

Metallurgical Residues and related materials, Gloucester Business Park, Brockworth

Summary

Small amounts of residue from pyrotechnological processes were recovered from a wide range of contexts. The dominant material is a “fluxed lining slag” which occurs in contexts from Phase 2.1 to Phase 5. These slags are the result of partial melting of “clay” as a result of fluxing by the alkali-rich ash of the fuel. The analysed specimens show no enhancement in metal content, nor any textures suggestive of incorporation of metallic blebs or particles. These slags might have an origin in a process where the metal is confined to a crucible (i.e. non ferrous metal casting), but could equally have had their origin in any process where clay, including the local soil or subsoil came into contact with a fire and was heated to temperatures in excess of approximately 900°C. This would not be normal in a domestic hearth, but is possible (intentionally or otherwise) in a wide variety of situations. It is unlikely that sufficient temperatures would be produced in the ground below a funeral pyre, but given the close association of some of the earlier of this material with cremations this remains a slight possibility.

Two crucible fragments derive from phase 3.1 contexts. One of these provides good microanalytical data to show it was used for handling a tin bronze. The second crucible fragment and a fragment of hearth lining do not reveal contamination from the metal, but do show elevated iron contents. The significance of this is uncertain (iron itself could not have been worked in the crucible). It is possible that some iron working was taking place, but the current evidence is really insufficient to demonstrate this conclusively. It is interesting that the crucible fragments are apparently not accompanied by the glassy slags seen in the other phases.

The post-medieval and undated material includes pieces of iron working slag and coked coal which are typical of the addition of domestic and industrial “ash” as a component of agricultural practice. There is one piece of irregular iron associated with this material which might be a piece of raw material (possibly even from a bloom) or blacksmith’s scrap.

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Catalogue

Context	Wt.	Comment
608	270	irregularly wedge-shaped fragment of iron. Probably waste, possibly a fragment of a part-consolidated bloom.
1007	30	large piece of coke
1011	5	very abraded fragment showing junction between grey vesicular fluxed lining slag, and pale grey lining
2026	5	eight coke fragments
2028	40	dense dark slag, varying from glassy (particularly near clay inclusions) to iron oxide-rich, smaller fragments bear shale and coke inclusions
2062	<5	coke
2166	5	small fragments of mid-grey vesicular fluxed lining slag, some coating small pebbles
2166	5	mid grey, finely vesicular fluxed lining slag
2190	<5	grey vesicular fluxed lining slag - tiny fragment
2632	10	green-blue fuel ash slag, draping ?partially melted pebble
2890	200	grey vesicular fluxed lining slag in fragments up to 5cm
2906	5	small fragment from rim of small (?4cm diameter) crucible
2933	5	single piece of grey fluxed lining slag, mainly bleached
3071	10	single piece (3.5cm) of vesicular grey fluxed lining slag, bearing small reddened areas
3246	10	grey vesicular fluxed lining slag in a single fragment of 3cm
3274	<5	1 piece from lower part of wall of small crucible, fluxed inner surface; 1 piece slagged hearth lining; 1 tiny piece grey lining/pottery

Description by Groups

Group 1. Phase 5 & ?. Coke (1007 / 2026 / 2062 / 2028)

Contexts 1007, 2026 and 2062 yielded coke alone; context 2028 contains some dense iron working slag associated with the coke. Although strictly non-diagnostic, the surface texture of the slag in 2028 closely resembles material from industrial forges. This group probably represents post-Medieval “fertiliser”.

Group 2. Phase 5. Iron (608).

This piece is very irregular and might just be a piece of relatively raw bloom. It is not a fragment of a finished artefact, but might be metal debris associated with the forge refuse of Group 1.

Group 3. Phases 3.2-5. Grey glassy, vesicular slags (1011 / 2632 / 2890 / 2933 / 3071 / 3246)

These slags are vesicular slags of the kind sometimes referred to as “fluxed lining slags” (Crew 1996). However, they may have an origin in various processes, not only as the product of fluxing of the hearth lining by the fuel ash in a metallurgical hearth (either ferrous or non-ferrous), but in various other sorts of hearths and ovens, or even during accidental burning of clay-rich materials. It is therefore possible that the material in these various contexts does not derive from the same process, despite the similarity of the residues.

Most of the material was rather small (these slags are very fragile), but context 2890 yields a significant quantity of larger pieces.

The analytical procedures applied to slags of this type were intended to reveal any evidence of metallurgical processes. Such indications might come from the chemical composition (raised proportion of iron, or non-ferrous metals) or from textural studies (traces of included hammer scale or blebs of metal).

GBP2 GPB98/32 2890

context	phase	SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	total
GBP1 (2166)	2.1	62.44	13.18	8.80	0.13	1.10	4.20	0.50	2.71	0.84	2.25	1.98	98.13
GBP2 (2890)	3.2	64.61	10.78	5.01	0.17	1.89	6.78	0.86	5.23	0.71	2.52	1.01	99.56

Table 1. Major element composition of samples GBP1 and GBP2, expressed as wt% oxide. LOI = loss on ignition. All iron is expressed as FeO. Samples analysed by XRF.

Sample GBP2 (a representative piece from context 2890) is very similar with respect almost all elements to sample GBP1 (context 2166, discussed below), as demonstrated by the major elements (Table 1), trace metals (Table 2) and rare earth elements (REE; Figure 1). Although the major elements are rather different (in particular the lime content of the Brockworth samples is much lower), the upper crust normalised REE profile (Taylor & McLennan 1981) of these samples corresponds closely with that from a sample of subsoil clay from Frocester (sample FC016), a locality with a similar geological setting. The REE profiles are flat lying, at a value close to 1, with only a very slightly middle REE hump.

	Cr	Cu	Zn	As	Mo	Pb
GBP1	104.19	37.052	76.679	8.449	3.677	5.973
GBP2	78.524	34.053	191.57	6.227	4.565	5.954
FC016	48.507	14.62	85.353	12.53	0.741	35.76

Table 2. Concentration of selected trace metals in samples GBP1 and GBP2, expressed as parts per million (ppm) element. FC015 is a comparative sample of subsoil clay from a comparable geological setting. Samples analysed by ICP-MS.

The content of the economic metals and associated elements (Fe, Cr, Cu, Zn, As, Mo, Pb) are all very low, and within the range of subsoil clays, differing little from the Frocester clay sample (Table 2). There is therefore no evidence for the input of metals to these samples from metallurgical processes. Ca, K, P, Mo are slightly raised in GBP2, suggesting a slightly higher contribution from fuel ash in GBP2 than GBP1. It is also worth noting that the levels of As and Mo are relatively low, and these element typically show a high degree of enrichment when coal is employed as fuel. That possibility (raised in the initial evaluation of this material) can therefore be discounted.

In view of the similarity of these two materials (GDP1 & 2), the SEM investigation has been focused on just one of the samples, GBP2. This sample is highly vesicular, with the vesicles ranging from a few microns (e.g. Plate 1, g) up to several millimetres (Plate 1, b). The slag phase bears quartz grains of up to 500µm (Plate 1, c) in a groundmass which is dominantly glass, but which shows a significant degree of crystallization (Plate 1 d-g).

The typical microstructure (Plate 1, e-g) comprises two crystalline phases in a glass. The earliest crystalline phase, clearly seen in the margins of vesicles (Plate 1, g) has an acicular morphology (needles up to 20µm in length and less than 2µm wide), apparently with a hollow core. These needles appear to grade outwards from the vesicles into lath shaped crystals (up to 5 x 20 µm), showing a zonation from core with lower electron backscatter coefficient (i.e. darker on BSEM images) to rims with a higher coefficient (i.e. brighter). The second crystalline phase occurs as a patchy distribution of extremely small (<2µm across) crystals (e.g. Plate 1, e; just above and to the upper right of the quartz grain in the lower left).

These phases are all too small for single crystal EDS analysis, so the analyses in table 3 are all from mixed phases. Spots 5 and 7 on the lath-shaped crystals provide analyses suggestive of a mixture of glass (using the compositions given by spots 6 and 8) and a salite pyroxene with octahedral substitutions of approximately $\text{Ca}_{1.0}\text{Fe}_{0.25}\text{Mg}_{0.75}$. The analysis of the acicular phase can be modelled as an approximately 50:50 mixture of such a salite and glass. The phosphate mineral composition can likewise be corrected by removal from the analyses of glass and a small salite component to leave a calcium phosphate (apatite).

spot/phase	Al	Si	Fe ^{II}	Mn	Ti	Mg	Ca	Na	K	S	P	Ni	interpretation
5 lath	1.79	47.77	6.08	0.00	0.74	12.21	25.96	<	0.62	<	4.64	0.19	salite, minor glass & apatite
7 lath	2.78	52.37	7.01	0.53	1.07	11.45	23.01	<	1.28	<	0.49	<	salite, minor glass
10 hollow needle	6.61	57.64	6.26	0.46	0.81	6.85	17.23	<	3.66	<	0.50	<	salite / glass
6 glass	11.86	63.90	7.41	0.27	0.90	0.60	4.88	<	9.26	<	0.58	0.19	glass
8 glass	12.49	62.99	6.14	0.40	1.22	0.89	5.96	<	8.60	<	1.31	<	glass
9 phosphate	2.51	27.46	4.19	0.29	0.46	5.95	33.37	<	1.56	<	24.00	0.20	apatite / glass / salite
11 phosphate	4.92	29.15	4.15	0.00	0.42	3.74	31.47	<	3.21	0.15	22.80	<	apatite / glass / salite

Table 3. EDS microanalyses from GBP2. Values quoted as wt% oxide normalised to 100% to facilitate comparison.

In some areas of the specimen the apatite phase can be seen (Plate 1, d) to form larger, hexagonal sectioned crystals up to 8µm across.

There are very few detailed descriptions of slags like these in the literature, probably because they are generally considered non-diagnostic. However, study of similar materials from other sites has shown that small pieces of hammerscale can usually be seen in slags like these where they are associated with blacksmithing. This was not the case with the material examined here. If the material had been associated with the working of non-ferrous materials, then equally a small amount of contamination of the hearth residues by the metal might be expected, but again this is not evident in this material. Casting of non-ferrous metals can produce minimal contamination of the hearth, for the metal is enclosed in a crucible, and there is no means for the positive identification of such an activity from the hearth residues in the absence of crucible or mould fragments.

Group 4. Phase 3.1 Non-ferrous metalworking. Crucible fragment 2906. Crucible/mould fragment 3274 (also 2 pieces furnace wall)

Two crucible fragments were carbon coated and mounted for SEM examination. One specimen of probable hearth lining was also examined. Because these are three-dimensional specimens fully quantitative micro-analyses cannot be obtained, so the analytical data quoted below (Table 3) are only semi-quantitative at best.

Despite this qualification the data are reasonably coherent. The crucible base (3274) has two analyses of the unaltered crucible ceramic, with different specimen orientation, but showing remarkably similar compositions (24-25% Al_2O_3 , 58-59% SiO_2 , 2-3% K_2O , 1% CaO , 2% MgO). The aluminium content seems reasonably high (25% is the minimum Al_2O_3 content for a fireclay), but if the alkalis are a primary component of the ceramic then they would have reduced the softening temperature considerably. The slag material is more aluminous (relative to the silica content) than the ceramic, is enriched slightly in iron, but strongly in calcium and phosphorus. The non-ferrous metal content of the slag includes up to 3.4% Cu expressed as CuO and up to 30% Sn expressed as SnO. The high tin:copper ratio is commonly seen in slags of this nature, and appears to reflect the preferential leaching of copper in post-depositional alteration, rather than being an indication that the crucible was used for metallic tin.

The crucible rim (2906) has been rather thoroughly cleaned, but shows a very different suite of analyses. The surface of the rim, and the upper part of the vesicular material inside (probably itself mainly melted crucible rather than a separate slag phase) show elevated iron contents (equivalent to 29 - 54% FeO). It is unlikely that such iron-rich material comprises a great thickness, but none the less, the levels are extremely high. Within the thickness of the vesicular material the iron contents fall rapidly to close to those observed in the body of the (3274) crucible fragments (5-6% FeO). The composition recorded for points within the vesicular layer is close to the composition of a crucible slag from Porth-y-Rhaw, probably of Roman age (author's unpublished report for Dyfed Archaeological Trust). Phosphorus and calcium show irregular enrichment within the vesicular material, presumably again reflecting reaction with the fuel.

An elevated iron content in some slags from copper alloy working has been noted previously (Tylecote 1986), and has been related to the iron content of the copper, deliberate use of iron oxides as a flux to clean the metal, or to the use of iron tools for manipulating the crucible. In this case, the significance of the iron-rich slag is uncertain, but it appears to form only a very thin veneer on the crucible.

The piece of probable hearth lining has a reddish, oxidised fabric, with an extremely vesicular surficial layer a few millimetres thick. Analyses of the fabric and vesicular layer include several clustering around Al_2O_3 of 24%, SiO_2 of 60%, CaO <1% and K_2O of 2-5%. These indicate a clay of broadly similar composition to that of the crucible. As with the crucible slags the clay shows substantial fluxing by the fuel ash with Ca and P both markedly enriched in spots 3, 6, and 8. The same spots show enrichment of iron, providing some suggestion that the piece is from an iron-working hearth, but as noted above local enrichment of iron is possible under other circumstances, so identification of iron working on the basis of this one fragment would be premature.

Group 5. Phase 2.1 Grey glassy vesicular slags (2190 & 2166)

These slags are present as rather small fragments of overall appearance similar to those of Group 3. A single specimen from context 2166 was selected for detailed study.

GBP1 GPB98/32 2166

Sample GBP1 was selected as being one of the larger pieces of material from these contexts. The specimen appeared slightly paler in colour than the "fluxed lining slags" described above as Group 3, but under the microscope the slags are indistinguishable (compare Plate 1 a and b) and the chemical analysis (as described above Tables 1 & 2, Figure 1) is very close to that from GBP1. Because of this similarity, the electron microscope studies were concentrated on gaining a full understanding of GBP2. The comments made about GBP2 are therefore believed to be applicable to GBP1.

References

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- TAYLOR, S.R. & McLENNAN, S.M. 1981. The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philosophical Transactions of the Royal Society*, **A301**, 381-399.
- TYLECOTE, R.F. 1986. *The Prehistory of Metallurgy in the British Isles*. The Institute of Metals, London.

	Al	Si	Fe ^{II}	Mn	Ti	Mg	Ca	Na	K	S (as S)	P	V	Ni	Cr	Cl (as Cl)	Cu	Sn	Analytical Total	
<3274> cruc. Base																			
1	25.15	57.76	6.21	0.00	0.46	1.97	1.11	2.49	3.41	0.00	0.96	0.00	0.00	0.00	0.00	0.49	0.00	88.55	
6	24.30	58.74	9.99	0.00	1.06	2.16	0.92	0.00	2.25	0.00	0.57	0.00	0.00	0.00	0.00	0.00	0.00	68.12	
2	9.40	18.38	4.90	0.00	0.00	4.34	13.91	0.00	0.49	0.29	15.41	0.00	0.00	0.00	0.00	2.64	30.24	56.33	
4	8.72	25.25	9.56	0.00	0.92	12.31	13.40	0.00	0.00	0.00	7.61	0.00	0.28	0.00	0.00	1.46	20.49	75.80	
3	7.79	15.41	6.79	0.00	0.71	3.86	33.61	0.00	0.00	0.00	26.19	0.00	0.00	0.00	0.00	1.93	3.72	65.10	
5	11.33	28.19	13.01	0.00	1.36	9.39	22.07	0.00	0.52	0.00	9.11	0.00	0.00	0.00	0.00	0.92	4.11	52.75	
7	20.49	19.33	10.87	0.00	0.99	2.97	13.91	0.00	1.25	0.00	25.04	0.00	0.00	0.00	0.00	3.40	1.76	100.19	
8	13.44	5.60	8.61	0.00	0.63	3.06	24.45	0.00	0.26	0.16	35.17	0.00	0.00	0.00	0.00	2.72	5.90	93.79	
<2906> cruc. Rim																			
11	6.01	36.23	53.55	0.00	0.42	1.80	0.69	0.00	0.54	0.00	0.77	0.00	0.00	0.00	0.00	0.00	0.00	111.66	
12	17.36	29.05	41.61	0.49	1.39	1.35	2.88	0.00	4.02	0.00	1.42	0.00	0.42	0.00	0.00	0.00	0.00	37.62	
20	12.07	31.79	48.68	0.00	1.17	1.10	1.71	0.00	0.90	0.00	2.57	0.00	0.00	0.00	0.00	0.00	0.00	77.97	
14	35.11	50.54	7.44	0.00	0.38	1.34	1.30	0.00	2.76	0.00	1.14	0.00	0.00	0.00	0.00	0.00	0.00	92.07	
18	16.87	16.82	32.44	0.00	2.50	0.00	7.84	0.00	0.74	0.26	22.33	0.00	0.00	0.00	0.20	0.00	0.00	61.91	
19	27.27	46.36	10.69	0.00	0.80	1.74	5.54	0.00	2.04	0.00	5.32	0.00	0.00	0.00	0.23	0.00	0.00	98.79	
9	8.79	34.86	37.71	0.00	0.85	0.00	5.90	0.00	2.15	0.15	9.58	0.00	0.00	0.00	0.00	0.00	0.00	86.52	
13	13.62	37.09	28.96	0.00	1.28	1.28	4.92	1.59	1.80	0.20	9.12	0.00	0.14	0.00	0.00	0.00	0.00	92.56	
16	32.43	47.26	13.10	0.00	1.42	1.83	0.58	0.00	3.15	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	102.63	
15	30.92	40.74	14.72	0.00	1.67	2.84	1.79	0.00	2.65	0.13	4.39	0.00	0.15	0.00	0.00	0.00	0.00	103.00	
10	39.14	26.85	11.40	0.00	1.03	1.61	4.46	0.00	1.35	0.18	13.98	0.00	0.00	0.00	0.00	0.00	0.00	120.76	
17	13.43	70.90	5.84	0.00	0.60	1.00	1.62	0.00	2.48	0.00	4.14	0.00	0.00	0.00	0.00	0.00	0.00	92.46	
<3274> lining?																			
a2	27.12	59.82	4.11	0.00	0.46	1.92	0.74	0.00	4.81	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	76.71	
a7	14.09	77.41	3.12	0.00	0.39	1.28	0.87	0.00	1.48	0.00	1.35	0.00	0.00	0.00	0.00	0.00	0.00	63.60	
a5	23.72	63.99	3.19	0.00	0.48	1.92	0.73	1.62	4.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	72.10	
a4	26.92	56.23	6.93	0.00	0.51	2.74	1.18	1.85	2.61	0.00	1.04	0.00	0.00	0.00	0.00	0.00	0.00	53.91	
a6	31.46	46.06	7.44	0.00	0.70	1.80	3.04	0.00	2.38	0.42	6.71	0.00	0.00	0.00	0.00	0.00	0.00	30.93	
a8	14.95	43.30	7.81	0.00	0.58	6.66	13.87	2.27	1.47	0.00	9.09	0.00	0.00	0.00	0.00	0.00	0.00	58.55	
a1	22.30	62.80	5.40	0.00	0.61	3.02	0.85	0.00	4.85	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	80.90	
a3	30.80	7.02	17.93	0.00	1.66	1.00	8.80	0.00	0.29	0.23	32.08	0.00	0.00	0.00	0.19	0.00	0.00	52.77	

Table 4. EDS microanalyses (semi-quantitative only) from mounted specimens. Figures quoted are wt% oxide, except for S and Cl, which are wt% of the element.

Figure Captions

Figure 1.

Upper crust normalised REE profiles for two slags from Brockworth, and a comparative clay sample from Frocester. The three samples are closely comparable, with the Frocester sample having just slightly lower concentrations of the heavy REE.

Plate 1.

All images are backscattered electron photomicrographs.

GBP1

a. Low magnification view, scale bar = 1mm

GBP2

b. Low magnification view, scale bar = 1mm

c. Detail from centre top of (b) showing residual quartz grains in dominantly glassy groundmass. Scale bar = 200 μ m.

d. Detail from mid right of (c) showing hexagonal apatite crystals in glass, adjacent to vesicle. Scale bar = 20 μ m.

e. More crystalline area of the specimen showing elongate crystals of salite and patches of tiny apatite crystals in glassy groundmass. Scale bar = 50 μ m.

f. Area immediately to right of (e) showing salite needles in vesicle walls. Scale bar = 50 μ m.

g. Detail from vesicle in lower right of (e) and lower left of (f) showing hollow salite needles in vesicle wall. Scale bar = 20 μ m.