (C22286, S2047; surface in moulding shop) A khaki-green glass in thick contorted flow. Bears particle of iron (or ferrosilicon?) which has high Si of up to 10% and Mn of up to 2.3%. More usual iron blebs have up to 2.8% Si, up to 1.5%P and about 0.5% Mn. [Plate A31 h Plate A32 a]

GOV9: (C22286, S2047; surface in moulding shop) A dense vesicular iron oxide slag. Where fresh this

appears to show a somewhat carious iron oxide as the primary phase, followed laths of fayalite. Where altered, the fayalite is replaced by a fine-grained mosaic of haematite, silica and possible mélonjosephite (an iron, manganese, calcium phosphate). The main iron oxide resembles magnetite morphologically, but analytically appears to be mainly haematite. In detail, the fayalite can be commonly seen to bear abundant rounded inclusions, probably of silica. This would be difficult to explain as an equilibrium assemblage. [Figure 2 c-d, Plate A32 b-h, Plate A33 a-h, Plate A34 a]

GOV10: (C22769, S2117; make-up from area of cupolas) This is a dense flow-lobed tapped fayalitic slag. The bulk material shows a coarsely dendritic/pseudodendritic wustite, partially altered to magnetite, with local growth of very coarse magnetite plates. The oxides are followed by a matrix of fayalite, which locally appears poorly preserved and some areas may have been glass.

Locally there are inclusions which appear to be rather thick flake hammerscale. Around these the slag is rather more siliceous and is dominated by a fayalite-wustite cotectic. The area around the hammerscale passes out into a zone with abundant and coarse platy magnetite. Analyses of magnetite close to the scale show high levels of phosphorus (up to 2%) and manganese (up to about 0.8%). [Figure 2 e-g, Plate A34 b-h, Plate A35 a-h, Plate A36 a-b]

GOV11: (C22769, S2117; make-up from area of cupolas) This is a dense flow-lobed tapped fayalitic slag. It shows a primary moderately coarse carious magnetite, possibly locally oxidised to haematite, particularly where interstitial rather than enclosed by the fayalite (but in a much lower proportion than in GOV10), followed by coarse elongate fayalite. The margins of the fayalite show an intergrowth and overgrowth of a siliceous material (possibly silica, but probably a siliceous glass) and there are small interstitial blebs of iron sulphide. [Figure 2 h, Plate A36 c-f]

GOV12: (C22363, S2147; within flue 23239, replacement/extension to flue 22336, W side of moulding shop) A sample from the margin of the iron flow in the flue adjacent to the supposed reverberatory furnace. The textures are extremely complex but appear to show a crudely fissured metal, probably mostly cementite, with slag penetration into the cracks (the slag containing pyrite, fayalite, leucite and mélonjosephite?). Thus in its present state the iron appears to be a white cast iron, but given the extraordinary occurrence this cannot be taken as indicative of the originally intended product. The iron is marginally oxidised and in contact with a slag including both coarse hercynite (particularly associated with the surface of the oxidised metal) and a fayalite wustite cotectic. [Figure 2 a-b, Plate A36 g-h, Plate A37 a-h, Plate A38 a-h, Plate A39 a, Plate C6]

GOV13: (C23140, S2144; machine base in Structure 14) thick flake scale

P1: (SO11-8, 14-16, 20). Thick, even flake hammerscale to 1640 µm, haematite to 18 µm (1%), magnetite 86 µm (5%), wustite layer 94%. [Figure 18 a-b, Plate A39 b-h, Plate A40 a,g,h, Plate A41 a,e]

P2: (SOI 9-13, 18-19, 21-24). Thick, even flake hammerscale to 1180 µm, haematite to 13 µm (1%) magnetite 58 µm (5%), wustite layer 94%. Shows development of a layer of voids above inner face – outside these wustite is columnar, inside is equant. The slagging near the inner face contains iron sulphide blebs and a very phosphatic glass. Really large voids cause the outer layers to be drawn down and the magnetite layer thickens to reach void. [Figure 18 c-d, Plate A40 b-f, Plate A41 c-d,f-h, Plate 42 a]

P3: (SOI 25-27). Thick, even flake hammerscale to 860 µm with large voids just above inner face, haematite to 9 µm (1%) magnetite 45 µm (5%), wustite layer 94%. [Plate A42 b-d]

P4: (SOI 28-29). Thick flake hammerscale to 1050 µm with large irregular voids in inner half – with more lagged material between them and inner face. Because of this the inner face is very irregular. Haematite to 9 µm (1%) magnetite 45µm (4%), wustite layer 95%. [Plate A42 e-f]

P5: (SOI 30-32). Thick, even flake hammerscale to 1410 µm, haematite to 18 µm (1%) magnetite 73 µm (5%), wustite layer 94%. [Plate A42 g-h, Plate 43 a]

P6: (SOI 33-34). Thick, even flake hammerscale to 1840 µm, haematite to 16 µm (1%) haematite to 88 µm (5%), wustite layer 94%. [Plate A43 b-c]

GOV14: (C22363, S2086; hearth base in boiler shop) thin flake hammerscale taken from same sample as the spheroidal hammerscale in GOV15.

P1: (SOI 1, 2) simple dense flake hammerscale with thick magnetite layer, overall 530 µm thick, haematite to 30 µm (5%), magnetite to 130 µm (25%), wustite layer 70%. [Plate A43 d-e]

P2: (SOI 3) possible flake hammerscale with internal contorted structure, 90 µm. [Plate A43 f]

P3: (SOI 4, 5) simple dense flake hammerscale 120 µm, haematite to 3 µm (3%), magnetite to 40 µm (33%), wustite layer to 64%. Has curious porous outgrowth up to 75 µm on the external surface mainly of magnetite, but with some outgrowth of wustite too. [Figure 18 e, Plate A43 g-h]

P4: (SOI 6) porous layered scale to 265 µm, haematite to 5 µm (2%) and magnetite to 24 µm (9%), wustite layer is 89%. [Plate A44 a]

P5: (SOI 7) dense flake hammerscale with minor grain boundary widening, 100 µm, haematite to 2 µm (2%), magnetite 8 µm (8%), wustite layer 90%. [Plate A44 b]

P6: (SOI 8-10) altered looking scale with granular texture locally, 80 µm. No measurable zonation, but local fine texture on one edge might be relict of haematite zone? [Plate A44 c-e]

P7: (SOI 11) fresh dense flake hammerscale with very thick columnar magnetite zone, 80 µm thick, haematite layer 3 µm (4%), magnetite layer to 46 µm (56%), inner magnetite zone 2 µm (3%), wustite layer 37%. [Plate A44 f]

P8: (SOI 12) altered granular scale, 160 µm, half of thickness appears to be equant corroded wustite, half is granular magnetite. [Plate A44 g]

P9: (SOI 13, 14) variably composed of granular and equant textures, to 100 µm. [Plate A44 h, Plate A45 a]

P10: (SOI 15, 16, 18, 19) open granular-textured flake scale largely altered to magnetite, to 100 µm. [Plate A45 b-c, e-f]

P11: (SOI 17) open-textured granular flake hammerscale with fine margins. To 265 µm thick. [Plate A45 d]

GOV15: (C22363, S2086; hearth base in boiler shop) spheroidal hammerscale taken from same sample as the flake hammerscale in GOV14.

P1: (SOI 4), spheroidal hammerscale 800 µm, thin shell with irregular internal pockets, internal coarse hercynite. [Plate A46 b]

P2: (SOI 5, 6, 7), spheroidal hammerscale 1200 µm, thick shell with large vesicles and small marginal ones, outer magnetite shell, then glass/fayalite filled vesicles, then equant magnetite passing into thick layer of wustite dendrites. Magnetite plates in contact zone. [Plate A46 c-e]

P3: (SOI 8,9), spheroidal hammerscale 900 µm, thick shell with few vesicles, equant magnetite overgrown by wustite dendrites throughout. [Plate A46 f-g]

P4: (SOI 10, 11), spheroidal hammerscale 1300 µm, thin shell, multicusate, outer equant magnetite grading to wustite pseudodendrites internally. [Plate A46 h, Plate A47 a]

P5: (SOI 12, 13, 14), spheroidal hammerscale 1200 µm, thick shell with large vesicles, outer equant magnetite grading to wustite dendrites internally, some plates near contact. [Plate A47 b-d]

P6: (SOI 15, 16, 17), spheroidal hammerscale 1900 µm, thick shell with vesicles, very thin outer crust, internally almost entirely wustite pseudodendrites/dendrites. [Plate A47 e-g]

P7: (SOI 18), spheroidal hammerscale 200 µm, dense angular wustite, dense angular wustite. [Plate A47 h]

P8: (SOI 19, 20), spheroidal hammerscale 700 µm, dense, with irregular embayments, dense equant magnetite with tiny o/g of plates and pseudodendrites of wustite. [Plate A48 a-b]

P9: (SOI 21, 22), spheroidal hammerscale 600 µm, dense with irregular partially filled voids and vesicles, primary equant magnetite, with plates, followed by wustite dendrites and late olivine. [Plate A48 c-d]

P10: (SOI 23, 24), spheroidal hammerscale 600 µm, medium shell multicuspate, dense angular ?magnetite. [Plate A48 e-f]

P11: (SOI 25, 26), spheroidal hammerscale 1000 µm, irregular shape with 2 large internal voids, residual quartz, complex intergrowth of magnetite. [Plate A48 g-h]

P12: (SOI 27,28), spheroidal hammerscale 400 µm, dense few vesicles, outer equant magnetite and crust, passing inwards to pseudodendrites with cores of magnetite. [Plate A49 a-b]

P13: (SOI 29), spheroidal hammerscale 200 µm, dense, single vesicle, sparse equant ?magnetite followed by laths of ?anorthite. [Plate A49 c]

P14: (SOI 30, 31, 32), spheroidal hammerscale 700 µm, early angular hercynite followed by hercynite?-sulphide intergrowth. [Plate A49 d-f]

GOV16: (C22806, S2133; hearth base, S end of smithy) thin flake hammerscale taken from same sample as spheroidal hammerscale in GOV17 (no microscopy undertaken).

GOV17: (C22806, S2133; hearth base, S end of smithy) spheroidal hammerscale taken from same sample as thin flake hammerscale in GOV16.

P1: (SOI 2, 3, 4), spheroidal hammerscale 1000 µm, dense with scattered vesicles, outer equant magnetite crust, thin, grades inwards to wustite pseudodendrites/dendrites, lots of plates in contact area. [Plate A49 h, Plate A50 a-b]

P2: (SOI 5,6), spheroidal hammerscale 700 µm, thin shell, multicuspate, outer equant magnetite grading to wustite dendrites. [Plate A50 c-d]

P3: (SOI 5,6), spheroidal hammerscale 700 µm, thin shell, dense angular and dendritic magnetite. [Plate A50 c-d]

P4: (SOI 7, 8), spheroidal hammerscale 800 µm, medium shell, rounded wustite lump, hercynite angular grains grading to plates, followed by tiny wustite dendrites and fayalitic groundmass. [Plate A50 e-f]

P5: (SOI 9, 10), spheroidal hammerscale 1000 µm, elongate, central voids, outer and possibly entrained crust of magnetite, with magnetite dendrites and plates, glassy matrix, passing inwards to wustite dendrites, also in glass. [Plate A50 g-h]

P6: (SOI 11, 12), spheroidal hammerscale 900 µm, irregular, one flat end with ?mullite, eccentric void with crust thinning away from

mullite, mainly equant magnetite in glass with some fine ?magnetite. [Plate A51 a-b]

P7: (SOI 13, 14), spheroidal hammerscale 1300 µm, dense with scattered vesicles, coarse polygonal wustite? [Figure 16 c, Plate A51 c-d]

P8: (SOI 15, 16), spheroidal hammerscale 1000 µm, very thin shell, coarse polygonal magnetite and magnetite dendrites inwards. [Figure 16 d, Plate A51 e-f]

P9: (SOI 17, 18), spheroidal hammerscale 700 µm, thin shell, coarse polygonal magnetite and magnetite dendrites. [Plate A51 g-h]

P10: (SOI 19, 20), spheroidal hammerscale 600 µm, thin shell, delicate magnetite dendrites in glass. [Plate A52 a-b]

P11: (SOI 21, 22), spheroidal hammerscale 800 µm, massive with two internal voids, coarse polygonal magnetite and magnetite dendrites, some glass. [Plate A52 c-d]

P12: (SOI 23, 24), spheroidal hammerscale 500 µm, thin shell, dendritic magnetite with plates and trace of wustite inwards. [Plate A52 e-f]

P13: (SOI 25, 26, 27), spheroidal hammerscale 700 µm, thick shell, outer crust of equant magnetite, passes inwards to polygonal and pseudodendritic wustite (via plates). [Plate A52 g-h, Plate A53 a]

P14: (SOI 28,29), spheroidal hammerscale 1000 µm, thick shell, outer dendritic magnetite in glass passes into wustite dendrites in fine fayalite via plates, fragments of enclosed possible flake hammerscale. [Figure 16 b, Plate A53 b-c]

P15: (SOI 30, 31), spheroidal hammerscale 700 µm, very thin crust, magnetite dendrites fine, in glass. [Plate A53 d-e]

P16: (SOI 32, 33), spheroidal hammerscale 500 µm, thick vesicular crust, delicate long dendrites of ?magnetite in glass. [Plate A53 f-g]

P17: (SOI 34,35), spheroidal hammerscale 1000 µm, thin shell, elongate, multicuspate, outer angular and dendritic magnetite with plates passes inwards to sparse wustite dendrites. [Plate A53 h, Plate A54 a]

P18: (SOI 36, 48, 49, 50), spheroidal hammerscale or clinker, 500 µm, solid, multi-component, glass + "mullite" in one, fayalite + magnetite, ?iron. [Figure 17 d, Plate A54 b, Plate A55 f-h]

P19: (SOI 37, 38), spheroidal hammerscale 1000 µm, medium shell, multicuspate void, outer angular and dendritic magnetite grading in to pseudodendrites. [Plate A54 c-d]

P20: (SOI 39, 40), spheroidal hammerscale 700 µm, medium shell, multicuspate void,

outer angular magnetite grading in to coarse dendritic magnetite. [Plate A54 e-f]

P21: (SOI 41, 42, 51), spheroidal hammerscale 800 µm, thin shell, fine magnetite dendrites in glass. [Plate A54 g-h, Plate A56 a]

P22: (SOI 43, 44), spheroidal hammerscale 800 µm, two voids in medium shell, very fine extensive dendrites - possible magnetite, in glass. [Plate A55 a-b]

P23: (SOI 45, 46, 52), spheroidal hammerscale 800 µm, thick shell, eccentric void, primary hercynite, followed by small dendrites of ?wustite. [Plate A55 c-d, Plate A56 b]

P24: (SOI 47), spheroidal hammerscale 200 µm, thick shell, multicuspate, outer angular magnetite grading in to coarse dendritic magnetite. [Plate A55 e]

GOV18: (C22726, S2060; hearth base, N end of smithy) thin flake hammerscale taken from same sample as spheroidal hammerscale in samples GOV19.

P1: (SOI1) dense simple flake hammerscale with variable thickness 400-500 µm, where thick, the haematite layer is 6 µm (1%) and the magnetite layer 90 µm(19%), but where the scale thins these thicken to 19 µm (5%) and 130 µm (33%) respectively. The wustite layer decreases from 80-62%. [Plate A56 c]

P2: (SOI 2-5) is a complex slaggy scale with numerous inclusions, voids and heterogeneous texture. Typically 360 µm thick. [Plate A56 d-g]

P3: (SOI 6-8) is a rather corrugated scale, mineralogically simple, except for slag penetrating between grains from inner face. 150 µm thick, the haematite layer is 3 µm (2%), the magnetite layer 13 µm (9%), the wustite layer is 80% of the thickness with an inner magnetite zone being 9%. [Plate A55 h, Plate A56 a-b]

P4: (SOI 9) is a rather folded scale, with some protrusions from the rear face behind hollows on the outside. The simple structure shows slag penetration from the inside. The scale is 80 µm, with a magnetite layer of 19 µm (24%). [Plate A57 c]

P5 (SOI 10, 23) corrugated flake hammerscale, to 180 µm. Outer magnetite layer is 18 µm (10%), inner magnetite is 10 µm (6%). [Plate A57 d, Plate 59 a]

P6: (SOI 11). Complex flake hammerscale with granular magnetite with plates, splits and voids. Scale is 150 µm thick. [Plate A57 e]

P7: (SOI 12-14) altered flake hammerscale comprising rather separated wustite grains, passing on inner surface into magnetite-rich material with filamentous secondary oxides. Scale is 170 µm thick with 5 µm magnetite layer (3%). [Plate A57 f-h]

P8: (SOI 15, 16) complex flake hammerscale apparently with melted slaggy zone inside scale. Scale overall 350 µm thick, with outer magnetite of 19 µm (5%), outer wustite 38 µm (11%) then a zone with strongly aluminous magnetite (40% hercynite) and magnetite plates, 63 µm thick (18%), then a zone of melted wustite with magnetite and some plates and large rounded voids of 190 µm (55%) thickness. [Plate A58 a-b]

P9: (SOI 17, 18) flake hammerscale with melt textures varying from 100-350 µm thick. Outer 9 µm (3%) is magnetite, but even this is superimposed on the melt texture. Outer surface curved, inner face planar. [Plate A58 c-d]

P10: (SOI 19-22) complex flake hammerscale apparently with melted zone outside intact scale. Scale is 800 µm thick overall, with up to 60% of thickness the outer wustite and magnetite melt. The original scale is 320 µm thick, has a 'normal' wustite microstructure, but with pores showing magnetisation and plate growth suggesting channels through the scale. [Plate A58 e-h]

GOV19: (C22726, S2060; hearth base, N end of smithy) spheroidal hammerscale taken from same sample as thin flake hammerscale in samples GOV18.

P1: (SOI 2, 3), spheroidal hammerscale 2000 µm, multi-component, voids close to margin on more iron rich side, fine angular and dendritic hercynite in glass, Al-rich zones with fine magnetite. [Plate A59 c-d]

P2: (SOI 4, 5), spheroidal hammerscale 1000 µm, thick wall, central cavity and array of more marginal ones, angular magnetite passing into pseudodendrites, via zone with plates. [Plate A59 e-f]

P3: (SOI 6, 7), spheroidal hammerscale 800 µm, open ended multicuspate? angular magnetite and magnetite dendrites in glass. [Plate A59 g-h]

P4: (SOI 8, 9), spheroidal hammerscale 500 µm, medium wall, angular magnetite, some dendrites. [Plate A60 a-b]

P5: (SOI 10, 11), spheroidal hammerscale 1000 µm, solid, with small elongate voids, central zone of polygonal wustite, passing out into pseudodendrites. [Plate A60 c-d]

P6: (SOI 12, 13), spheroidal hammerscale 600 µm, thin walled multicuspate, polygonal to slightly dendritic magnetite. [Figure 16 e-f, Plate A60 e-f]

P7: (SOI 14, 15, 16), spheroidal hammerscale 600 µm, thin walled multicuspate, magnetite dendrites. [Plate A60 g-h, Plate A61 a]

P8: (SOI 17, 18, 19), spheroidal hammerscale 600 µm, solid with small elongate voids, zones of dense polygonal wustite passing out to pseudodendrites and

to marginal angular magnetite via plates. [Plate A61 b-d]

P9: (SOI 20, 21), spheroidal hammerscale 700 µm, solid with irregular cavities, spiders web wustite dendrites in glass. [Figure 16 a, Plate A61 e-f]

P10: (SOI 22, 23, 24), spheroidal hammerscale or clinker, 600 µm, multiple vesicles, multi-component, various zones of glass with anorthite/pyroxene, plus more iron-rich blebs. [Figure 17 c, Plate A61 g-h, Plate A62 a]

P11: (SOI 25, 26, 27), spheroidal hammerscale 600 µm, thick walled, primary magnetite crosses and plates followed by tiny fayalite. [Plate A62 b-d]

P12: (SOI 28, 29), spheroidal hammerscale 1000 µm, very thin walled, magnetite dendrites in glass. [Plate A62 e-f]

P13: (SOI 30, 31, 32, 33), spheroidal hammerscale or clinker 2500 µm, multi-component, solid with irregular voids, 2 different glasses, one Fe rich with hercynite, the other with magnetite and sulphide blebs. [Plate A62 g-h, Plate A63 a-b]

P14: (SOI 34, 35), spheroidal hammerscale 1000 µm, thin walled multicuspate, marginal angular magnetite passing into pseudodendrites. [Plate A63 c-d]

P15: (SOI 36, 37), spheroidal hammerscale 700 µm, thin walled multicuspate, magnetite dendrites. [Plate A63 e-f]

P16: (SOI 38, 39, 40), spheroidal hammerscale 1200 µm, irregular, multi-component, elongate magnetite, curved dendrites and glass. [Plate A63 g-h, Plate A64 a]

GOV20: (C22512, S2088; hearth base in boiler shop) thin flake hammerscale taken from same sample as spheroidal hammerscale in samples GOV21.

P1: (SOI 1-4), flake hammerscale to 380 µm, haematite to 3 µm (1%), magnetite to 42 µm (11%), wustite layer 88%. Rather complex scale with very irregular profile, 'frayed' inner melted surface and high internal porosity [Plate A64 b-e]

P2: (SOI 5-7, 23-28), flake hammerscale to 200 µm, haematite to 2 µm (1%), magnetite to 23 µm (12%), wustite layer 88%. Fairly planar scale with a high proportion of magnetite. Inner surface slightly melted. Has an external adhering mass of porous magnetite attached near one end, which includes highly altered and eroded dendritic structures. [Plate A64 f-h, Plate A66 h, Plate A67 a-e]

P3: (SOI 8-13), flake hammerscale to 230 µm, haematite absent, magnetite 15 µm (7%), wustite layer 93%. Planar simple scale, with rather coarse grain structure showing widening of boundaries in outer part

of scale and associated development of magnetite plates. [Plate A65 a-f]

P4: (SOI 14-22, 29-30), flake hammerscale to 200 µm haematite absent, magnetite to 6 µm (3%), wustite layer 97%. Scale complicated by embayments below irregular developments of porous magnetite on outer face. Below these, not only is scale curved, but magnetite penetrates through most of the thickness. [Plate A65 g-h, Plate A66 a-g, Plate A67 f-g]

P5: (SOI 31-33), flake hammerscale to 340 µm haematite to 3 µm (1%), magnetite to 16 µm (5%), wustite layer 94%. Fairly simple thick scale, but contains numerous horizons of voids. [Plate A67 h, Plate A68 a-b]

P6: (SOI 34-41), flake hammerscale to 290 µm haematite to 5 µm (2%), magnetite to 14 µm (5%), wustite layer 94%. Slightly irregular scale with undulating surface. High areas on surface correspond to slagged areas below, with voids, fayalitic slag, rounded wustite and magnetite plates. Between these melted areas is dense wustite. Rear contains small iron nickel arsenide blebs (also with copper and sulphur). [Plate A68 c-h, Plate A69 a-b]

P7: (SOI 42-45), slag blisters with relict oxide horizons (remains of scale), but all largely reacted and melted with inner, fayalite dominated zone, then with wustite, then with wustite plus plates, then outer magnetite crust. [Plate A69 c-f]

P8: (SOI 46-50) Very complicated melted scale. Outer haematite/magnetite layer is mainly fairly solid. Half of the thickness of the remainder bears some wustite, but mainly as nodules within magnetite lamellae. There are also euhedral equant Al-magnetite crystals of up to 30 µm in this layer. Inner part of scale is dominated by wustite pseudodendrites (with some real dendrites too). Overall to 290 µm haematite to 5 µm (2%), magnetite to 14 µm (5%), wustite layer 94%. [Figure 18 g, Plate A69 g-h, Plate A70 a-b]

P9: (SOI 51-55) Simple flake hammerscale to 150 µm, haematite absent, magnetite to 29 µm (19%), wustite layer 81%. Inner margin is slagged and has 'frayed' appearance. [Plate A70 c-g]

P10: (SOI 56-59), flake hammerscale with even thickness of columnar wustite (c. 250 µm) on outside (with some widening of boundaries with magnetite plates forming 'stitching') then layer of voids, internally 0-400 µm thickness with more equant wustite. Overall to 650 µm, haematite absent, magnetite to 18 µm (3%), wustite layer 97%. [Plate A70 h, Plate A71 a-c]

P11: (SOI 60-64), flake hammerscale to 180 µm, haematite absent, magnetite to 9 µm (5%), wustite layer 95%. The flake shows well developed slagging and melting of inner face (with iron sulphide blebs), dense and simple outwards, but has large arching blisters as it leaves the substrate. [Plate A71 d-h]

P12: (SOI 65-70) very simple thick flake hammerscale to 960 µm haematite to 11 µm (1%), magnetite to 85 µm (9%), wustite layer 90%. Has minor grain boundary widening on inner face. [Plate A72 a-f]

GOV21: (C22512, S2088; hearth base in boiler shop) spheroidal hammerscale taken from same sample as thin flake hammerscale in samples GOV20. (no microscopy undertaken)

GOV22: (C22969, S2120; mixed make-up for moulding shop floor) thin flake hammerscale taken from same sample as the spheroidal hammerscale of GOV23.

P1: (SOI 1-3) very irregular flake hammerscale of roughly 350 µm, with magnetite-rich lumps (up to 80 µm) on exterior. The inner edge is slightly slagged and of frayed appearance. Outer and inner magnetite layers are 13 µm (4%), with the wustite layer 92%. [Plate A72 g-h, Plate A73 a]

P2: (SOI 4, 5) somewhat heterogeneous flake hammerscale to 410 µm, with internal slabs of dense scale surrounded by more granular zones. Haematite layer is 3 µm (1%), magnetite layer to 40 µm (9%) and has an inner magnetite zone of 3 µm (1%), leaving the wustite zone as 89%. [Plate A73 b-c]

P3: (SOI 6-8) heterogeneous scale, with inner dense primary layer (160 µm and an outer columnar (melted?) zone of 260 µm, giving a total thickness of 410 µm. The haematite layer is 3 µm (1%), the magnetite layer 25 µm (6%) and an inner magnetite layer is 9 µm (2%). [Plate A73 d-f]

P4: (SOI 9-13) simple scale, except for inward facing cavities with magnetite alteration and plates. Scale 205 µm thick, with haematite layer 9 µm (5%) and magnetite layer 22 µm (11%), both thickening inwards where cavities almost reach surface. Wustite layer is 84%. Voids also carry a very high phosphorous phase – possibly an apatite. [Figure 18 f, Plate A73 g-h, Plate A74 a-c]

P5: (SOI 14-16) flake hammerscale with simple outer section 150 µm thick with an internal up to 70 µm variable layer of slagged, melted material. Inner face bears particles of possible iron arsenide. Magnetite layer is 13 µm (9%) of outer layer. [Plate A74 d-f]

P6: (SOI 17-19) flake hammerscale with an outer part of simple scale, and an inner section of melted material, with slagging and 'stitching' of wustite grains by magnetite plates. Scale 200 µm thick, with haematite layer of 1 µm (1%), magnetite layer of 15 µm (7%). Wustite layer is 92%. Inner face bears small complex grains possibly with a CuFeS-Ni₂As eutectic. [Plate A74 g-h, Plate A75 a]

P7: (SOI 20-23) convoluted thin flake scale to 100 µm thick. Embayed sections show

outer filling of Al-magnetite cored on hercynite, with minor fayalite. Where simple the scale has magnetite layer of 13 µm (13%) and an inner magnetite layer of 4 µm (4%) with the wustite zone comprising 83%. [Plate A75 b-e]

GOV23: (C22969, S2120; mixed make-up for moulding shop floor) spheroidal hammerscale taken from same sample as the thin flake hammerscale of GOV22.

P1: (SOI 1, 2, 3) Melting slag spatter, very irregular (1.2 x 2.0mm) multi-component grain. Possible lime grains and fuel debris set in Ca-rich slag, with melilite, Fe-akermanite, Mg,Al-magnetite and Fe,Mg-hercynite. [Plate A75 f-h]

P2: (SOI 4, 5) Melting slag spatter(?), compositionally a Ca-rich clinker. Solid sub-spherical particle 3x2mm, with multiple vesicles and possible Fe-bleb (now oxidised). Mullite in glass with iron droplets (P-rich). Up to 5 wt% Ca in glass. [Plate A76 a-b]

P3: (SOI 6-9) Spheroidal hammerscale 1500 µm, with large attached flake hammerscale fragment. Central void and other vesicles. Spheroid has magnetite rim then plate-rich zone, internally wustite dendrites and fayalite. [Plate A76 c-f]

P4: (SOI 10-14) Melting slag spatter? 1800 µm spheroid with torn neck on one side. Multiple scattered vesicles in dense body. Some primary Al-magnetite in euhedral equant grains and also swallow-tailed anorthite, but most of grain is finely dendritic hercynite. [Figure 17 a-b, Plate A76 g-h, Plate A77 a-c]

P5: (SOI 15-17) Spheroidal hammerscale 1400 µm. Multicusped large central cavity. Thin magnetite crust but mainly wustite dendrites and pseudodendrites. Small fragment of flake hammerscale attached to exterior. [Plate A77 d-f]

P6: (SOI 18-22) Melting slag spatter? Bears marginal equant Al-magnetite, but internally dominated by curved sheaves of anorthite – which terminate abruptly at outer margin giving jagged appearance. 1500 µm diameter. [Plate A77 g-h, Plate A78 a-c]

P7: (SOI 23) burnt iron? Irregular particle, 3x1.8mm, with rounded wustite grains in core, outside is formed of wispy secondary oxides. [Plate A78 d]

P8: (SOI 24, 25) spheroidal hammerscale 1200 µm, thin magnetite crust, internally wustite dendrites with fayalite groundmass. Spheroid with central cavity and multiple vesicles. [Plate A78 e-f]

P9: (SOI 26) not a residue. [Plate A78 g]

P10: (SOI 27-29) 800 µm diameter particle of 'clinker'. The particle is multi-component. One area has angular particles apparently of coal set in a matrix of ?metakaolinite. The majority of the grain is of mullite, hercynite

and iron sulphide blebs in glass. The particle is dense and rounded. [Plate A78 h, Plate A79 a-b]

P11 (SOI 30-33) spheroidal hammerscale 1000 µm diameter. Dense core of pseudodendritic wustite with euhedral magnetite on margin. Large central cavity ad some other vesicles. Has minor included quartz. [Plate A79 c-f]

P12: (SOI 34-36) 2000 µm diameter irregular particle, multiple internal cavities – some filled with apparently secondary iron oxides. Primary mineralogy includes melilite, and Fe-Mg-rich melilite group phase and ? magnesio-wustite. [Plate A79 g-h, Plate A80 a]

P13: (SOI37) 500 µm grain not examined in detail. [Plate A80 b]

P14 (SOI38-39) melting slag spatter 1000 µm diameter. Grain has central void and several vesicles. Anorthite-rich glass with blebs of iron rich in Si, S and P. Also contains some quartz grains undergoing dissolution. [Plate A80 c-d]

GOV24: (C22421, S2042; pit in moulding shop) A large cupola slag mass with slag bearing droplets of iron, binding coke-rich material. GOV24 (no suffix) was a mounted specimen of slag with no large iron droplets, with an accompanying chemical analysis. GOV24a-c were polished mounts of individual iron blebs, with attached matrix. Sufficient observation of the slag made in the sample GOV24a, so GOV24 was not examined microscopically.

GOV24: Sample of slag. Sample not examined microscopically. The bulk analysis indicates a slag that is rather more siliceous than other glassy slags from the site and which has a high manganese content (>2wt% MnO)

GOV24a: Sample of slag with iron particle. The slag phase is a largely crystalline slag with anorthite (in the large prisms) and smaller more dendritic crystals of a calcium silicate, probably pseudowollastonite. There are complex blebby primary dendrites of MnS, in some cases probably nucleated on a titanium mineral. The slag bears lumps of metallic iron which have a high Si-content (9% Si, 0.3% P, 2.3% Mn). [Plate A80 e-h, Plate A81 a]

GOV24b: Sample of slag with iron particle. The slag is more heterogeneous than in GOV24a, but is generally more glassy, with finer-grained crystalline phases of anorthite and manganese sulphides (probably nucleated on titanium minerals) in glass. The glass also bears partially reacted quartz grains. The iron particles show Si contents over 8-9% and over 2% Mn [Plate A81 b-h]

GOV24c: Sample of slag with iron particle. Shows similar slag phases but also some possible small clinopyroxene. The enclosed iron particles are rather corroded, but contain large graphite flakes, and have 8-

10% Si, 2.2% Mn and 0.3% P. [figure 4 e, Plate A82 a-g]

GOV25: (C22139, S2061; floor of building SE of pattern shop) cast iron in a "floor" formed of iron oxide-cemented sand,

GOV25a: heterogeneous cast iron, central area of grey cast iron with graphite flakes, cementite and steadite eutectic (therefore about 4% carbon). The area surrounding it consisted of pearlite and cementite, in a widmanstatten or dendritic form. Iron has numerous manganese sulphide inclusions. Near the edges the pearlite is replaced by slag. Iron has about 1.6% Si and variably 1-4% Mn [Plate A82 h, Plate A83 a-g, Plate C7]

GOV25b: concretionary deposit of quartz and coal cemented by iron oxides, with very weathered iron particles. [Plate A83 h]

GOV25c: concretionary deposit of quartz and coal cemented by iron oxides. Contains a substantial piece of weathered grey cast iron with significant steadite development (Plate A84 a). Also bears a grain of uncertain nature, possibly an abrasive (Plate A84c). [Plate A84 a-c]

GOV26: (C22803, S2076; concreted block from "pit" in finishing shop)

GOV26a: concretionary material with wide variety of materials cemented by iron oxides, including fragments of leaded gunmetal (78% Cu, 8%Zn, 4%Pb, 1%Sn and 0.4% As, with 4% S), as well as particles of natural emery, quartz, coal, charcoal?, weathered grey cast iron and silica- and iron-rich copper slag (one texture has olivine with composition Fa90Fo10 with 2% Zn, copper and copper-iron sulphides in glass, with bulk composition including 0.4% Cu and 0.8% Zn; a second texture shows a probable aluminous pyroxene with 1%Zn). [Figure 19 a-e, g, Figure 21 b, Plate A84 d-h, Plate A85 a-e]

GOV26b: concretionary material with wide variety of materials cemented by iron oxides, including fragments of leaded gunmetal, as well as particles of natural emery, quartz, coal and weathered grey cast iron. [figure 21 c-d, Plate A85 f-g]

GOV27: (C22067, S2152; concreted floor from finishing shop) particles in "floor"

GOV27a: concretionary material with wide variety of materials cemented by iron oxides, including fragments of leaded gunmetal, as well as particles of natural emery, quartz, coal and weathered grey cast iron (some highly deformed swarf) [Figure 19 f, h, Plate A85 h, Plate A86 a-f]

GOV27b: concretionary material with wide variety of materials cemented by iron oxides, including fragments of leaded gunmetal, as well as particles of quartz, coal and

weathered grey cast iron (some highly deformed swarf), clinkery slags (Al-magnetite dendrites in glass) and flake hammerscale. [Plate A86 g-h, Plate A87 a-d]

GOV28: (C22067, S2152; concreted floor from S part of turning shop) porcellaneous grading to blue glass. Somewhat skeletal or dendritic crystals of 300 µm x 20 µm of pseudowollastonite in glass, with fine needles of sulphides probably nucleated on titanium minerals (nitrides?). [Plate A87 e-h]

GOV29: (C23203, S2145; "T" structure in NW) altered flue. No microscopy.

GOV30: (C22969, S2120; mixed make-up for moulding shop floor) dark green grey homogenous glass (No microscopy).

GOV31: (C22286, S2047; surface of moulding shop) white, slightly altered firebrick (No microscopy).

GOV32: (C22286, S2047; surface of moulding shop) grey-red reduced brick (No microscopy).

GOV33: (C22363, S2086; hearth base in boiler shop) smithing slag from same context as hammerscale samples GOV14 and 15 (No microscopy).

GOV34: (C22512, S2088; hearth base in boiler shop) clinker from same context as hammerscale samples GOV20 and 21 (no microscopy).

GOV36: (C23150, S2137; pit in structure 14) thin and thick flake hammerscale from same context as spheroidal hammerscale in GOV37.

P1: (SOI 1-7), flake hammerscale to 1050 µm, haematite to 4 µm (0%), magnetite to 50 µm (5%), wustite layer 95%. Simple thick scale, but with development of pores from rear face. Pores associated with development of magnetite plates, and some slaggy textures (including localised wustite dendrites). [Figure 18 b, Plate A88 b-h]

P2: (SOI 8-11), flake hammerscale to 1100 µm, haematite to 4 µm (0%), magnetite to 42 µm (4%), wustite layer 96%. Simple thick scale with boundary and pore enlargement near rear face and a few surface-normal narrow pores or fissures. Some of the pores show sulphidised margins and magnetite plates. [Plate A89 a-d]

P3: (SOI 12-16), flake hammerscale to 900 µm, haematite to 20 µm (2%), magnetite to 100 µm (11%), wustite layer 87%. Simple thick scale with a layer of voids just inside inner margin – it must have almost detached on this line. Some areas show the development of fine surface normal channels. [Plate A89 e-h, Plate A90 a]

P4: (SOI 17-18), flake hammerscale to 800 µm, haematite to 7 µm (1%), magnetite to 38 µm (5%), wustite layer 94%. Thick scale

shows pore development just inside rear face. Pores and grains slightly oblique suggesting some shearing. [Plate A90 b-c]

P5: (SOI 19-21), flake hammerscale to 700 µm, haematite absent, magnetite to 40 µm (6%), wustite layer 94%. Simple thick scale with some melting and slagging (with magnetite plates) of rear face. [Plate A90 d-f]

GOV37: (C23150, S2137; pit in structure 14) spheroidal hammerscale from same context as flake hammerscale in GOV36.

P1: (SOI 1,2), clinker 1200 µm, solid, small central cavity, glass - mullite? - iron sulphide. [Plate A90 g-h]

P2: (SOI 3,4), spheroidal hammerscale 700 µm, multicusped, thin wall, magnetite, angular on edge, more dendritic inwards, possible fayalite intergrowths on magnetite margins. [Plate A91 a-b]

P3: (SOI 5,6), spheroidal hammerscale 300 µm, solid with relatively small vesicles, magnetite, angular on edge but internally dendritic. [Plate A91 c-d]

P4: (SOI 7,8,9,10), spheroidal hammerscale 700 µm, solid with relatively small vesicles, very delicate iron oxide dendrites in ground mass of feathery fayalite. Outer marginal zone of 50 microns shows typical angular magnetite dendrites, then zone with plates 30 microns, then inwards to very delicate large dendrites of wustite. [Plate A91 e-h]

P5: (SOI 11,12), spheroidal hammerscale 600 µm, many vesicles, but they are largely separate so not quite multicusped, marginal magnetite dendrites pass inwards to mixed zone in which appears to overlie magnetite in the dendrites. Plates present in the mixed zone. [Plate A92 a-b]

GOV38: (C22945, S2123; fill of wood-lined pit in turning shop) iron (equant fragment)

GOV38a: [Plate A92 c-d]

GOV39: (C22422, S2121; sand from moulding shop)

Description of residue classes

Iron (Figure 1)

The iron sampled in this project has not included any examples of true products. Most samples analysed were of iron either as droplets present as inclusions within slags (mainly interpreted as melting slags from cupola furnaces) or were pieces of swarf from the finishing of castings.

The majority of examples of iron studied were of grey cast iron – that is to say iron containing free carbon as graphite flakes. Some samples did not show graphite, or showed an absence of graphite towards the margins. In such samples it may be difficult or impossible to assess whether the pieces represent evidence for a different material being worked, or simply inhomogeneity within materials. The lack of graphite on the margins of some of the larger pieces of what are clearly, in bulk, grey cast irons, makes problematic, in particular, the interpretation of small swarf fragments lacking graphite, since the turning and grinding residues may preferentially contain material removed from the very external surfaces of the castings.

In many cases, but particularly with samples from the Caledonia Foundry, the phosphorus content of the grey cast irons is very high (0.8-1.2% P). The analysed silicon content of the iron is very high too, with occasional particles of compositions corresponding to a ferrosilicon. It would appear likely, although there is a complete lack of ancient or modern comparative examples, that the silicon content of droplets of iron isolated within the cupola slag is vastly exceeding the content which would have been present in the bulk metal. The analysis of such droplets may therefore be a very poor guide to bulk metal composition in general.

Within the grey cast irons the most common inclusions are of manganese sulphides. In several examples the level of such inclusions exceeds that likely in a bulk metal, so once again the utility of the analysis of cupola residues for determining casting metal composition must be questioned.

For the swarf samples, the interpretation of the original metal type and composition is complicated by the loss of the original microstructure during the deformation induced by the turning process. Many of these samples come from deposits associated with the later phases of activity in the Scotland Street Engine Works, perhaps dating from the early decades of the twentieth century. It is possible that these samples, which apparently contain small, equant, graphite inclusions may represent spheroidised (malleable) cast iron, but that interpretation is tentative on the present material. Swarf from the much older Govan Ironworks Foundry is generally badly corroded, but where visible, the textures seen are indicative of grey cast iron.

Iron-rich slags (Figure 2)

Three samples of extremely iron-rich residues were selected from the materials from the Govan Ironworks Foundry (GOV9, GOV10 and GOV11). The sample of the flow of iron recovered from the base of the flue below the presumed reverberatory melting furnace (air furnace) proved to be associated with a veneer of slag, and that too is discussed here (GOV12).

Slag from the reverberatory furnace leak:

The sample of iron (GOV12) had a granular microstructure, most likely mainly of cementite, and had approximately 0.2% phosphorus, but no other detectable alloying elements. Towards the margins the iron was deeply fissured with thin seams of dark-coloured slag. The origin of the fissures is unknown, although their general apparent morphology somewhat resembles that of the graphite flakes in a grey cast iron. The slag in the fissures within the iron had a complex mineralogy. There was a small amount of subhedral pyrite, growing directly on the iron substrate. The principal phase was fayalite with about 3% Mn-substitution. The fayalite was intergrown with leucite in its outer margins. The subsequent phases included leucite in large crystals, small crystals of an Al and Ti-rich magnetite and a phosphate mineral (possibly mélonjosephite). The slag phase outside the main mass of iron included complex masses of iron oxides, apparently aggregates of spheroidal droplets, now of mixed oxides. The main phase was usually fayalite, in part as a cotectic with wustite and in part intergrown with coarse crystals of hercynite.

The unusual history of this iron (having apparently leaked from the reverberatory furnace in a catastrophic failure and flowed into the out-going gas flue, with a fall of several metres) means that there has been much scope for modification of the iron and its associated slag from the materials that were initially present in the hearth.

There are no published descriptions of reverberatory melting furnace slags available, either in the modern archaeological literature or in the contemporary technical literature. What one might expect would be interaction between the melting iron and the sand bed of the furnace, to develop a broadly fayalitic slag phase. That slag might be expected to provoke a redistribution of some 'contaminant' elements between the molten iron and the slag phase. In this instance, the slag close to the iron shows elevated contents of sulphur (now present in iron sulphides), phosphorus (now present in mélonjosephite) and manganese (present in fayalite) suggesting acquisition of the elements by the slag from the iron.

Dense granular iron oxide slag:

The vesicular, massive, iron oxide-dominated sample from the moulding shop (GOV9) also showed some rather problematic microstructures. The sample was dominated by equant rather coarse (up to 0.5mm) grains, apparently of haematite. The morphology of the grains resembled that of magnetite in hammerscale, with rounded grain boundaries and numerous rounded cavities. Veins, cavities and vesicles within the structure of the iron oxide were filled either with a fine-grained mosaic of haematite, a silica phase, and a phosphate mineral (probably mélonjosephite) or by what appear to be crystals of fayalite, but containing myriads of droplets of silica (locally either in random distributions or in arrays in particular crystallographic orientations within the fayalite).

Interpretation of this material is difficult, but the bulk composition of 87% iron expressed as Fe_2O_3 and 11% SiO_2 with just 0.2% MnO and 0.5% P_2O_5 , means that is likely that this material can be considered to be oxidised iron with a little admixed silica.

The oxidation of the iron, the reaction to produce fayalite and the probable free silica, might be taken as evidence for oxidation of iron during a refining process. However, it is equally possible that some oxidation of

iron would occur in the reverberatory melting furnace. The location of this sample within the moulding shop and the mineralogical links to the slag coating the iron found in the flue, strengthen the latter interpretation. This material may accordingly be interpreted as a probable residue from the reverberatory furnace.

Flowed-lobed dense slags:

Samples GOV10 and GOV11 both showed a flow-lobed structure suggesting that were slags tapped from a furnace. Such slags are usually assumed to have been tapped from a puddling furnace, but other processes might also have generated similar compositions and textures and tapping of slag from a reverberatory melting furnace must also be considered.

These two samples have quite distinct compositions, with that of GOV10 being similar to that of GOV9 (11% SiO₂ and the remainder almost entirely iron oxides) whereas GOV11 has 24% SiO₂ and 1.4% Al₂O₃. The trace element contents of these two samples are very similar to that of GOV9, with the REE profile of GOV11 particularly similar to that of GOV9.

GOV10 has an unusual microstructure, which, where homogeneous, is of a partially oxidised slag of coarse wustite dendrites in a fayalite matrix. The wustite shows substantial alteration to magnetite (with microtextures similar to that seen in hammerscale) and also overgrowth by magnetite leading to some small almost subhedral equant growths and more generally the development of coarse lamellar magnetite (similar very coarse magnetite lamellae have been reported from probable puddling slags by Young (2009)). These plates show high levels of silica on EDS analysis, and may be intimately intergrown with fayalite). Where less homogeneous the slag shows a more siliceous composition, being mainly an oxidised fayalite-wustite eutectic intergrowth, but in contact with relatively unaltered large pieces of coarse flake hammerscale. The contact between the two textures appears to coincide with the margin of a flow lobe, and it is possible that the inhomogeneous slags are external to the main flow. The flake scale included in the sample is approximately 800 µm thick and shows the extensive development of tabular porosity just above the basal surface. Similar scale (cf. GOV13 particles 3 and 5, GOV37 particle 3) was only observed in hammerscale samples taken from in Structure 14.

In contrast, GOV11 shows a microstructure of elongate fayalite in close association with equant euhedral grains of magnetite. The margins of the fayalite show intergrowths with, and rounded blebs of, a silica-rich material that appears to be a glass (detectable levels of potassium, calcium, phosphorus and aluminium), rather than silica itself. These peripheral structures may therefore represent a product of liquid immiscibility, but the intergrowths are too fine-grained for good quality microanalysis. The interstitial areas also contain small blebs of iron sulphides. The flow lobes are bounded by surficial zones of magnetite. These features clearly indicate that GOV11 is the product of solidification of a free-flowing, homogeneous melt.

One important characteristic of these three samples is that they have uniformly low sulphur content. Despite the blebs of sulphide visible in the section of GOV11, the XRF values for sulphur are 0.04, 0.04 and 0.08wt% for GOV9, 10 and 11 respectively. The phosphorous contents of the three slags are low too (0.46, 0.68 and 0.89 expressed as wt% P₂O₅).

The low phosphorus and sulphur contents of the tapped slags, GOV10 and GOV11, differ markedly from the high contents reported in most historical and recent analyses of both 'wet' and 'dry' puddling slags (see Table 3 of Young 2009). However, exceptions to this are to be found and it is not possible to exclude these slags having had an origin during puddling on this basis. However, it could be argued that by melting pig iron in a puddling furnace, impurities in the pig, such as phosphorus may have become concentrated in the molten slag rather than the nascent bloom. In a reverberatory air furnace the iron is maintained as a melt – so may retain these impurities and they may not necessarily become concentrated into any slag generated through reaction of iron and sand bed.

The significance of the hammerscale in GOV10 is unclear. It is certainly possible that the hammerscale was picked up by the tapped slag from the fettling of a puddling furnace. The presence of a 'halo' of coarse lamellar magnetite is significant. This texture has been associated with situations involving the oxidation of wustite. Similar microstructures have been recorded here in hammerscale, following earlier identification of the microstructure in residues from the fettling of puddled iron blooms at Llynfi Ironworks, Maesteg (Young 2009). The oxidation of a wustite-rich microstructure in a zone surrounding the scale would be compatible with what is known of reactions during the puddling process.

The detailed interpretation of these specimens must remain uncertain. The high degree of oxidation of GOV11 suggests an origin in refining, but equally it has been argued above that some slags may become oxidised in the melting furnace. For GOV10, the presence of coarse scale may be suggestive of this material being a puddling slag, from the process of wet puddling (pig boiling) which might have been employed in the Govan Bar Iron Works (although the evidence for refineries in the Pig Iron Works suggests that dry puddling was employed). However, since a reverberatory furnace might be charged with scrap, it is possible that scale might enter that system too (albeit not deliberately) from recycled material from the works that had not been descaled.

Iron-poor slags (Figure 4)

Iron poor slags generated during the melting of iron in a cupola furnace differ markedly from the slags formed when iron is melted in a reverberatory furnace because, firstly, the iron is melted in contact with the fuel, and secondly, if large quantities of iron are to be melted then it may be advantageous to flux the alumina-silicate slag with lime to ensure the cupola shaft does not become clogged. Under these circumstances the chemical composition of the slag generated may approach that of the slag generated during iron smelting in a blast furnace.

Caledonia Foundry:

During the present study it became clear that certain textures of slag could be associated with residues from cupola melting. These slag masses were in the form of lenticular masses probably originally 0.3 to 0.6m in diameter. The masses were extremely inhomogeneous, containing rather variable slags, coke, and iron droplets. Such slags formed the majority of the significant slag dumps on the Caledonia Foundry site, although the slag masses were rarely preserved as particularly large fragments. Samples LP4-05, LP4-

06, LP4-07, LP4-08, LP4-09, LP4-10, LP4-11 and LP4-13 were all drawn from such material; LP4-14 may also have been. Only LP4-12 (of the slags from the Caledonia Foundry) appears not have been of this form – and was from a pale stony slag flow with the surface associated with fine coke particles.

The analyses of the Caledonia Foundry cupola slags were rather variable, in part due to the sample volume being small compared with the scale of observed slag inhomogeneity. Factors that most of the analyses share include elevated titanium contents (1.4-2.1wt% expressed as TiO_2), a low $SiO_2:Al_2O_3$ ratio (<2.1 for the five low Mn slags; but >3.5 for the high Mn samples, LP4-11 and -13), low magnesium (<1.1% MgO, except for LP4-13 at 2.50wt% MgO), low calcium (<3wt% CaO), except for LP4-13 at 11.5% CaO), high silica (>50wt% SiO_2 except for LP4-07 at 36%) and high alumina (>28wt%, except for the high Mn slags, LP4-11 and -13 at 13% and 14% respectively). The slags show a close correlation between iron content and phosphorus, suggesting that the phosphorus is mainly contained with the metallic iron blebs. There is also a close correlation between elevated manganese and sulphur contents, although sulphur contents are generally low (0.04wt%S or below for all samples with low manganese, 0.10% and 0.22% for the high Mn samples, LP4-11 and -13 respectively). For all the low-iron slags from the Caledonia Foundry, the Upper Crust normalised REE profiles are rather flat (Figure 5).

The simplest way to explain these data is to model the low manganese slags (LP4-07, -08, -09, -12 and -14) as being dominated by fuel ash, with inputs from any other source being low.

For the high manganese slags (LP4-11 and LP4-13), the issue is not simply of manganese, but considerably extra silica is present. For LP4-13, the composition has also been modified by the addition of lime, raising the CaO content to 11.5% and the MgO to 2.50%. Either by coincidence or design the total of the additional SiO_2 , MnO, MgO and CaO required in this model (calculated by comparing the high-Mn slags to the average composition of the low-Mn slags) is the same for the two samples (amounting to approximately 53% of the total slag), but for LP4-11 23% of this addition is MnO, 70% SiO_2 , 1% MgO and 4% CaO, whereas for LP4-13 the values are 9%MnO, 63% SiO_2 , 4% MgO and 22%CaO.

If the calcium and magnesium are assumed to be a result of using a limestone flux, then the remaining addition to the average low-Mn cupola slag was 77% SiO_2 / 23% MnO for LP4-11 and 87% SiO_2 / 13% MnO for LP4-13.

The interpretation of the high-manganese slags is problematic. There are two main possible interpretations:

Firstly it is possible that the elevated manganese and silicon contents of the slags represents deliberate additions to boost the manganese and silicon content of the iron (for instance to compensate for a batch of iron with a particularly high sulphur content and to promote graphite formation). However, manganese control would normally be effected through additions to the iron in the ladle, rather than the furnace. In addition, it is worth noting that the sulphur contents of these samples is very low – with sulphur at about 2% of the level of Mn expressed as MnO – suggesting that manganese has not been used here a de-sulphidising agent.

The second alternative is that the elevated contents of silicon and manganese represent elements partitioned out of the melting metal and into the slag phase. Such a situation might arise if the material being melted was either pig rich in these elements, or perhaps recycled scrap steel.

In summary, the cupola slags at the Caledonia Foundry show that generally the melting was undertaken with no limestone flux. Some samples showed high manganese contents, possibly derived from recycling. One of the high-Mn samples was the only sample to show any indication of the use of a limestone flux.

Govan Ironworks Foundry:

Identification of the iron-poor slags at the Govan Ironworks Foundry was complicated by the use of large quantities of probable blast furnace slag as make-up for the foundry site during its construction.

Amongst the sampled material was just one large block which satisfied the criteria for recognition of cupola slag on textural criteria described above (GOV24). This block showed a khaki-cream mottled slag, with coke and large iron inclusions.

The whole-sample chemical analysis of the slag from this block shows that is markedly less calcic than most of the other low iron slags, with only the khaki glass GOV8, showing a similar bulk composition.

Plotting the composition of the spheroidal micro-residues interpreted as being cupola slag spatter and clinker, together with the smithing clinkers on the $CaO-SiO_2-Al_2O_3$ ternary diagrams (Figure 6; upper diagram shows relationships at 1600C, the lower at 1400C) shows a distribution involving low-calcium examples distributed in the region of the diagram between tridymite and mullite, but with a concentration of microresidues and the macro-clinkers at $SiO_2:Al_2O_3$ of 74:26 (molar oxide ratio; equivalent to molar Si/Al of 1.42). From this focus of "clinker" a scatter comprising most of the microanalyses from micro-particles texturally identified as cupola spatter forms an array of points towards the CaO pole.

Most of these spatter microanalyses lie in an area of the $CaO-SiO_2-Al_2O_3$ diagram in which the liquidus lies below 1600C. Very few of the analyses lie close to those of the low-iron macroscopic slags, which are sufficiently calcic to lie in an area in which the liquidus lies below 1400C.

The slag analysis from the macroscopic cupola slag (GOV24) is peripheral to the field of microanalyses of spatter particles, but not sufficiently distant to indicate that the macroscopic slag need be of a different origin to the spatter.

The analytical data therefore suggest a model in which slag samples GOV1-6, a tightly clustered group of analyses are interpretable as blast furnace slags. These slags show the maximum amount of lime that could be added to the melt without causing a significant rise in liquidus temperature. They can be subdivided into two subgroups (groups 1a and 1b) on the basis of trace element composition, but are all relatively basic, calcic, iron-poor (with no iron droplets recorded) and mostly moderately sulphidic (0.60 to 2.3 wt% S; most show oldhamite).

The differences observed in trace element chemistry between groups 1a and 1b, are probably related to a major difference also in their major element chemistry: group 1b have a much higher magnesium content than all the other low iron slags. Such a difference might result from the smelting of different ore (Young 1993 table 9.1 records significant variation in the magnesium contents of both blackband and claystone ironstones), but might equally result from the use of a somewhat dolomitised limestone as flux.

GOV28 and 30 are a pair of samples with similar chemical properties (group 2). They are slightly less calcic than the group described above. They have very flat upper crust-normalised REE profiles. On discriminants associated with the REE they behave close to the sample of cupola slag GOV24. On other trace element and major element discriminants they behave rather independently of both cupola slag and blast furnace slag. They have a much Si:Al ratio than the other low-iron slags. GOV28 was a variable stony-blue glass slag resembling GOV3 and GOV4 in appearance. GOV30 was a homogeneous dark grey-green glass, with an overall appearance somewhat similar to GOV7 and GOV8.

GOV7 and 8 are also a pair of samples (group 3) with properties between the blast furnace slags and the cupola slag, GOV24 (group 4). They show REE distributions (figures 10, 11) which are dissimilar to those of the cupola slag, but on other trace and major elements they are very similar to the cupola slag (figures 12-14; although slightly more calcic). Both samples contained iron blebs rich in Mn, Si and P.

The overall pattern of composition of these four groups is complicated. The diagrams in figures 10-15 show no single simple control, or differentiation between the classes. Changes to the fuel chemistry, the flux chemistry and the ore chemistry may all have affected both smelting and melting slags in various ways.

It is tentatively suggested that GOV7 and 8 are probably cupola furnace slags, whereas GOV28 and possibly GOV30 are less certainly so, but there is considerable uncertainty over the origin of these intermediate materials. If GOV28 and GOV30 were to be interpreted as smelting slags, then they might, arguably, have originated from the use of a more siliceous ore.

The group of possible cupola melting slags (chemical groups 2, 3, 4; GOV7, 8, 24, 28, 30) are linked by being less sulphidic than the probable blast furnace slags (0.35 – 0.50 wt% S; none shows the development of oldhamite).

The origin of the samples provides some supporting evidence for the interpretation of this entire group (i.e. chemical groups 2, 3 and 4) as cupola slags. The blast furnace slags GOV1-6 derive from slag-dominated make-up deposits ([22061], [23119]) that are probably early in the development of the site (and are very likely to be make-up prior to foundry construction). The problematic slags GOV7 and GOV8 both derive from surface deposits within the moulding shop [22286]. GOV28 was within a layer which was probably make-up for a floor [22067] in the southern part of the turning shop. GOV30 derives from an internal make-up deposit [22969] within the moulding shop (which also yielded the assemblage of melting slag spatter GOV23).

Clinker and smithing slag

Only a small number of samples were taken of macroscopic clinkers and smithing slags.

Samples LP4-18 and LP4-19 from WP3-LP4 were both from a fill of pit 60419 in casting floor (as were the microresidue samples LP4-24 and -25). LP4-19 was not examined microscopically, but its general morphology and chemical composition were broadly similar to LP4-18. Both samples had a morphology suggesting that they were smithing slags, but their iron contents were very modest (19.0 and 19.5wt% calculated as Fe_2O_3) suggesting that they might have been simple clinkers.

Two samples of similar materials were recovered from hearth bases in the boiler shop at Govan Ironworks Foundry (GOV33 and 34, from [22363] and [22512] respectively). These two samples showed significantly elevated iron contents (41wt% and 29wt%, respectively, calculated as Fe_2O_3). Neither of these samples was examined microscopically.

Despite their variation in iron content (and also in some of the other elements associated with iron, such as cobalt and nickel) these four samples show a good degree of consistency in their composition, which can therefore be taken as indicative of the composition of the coal residues.

Microresidues (Figures 16-18)

Microresidues remain a rather poorly-understood facet of archaeometallurgy. This study continues the approach of several recent investigations (Young 2008, 2009a, 2009b, 2010), but represents the first investigation (to the author's knowledge) of ferrous microresidues from an industrial context, apart from the rather different bloom-shingling microresidues described from Maesteg (Young 2009b).

When iron or steel is heated in air it will undergo superficial oxidation and, indeed, at high temperatures will readily burn. The oxidised surface layer of the iron is termed scale. Archaeological finds of detached scale are usually, particularly in pre-industrial contexts, derived from forging, so are termed hammerscale. Modern industrial practice means that scale is especially encountered during hot-rolling (the forming technique applied to most steel produced today), therefore the term millscale is more generally encountered in the modern literature.

Previous published studies of hammerscale from an archaeological perspective (e.g. Allen 1986; Unglik 1991) have focussed primarily on early smithing residues, but the experimental work of Dungworth and Wilkes (2009) carries more relevance for the present work because it was undertaken in a modern steel coke-fired hearth with an iron tuyère, and involved the smithing of both modern mild steel and late C19/early C20 puddled wrought iron.

There has been considerable modern research into the nature of millscale, but that work cannot, in general, be applied directly to archaeological materials, partly because of the differences in forming techniques being employed, but principally because of the differences between modern steels and historical or ancient wrought irons. In particular scaling behaviour is likely to have been different with historic materials because of the high slag content of wrought iron.

This investigation has examined two classes of scale – flake hammerscale produced during the surface oxidation of the workpiece (and broadly comparable to millscale) and spheroidal hammerscale, formed from droplets of molten material expelled during rapid squeezing of the workpiece at very high temperatures (typically from hammering, especially during forge welding).

Spheroidal particles:

The descriptions above demonstrate that a wide variety of broadly spheroidal particles were found in samples of microresidues. These range from the high sphericity particles of iron oxide-, or iron silicate-rich composition that can be identified as spheroidal hammerscale (Figure 16), through to much lower sphericity, often multi-component, grains indicative of formation from much more viscous, often clinker-like, materials (Figure 17).

The microresidue samples were taken from a wide variety of contexts. Some were taken from within the brick bases of smithing hearths in the smithy and boiler shop at the Govan Ironworks Foundry, and these might be expected to provide a baseline for residues from the hot-working of iron. These three samples (two from the smithy and one from the boiler shop) yielded abundant spheroidal particles (GOV15, GOV17, GOV19), of which 54 were examined on the SEM. Of these, 46 particles would be identified as spheroidal hammerscale, including one with an included quartz grain, thirteen with a large multicuspate central cavity and four with the shell reduced to an extremely thin layer. Eight grains did not fall within the definition of spheroidal hammerscale, and of these six were calcium-poor and two calcium-rich.

Aspects of this assemblage are unusual, in particular the common occurrence of particles with a large multicuspate central cavity (Figure 16 e, f). This particular morphology had a restricted range of mineralogy, being typically dominated by equant to stubbily-dendritic aluminous magnetite. Such grains are not typically encountered in welding residues from the use of wrought iron in earlier periods, but it is not currently known what facet of 19th century materials or techniques promotes the formation of spheroidal hammerscale of this morphology. It is noteworthy, however, that these large central cavities are associated with an oxygen-rich mineralogy, so exsolution of oxygen from the cooling melt may have been a major factor in development of the texture.

The relatively aluminous composition of many of the spheroids is probably a reflection of the interaction between the parent scale and clinker in the hearth – as demonstrated by several pieces of flake hammerscale (see below) with external masses of coarse Al-magnetite or Fe-hercynite.

The presence of quartz grains within otherwise iron oxide-dominated spheroidal hammerscale grains (examples from GOV15 and LP4-25) may tentatively be held of evidence for the use of a sand welding flux. The use of a flux to assist in forge welding (using either a quartz or a borax flux) became widespread, almost indiscriminate, in the 20th century with the ubiquity of mild steel, but in the 19th century might be expected to be more closely associated with the use of steel than the use of wrought iron (the low carbon content of wrought iron raises its welding temperature into the range in which the oxide scale is molten and the welding properties are also enhanced by the low melting point slag inclusions; in steels the lower melting point of the steel means that in the

temperature range desirable for welding the oxide scale may still be solid – and therefore an obstacle to obtaining a clean weld).

A somewhat similar assemblage, although with very few particles, was recovered from a pit in Structure 14 (GOV37) and it is possible that these grains were derived from the boiler shop to the east.

Assemblages of spheroidal particles from within the foundry areas at both the Caledonia Foundry and the Govan Ironworks foundry show significant numbers of particles with variants of a glass-mullite-spinel-iron mineralogy, or with related compositions bearing lime, melilite, anorthite or corundum (Figure 17). Such particles include six out of the twenty spheroidal particles in sample LP4-25 and seven out of thirteen particles from GOV23. These particles can be identified as minute droplets (spatter) of cupola furnace slag and their bulk composition plots across a similar field to those of the macroscopic cupola slags (Figure 6). These grains differ from the low-sphericity grains with multiple compositional domains, often with indications for not having been fully liquid or fully homogenised, that can be attributed to clinker (coal fuel ash), and which occur at low levels of abundance in coal-fuelled smithing microresidues. Such particles occurred in samples GOV17 and GOV19 from the Govan Ironworks Foundry smithy.

Tabular particles:

The microresidue samples also yielded abundant grains with a tabular morphology, most of which could be described as flake hammerscale (Figure 18 a-e), although some particles showed a silica-rich composition and a texture indicating solidification from a melt (Figure 18 g-h). These particles would be described as slag flats. There was a considerable degree of gradation between these two classes, with many flake hammerscale particles showing development of melt-textures along or near their basal detachment surface, while others showed the granular oxides of the scale reduced to islands within a slag matrix. Several particles showed adhering, relatively aluminous, material on the outer surface (e.g. Figure 18 e) – and these are interpreted as showing the influence of interaction with clinker.

For the samples from the boiler shop and smithy (mentioned above as yielding spheroidal hammerscale from brick hearth bases), the flake hammerscale assemblage examined under the SEM amounted to a total of thirty three particles. Of these, three particles were simple flake hammerscale with a fairly thin magnetite layer (up to 5% of the scale thickness; see material from Structure 14 below). A further eight particles showed a similar simple structure, but with the magnetite layer 7% - 12% of the thickness of the scale and six other examples had a much thicker magnetite layer (19-56%). Two of these particles showed evidence for interaction with clinker in the hearth (i.e. had aluminous material attached to their outer faces). Nine particles from these samples showed evidence of being substantially melted. Five particles showed the development of a rather porous structure of granular magnetite. Some of the above features resemble the rather complex variety of scale formed at temperatures of 570-700C, with a relatively much thicker magnetite layer than recorded at higher temperatures, particularly when cooled slowly (Chen & Yuen 2002).

The modern literature on oxide scale formation, however, deals almost exclusively with low carbon

steels, and the differences between modern millscale and the variety of materials described above may represent, at least in part, the diversity of ferrous materials being employed in the mid to late 19th century, including a variety of cast irons, steels and wrought iron.

There are several features of the scale from this assemblage that may aid interpretation. The interaction with clinker in the hearth has already been mentioned. This has generated external growths of coarse Al-magnetite and Fe-hercynite, often associated with irregularities in the overall growth form of the scale.

Some of the scale, in contrast, shows various changes to the scale structure starting at the basal surface. In simple oxide scale the basal surface may show minor development of a fayalitic intergranular film (e.g. Figure 18 c). Further degrees of slag development result in higher proportions of this fayalitic slag (which is also often highly phosphatic). In the fayalitic zone the oxide grains become reduced in size and frequently oxidised to magnetite. As the altered zone progresses towards the outside of the scale the leading edge of the alteration becomes characterised by the development of magnetite in a lamellar habit (e.g. Figure 18 f, g). Initially this appears a structure bridging the widened gaps between adjacent wustite grains (and resembling stitching), but may become a major phase in a fayalite-dominated microstructure. In the most molten textures, the external surface of the largely fayalitic scale may develop a thin oxide (probably mainly magnetite) crust very similar to that seen on slag-textured spheroidal hammer scale (Figure 18 g, h).

These textures appear to provide evidence for fluxing of the oxide scale by silicate-rich materials derived from within the oxidising material, rather than from outside. There are two potential sources for such silicate-rich materials – firstly the melting of slag inclusions within the metal (particularly perhaps in the case of wrought iron) and secondly the liberation of silicon from the alloy itself (likely to be particularly the case with cast irons). There is a very limited literature on scale formation on cast iron (e.g. Jedrzejczyk *et al.* 2008) and the reported porous textures do not appear to be similar to those seen here.

In contrast to the complex, partially melted scale of the smithing assemblages, Structure 14 yielded a rather different assemblage of flake hammer scale with a simple structure (Figure 18, a-d). This scale was thick (range 700 – 1840 µm, mean 1140 µm), even structured, externally smooth and planar, with (in all but one case) the wustite, magnetite and haematite layers very close to the 95:4:1 thickness ratio described by Chen & Yuen (2003) for scale formation at temperatures over 700C.

Suarez *et al.* (2006) give thickness-time curves for scale development on ultra low carbon iron. At 1200C they show scale grown in air could reach the 1800µm thickness observed here in approximately 300 seconds (5 minutes), but that at 1050C, it would take around 5000 seconds (approximately 80 minutes). They also showed that growth of the magnetite layer to the 88µm observed maximum would take around 2200 seconds (approximately 40 minutes) at 1200C and 5000 seconds (approximately 80 minutes) at 1050C. Clearly given the uncertainty over the nature of the substrate and conditions, detailed interpretation of heating history cannot be made, but it would appear unlikely that the scale from Structure 14 could have been grown in a heating period of less than 40 minutes, and given that the amount of slag migration observed close

to the basal surface of the scale was small, the temperature may have been closer to 1050C than 1200C, giving a minimum heating period of well over one hour. The scale structure certainly indicates heating at over 700C, and the diagrams of Suarez *et al.* would indicate heating periods of many hours would be required if the temperature were to have been much below 1000C.

The assemblage of tabular microresidue material from the backfill of pits in the moulding shop of the Caledonia Foundry resembles that from the boiler shop at the Govan Ironworks Foundry. Of the fifteen particles examined, seven showed evidence of having been molten, four were simple oxide scale, one was simple oxide scale with substantial basal melting and two were oxide scale with abundant magnetite plate development.

Grinding and turning waste (Figure 9)

Detritus from finishing processes was recovered from various locations with the Scotland Street Engine Works and the Govan Ironworks Foundry's finishing shop.

The Scotland Street works produced fine grained grinding waste from the east end of the Scotland Street block and much coarser swarf from the Paterson Street block (with its evidence from the plinths for large lathes or other turning machines). No metallurgical data could be obtained from the corroded fine-grained waste, and the metallography of the coarse swarf has been discussed above.

Deposits from both floor levels and within a pit in the finishing shop at the Govan Ironworks Foundry (GOV26, 27) yielded a more interesting set of fine-grained finishing residues, including abundant natural emery particles (produced at that period almost entirely from Naxos in Greece) together with quartz grains, coal dust and slag particles of a type not seen elsewhere on the site.

The slag grains include glassy slags with large laths of Zn-bearing olivine, possible Zn-bearing aluminous pyroxene, copper sulphides and copper-iron sulphides (Figure 19 a, c, d). The olivine bearing slags also (e.g. Figure 19 c) contain grains of quartz with rounded outlines suggesting reaction with the liquid phase. Although these fragments are too small for positive identification, they resemble slags from copper smelting. Copper slags were (and are) widely used as an abrasive after the introduction of air abrasion techniques. Sand blasting was first patented in 1870 (by Benjamin Tilghman) in the United States, but he moved to Britain to set up a works in Altrincham in 1879. Compressed air was not used in the process until after 1904, and most commentators assume that copper slag was not used as an abrasive in the process until after that development. Since then it has been widely used as an abrasive for cleaning metals (e.g. for removal of millscale). Whether the Govan works was employing copper slag at a much earlier period cannot be ascertained on the present material, but it is certainly a possibility.

Some of the samples of finishing waste (e.g. GOV26a and b from Govan Ironworks Foundry finishing shop and LP4-15 from STR17 in the Paterson Street building of the Scotland Street Engine works) contained small chips or swarf of copper alloy, discussed further below.

Brass foundry slags (Figure 20)

The compositions of the analysed samples are very variable; some show elevated very strongly elevated zinc and lead (to 20% and 1.9%, quoted as wt% oxides). These samples also show elevated sodium, and to a lesser extent potassium. This pattern suggests that for these samples the slags were generated through reaction with vapours. The lack of clear relationship between the slags and the structures, together with this evidence that they did not form directly within a metallurgical reaction, means that they do not meaningfully contribute to site or process interpretation.

Copper alloys (Figure 21)

Copper alloys were recovered from the crucible furnace shafts in the Scotland Street Engine Works (LP4-1, -2, -3, -4) where the copper prills probably represented accidental spillage, and also as chips and swarf from the Govan Ironworks Foundry finishing shop (GOV26a, b) and from machine base STR17 in the Paterson Street building of the Scotland Street Engine works (LP4-15).

In all cases the alloys found were leaded gunmetal (an alloy of copper containing lead, zinc and tin, as well as other trace metals) suitable for general purpose castings.

Discussion by site

WP3-LP3: Dundas Street Brass Foundry

The evidence from this site comprises various zinc-rich slags from the backfill of the flues associated with the foundry. Zinc is an easily vaporised element, so its concentration in residues in the foundry's flues would be expected, and unfortunately, provides little information on the activities being undertaken.

WP3-LP4: Caledonia Foundry/Scotland St. Engine Works

The evidence for the work of the Caledonia Foundry (c.1835-1867) is principally in the large quantity of cupola slags in the area of the yard. These demonstrate that the foundry was casting grey cast iron and that little, if any, flux was typically being used. Although a probable base for a cupola furnace of this phase was discovered, it gave little indication of the original size of the furnace.

The use of a flux in 19th century founding was clearly very variable. Some contemporary manuals do not even mention the possibility of working without a flux. Kirk (1899, p. 84) describes the use of a flux to produce a tappable slag (at 30-100lbs of limestone per ton of iron melted, with lower amounts corresponding to a charge with abundant dirty scrap or sand-coated sprues and gates). He states that if tapping slag is not required, flux may be added at 5-10 pounds per ton, to produce a brittle slag. He also notes that intermediate amounts of flux may be employed to promote slag formation to act as a "filter" to remove impurities from the iron. Such an effect might, for instance, be behind the high levels of manganese in two of the cupola slags from the Caledonia Foundry that had very high manganese contents.

West (1885) advocated use of small quantities of flux late in the heat, allowing the furnace to be cleaned, to drop better and to glaze the lining.

Palmer (1919, p. 306) suggested that some founders do not use a slag because they are using a large cupola for small heats, thus with little problem with blocking; that must be considered an alternative possibility here.

Tate (1904) also refers to the use of flux for long heats, but not for short ones.

The apparent lack of flux in most of the analysed samples may well be associated with the use of small 'heats', probably for the production of small castings and the use of a small furnace is probable indicated.

The grey iron samples seen were largely as blebs within the slags and, as discussed above, analyses of such blebs may not be entirely reliable as estimates of bulk metal composition, but high phosphorus contents were widespread, and this may, if deliberate, have been to promote fluidity of the iron during intricate castings.

The later history of the Engine Works was mainly documented through the presence of swarf in various machine settings. The deformation (cold working) of these samples rendered identification of the metal problematic, but the material in the late machine bases may be steel. The late works contained a crucible furnace for making small castings in gunmetal. A small fragment of a similar (although not quite identical) gunmetal in one of the machine bases of the Paterson Street block was probably indicative of the finishing of such components.

WP5: Govan Ironworks Foundry

The materials from the Govan Ironworks Foundry are principally residues from activities within the foundry with the exception of the initial site make-up, composed of blast furnace slag.

The blast furnace slag samples show well-fluxed compositions giving appropriately low melting points. The colours and textures of these samples correspond to those usually held to be indicative of the use of a hot blast. The stratigraphic origin of these samples is not quite precisely controlled, but it appears likely that the originating context is part of the make-up of the site prior to construction of the foundry. If that is the case, then these samples date to the early 1840s, the first few years of operation of one of the very first ironworks purpose-built to operate on the hot blast system.

Within the materials identified as blast furnace slags, the major group shows an elevated magnesium content compared with the other low-iron slags, possibly indicating either a different ore, or the use of a partly dolomitised limestone flux.

The core activity of the foundry is represented by residues, macroscopic and microscopic, of both cupola and reverberatory melting furnaces. In contrast to the contemporary activities at the Caledonia Foundry, the cupola furnaces at the Govan Ironworks Foundry were well-fluxed, reflecting the requirements for large heats for big castings. The amount of flux used was apparently variable, with the most highly fluxed materials having fluxing levels similar to that employed in a blast furnace. However, it must be remembered

that addition of flux during a heat is not normally a constant, so the waste materials will vary both with time through the heat and often with in homogeneity within the furnace too.

The site also employed at least one reverberatory melting furnace. The possible residues from this furnace are problematic – and certain discrimination from slags from the puddling process (which also involves a reverberatory furnace) is not currently possible. The failure of the furnace into the underlying gas flue does, however, provide an insight into the nature of the slag, albeit an unusual one.

Finishing processes included grinding and the recovery of grains of natural emery from the finishing shop indicates one of the abrasives employed. The sample deposits also included grains of slag with zinc-bearing olivine and copper sulphides, but also bearing partly dissolved grains of quartz. These appear to be grains of copper slag – a material widely used in the twentieth century as an abrasive. It is unclear whether these particles in the finishing shop are indeed actually an early use of this abrasive, or whether they are indicators of some unidentified process of non-ferrous metalworking on the site.

The hot-working of ferrous materials in the smithy and boiler shop gave rise to diverse assemblages of micro-residues. This diversity suggests that various metals were being worked, but a lack of comparative materials makes the assemblage difficult, at present, to decode.

The most puzzling aspect of the Govan Ironworks Foundry is 'Structure 14'. This structure contained a furnace which was both attached to, and by-passed by the exhaust gas system. The furnace shows an inclined array of internal supports, but has not yet been identified. The residues from this building were dominated by extraordinarily-thick flake hammerscale, which appears to suggest a process involving a prolonged heating of the iron. However, a lack of significant quantities of spheroidal microresidues makes it unlikely that this was a refining process, or one involving working with a hammer. Some form of heat treatment - perhaps making castings malleable might be the answer, but this is speculative. Interestingly, the scale from this structure closely resembles the scale inclusions found within one of the flow-lobed iron-rich slags of problematic origin.

References

- Allen, J.R.L. 1986. Interpretation of some Romano-British smithing slags from Awre, Gloucs. *Historical Metallurgy*, **20**, 97-104.
- Chen, R.Y. & Yuen, W.Y.D. 2003. Review of the high-temperature oxidation of iron and carbon steels in air or oxygen. *Oxidation of metals*, **59**, 433-468.
- Dungworth, D. & Wilkes R. 2009. Understanding hammerscale: the use of high speed film and electron microscopy. *Historical Metallurgy*, **43**, 33-46.
- Jedrzejczyk, D., Hajduga, M & Loreket, R. 2008. *High temperature oxidation as the method of surface treatment of cast iron*. Metal 2008 (<http://www.metal2011.com/data/metal2008/sbornik/Lists/Papers/030.pdf>)
- Kirk, E. 1899. The cupola furnace: A practical treatise on the construction and management of foundry cupolas. Henry Carey Baird & Co.
- Païdassi, J. 1956. Sur l'oxydation du fer dans l'air dans l'intervalle 400°–700°C. *Acta Metallurgica*, **4**, 227-229.
- Païdassi, J. 1958. Sur la cinétique de l'oxydation du fer dans l'air dans l'intervalle 700–1250°C. *Acta Metallurgica*, **6**, 184-194.
- Palmer, R.H., 1919. *Foundry practice; a text book for molders, students and apprentices*. John Wiley & Sons
- Tate, J.M. 1904. *Foundry Practice*. John Wiley & Sons.
- Taylor, S.R. & McLennan, S.M. 1981. The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philosophical Transactions of the Royal Society*, **A301**, 381-399.
- Unglik, H. 1991. Observations on the structures and formation of microscopic smithing residues from the Bixby Blacksmith Shop at Barre Four Corners, Massachusetts, 1824-55. *Historical Metallurgy*, **25**, 92-98.
- West, T.D. 1893. *American foundry practice: treating of loam, dry sand and green sand moulding, and containing a practical treatise upon the management of cupolas and the melting of iron (9th ed.)*. J. Wiley & Sons.
- Young T.P. 1993. Sedimentary Ironstones. pp. 446-489 In: PATTRICK, R.A.D. & POLYA, D.A. (eds) *Mineralization in Britain*, Chapman & Hall.
- Young, T.P. 2008a. *Archaeometallurgical residues from Coolamurry 7, 04E0323*. GeoArch Report 2006/10. 46pp.
- Young, T.P. 2008b. *Evaluation of archaeometallurgical residues from the M74 Completion: WP5, The Govan Ironworks Foundry*. GeoArch Report 2008/13. 7pp
- Young, T.P. 2008c. *Evaluation of archaeometallurgical residues from the M74 Completion: WP3-LP4 Dundas St Foundry*. GeoArch Report 2008/14. 2pp
- Young, T.P. 2008d. *Evaluation of archaeometallurgical residues from the M74 Completion: WP3-LP3 Caledonian Foundry/Scotland St Engine Works*. GeoArch Report 2008/15. 9pp
- Young T.P. 2009a. *Archaeometallurgical residues from Crickhowell Road, Trowbridge, Cardiff*. GeoArch Report 2009/02. 11pp.
- Young, T.P. 2009b. *Archaeometallurgical residues from Llynfi Vale Ironworks, Maesteg*. GeoArch Report 2009/18, 23 pp.
- Young, T.P. 2010. *Archaeometallurgical Residues from Portwall Lane, Bristol (BSRMG 2006/17)*. GeoArch Report 2009/34. 54 pp.

Illustration Captions

Figure 1. Examples of ferrous microstructures

- a. Caledonia Foundry. LP4-05. BSEM image of grey cast iron. Scale bar 2mm.
- b. Caledonia Foundry. LP4-05. BSEM image grey cast iron. Detail showing steadite between rounded grains in a graphite-poor area of the sample. Scale bar 100µm.
- c. Caledonia Foundry. LP4-06. BSEM image of grey cast iron bleb in glassy cupola slag. Scale bar 3mm
- d. Caledonia Foundry. LP4-06. Reflected light photomicrograph of same bleb as (c). Scale bar 1mm.
- e. Caledonia Foundry. LP4-06. Reflected light photomicrograph of same bleb as (d). Detail showing relationship of graphite, pearlite, cementite and steadite.
- f. Caledonia Foundry. LP4-07. BSEM image of grey cast iron with inhomogeneous texture.
- g. Caledonia Foundry. LP4-10. BSEM image of grey cast iron with strongly developed dendritic structure.
- h. Scotland Street Engine Works, Phase 2. LP4-21. Strongly deformed swarf with bands of pearlite and cementite, possibly steel. Scale bar 0.5mm.

Figure 2. Iron-rich slags

- a. Govan Ironworks Foundry. GOV12. Iron from flue below moulding shop. BSEM image near margin of iron flow showing fissured iron (white), with slag infill with iron sulphide, fayalite, leucite and mélonjosephite.
- b. Govan Ironworks Foundry. GOV12. Iron from flue below moulding shop. Reflected light photomicrograph, showing slag filled fissures (dark) in granular cementite (pale). Scale bar 0.2mm.
- c. Govan Ironworks Foundry. GOV9. Iron oxide-rich slag from moulding shop. BSEM image, showing typical texture of granular haematite/magnetite with minor secondary (altered?) fayalite. Scale bar 2mm.
- d. Govan Ironworks Foundry. GOV9. Iron oxide-rich slag from moulding shop. BSEM image, showing detail of texture of intergranular space, with fine granular haematite (white), silica (black) mélonjosephite (mid grey) and relict fayalite or fayalitic glass (pale grey). Scale bar 50µm.
- e. Govan Ironworks Foundry. GOV10. Flow lobed slag from near moulding shop. BSEM image showing hammerscale inclusion surrounded by fayalitic slag. Scale bar 500µm.
- f. Govan Ironworks Foundry. GOV10. Flow lobed slag from near moulding shop. BSEM image showing lamellae of magnetite overgrowing wustite in oxidised corona around hammerscale particle. Scale bar 100µm.
- g. Govan Ironworks Foundry. GOV10. Flow lobed slag from near moulding shop. BSEM image showing lamellae of magnetite overgrowing wustite in oxidised corona around hammerscale particle. Scale bar 250µm.
- h. Govan Ironworks Foundry. GOV11. Flow lobed slag from near moulding shop. BSEM image showing typical texture of fayalite plus magnetite. Centre of image shows oxidised flow lobe margin. Scale bar 500µm.

Figure 3. Upper Crust-normalised REE profiles for iron-rich slags (GOV9,10,11), coarse flake hammerscale (GOV13), thin flake hammerscale (GOV22), spheroidal microresidues dominated by cupola spatter (GOV23), variably altered firebrick (GOV29,31,32) and smelting slag/clinker (GOV33,34). All samples from Govan Ironworks Foundry.

Normalisation factors after Taylor and McLennan (1981).

Figure 4. Iron-poor slags (BSEM images)

- a. Govan Ironworks Foundry. GOV3. Blast furnace slag (chemical group 1b). Glass with dendritic oldhamite (white) and melilite (pale grey). Scale bar 30µm.
- b. Govan Ironworks Foundry GOV1. Blast furnace slag (chemical group 1a). Anorthite (dark) and Fe-Mn sulphides (white) in glass. Scale bar 100µm.
- c. Govan Ironworks Foundry GOV4. Blast furnace slag (chemical group 1b). Melilite slag with oldhamite. Scale bar 100µm.
- d. Govan Ironworks Foundry GOV5. Blast furnace slag (chemical group 1b). Melilite slag with voids after oldhamite. Scale bar 100µm
- e. Govan Ironworks Foundry GOV24c. Cupola slag.
- f. Caledonia Foundry. LP4-18. Cupola slag. Finely crystalline slag with multiple spinels and feldspar. Scale bar 60µm
- g. Caledonia Foundry. LP4-08. Cupola slag. Glassy slag with needles of mullite. Scale bar 600µm.
- h. Caledonia Foundry. LP4-14. Cupola slag. Mn- and Ca-enriched glassy slag with needles of mullite and dendritic Mn- and Al-rich magnetite. Scale bar 70µm.

Figure 5. Upper Crust-normalised REE profiles for iron-poor slags (cupola slags) from the Caledonia Foundry. Normalisation factors after Taylor and McLennan (1981).

Figure 6. Iron-poor slags displayed on SiO₂-CaO-Al₂O₃ ternary diagram. Upper diagram shows fields at 1600C, lower at 1400C. Fields based on information from FactSage. Shaded areas liquid.

- Red circles: iron-poor slags of chemical groups 1a, 1b and 2. (Govan Ironworks Foundry)
 Pink circles: iron-poor slags of chemical group 3. (Govan Ironworks Foundry)
 Blue circle: iron-poor slag of chemical group 4. (Govan Ironworks Foundry)
 Green circles: iron-poor slags (Caledonia Foundry)

- Blue crosses: area analyses from microresidue particles interpreted as cupola spatter (Caledonia and Govan Ironworks foundries)
 Blue triangles: area analyses from microresidue particles interpreted as clinker (Caledonia and Govan Ironworks foundries).

Red trend line is for specimens interpreted as blast furnace slags. Blue trend line is for microresidues interpreted as cupola spatter.

Figure 7. Plot of CaO+MgO against SiO₂ (values in wt%) for the low-iron slags from the Govan Ironworks Foundry (Groups 1-4) and from the Caledonia Foundry.

Figure 8. Plot of Al₂O₃ against SiO₂ (values in wt%) for the low-iron slags from the Govan Ironworks Foundry (Groups 1-4) and from the Caledonia Foundry.

Figure 9. Upper Crust-normalised REE profiles for low-iron slags from the Govan Ironworks Foundry. Normalisation factors after Taylor and McLennan (1981). Scaling as for figures 3 and 5.

Figure 10. Upper Crust-normalised REE profiles for low-iron slags from the Govan Ironworks Foundry. Normalisation factors after Taylor and McLennan (1981). Expanded y-axis to show discrimination of groups.

*Upper plot shows groups 1a and 3.
Middle plot shows group 1b
Lower plot shows groups 2 and 4.*

Figure 11. Bivariate plots showing ratios of Upper Crust-normalised REE concentrations, which describe the shape of the REE profile, for the groups of low-iron slag from the Govan Ironworks Foundry.

Figure 12. Bivariate plots showing the variation of Ba (ppm), U/Th (by elemental weight), Sr (ppm) and TiO₂ (wt%) with SiO₂ (wt%) for the groups of low-iron slag from the Govan Ironworks Foundry.

Figure 13. Bivariate plots showing the relationship between U (ppm), Th (ppm) Rb (ppm) and the total of the REE (Σ REE; ppm) for the groups of low-iron slag from the Govan Ironworks Foundry.

Figure 14. Bivariate plot showing the relationship between MgO and CaO (both wt%) for the groups of low-iron slag from the Govan Ironworks Foundry.

Figure 15. Bivariate plots showing the relationship of various siderophile elements (Mo, Ni, Cr, V, Cr in ppm; MnO in wt%) with iron (as wt% Fe₂O₃) for the groups of low-iron slag from the Govan Ironworks Foundry.

Figure 16. BSEM images of spheroidal hammerscale. All illustrated particles are from the Govan Ironworks Foundry smithy.

- GOV19, particle 9. High sphericity particle with delicate wustite dendrites in glass. Scale bar 600 μ m.*
- GOV17, particle 14. Magnetite external crust, internally wustite dendrites in glass. Bears remnant fragments of flake hammerscale. Scale bar 800 μ m.*
- GOV17, particle 7. Dense wustite particle, locally with polygonal grain boundaries. Scale bar 1mm.*
- GOV17, particle 8. Thin outer shell of magnetite with equant and dendritic forms. Scale bar 700 μ m.*
- GOV19, particle 6. Spheroid with multicuspate central cavity. Scale bar 600 μ m.*
- GOV19, particle 6. Detail of particle shown in (e) to show variation of polygonal equant grains to short angular dendrites of magnetite. Scale bar 100 μ m.*

Figure 17. BSEM images of spheroidal particles interpreted as clinker or cupola furnace spatter.

- Govan Ironworks Foundry moulding shop. GOV23, particle 4. Slightly irregular spheroid with multiple*

vesicles and inclusions of probable fuel ash. Scale bar 1mm. Interpreted as cupola spatter.

- Govan Ironworks Foundry moulding shop. GOV23, particle 4 (as (a)). Detail to show microstructure of swallow-tail twinned anorthite, set in a groundmass rich in dendritic hercynite. Scale bar 70 μ m.*

- Govan Ironworks Foundry smithy. GOV19, particle 10. Complex multi-component grain locally rich in anorthite and pyroxene. Interpreted as clinker droplet. Scale bar 500 μ m.*

- Govan Ironworks Foundry smithy. GOV17, particle 18. Complex multi-component grain with zones of (i) oxidised iron, (ii) of glass rich in mullite and (iii) of a fayalite plus magnetite slag. Interpreted as clinker-rich smithing slag droplet/spheroidal hammerscale. Scale bar 400 μ m.*

- Caledonia Foundry moulding shop. LP4-25, particle 1. Clinker-influenced particle with possible flake scale adhering to exterior. Interpreted as clinker-rich smithing slag droplet/spheroidal hammerscale. Scale bar 100 μ m.*

- Caledonia Foundry moulding shop. LP4-25, particle 3. Slightly irregular particle with primary coarse hercynite with reaction rims to magnetite + corundum, set in groundmass of spinels and probable Fe-gehlenite. Scale bar 100 μ m.*

Figure 18. BSEM images of flake hammerscale.

- Govan Ironworks Foundry 'structure 14'. GOV13, particle 1. Thick flake hammerscale showing simple structure. Scale bar 1mm.*

- Govan Ironworks Foundry 'structure 14'. GOV36, particle 1. Thick hammerscale, detail showing haematite and magnetite layers (somewhat damaged during specimen preparation), together with fine-scale exsolution of magnetite within the wustite layer. Scale bar 100 μ m.*

- Govan Ironworks Foundry 'structure 14'. GOV13, particle 2. Thick hammerscale showing simple structures in outer layers, large voids near basal surface, with grain boundary widening and slagging on basal margin. Scale bar 1mm.*

- Govan Ironworks Foundry 'structure 14'. GOV13, particle 2 (field of view immediately to the right of that in (c)). Large void, with characteristic downturned margins, in centre of flake has inhibited iron migration, so the outer magnetite zone is greatly thickened. Scale bar 1mm.*

- Govan Ironworks Foundry smithy. GOV14, particle 3. Thin flake hammerscale with very thick magnetite layer, simple internal structure and rounded surfaces on basal detachment, but with irregular aluminous outgrowth probably produced by adherence or reaction of clinker. Scale bar 100 μ m.*

- Govan Ironworks Foundry moulding shop. GOV22, particle 4. Thin flake hammerscale showing cavities close to basal surface in which lamellar magnetite overgrowths on oxidised wustite have formed. Smaller lamellae occur as 'stitching' across the widened grain boundaries. Scale bar 100 μ m.*

- Govan Ironworks Foundry boiler shop. GOV20, particle 8. Complex melt-textured flake hammerscale. Has outer magnetite-haematite crust, then thick layer with development of lamellar magnetite with large equant hercynite grains. The inner zone is composed of rounded wustite pseudodendrites (and locally true dendrites). Scale bar 300 μ m.*

- Caledonia Foundry moulding shop. LP4-24, particle 10. Melt textured hammerscale (or slag flat). Shows outer columnar/dendritic magnetite zone, a central zone of blebby to dendritic wustite and an inner zone dominated by fayalite (with a wustite cotectic). Scale bar 100 μ m.*

Figure 19. BSEM images of grinding residues. Govan Ironworks Foundry, Finishing Shop (see also plate 21, b-d)

- a. GOV26a. View showing corroded grey cast iron particle at top, with small particles cemented by iron oxides (including both emery and possible copper slag) towards base. Scale bar 700µm.
- b. GOV26a. Multiple particles of natural emery, together with grains of quartz, coal and corroded iron, bound by iron oxides. Scale bar 600µm.
- c. GOV26a. Detail of possible copper slag particle seen in (a). Elongate crystals are of olivine. Dark grains to left with resorption textures are quartz. Scale bar 100µm.
- d. GOV26a. Detail of a second possible copper slag particle. Elongate Zn-bearing olivines in glass with iron-copper sulphide blebs. Scale bar 100µm.
- e. GOV26a. Detail of an emery particle. Scale bar 100µm.
- f. GOV27a. Angular grain of glassy slag bearing skeletal magnetite. Scale bar 200µm.
- g. GOV26a. Detail of an emery particle. Scale bar 100µm.
- h. GOV27a. General view of 'floor' deposit showing quartz, coal and iron oxide particles bound by iron oxides. Scale bar 1mm.

Figure 20. BSEM images of zinc-rich slags. Dundas St. Brass Foundry

- a. LP3-1. Zincite particle in calcic glass, which also bears small gahnitic spinels. Scale bar 600µm.
- b. LP3-4. Coarse melilite laths in glass with small Al-diopside dendrites. Scale bar 200µm.
- c. LP3-2. Zincite, altered to willemite, overgrown by elongate prisms of willemite. The glassy matrix also bears euhedral grains (dark) of gahnite with franklinite rims. Scale bar 100µm.
- d. LP3-2. Zincite, altered to willemite, overgrown by elongate prisms of willemite. The glassy matrix also bears euhedral grains (dark) of gahnite with franklinite rims. Scale bar 600µm.

Figure 21. BSEM images of copper alloys

- a. Scotland Street Engine Works. LP4-01. Prill of leaded gunmetal from crucible furnace. Scale bar 200µm.
- b. Govan Ironworks Foundry, Finishing Shop. GOV26a. Leaded gunmetal fragment. Scale bar 700µm.
- c. Govan Ironworks Foundry, Finishing Shop. Leaded gunmetal swarf. GOV26b. Scale bar 1mm.
- d. Govan Ironworks Foundry, Finishing Shop. GOV26b. Leaded gunmetal swarf. Scale bar 600µm.

Table 1: Samples selected for analysis from WP3

name	SEM	EDS	Chem	sample	source	
LP3-01	x	x	x	<5001>	50261, backfill of flue	green viscous glassy slag
LP3-02	x	x		<5001>	50261, backfill of flue	dark glassy slag flow
LP3-03	x	x		<5010>	50275, backfill around furnace 50164	purple clinker
LP3-04	x	x	x	<5010>	50275, backfill around furnace 50164	grey vesicular stony slag
LP3-05	x		x	<5005>	50244	pale sand
LP3-06	x		x	<5006>	50405	dark sand
LP4-01	x	x		<6002>	60422, in crucible chamber 60409, STR1	small Cu-alloy prill
LP4-02	x	x		<6002>	60422, in crucible chamber 60409, STR1	small Cu-alloy prill
LP4-03	x	x		<6002>	60422, in crucible chamber 60409, STR1	small Cu-alloy prill
LP4-04	x	x		<6002>	60422, in crucible chamber 60409, STR1	large Cu-alloy flow
LP4-05	x	x		<6040>	60594, slag deposit, Area III, E Courtyard	iron particle from large cupola slag mass (shows considerable entrainment of sand)
LP4-06	x	x		<6040>	60594, slag deposit, Area III, E Courtyard	iron particle from large cupola slag mass
LP4-07	x	x	x	<6042>	60598, ashy gravel, S of sandstone bldg B60861	isolated iron particle for SEM and pale grey slag sample for chem
LP4-08	x	x	x	<6042>	60598, ashy gravel, S of sandstone bldg B60861	grey slag
LP4-09	x	x	x	<6043>	60599, ashy gravel, S of sandstone bldg B60861	cupola slag, SEM sample has iron bleb
LP4-10	x	x		<6043>	60599, ashy gravel, S of sandstone bldg B60861	isolated iron bleb, close to LP3-09
LP4-11	x	x	x	<6015>	60262, slag rich ashy deposit, B60256	dark brown glassy slag from large coke rich flow puddle coke rich white stony flow with clinkery surface (SEM mount hoped to have slag and isolated bleb)
LP4-12	x	x	x	<6015>	60262, slag rich ashy deposit, B60256	
LP4-13	x	x	x	<6021>	60537, mixed slag/fuel deposit, Patterson St block W of machine row	dark brown glassy slag, with iron bleb in SEM block
LP4-14	x	x	x	<6016>	60263, slag-rich brown deposit, B60256	pale stony slag ball surrounded by clinkery slag
LP4-15	x	x		<6035>	60573, loose red deposit, assoc M/B 060531, STR17	fine particles
LP4-16	x	x		<6035>	60573, loose red deposit, assoc M/B 060531, STR17	aggregate
LP4-17	x	x		<6035>	60573, loose red deposit, assoc M/B 060531, STR17	large particles
LP4-18	x	x	x	<6006>	60344, dark deposit, casting pits?, pit 60419	smithing slag #1
LP4-19			x	<6006>	60344, dark deposit, casting pits?, pit 60419	smithing slag #2
LP4-20	x	x		<6037>	60592, loose deposit in concrete box STR19	medium swarf
LP4-21	x	x		<6044>	60592, fill of M/B STR19	medium-small swarf
LP4-22	x	x		<6087>	60993, machine chamber STR2	very large swarf
LP4-23	x	x		<6006>	60344, pit 60419, casting pits	clinker
LP4-24	x	x		<6006>	60344, pit 60419, casting pits	flake
LP4-25	x	x		<6006>	60344, pit 60419, casting pits	spheroids
LP4-26	x			<6073>	60912, moulding sand, fill of ?furnace 60906, STR13	fresh "sand"
LP4-27	x			<6027>	60664, loose silty sand within brick walls 60663	fresh "sand"
LP4-28	x	x		<6018>	60454, black moulding sand, Patterson Street, W of machine row	used sand

Table 2: Samples selected for analysis from WP5

specimen	context	sample	location	material	notes	SEM	EDS	Chem.
GOV1	22061	2053	Site make-up	blast furnace slag	dark glass with convoluted surface	x		x
GOV2	22061	2053	Site make-up	blast furnace slag	dark glass with convoluted surface grading into honeycomb texture	x		x
GOV3	22061	2053	Site make-up	blast furnace slag	porcellanous grading to blue glass	x		x
GOV4	22061	2053	Site make-up	blast furnace slag	stony with marginal blue glass, dimpled base with coke	x		x
GOV5	23119	2124	Site make-up	blast furnace slag	stoney, vesicular dense	x		x
GOV6	23119	2124	Site make-up	blast furnace slag	stoney, vesicular, lobed top	x		x
GOV7	22286	2047	Moulding shop	blast furnace slag	blue-green glass in thick contorted flow	x		x
GOV8	22286	2047	Moulding shop	blast furnace slag	khaki-green glass in thick contorted flow	x		x
GOV9	22286	2047	Moulding shop	refining slag	dense vesicular iron oxide slag - ?refining	x		x
GOV10	22769	2117	Make-up ear cupola base	refining slag	puddling tapped slag	x		x
GOV11	22769	2117	Make-up ear cupola base	refining slag	puddling tapped slag	x		x
GOV12	22336	2147	Flue below moulding shop	iron	iron flow in flue	x		
GOV13	23140	2144	structure 14	scale	thick flake scale from Structure 14	x		x
GOV14	22363	2086	smithy hearth, boiler shop	scale	thin flake h/s	x		
GOV15	22363	2086	smithy hearth, boiler shop	scale	spheroidal h/s	x		
GOV16	22806	2133	fill of hearth in S end of smithy	scale	thin flake h/s	x		
GOV17	22806	2133	fill of hearth in S end of smithy	scale	spheroidal h/s	x		
GOV18	22726	2060	small smithy hearth	scale	thin flake h/s	x		
GOV19	22726	2060	small smithy hearth	scale	spheroidal h/s	x		
GOV20	22512	2088	smithy hearth, boiler shop	scale	thin flake h/s	x		
GOV21	22512	2088	smithy hearth, boiler shop	scale	spheroidal h/s	x		
GOV22	22960	2120	makeup	scale	thin flake h/s	x		x
GOV23	22960	2120	makeup	scale	spheroidal h/s	x		x
GOV24	22421	2042	Moulding shop	melting slag	slag from possible bear	x		x
GOV24A	22421	2042	Moulding shop	iron	large cast iron particle from possible bear	x		
GOV24B	22421	2042	Moulding shop	iron	small cast iron particles from possible bear	x		
GOV24C	22421	2042	Moulding shop	iron	cast iron in coke from possible bear	x		
GOV25A	22139	2061		iron	cast iron in "floor"	x		
GOV25B	22139	2061		iron	cast iron in "floor"	x		
GOV25C	22139	2061		iron	cast iron in "floor"	x		
GOV26A	22803	2076	"pit" in finishing shop	iron?	particles in "pit" in finishing shop	x		
GOV26B	22803	2076	"pit" in finishing shop	iron?	particles in "pit" in finishing shop	x		
GOV27A	22067	2152	"floor" in finishing shop	iron?	particles in "floor"	x		
GOV27A	22067	2152	"floor" in finishing shop	iron?	particles in "floor"	x		
GOV28	22067	2152	Turning shop	blast furnace slag	porcellanous grading to blue glass	x		x
GOV29	23203	2145	"T" shaped feature in NW	ceramic	altered flue	x		x
GOV30	22969	2120	Moulding shop	blast furnace slag	dark green grey homogenous glass	x		x
GOV31	22286	2047	Moulding shop	ceramic	white, slightly altered firebrick			x
GOV32	22286	2047	Moulding shop	ceramic	grey-red reduced brick			x
GOV33	22363	2086	smithy hearth, boiler shop	smithing slag	smithing slag	x		x
GOV34	22512	2088	smithy hearth, boiler shop	fuel residue	clinker			x
GOV36	23150	2137	structure 14	scale	thin and thick flake h/s	x		
GOV37	23150	2137	structure 14	scale	spheroidal h/s	x		
GOV38A	22945	2123	"pit" in finishing shop	iron	iron from "pit" in finishing shop (equant fragment)	x		
GOV38B	22945	2123	"pit" in finishing shop	iron	iron from "pit" in finishing shop (large platy fragment)	x		
GOV39	22422	2121	Moulding shop	sand	sand from moulding shop	x		

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