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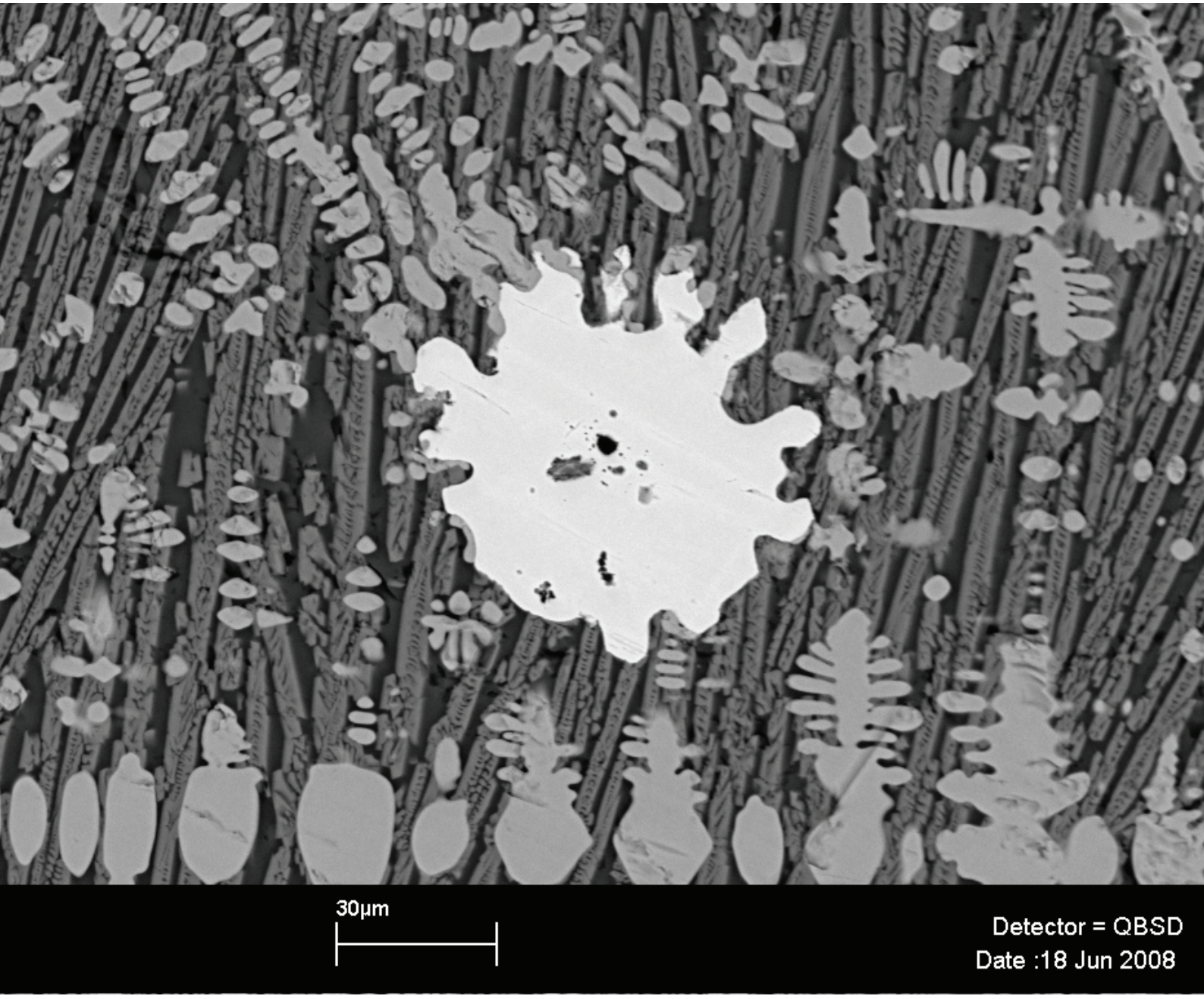
REDCLIFF, WELTON, EAST YORKSHIRE
AN EXAMINATION OF THE SLAG

TECHNOLOGY REPORT

David Dungworth



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AN EXAMINATION OF THE SLAG

David Dungworth

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SUMMARY

The excavation of a coastal trading settlement of the first century AD on the northern shore of the Humber recovered a small quantity (10kg) of iron-working slag. A careful examination of the material suggests that this was generated during primary manufacture (smelting). The assemblage included samples of iron-rich material that appear to represent the metal that was produced — a carbon-rich steel.

ACKNOWLEDGEMENTS

I would like to thank Steven Willis and John Creighton for allowing me to work on the Redcliff iron-working assemblage. I am particularly grateful to them for their patience in allowing me to re-examine the material. I apologise to them for the rather misleading nature of the first (2000) report and hope that the current report can be taken as the basis for the published account of the ironworking at Redcliff. I would like to thank James Folkes who helped with the examination of the slag in the 1990s (but who cannot in anyway be held responsible for my misidentifications). I would like to thank Sarah Paynter who provided a second opinion on the Redcliff slag during the re-examination in 2007–8.

ARCHIVE LOCATION

The slags are currently held by Steven Willis, Canterbury University but will be deposited with Kingston-upon-Hull Museum

DATE OF RESEARCH

1995–2008

CONTACT DETAILS

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INTRODUCTION

This report describes the examination and scientific analysis of ironworking debris recovered during the archaeological excavations at Redcliff. The assemblage was first examined by the author in the 1990s and a report submitted to the excavators in 2000 (a copy forms part of the site archive held by Steven Willis). The 2000 report concluded that the assemblage comprised almost exclusively iron smithing slag. In the years that have followed the author has had the opportunity to examine many other ironworking assemblages. Suspicions about the conclusions of the 2000 report were such that in 2007 the author requested the opportunity to re-examine the whole assemblage. Between 2007 and 2008 the assemblage was re-examined, existing samples re-analysed and new samples selected for further study. As detailed below, the assemblage is now interpreted as a smelting assemblage. This report should completely replace the 2000 report.

SITE BACKGROUND

Redcliff lies on the north shore of the Humber (NGR SE 981 249) close to North Ferriby. An area of almost 1000m^2 was excavated between 1986 and 1988 by a team which included David Crowther, Steven Willis and John Creighton (Crowther 1987; Crowther *et al* 1989; 1990). The excavation revealed signs of habitation dating mainly to the first century AD. The richness of the artefactual record suggests that Redcliff was an important trading site during the period between the Roman conquest of southern Britain and the early 70s when northern England was conquered. During this period Redcliff would have been on the edge of (but just outside) the Roman empire.

TECHNOLOGICAL BACKGROUND

The visual appearance of the slags examined (see Figures 1–4) leaves little doubt that they have resulted from the production and/or manipulation of iron (or iron alloys) rather than from the working of other metals (eg copper alloys). During the period of occupation at Redcliff the production of metallic iron (and occasionally steel) was carried out using the bloomery process (Bayley *et al* 2001; Crew 2000; McDonnell 1986; Paynter 2007a; Tylecote *et al* 1971) in which some of the iron in the iron ore was reduced to metallic iron (in the solid state) while the remainder reacted with gangue minerals in the ore, clay furnace lining and charcoal ash to form a liquid slag. Two separate *chaînes opératoires* for the bloomery smelting process have been identified: in the first the waste slag is simply allowed to collect at the base of the furnace, while in the second the furnace is provided with an opening near the base through which slag is removed. Even where the furnace superstructure does not survive, it may still be possible to identify the *chaîne opératoire* through the morphology of the slag. Where the slag is removed from the furnace by

allowing it to flow through the opening near the base it takes on a characteristic 'tapped' morphology (Bayley *et al* 2001; McDonnell 1983). In contrast, the slag which simply collects within the furnace often forms at the base of the furnace and forms a plano-convex 'furnace bottom' (Paynter 2007a), examples of which can reach substantial dimensions (up to 1m in diameter and 0.5m thick). The manipulation (smithing) of iron also produces characteristic slags which allow the identification of this process. The heating of iron as part of smithing usually leads to some oxidation of the surface and fragments of this oxidised surface (hammerscale) can form substantial proportions (in excess of 50% by weight) of contexts associated with iron smithing (Mills and McDonnell 1992; Dungworth and Wilkes 2005). Even where a deliberate hammerscale sampling strategy has not been employed, hammerscale is often recovered from environmental soil samples. Smithing also usually produces concave-convex lumps of slag which are substantially smaller (and more porous) than furnace bottoms, typically 0.15m in diameter and 0.05m thick.

AIMS AND OBJECTIVES

This report aims to provide a comprehensive account of the ironworking debris that was recovered during the archaeological excavation at Redcliff. The main objective (of this and the 2000 report) has been to identify the nature of the metalworking processes which produced this debris and their significance for our understanding of the site in the first century AD.

METHODS

The assemblage of ironworking debris from Redcliff was examined visually. This methodology is well-established (Bayley *et al* 2001; Crew 1995; McDonnell 1983; Paynter 2007a) and relies on the identification of distinctive traits such as colour, size, shape, and surface texture which can be used to relate individual fragments of ironworking debris to particular processes.

As will be seen below, the Redcliff assemblage contains very few distinctive fragments and the author's examination in the 1990s led to the misidentified of most of the pieces. The 2007–8 re-examination has benefited from the extra experience gained by the author since the first examination. In addition, the author has sought second opinions from colleagues who have further experience of prehistoric iron smelting debris.

The Redcliff assemblage contains few of the more commonly reported categories of ironworking debris and so a high proportion of the assemblage has been sampled for scientific examination. The samples (25 in total) were selected to reflect the widest range

of types, sizes and shapes of material present with an emphasis on material from secure contexts. The selected samples were detached using a rock saw and embedded in epoxy resin. The embedded samples were ground and polished to a 1-micron finish. The samples were examined first using an optical microscope and then with a scanning electron microscope. The chemical composition of the samples was determined using an energy dispersive X-ray detector attached to the scanning electron microscope. The chemical compositions were determined by analysing a series of areas (each usually 0.02–0.1mm^2). Each area was carefully positioned to avoid parts of the sample which had undergone post-depositional alteration. The number of areas analysed on each sample was varied depending on sample homogeneity/heterogeneity (minimum = 4, maximum = 10).

The analysis of multiple areas of each sample allowed the quantification of sample homogeneity/heterogeneity. A value H was calculated for each sample by summing the product of the standard deviation and mean for each oxide present. Few assemblages have been approached in this way, but comparisons can be made with the author's data from Heckfield (Dungworth 2007) and Trevelgue (Dungworth forthcoming) and data from McDonnell's PhD thesis (McDonnell 1986). Samples of tap slag (the most common form of iron smelting slag in the Roman and medieval periods) usually have consistently low values of H (that is 1.2±0.5) indicating that the slags are very homogeneous. It should be noted that all of the H values considered here have been calculated using the same technique (SEM-EDS analysis of multiple areas) and the precision of this technique is such that a perfectly homogeneous sample of bloomery slag is unlikely to yield a H value of less than 0.5. This is due to the size of the crystalline phases present (up to 0.2mm^2) compared to the areas analysed (up to 0.1mm^2). The calculation of H values for an analysed sample of ironworking debris also addresses a perennial problem with SEM-EDS analyses, how many areas should be analysed to obtain data that is representative of the sample as a whole. H values were calculated for each sample after the collection of data from each area and analysis of a sample was stopped only once H values had reached stable minima. Smithing slags tend to give rather high H values (6.7±4.1) reflecting their heterogeneity due to the fact that they have largely formed at temperatures below that required to fully melt them. The iron smelting slags of the pre-Roman period are usually not tap slags and these frequently have H values (2.4±1.0) between those of tap slags and smithing slags.

DESCRIPTION OF THE ASSEMBLAGE

The assemblage comprises 10kg of ironworking debris. This includes several fragments of furnace bottoms, slag prills and vitrified ceramic lining, but most fragments are lumps which lack any distinctive morphology which would clearly indicate the process(es) which produced them (Table 1).

Table 1. Summary details of the different types of slag recovered (weights in grams, density in grams per cubic centimetre)

Type	Abbrev.	Weight	Number	average weight	average density
Furnace bottom	FB	1238	1	1238	3.3
Furnace bottom (possible)	FB?	2264	4	566	2.9
Dense iron silicate	DIS	141	2	71	3.7
Slag prills	PRILL	663	10	66	3.3
Slag lump with abundant charcoal impressions	SLIC	48	1	48	2.5
Vitrified ceramic lining	VCL	821	6	137	1.5
Non-diagnostic ironworking slag	ND	3971	48	114	2.8
Ore	ORE	228	2	114	3.4
Metallic iron	Fe	975	13	75	
Total		10349	87	119	2.8

Table 2. Total weights of slag recovered per phase (grams)

Phase	Weight
1–3	13
2	758
3	1166
4	3018
5	5343
us	51

As described above, furnace bottoms are plano-convex lumps of slag which are substantially larger than smithing hearth bottoms (cf Bayley *et al* 2001). They are characteristic of iron smelting where the slag was not tapped from the furnace but instead was allowed to collect in the base of a smelting furnace (Paynter 2007a). The single certain fragment of furnace bottom from Redcliff (Figure 1) is rather smaller and weighs only 1.2kg. When complete it is likely to have been approximately 0.3m in diameter, 0.1m thick and weighed around 2.5kg. The fragments of possible furnace bottom are less complete but give no indication that any were originally any larger. These lumps of slag are substantially larger and more dense than smithing hearth bottoms. The examination of iron smelting slags from other prehistoric sites in Britain suggests that such small furnace

bottoms are not unique to Redcliff. Despite their small size, the Redcliff furnace bottoms indicate that iron smelting took place.

Figure 1. Fragment of furnace bottom (sample # 22)

Figure 2. Fragments of possible furnace bottom (sample #18)

Two fragments of dense iron silicate were recovered from Redcliff. Dense iron silicate slag is easily recognised by its high density and the fact that most surfaces are fractured, however, the process(es) which produced this type of slag is not obvious. The high density (and lack of porosity) of this type of slag suggests that it was probably produced during iron smelting rather than smithing. It is possible that dense iron silicate slag comprises fragments of furnace bottoms; these may have been removed from the furnace and have been broken in the process.

One of the types of slag recognised among the Redcliff assemblage is slag prills (Figures 3 and 4). This is characterised by well melted surfaces and evidence that it had flowed but, unlike tap slag, the flow appears to have been predominately vertical rather than horizontal. This suggests that the movement of slag prills occurred entirely within a furnace. In addition, the contorted shapes of some examples suggest flow around obstacles, possibly charcoal. The smooth surfaces of slag prills show that the slag had a high surface tension and did not 'wet' the surface of the charcoal. The small size of slag prills indicates that they did not travel significant distances inside the furnace and remained isolated from each other (otherwise they would have formed larger masses of slag such as furnace bottoms). Slag prills are not widely reported in the archaeometallurgical literature although references to them are limited to iron smelting sites (see Crew 1995; 2000, 39;

Dungworth in preparation; Dunikowski and Cabboi 1995, Fig 100; McDonnell 1988; Paynter 2007a).

Figure 3. Slag prill (sample #70)

Figure 4. Slag prill (sample #27)

A single lump of slag which had a surface almost completely comprising the impressions of charcoal was noted. This type of slag is more abundant among some other early iron smelting assemblages, such as North Cave (McDonnell 1988) and Trevelgue Head (Dungworth forthcoming).

Vitrified ceramic lining consists of parts of the furnace superstructure which have survived due to the vitrification of the inner surface.

Almost 40% of the assemblage of slag from Redcliff comprises non-diagnostic slag. The density and colour of the non-diagnostic slag leaves little doubt that it was produced by ironworking rather than the production or manipulation of other metals, such as copper alloys, but it lacks any diagnostic characteristics that allow it to be associated with any particular ironworking process. In particular it is not possible, on the basis of the visual examination of this material, to be certain whether it was produced by iron smelting or iron smithing. The absence of any materials diagnostic of iron smithing (hammerscale or smithing hearth bottoms) make it likely that all of the non-diagnostic ironworking slags from Redcliff were produced by iron smelting. While non-diagnostic ironworking slags rarely form significant elements within smelting slag assemblages where the slag was tapped from the furnace, they are often present in significant proportions among assemblages where slag collected within the furnace. Among iron smelting assemblages, non-diagnostic slags appear to be most abundant when large furnace bottoms were not

formed (eg Dungworth forthcoming; cf McDonnell 1988). The initial classification of the Iron Age bloomery slags from Bryn Y Castell included over ten types but almost half the assemblage was recorded as 'unclassified' (Crew 1986a; 1986b).

MICROSTRUCTURES

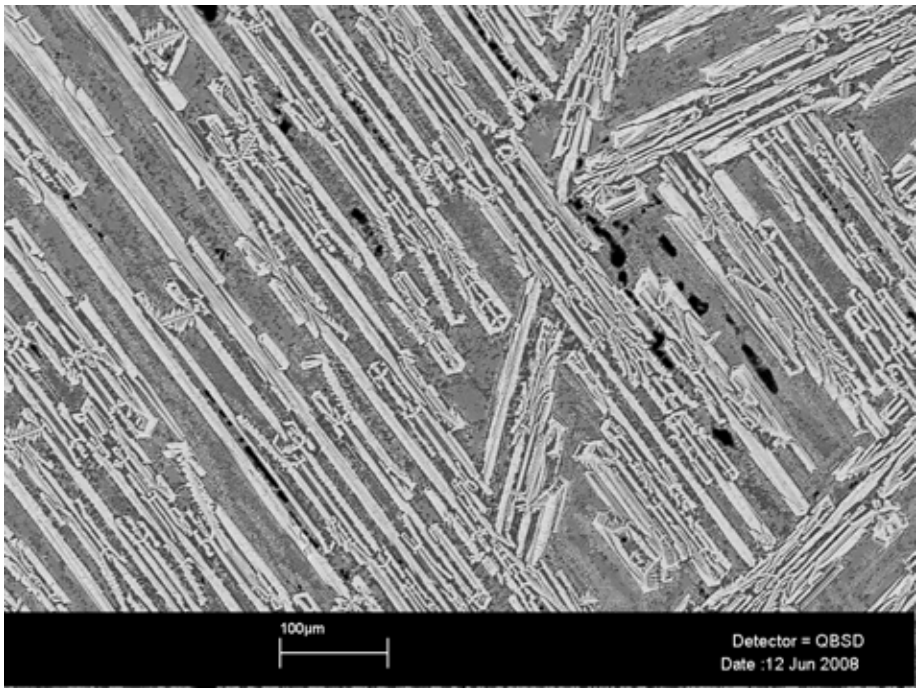

Figure 5. SEM image of sample #86 (back-scattered electron detector) showing long, thin light grey crystals of fayalite (Fe_2SiO_4).

The 25 samples selected for chemical analysis were also inspected using optical and scanning electron microscopes and microstructural features noted. In most respects the samples contain the range of phases that are routinely observed in bloomery smelting slags: fayalite, wüstite and a glassy groundmass (Morton and Wingrove 1969; McDonnell 1986). All samples contain substantial proportions of the mineral fayalite (Fe_2SiO_4) but the crystal form varies from the very long but thin laths of sample #86 (Figure 5), through thicker laths (eg sample #18, Figure 6), to the relatively large euhedral crystals of sample #05 (figure 7).

Between the fayalite crystals there is a glassy groundmass which is difficult to characterise chemically. The glassy groundmass is found throughout the slag but in small areas which are generally too small to allow meaningful analysis of this phase alone with the techniques available. In addition, the glassy groundmass is rarely homogeneous but frequently has a complex eutectic microstructure (cf Figure 8). Given the overall

composition of the slags and the range of phases present, the groundmass is likely to be rich in silica, alumina, phosphorus, potassium, magnesium and calcium.

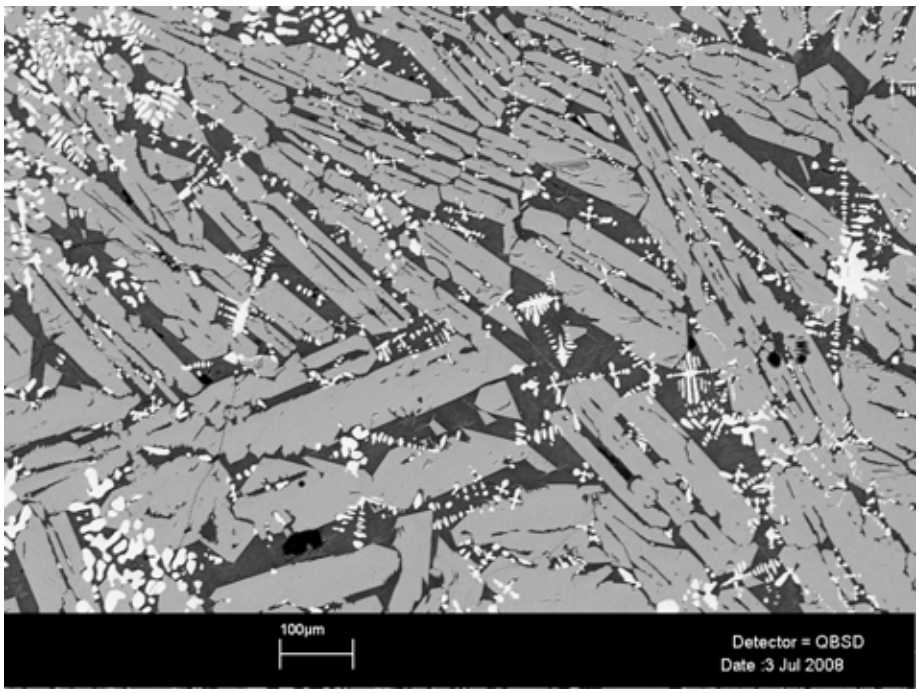

Figure 6. SEM image of sample #18 (back-scattered electron detector) showing laths of fayalite (mid grey)

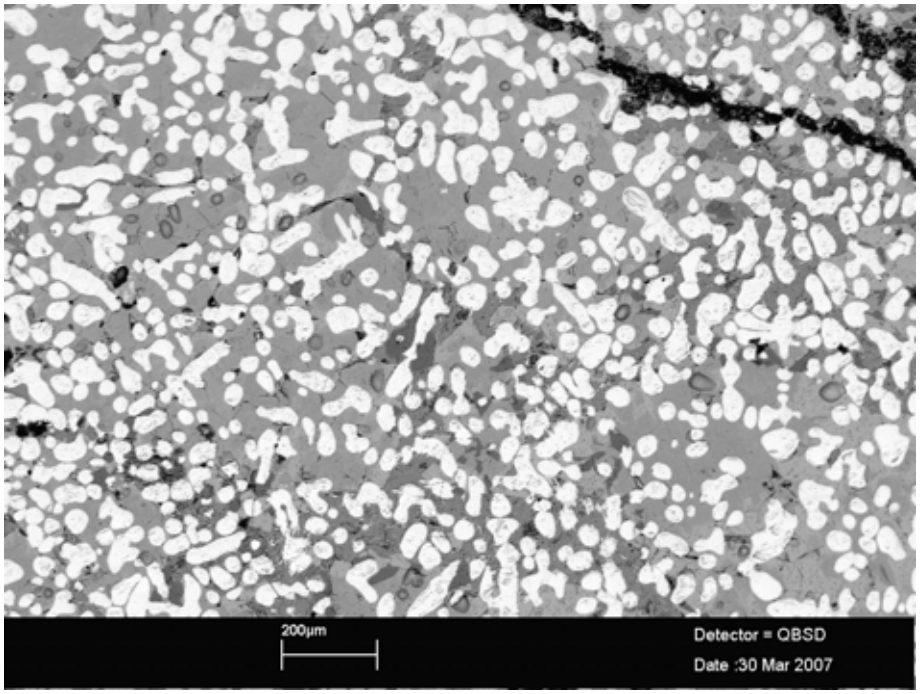

Figure 7. SEM (back-scattered electron detector) image of sample #05 showing abundant droplets of wüstite (FeO, white) and euhedral grains of fayalite (light grey)

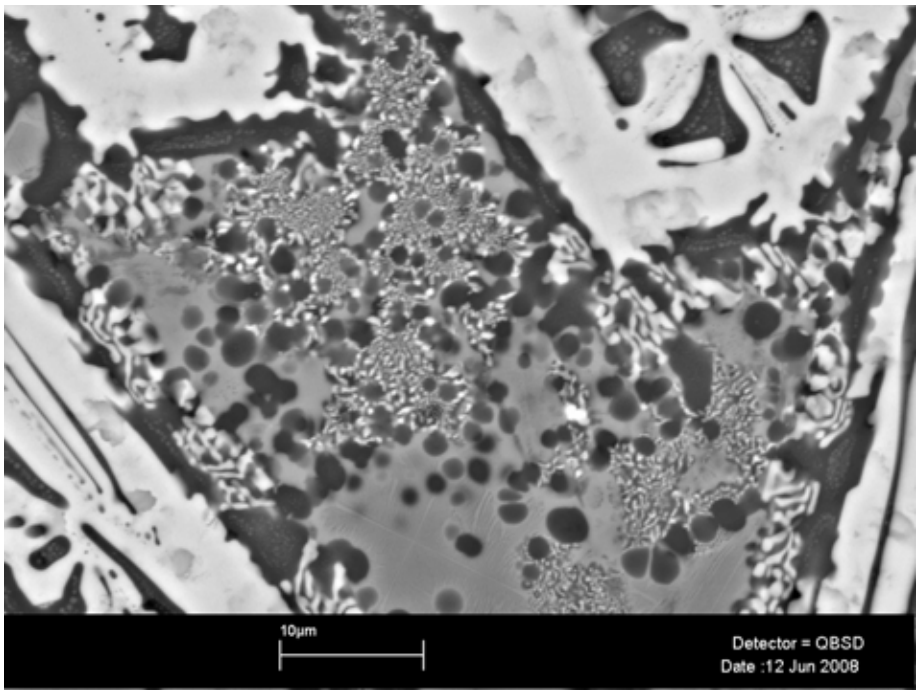

Figure 8. SEM image of sample #86 (back-scattered electron detector) showing the complex glassy matrix. This contains at least three phases (dark and light droplets in a grey matrix).

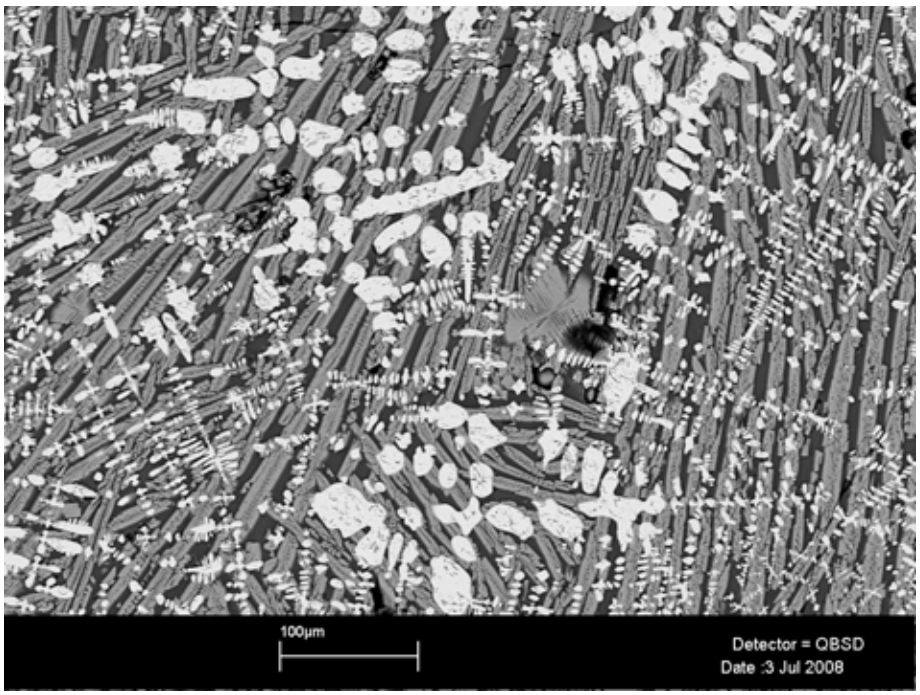

Figure 9. SEM (back-scattered electron detector) image of sample #54 showing fine dendrites of wüstite (FeO, white) and laths of fayalite (Fe_2SiO_4; mid grey)

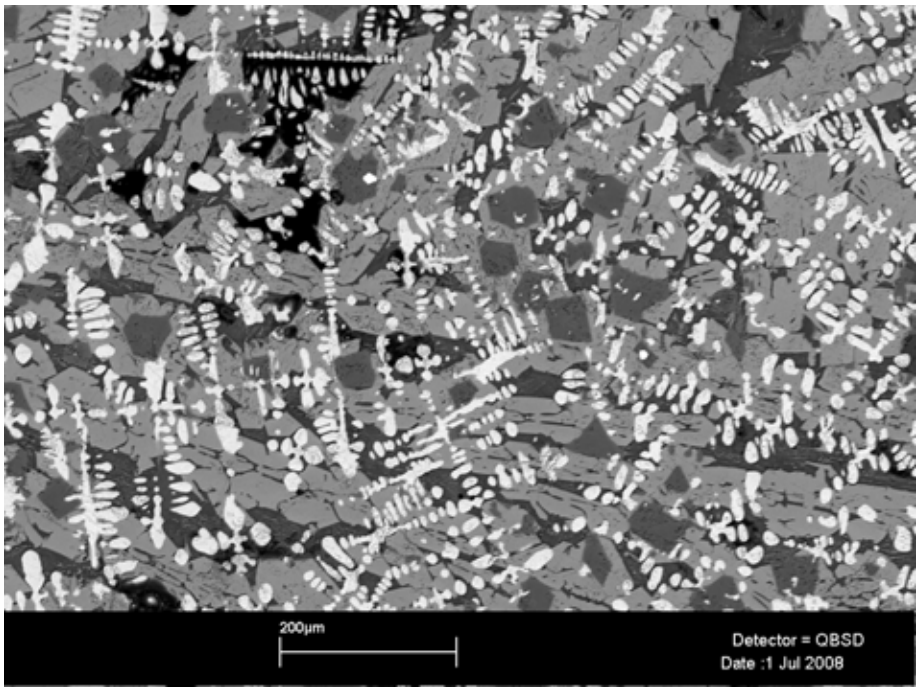

Figure 10. SEM (back-scattered electron detector) image of sample #16 showing fine dendrites of wüstite (FeO), laths of fayalite (Fe_2SiO_4) and euhedral crystals of hercynite ($FeAl_2O_4$) (in order of descending brightness)

Most samples also contain variable amounts of the iron oxide wüstite (FeO). The form of the wüstite varies from fine dendrites (Figure 9) to droplets in a vaguely dendritic arrangement (Figure 7). Hercynite ($FeAl_2O_4$) is present in small proportions in most samples (eg sample #16, figure 10). Hercynite is an uncommon mineral in bloomery smelting slags and is only usually present where the ore contained high proportions of alumina.

The samples selected for microstructural examination and chemical analysis included several amorphous iron-rich lumps. In addition, several samples of slag contained metallic droplets. The microstructure of these metallic samples provides supporting evidence for the interpretation of the assemblage as deriving from the production rather than manipulation of ferrous alloys, and gives some indication of the nature of the alloys that were produced.

Sample #86 (dense iron silicate) contained a droplet of iron with a very porous texture (Figure 11; cf Paynter 2007b, fig 9). Iron with this microstructure has been noted by Tholander (1987; Blomgren and Tholander 1986) as partially smelted iron and dubbed 'coral iron'. Other samples (eg #54, Figure 12) contained numerous small droplets of iron which had failed to coalesce into a bloom and had been lost in the slag. Analysis of metallic iron failed to detect any elements (in particular phosphorus) other than iron.

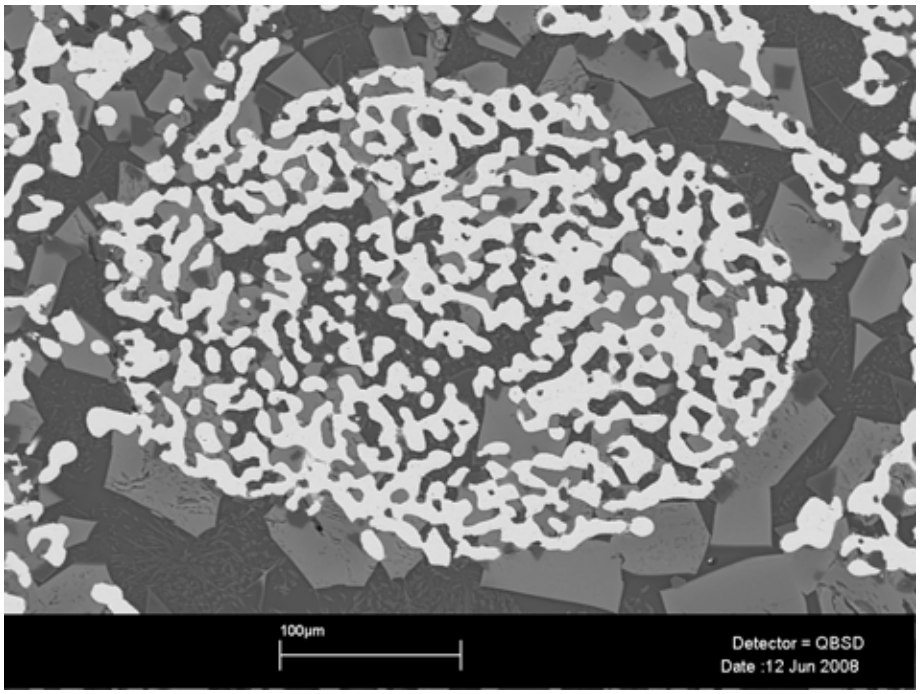

Figure 11. SEM (back scattered electron) image of slag #86 showing the presence of 'coral iron', fayalite, hercynite and a eutectic glassy ground mass (in order of descending brightness)

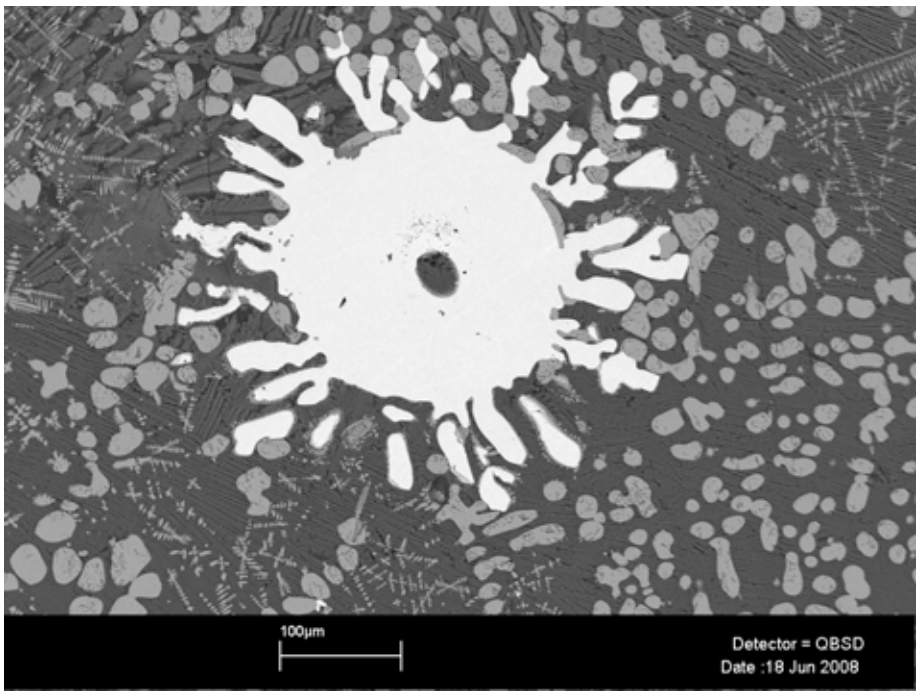

Figure 12. SEM (back scattered electron) image of part of slag #54 showing the presence of metallic iron, wüstite, fayalite and a eutectic glassy ground mass (in order of descending brightness)

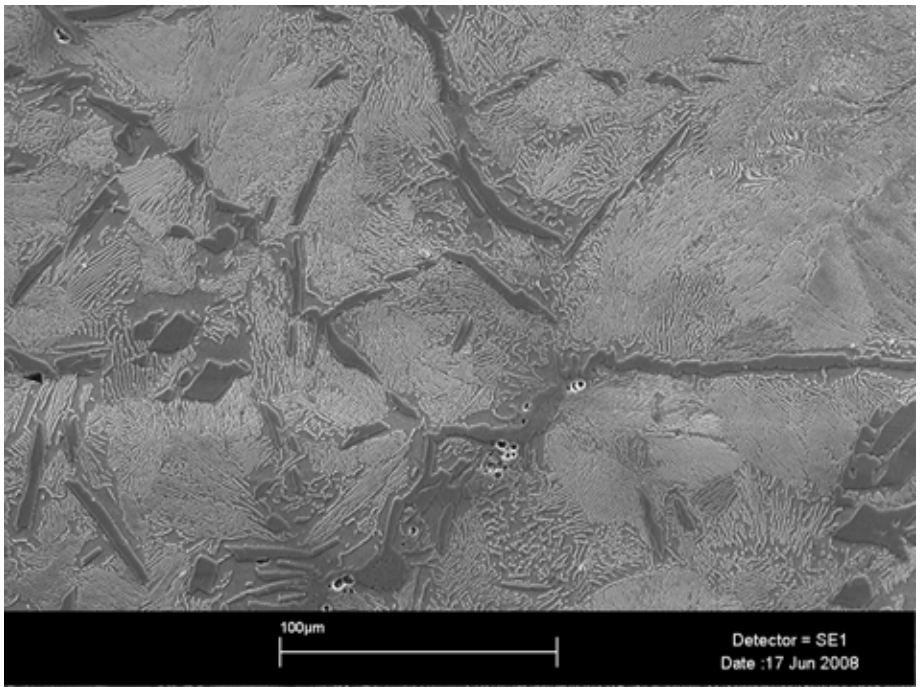

Figure 13. SEM (back scattered electron) image of sample #02 showing the presence of pearlite and cementite

The use of metal detectors during the excavations ensured the recovery of considerable amounts of iron-rich material which because it was amorphous was classified as slag. Two samples of this iron-rich material were selected for examination and analysis. The first (sample #02, Figure 13) was a carbon-rich iron alloy (steel). Figure 13 shows the sample is composed primarily of pearlite with cementite at the grain boundaries. This indicates that it is a hypereutectoid steel with a carbon content of approximately 1%; analysis failed to detect any phosphorus in this sample (the detection limit for phosphorus in metallic samples being 0.1wt%). The second metallic sample (#12) was composed almost entirely of ferritic iron (no phosphorus detected) with some pearlite. Sample #54 contained areas of corroded iron with a relict microstructure similar to that of sample #02 (ie a hypereutectoid steel) as well as regions of slag and ore. The intimate mixture of steel, slag and ore suggests that this steel was a natural steel produced within a bloomery furnace by the correct manipulation of smelting conditions, rather than by the secondary carburisation of iron.

The bloomery process yields metallic iron but this iron remains as a solid so the bloom is unlikely to be completely homogeneous; the concentrations of elements such as phosphorus and carbon are likely to vary in different parts of the bloom. Nevertheless, the fragments of iron examined here suggest that the bloom would have contained negligible concentrations of phosphorus (<0.1wt%) but significant concentrations of carbon (0.5wt%).

CHEMICAL COMPOSITION OF THE EXAMINED SAMPLES

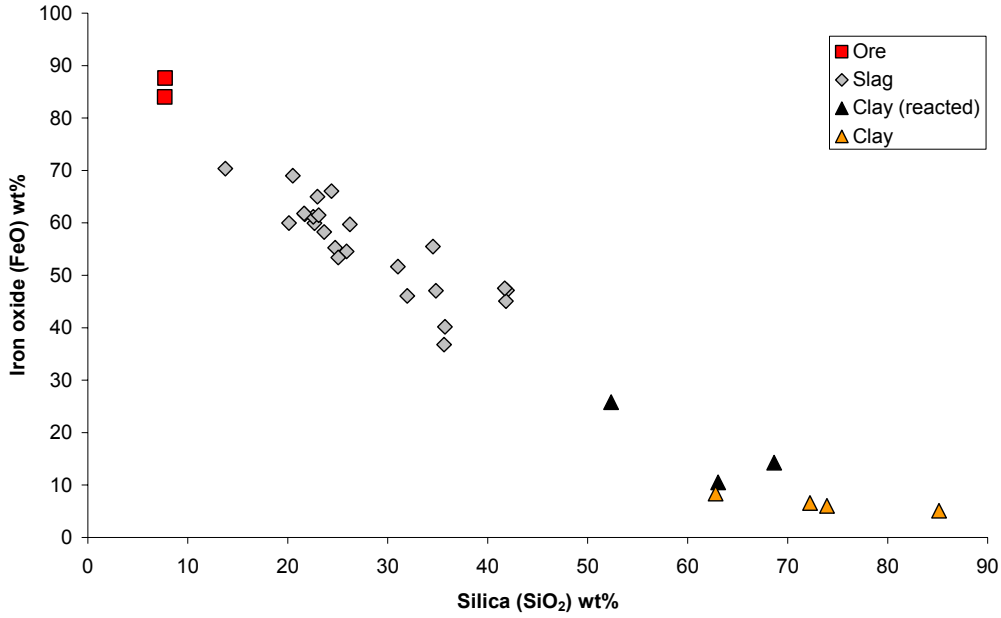

Figure 14. Plot of silica and iron oxide concentrations for various analysed samples

The chemical composition of the analysed samples provides information about a number of aspects of the process which produced them. In general, the slags have compositions similar to those from other iron smelting sites of similar age (cf Morton and Wingrove 1969; Paynter 2006). The slags are rich in iron oxide and silica; these two oxides account for 75–90wt% of each sample. The remainder of the composition is contributed by alumina, lime, potash, phosphorus oxide, magnesia and soda (other oxides are present but at very low concentrations, see Table 3 and Appendix 2).

Table 3. Summary chemical compositions (averages)

	Slag	Ore	Furnace Clay
Na_2O	0.76	0.31	1.15
MgO	1.01	0.49	1.24
Al_2O_3	8.04	3.16	13.19
SiO_2	27.84	7.72	73.53
P_2O_5	1.12	1.54	0.04
K_2O	1.42	0.23	2.67
CaO	3.86	0.53	0.92
TiO_2	0.20	0.09	0.68
MnO	0.16	0.09	0.07
FeO	55.60	85.83	6.50

In some respects the composition of the slag reflects the ore which was smelted, in particular the relatively high concentration of alumina and the low levels of manganese. The ore itself, however, cannot be the only raw material which contributes to the formation of the slag. This can clearly be seen in the alumina:silica ratios of the ore and slag. In the ore this ratio is 0.41 but the same ratio in the slag is 0.30; the slag must therefore include some material with a much lower alumina:silica ratio. It seems likely that the clay fabric of the furnace has reacted with some of the ore to form the slag. Similarly the slag contains higher concentrations of potash and lime than could be provided by the ore and the clay and it is likely that the ash of the charcoal fuel made small contributions to the formation of the slag. The contributions of furnace clay and fuel ash to the slag are discussed in more detail below (materials balance).

The chemical composition of the slag provides some information about the likely furnace conditions. The slag is composed primarily of three oxides, FeO, SiO_2 and Al_2O_3 (these account for 85–95wt%), and an estimation of the slag melting temperature can be made using the relevant phase diagram (Levin *et al* 1956, fig 373). The Al_2O_3–FeO–SiO_2 phase diagram indicates that the Redcliff slag would have a liquidus temperature close to 1150°C, comparable with other contemporary iron smelting slags (cf Paynter 2007a, 207). As at least some of the slag is dense and well consolidated, it is likely that furnace temperatures were in some areas perhaps 100°C higher than the liquidus temperature. Other, less well consolidated lumps of slag are likely to have formed at lower temperatures.

Paynter (2006) has demonstrated that Iron Age and Roman iron smelting slags have regionally distinct chemical compositions, for example those from the Forest of Dean have high potash concentrations while those from the Midlands Jurassic Ridge have high titanium oxide concentrations. The Redcliff slags, however, do not closely match those of other analysed smelting slags from lowland East Yorkshire. The slags from North Cave (McDonnell 1988) and Welham Bridge (Clogg 1999) are similar to each other and indicate the use of similar smelting procedures and resources (bog iron ore). The Redcliff slags, however, contain much higher concentrations of alumina, potash and lime, and lower concentrations of manganese oxide compared to other East Yorkshire sites. The chemical composition of the Redcliff slags cannot be linked to any other region discussed by Paynter but this may simply reflect the fact that many regional iron ore sources and their associated slags have not be characterised in this way (Paynter 2006, 290). The XRD analysis of a sample of ore indicated the presence of the mineral goethite (FeOOH). While significant iron ore outcrops are known in the area, such as the Frodingham ironstone, and these are mostly shelly oolitic limonites (ie hydrated goethite), they usually contain rather low concentrations of iron compared to the samples analysed from Redcliff.

MATERIALS BALANCE CALCULATIONS

During the bloomery smelting of iron ores the iron ore reacts with a proportion of the clay lining and charcoal ash to form metallic iron and waste slag (Crew 2000). This reaction can be represented by the formula below in which P stands for the proportion of each component

$$P_{ore} + P_{clay} + P_{ash} = P_{slag} + P_{metal}$$

The values of P can be estimated by materials balance calculations for those oxides in the inputs (ore, clay and ash) which are found in the slag but not in the metal (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2 and MnO):

$$(C_{ore} \times P_{ore}) + (C_{clay} \times P_{clay}) + (C_{ash} \times P_{ash}) = (C_{slag} \times P_{slag})$$

where C is the concentration of the oxide. The calculation of the proportions of inputs (P_{ore}, P_{clay} and P_{ash}) was achieved using a computer spreadsheet so the concentration of all oxides (except P_2O_5 and FeO) matched as closely as possible to the actual slag composition. The result (see Total column in Table 4) contains concentrations of P_2O_5 and FeO above those seen in the actual slag. Phosphorus is known to enter both slag and metal in varying proportions and some may be lost completely as vapour. The difference in the concentration of FeO in the Total column and in the actual slag gives the amount of FeO which is reduced to metallic iron. The agreement between the modelled slag and the actual slag is striking and suggests that the model is reliable. In most cases, the differences in concentrations of particular oxides are only slightly greater than the precision of the technique used to determine chemical composition (SEM-EDS). The lack of a perfect fit can probably be explained by reference to the heterogeneous nature of the smelting process, the limited number of samples (especially for ore) and the lack of chemical analyses of Redcliff charcoal ash.

The materials balance approach suggests that the observed slag would be produced when 1.6745kg of ore, 0.1988kg of clay and 0.0474kg of ash reacted to give 1kg of slag and 0.6957kg of metallic iron (the 0.8945kg of FeO contains 0.6957kg of metallic iron). A materials balance approach will probably slightly overestimate the amount of metallic iron which would form a bloom for two reasons. Firstly, it assumes that all of the inputs react fully to give slag and metal, however, several samples of slag examined contain small areas of unreacted ore. Secondly, it assumes that all of the reduced iron collects to form a single bloom and many of the samples examined contained at least some metallic iron droplets which had been lost in the slag. The iron bloom would also require smithing to transform it into stock ready for the production of artefacts, and such smithing can lead to considerable loss of metal (mostly as hammerscale, cf Crew 1991).

Table 4. Materials balance calculations for Redcliff iron smelting (the composition of ash is an average based on published data, eg Turner 1956).

	INPUTS			OUTPUTS			
	Ore	Clay	Ash	Total	Modelled Slag	'Metal'	Actual Slag
Proportion	1.6745	0.1988	0.0474	1.9207	1.0000	0.9207	
Na_2O	0.31	1.15	2.71	0.88	0.88		0.76
MgO	0.49	1.24	6.28	1.37	1.37		1.01
Al_2O_3	3.16	13.19	0.47	7.93	7.93		8.04
SiO_2	7.72	73.53	6.05	27.84	27.84		27.84
P_2O_5	1.54	0.04	6.40	2.90	2.90		1.12
K_2O	0.23	2.67	17.39	1.74	1.74		1.42
CaO	0.53	0.92	58.91	3.86	3.86		3.86
TiO_2	0.09	0.68	0.02	0.28	0.28		0.20
MnO	0.09	0.07	1.22	0.22	0.22		0.16
FeO	85.83	6.50	0.53	145.05	55.60	89.45	55.60

The concentration of phosphorus oxide in the modelled slag (2.9wt%) is significantly higher than in the actual slag (1.12wt%). This indicates that at least some of the phosphorus should have been reduced into the iron bloom. The analyses of several fragments of iron, however, indicate that the smelted iron contained little or no phosphorus. The 'missing' phosphorus almost certainly was lost as vapour, as both phosphorus and phosphorus oxide are relatively volatile (Tylecote *et al* 1971).

DISCUSSION

The examination of the ironworking slags from Redcliff has shown that they were produced during the smelting of iron in a furnace where the slag collected within the furnace and was not tapped from it. This places it within the Iron Age tradition of iron smelting (Paynter 2007a) and contrasts with the Roman technology which employed regular removal of slag from the furnace by tapping. The composition of the slag, when compared to the available data on raw materials (ore, clay furnace lining and charcoal ash) indicates that the smelting process yielded slightly less than 0.7kg of raw iron for every 1.7kg of ore used. The 1.7kg of ore would react with 0.2kg of clay lining and 0.05kg of charcoal ash to produce the iron and 1kg of slag.

The quantity of slag recovered is small and on its own indicates the production of little more than 4kg of raw iron bloom. Nevertheless, the limited extent of the excavation and the loss of some of the site by river erosion make it likely that more than 4kg of iron was produced. It is possible that the production of iron was undertaken, at least partially, with a view to trading with settlements to the south which then lay within the Roman empire.

The iron and steel fragments examined are certainly fragments of metal produced at Redcliff but which failed to be consolidated into a bloom. Two fragments of metal were hypereutectoid steels (roughly 1% carbon), while other fragments and droplets trapped in slag were plain iron and contained no detectable carbon or phosphorus. While the blooms produced were likely to be heterogeneous, it is probable that they contained at least some carbon. If the fragments of metal are representative of the blooms produced these would have an average carbon content of 0.5%.

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APPENDIX 1: DETAILS OF SLAG EXAMINED

Details of the Type of slag can be found in Table 1

#	Context	Phase	Weight	Density	Type	Notes
1	TSS	5d	79		Fe?	Slightly magnetic, iron-rich but highly corroded
2	251	5a	20		Fe?	Magnetic, iron-rich but highly corroded
3	302	4	51		Fe?	Magnetic, iron-rich but highly corroded
4	1	5d	20		Fe?	Slightly magnetic, iron-rich but highly corroded
5	1	5d	42		Fe?	Slightly magnetic, iron-rich but highly corroded
6	TSS	5d	35		Fe?	Slightly magnetic, iron-rich but highly corroded
7	TSS	5d	57		Fe?	Slightly magnetic, iron-rich but highly corroded
8	TSS	5d	49		Fe?	Slightly magnetic, iron-rich but highly corroded
9	TSS	5d	81		Fe?	Slightly magnetic, iron-rich but highly corroded
10	301	4	111		Fe?	Slightly magnetic, iron-rich but highly corroded
11	TSS	5d	143		Fe?	Magnetic, iron-rich but highly corroded
12	303	3d	269		Fe+slag?	Magnetic, iron-rich but highly corroded
13	us	-	18		Fe?	Slightly magnetic, iron-rich but highly corroded
14	761		3		ND	
15	354		19		ND	
16	290	5a	81		ND	Magnetic, iron-rich.
17	302	4	69		ND	
18	302	4	1273	3.1	FB?	Very fragmentary.
19	302	4	650	2.6	ND	
20	290	5a	268	2.6	ND	
21	66	3a/c	123	2.9	ND	
22	1	5d	1238	3.3	FB	160mm by 120mm by 50mm. Approximately one quarter of its likely original size (200mm diameter).
23	25	2	634	2.8	FB?	110mm by 110mm by 50mm. Some areas with fluid flow.
24	25	2	17.1	2.8	ND	
25	300	4	193.8	2.3	ND	Yellow powdery surface
26	251	5a	287.2	3.2	ND	Dense puddle?
27	5	5a	99.0	2.7	PRILL?	
28	354	?	440.6	3.3	PRILL	
29	968	3	357.3	2.8	FB?	100mm by 75mm by 40mm
30	302	4	227	2.9	ND	Vitrified lining attached
31	290	5a	206	2.7	ND	
32	290	5a	19	1.6	ND	
33	TSS	5d	36	2.5	ND	
34	768	4	48	2.5	SLIC	
35	300	4	85	2.5	ND	
36	251	5a	149	3.2	ND	
37	251	5a	104	2.2	ND	Yellow powdery surface
38	251	5a	33	2.7	ND	
39	251	5a	25	3.0	ND	

#	Context	Phase	Weight	Density	Type	Notes
40	300	4	147	2.7	ND	
41	300	4	98	2.0	ND	Vitrified lining attached?
42	284	5a	52	2.8	ND	
43	779	4	67	2.4	ND	
44	250	5d	20	1.9	ND	
45	TSS	5d	39	2.7	ND	
46	322	2	43	3.7	PRILL?	
47	967	3	9	3.0	ND	
48	10	5a	133	2.5	ND	
49	10	5a	4		ND	
50	TSS	5d	52	4.0	ND	
51	1	5d	14	3.0	ND	
52	251	5a	68	2.9	ND	
53	290	5a	81	2.2	VCL	
54	290	5a	278	2.8	ND	Some signs of flow
55	TSS	5d	84	3.1	ND	
56	302	4	109	2.8	ND	Vitrified lining attached?
57	251	5a	96	3.6	DIS	
58	us	-	30	3.9	ND	
59	TSS	5d	6		FLOW	
60	77	2	19	2.7	ND	
61	5	5a	40	3.2	ND	
62	251	5a	14	3.4	FLOW	
63	298	3d	10		ND	
64	250	5d	41	2.8	VCL	
65	5	5a	37	2.8	ND	
66	251	5a	30	3.0	FLOW	
67	251	5a	1		ND	
68	67	1 to 3	10	2.8	ND	
69	250	5d	8		ORE	
70	5	5a	8		FLOW	
71	TSS	5d	4		ND	
72						BURNT BONE
73	TSS	5d	8		ND	
74	251	5a	13	3.6	FLOW	
75	251	5a	14	2.8	ND	
76	250	5d	29			GEOLOGICAL
77	TSS	5d	12	3.2	ND	
78	TSS	5d	11		ND	
79	290	5a	4		VCL	
80	251	5a	6	3.6	FLOW	
81	314	3b	3		FLOW	
82	290	5a	41	1.2	VCL	

#	Context	Phase	Weight	Density	Type	Notes
83	1	5d	3		ND	
84	251	5a	4		VL	
85	111		3		ND	
86	295		45	3.8	DIS	<545>
87	251	5a	220	3.4	ORE	
88	79?		50	2.1		PUMICE <541>
89	85		220	2.0		PUMICE
90	793		650	<1.0	VCL	

APPENDIX 2: SEM-EDS DATA FOR ANALYSED SLAG SAMPLES

#	Context	Phase	Type	Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO
10	301	4	Fe	All	1.06	1.33	11.85	35.64	2.08	3.49	7.12	0.36	0.29	36.80
12	303	3d	Fe	All	0.51	0.62	6.80	26.22	0.76	1.61	3.57	0.11	0.08	59.72
16	290	5a	Fe	All	0.41	1.08	3.39	34.52	0.27	1.07	3.57	0.11	0.11	55.47
18	302	4	FB?	All	0.62	0.49	3.73	24.37	0.65	1.18	2.76	0.05	0.09	66.06
21	66	3a/c	ND	All	0.88	1.07	8.98	21.63	1.47	0.24	3.46	0.24	0.25	61.78
22	1	5d	FB	All	1.07	1.90	11.10	31.96	1.99	1.08	4.42	0.20	0.21	46.06
23A	25	2	FB?	1	1.15	1.27	11.56	35.71	1.58	1.76	6.34	0.25	0.20	40.17
23B	25	2	FB?	2	0.58	1.42	8.81	13.76	1.06	0.48	3.28	0.09	0.16	70.35
25	300	4	ND	All	0.78	0.49	5.49	41.82	0.64	1.84	3.53	0.26	0.08	45.07
28	354	?	PRILL	All	0.69	1.21	8.61	22.55	1.51	0.98	2.91	0.17	0.19	61.18
29	968	3	FB	All	1.31	1.03	9.81	34.82	0.18	2.06	3.26	0.40	0.08	47.05
31	290	5a	ND	All	1.16	1.32	10.51	31.02	1.49	0.76	1.73	0.22	0.12	51.67
34	768	4	SLIC	All	0.56	1.04	9.00	20.13	1.40	1.52	6.07	0.10	0.19	59.97
36	251	5a	ND	All	0.65	0.63	4.79	22.97	0.96	1.33	3.43	0.12	0.10	65.02
41c	300	4	ND	Clay	0.57	0.23	4.94	85.14	0.00	2.12	1.50	0.38	0.05	5.07
41s	300	4	ND	Slag	0.51	0.41	4.40	41.70	0.33	1.66	3.15	0.30	0.00	47.53
46	322	2	PRILL	All	0.59	0.65	4.92	20.51	0.74	1.13	2.33	0.09	0.06	68.99
53	290	5a	VCL	All	0.90	1.08	13.95	73.94	0.00	2.61	0.79	0.65	0.08	6.00
54o	290	5a	ND	Ore	0.32	0.18	0.91	7.74	2.20	0.11	0.79	0.02	0.10	87.63
54s	290	5a	ND	Slag	0.75	0.89	7.43	23.09	0.94	1.60	3.51	0.17	0.15	61.46
56c	302	4	ND	Clay	0.43	0.72	9.63	68.65	1.24	1.01	3.47	0.39	0.19	14.26
56s	302	4	ND	Slag	0.79	1.07	11.62	25.05	1.74	1.54	4.26	0.27	0.24	53.41
79	290	5a	VCL	All	0.75	1.19	14.84	72.24	0.00	2.68	0.90	0.76	0.05	6.59
80a	251	5a	PRILL	1	0.58	1.17	9.29	23.65	1.39	1.37	3.83	0.23	0.24	58.26
80b	251	5a	PRILL	2	0.61	1.14	8.60	21.71	1.23	1.22	3.43	0.20	0.23	61.63
81	314	3b	PRILL	All	0.77	1.08	9.48	25.88	1.47	1.74	4.49	0.27	0.25	54.56
82c	290	5a	VCL	Clay	0.86	1.47	18.42	63.04	0.59	2.70	1.30	1.01	0.11	10.50
82s	290	5a	VCL	Slag	0.82	1.26	7.60	52.34	0.88	4.77	5.96	0.43	0.13	25.82
86	295	?	DIS	All	0.75	0.35	3.55	41.93	0.39	1.88	3.82	0.14	0.06	47.13
87	251	5a	ORE	All	0.30	0.81	5.40	7.71	0.89	0.35	0.27	0.15	0.09	84.04
88	79?	?	Rock?	All	5.20	4.05	18.06	50.04	0.37	5.17	8.85	1.84	0.18	6.24
90	793	?	VCL	All	2.39	2.44	19.04	62.80	0.17	3.28	0.49	0.94	0.10	8.35

Note: each result is the normalised average of 4–10 separate areas






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