Metallurgical residues from Porth-y-Rhaw, Dyfed

Summary: Material was submitted from 19 contexts. These contexts divided into 5 groups; one group including the general occupation deposit and unstratified material, but with four representing discrete stratified settings: (1) Iron Age features, (2) contexts associated with a furnace or hearth, (3) a posthole near the entrance, and (4) deposits of C2 age mainly associated with the roundhouse. These four settings yielded correspondingly discrete assemblages of metallurgical residues. The Iron Age deposits yielded three fragments of a dense grey slag derived from a smithing hearth cake. The furnace-associated features contained 3 sherds of a metallurgical crucible (a single sherd was also present in the general occupation deposit), and one of a probable crucible lid, together with some small fragments of smithing slags. The posthole contained a considerable quantity of smithing slag cake fragments, together with material from the furnace wall. The deposits associated with the roundhouse contained fragments of vitrified clay, probably from the wall of a metallurgical hearth.

The crucible contained traces of a tin oxide-rich material (both internally as a slagged residue, and as tiny blebs up to 50µm across on the external vitrifed surfaces of the crucible), representing a decomposed tin bronze, from which the copper had been largely lost by dissolution. The decomposed nature of the metal blebs means that no determination of the original metal composition was possible. Concentrations of copper were, however, significantly high to suggest that the crucible had been used for melting bronze rather than tin itself.

The crucible fragments were tantalisingly incomplete, but appear to be of a form without exact parallel elsewhere. The crucible appears to have been of roundedly triangular shape, with one extremely thickened angle, leaving an almost circular "well". The most likely reconstruction of form would suggest some similarity with the "D" shaped crucibles representing the development of the native triangular crucible during the Roman period, such as have been recorded from Exeter (Fox 1952) and Sutton Walls (Kenyon 1953) in 1st Century AD contexts.

The iron-working slags are typical of the varied slags produced during blacksmithing. They vary in chemical and mineralogical composition, possibly reflecting a spectrum of activity from high (context 1225) to low (context 1251) temperature processes. The total weight of iron-working slags recovered is very small and it is therefore difficult to judge the significance of this activity for the site.

Context	Sample	Weight	Age	Setting	Residue	Analyses
Group 1						
1225		50	IA		Dense grey slag	SEM amd w/r
1339			IA		Dense grey slag cf 1225	
Group 2						
1251				Occupation near furnace	Broken dense slag	SEM
1285		40		P/h near furnace	Fired clay?	
1286				Fill of cut near furnace	Small pieces pale slag. Crucible 473	Rock frags?
1760				Adjacent to furnace	? crucible lid	
Group 3						
1763				Upper fill of p/h near ent.	Smithing cake and cinder	SEM + w/r
1795				Upper fill of p/h near ent.	Large amount of furnace debris from near blowhole, some denser flaps and poor cake	
1298		335		? 1795	Smithing slags	
Group 4						
1217	576	800 bs	C2	Roundhouse floor		
1217			C2	Roundhouse floor	Light frothy clinker	
1234			C2	Over roundhouse porch	Light frothy clinker	
1235?			C2		Light frothy clinker - large pieces	
1235			C2		Light frothy clinker - large pieces	
1236?			C2			
1236			C2		Light frothy clinker - large pieces	
1770				Stake hole	Light frothy clinker	
650			C C2	Wall tumble	Light frothy clinker	
Group 5						
604			Genera l	Occupation	Mainly light frothy clinker, 1 piece dense grey slag cf. IA material. crucible	Glass + stone
1761				Unstrat.	Light frothy clinker	

Table 1. Summary of the residue archive

Crucibles

Description

(1) Context 1286

Three conjoining fragments of a crucible were recovered from context 1286 (object 473). A single fragment with identical form was recovered from the occupation material, context 604. A similar, but much thinner, fragment was in context 1760. Both contexts 1760 and 1286 are associated with the small hearth.

The crucible (object 473) represented by three sherds is illustrated in figure 1 A-C. The base of the crucible is missing, as is around 40% of its wall. The crucible is rounded, but with slightly tighter curvature at two points giving a slightly sub-angular outline. The wall has a rounded rim, dropping vertically internally, but swelling slightly externally, to give the widest point approximately 13mm below the rim. The surviving piece has one of the slightly angular regions at one end, the other angular region centrally and a substantially thickened area at the opposing end. The unfortunate position of the breakage through this thickened area makes its interpretation difficult. The thickening involves the wall increasing from its typical 10mm thickness, to around 15mm at a point 7 mm below the rim. The internal margin of the thickened area is damaged, but appears steep, and continues the curve of the internal face of the wall from the adjacent area of normal wall. The internal well of the crucible is therefore sub-circular, with a diameter of approximately 38mm, a maximum preserved depth of 20mm, and an estimated original depth of approximately 29mm, giving a volume of approximately 26cm^3.

The crucible has a grey fabric bearing quartz grains of up to 4mm. The surface of the crucible is vitrified to approximately 10mm below the rim on the side away from the thickening, but extending to at least 20mm below the rim in the thickened area. The inner face is also well vitrified to at least 10mm below the rim, but below that is generally covered with a skim of slag, which thickens to 2mm in a few places. The external vitrification is dominantly black in colour, change to a reddish tinge over the top of the rim and on to the internal face.

The area in which the wall starts to thicken is marked by a partly annealed fracture running over the rim, and two further fractures cut the thickened area. A region 16mm wide by 13mm high spanning this second crack forms a flat surface, with a less highly efelctive vitrified surface. It is possible that this may represent mark formed by contact with tongs.

(2) Context 604

A fragment of a crucible similar to that described above. The rim bends markedly along the 15mm length of the piece, suggesting that the fragment comes from one of the subangular bends described above. The inner face appears not to be vitrifed, but is covered at least in part by a skim of slag. The external vitrification is red for 5mm below the rim and black for at least 15mm below this.

(3) Context 1760

A small fragment (figure 1, D-E) of similar fabric to the crucible fragments described above, but considerably thinner. The piece has one slightly concave, but almost planar face, showing black vitrification, which turns red near the margin and along the edge of one of the fractured margins. The other face curves around to the margin of the fragment, which is 3mm thick at 3mm from the margin and 5mm at 15mm from the margin. This more strongly curved face appears to be less vitrified. The original margin of the fragment is irregularly curved, with a radius of curvature somewhat larger than that of most of the lip of the crucible (473) described above. The planar nature of this piece, and the apparently strong difference in vitrfication between surfaces, suggests that this may be a fragment of a crucible lid.

Analysis

Several small samples were taken for analysis from the larger crucible fragments:
sample a: a <500µm wide flake of black vitrified surface from the outside of the crucible, for SEM.
sample b: a <500µm wide flake of red vitrified surface from the inside of the crucible, for SEM.
sample c: a <1000µm wide flake of slag from the inside of the crucible, for SEM.
sample d: a <3000µm wide flake of slag from the inside of the crucible, for ICP-MS.

Sample (a) showed a well-preserved vitrified surface. At intervals across the surface lay individual grains, or clusters of elongate crystals of a tin oxide. Individual crystals were needles of up to 20µm in length, and typically <1µm across. These crystals were either isolated, or more commonly randomly oriented within patches of up to 50µm diameter (Plate 1a).

The vitrified surface of sample (b) showed an elevated concentration of copper, which is usually associated with the generation of the red colouration. Small particles of an iron oxide were present on the surface, and it is uncertain whether these were associated with the slag phase, or were a component of the crucible clay.

The slag, sample (c), showed a layered structure (Plate 1b), with laminae rich in elongate tin oxide crystals alternating with fine grained, probably highly altered, silicate slag (Plate 1, B). The tin oxide crystals formed needles, typically of up to 100µm and locally up to 200µm in length and 1-10µm wide. A larger crystal gave an EDS analysis, which was contaminated by slag, but which suggested a compostion of >85% tin oxide and 4% copper oxide. The chemical and mineralogical form of the copper remains unknown. The slag material appeared amorphous and was cracked. This appearance suggested a weathering product rather than a primary slag phase, a proposition supported by the detectable quantites of chlorine present in the microanalysis. One larger (approximately 20µm diameter), inhomogeneous metal oxide bleb in the slag gave analysis equivalent to >85% tin oxide with around 5% copper oxide. The slag phase contained very little copper, but did contain a very high level of phosphorus (9% as oxide, correpsonding to 4 wt% of the element). Such high levels of phosphorus might be associated with alteration, but are more likely to indicate that the crucible contents came into contact with the fuel (possibly also indicated by the high alkali content).

	Na	Mg	Al	Si	P	Sn	K	Ca	S	Ti	Mn	Fe	Cu	Cl	total	total *
Tin oxide on ext.	<	<	0.5	0.8	0.3	67.4	0.3	<	<	<	<	0.4	<	<	70	78
Tin oxide in slag	<	<	1.1	3.4	1.2	75.3	<	<	<	<	<	1.3	2.9	<	85	94
Bleb in slag	<	0.7	2.0	1.4	1.8	64.7	0.6	<	0.2	<	<	2.0	4.3	<	78	85
Altered slag matrix	5.5	5.6	9.7	32.7	9.2	15.3	2.9	5.1	0.2	0.6	0.3	12.2	0.4	0.1	100	102

Table 2. EDS analyses from crucible material quoted as wt% of oxide. The totals of material analysed on rough surfaces is very low, so those analyses should only be used as a semi-quantitive guide to composition. Total is given as a hypothetical value were the tin present as a hydrated oxide. < indicates element below detection. The samples did not contain lead, zinc or arsenic in detectable quantites.*

Discussion

The retrieval of only a part of crucible (473) makes comparison with other examples difficult. There are three possible interpetations for the thickened region of the crucible. Firstly it is possible that this not a deliberate feature, and that the crucible is essentially of a sub-angular form. Although some early crucibles are highly irregular in shape (e.g. some of the Glastonbury examples, Bulleid & Gray 1911) the degree of regularity of the remainder of this specimen makes this unlikely. Secondly the crucible could be of a pinched form (cf. Tylecote 1986 form D1), but one might have expected to be able to see an out-turn of the external surface approaching the "handle region", but this is not present. The third, and most likely, interpretation, is that the thickened region represents the thickened elongated corner of a D-shaped crucible (Tylecote 1986 form A3).

The earlier Iron Age (?4th-5th centuries BC) seems to be typified, at least in western Britain, by cup-shaped crucibles (Old Oswestry, Llwyn Bryn-Dinas, Berth, Danebury); the later Iron Age (1st-?2nd centuries BC) by triangular forms (Glastonbury, Gussage, Collfryn, Castell Henllys). D-shaped crucibles are of a shape intermediate between these triangular forms and the circular crucibles common on Roman sites. Tylecote (1986) illustrated the form of these D-shaped crucibles with an example from Sutton Walls (Herefordshire), probably dating to the first century AD (Kenyon, 1953). The Sutton Walls example has walls which diverge evenly upwards, giving an open shape, markedly different to the slightly inverted rim form of this specimen. A very similar wall profile to the Porth-y-Rhaw specimen is seen in an example from Exeter, also of first century AD date, described as being sub-angular (Fox, 1952). Neither the Exeter nor the Sutton Walls examples shows the marked thickening of the Port-y-Rhaw specimen, but the Sutton Walls specimen does show some slight thickening.

Thus, although the material is incomplete, and is without exact parallel, it appears to fit best with sub-angular to D-shaped crucibles representing the evolution of the triangular crucible during the Roman period.

The residues on the crucible surface and within the altered remnant of crucible slag were extremely tin-rich. The precise mineralogical phase was not identified, but the material was not tin ore (cassiterite), and was probably a hydrated oxide of tin. The persistent, if low, quantities of copper present in the altered patches and in the slag strongly suggest that the tin-rich patches are the result of the decompostion of tin bronze, with subsequent dissolution of the copper-bearing weathering products. An extreme example of this process was quoted by Tylecote (1986). The highly altered composition of these residues means that it is not possible to use the absence of arsenic, zinc and lead as a provenance indicator. There is no evidence that the crucible was used for making bronze, rather than for remelting.

The Iron-working Slags

Description

The iron-working slags are all rather fragmentary, so little interpretation can be made of their overall morphology, or the original slag cake size. They are all of moderate density and the specimens were all consistent with identification as hearth cake fragments from blacksmithing. However, the identification of non-ferrous metworking on the site meant that close analysis of representative material was desirable, in order to confirm the nature of this material. Four specimens from three contexts were examined by electron optical techniques (together with an additional four small specimens from two contexts which were problematic in hand specimen, but which proved to be various natural iron-rich rocks, and which are not described further). A single sample was given a full chemical analysis.

Petrology

Sample e: context 1763 (upper fill of posthole near entrance)

This sample is of a fayalite-wüstite dominated slag. Wüstite dendrites of up to 500µm occur distributed throughout, but are particularly spatially associated with the abundant, and often large, fragments of hammerscale (e.g. Plate 3c). Hammerscale is up to 2mm in width and 200µm thickness. The matrix to the dendrites is formed of densely-packed laths (500µm x 20µm) of fayalite (generally with a small amount of Ca substitution) (e.g. Plate 3b). This slag is noticeably richer in fayalite than those from contexts 1225 and 1251. The wüstite is locally altered to and/or overgrown by magnetite.

Sample f: context 1251 (Occupation deposit near hearth)

This low density material proved to be mainly a partially melted fragment of sedimentary rock (probably once an inclusion in a hearth wall). At one end the rock is in contact with a fayalite-wüstite slag, similar to that of sample g, but bearing small grains of hercynite (reflecting increased Al supply from the melting rock fragment).

Sample g: context 1251 (Occupation deposit near hearth)

This slag is dominated by wüstite. It contains abundant hammerscale (Plate 3a). Details of the silicate mineralogy are frequently obscured by weathering, but subordinate fayalite is present. Irregular regions may contain grains with a leucite-wüstite eutectic. This sample is much poorer in silicate minerals than those from contexts 1225 and 1763. The decreased significance of the silicate component, plus the abundance of hammerscale, may suggest that this sampple was produced during relatively low temperature blacksmithing.

Sample h: context 1225 (IA gully below roundhouse)

This material was grey in colour and rather uniform in hand specimen, in contrast to the darker and more heterogeneous materials from contexts 1251 and 1763. The slag was, however, heterogeneous on a fine scale (Plate 2a). It was characterised by the co-occurrence of coarse granular wüstite and magnetite (Plate 2b,c,d). These granular crystals were up to 150mm in diameter. Wüstite crystals were rounded, and bore rounded cavitities; the magnetite grains were angular and bore planar crevices. Some grains contained both minerals, and there was some indication that alteration and/or superposition of these two phases occurred in both directions. Finer wüstite dendrites also occurred. Fayalite occurred as large laths (upper centre of Plate 3a), possibly up to 1mm in length in some areas, but in others (e.g. Plate 3c) fayalite was seen mainly in tiny late-stage dendrites in the glassy matrix. Leucite (commonly as a leucite-fayalite? eutectic) and hercynite occur sporadically, particularly near the vesicles. The texture of this slag is suggestive of its generation in a higher temperature process (e.g. welding) than that producing the slags of samples e, f and g.

Some limited EDS analysis of sample h was undertaken from the area illustrated in Plate 2c, to clarify the mineral compositions involved (Table 3a-c).

	Tetrahedral	Octahedral					End Member composition		
	Si	Ca	Fe2	Mn	Mg	total	Fa	Fo	"Ca2SiO4"
olivine edge	1.022	0.017	1.755	0.000	0.183	1.96	90	9	1
olivine core	1.014	0.012	1.685	0.000	0.276	1.97	85	14	1

Table 3a. Mineral formulae for EDS analyses of olivines, based on a structure with 4 oxygens (context 1225: sample h)

	Tetrahedral				Octahedral					
	Fe3	Si	Al	total	Fe2	Mn	Ca	Ti	Mg	total
magnetite	13.59	0.15	2.26	16.00	7.38	0.00	0.00	0.13	0.00	7.51

Table 3b. Mineral formula for EDS analysis of magnetite, based on a structure with 32 oxygens and 16 filled tetrahedral sites. (context 1225: sample h)

	Tetrahedral		Octahedral							Interlayer				Other	
	Si	Al	Al	Fe2	Fe3	Mn	Mg	Ti	total	Ca	Na	K	total	S	P
glass	10.047	4.011	0.000	2.742	0.000	0.000	0.000	0.000	2.74	1.289	1.42	2.30	5.01	0.04	0.22

Table 3c. Model mineral formula for EDS analysis of glass, calculated as if it were a feldspar with 32 oxygens. (context 1225: sample h)

The initial olivine phase is sufficiently Mg-rich to be a ferro-hortonolite (Fo 14), but the margins are fayalite (Fo 9). The magnetite is very heavily substituted (approximately 13% hercynite, 2% ülvospinel). The glass phase contains most of the Ca, Na, K, S and P. The glass is very low in S (as also were the glasses of the other specimens examined only semi-quantitively), confirming the fuel used was not coal.

Chemistry

Sample i: context 1225 (IA gully below roundhouse)

The composition of a sample of the slag from context 1225 was determined by XRF (for major elements) and by ICP-MS (for minor and trace elements).

SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
12.46	3.94	42.59	37.41	0.04	0.54	0.73	0.00	0.94	0.27	0.27

Table 4 XRF major element analysis of iron-working slag sample (sample I) from context 1225.

The composition is entirely consistent with these slags being iron-working slags. The low take-up of elements present in the fuel is typical of the dense smithing slag cakes on other sites, in which the composition is determined by partial melting of the hearth wall, and the reaction of that melt with iron and iron oxides from the workpiece.

Discussion

The material studied was typical of early smithing residues. The analytical work undertaken confirmed rhis interpretation and revelaed no evidence that any of these slags was associated with non-ferrous metalworking. The sample size was very small, but the studied slags were extremely varied, suggesting a range of iron-working tasks was being carried out on site. None of the iron slags is likely to have been associated with smelting, and none of the smithing slags need be associated with bloomsmithing. The material from context 1225 did not contain significant hammerscale, but is more likely to be associated with welding, than with any stage of the primary production process.

References

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Figure Captions

Figure 1. Crucible material from context 1286
Pale stipple shows the distribution of internal slagged deposit.

A. Plan view of three conjoining sherds of crucible (object 473).
B. Lateral view of two sherds of object 473, to show vertical extent of slagging.
C. Reconstructed profile of object 273, viewed from thickened corner.
D. Plan view of probable crucible lid sherd.
E. Lateral view of probable crucible lid sherd. Profile suggests this orientation, but intensity of vitrification hints the lid may have been the other way up.

Plate 1. Backscattered electron photo micrographs of crucible material from context 1286

a. Bleb bearing acicular tin oxide(?) crystals on exterior surface of crucible object 473. [*862/20*]

b. Layered slag deposit bearing laminae rich in elongate tin oxide(?) crystals, removed from inside of object 473. [*862/22*]

Plate 2. Backscattered electron photo micrographs of iron-working slag (sample h) from context 1225.

a. Typical textures of slag, showing heterogeneous composition even within a small area. Upper left part of area between vesicles shows equant iron oxide crystals (both wüstite and magnetite), upper centre is much richer in fayalite laths, whereas lower centre is dominated by wüstite dendrites. [862/12]

b. Detail of an area with wüstite dendrites together with some coarser wüstite grains (wüstite is bright and shows rouded outlines). Magnetite occurs as angular crystals (pale grey). Elongate fayalite laths (mid-grey) are also present. The crystalline phases are contained in a glass matrix (dark). [862/11]

c. Detail of an area where the wüstite dendrites are absent. Texture dominated by large angular magnetite (mid-grey) and rounded, carious, wüstite (bright). Matrix of glass (dark) bears small dendrites of olivine (mid grey). [862/23]

d. Detail of an area with abundant wüstite grains set in a strong fabric of aligned olivine (fayalite?) laths, with co-aligned magnetite grains. Small areas (e.g. Just below centre left) show leucite (dark grey)-wüstite eutectic intergrowths. [862/13]

Plate 3. Backscattered electron images of iron-working slags from contexts 1251 and 1763

a. Context 1251 Sample g. Hammerscale (vertically oriented on left) shows typical assymetric structure. Right side of scale shows rounded blebs wustite-fayalite eutectic. Left side of scale more abrupt. Typical slag texture is heterogeneous, with abundant wüstite dendrites (bright), fayalite laths (mid-grey) and minor glass (dark). Some areas (e.g. left of centre bottom) show wüstite (bright)-leucite (dark) eutectic structures. [*862/16*]

b. Context 1763 Sample e, typical fabric. Small patches dominated by wüstite probably represent relict scale. Wüstite generally subordinate to fayalite laths. Very little glass present. [*862/18*] 1763 typical, S-free glass, fay slightly Ca close to e/m

c. Context 1763 Sample e. Large assymetric hammerscale. As with (b) the typical composition is dominated by fayalite; wustite only dominant near scale [862/19].

d. Context 1763 Sample e. Somewhat weathered hammerscale example, but shows (e.g. lower left) alteration of original wüstite to magnetite (dark rims on wüstite dendrites). Alteration is shown by the poor polish, and the secondary deposits inside the vesicles [862/17]