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BLACKSMITHS' FUEL THE ANALYSIS OF SLAGS FROM ARCHAEOLOGICAL AND CONTEMPORARY IRON-WORKING

TECHNOLOGY REPORT

Joanna Dunster and David Dungworth



INTERVENTION
AND ANALYSIS



ENGLISH HERITAGE

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Blacksmiths' Fuel

The analysis of slags from archaeological and contemporary iron-working

Joanna Dunster and David Dungworth

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SUMMARY

This study investigates the slag produced by iron-smithing in an attempt to identify features which can be used to identify the fuel used. Slag from archaeological contexts and from contemporary blacksmithing is examined using scientific techniques to characterise its microstructure and determine its elemental and mineral composition. The results are compared and consistent distinguishing features are identified and discussed.

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INTRODUCTION

Smithing is the process by which the metallic iron (Fe) product of smelting is further purified and worked into useable shapes. The basic technique is to heat the metal to a soft consistency below its melting range, which allows it to be hammered without breaking, and mobilises particles of molten slag within the metal (Bealer 1995; Craddock 1995; CSIRA 1955).

The most common waste product of smithing is slag or clinker, which is the mixed remains of oxidized flakes of metallic iron with the fuel ash, other contamination debris such as flux and the lining of the hearth (McDonnell 1991; Semeels and Perret 2003). This study aims to identify differences which can be attributed to the source of fuel (coal or charcoal) used during the smithing process. If a reasonable conclusion as to the fuel used can be gained by examination of the smithing slag, it will improve our knowledge of the process of smithing in Britain throughout history, and also of the choices made about fuel for industry in general.

The objectives of this project are:

- o to collect data from archaeological and contemporary iron-smithing slag using a range of techniques to obtain the microstructure, elemental composition and mineral phases
- o to compare the results of these analyses to identify consistent significant differences between slag known to have been produced in a reaction using charcoal fuel and coal fuel
- o to explore the reasons for these differences, and for other variations in the slag composition which could be misleading
- o to propose the most reliable features for future analysis of smithing slag in which the fuel is unknown

PREVIOUS INVESTIGATIONS OF IRON SMITHING

Iron smithing has been recognised in the archaeological record through a variety of structures, slags and micro-residues (McDonnell 1986a; Pleiner 2006, 112–122). The durability of slags has meant that these are the most frequently recovered evidence for iron smithing.

Iron smithing slags

The most diagnostic slags are the smithing heath bottoms which are plano-convex or concave-convex slag cakes (Bayley *et al*/2001, Fig 21; McDonnell 1983). These usually

have fairly smooth upper surfaces (plane or concave) and rougher lower surfaces (convex), often with charcoal fuel impressions (Figure 1).

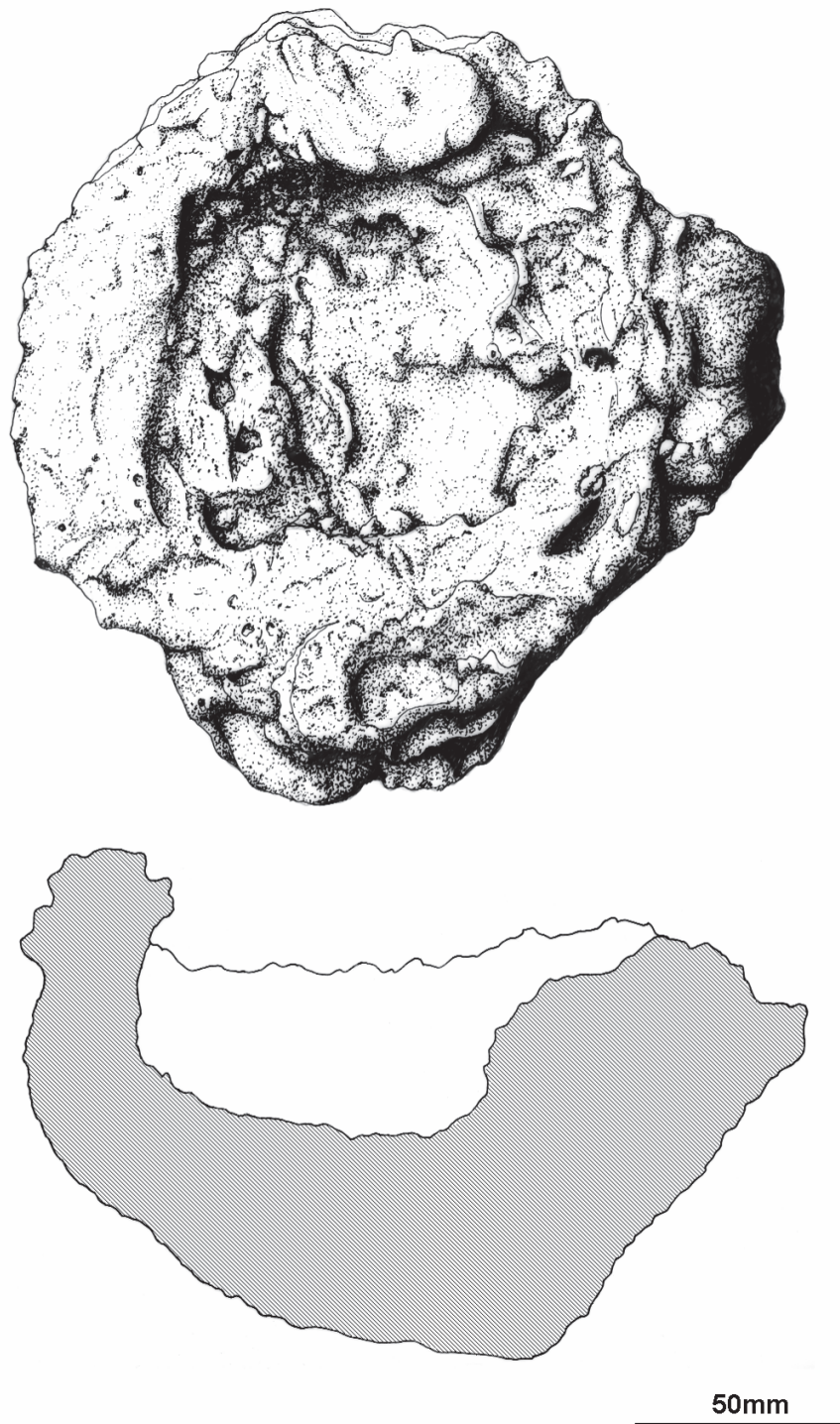


Figure 1. Drawing (plan and cross-section) of a medieval smithing hearth bottom (Retford, Nottinghamshire, see Ross and Davies 1995)

Smithing hearth bottoms are assumed to form in the hottest zone of the blacksmiths' hearth (McDonnell 1991). Smithing hearth bottoms share some morphological characteristics with a category of iron smelting slags: furnace bottoms. Nevertheless, furnace bottoms can usually be distinguished by their larger size (Paynter 2006). Less easily recognised, are the amorphous smithing slags which may form up to half of the slag from a smithing site (McDonnell 1986a). Scientific investigation of smithing hearth bottoms and amorphous iron-working slags (from the same assemblages) has shown that these are usually indistinguishable.

The presence of hammerscale (flakes and spheres of oxidised iron produced by heating and then forging iron) is diagnostic of smithing (Dungworth and Wilkes 2009). Hammerscale is frequently found in blacksmithing workshop floor deposits (Mills and McDonnell 1992) but it is widely assumed that a proportion falls into the blacksmith's hearth where it contributes to the formation of smithing slags (McDonnell 1991).

In a smithing hearth, the volume of slag would be determined by the type of item under construction (larger objects obviously requiring a larger volume of metal and therefore producing more slag), by the duration of the smithing activity, the temperature in the hearth, by the purity of the metallic iron at the start of the process, and the frequency with which any slag accumulations were cleared out.

Semeels and Perret (2003) propose a division of smithing slags into three categories based on size, colour, shape and density (with some supplementary data coming from chemical analysis). The first is a dense grey slag (SGD, *scorie grise dense*) which is routinely identified as classic iron smithing slag. The second is a rusty iron-rich slag (SFR, *scorie ferreuse rouillée*) which largely comprises fragments of iron which have become detached during smithing. The last type is a sandy-clayey slag (SAS, *scorie argilo-sableuse*) which has a low density and is rich in sand (possibly applied as a flux) as well as clay from the lining of the hearth.

Scientific investigation of smithing slags

Smithing hearth bottom slag and amorphous smithing slag lumps generally share the same microstructure, and elemental and mineral composition. The composition is highly variable even among samples from a single assemblage (Tables 1 and 2). The slags are rich in iron with varying proportions of silica and a range of other elements that are also found in bloomery iron smelting slags (Table 1). In almost all respects the range of elements present and their concentrations are within the same range. McDonnell (1986b) found that manganese (Mn) was found in many iron smelting slags but was generally found in only low concentrations in smithing slags (Table 1). Slags with more than ~0.3wt% MnO can usually be identified as iron smelting slags; however, not all iron smelting slags contain elevated levels of manganese.

There do not appear to be any clear differences in the chemical composition of smithing slags produced at different times (Table 2). The iron content *seems* to be highest in the prehistoric smithing slags and lowest in the medieval slags; however, the numbers of analysed samples from these periods are low. In addition, the standard deviations are sufficiently high that no significance should be read into these slight differences.

Table 1. Average chemical composition of iron smithing slag and iron smelting slag compared (after Fulford and Allen 1992; McDonnell 1983; 1986; 1992; Morton and Wingrove 1969; 1972; Paynter 2002; 2006a; Starley 2003; 2009)

	Smithing	Smelting
Na ₂ O	0.4±0.4	0.4±0.3
MgO	0.5±0.3	0.8±0.7
Al ₂ O ₃	4.3±2.3	4.0±2.2
SiO ₂	24.7±8.7	24.0±5.3
P ₂ O ₅	0.7±0.6	1.3±0.9
S	0.1±0.1	0.1±0.1
K ₂ O	1.3±0.9	1.0±0.7
CaO	2.7±2.1	1.9±1.0
TiO ₂	0.2±0.1	0.2±0.1
MnO	0.1±0.1	1.0±1.8
FeO	64.9±11.9	65.0±7.1

Table 2. Average chemical composition of iron smithing slag from different periods (after McDonnell 1983; 1986; 1992; Paynter 2002; 2006a; Starley 2003; 2009)

	Prehistoric	Roman	Post-Roman	Medieval
Na ₂ O	0.2±0.2	0.4±0.4	0.9±0.5	0.4±0.2
MgO	0.4±0.3	0.5±0.2	0.6±0.5	0.4±0.1
Al ₂ O ₃	4.4±2.3	4.2±2.2	2.8±1.7	5.6±2.5
SiO ₂	19.8±3.1	25.9±7.3	23.2±10.9	27.5±10.5
P ₂ O ₅	0.4±0.5	0.8±0.6	0.6±0.5	1.0±0.8
S	0.2±0.2	0.1±0.1	0.2±0.2	0.1±0.1
K ₂ O	1.3±0.7	1.3±0.9	1.3±0.8	1.2±1.1
CaO	2.4±1.8	2.9±1.9	2.8±2.5	2.4±2.3
TiO ₂	0.2±0.1	0.2±0.1	0.1±0.1	0.2±0.1
MnO	0.1±0.1	0.2±0.2	0.2±0.2	0.1±0.1
FeO	70.6±6.7	63.4±10.2	67.39±14.9	61.0±13.7

An examination of the microstructure of iron smithing slags shows that (like bloomery smelting slags) these are generally rich in fayalite with varying proportions of other phases that are also found in a range of bloomery smelting slags (eg wüstite, hercynite and leucite). The proportions of these phases varies considerably even within samples from a single assemblage. The texture of the microstructures of iron smithing slags often shows some slight differences compared to many iron smelting slags. While smelting slags which have cooled quickly (especially tap slags) will have long thin fayalite crystals and (where it

is present) fine dendrites of wüstite; iron smithing slags tend to have more equiaxed fayalite grains and coarse and rather 'blobby' wüstite. Unfortunately, iron smelting slags which have cooled slowly (especially furnace bottoms) tend to have equiaxed fayalite and blobby wüstite, and so resemble iron smithing slags.

It has often been noted that iron smithing slags are heterogeneous and that this can exist within a single sample (McDonnell 1991; Semeels and Perret 2003). McDonnell (1991) identified four zones within smithing hearth bottoms: the upper surface, the core, the base and a side (often with adhering ceramic hearth lining).

Modelling the formation of iron smithing slags

Iron smithing slags form within the blacksmith's hearth. The key factors which will affect the formation of slag are the temperatures produced within the hearth, the range of materials within the hearth and blacksmithing practice.

Most blacksmithing required elevated temperatures and these have been achieved by burning fuel in a restricted space (hearth). It is assumed that most early smithing made use of charcoal as a fuel. When burnt charcoal produces a high temperature but also a reducing atmosphere and so prevents excessive oxidation (and so loss) of metal. In order to achieve temperatures sufficient to forge and weld iron it would be necessary to force air into the hearth. The temperatures produced within a blacksmith's hearth will have varied depending on the nature of the work being undertaken and this will have had an influence on the formation and final appearance of the slag. Most forging was carried out at temperatures in the range 700–1000°C and these sorts of temperatures would be maintained routinely in a hearth. Nevertheless, once the iron was removed from the fire and forged on the anvil, the air blast would be reduced and the hearth would cool somewhat. Welding would require higher temperatures (1100–1300°C, depending on the nature of the iron alloy). Welding temperatures are likely to have been achieved episodically and maintained for only short periods of time. The temperatures within a hearth would not be uniform throughout but would be hottest close to where the air blast (via the tuyère) entered the fuel bed. A smith who never welds would probably produce slag of a somewhat different character compared to one who does.

The size, shape and inclination of the tuyère, as well as the nature of the fuel bed and the overall form of the hearth will all have had an influence on the size and shape of the hottest zone, and this will in turn have affected the size and shape of the slag that formed. The concave upper surface of many smithing hearth bottoms (Figure 1) suggests that they formed at the base of the hottest zone (cf Figure 2). Smithing practice will also have had an impact on the size and shape of the slag that formed,

Clinker is the blacksmith's worst trouble. Cold, clinker is like a crude black glass; hot, it is like black treacle. . . . As the fuel burns, clinker is formed in a molten state and trickles down to the bottom of the fire, just in front of the blast hole. Here the

clinker obstructs the blast and bits are blown upwards and stick to the hot metal giving it a molten coating. Metal in this state cannot be welded and when it is struck, the molten clinker spurts out from under the hammer and burns the hands. . . . The blast is then cut for a few minutes to allow the clinker to cool and solidify sufficiently to be hooked out in one piece with the tip of the poker. . . . Sometimes the clinker does not form into one lump or else the lump breaks up . . .
CSIRA 1955, 17–18

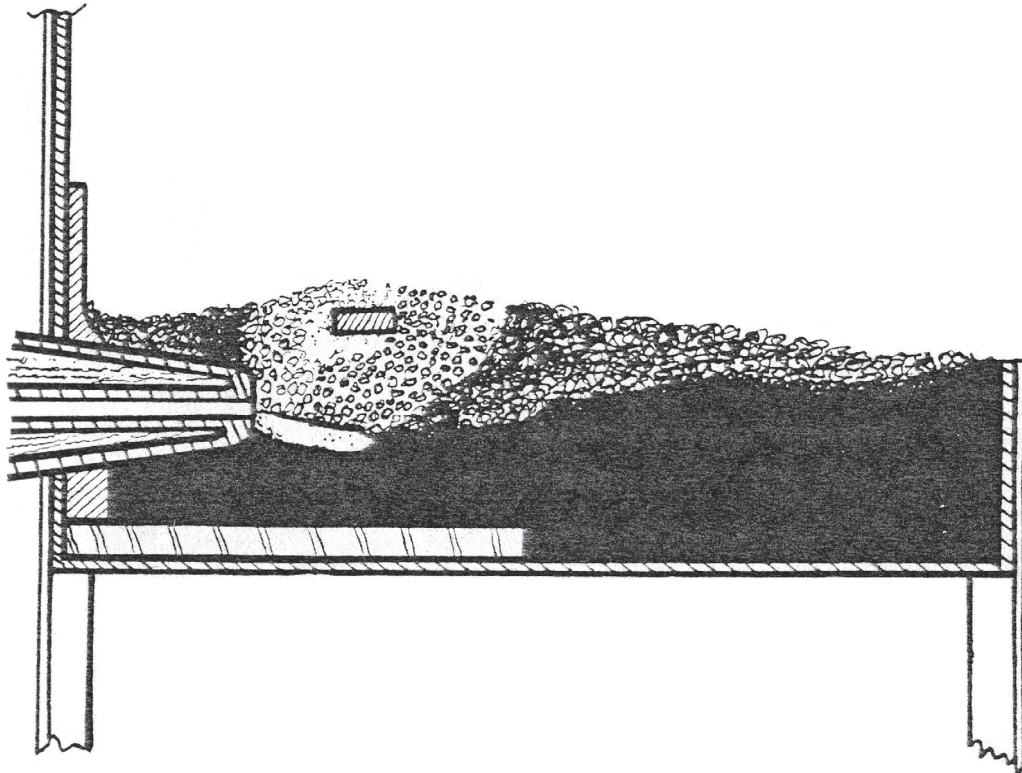


Figure 2. Cross-section through a modern blacksmith's hearth showing the tuyère, with the clinker forming in front and slightly below the end of the tuyère (CSIRA 1955, Figure 28)

It is not uncommon for modern smiths to remove cold clinker from their hearths four times a day: before starting working in the morning, after a morning break, after lunch and after an afternoon break. More frequent removal of clinker would yield smaller more amorphous lumps, while less frequent removal would increase the likelihood of producing a plano-convex cake of slag.

There are a number of other possible materials which could contribute to the formation of iron smithing slags. These include the fuel, a flux, the iron and the hearth lining.

The fuels used by blacksmiths are rich in carbon and produce intense heat as the carbon oxidises (to carbon monoxide and then carbon dioxide). These fuels also contain a non-combustible residue (ash). The proportion of ash and its chemical composition will vary

depending on the nature of the fuel and the way in which it has been prepared and processed prior to use by the blacksmith.

It is widely assumed that charcoal was the most frequently used blacksmithing fuel up to the medieval period. Charcoal is partially burnt wood which has lost most of its volatile components. It is rich in carbon and has been used for various metallurgical operations for millennia. The ash content of wood and charcoal (Table 3) is generally rich in calcium and potassium with lesser amounts of other elements (magnesium, silicon, phosphorus and manganese). These elements will usually be present as compounds: commonly carbonates but also oxides and sulphates, depending on the nature of the charcoal and the temperature of combustion. The composition of wood ash can vary depending on the species of tree, the time of year the wood was cut, the part of the tree used and the nature of the underlying geology on which the tree grew (Sanderson and Hunter 1981; Stern and Gerber 2004; Turner 1956). The way in which the charcoal was prepared will also have an effect on its ash composition. It is likely that the sulphur content of charcoal ash will be consistently lower than the sulphur content of coal ash.

Table 3. The range of compositions of wood ash and coal ash

	Wood	Coal
Na ₂ O	0.2–2	0.2–2
MgO	4–10	0.2–10
Al ₂ O ₃	0.1–2	5–40
SiO ₂	2–10	10–60
P ₂ O ₅	2–15	0.1–2
S	0.1–4	0.1–4
K ₂ O	10–40	0.2–4
CaO	10–70	1–40
TiO ₂	~0.1	0.1–1.0
MnO	0.1–10	<0.3
Fe ₂ O ₃	0.2–3	4–40

Coal is widely used as a fuel by modern blacksmiths (CSIRA 1955) and has been used by some smith as early as the Roman period (Tylecote 1986, 225–226). Coke (the solid residue left after the partial combustion of coal) has often been preferred for metallurgical uses. The heating process employed in converting coal into coke will have removed a proportion of the sulphur, although most coal used for making coke was carefully selected from low sulphur coals. Coal and coke generally have much higher ash content compared to wood and charcoal and so may make a more significant contribution to smithing slag formation when they are used. Coal and coke ash generally contain more aluminium, silicon and iron compared to wood and charcoal ash.

Smithing slags are also formed in part through a contribution from the iron placed in the fire. The blacksmith would place iron in the hot zone of the hearth (cf Figure 2) and heat it so that it was soft enough to forge or weld. While in the hot zone the surface of the iron would tend to oxidise and form a skin of iron oxides. Smiths are often encouraged to

carefully place the iron in the least oxidising portion of the fire (CSIRA 1955, 18), however, some oxidation is inevitable. The skin that forms on the heated iron (composed of thin layers of hematite, magnetite and wüstite) would be relatively brittle compared to the underlying metal and so would be easily detached during smithing. Nevertheless, some flake hammer scale is likely to have become detached from the surface of the iron while it was in the hearth. If the iron was inadvertently overheated or placed in an excessively oxidising zone of the hearth, it would be possible to burn the metal. This would introduce large quantities of metal and metal oxides into the hearth. In general steels will burn at a lower temperature than plain iron; it is likely that phosphoric irons will also burn more easily than plain iron but these alloys have been less studied. Non-metallic inclusions within the iron or iron alloy (especially slag inclusions) would usually be liquid at welding temperatures and so would drip into the hot zone of the hearth.

The forge welding of iron relies on the application of pressure (hammer blows) to metal which is sufficiently hot to allow two pieces of metal to bond to one another. If the metal surfaces acquire an oxide skin during heating then this can prevent effective bonding of the metal and many smiths recommend the use of a flux to 'glaze the surface of the metal' (Bealer 1995, 130). A wide variety of materials have been recommended for use in fluxes, including clean sand, iron filings, borax, common salt, sal ammoniac (ammonium chloride), and combinations of all of these. If it is used, some flux will inevitably fall into the hearth and can contribute to the formation of the smithing slag. It is not certain to what extent fluxes were used (or the nature of these fluxes) before the post-medieval period.

Modern blacksmith's hearths (Figure 2) are designed to accommodate a bed of fuel substantially larger than the actual combustion zone. This ensures that the sides and base of the hearth rarely get hot enough to begin to oxidise and react with other materials in the hearth. Earlier practice is less well known but the frequent observation of partially vitrified ceramic material adhering to one side of a smithing hearth bottom is consistent with the construction of small bowl-shaped hearths, often at ground level. In such a hearth, the clay lining and any clay tuyère would have been sufficiently close to the hot zone that they could vitrify and even melt, and so could contribute to the formation of smithing slag.

Although studies of iron smelting slags have made some use of materials balance calculations to examine the relationships between raw materials and products, the same has not been tried for smithing slags. The variety of different materials which could contribute to the formation of smithing slag would make such a model rather uncertain.

THE ASSEMBLAGE

In order to further investigate the possible relationships between fuel and iron smithing slag samples of materials from a variety of sources were analysed (Table 4). This included both modern and archaeological material where some information was available on the nature of the fuel used.

Fox's Field, Ebley is an early Roman-period settlement site which yielded evidence for small-scale iron smithing (Bateman 2011). Coal was recovered from the same contexts as the iron smithing slag and some coal appeared to be embedded within the smithing slag. The Anglo-Saxon settlement at Bloodmoor Hill, Carleton Coalville produced evidence for iron, including hammerscale and smithing slags, some of which were found incorporated within the slags (Lucy *et al*/2009). Excavations at Stafford Castle found iron smithing slag in a 13th- and 14th-century ditch (Soder 2007). The well-known medieval smithing site at Burton Dassett (McDonnell 1992) produced 365kg of iron smithing slag (including hammerscale). Some of the fragments of iron smithing slag recovered from Burton contain small (<2mm) fragments of coal.

Table 4: Sources of slag used

	Site/Smith	Fuel	Bellows	Description
#01	Hector Cole	Coal	Electric	Clinker with red-orange ceramic-like material
#02	Hector Cole	Coal	Electric	Clinker
#03	Hector Cole	Coal	Electric	Clinker
#04	Hector Cole	Coal	Hand	Clinker with red-orange ceramic-like material
#05	Hector Cole	Coal	Hand	Clinker
#06	Hector Cole	Coal	Hand	Clinker
#07	Lucille Scott	Coke	Hand	Clinker
#08	Lucille Scott	Coke	Hand	Clinker
#09	Lucille Scott	Coke	Hand	Clinker with red-orange ceramic-like material
#10	Ebley	Coal?	Hand?	Amorphous lump of smithing slag
#11	Ebley	Coal?	Hand?	Amorphous lump of smithing slag
#13	Carleton Coalville	Charcoal?	Hand?	Amorphous lump of smithing slag
#14	Carleton Coalville	Charcoal?	Hand?	Vitrified ceramic
#15	Carleton Coalville	Charcoal?	Hand?	Amorphous lump of smithing slag
#16	Stafford Castle	Charcoal?	Hand?	Smithing Hearth Bottom
#17	Stafford Castle	Charcoal?	Hand?	Vitrified ceramic
#18	Stafford Castle	Charcoal?	Hand?	Vitrified ceramic
#19	Burton Dassett	Coal?	Hand?	Amorphous lump of smithing slag
#20	Burton Dassett	Coal?	Hand?	Amorphous lump of smithing slag
#21	Burton Dassett	Coal?	Hand?	Amorphous lump of smithing slag
#25	Hector Cole	Coal	Electric	Clinker
#26	Hector Cole	Charcoal	Hand	Clinker
#31	David Dungworth	Charcoal	Hand	Amorphous lump of smithing slag
#32	David Dungworth	Charcoal	Hand	Amorphous lump of smithing slag
#33	David Dungworth	Coke	Electric	Clinker

METHODS

Macroscopic examination

Smelting slags are heterogeneous, and the composition can vary between different areas sampled. To allow the most representative data to be collected from the slags, three samples were extracted from each source. Once analysis was complete it became clear that some of the selected samples were actually hearth lining rather than smelting slag. Project timetabling constraints unfortunately prevented the selection of replacement samples.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

The mounted samples were viewed using a FEI Inspect F Scanning Electron Microscope (SEM) fitted with a back-scattered electron detector. All images of the sample microstructure (Figures 3–16) were obtained using a back-scattered electron detector. An attached Oxford Instruments X-Act SDD Energy Dispersive Spectroscopy (EDS) was used to obtain the elemental composition. The SEM was operated at 25kV and 1.2nA with a working distance of 10mm. Readings were taken for 100 seconds, and the spectra were quantified using Oxford Instruments INCA software. For each sample, several readings were taken from large representative areas for bulk analysis. The number of readings (3–10) was varied depending on the heterogeneity of the samples.

RESULTS

Microstructure

The microstructures are very variable but fall into three main groups: glassy slags with very fine laths and dendrites, coarser fayalitic slags and vitrified ceramics. The glassy slags are the most abundant group and display the most variability in terms of the phases present. It was in many cases difficult to characterise these phases: they generally made up a small proportion of the samples volume and were often present as such small crystals or dendrites that discrete SEM-EDS analysis was not possible. Magnetite (Fe_3O_4) is present in over half of the glassy samples (Figures 3–8) as recrystallised dendrites (Figures 4 and 6) or the more typical equiaxed grains of spinels (Figure 8). In many cases, some of the iron in the magnetite has been replaced by aluminium and a few crystals of hercynite (Fe_2AlO_4) are also present. Larger masses of magnetite (or possible wüstite, FeO) are also present in some samples (Figure 5) and probably represent partially reacted fragments of hammerscale.

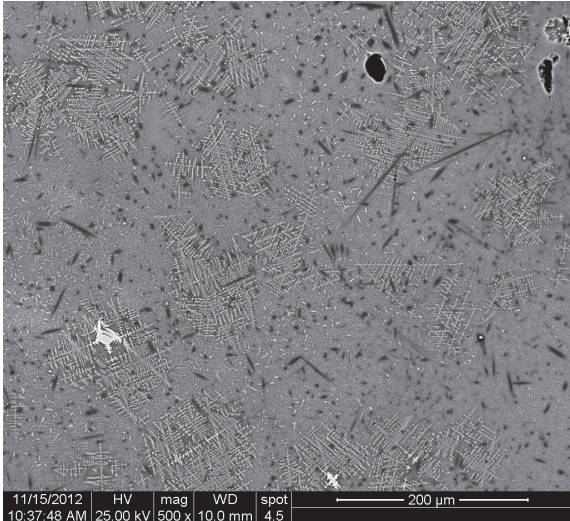


Figure 3. SEM image of sample 01

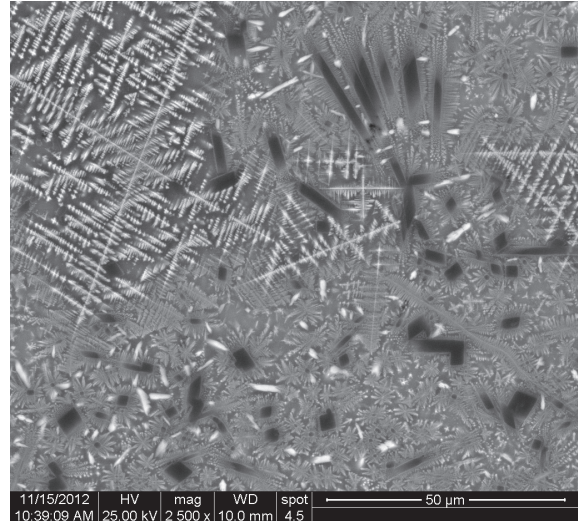


Figure 4. SEM image of sample 01 showing magnetite dendrites (white) and laths of an aluminium silicate

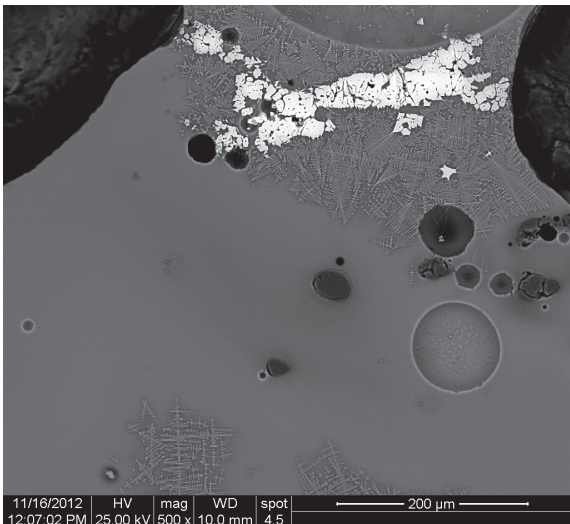


Figure 5. SEM image of sample 07. Note the mass of iron oxide near the top (possible relict hammerscale)

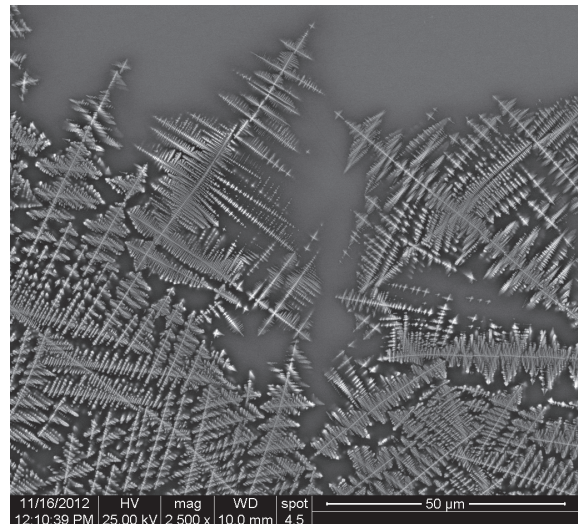


Figure 6. SEM image of sample 07 showing iron oxide dendrites (probably magnetite)

Aluminium silicate crystals were also noted in several samples (Figure 4) which may be kyanite (Al_2SiO_5) and/or mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). Calcium aluminium silicate crystals were also present in some samples; these are probably anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Silica-polymorphs are present in a few of the glassy slags (Figure 5).

The fayalitic slags all contain fayalite and this is usually the most abundant phase (Figures 9–14). The fayalite is usually present as laths (Figure 10) but occasionally these tend towards being equiaxed (Figure 13). The size of the fayalite crystals varies considerably: some laths are barely $10\mu\text{m}$ across while others are almost 1mm across. Iron oxide is frequently (but not universally) seen in the fayalitic slags. It usually has a dendritic distribution and with the rather rounded character typical of wüstite (Figures 11 and 12).

Equiaxed hercynite crystals are present in several of these samples (Figure 10). Leucite is also occasionally present; usually as a leucite-wüstite eutectic (Figures 13 and 14).

The ceramic samples all contained abundant silica grains. In some cases, the matrix showed little vitrification: the samples retain considerable porosity and this tended to be irregularly shaped (Figure 15). In other cases, vitrification was sufficiently advanced for most porosity to be present as a small number of near spherical pores (Figure 16).

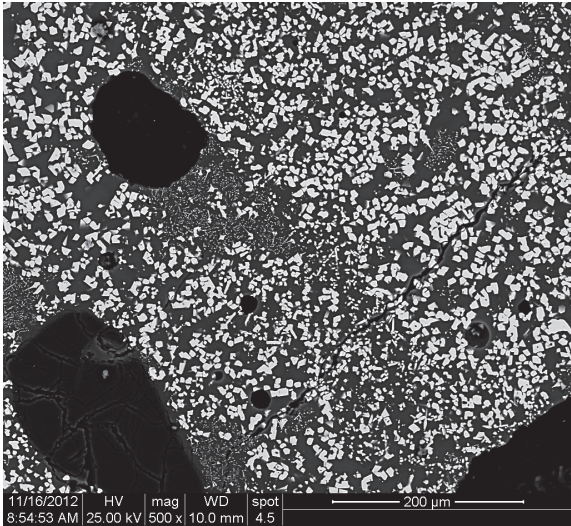


Figure 7. SEM image of sample 20 showing equiaxed spinels (magnetite)

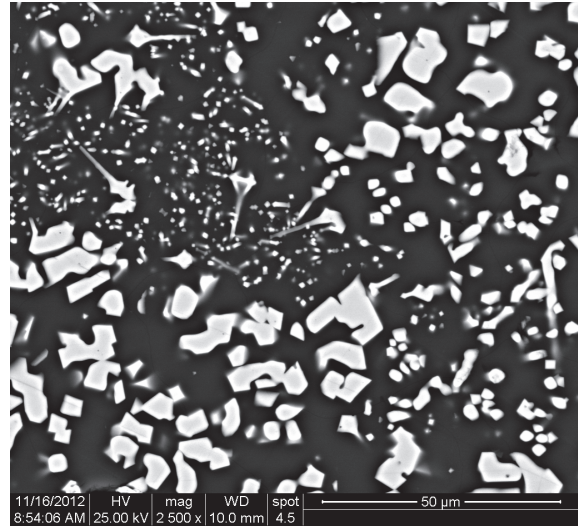


Figure 8. SEM image of sample 20 showing equiaxed spinels (magnetite)

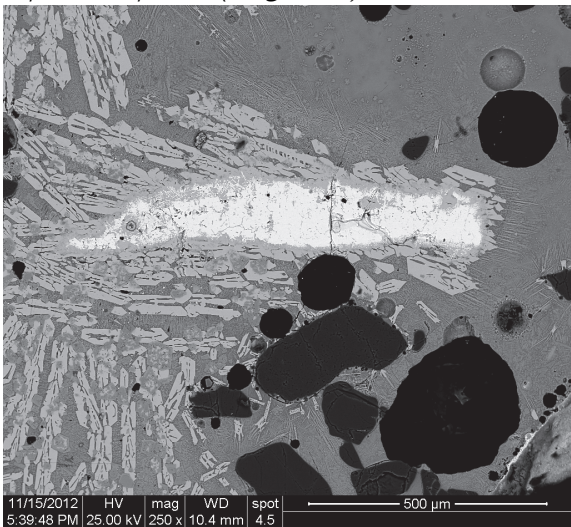


Figure 9. SEM image of sample 19

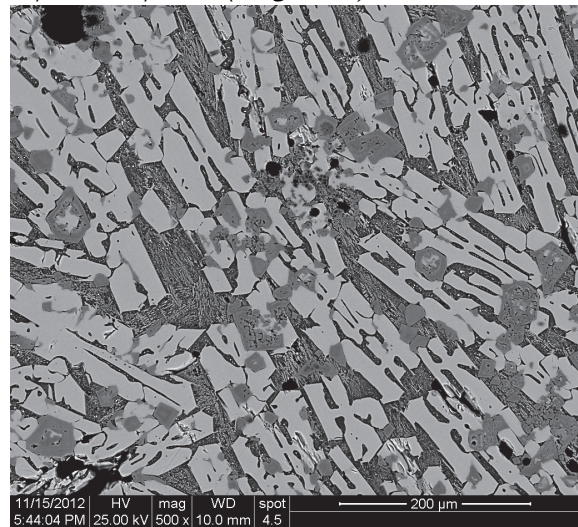


Figure 10. SEM image of sample 19

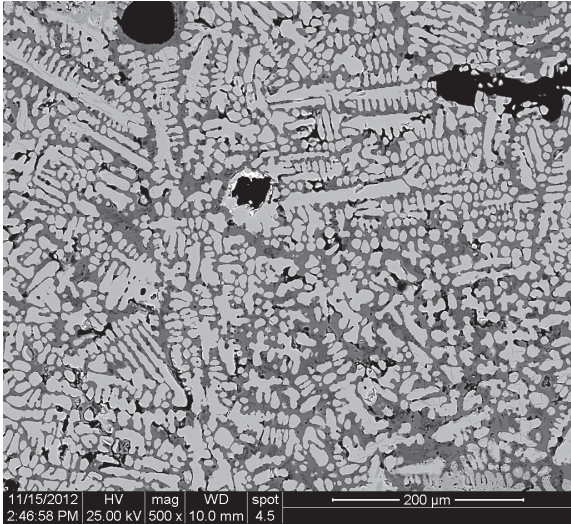


Figure 11. SEM image of sample 05

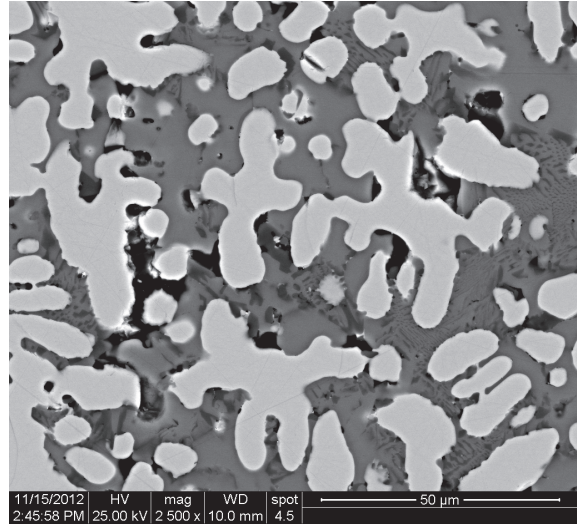


Figure 12. SEM image of sample 05

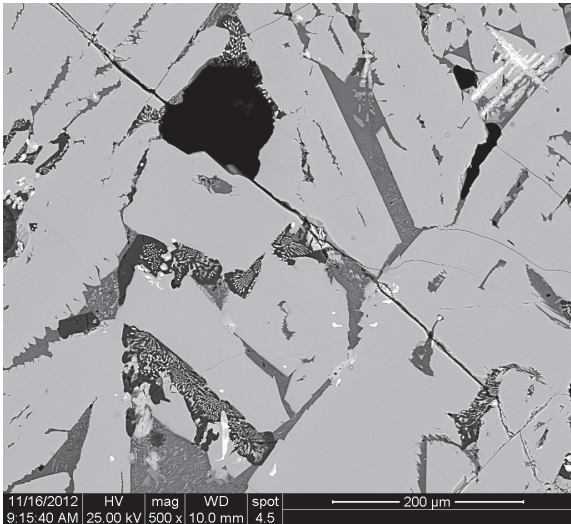


Figure 13. SEM image of sample 21

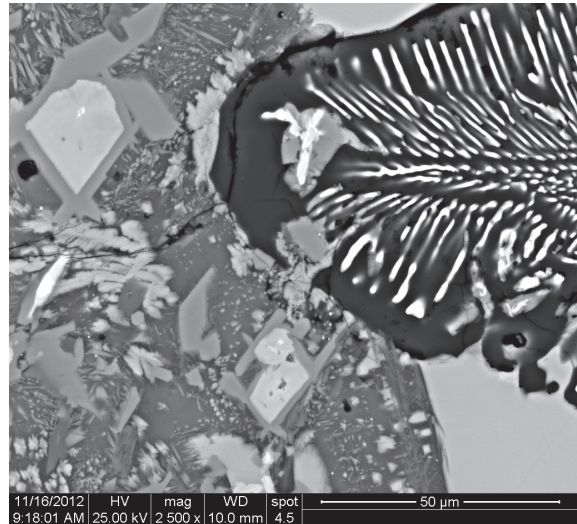


Figure 14. SEM image of sample 21

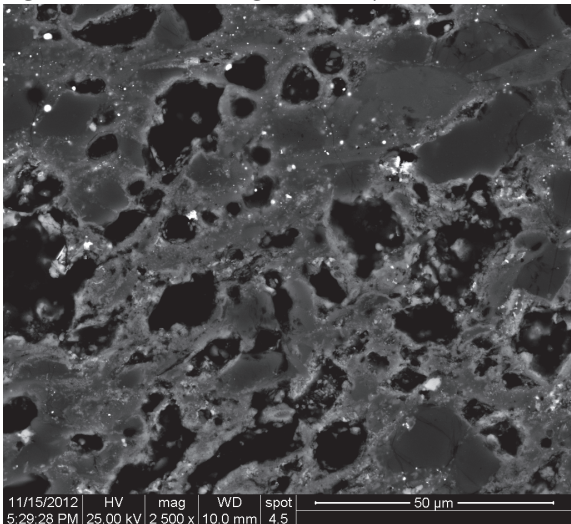


Figure 15. SEM image of sample 18

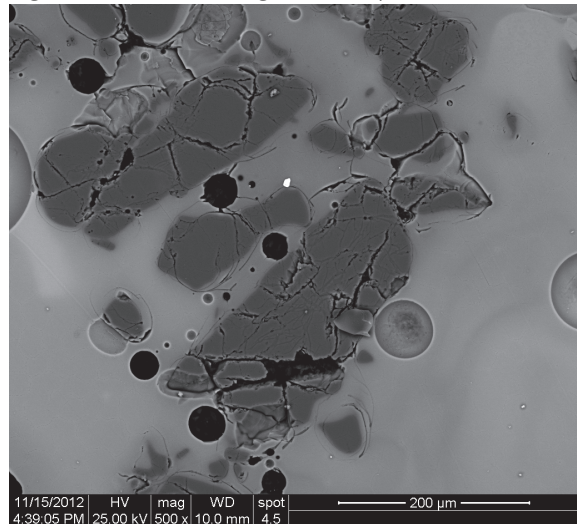


Figure 16. SEM image of sample 14

Table 5. Summary of microstructure of smithing samples

	Fuel	Type	Comments
#01	Coal	Glassy	Very fine magnetite and aluminium silicate
#02	Coal	Glassy	Very fine aluminium silicate
#03	Coal	Glassy	Very fine magnetite and aluminium silicate
#04	Coal	Fayalitic	Fayalite laths, hercynite, wüstite and iron sulphide
#05	Coal	Fayalitic	Fayalite and abundant wüstite
#06	Coal	Glassy	Very fine magnetite and aluminium silicate
#07	Coke	Glassy	Very fine magnetite
#08	Coke	Glassy	Very fine magnetite
#09	Coke	Glassy	Very fine magnetite
#10	Coal?	Fayalitic	Fayalite laths, hercynite and wüstite
#11	Coal?	Glassy	Fine-coarse magnetite
#13	Charcoal?	Fayalitic	Fayalite laths and wüstite
#14	Charcoal?	Ceramic	Silica inclusions
#15	Charcoal?	Fayalitic	Fayalite laths
#16	Charcoal?	Fayalitic	Fayalite and hercynite
#17	Charcoal?	Ceramic	Silica inclusions
#18	Charcoal?	Ceramic	Silica inclusions
#19	Coal?	Fayalitic	Fayalite laths and hercynite
#20	Coal?	Glassy	Fine magnetite
#21	Coal?	Fayalitic	Fayalite (with some wollastonite), leucite and wüstite
#25	Coal	Glassy	Silica inclusions
#26	Charcoal	Glassy	Anorthite
#31	Charcoal	Fayalitic	Fayalite and wüstite
#32	Charcoal	Fayalitic	Fayalite and wüstite
#33	Coke	Glassy	Fine magnetite

Chemical Composition

The chemical composition of the samples (Table 6) reflects their microstructure: the glassy slags tend to be rich in aluminium and silicon and the fayalitic slags contain higher proportions of iron (Figure 17). The ceramic samples often contain high levels of silicon but the compositions vary depending on the degree of vitrification and possible reactions with other materials (fuel ash, slags, etc). The glassy samples tend to have higher levels of magnesium and titanium than the fayalitic slags (Figures 18 and 19), many other elements (eg sodium, potassium and calcium) show no consistent differences between glassy and fayalitic slags (Table 7; Figures 19 and 20).

Table 6. Average chemical composition of the analysed samples of smithing slag and related materials

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	K ₂ O	CaO	TiO ₂	MnO	FeO
#01	0.6	0.8	23.7	50.6	0.4	<0.1	1.6	2.9	1.3	<0.1	17.7
#02	0.7	1.0	23.1	52.0	0.2	<0.1	3.1	1.6	1.1	<0.1	16.8
#03	0.9	0.7	18.9	51.2	0.5	<0.1	1.7	3.4	0.9	<0.1	21.4
#04	0.6	0.3	8.9	24.6	0.3	0.8	0.8	1.3	0.4	0.3	60.3
#05	0.2	0.2	5.2	10.6	0.3	0.2	0.2	0.3	0.1	0.5	81.9
#06	0.7	1.0	19.6	56.4	0.3	<0.1	2.3	1.5	1.0	<0.1	16.8
#07	2.3	1.3	21.9	50.9	0.3	<0.1	1.7	2.8	1.2	<0.1	17.2
#08	2.3	1.5	21.9	51.6	0.2	<0.1	1.5	2.3	1.2	<0.1	17.2
#09	1.4	1.6	21.9	61.6	0.2	<0.1	3.3	1.0	1.0	<0.1	7.5
#10	0.7	1.1	10.6	23.3	0.5	0.3	1.3	4.6	0.3	<0.1	56.4
#11	0.7	1.6	22.9	52.2	0.5	<0.1	3.5	4.2	0.7	<0.1	13.3
#13	0.7	0.2	2.7	30.4	0.5	<0.1	3.9	3.6	0.2	<0.1	57.5
#14	0.4	0.5	7.4	72.0	0.4	<0.1	2.0	1.1	0.4	<0.1	15.5
#15	0.7	0.4	2.3	42.9	0.6	<0.1	4.0	4.0	0.1	<0.1	44.6
#16	0.2	0.5	6.6	18.1	1.1	0.2	0.3	0.8	0.1	0.3	71.4
#17	0.5	0.7	12.7	72.5	0.4	<0.1	2.5	0.4	0.7	<0.1	9.2
#18	0.8	4.2	13.9	60.2	<0.2	0.6	3.6	9.1	0.7	0.1	5.6
#19	0.3	0.4	13.5	27.2	0.5	0.4	1.0	1.6	0.4	<0.1	54.1
#20	0.5	0.7	18.9	40.4	2.8	<0.1	1.3	5.0	0.5	<0.1	29.6
#21	0.5	0.3	6.1	29.9	1.0	<0.1	2.1	3.8	0.2	0.1	55.7
#25	1.3	1.8	17.0	68.8	<0.2	<0.1	2.7	0.6	1.0	0.2	6.0
#26	1.0	2.3	9.8	53.2	1.4	0.1	5.1	19.9	0.8	0.1	5.8
#31	0.2	0.3	9.3	31.4	0.2	<0.1	1.8	5.2	0.3	<0.1	50.8
#32	0.3	0.4	7.9	29.8	0.2	<0.1	1.5	4.4	0.2	0.1	54.8
#33	1.4	1.7	23.4	55.2	<0.2	0.1	3.0	1.1	1.3	<0.1	12.6

Table 7. Average composition of fayalitic and glassy slags

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	K ₂ O	CaO	TiO ₂	FeO
Fayalitic	0.4	0.4	7.3	26.8	0.5	0.5	1.7	3.0	0.2	58.76
	±0.2	±0.3	±3.5	±8.6	±0.3	±0.6	±1.3	±1.8	±0.1	±10.6
Glassy	1.1	1.3	20.3	53.7	0.6	<0.1	2.6	3.9	1.0	15.1
	±0.6	±0.5	±3.9	±6.8	±0.8		±1.1	±5.2	±0.2	±6.8

An examination of the data on the composition of the smithing slag, taking into account the type of fuel known (or believed) to have been used (Figures 21 and 22), shows considerable overlap between charcoal and coal/coke (Table 8). The slags produced using coal or coke include some with high iron and low silica and some with low iron and high silica. The slags from charcoal hearths tend to have moderate proportions of both of these elements (Figure 21). The charcoal slags tend to have lower sodium to potassium ratios and higher aluminium to silicon ratios (Figure 22), although there remains some overlap.

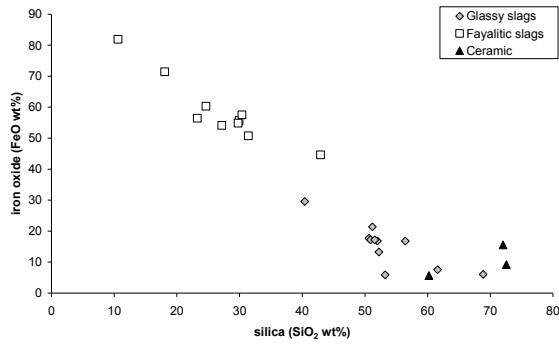


Figure 17. Silica and iron oxide content of smithing slags

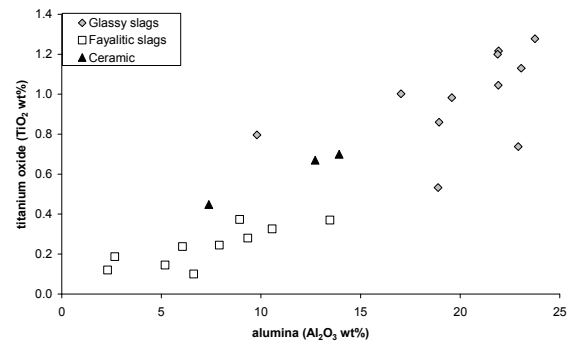


Figure 18. Aluminium oxide and titanium oxide content of smithing slags

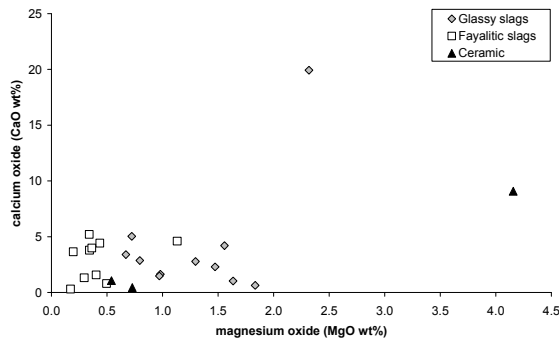


Figure 19. Magnesium oxide and calcium oxide content of smithing slags

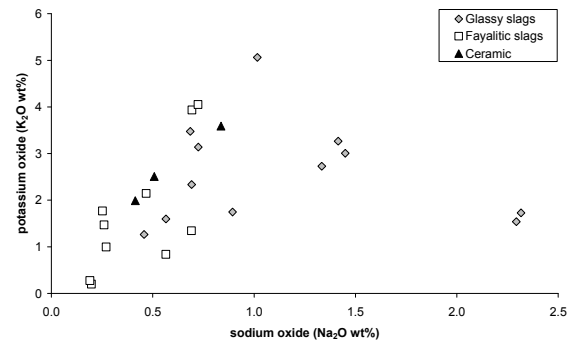


Figure 20. Sodium and potassium oxide content of smithing slags

Table 8. Average composition of slags by known or assumed fuel type

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	K ₂ O	CaO	TiO ₂	FeO
Charcoal	0.5	0.7	6.4	34.3	0.7	0.2	2.8	6.3	0.3	47.5
	±0.3	±0.8	±3.3	±12.2	±0.5	±0.2	±1.9	±6.8	±0.3	±22.3
Coal/Coke	0.9	1.0	17.3	44.2	0.5	0.3	2.0	2.4	0.8	30.3
	±0.7	±0.6	±6.6	±16.8	±0.2	±0.5	±1.0	±1.3	±0.4	±24.1

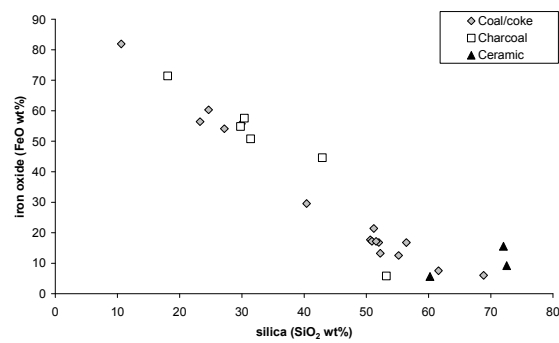


Figure 21. Silica and iron oxide content of smithing slags

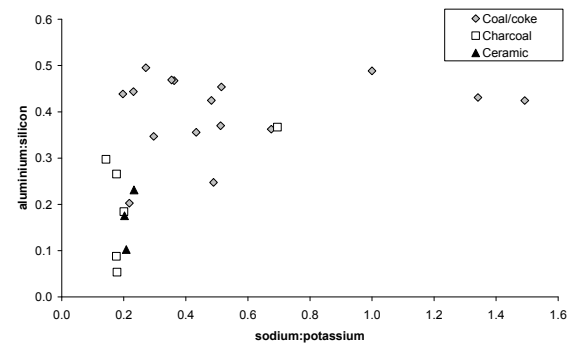


Figure 22. Alkali ratio and alumina to silica ratio of smithing slags

DISCUSSION

The examination and analysis of a range of iron smithing slags has shown that these have varied microstructures and contain a suite of elements which vary across considerable concentrations. Some of these slags are fayalitic in nature while others are glassy, although the latter usually show the presence of some very fine crystalline phases. There is no clear relationship between the slag microstructure and the type of fuel used or the date of the slag. The slag known (or thought) to have been produced using charcoal tends to have lower Na: K ratios than those produced using coal or coke. In addition, the Al:Si ratios are usually higher for coal/coke slags than charcoal ones, although there are occasional exceptions. Sulphur is detected in some slags and in a few cases at quite high levels. It seems logical that sulphur would derive from coal or coke, however, the selection of low-sulphur coal for metallurgical applications would mean that not all coal/coke smithing slag would contain high levels of sulphur.

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