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Analysis of materials from Porth y Rhaw

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Abstract

This report details the analytical investigation of three items from the excavations conducted at Porth y Rhaw by Dyfed Archaeology in 2019-2022: two sherds of crucible and a sample of fuel ash slag.

On of the two crucible sherds, <8>, was probably used to handle leaded gunmetal, a widely used alloy castings in the Roman period. The other sherd, <24>, was probably employed for the handling of leaded bronze, another alloy commonly employed in the Roman period.

The fuel ash slag shows a composition with a lower overall total of the alkali and alkaline earth elements and lower phosphorus than other analysed examples of fuel ash slags. Its composition resembles the non-iron contribution to an iron working slag previously analysed from the site. These observations suggest that it may be a relatively simple hearth ash, albeit with a slightly elevated sodium content – potentially because of the cliff top location and the likelihood that the substrate is affected by sea spray. Thus, the analyses provides no additional direct information as to the use of hearth (2223).

Contents

Methods

Project rationale and history

The assessment of pyrotechnological residues from the 2019-2022 excavations at Porth y Rhaw was conducted in January 2024 (Young 2024). The assessment made the recommendation that two crucible sherds be investigated by pXRF to determine the metals handled and that elemental analyses be conducted of fuel ash slags associated with a hearth of unknown purpose located within the roundhouse. Analysis of the crucible sherds as undertaken in 2024, with the analysis of the fuel ash slag and the reporting following in 2025.

Previously, the archaeometallurgical residues from the 1995-98 excavations were analysed in 1999 (Young 1999a, b) and published in 2010 (Young 2010a).

Analytical methods

Bulk elemental analysis by XRF and ICP-MS

Bulk chemical analysis was undertaken using two techniques. The major and minor elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P and S) were determined on a fused bead using wavelength-dispersive X-Ray fluorescence (WD-XRF). Whole-specimen chemical analysis for thirty-six trace elements (Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, and U) were undertaken using a sample in solution by Inductively-coupled Plasma Mass Spectrometry (ICP-MS). Both XRF and ICP-MS analyses were commissioned from ChemoStrat Ltd (Welshpool, UK).

For XRF analysis, samples were ground using a tungsten carbide shatter mill, dried at 105C overnight and then 0.5g was mixed with 6.5g of 50:50 LiT/LiM flux and fused to produce a glass disk using a Claisse M4 Fluxy automatic fused disk maker. The samples were analysed using a Bruker S4 WDXRF using the default wavelengths for the elements identified. Calibration was via a selection of iron slag reference materials and geological reference materials.

Samples for trace elemental analysis by ICP-MS were drawn from a second aliquot of the powdered material using the alkali fusion method (Jarvis & Jarvis 1992a and 1992b; Pearce *et al.* 1999). Once prepared, the samples were then all subjected to analysis using a Thermo Scientific XSERIES 2 ICP-MS. Data quality was strictly monitored in terms of precision and accuracy by five international rock standards of known concentration and varying compositions which are run after every 20 unknown samples. In addition, external monitoring of data quality is carried out four times a year via the GeoPt round robin proficiency testing program (*http://www.geoanalyst.org/ overview.html*).

The results of the elemental analyses are presented in Tables 2, 3 and 4 of this report.

Qualitative analysis by pXRF

The specimens were analysed at selected places on a semi-quantitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 40s. The instrument was controlled by a PC running Bruker's S1PXRF with spectra stored as pdz files and csv files.

Results

Crucibles

The collection includes two sherds of crucible.

SF <8>. A 3.4g sherd from context (109) was thin, with a sharp angular rim. It was straight and vertical internally, but inturned externally. The fabric was pale and very fine fabric, bearing only rare sand grade quartz. The glaze was dark and bright red internally, locally intruding the wall, but clearer outside below the rim.

Analysis by pXRF (Figure 1, upper) shows the exterior of the sherd to be contaminated by (in decreasing order of peak height) copper, tin, zinc and lead. The interior shows contamination zinc, copper, tin and lead. Iron forms a prominent component of both analyses but shows an approximately constant relationship in peak height to strontium and zirconium, so is likely to be largely within the crucible fabric.

SF <24>. A 4.5g sherd from context (103) was from the wall extending to the rim. It was thick-walled, probably inturned, with red splashing (copper contamination) on the otherwise green glaze near the rim. The fabric was sandy with quartz grains to 4mm.

Analysis by pXRF (Figure 1 lower) shows the exterior of the sherd to be enriched in strontium, calcium and potassium with respect to the interior and also contaminated by copper. Zinc and lead are present in trace amounts. The interior of the sherd shows slightly lower amounts of copper, but increased levels of lead and tin. Zinc remains at trace levels on the interior.

The conversion of pXRF analyses of crucibles into an identification of the metal being handled carries considerable caveats. The four main metals present in the ally all behave differently: zinc tends to be volatilised and permeates the crucible wall (often leading to it appearing more abundant than it would have been in the ally), lead may form a slag with the crucible ceramic, and tin may be concentrated where it is oxidised, often in a dross. Enhanced levels of strontium (together with potassium and calcium, whose peaks are outside the range emphasised by the filter employed here) may be an indicator of a fuel ash slag/glaze.

In this instance, all four metals are well represented in analyses of SF<8> with, as is typical, copper particularly prominent external, but with zinc, lead and tin relatively enhanced internally. It is probable that this vessel was handling a quaternary alloy, probably a leaded gunmetal.

In SF<24> the amount of contamination by metals is much less, leading to a lower degree of certainty of identification. In these analyses zinc plays only a very minor role and it is likely that the alloy did not have a significant proportion of zinc. The alloy being handled is very tentatively suggested to be a leaded bronze.

Fuel ash slag

The elemental analysis of the fuel ash slag (sample taken from the assemblage from (2223)) is presented in Tables 2, 3 and 4.

The major element composition is broadly typical of a fuel ash slag, with SiO_2 + Al_2O_3 over 80% and with a high total for the alkali and alkaline earth elements (MgO + CaO + Na_2O + K_2O) at 9.24%. P_2O_5 is rather low at 0.67%.

The trace element composition is largely unremarkable. The rare earth elements (REE) show a close to horizontal profile (Figure 2).

If the composition of the sample is compared to the composition of the analysis of a smithing hearth cake fragment (SHC) from the previous excavations on the site, there is a reasonably constant factor of dilution (0.24 to 0.40) for most trace elements – consistent with the smithing hearth cake having incorporated hearth materials (i.e. hearth ceramic plus fuel ash) of a very similar composition to that recorded for the fuel ash slag sample. Amongst the major element oxides, Al_2O_3, MgO, K_2O, and TiO_2 show dilution factors in the same range. The dilution of CaO and P_2O_5 fall outside this range (at 0.69 and 0.43 respectively) suggesting they have been slightly relatively enriched in the fuel ash compared with the hearth contribution to the iron working slag. Na_2O was below detection limits in the slag, so cannot be compared in the same way.

Interpretation

Crucibles

The thin-walled vessel <8> was probably used to handle leaded gunmetal. This alloy was widely used for copper alloy castings in the Roman period, with the quaternary alloy reflecting a high degree of recycling. Gunmetal persists into later periods too, but not quite a pervasively as in the Roman period.

The thick-walled vessel <24> was probably used to handle either bronze, or possibly more likely leaded bronze. Leaded bronze is commonly encountered in the Roman and early medieval periods.

The previous studies of crucible sherds from Porth y Rhaw investigated crucible sherds from three contexts, but only one of the crucibles, interpreted as being of Roman age, was investigated in detail and that proved to have been used for handling bronze.

Fuel ash slag

The interpretation of the use of the hearths within the excavated roundhouse is problematic. Analysis of fuel ash slag from (2223) offers little positive evidence. The fuel ash slag shows elevated levels of all the analysed alkali and alkaline earth elements, but a relatively low level of phosphate.

Comparison with other analysed examples of fuel ash slags (of which there are relatively few), suggests that an elevated phosphorus content is typical of many fuel ash slags (Figure 3). Samples from Bornais, S. Uist (Young 2002, 2005), Ysgol Bro Dinefwr, Llandeilo (Young 2015) and South Hook, Pembs. (Young 2010b, c), all from slags derived from cereal-drying kilns, and those from Brockworth, Glos. (Young & Bowstead-Stallybrass 2003) of uncertain context, all show an elevated phosphorus content (all with P_2O_5 greater than 1.9%). Also included in Figure 3 are analyses of ceramic materials (hearth lining, furnace lining and heat altered substrate) that approach fuel ash slags, from amongst Roman metalworking waste in Priory Field, Caerleon (Young 2017). The Porth y Rhaw sample plots closer to this second group in Figure 3, than it does to the true fuel ash slags. It is therefore likely to include a high contribution from the substrate and a low contribution from organic matter.

For ash residues to be fusible into a slag, typically requires a considerable input of the alkali (mostly sodium and potassium) and alkaline earth (mainly calcium) elements. These may be derived from the fuel ash (for instance wood ash is rich in both potassium and calcium) and the substrate (Bornais lies on calcareous sand and Brockworth on a limestone gravel).

The contribution of the various oxides to the over composition of these materials is illustrated in Figure 4. The high contribution of CaO (probably including a significant substrate contribution) to sample from Brockworth and Bornais is evident. The contribution of MgO is particularly high in those samples certainly originating from cereal drying kilns. The proportionately high contribution from Na_2O at Porth y Rhaw, despite the overall low total, is noticeable. A higher proportion of Na_2O might reflect the influence of saltwater spray on the substrate, rather than any specific marine input, although that cannot be excluded.

In summary, the composition of the fuel ash slag from Port y Rhaw sheds little light on its origin. It does not show the uptake of phosphorus and magnesium that appears typical of the cereal drying kilns, it shows a strong, but not excessive, input of sodium, potentially explained by its cliff-top location. It is unlikely that the seawater provided a direct source of alkalis, as it might during brine evaporation for instance.

Figure captions

Figure 1. pXRF spectra for analyses on the inside and outside of sherds of crucibles SF <8> and SF <24>.

Figure 2. Upper crust-normalised rare earth element (REE) profiles (normalisation after Taylor & McLennan 1981).
Sample POR: fuel ash slag from hearth deposit (2223).

Sample PYR1225: sample from a ironworking slag from (Young 1999a,b)

Figure 3. Plot of P_2O_5 (wt%) against the sum of the alkali and alkaline earth elements (wt%) for analyses of the fuel ash slag from Porth y Rhaw (2223) in comparison with examples from:
Priory Field, Caerleon (Young 2017)
Bornais, S. Uist (Young 2002, 2005)
Ysgol Bro Dinefwr, Llandeilo (Young 2015
South Hook, Pembs. (Young 2010b, c)
Brockworth, Glos. (Young & Bowstead-Stallybrass 2003)

Figure 4. Contribution of MgO, CaO, Na_2O and K_2O to the composition of analyses of examples of fuel ash slags. The localities are as Figure 3.

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Table 1: major element analyses by XRF expressed as wt% for macroscopic materials. Raw measured values, except for calculated columns for FeO (as an alternative to Fe_2O_3). < = below detection.

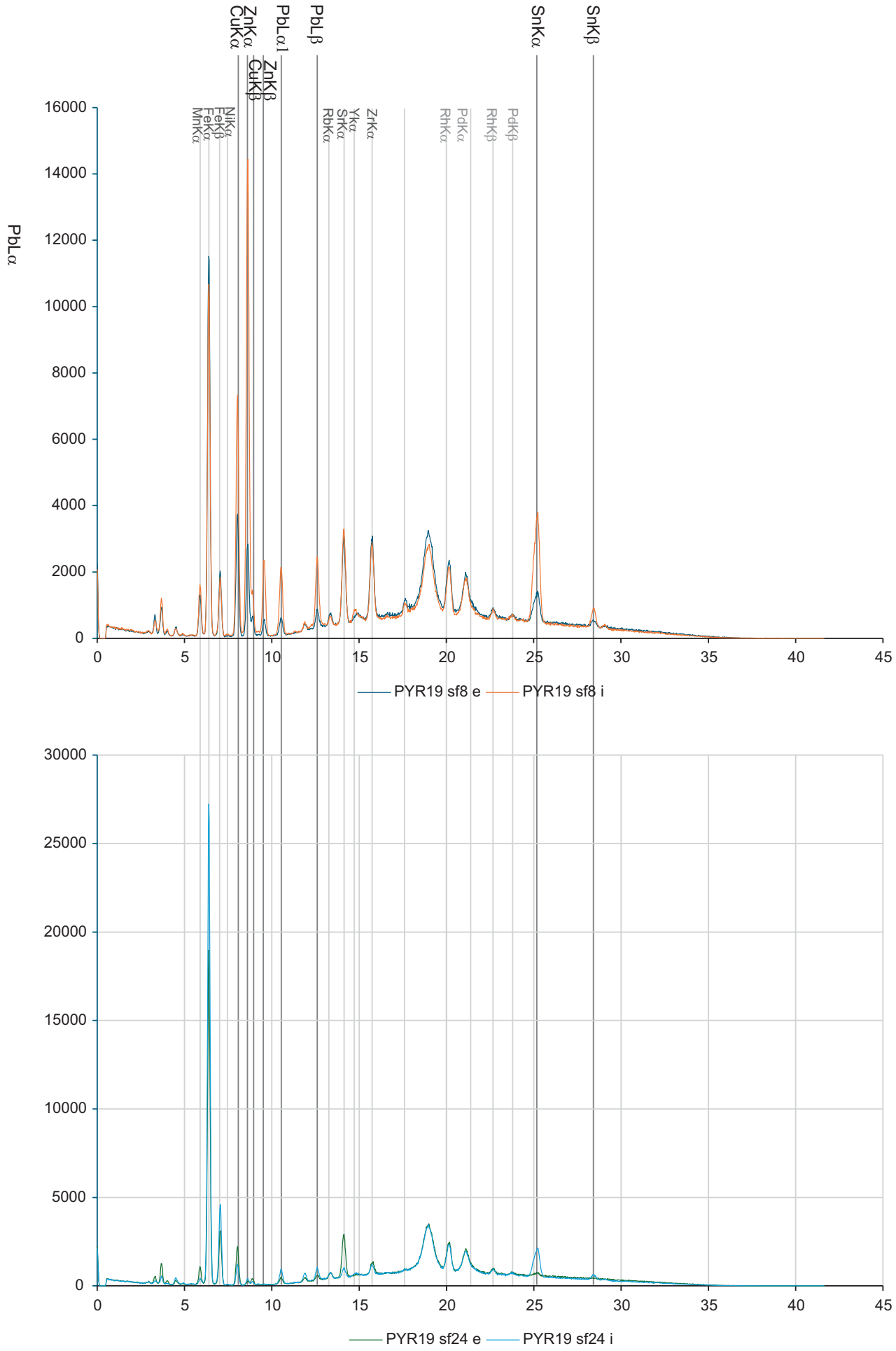
Sample	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**FeO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**SO_3**	**LOI**	**total**
POR1	68.62	13.80	5.32	4.79	0.44	1.80	1.14	2.76	3.54	0.95	0.67	<0.15	1.60	99.75

Table 3: trace element analyses by ICP-MS for macroscopic materials (part 1). Raw numerical values in ppm. < = below detection.

Sample	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba
POR1	1.79	95.8	76.1	15.8	22.6	269.2	83.2	14.47	86.96	176.0	23.46	187.3	12.30	1.65	1.48	2.10	506.0

Table 4: trace element analyses by ICP-MS for macroscopic materials (part 2). Raw numerical values in ppm. < = below detection.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
POR1	30.18	61.07	6.94	24.92	4.79	1.00	4.19	0.66	4.16	0.84	2.52	0.36	2.41	0.37	5.20	0.93	1.80	5.77	8.00	2.22


PbLα
PbLα1
PbLβ
SnKα
SnKβ
CuKα
ZnKα
CuKβ
ZnKβ
MnKα
FeKβ
FeKα
NiKα
RbKα
SrKα
YKα
ZrKα
RhKα
PdKα
RhKβ
PdKβ
PYR19 sf8 e
PYR19 sf8 i
PYR19 sf24 e
PYR19 sf24 i

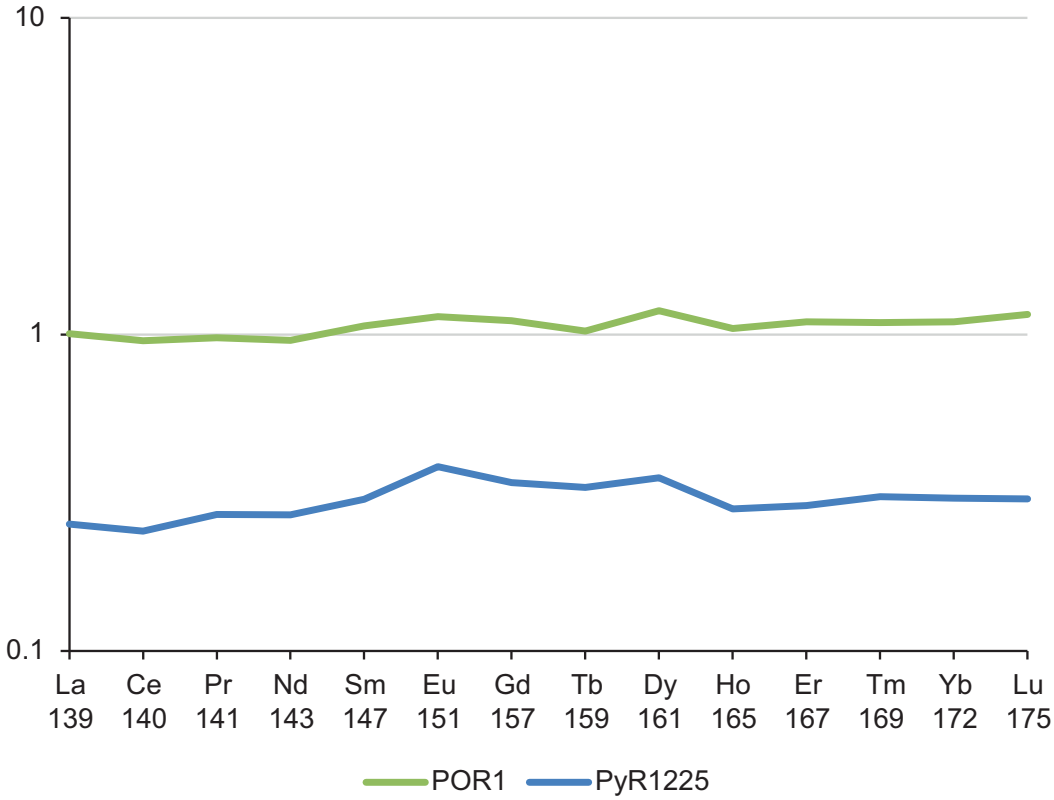

10
1
0.1
La 139
Ce 140
Pr 141
Nd 143
Sm 147
Eu 151
Gd 157
Tb 159
Dy 161
Ho 165
Er 167
Tm 169
Yb 172
Lu 175
POR1
PyR1225

Figure 3

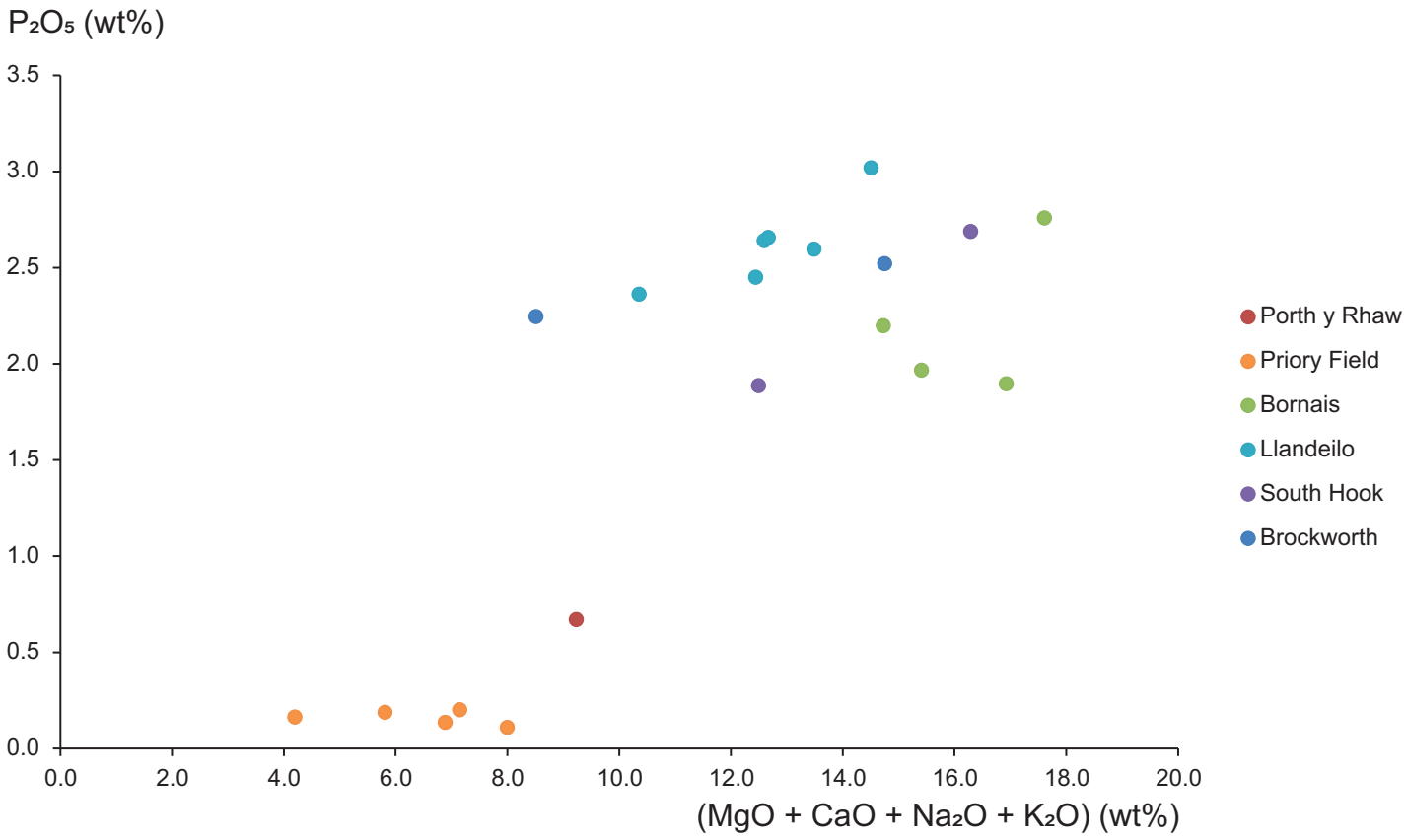
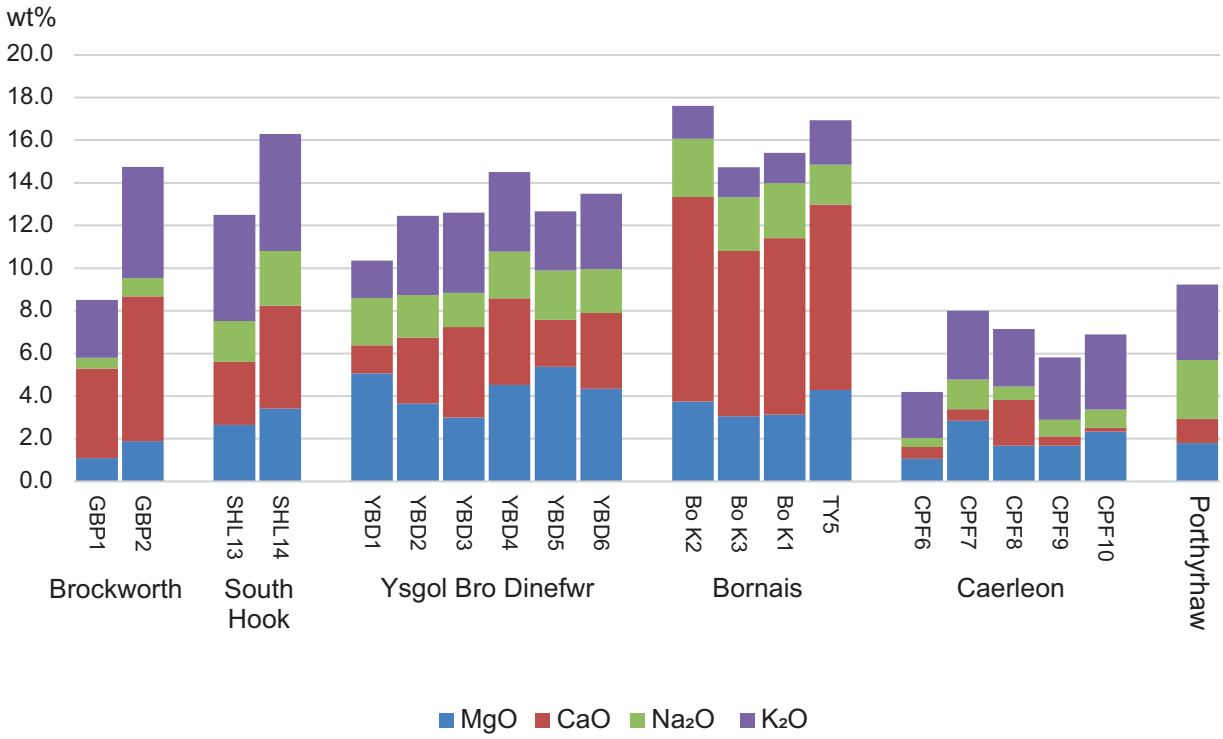

P2O5 (wt%)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
(MgO + CaO + Na2O + K2O) (wt%)
Porth y Rhaw
Priory Field
Bornais
Llandeilo
South Hook
Brockworth

Figure 4


wt%
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
GBP1
GBP2
SHL13
SHL14
YBD1
YBD2
YBD3
YBD4
YBD5
YBD6
Bo K2
Bo K3
Bo K1
TY5
CPF6
CPF7
CPF8
CPF9
CPF10
Porthyrhaw
Brockworth
South Hook
Ysgol Bro Dinefwr
Bornais
Caerleon
MgO
CaO
Na₂O
K₂O

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