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Summary

A model is proposed for the formation of smithing slags, in particular the characteristic plano-convex hearth bottom. The composition of smithing slags is given and the source of the major and minor oxides is discussed. The model suggests the mechanisms which account for the observed mineral textures.

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A Model for the Formation of Smithing Slags

Dr Gerry McDonnell

1 Introduction

The majority of ironworking slag studies have been focused on iron smelting slags in order to investigate smelting technology, eg furnace temperatures, and ore sourcing. The smithing slags have received little attention, despite the fact that greater quantities of smithing slag than smelting slag are recovered from excavations of settlement sites. One reason for this is the belief that no useful data can be obtained from their analyses. Since very few have been investigated this is as yet an unproven argument. In fact with sufficient analyses, details concerning smithing technology can be elucidated.

Smithing slags are commonly found on settlement sites in Britain from the Iron Age onwards. Their form, size and texture may vary with period and settlement type (eg rural farmstead or urban smithy), but in general they all have some common attributes. This paper will discuss smithing slags in general and will draw on examples from different periods and geographical locations. The time span is restricted to that in which the direct method of iron production was in use, ie from the Iron Age (c700BC in Britain) to the medieval period (c1500AD)when the indirect method of iron production became dominant. The purpose of this paper is to investigate the mechanism of smithing slag formation, in particular that of the characteristic plano-convex slag agglomeration, termed hearth bottoms.

2 Definition

Smithing slags were formed during the secondary smithing process, i.e. during the manufacture and/or repair of artefacts. In this paper primary smithing slags, i.e. those generated during the refining of the bloom, are not discussed, although many of the points discussed in this paper will be relevant to the formation of primary smithing slags. To examine the mechanism of slag formation, hearth bottoms rather than smithing slag lumps were analysed because the "way-up" in which they formed in the hearth can be determined by morphological examination. It is assumed that the convex surface was the underside of the hearth bottom and the flat surface (often with a central depression due to the air blast) formed the upper surface. To confirm or refute this assumption the magnetic declination of three samples was examined using a spinning magnetometer. This confirmed that the declination was negative, i.e. pointing down to the centre of the earth when they were measured in the correct "way-up" position. This confirmation of the slag orientation does assume that the hearth bottoms cooled and passed through their Curie Point in-situ. If they had been extracted from the hearth and cooled in another orientation then the declination would be different.

Hearth bottoms are the characteristic form of smithing slag, but they do not form the majority (by weight) of smithing slag recovered from archaeological sites. This is demonstrated by Table 1, which gives the weight of smithing slag lumps (SSL) and of hearth bottoms (HB) recovered from seven sites, together with the weight percentage of the hearth bottoms. Hearth bottoms normally (as here) represent less than 33% by weight of smithing debris recovered from excavations.

TABLE 1 Weights of Smithing Slag Lumps and Hearth Bottoms Recorded From English Excavations

		Weight (kg)		Weight %
Site	Date	SSL	HB	HB
Beckford, Hereford & Worcester	I.A.	4.8	0.7	13
Dorchester, Dorset	R.B.	308.6	3.2	1
Tiddington, Warwickshire	R.B.	136.5	2.5	2
Wickford, Essex	R.B.	52.4	16.2	24
Raunds, Northamptonshire	A.S.	29.2	14.0	32
Wharram Percy, Yorkshire	A.S.	74.2	5.1	6
Burton Dassett, Warwickshire	Med	310.3	34.5	10

I.A. = Iron Age; R.B.=Romano-British; A.S.=Anglo-Saxon; Med=Medieval

Other residues including hammer scale, hearth lining, cinder and fuel ash slag were also formed during the smithing process. These residues are relevant to the formation of smithing slag but are not discussed individually in detail. A brief description of each type is given in Table 2.

Table 2 Description of Other Residues Formed During the Smithing Process

Hammer Scale	- Flake hammer scale are flakes of iron oxide or slag that detatch from the artefact during working. - Spheroidal hammer scale are droplets of slag expelled during welding.
Hearth Lining	- The fired and/or vitrified clay lining of the hearth. It may become attached to slag pieces.
Cinder	- An intermediate product between hearth lining and smithing slag, normally considered a silica rich slag
Fuel Ash Slag	- High silica slag formed from the ash of the fuel reacting with silica-rich materials

3 Smithing Slag Morphology

Smithing slags have two forms, diagnostic hearth bottoms, and randomly shaped smithing slag lumps. The hearth bottoms are plano-convex accumulations of slag and are usually sub-circular in plan, although secondary growth can lead to a wide range of shapes. They range in size from tens to hundreds of millimetres in diameter and ten to a hundred millimetres in depth. The weights of hearth bottoms are more varied due to the variation in "overall density" (usually because of differences in vesicularity), ranging from tens of grammes to thousands of grammes. The dimensions of hearth bottoms recovered from the Anglo-Scandinavian and medieval site (9th-13th Century A.D.) at Coppergate, York (Yorkshire) are given in Table 3 and the range of hearth bottom weights is shown in Figure 1. Both sets of data demonstrate the wide variation in hearth bottom dimensions that may be present on one site.

TABLE 3 Dimensions of Hearth Bottoms Recovered from Coppergate, York

Dimension	Range	Mean	Standard Deviation
Weight (gms)	45-2100	385	304
Major Diameter (mm)	40-900	95	30
Minor Diameter (mm)	30-170	75	20
Depth (mm)	10-100	40	15

Smithing slag lumps can be considered as irregularly shaped, part-formed hearth bottoms. They can range in weight from a few grammes to several hundred grammes.

Hearth bottoms and smithing slag lumps show great variation in surface texture, ranging from a rough, agglomerated appearance to distinctly flowed or ropey forms. Non-slag inclusions, in particular stone fragments and charcoal, are commonly incorporated in the slags. The texture of the cross-section ranges from heavily vesicular to fine-grained and smooth, though vesicularity (coarse or fine) is more typical.

4 Chemical and Mineral Composition

Hearth bottoms and smithing slag lumps have the same origins and are thus merely morphological variations of the same material, so their chemical and mineral compositions may be discussed together. The bulk analyses were obtained using a Scanning Electron Microscope (SEM) with an attached energy dispersive X-ray analyser in the raster scan mode on a prepared section. Five different areas on each sample were analysed at magnifications of greater than x200. The mean chemical compositions of 14 samples from 6 sites are given in Table 4 and show an overall fayalitic composition with minor percentages of alumina, lime, and potash. The standard deviations indicate a considerable variation in composition. The slags usually comprise three phases, silicate (normally fayalite), free iron oxide and a glassy matrix, although in some cases such as Beckford (McDonnell 1986, 157) the glass phase was absent. The mean phase compositions are given in Table 4 and confirm the silicate phase as fayalite with minor percentages of other oxides present, in particular magnesia. The glass phase shows a typical composition, being rich in silica, alumina, lime and potash. The iron oxide content of the glass shows great variation, being as low as 10% in some cases. The iron oxide phase sometimes contains minor levels of silica and if the oxide occurs as magnetite rather than wustite, alumina and titania may also be present.

TABLE 4 Smithing Slag Mean Bulk and Phase Analyses

	BULK		SILICATE		GLASS		IRON OXIDE	
	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
Na_2O	0.4	0.5	0.2	0.2	1.0	0.8	0.1	0.1
MgO	0.4	0.3	1.1	0.8	0.0	0.1	0.3	0.3
Al_2O_3	3.7	1.7	0.3	0.9	10.7	4.8	0.8	0.6
SiO_2	25.8	8.0	29.3	2.2	40.6	8.3	1.2	1.5
P_2O_5	0.8	0.9	0.4	0.6	3.0	3.0	0.0	0.1
S	0.1	0.1	0.0	0.1	0.3	0.3	0.0	0.1
K_2O	1.7	0.9	0.1	0.4	7.6	5.0	0.0	0.1
CaO	3.6	2.4	1.9	1.3	10.8	7.2	0.1	0.1
TiO_2	0.2	0.1	0.0	0.1	0.4	0.3	0.4	0.6
V_2O_5	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Cr_2O_6	0.1	0.1	0.0	0.0	0.1	0.2	0.0	0.1
MnO	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1
FeO	61.9	10.8	66.5	3.3	24.3	10.9	93.9	5.0
CoO	0.1	0.2	0.1	0.2	0.0	0.1	0.1	0.2
NiO	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1

The texture of individual minerals shows great variation, the silicate ranging from lath (Plate 1) to massive (Plate 2), while the iron oxide is predominantly globular dendrites although in some cases fine skeletal dendrites are present. If the oxide is present as magnetite the crystals may be cubic. The glass phase occurs at the mineral boundaries and usually contains fine crystallites of silicate. The proportion of the phases shows great variation (Plate 3), not only between samples but also within samples, leading to mineral and chemical heterogeneity. Table 5 presents the mean volumetric phase percentages, determined by optical microscopy of the samples whose mean analyses are given in Table 4. They confirm the essentially silicate (fayalitic) composition of the slags, and confirm the large variation in all the phases, particularly the glass and iron oxide phases.

TABLE 5 Volumetric Phase Percentages, Mean Values and Standard Deviations

	Silicate Phase	Glass Phase	Iron Oxide Phase
Mean	53	23	24
S.D.	16	12	20

5 The Principal Sources of the Major and Minor Elements

In general the composition of smithing slags is essentially fayalitic, the dominant oxides being those of iron and silicon. The minor oxides are alumina, potash, and lime. The most likely sources of these oxides is discussed below.

It is proposed that the slag inclusions in the iron being worked do not make a major contribution to the formation of smithing slag. There are two reasons for this, firstly that in the majority of iron the slag inclusion content is low, probably less than 5-10% by volume. In order to release a significant volume of slag inclusions a far larger volume of iron would have to be oxidised, causing the slag inclusion component to be only a minor constituent of the resulting slag. The second reason is that if inclusions of smelting slag in the iron were incorporated into the smithing slag to a significant extent then the level of manganese oxide in many smithing slags would be much higher. The high levels of manganese oxide found in many smelting slags is due to its preferential partioning to the slag rather than the metal during the smelting of manganese bearing ores(McDonnell 1986).

5.1 Iron Oxide

The iron oxide derives from oxidation of the iron being worked. The oxide scale formed on the surface of the metal would be a major contributor to slag formation if it parted from the metal and fell into the hearth.

5.2 Silica

The silica component of the slag came from two sources. The major contribution was from sand fluxes applied to the surface of the iron being worked. The flux cleaned the surface of the metal by reacting with the iron oxide scale and any other oxides to form a thin coating of fayalite and/or slag.

This layer is oxygen impervious and so prevents further oxidation of the iron. The melting point of fayalite is 1177°C but it may form by solid state reaction at temperatures as low as 660°C.

The second source of silica was the hearth lining. The physical attachment of the slag to the hearth lining and the formation of cinder between the lining and the slag proves that migration of silica occurred. The extent of silica diffusion cannot be measured, but examination of hearth bottoms with attached lining and slagged lining fragments shows that only a small portion of lining is absorbed by the slag.

5.3 The Source of the Minor Elements (Al,K,Ca)

The minor elements derive from the hearth lining, and perhaps the flux used to clean the iron, and also from the ash produced by the fuel.

6 A Model For Slag Formation

The formation of iron oxide and fayalite on the surface of the iron while it is being worked is the primary mechanism of smithing slag formation. This slag would fall from the iron and accumulate in the hearth. Since the smith would carry out most of the work in the tuyere zone of the hearth, where the temperatures are highest but oxidising conditions prevail, the slag would develop in front of the tuyere. As the slag developed in the hearth, reactions would occur between slag and hearth lining as described above.

Using this model some predictions as to the variation in the chemical and mineral composition in different zones of a hearth bottom can be made. There are four areas of interest in a hearth bottom (Figure 2), the upper surface which should contain the the last material to join the hearth bottom, the central core which should display a fully developed slag texture, the basal zone which should contain the first slag formed and may show evidence of reactions between the slag and the fuel ash and/or the base of the hearth and, finally, the reaction zone between the slag and the hearth lining. During routine slag analysis samples from the centre of a slag lump are selected for study because the peripheries may have suffered excessive corrosion during burial. Therefore the edges (i.e. upper, basal and the reaction zone) are not normally investigated. Analysis of these zones in five specimens show a range of structures, most of whose variation falls within the expected textural heterogeneity of smithing slags. Normally the upper surface (Plate 4) displays similar mineral textures to those observed in the core of the slag (Plate 5). The mineral texture may vary from sample to sample, ie some may be iron rich with rounded iron oxide dendrites and others may be deficient in iron oxide, but the upper and core zones display the same overall texture within the heterogeneous variation. The basal zone is normally more vesicular (Plate 6) than the core zone but usually displays a texture broadly similar to the core zone. If the free iron oxide content is high then corrosion severely affects this zone. The high vesicularity is probably the normal texture of the slag as it forms, and the less vesicular slag in the core of the hearth bottom results from compression of the slag at a sufficiently high temperature during its accumulation in the hearth. The basal zone retains the vesicular texture because it was never heated to a high enough temperature after its formation.

The reaction zone normally displays a silicon gradient from lining to slag, but there are well defined boundaries (Plate 7) present in the structure.

One analysis of a typical hearth bottom (Figure 2) showed that the reaction zone had the expected silica-rich microstructure (Plate 6,Table 6), with potassium-aluminium silicate inclusions (Phase P2 in Table 6) surrounded by a glass/fayalite groundmass (Phase P1 in Table 6). Higher free iron oxide contents might be expected in the upper and basal surfaces (Plates 4 and 6) but the iron oxide content was low throughout the slag (Table 7); in three areas (B1-B3) the analyses approximate to fayalite. In the other two, the iron oxide content is very low and the slag is rich in lime. This low iron oxide content is not unusual in smithing slags.

Identifiable hammer scale structures may also be expected, ie remnant flakes or spheroids might be present in the peripheries of the slag prior to their absorption into the slag structure, but in only one case have these structures been observed. These structures may be more highly susceptible to corrosion, especially if the free iron oxide content is high, but it is more probable that they are rapidly absorbed into the slag, hence rapidly loosing ther morphology. It is also surprising to observe silicate lath structures (Plate 1) since they are typical of fast cooled structures (Donaldson 1976, 1979), which would not be expected in the normal course of events in a hearth bottom. Their presence is probably due to dendritic crystal growth in the solid or plastic state, rather than rapid cooling from the liquid state; they represent low temperature growth rather than high temperature growth.

Table 6 Analyses of the Silica Rich Zone from Sample Bragny4a

	B1	P1	P2
MgO	0.0	0.0	0.0
Al_2O_3	8.0	10.9	12.9
SiO_2	53.7	55.6	44.6
P_2O_5	0.0	0.0	0.0
S	0.1	0.0	0.0
K_2O	16.1	16.1	42.3
CaO	1.7	2.9	0.0
TiO_2	0.4	0.4	0.0
Cr_2O_3	0.0	0.0	0.0
MnO	0.0	0.1	0.0
FeO	18.3	14.4	0.1
CoO	0.2	0.1	0.0
NiO	0.0	0.1	0.0
CuO	0.1	0.0	0.0
TOTAL	98.6	100.6	99.9

B1= Bulk Area Analysis; P1 phase around phase P2

Table 7 Bulk Area Analyses of Slag Zone in Sample Bragny4a

	B1	B2	B3	B4	B5
MgO	0.0	0.0	0.0	0.0	0.0
Al_2O_3	3.8	3.5	4.1	7.7	6.3
SiO_2	21.3	21.3	19.1	24.3	26.7
P_2O_5	0.0	0.0	0.0	0.0	0.0
S	0.1	0.0	0.0	0.1	0.1
K_2O	3.6	3.8	3.2	12.8	9.4
CaO	0.6	0.5	0.7	1.4	1.3
TiO_2	0.2	0.3	0.2	0.3	0.1
Cr_2O_3	0.1	0.0	0.0	0.0	0.0
MnO	0.4	0.2	0.1	0.1	0.1
FeO	68.3	68.7	70.2	53.0	54.5
CoO	0.0	0.1	0.0	0.0	0.1
NiO	0.0	0.1	0.0	0.0	0.0
CuO	0.1	0.1	0.2	0.1	0.0
TOTAL	98.5	98.6	97.8	99.8	98.6

8 Summary

It is argued that smithing slags, in particular hearth bottoms were formed from the oxide scale of the iron being worked and the flux used to clean its surface and protect it from oxidation while in the hearth. Slag-hearth lining reactions were important, and contributed to the overall chemistry of the slag. Slag inclusions in the metal did not make a significant contribution to slag formation. Smithing slags are chemically and mineralogically heterogeneous, but less so than might be expected. This is due to solid state reactions, eg formation of fayalite, driving the composition towards equilibrium.

The results obtained from a general study of a broad range of smithing slags and hearth bottoms and detailed study of selected hearth bottoms indicate that the model outlined above satisfies most of the observations and data. However, there are some discrepancies, in particular the absence of residual hammer scale structures, and it would be possible to interpret the data in a different way. It is therefore necessary to pursue the study of smithing slags to investigate these discrepancies, which if understood would enable technological interpretations to be drawn from smithing slag analyses.

References

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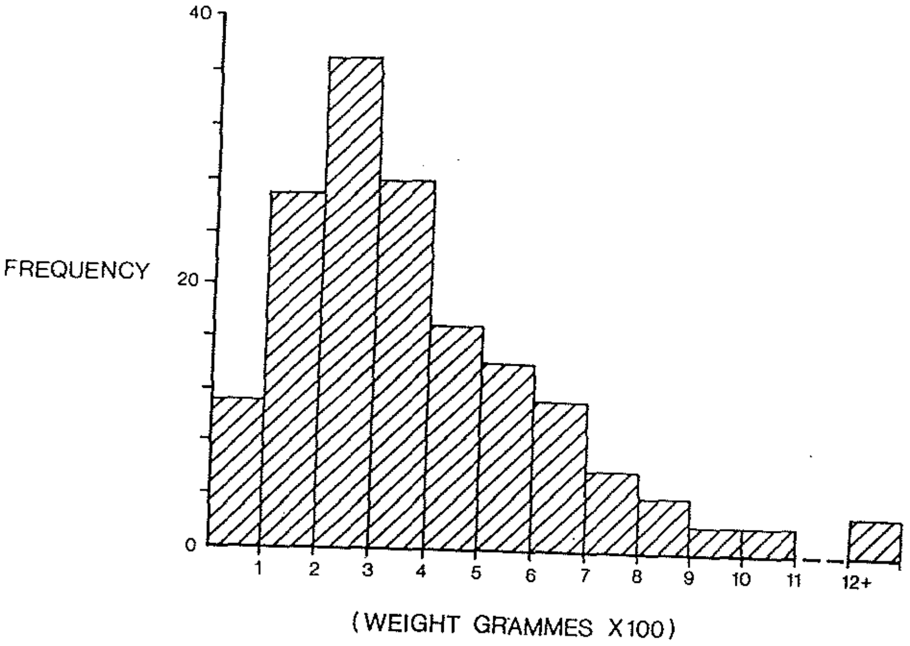

FIGURE 1 Histogram of Hearth Bottom Weights from Coppergate, York

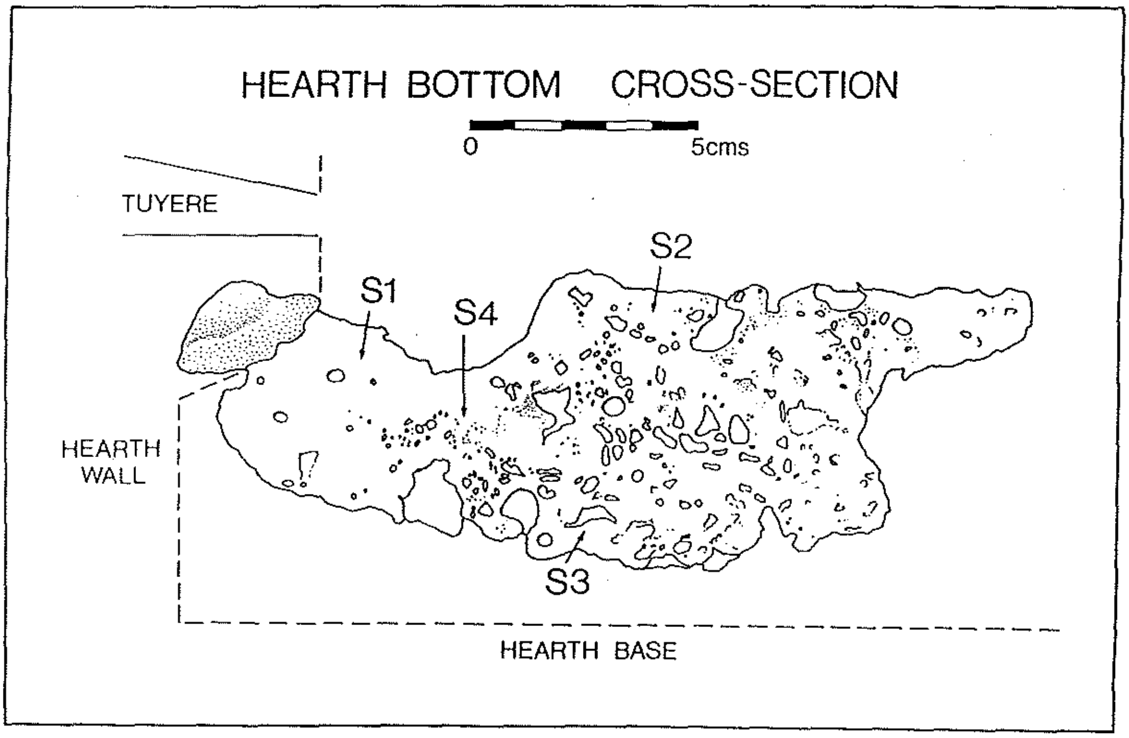

FIGURE 2 Hearth Bottom Cross-Section

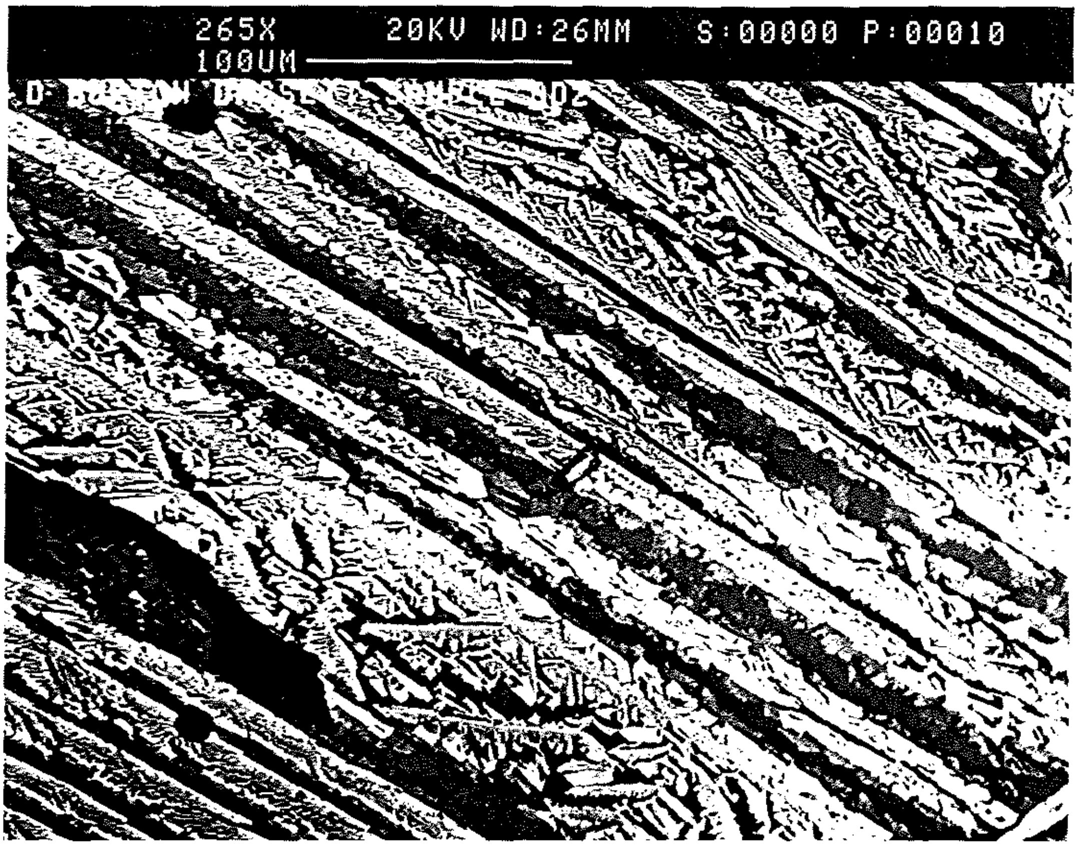

PLATE 1 Back Scattered Electron (BSE) Image of silicate (fayalite) laths (grey). (Sample BD2 Burton Dassett, Warwickshire)

PLATE 2 BSE Image of massive silicate (fayalite, grey) with rounded wustite (white) and the glassy groundmass (black) (Sample SOU14601 Hamwih, Southampton)

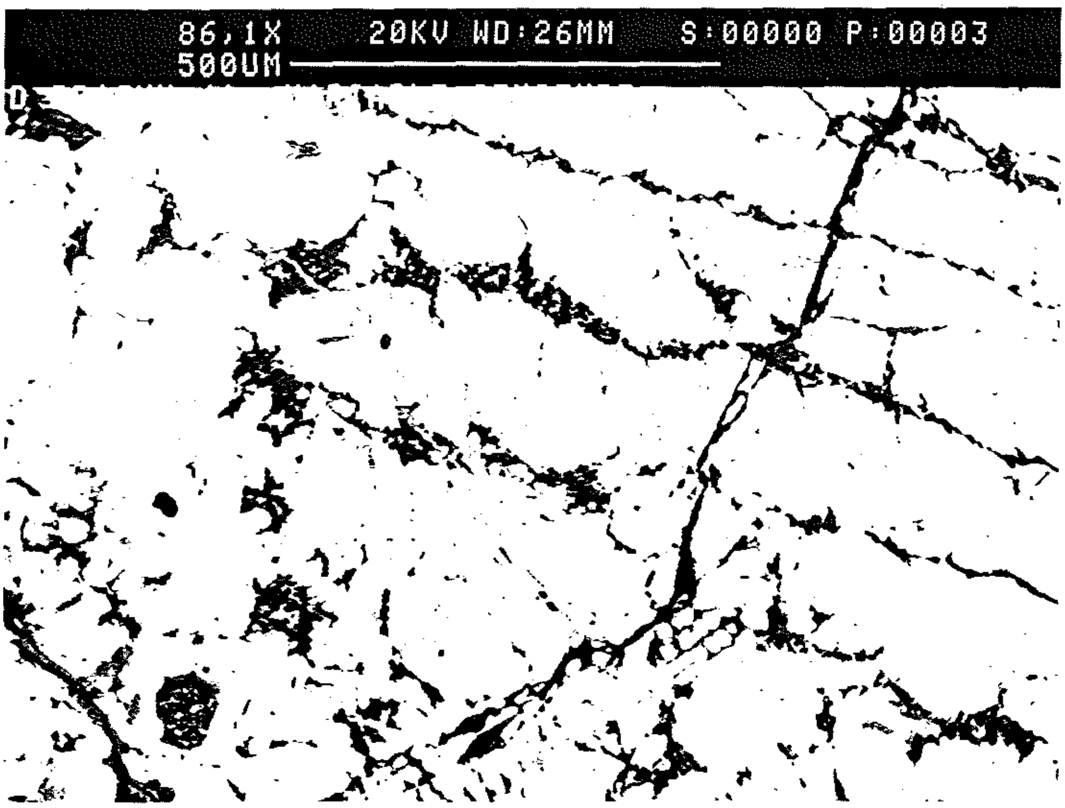

PLATE 3 BSE Image of varied structure. White iron oxide dendrites (wustite?) and silicate laths (grey) in a glassy groundmass (black). (Sample B4a, Bragny, Burgundy, France).

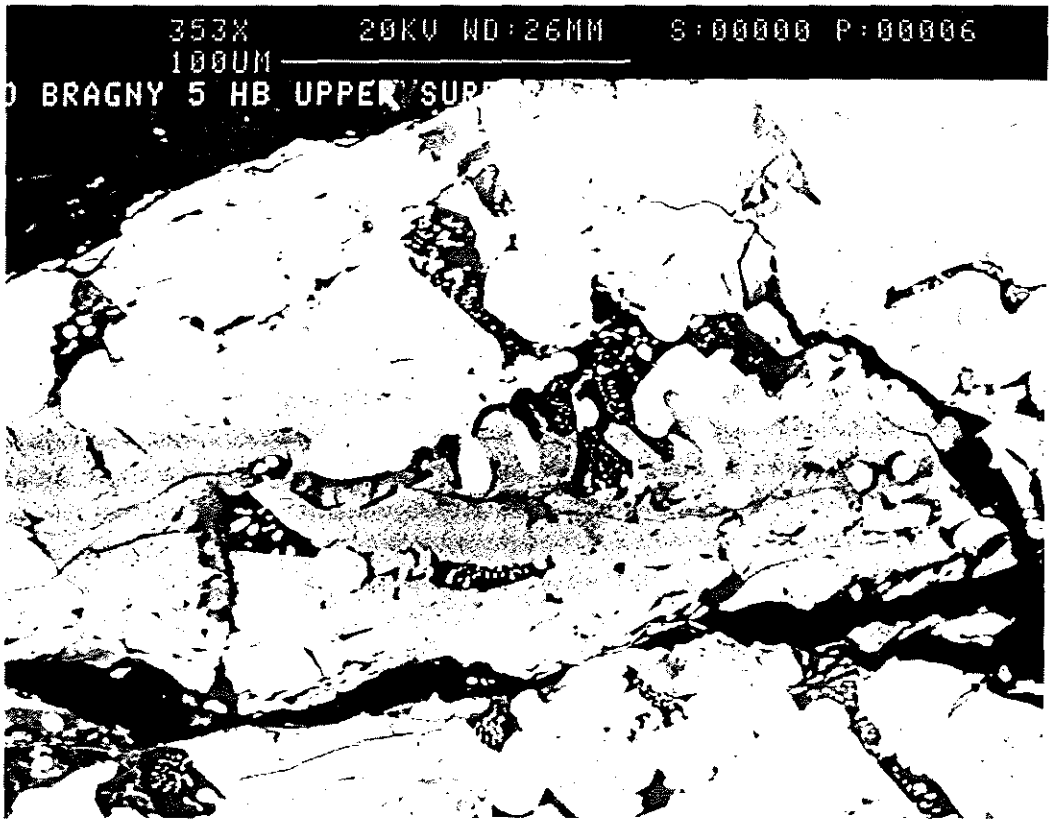

PLATE 4 Rounded iron oxide dendrites (white) and silicate (grey) in glassy groundmass (black) in the upper surface of a hearth bottom (Sample B5, Bragny, Burgundy, France).

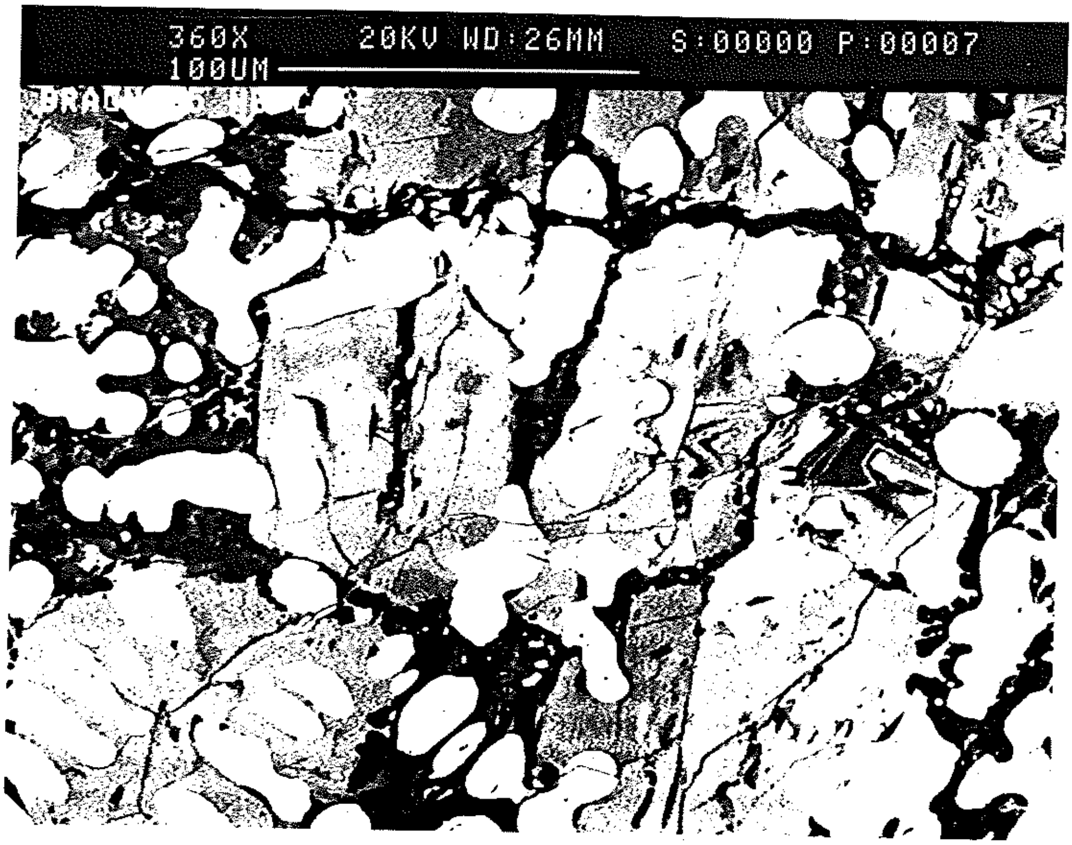

PLATE 5 Similar structure to Plate 4 but in core of the slag.

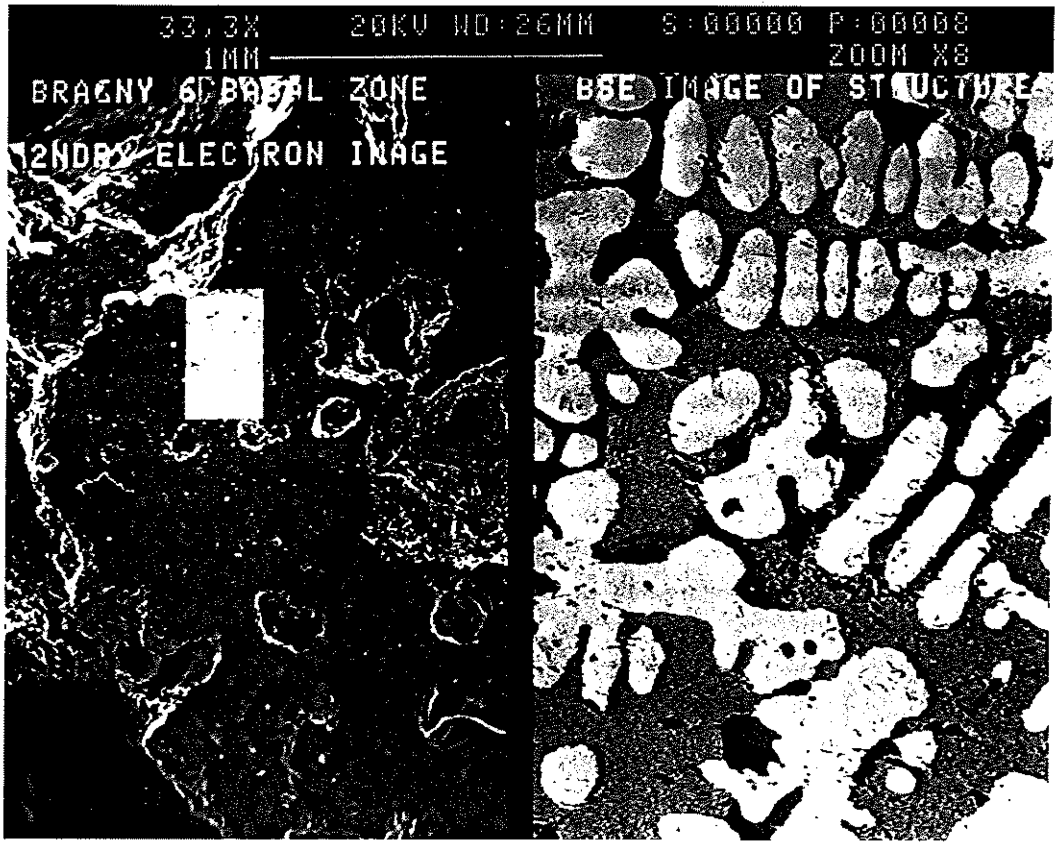

PLATE 6 Basal zone of Sample B5 Bragny (Burgundy, France). The lefthand image is a secondary electron image showing vesicular structure. The righthand side is a BSE image of the highlighted square, showing essentially the same structure as Plates 4 and 5.

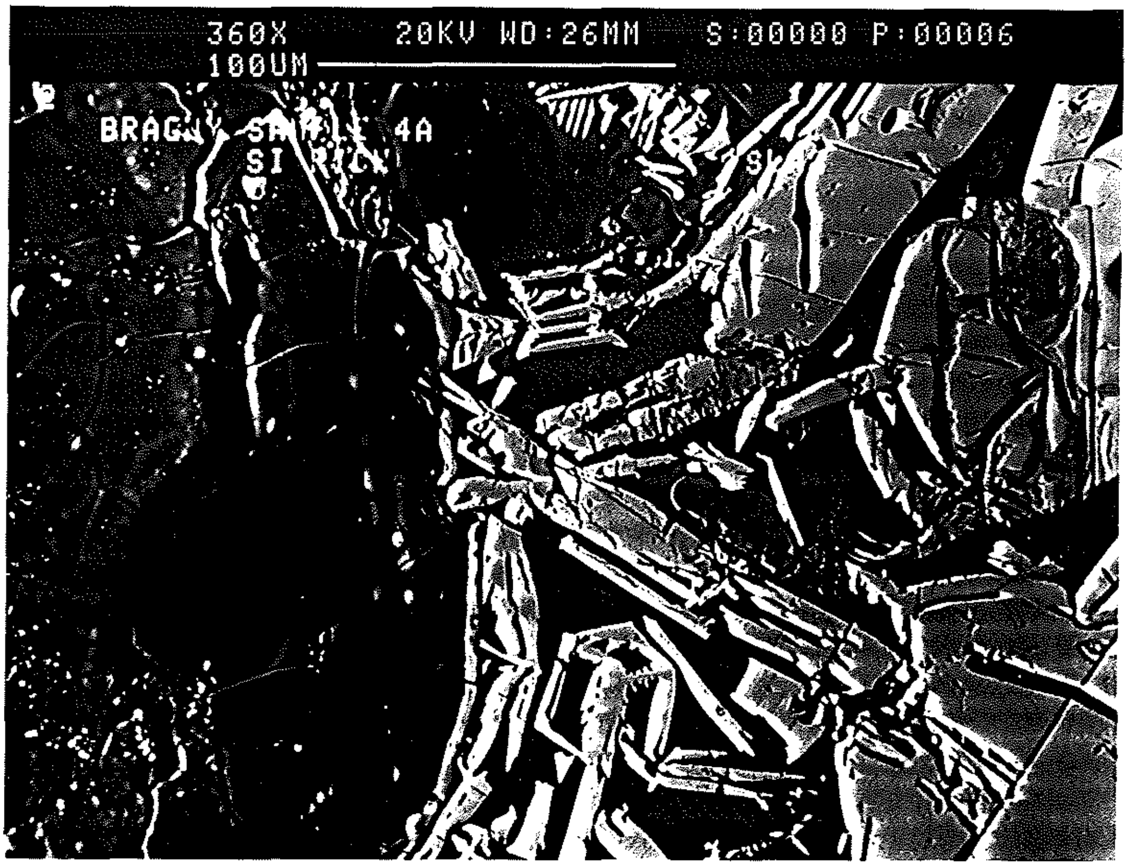

PLATE 7 BSE Image of Sample B5 Bragny (Burgundy, France) showing sharp interface between high silica zone (left hand side)and more typical slag structures (right hand side, white lath structures).