

Slag and related materials from Bornish, S. Uist

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Abstract

Large collections of slag were made from both Iron Age and Norse contexts. The slags are characterised by low density, porous, clinkery material, ranging from sub-mm particles up to blocks weighing several hundred grams.

Closely spaced sampling of floor deposits associated with an Iron Age corn-drying kiln on Mound 3 (FD) demonstrates that it produced considerable quantities of slag, particularly of fine particles. The use of iron-bearing peat as fuel allowed for the production of at least partial melting of both the sand included in the peat, and the wind-blown lime-rich sands of the locality. A similar, but less well marked, relationship is seen between the distribution of slag across Iron Age house floors on Mounds 3 (DD) and 1 (CB) and the position of the hearths. The non-metallurgical origin of these slags allows a similar interpretation to be suggested for the larger blocks of slag associated with the Norse "industrial" hearth pits (CE) on Mound 1.

The substantial slag blocks recovered from the Norse "industrial" contexts on Mound 1 have been investigated texturally, mineralogically and chemically. The slags frequently show a mineralogy involving clinopyroxene and plagioclase. In the most iron-rich areas the assemblage may also include iron oxides and olivine. The unusual nature of these slags is interpreted as a product of the highly calcareous nature of the sand into which the hearths were constructed (and also which are included within the peat fuel), coupled with the high iron content of the peat. These slags can be demonstrated to result from flowage of a partial melt of a mixture of sand (from the walls of the hearth), disaggregated bedrock (from blocks lining the hearth) and peat ash, from the hotter parts of the hearth and producing a sintering of the sand on the hearth floor. This material would have needed clearing from the hearth on a regular basis. The purpose of these hearths is uncertain, but one slag block appears to contain the remnants of a pot base. The analytical studies provide no evidence for slag production involving any metallurgical process.

The slag material recovered from sieved micro-residues, particularly from the floor adjacent to the corn drying kiln on Mound 3, but also from the Mound 1 house floor, includes a significant proportion of magnetic spheroids. These bodies might easily be confused with those produced during the welding of iron, but are less perfectly spherical and have an irregular surface. The discrimination of these two classes of spheroid has implications for the interpretation of magnetic residues from other sites.

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Analytical Methods

Analytical work was undertaken using the Philips PW 1400 X-ray fluorescence spectrometer (XRF) and the Perkin-Elmer Elan 5000A inductively coupled plasma - mass spectrometer (ICP-MS) of the Earth Sciences Department, Cardiff University. The electron microscope and microanalytical work was initially undertaken on the Cambridge Instruments S360 scanning electron microscope (with a Link Analytical Ltd. AN10000 energy dispersive X-ray analysis system) of the Earth Sciences Department, Cardiff University and later on the Camscan Maxim 2040 scanning electron microscope with Oxford Instruments energy-dispersive and wavelength-dispersive analytical systems of the Archaeology Section, The School of History and Archaeology, Cardiff University.

Material and Project History

The project to investigate the slags from Bornish commenced with a chemical investigation of unstratified material from mound 1. Two specimens (BO.A and BO.B; from material marked "*Mound 1 unstratified material 24/6/96*") were analysed, with the intention that chemical analysis (XRF and ICP-MS) alone might give a clue to the nature of the slag material, in particular as to whether it was of metallurgical origin. The samples were selected because of the presence of a dense, greenish, glassy, phase, which appear to be closest out of the available material to typical metallurgical slags. Neither specimen had any morphological features to assist with interpretation. In addition, similar analysis was made of a sample of sand from the site (BO.C).

The wholerock analyses are presented in Table 1. The analyses for BO.A and BO.B have high iron contents, equivalent to approximately 19% when calculated as Fe_2O_3 . Both samples showed a slight weight gain on ignition, and this is most likely due to a significant proportion at least of the iron being present as Fe (II), rather than as Fe (III). The chemical composition shows enrichment in many elements besides iron, compared with the sand sample BO.C. Some of this enrichment may be due to the use of a rock lining in the hearth, rather than the simple sand, but it is probably mostly due to material introduced in the ash fraction of peat. In particular U, V, Mo and P show major enrichment in the slags, and these are elements associated with the organic material in peat. The "immobile" elements (the rare earth elements, Y, Nb, Ti and Zr) are also enriched in the slags, suggesting the possible involvement of resistate material - perhaps a weathered bedrock, but might also reflect the concentration of these elements, often described as being among the "incompatible" elements, into the partial melt. The high iron contents and the reduced nature of the iron are both features which might be found in iron-working slags, and this was how the material was interpreted in the first report (Young & Thomas 1997).

As a second phase to the investigation, three additional pieces of unstratified slag were examined using the BSEM (BO.D, BO.E, BO.F) to provide mineralogical and textural information. The BSEM investigation was extended to the sample of the sand from the site (BO.C). In addition three samples of peat from the area were ashed and analysed geochemically (BO.P1, BO.P2, BO.P3).

The third phase of the project followed the 1997 field season. Two large lumps of slag were picked from a stratified collection (context 379, >100 mm). They were selected because of their stronger overall morphological resemblance to more conventional smithing slag hearth cakes, despite the previous studies having failed to demonstrate conclusively that the slags from the site had a metallurgical origin. These two specimens were sliced and subdivided. One piece proved to be internally layer, and was sliced to give two samples for geochemical analysis (BO.J - a representative fragment; BO.H - a piece of one of the white coarse layers). The lower part of the specimen was reserved for inspection by BSEM as two pieces BO.I1 and BO.I2. This specimen was subsequently recognised as a strongly altered and slagged fragment of Lewisian Gneiss. The second selected specimen

was from a low density plano-convex sheet. Four subsamples were removed: BO.K4 from the centre for BSEM, BO.K1 (base), BO.K2 (top), and BO.K 3 (margin) for chemical analysis.

In 2001 the entire macroscopic (>10 mm) slag collection from mounds 1 and 3 was examined, and representative materials from the sieved fines also examined (the sub-10 mm sieved fines are described throughout this report as the microscopic slags). Data on the distribution by weight of both slag material from the coarse and sieved fine fractions was assembled for several key horizons, so that the spread of material with respect to various features could be determined. Detailed examination of examples of fines material from mound 3 was undertaken, including magnetic separation and examination under the SEM.

Mound 3

Distribution of slags: Mound 3

The controls on the distribution of slag have been investigated through examination of the samples taken across three surfaces: two successive floors (contexts 276 and 269; Figure 1) within the granary building and a house floor (context 614; Figure 2). The distribution of slag particles in the sieved fine residues shows a strong relationship to the position of the kiln in the granary structure.

Several different measures of the slag distribution are given. The samples from each grid square were generally not completely picked, so a correction factor has been applied to each subsample to derive:

1. the weight of slag per square metre
2. the weight of slag per litre of deposit sampled

In addition, a third indicator, the proportion of slag in the assemblage >10mm, was also mapped.

For the early floor (276) in the granary, the total slag distribution shows a bias towards the centre of the structure, but when the weight/litre of deposit shows the greatest proportion of slag lying in front of the mouth of the kiln, with the greatest density of material lying about 2m from the kiln (with over 11 g/l deposit). The distribution of the coarse fraction is more patchy with peaks in front of the kiln, in the centre of the structure and a further peak in the SE corner of the building.

Within the second floor (269) of the granary, the total slag distribution shows the material dominantly occurring in the SE part of the structure, where the layer was thickest. The weight/litre, however, again shows a distribution along the western wall of the structure, extending out from the kiln (with a peak of 26 g/l in the mouth of the kiln) to the entrance passage, with a second accumulation towards the NE of the structure; an area which also shows the highest proportion of coarse material.

These data support the suggestion that the slags are derived from the kiln. The highest proportion of slag fines on both floors occurs in the area in front of the kiln. Measures of total slag are influenced by the

thickness of the deposit and indicate a large proportion of the slag was finally deposited where the overall accumulation was greatest. The distribution of the small quantity of coarse-grained material was more patchy on both floors, and showed a less close relationship to the position of the kiln, probably reflecting the ease with which coarser particles would be redistributed by secondary processes.

In the Iron Age building (DD) the amount of slag recovered from the sieve samples was very small (maximum of 1.6g / litre of deposit), and the distribution maps are strongly influenced by the occurrence of a small number of larger slag fragments. The results are of therefore rather dubious significance. The total slag distribution and weight per litre give rather similar distributions, with most material lying between the hearth and the north wall. The weight per litre also suggests that slag accumulated to a lesser extent in the southern half of the building. Both distributions include an anomalously high value in the middle of the floor, of uncertain cause. The distribution of the coarse fraction is patchy, but shows accumulation close to the house walls around the northern end of the building, perhaps indicating areas where the floors were kept less clean.

Although the situation in the house is far less clear than in the granary, it seems likely that the slag distribution is controlled by the position of the hearth.

Description of slags: Mound 3

The slags from Mound 3 are characterised by their occurrence in very small pieces. The archive includes only 3 pieces of slag over 10g (11, 15 and 18g) and the remainder of the collection includes only slag fragments below 3g. This is in stark contrast to the large slag blocks on Mound 1 (see below). There are two logical interpretations for this lack of large pieces. One possibility is that they were removed and deposited elsewhere; the other that they were not produced by the activities taking place in the Mound 3 structures. The complete lack of large blocks, or even of small pieces likely to have been derived from the sort of slag sheets recorded on Mound 1 strongly suggests that they were not being produced in the Mound 3 hearths.

A high proportion (approximately 15% in the samples examined) of the slag fines from Mound 3 are magnetic, and can be easily separated from the pickings by magnet. These magnetic fines are typically brownish in colour and are dominated by small spiky sintered fragments, but also include blebs and spheroids suggestive of a more freely flowing material. The spheroids are particularly interesting because of their resemblance to spheroidal hammer scale (Plate 1). They differ from spheroidal hammer scale in being less perfectly spherical and in having a more irregular surface when seen under the SEM (Plate 1, B). At the scale of observation when being picked from the sieve residues under a binocular microscope the two particle types would not be easily separable.

The non-magnetic fraction is dominated by pale grey to creamy yellow fragments of sintered sand and glassy slag. These textures also dominate the coarser fraction of the slag. They are typical porous and friable. Their low density means that few of the slag pieces of this

type in the >10mm fraction weigh more than 2g. A few of the glassy slag fragments are darker, sometimes almost black, but typically still bearing pale quartzofeldspathic grains. The only pieces greater than 10mm are all of a dark glass, presumably of a more iron-rich composition and more free-flowing.

Mound 1

Distribution of slags: Mound 1

Slag was recovered from most sieve samples taken on Mound 1, occurring in 71% of 204 samples from Iron Age horizons and in all 19 samples from Norse contexts. Slag fragments in the sieved samples only rarely exceed 3g, and much of the assemblage is represented by collections with an average slag particle of 0.04g.

The distribution of slag particles in the sieved residues from the closely sampled late Iron Age horizons on Mound 1 (unit CB) shows a strong control by the position of a large hearth. This is illustrated in Figure 3 for contexts 397 and 482 (397 is a floor for the 2nd Iron Age house, CB, with 482 the pit dug for the hearth construction). The overall bulk quantity of slag and the weight of slag per litre of sediment both show concentration of the slag close to the hearth. A similar distribution can be seen in equivalent measures of charcoal and burnt organic matter distribution. Unlike the Mound 3 granary floors, the surfaces around the hearth did not yield a slag component greater than 10mm on sieving.

In contrast, the deposits associated with the Norse "industrial" activity (unit CE) include a significant proportion of coarse grained slag material (ranging up to >100mm). The first significant appearance of a coarse fraction is in a brown sand (contexts 372, 400; total 1.7kg) overlying the Iron Age features, but grouped with the Norse features which cut it. The main concentrations of coarse material occur in pit 389 (context 373; 0.4kg), pit 433 (contexts 379, 390, 403, 416; total 12kg) and a sand deposit lying over the pit (contexts 371, 374, 382; total 4.9kg). The occurrence of slag in these features is interpreted as linked to the adjacent hearth pits. A small amount of coarse slag also occurs in the Norse midden deposits (e.g. context 395).

Description of slags: Mound 1

General Account

The macroscopic slags from Mound 1 are dominated by material comprising friable, sintered sand, mixed with varying proportions of flowed melt. The melted material is dominantly pale, frequently pale greyish in colour, although the variation is from almost white to almost black. The smaller fragments typically show little overall form, but the larger pieces suggest that much of this material originated from the breaking up of sheets of slag. These sheets typically have a base dominated by sintered sand, and an upper part bearing more melted material, often with a glassy upper surface. Several

pieces show that the sheets often had raised or thickened margins, often showing incorporation of much larger (up to 6mm) crystalline grains than the sand on the base of the sheets.

The form of the slag sheets is interpreted as indicating their formation on the base of hearths floored with sand. The silicate melt appears to be partially derived from above (leading to a blebby and glassy upper surface), but with much of the material derived from the margins of the hearth, leading to the thickened and/or upturned edges to the slag sheets in some instances, often also with a higher proportion of coarse material derived from degradation of the stones lining the hearth edges. The base of the sheets is typically almost planar, with blebs and lobes of melt descending from above and incorporating or sintering the sand on the hearth base.

The microscopic slags from Mound 1 are broadly similar to those from Mound 3. Typical samples from Iron Age and Norse contexts were examined, and although the materials present are broadly similar there are some differences:-

A sample from the Norse "industrial" phase (5661, context 382; a sand deposit over pit 433) contained approximately 50% magnetic materials. These included material ranges in size up to 10mm. The particles have similar textures to those observed in the Mound 3 material, with much of the magnetic material being in the form of blebs and drops. Many of the blebs are conjoined, meaning there appear to be fewer individual spheroids present. The spheroidal blebs are mainly in the range of 1-2mm in diameter, but they grade up into much less spherical blebs of up to 8mm maximum diameter. Most of the magnetic material is in the form of irregular blebs and short runs of dark glass, sometimes with a reddish bloom on the surface, with abundant included quartzo-feldspathic grains. The non-magnetic fraction also includes glassy materials and blebs, but these glasses are dominantly pale, ranging from almost colourless, through creamy white and grey, to a pale green. Most show included grains.

In contrast a sample from the Iron Age house (8392, context 397; the most slag-rich sample from the surface mapped in detail, see above) was very fine-grained, and more similar to the Mound 3 examples. The magnetic component comprises around 15% of the sample, and is dominated by material that is dark, or black. Some of the dark magnetic material has pale sand grains adhering to the surface, some larger pieces have included grains. The spheroids are clustered between 800 and 1200µm, with most being close to perfect spheres. The spheroids form less than 10% of the magnetic assemblage, most of which comprises more amorphous blebs of dark glass, but with a similar size range to the spheroids. In some cases the dark magnetic material can be seen to form thin sheets, and to bind sand particles together to form clumps up to 8mm across. The non-magnetic fraction is very pale, ranging from white through to a translucent grey glass, including many quartzo-feldspathic grains with grain size in the range 100-200µm. Sub-spherical blebs of the pale glass also occur, and range up to about 2mm, significantly larger than the magnetic spheroids.

The differentiation of the slags from the "industrial" activity, from those of the domestic floors and granary, appears to be dominated by the amount of melted

material. In the domestic contexts the slags are limited to non-magnetic forms, in which sand is bound by small amounts of melt, or more discrete blebs of melt forming particles up to a few mm, and magnetic forms, with spheroids of up to 1200µm and also amorphous blebs binding grains into particles up to a few mm. In the "industrial" settings the melt phase is sufficiently abundant to bind together slabs of material up to at least 100mm wide (possibly much more; all the large fragments are broken sheets) and up to 40mm thick.

The most likely explanation for the difference in scale of the slags formed would be the length of time the hearths were maintained in use. The slags in the two contexts are similar, but those in the "industrial" setting develop into larger bodies, through the maintenance of high temperatures for long periods of time. If the difference between the two settings was the process, or the temperature, then the slag materials might be expected to be more different from each other.

Description of major pieces of archived material of >10mm

BO97. 371 >100mm

A slag piece, 126 x 64 deep x 70mm wide, with a flat sintered base which only extends over part of the piece. The lower surface angles up to 40mm above lowest point on the flat base at the high end. The angled surface reaches the flat base 60mm from the margin of the block. There is a 12-16mm thick basal layer, overlain by a rather more blebby upper layer. The raised portion is red above and below. The slag appears to be mainly crystalline, despite its glassy upper surface.

BO97. 373. >100mm

The form of this piece hints at it having been part of a 250 mm diameter bowl -shaped cake, 40mm thick centrally but reducing to 12mm laterally. The are some 30 x 30 x 20 mm cavities/depressions. The slag is glassy, with red, black and white swirls on upper surface. The lower surface has deep layer of sintered sand, with bright red colours. Internally the slag is crystalline, but black and glassy in uppermost 5mm. The colours on the upper surface here are unusual and represent a feature not observed in the remainder of the material.

BO97. 379. 11.2-100mm

This is the largest single slag collection from Mound 1, totalling 8.7kg at this grade (but also with 1.0kg <11.2mm and 0.77kg >100mm). Most of the smaller pieces are rather amorphous, but the larger pieces are more revealing. Many of these have a flat basal surface with sintered sand, and several of these show steeply inclined lateral contacts, suggesting they come from the base of the hearth wall. In these cases the upper surface is steeply inclined. This suggests that the principal reaction is not in the base of the hearth, but in its walls. Some of the lateral surfaces and tops show accumulations of coarse grains, of a size much larger than that of

the blown sand, suggesting that rocks are being corroded, disaggregated and incorporated and not just the dune sand. The >100mm fraction from this context was sampled for specimens BO.H, BO.J, BO.I and BO.K as described below.

BO97.379 > 100mm

1. 115 x 75 x 40mm. It has an irregularly lobed top of dark glass, bearing a few large quartzo-feldspathic grains. The lower face also very irregular, with a few glass lobes, but most of surface has sand fused onto glass. The slag is internally pale- to mid-grey with abundant included quartzo-feldspathic grains.

2. 135 x 95 x 30mm. A wedge shaped slag block, of which one edge is the margin of a slag sheet. The slag has fairly low vesicularity and has a dense 5mm thick basal layer. This layer thickens to 25mm away from the sheet edge. One face has sand sintered to surface, forming an almost planar surface concealing the lobate nature of slag above. The other face shows lobate slag surface in runnels parallel to thin edge. Several areas of this face show iron staining, which takes the form of small brown flakes and patches adhering to surface.

3. 110 x 80 x 25mm. The slag is distinctly paler than 1 and 2, with a slight greenish tint. These are abundant included quartzo-feldspathic grains. There is some adhering pale ashy/calcareous material. The "upper" surface has more 2-3mm diameter blebs than the previous specimens. The lower surface is irregular, but broadly similar to the other specimens from this horizon.

4. 100 x 70 x 20mm. A dark slag with a smooth lobate surface upper surface, bearing a pale crust. The lower surface is planar, with slag sintered to sand. One edge of the specimen has a suggestion of down turning of the slag, suggesting deformation during extraction.

plus specimens of BO.K and BO.H/I/J (see below)

BO97. 382 >100mm

A single piece of slag, 100 x 80 x 40 mm in two flows (the upper 15, the lower 25 mm thick). The lower flow has a mammilated base with sintered sand, which forms a hollow to one side of arcuate piece of unvitified, cracked material, which may be a piece of broken pottery. A possible interpretation of this piece is that the base of a pot stuck to the forming slag in the base of the hearth, the pot (minus its base) was then removed, leaving a void filled by mammilated slag, before the final upper layer formed across the top.

BO99 Mound 1. 382B baulk, slag >11.2mm

The largest fragment is 60g, 87x58x32 mm, with an oblique wedge-shape, dominantly of dark sandy glass. Most of the base is flat with sintered sand. A tall narrow protruding end rises off this base, but it is not clear whether this is original or a deformation produced during extraction. The upper surface

shows red-brown spiky sintered material, thickening on to the long raised edge, where the vesicular slag is also brownish. Raised corner shows best development of bulbous lobes of slag.

A 30g fragment from a sheet 28mm thick. The lower surface shows flat surface of sintered sand, but is very brownish. The upper surface shows a curious brownish sheen, possibly an alteration product of the iron-rich glass. Internally it is brown/grey and vesicular.

A 30g fragment from sheet with a curved base 7-17mm thick. The thin edge is dark, whereas the thick area is a rivulet of very pale glass. Lower face of brown spiky sintered material arranged in crude linear structures. The upper surface is glassy.

A 5g rather amorphous fragment, which shows irregular sandy base overlain by bleb of glass separating two concavities. Each concavity bears Fe-oxide structures with crude platey arrangement.

There are also several small pieces which show concave basal sand attachment, suggest flowage/formation as drape - but may be associated with extraction in some cases.

BO97. 390 >100mm

This is a single block of slag, 45 x 100 x 70mm, 170g, with a flat sintered base over part of its area. The taller end shows very coarse grains on the upper surface, suggesting derivation from decomposing rock. There are complex internal voids of 40-50mm. The slag is internally crystalline, and grey.

BO97. 416 >100

A slag piece, 105x80x50 mm, probably from a 30mm thick sheet, but it is very irregular. It bears lots of inclusions from sandy clay through to very Fe-rich material.

BO97 Mound 1 unstratified

A large block of gneiss with adhering slag phase. Thin coatings on the steep surfaces of the block tend to have yellow colour. Rather thicker, darker slag seems to have accumulated on what are interpreted as horizontal surfaces on the block. The thickest slag is about 30mm thick. The slag appears to have under-run the block too. The block is presumably from the wall of a hearth, but could be a block within a hearth.

Mound 1: unstratified

A single piece of slag, 358g, 28-38mm thick sheet, 110x160 mm. The lower face is formed of a rough sandy sinter, with some sub-spherical blebs. A vesicular slag with large voids and dimples on its upper surface forms the upper part. The specimen probably grew as 2-3 thinner sheets, each of c. 16mm thickness. One end shows lots of grit,

suggesting proximity to disaggregating and decomposing rock. The upper surface has some coarse grit to 6mm. The slag is crystalline, sandy, and locally with Fe-oxide coloured surface.

Analytical investigation of slags from Mound 1

Petrography and mineralogy

BO.C

The geochemistry of the sand sample (see below) corresponds in composition to a mixture 10-15% calcium carbonate sand (of biological origin) with 85-90% of siliciclastic sand, with a composition only slightly more silicic than the local Lewisian Gneiss (Fettes *et al.* 1992). This broad mixture was supported during examination of a strew mount under the analytical SEM. Only a small proportion of grains were investigated in detail and analysed, but the identified grains included quartz, biogenic calcite, alkali (dominantly potassium) feldspar, plagioclase (mainly of labradorite/bytownite composition, but with some oligoclase), hornblende and garnet.

BO.D, BO.E and BO.F

Three slag specimens (BO.D, BO.E and BO.F) were selected for petrographic study because of their superficial resemblance to BO.A and BO.B.

Bo.D

In hand specimen shows yellow/orange feldspar grains set in a variably dark green to black matrix. The feldspars are typically coarse (1-2 mm), but finer white quartz-feldspathic grains are also present. The specimen contains a few large 4-7mm vesicles, but is noticeably denser and less vesicular than most of the material. This specimen may be a partially-melted pebble; the large feldspars certainly indicate strong bedrock influence.

This sample comprises sintered quartz-feldspar-hornblende grains. Some flowage of the melt phase has occurred (particularly the more iron-rich component). SEM investigation showed the melt to have solidified as a glass locally, but more commonly as an extremely finely crystalline matrix, but with slightly coarser crystallites (although still too small for meaningful analysis) suggestive of a feldspar (Table 5A, 40) and iron-rich olivine (Table 5B, 62) growing on the surface of relict grains (Table 5A, 37-39). These microcrystalline zones become progressively Ca and Fe poorer (Table 5B, 63-67) away from the substrate, until they attain a bulk composition close to that of an alkali feldspar. In other areas there are large (4mm) zones of hornblende (Table 5A, 22-25), with rather diffuse margins, suggestive of breakdown of the original rock.

Bo.E

This includes a dark red slag phase, which is vesicular, bearing sand grains and a large cracked rock fragment (10 mm).

SEM investigation showed the slag to be highly vesicular, with a much higher proportion of melt than BO.D. The relict grains are dominantly quartz, with a grain size of 100-1000µm, probably with some plagioclase (labradorite; Table 5A, 29). The crystallization of the slag has developed in a patchy manner, with clusters of laths of plagioclase (bytownite; Table 5A, 30, 32) and amphibole (gedrite rather than the hornblende seen in other samples; Table 5A, 26), between which are more glassy (and/or microcrystalline) areas (Table 5B, 51) bearing small crystals (5µm) of olivine, probably of a hortonolite composition (Table 5B, 68).

BO.F

This is a pale highly vesicular slag, dominated by a glassy matrix glasses bearing small grains of quartz (typically 200µm, rarely up to 1.5mm). Part of the lump shows a red-brown colouration suggestive of Fe enrichment.

Under SEM examination areas where feldspars had been breaking-up there were electron low-density laths (20-100µm x 2-10µm) which had a labradorite and andesine compositions (Table 5A, 33, 34), where measured. Further from the decomposing feldspars, a glass bore elongate (<100µm x 20µm) crystals of salite (Table 5A, 13,14) in glass (Table 5B, 50). As with BO.E, it is suggested that these laths include both relict material and neomorphic phases; in this case the salite appears to be neomorphic, but the plagioclase may, at least in part, be relict.

BO.H, BO.J, BO.K and BO.I

New material from the 1997 season (BO97, M1, slag 379 >100mm) allowed investigation of two further specimens where the gross morphology was clearer:-

BO.H/I/J. *This is a block of degraded Lewisian gneiss, with a slag coating. 4 subsamples were taken:*
BO.J = analysis of representative area of gneiss
BO.H=analysis of the felsic component of gneiss
BO.I1= SEM block mainly gneiss
BO.I2= SEM block gneiss and adhering slag

BO.K. *This is a rather atypical slag texturally, in having large (cm-scale) vesicles, but the pale grey slag appeared reasonably compositionally typical of the assemblage and the overall form of the piece, suggestive of being part of a broad, thin, plano-convex sheet. BO.K1-4 are subsamples from different areas of the block. BO.K4 is a polished block for SEM examination from the centre of the block; Bo.K1-3 are subsamples for chemical analysis - 1 from near the base, 2 top surface near the margin, 3 top surface away from the margin*

Bo.I1

A quartz and plagioclase (oligoclase) dominated specimen. Areas of glass extend along many grain boundaries. Localised patches of speckled appearance under backscattered electron imaging, are very finely crystalline iron oxides in glass (Table 5B, 53-56), with development of clinopyroxene (augite; Table 5A, 8-11) against the adjacent quartz grains.

Bo.I2

The slag material shows a very variable nature under the SEM. One area shows a concentrically zoned structure around small patch (about 150µm in diameter) of iron oxide crystals.

In an inner zone (Plate 3, A) up to 300µm wide are Fe oxides (2-15µm), which are rather indistinct and overgrown by zoned olivine (with chrysolite cores and hortonolite outer layers; Table 5A, 1-4). These olivines have a bright, electron-dense rim which is too thin to analyse. The olivine is surrounded by a material, probably clinopyroxene, trending from an omphacite to a diopside composition (Table 5A, 18-20).

This inner zone is surrounded by a zone 150 µm wide (Plate 3, B) bearing lath- to dendritic-shaped olivine (100µm long up to 5µm wide). These show cores of chrysolite and outer regions of hyalosiderite (Table 5A, 5-7). These dendrites are overlain by clinopyroxene (20 x 5 µm) with cores of augite and no visible zonation (Table 5A, 12). The surrounding material is again of omphacitic composition (Table 5A, 21).

In a separate area, within the gneiss, the glass between quartz grains was analysed and was found to be relatively high in Mg, Ti, and K (Table 5B, 57-58). A grain of oligoclase (Table 5A, 35) in this area was found to have a reaction rim, probably of scapolite (Table 5A, 28). In a nearby area a zone was found with grains with a laminated porous structure (Plate 2, B). Microanalysis of the silicate material between the voids gave a composition close to biotite (Table 5B, 61).

Some areas within the gneiss are extremely rich in Fe-Ti oxides (ilmenite?); it is unclear whether these are relict, or a product of the liberation of titanium from the decomposition of biotite (Plate 2, D).

Bo.K4

This is a highly vesicular clinkery slag (cf. Bo.F) of a dark brownish grey colour. The colour darkens slightly towards what is interpreted as the lower face, which has a dark grey colour with a purple tint. There is much sintered sand on this face. The upper face is characterised by a smoother surface, locally with a greenish tint.

SEM studies indicate that this specimen is internally homogeneous and highly vesicular. The slag comprises sintered sand grains (of a size consistent with derivation from blown sand rather than directly from degradation of gneiss), bound by a glassy and microcrystalline phase (Plate 2, A). Larger crystallites within this matrix were analysed and showed the

presence of neomorphic clinopyroxene (salite; Table 5A, 15-16) and plagioclase (andesine; Table 5A, 36).

Summary

The petrography of the slags shows two major sources of the silicate component: blown sand and Lewisian gneiss. BO.I2 shows the interior of a pebble of gneiss, with abundant indicators of heating, including cracked grains and possible remnants from biotite dehydration. Biotite dehydration melting might be expected to occur in a gneiss at approximately 750-800C. BO.I1 shows areas of gneiss showing considerably more melting, with the melt showing development of iron oxide (magnetite?) and augite. Localised areas of higher degrees of iron enrichment were recorded within the slag part of BO.I1 and BO.D (another specimen interpreted to be largely partially-melted gneiss) and in these the neomorphic mineral phases included iron oxides and olivine. In The BO.I1 case, at least, the iron-enrichment was focussed on the margin of the slag, suggesting that the addition may have been derived from iron-rich peat ash, rather than from the ferromagnesian minerals of the gneiss itself.

The slags formed by the sintering of loose sand include BO.F and BO.K4. In both cases the glass phase contained some crystalline materials, including salite and plagioclase. These phases suggest a high temperature of formation (probably significantly in excess of 1000C), but experimental studies would be desirable to clarify this.

Chemical Analysis**The Components****Sand**

The sample of sand (BO.C) shows a reasonably good major element analytical total. The major element analysis could be expressed approximately as a mixture of end members 48% quartz, 18% anorthite, 15% albite, 4% orthoclase and 10% calcite. This composition complements the mineralogical observation of quartz, plus a somewhat calcic plagioclase, mixed with some alkali feldspar and rarer ferromagnesian minerals.

The chondrite-normalised REE profile shows a gentle enrichment of LREE, with a very slight positive europium anomaly (LaN/YbN = 9.1; ΣREE = 33.7).

Peat

Interpretation of the analyses of the peat is hampered by poor analytical totals. The low totals (BO.P1 64.2%; BO.P2 63.0%; BO.P3 77.2%) are indicative of incomplete ignition of the samples during preparation; the samples were ashed following the preparation routine developed for charcoals. To make comparison with other materials easier, the analyses are presented both raw, and normalised to 100%. Sample BOP1

yielded too little residue after ignition for minor and trace element analysis.

BO.P1 and P2 have a major element composition dominated by magnesium and calcium. No mineralogical data is available to determine how these materials are held in the peat, but such high levels will be a major influence on the fuel ash and its reactivity. Both samples have a moderate iron, low manganese, low alumina and silica, but high potash content.

The sample BO.P2 has a chondrite-normalised REE profile very close to that of the blown sand (BO.C), apart from having a slight negative europium anomaly ($\text{La}_N/\text{Yb}_N = 9.1$; $\Sigma\text{REE} = 52.4$).

In contrast, sample BO.P3 shows higher concentrations of the REE ($\Sigma\text{REE} = 106$ after normalisation), with greater enrichment of the LREE than in BO.P2 ($\text{La}_N/\text{Yb}_N = 12.4$). BO.P3 is much richer in alumina and silica than the other two peat samples, and also is very iron rich (with an accompanying enrichment in manganese). This sample shows lower levels of potash and phosphorus than P1 and P2.

Gneiss

Sample BO.J was taken in an attempt to obtain a balanced wholerock analysis for the degraded gneiss block included in slag. Sample BO.H is a sample of the quartzo-feldspathic component of the gneiss.

These two samples have chondrite-normalised REE profiles which can be distinguished from all the other analyses from site in being much flatter, particularly for the HREE (La_N/Yb_N is 5.3 for BO.H and 3.7 for BO.J; Figures 4A and 5A, ΣREE is 68.4 for BO.H and 125.1 for BO.J). These figures show that the ferromagnesian mineral bands have a strong enrichment in the REE, but a low degree of fractionation.

The Slags

The analysed slags fall into two groups. The initial survey started with the analysis of two slags expected to be iron-rich, and BO.A has 16.5% Fe_2O_3 and BO.B 17.7%. These slags have a low silica content of approximately 54%, but high CaO (12.8 and 7.7% respectively). The second group of analyses are all from the same slab, chosen as macroscopically being more typical of the assemblage. They show a low iron content (approximately 4.5% Fe_2O_3), silica of 62% and lime of 8-9%.

The iron-poor slags show enrichment of several elements associated with the fuel (K, P, Mo, As, U) compared with the iron-rich slags.

The chondrite-normalised REE profiles of the slags known to be dominated by sintered sand (BO.K1-3) are very similar to those of the iron-rich slags (BO.A and B; Figure 4B). However, the iron-rich slags show a slightly more fractionated profile, being particularly steeper at the extreme light end (La_N/Yb_N : BO.A 13.3, BO.B 13.5, BO.K1 9.5, BO.K2 9.4, BO.K3 9.9). This LREE enrichment gives the iron-rich slags a slightly higher ΣREE (BO.A 108, BO.B 111, BO.K1 74, BO.K2 98, BO.K3 109).

Summary

The investigation of the chemistry of these materials is hampered by the small number of analyses undertaken; it remains unclear to what extent the single sand sample is representative of the sands on the mounds as a whole, and the diversity of the peat analyses means there is great uncertainty about the possible range of peat ash composition. However, some tentative conclusions and modelling can be undertaken.

The chemical analyses cluster into three groups on the basis of their REE chemistry. These groups are particularly well shown on a diagram of total REE vs. La_N/Yb_N (a measure of the slope of the REE profile and therefore differentiation; Figure 5A).

The central cluster includes samples with La_N/Yb_N in the range 9-10. This cluster includes the blown sand sample (BO.C), a peat sample (BO.P2) and the relatively iron-poor slags formed of sintered sand (BO.K1-3). The samples in the cluster differ markedly in their total REE content, with ΣREE ranging from 33.7 ppm for BO.C to 108.7 ppm for BO.K3. The upper limit of the range is quite close to the average upper crustal value ($\Sigma\text{REE} = 146.4$ ppm, $\text{La}_N/\text{Yb}_N = 9.2$). The major element composition of the members of this group shows considerable variation. The slags are all less siliceous than the sand sample, but they show enrichment in Fe, Mg, Ti, K and P (together with trace elements like U, V, and Mo). Most of these elements (Fe, Mg, K, P, U, V, Mo) are enriched in the peats, relative to the sand. Many of the elements (Fe, Mg, Ti, K) would also be relatively abundant in the ferromagnesian fraction (particularly the biotite) of the gneiss.

A second group is formed by the iron-rich slags (BO.A and BO.B) together with the iron-rich peat (BO.P3). They have ΣREE of 106-111 ppm and La_N/Yb_N of 12.4 – 13.5. The iron-rich slags have a much more siliceous bulk composition than the other materials ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 6-7. These samples were originally selected because of their resemblance to "conventional" iron slags, so one possible explanation of these samples is that they represent flowed iron-rich melt. The production of such a melt would trend towards the composition of olivine and might be expected to show a more fractionated composition, including a steeper REE profile, than its parent material. Material closer to an olivine composition was observed, for instance, in the centres of areas interpreted as reactions between partially-melting silicates and iron-rich fuel ash in BO.I2 (see above; Plate 3A and B).

The third group comprises the two samples of gneiss (BO.H and BO.J), and is characterised by a low gradient to the REE profile, with La_N/Yb_N of 3.7 and 5.3.

If the REE data are plotted against components of the major element chemistry (e.g. Al_2O_3 , Figure 5B), however, these groups break down, and the controls on the chemistry are shown to be more complex.

One aspect of high calcium systems is their ability to fix large amounts of phosphorus (and also uranium). The relationships between these elements in the Bornish slags are illustrated in Figure 6. It would appear that the calcium-rich slags have absorbed preferentially

phosphorus and uranium, in a linear relationship, from the fuel ash. Thus these two elements have become concentrated with respect to calcium. Another element likely to enter slags preferentially from fuel ash is potassium. Figure 7 shows the relationship between phosphorus and potassium. Approximately linear relationships are shown for the slags, and for the sand, gneiss and peat. This again shows that phosphorus has been preferentially absorbed by the slags, leading to a much high P:K ratio in the slags than the source materials.

The slags can be modelled in terms of their major element chemistry as a mixture of the components (sand, gneiss, peat), but the trace element chemistry is more complex. Whether that complexity derives from fractionation process produced by the partial melting of the components and migration of the melt, or from the scavenging properties of the partial melt preferentially including certain elements from the fuel ash, or whether there is an additional, as yet unrecognised, source for some of the trace elements cannot be resolved on the evidence of the present data set. One possibility for an additional component is suggested by the iron-rich peat (BO.P3), which has a relatively high alumina:silica ratio, suggestive of the presence of clay minerals. Any attempt to define mixing or differentiation trends would need to be based on a large sample database.

Modelling of slag chemical composition

The earlier report on the Bornish material suggested that samples BO.A and B could be modelled as mixtures of 30-60% sand and 70-40% peat ash, with some added iron. This model can be now be improved, but simple mixing models do not adequately explain all features of the chemical composition. If the sand and peat samples examined in this study are representative, then it follows that slags BO.A and B cannot be the products of mixing, since they have the most fractionated REE profiles, close to that of one of the peat samples, but they differ strongly in major element chemistry from that peat.

Similarly the slags dominated by sintered sand (BO.K) show REE distributions close to the blown sand, and another one of the peat samples, but show degrees of total REE enrichment beyond that which could be explained by mixing and loss of carbonate.

The solution to these problems must lie in the nature of the partitioning of elements during the partial melting process, but the precise pathways cannot yet be determined. The enhanced levels of P, U, Mo and K shown by the low-iron slags, show they have absorbed more ash from the organic component of their fuel than the high-iron slags. The high-iron slags have presumably been the product of reaction with a high-iron peat (with a more strongly fractionated REE component).

Despite the problems in identifying appropriate mixing and fractionation process to derive the observed slags, there is good petrographic and chemical evidence that they are derived from the parent materials: sand, gneiss and peat ash. The very high iron content of some of the peat samples removes any need for iron to have been

added to the system; those areas of iron-enrichment identified petrographically are related to points of likely contact with fuel ash and zones of reaction of the ferromagnesian minerals in the gneiss. There is no remaining evidence to support input of material from any metallurgical process.

Conclusions

A full understanding of the controls on the composition of the macroscopic slags has not been achieved, but they appear to be products of mixing and partial melting of the inorganic components of the fuel and hearth walls. There is no chemical or mineralogical evidence for addition of material from the use of the hearth for metallurgical purposes.

It would appear that the dominant form of slag has a relatively low iron content, and contains a high proportion of sintered grains. These grains include blown sand from the hearth floor and walls, fragments of gneiss from the hearth setting and the sand component included within the peat. The grains are surrounded by a glassy phase, with local crystallisation of clinopyroxene (salite) and probably plagioclase feldspar. In some areas where the input of iron (from the fuel ash) was particularly marked, the slags show sequential development of magnetite, olivine (Fa₁₂₋₅₈) and augite. These slags have an enrichment of incompatible trace elements, including the REE, but show a REE profile close to that of the parent materials. Other elements preferentially enriched in the slag are those scavenged from the fuel ash, including Mo, U and V. This scavenging behaviour may be linked to the high calcium content of the slags. This high calcium content is linked to the high proportion of biogenic calcite in the blown sands, and also to a high calcium content of some of the peats.

Where these slags have formed adjacent to blocks of Lewisian Gneiss, their petrology is strongly influenced by the input of material derived from the breakdown of biotite, and probably locally of hornblende as well. These areas of slag show mineral assemblages with Fe and Fe-Ti oxides, in glass, locally with crystallites of augite.

The behaviour of calcium-rich systems of this type is not well described in the literature, but it is likely that the reactivity of the system is driven by reactions between calcite and the silicate minerals during thermal breakdown of the calcite at temperatures from as low as 600°C, although high degrees of partial melting must have occurred at significantly higher temperatures. The generation of clinkery slags has been recorded from other archaeological sites where hearths are on calcite-rich substrates. A site at Gloucester Business Park (Young 2000) lying on limestone gravels in the Severn Valley, produced assemblages of apparently non-metallurgical slag, which also showed evidence for slag phosphorus scavenging and which had a glassy matrix bearing crystals of salite. Analytical data demonstrate a linear relationship between the P and U held in the Bornish slags (Figure 6A), and the Gloucester Business Park slag analyses also lie on this trend. The relationship between Ca and P in the slags is slightly less close (Figure 6B), but nonetheless a linear relationship exists. The EDS microanalyses of the glass

phase in the Bornish slags also lies on the same line (Figure 6B), suggesting that in the Bornish material it is the glass phase that is the carrier for P and U.

A second, rarer, form of slag possesses a much higher iron content, a more fractionated REE profile and a rather siliceous bulk composition. These slags appear to represent either the influence of an additional, as yet unrecognised, parent material, or, perhaps more likely, the production of more mobile, iron-rich, fractionated melts. These may have been produced through the local attainment of higher temperatures in the hearth, or through the occasional occurrence of particularly iron-rich peats in the fuel.

The microscopic slags from several occupation surfaces show distributions controlled by the position of domestic hearths and kilns. These slags, too, can confidently be assigned a non-metallurgical origin.

The microscopic slags show a similar range of composition as the macroscopic examples, and include what appear from microscopic examination to be both iron-rich and iron-poor particles. The iron-poor particles are often sintered grains and/or pale glassy materials. The iron-rich materials include browner materials, some rather spiky appearing sintered masses, but others occur as spheroidal particles. Both spiky sinters and spheroidal particles are readily separated from the sieved residues by a magnet, and it is assumed (although SEM examination of the internal nature of these particles has not yet been undertaken) that they contain magnetite, as do iron-rich patches within the macroscopic slags.

The presence of microscopic iron-rich, magnetic, spheroidal particles has implications for the interpretation of sieved residues in general. Well-formed magnetic spheroids are usually associated with spheroidal hammerscale (Allen, 1986; Crew, 1996; Starley, 1995). Spheroidal hammerscale is produced through expulsion of liquid slag from an iron workpiece during fire welding. They are particularly common in residues associated with bloomsmithing, during which process a bloom is worked down to a billet through welding and working of the raw material. The present material is microscopically distinct from the more perfect spheroids recovered from iron-working sites, but this distinction is only readily apparent under the electron microscope and not under the low-powered binocular microscopes commonly employed during the sorting of sieve samples. The occurrence of high-iron fuel ashes of this type is unusual, however, and these spheroids may well provide an indicator of the use of iron-rich peats.

Acknowledgements

Dr Gary Thomas undertook much of the early stages of the analytical work for this project. The help provided by the technical staff in the Earth Sciences Department of Cardiff University, particularly Mr C. Lewis is also gratefully acknowledged

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