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Analysis of archaeometallurgical residues from Cleobury Park Furnace, Shropshire

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Abstract

This report presents analyses of three samples of blast furnace slag recovered from the surface of the Cleobury Park furnace site during surveying.

The analyses show the slags to be closely comparable with other analysed 16th century blast furnace slags from Britain.

Full quantitative interpretation of the analyses is not possible, because of a lack of corresponding analyses of the ore and possible limestone flux. Some interpretation may be made on the basis of what are probably similar ores from other sites.

Approximate modelling on this basis suggests that 1kg of slag was the residue from the smelting of 3.1kg of raw (unroasted) ore (or approximately 2.6kg of roasted ore) with 0.3kg of limestone to produce 1.4kg of metallic iron. Such a model is, however, extremely tentative and has large potential errors. Some support for such a model may be sought in the Sidney accounts of their Glamorgan ironworks of the 1560s in which 2.5 loads of marl were added to 24 loads of ore during the casting of sows.

Contents

Methods

Three surface finds of glassy blast furnace slag made during the field survey of the site (Young 2011a) were taken forward for detailed analysis.

Chemical analysis was undertaken using two techniques. The major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P) were determined by X-Ray Fluorescence using fused beads on the Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) system in the department of Geology, Leicester University (this also generated analyses for S, V, Cr, Sr, Zr, Ba, Ni Cu, Zn, Pb and Hf). Whole-specimen chemical analysis for minor and trace elements was undertaken using samples in solution on the ThermoElemental X-series Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth and Ocean Sciences, Cardiff University.

Results

The results are presented in Tables 1-4.

The three samples were very similar in overall composition. The iron contents are low, and are likely to reflect, at least in part, entrained blebs of metallic iron in addition to the iron actually contained in the glass.

The lime content of the slags is comparable with that quoted by Tylecote (1986, Table 106) for a variety of 16th century blast furnace slags from the smelting of ores of quite diverse geological origin and composition.

The likely ore source for the Cleobury furnaces (within Cleobury Park itself, Young 2011a) lies at the same (or very close) geological horizon as that for the source of the ore for the medieval bloomery sites of Cindermill and Ned's Garden (a horizon within the Carboniferous Coal Measures). The rare earth elements (REE) do indeed show upper crust-normalised profiles (Figure 1) similar to those of the better ores analysed from those medieval bloomeries (Young 2011b).

The blast furnace slags show REE contents approximately 2.6 times those of the ores, which corresponds to the enrichment predicted by the extraction of the iron.

Interpretation

The key question in the interpretation of late 16th century blast furnace slags is whether they can show evidence for the use of a flux. The addition of limestone as flux is well attested from the mid-17th century onwards (Tylecote1986), but is not well-known for the 16th century. Documentary evidence from the Sidney ironworks in Glamorgan (Crossley 1975, 246-247) shows an addition of 2.5 loads of marl to 24 loads of ore during the smelting of a rich oxide ore for sows and a slightly higher use of lime (4 loads of marl and 1 load of limestone to 20 loads of ore) during the casting of plates for steelmaking. The ores employed in this operation were entirely different to those of Cleobury Park, but these accounts at least establish the fluxing with limestone was practised in the mid-16th century.

In the Cleobury Park instance, the evidence is slightly ambiguous. The strong relationship between the REE profiles of the blast furnace slags and those of ore samples from medieval sites a few kilometres to the north, supports a derivation from similar ores and would suggest that there has been little modification of the REE profile by any flux. The local iron ores are known to be rather variable in their lime content (Young 2011b). On this basis it might be argued that the ore was simply a calcareous variant of the local Carboniferous ores.

On the other hand, if the REE content of the limestone was low, and the proportion of flux employed was small (both likely propositions), then the slag REE profile might indeed be very close to that of the ore.

An approximate modelling of the mass balance has been created. This employed a weighted mixture of the two high grade ores from the medieval sites (Young 2011b, samples NG11 and FID8) to attain the same silica to alumina ratio as that of the blast furnace slags. This mixture would require an enrichment of the alumina and silica by a factor of 2.6 to reach the concentration seen in the slag. There is then a shortfall in the concentrations of magnesium and calcium which must be addressed by the incorporation of a 'limestone' into the calculation. This addition is most likely to be a deliberate flux, but the use of a more calcareous ore than the model one is also possible.

Recasting this model suggests that 1kg of slag was the residue from the smelting of 3.1kg of raw (unroasted) ore (or approximately 2.6kg of roasted ore) with 0.3kg of limestone to produce 1.4kg of metallic iron.

This model is extremely tentative and relies on many approximations and assumptions, but provides at least a starting point for the understanding of the process that might, in the future, be refined by analysis of the actual raw materials. Bearing in mind the Sidney accounts discussed above, the addition of 10% flux is not an unreasonable proposition.

References

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TYLECOTE, R.F. 1986. *The prehistory of metallurgy in the British Isles*. The Institute of Metals. 257pp.

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Figure Caption

Figure 1: upper crust-normalised (factors after Taylor and MacLennan 1981) rare earth element profiles for samples CPF1-3 and for ore samples from nearby medieval sites (NG11 from Ned's Garden and FID8 from Cindermill, Young 2011b).

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	LOI	total	SiO_2
CPF1	56.05	15.52	3.02	2.72	0.90	2.38	18.76	0.08	2.10	0.94	<0.002	-0.28	0.09	100.08	0.97
CPF2	57.41	11.80	7.08	6.37	0.65	1.69	17.39	0.04	1.89	0.84	0.05	0.75	1.50	99.13	0.70
CPF3	52.23	14.31	7.49	6.75	1.07	2.31	19.34	0.08	1.79	0.96	0.06	-0.61	0.22	99.96	1.15

Table 1: Major elements as wt% oxide. Determined by XRF. LOI = loss on ignition (negative = weight gain). Iron is presented as Fe_2O_3, with an alternative recasting of the iron as FeO presented in the coloured columns.

	SO_3	V_2O_5	Cr_2O_3	SrO	ZrO_2	BaO	NiO	CuO	ZnO	PbO	HfO_2
CPF1	0.087	0.012	<0.004	0.034	0.032	0.093	<0.002	<0.002	<0.001	0.004	<0.004
CPF2	0.127	0.022	<0.004	0.022	0.033	0.055	<0.002	<0.002	<0.001	0.005	<0.004
CPF3	0.061	0.022	0.006	0.029	0.033	0.061	0.007	0.002	<0.001	0.002	<0.004

Table 2: Minor elements as wt% oxide. Determined by XRF.

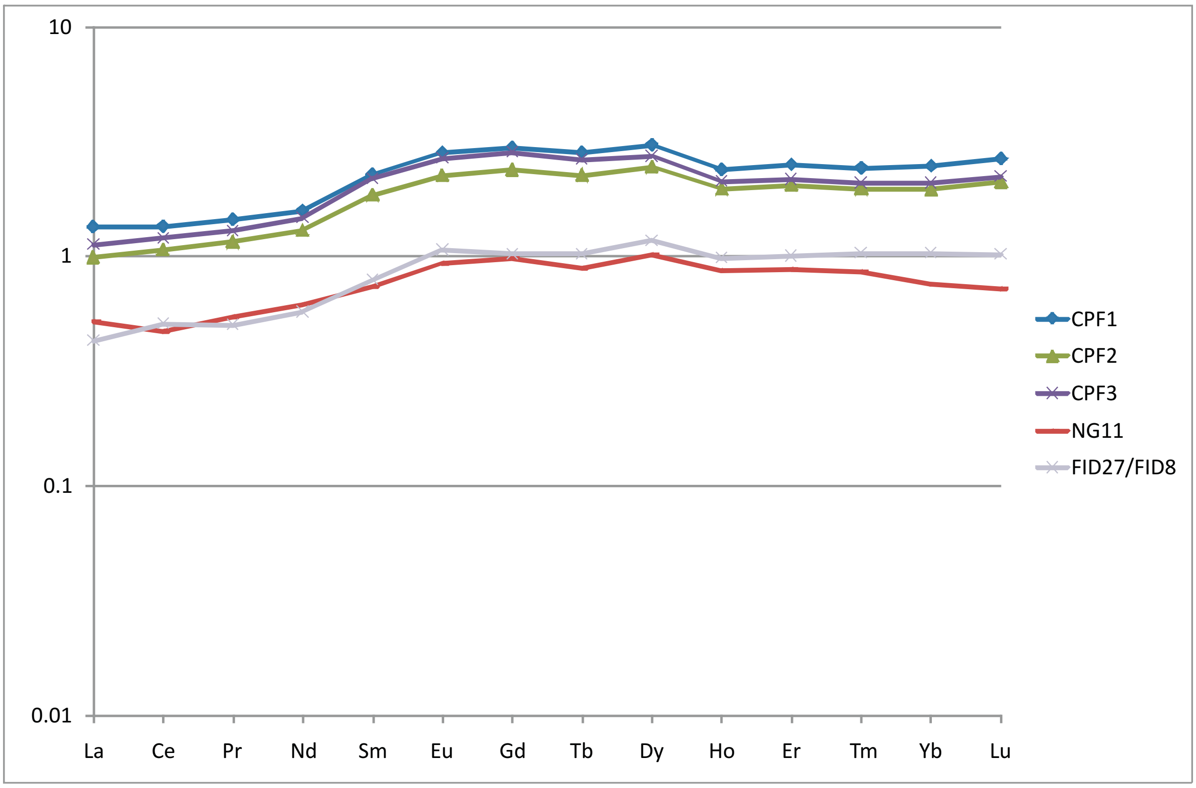
	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba
CPF1	38.3	56.1	26.1	0.9	25.0	8.7	21.3	2.0	64.6	252.2	64.3	279.7	6.75	0.76	0.90	5.50	704.3
CPF2	29.1	76.9	40.4	5.9	12.3	7.5	21.6	2.8	55.0	202.0	49.1	269.2	8.28	0.85	0.83	5.27	425.0
CPF3	32.1	85.4	62.1	0.9	18.9	91.1	29.5	3.0	55.9	197.8	54.3	232.5	7.96	1.02	1.54	5.19	451.0

Table 3: Trace elements in elemental ppm. Determined by ICP-MS.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
CPF1	40.09	86.25	10.21	41.11	10.19	2.48	11.31	1.81	10.70	1.90	5.77	0.80	5.43	0.85	6.62	0.63	1.96	8.65	4.28
CPF2	29.77	68.41	8.22	33.75	8.33	1.98	9.02	1.44	8.58	1.57	4.69	0.65	4.31	0.67	6.79	0.67	2.30	7.40	3.90
CPF3	33.72	76.71	9.18	38.20	9.80	2.35	10.78	1.69	9.57	1.70	4.98	0.69	4.59	0.71	5.83	0.70	2.19	7.64	4.37

Table 4: Trace elements in elemental ppm (contd). Determined by ICP-MS.

Figure 1



10
1
0.1
0.01
La
Ce
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Dy
Ho
Er
Tm
Yb
Lu
CPF1
CPF2
CPF3
NG11
FID27/FID8

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