Cefn Du, A30/99

Summary

The stratified metallurgical residues from this site comprise 1.1kg of vesicular slags from pit F351 within structure S3 (workshop?), together with a small fragment of furnace lining from linear F253; both contexts are attributed to Period 2. The vesicular slags produced no definitive evidence for the nature of their generation, but their high temperature of formation and overall morphology are strongly suggestive of a metallurgical process. The slags contain no evidence for metal contamination, so are most likely to derive from non-ferrous metal processing or casting, in which the metal was securely contained within a crucible. The relatively small amount of slag retrieved would argue against metalworking being a substantial component of the site's economy.

The micro-residues recovered by flotation are dominated by small hollow spherules. These spherules are non-magnetic and pale, close to the colour recorded for the macroscopic vesicular slags from pit F351. In some cases at least, they appear to be vitrified remains of individual sediment grains. They presumably reflect individual granules of sediment or hearth lining, caught up in the hearth. They are again evidence either for friable hearth walls, or for the use of fuel (e.g. peat) containing sediment grains. They are not indicative of any particular metallurgical process (unlike the dense, iron-rich magnetic spherules of other sites, which are indicative of fire-welding). The micro-residues from F404 are more massive, and although in small pieces are similar to those from F351. In such a small quantity they are not readily interpretable.

In addition the site yielded an unstratified piece of iron bloom. These are very rare finds, and an understanding of the chemistry of this example adds considerably to regional knowledge. The high phosphorus and high arsenic contents compare favourably with what has been interpreted to be the composition (Crew and Salter 1993) of Iron Age currency bars from Anglesey (although those bars still await formal description). The bloom is very likely to have been of local production, but no iron working or smelting slags were identified in the material from the site.

Catalogue and detailed descriptions

SF 005, context 4000, undated [topsoil]

Description
A small partly compacted piece of iron bloom, of weight 390g. The corroded mass measures 80 by 87mm with a maximum thickness of about 25mm. It has an irregular outline. The piece is very irregular but has a slightly dished concavo-convex profile. X-radiographs (Figure 1d) show dense metal along one edge, but increasing evidence for cavities towards the opposite edge.

The bloom was cut and a complete polished transverse section produced. This section was 78mm in length with a maximum thickness of 18mm. The bloom contained a significant proportion of metal, with corrosion forming a crust up to 4mm thick locally, but typically much less. The section shows numerous cavities in the metal, up to 7mm maximum dimension. These cavities are mainly filled with corrosion products, but locally they contain slag, particularly in the smaller examples. The cavities often have lobate outlines, and they appear be original features of the bloom, rather than products of corrosion.

The section was polished for inspection under the analytical SEM, and then repolished and etched in nital for optical metallographic investigation.

On a macroscopic scale (Figure 1a and b), the polished surface shows evidence for the bloom comprising small, irregularly sutured blebs of iron, with particularly marked sutures (welds) with an apparent inclination of approximately 45° to the length of the slab.

In optical investigation after nital etching, only local areas of the upper face (sensu Figure1, Figure 2) show an elevated carbon content, and the occurrence of pearlite within 2.5mm of the margin (Figure 2). Within this carburised zone the cavities are small. Large cavities appear close to the level of the disappearance of the pearlite, and accompany a purely ferritic microstructure through the remainder of the thickness. The ferritic iron shows phosphoric "ghosting" (Stewart *et al.* 2000), compatible with the level of phosphorus recorded by EDS. Such ghosting has been attributed to the differential phosphorus content of the ferrite as a result of partial segregation of phosphorus during the austenite-ferrite transformation.

Several small slag inclusions were examined in detail in the SEM. They were found to be very variable both chemically and mineralogically. Some larger inclusions had mineralogies and microstructures typical of iron smelting slags (e.g. Figure 3); they showed either wustite alone, or wustite and fayalite, in a glassy groundmass.

Other smaller inclusions (e.g. Figure 4) show glass, sometimes with phosphorus contents as high as 5-6wt%. Elemental mapping suggests that these high-P glass-filled voids are fringed with small crystals of a material rich in silicon and potassium, and this is interpreted to be leucite. This relationship suggests that these small voids may be filled with a slag dominated by fuel ash (of which the major elemental components will be K, Ca and P).

EDS analyses of metal close to the lower margin (as shown in Figure 1) show P contents of about 0.35wt% and As of 0.7 – 1.2wt%. In both cases these figures must be regarded as provisional estimates.

Discussion

The production of high P iron from smelting of bog ores has been attested in North Wales through the work of Crew (e.g. Crew 1991, 1998; Crew & Salter 1993). Crew and Salter (1993) related the composition of the bog-iron production to the morphology of the Llyn Cerrig Bach-type currency bars, with welded tips. Furthermore, they speculated that the welding might possibly be associated with, and be a demonstration of, a high As content, which would improve the ease of welding. Arsenic can be concentrated in ferric materials in contact with groundwater (ferric substrates are employed in As pollution remediation), so high As contents might be expected in bog-ores generated in areas with moderate As in the groundwaters. These conditions might be expected to occur particularly in areas of sulphide mineralisation (such as parts of Snowdonia, or Anglesey around Parys Mountain).

Crew later (1995) separated the two forms of currency bar with welded tips from his 1993 paper into Type E (Orton, high P, variable C) and Type N (Llyn Cerrig Bach, ?low P), but it is unclear what was his basis for the assertion that the Llyn Cerrig bars are low P.

It is unfortunate that this specimen is unstratified, given the wide (prehistoric to post-Roman) age range proposed for the Cefn Du site. There is no supporting evidence for iron-making amongst the remainder of the material from Cefn Du, although it is unlikely that a small, semi-compacted bloom (or bloom fragment) such as this, would have been transported far from its place of origin. The small size of the piece (390g) contrasts with the weights of 508 and 818g recorded for the two complete currency bars from Llyn Cerrig Bach (Crew & Salter 1993), which have been taken as suggesting raw bloom weights in excess of 2kg (cf. Crew 1991). It seems likely therefore that the current specimen is an incomplete bloom; perhaps one which was incompletely consolidated in the furnace.

SF 120, context 4176, Phase 2 [Structure S3, workshop?, fill of pit F351]

Description

An assemblage dominated by highly vesicular slags of a type commonly formed by reaction of the fuel ash with the hearth lining. Some small lining fragments are also present. A small number of denser slag pieces appear to be partially melted rock fragments. The total group weighs 1112g.

The larger pieces (weight up to 190g) show an overall morphology similar to some slags from iron-working. They have a crudely plano-convex form, 10-15cm across, with a short "spike" of slag of 15mm diameter extending at an acute angle from the convex surface. This morphology is interpreted as being generated by formation of a slag cake in the angle of the hearth wall and hearth floor, below the blow hole, and the periodic removal of the cake by means of a poker inserted horizontally along the hearth floor and slightly penetrating the hearth wall (thereby generating a hole subsequently filled with slag to form the “spike”).

In contrast to the slag morphology, the slag chemistry shows little evidence of generation during metallurgical processing. Elemental analysis of a sample of slag taken from one of the larger cakes, was supplemented by similar analyses of a small piece of friable hearth wall present as an inclusion within the slag, and a separate piece of hearth wall.

	LOI	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
baked lining	2.2	76.8	11.1	5.9	0.10	1.17	0.57	1.16	1.50	0.93	0.19
lining within slag	3.9	75.9	12.7	6.5	0.29	0.78	0.42	1.00	1.50	1.10	0.62
slag	1.8	(74.7)	11.5	5.8	0.22	1.36	1.03	1.34	2.42	1.00	0.56

Table 1. X-ray fluorescence analyses for major elements on fused beads. Samples include a typical piece of the slag, a soft brown clay inclusion within the slag, and a discrete hearth wall fragment.
LOI = loss on ignition. Value in parenthesis adjusted.

Chemical analyses (Table 1) of the slag, together with the inclusion and the hearth lining fragment provide very similar compositions. There is very slight enrichment from clay to slag in calcium, potassium and phosphorus, the three most abundant elements in wood ash, suggesting that the slag comprises approximately 2-3% admixture of fuel ash to the earth lining. There is no enrichment in iron.

Electron optical examination and EDS microanalysis of a polished block of slag provided very similar results to the whole-sample analyses. The slag proved to comprise grains of quartz, feldspar and minor Fe-Ti oxides, showing signs of cracking and reaction, set in glassy matrix. In addition to supporting the whole-sample chemical data, the microanalyses revealed no detectable quantities of copper, lead, tin or zinc.

Discussion
The morphology of the larger slag pieces strongly suggests their generation in a similar mode to the generation of low-density blacksmithing slags, on the hearth wall below the blowhole. The complete absence of iron-enrichment in this assemblage makes it rather unlikely that these slags are from iron-working. Surficial oxidation of the workpiece will inevitably lead to loss of “hammer-scale” to the hearth during blacksmithing. The degree of partial melting of the hearth lining can be matched at other sites (in particular where hearths have been dug into a friable, unconsolidated, subsoil or into loose sand), in hearths which were associated with iron-working, so production of these slags at a similar temperature to that of an iron-working hearth is indicated. A metallurgical process involving containment of the metal inside a crucible seems more likely, and although there is no direct evidence for these slags having originated during non-ferrous metalworking, this appears probable.

SF 121, context 4176, Phase 2 [Structure S3, workshop?, fill of pit F351]

Description
Three small pieces of fuel ash/lining slag.

Discussion
The slag fragments resemble the larger pieces of SF120, from the same context, and require no further comment.

SF 125, context 4063, Phase 2 [Fill of linear F253]

Description
Small fragments (12g) of a hearth or furnace wall. The highly fired and reduced surface shows some evidence of having been relined.

Discussion
Not certainly from a metallurgical hearth or furnace, although this is very likely.

S11, context 5078 (micro-residues by flotation)

Description
Small quantity of porous pale silicate slag, dominated by hollow spherules 1-1.5mm diameter.

S14, context 5141 [pit F404, near corn drier] (micro-residues by flotation)

Description
Porous grey vitreous slag (10g) in pieces up to 15mm. Some fragments are slightly magnetic. Outer surface of some fragments shows reddening.

S43, context 4266 [Structure 3, Phase 1, ?workshop, posthole F371] (micro-residues by flotation)

Description
Small quantity (approximately 15) of small (800-2000µm) spherules and/or droplets of pale silicate slag. Dominantly non-magnetic.

Cefn Cwmwd, C15/99

Summary

Metallurgical residues from Cefn Cwmwd are limited to a single blacksmithing hearth cake and a small piece of pure copper, neither from truly stratified contexts. Micro-residues from Cefn Cwmwd resemble those from Cefn Du and are not diagnostic, and not necessarily metallurgical.

Catalogue and detailed descriptions

SF 135, context 1001, cleaning layer (above structure S6)
Description
Dense, plano-convex blacksmithing hearth cake.

Discussion
This is a typical smithing hearth cake, of the kind generated by smithing activity in a clay hearth. The relatively small size (355g) argues for an origin in blacksmithing rather than bloomsmithing. The close association of this slag cake with hearth structures (F387 & F720) raises the possibility of these structures being metallurgical hearths, but this tiny amount of slag only emphasises the general lack of metallurgical residues on the site.

SF 156, context 1060, ?Period 1
Description
Small fragments (5g) of burnt clay bearing small charcoal fragments.

Discussion
Origin not necessarily metallurgical.

SF 169, context 1000, unstratified (topsoil)
Description
A small piece (40g) of copper metal. The piece shows a compact outer crust (Figure 5), with a porous, locally crudely dendritic internal structure, indicative of shrinkage during solidification. There are numerous included grains of quartz, mica and other minerals. The copper is likely to have fallen molten to the floor of the earth and then solidified incorporating various pieces of detritus from the hearth. Under the electron microscope EDS microanalysis of the copper in polished section shows no accessory metals above the detection limits.

Discussion
That this metal is pure copper is interesting and suggests it is in its first cycle of use. The presence of copper resources on Anglesey raises the possibility that this piece represents metal lost during primary smelting, although there is nothing here which precludes the metal having been lost during melting for alloying or refining.

SF 261, context 1907
Description
Porous fired clay; not slag.

Discussion
Origin not necessarily metallurgical.

S32, context 1446 [pit SW of structure S6, phase S6.5, 3rd century?)

Description
Small quantity of porous pale silicate slag, dominated by hollow spherules 1-1.5mm diameter.

S34, context 1466 [pit F0451, phase S6.1, late IA – early Roman]

Description
Fine debris of fragmented silicate slag.

Melin y Plas, C17

Summary

None of the material from this site is necessarily metallurgical.

Catalogue and detailed descriptions

SF090, context 230
Small chip (<5g) of calcined shale. This sort of material may originate from the burning of dirty coal, as well as by other means.

SF127, no context given
A small pebble, incompletely vitrified (<5g) with two adhering smaller vitrified pebbles. The temperature required to produce this vitrification is not likely in a domestic hearth, but would be more likely in a metallurgical hearth, such as a blacksmiths.

Material rejected as not being metallurgical residue

Cefn Du, A30/99

SF106
Description: These are badly decomposed fragments of a basic igneous rock.
Comment: Natural

Cefn Cwmwd, C15/99

SF089
Description: Rock fragments
Comment: Natural

SF203
Description: Two small pieces, one probably entirely natural, the other a concretionary growth around a small piece of iron
Comment: Further analysis not required.

SF249
Description: Sedimentary rock which originally contained carbonate concretions, now weathered out.
Comment: Natural.

Melin y Plas, C17

SF025, context 056
Description: Iron with thick smooth corrosion layer, 5g
Comment: Further analysis not required.

SF289, Pit 793
Description: iron pan in porous, angular gravel (130g).
Comment: Probably natural, but might be associated with corrosion of iron artefact.

Figure Captions

Figure 1. Iron bloom, Cefn Du, SF005.
(a) drawing of polished block showing major civilities and distribution of areas of elevated C and P.
(b) reflected light photograph of polished section, showing major diagonal welds.
(c) drawing of upper face of bloom
(d). X-radiograph of bloom. Both c and d show position of cut section.

Figure 2. Reflected light photomicrograph montages showing:
(a) cross section of bloom, C enriched zone at top, phosphoric ghosting present in most of lower part.
(b) detail of carburised upper surface
Scale bars 1mm. Iron bloom, Cefn Du, SF005.

Figure 3. Backscattered electron photomicrograph and energy dispersive spectrometry element maps for P, Cl, Fe and Si, of large slag inclusion, showing wustite and glass, together with weathered areas. Iron bloom, Cefn Du, SF005.

Figure 4. Backscattered electron photomicrograph and energy dispersive spectrometry element maps for Fe, Si, P and K, of small slag inclusions (lower bottom edge of Figure 3), showing leucite developed on the margins of a P-rich glass. Iron bloom, Cefn Du, SF005.

Figure 5. of copper fragment Cefn Cwmwd SF169 , context 1000.

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