Geochemical Investigation of slag samples from Caerleon

Abstract

Geochemical analyses of two samples of tap slags from Caerleon have been undertaken. The two samples are geochemically rather similar, although the incompatible elements are enriched in Cl 1. The composition of both samples is close to that of slags from other sites believed to working Forest of Dean ores (Ariconium, Usk, St Briavels and Frocester Court). Both samples have a relatively low iron content. The rare earth element (REE) profiles from the specimens are parallel, with Cl 1 being enriched in REE relative to Cl 2. The two samples show characteristic moderately high uranium contents and uranium/thorium ratios; a feature apparently associated with ore sources on the western side of the Forest of Dean rather than the eastern, and which has also been observed in slags from Usk (2 of 6 analysed tap slags) and St Briavels (2 of 2 analysed tap slags).

i. Techniques

All specimens were examined macroscopically and 2 tap slag specimens (Cl 1 and Cl 2) were the subject of further detailed study. The detailed investigation of the samples included geochemical analysis using X-ray Fluorescence (XRF) of fused beads (major elements) and powder pellets (minor and trace elements) and geochemical analysis using Induction Coupled Plasma - Mass Spectrometry (ICP-MS) of solutions (minor and trace elements).

X-Ray Fluorescence Analysis (XRF): The XRF is a Philips PW 1400 sequential spectrometer incorporating a rhodium side window x-ray tube, a 6 position pre-aligned crystal changer, a scintillation detector, a gas flow detector and a 72 position automatic sample changer. The system is controlled by a Digital PDP 11/34 computer running X-14 software. The principal application is the whole analysis of rocks, whereby the major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe) are determined using a fused bead in order to overcome grain size effects and 34 minor/trace elements are determined using compressed powder briquettes. Loss on ignition is determined prior to preparing the fused beads and is incorporated in the results. The machine is calibrated against > 30 international rock standards.

Inductively Coupled Plasma - Mass Spectrometer (ICP-MS): The instrument is a Perkin-Elmer Elan 5000A ICP-MS. the sample is introduced into an inductively coupled argon plasma where it is ionised. Sample ions are drawn through an orifice, focused by a series of electrostatic lenses, filtered by a quadropole mass analyser and finally detected by an electron multiplier. For undiluted freshwater solutions detection limits are <10 ppb for REE, Y, Th, U, Cs, Be, Bi, 10-50 ppb for Ag, Cd, Ga, Rb, Sn, Sb, Ta, Nb, Tl, 50-100 ppb for Ba, Pb, Sc, Sr, Co, Ge, W, Mo and 100-200 ppb for V. Cr and Cu. Other elements are being added to list, and the machine can now be used, in addition, for Ca, Ti, Mn, Fe and Al. Typically 100-200 mg solid samples are dissolved using a variety of acids to a dilution of 2000, but higher dilutions (up to 10,000) are required for iron rich materials because of clogging of the orifices, giving typical detection limits for the REE of 20 ppb in these materials.

ii. Description

Material analysed

Cl 1 (CL82 E21; 393 g): This specimen appears to be a tapped bloomery slag, although the upper surface is only preserved over a relatively small area and the flow structures are imperfect. The lower part of the slag comprises a coarsely crystalline silicate slag; the upper part is a finer grained material which is rather weathered. The lower part was sampled for the geochemical analysis. Analysis showed a lower iron content than is typical for slags of this type, in fact both samples show iron contents close to the value for an melt of olivine composition; this is reflected in the silicate-rich wüstite-poor mineralogy seen in hand specimen.

Cl 2 (CL82 D u/s; 33.7 g): The specimen is a small fragment of bloomery tap slag. The chemical composition of this specimen was broadly typical of tap slags derived from Forest of Dean ores and plots

Other material

CL82 D5: small quantity of badly fragmented smithing slag with abundant charcoal impressions.

CL82 D4: 2 large pieces of smithing hearth bases. One has iron oxide-rich accumulation in lower part, which appears to contain abundant hammer scale (this will be examined petrographically in the future). 3 small pieces of smithing slag.

u/s: 1 small piece of dark glassy slag with coke fragments - probably an industrial forge slag. 1 small fragment of bloomery tap slag. 1 piece of very corroded iron pan material. 1 piece of smithing slag with abundant charcoal impressions. 1 piece of slag adhering to partly vitrified furnace wall material; furnace wall with sandstone fragments in clay matrix.

CL82 D u/s: 1 piece of corroded iron-pan material, not slag.

iii. Discussion

The high values of SiO_2/Al_2O_3 and U/Th for the Caerleon material (Figure 1) are both good indicators that the ores being utilised were not derived from the Carboniferous Coal Measures (claystone ironstones) despite the close geographical proximity of suitable resources. Instead, the source of the ores is likely to have been in the Bristol Channel iron orefield, probably either the Forest of Dean or the Vale of Glamorgan.

A key property of the chemical composition of the slag specimens from Caerleon is their high U content (18.30 ppm in Cl 1 and 16.51 ppm in Cl 2). These concentrations would be expected to correspond (authors' unpublished modelling of slags from Usk) to about 8-10 ppm in the original ore. This differs (Figure 2) from the slightly lower levels recorded in lump ores from the eastern outcrop of the Forest of Dean (Shakemantle, Edgehills, Drybrook; m = 4.20 ppm, s = 1.58, n = 12, range 2.35 - 7.91 ppm) and the western outcrop (Clearwell, Scowles Quarry, Blakes Wood; m = 4.85 ppm, s = 2.93, n = 12, range 2.16 - 7.52 ppm), but is more compatible with the range of uranium in ochres from the western side of the Forest of Dean (7.29 - 25.89 ppm). The fault-hosted ores of the western margin of the Worcester Graben (e.g. Iron Acton and Newent) have a much lower uranium content (m = 0.85 ppm, s = 0.47, n = 4), whereas the Glamorgan ores are very variable, but most outcrops have yielded some very high uranium material (Figure 3). This provides some tentative suggestion of derivation from the western side of the Forest of Dean. A western Dean origin for ores used to generate the high U slags is supported by the occurrence of high U slags at St Briavels (2 of 2 tap slags) and Usk (2 of 6 tap slags), but their absence from collections from Ariconium (9 analysed tap slags) and Frocester Court (10 analysed tap slags). An origin from the Glamorgan ores is also possible, but the U content of smelting slags from working of these ores has not yet been determined.

In the absence of analyses of furnace linings from Caerleon, more detailed modelling of the mass-balance for the smelting furnace is not possible. This means it is not yet possible to utilise the rare earth elements (REE) to provide provenance evidence. However, the parallel nature of the REE profiles (Figure 3) indicates a similarity of materials (both furnace lining and ore) despite the preferential concentration of REE in the silicate-rich slag Cl 1. In detail, Cl 1 is relatively enriched in the heavy REE relative to Cl 2 (Table 3c), suggesting that the increased silicate content of this slag is at least in part due to an increased relative importance of fine-grained sediment - but does not allow distinction between the incorporation of such material from the ore or from the furnace lining.

iv. Future work

It is our intention to pursue identification and microanalysis of individual phases within the slag, when machine-time permits. The significance of silicate-rich slags needs to be explored to determine whether they represent deliberate manipulation of the furnace chemistry, or whether they are generated by physical separation during the tapping process.

Reference

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.

Figure Captions

Figure 1 (a). Plot of total REE (Σ REE) in ppm against U/Th. **(b)**. Plot of SiO2/Al2O3 against U/Th. Low SiO2/Al2O3 and U/Th are typical of fine-grained sediments (such as is typically used for furnace linings) and therefore of claystone ironstones (Weald data shown for illustration, but the as yet unanalysed local coal measures ironstones are expected to be similar).

Figure 2. Map showing the mean (filled circle) and maximum (open circle) uranium content of samples from ores of the Bristol Channel orefield. Grey: Carboniferous limestone outcrop; black: faults of Worcester Graben.

Figure 3. Upper crust-normalised (Taylor & McLennan 1981) REE profiles.

Data tables

oxide	SiO_2	Al_2O_3	Fe as Fe_2O_3	Fe as FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	$P2O_5$	*total (with Fe as FeO)*
Cl 1	33.73	4.48	58.19	52.36	0.40	1.92	3.83	0.17	1.80	0.25	0.19	99.13
Cl 2	25.89	4.11	69.34	62.40	0.17	1.02	3.10	0.48	1.58	0.24	0.28	99.26

Table 1: Major elements (expressed as wt% oxides) determined by XRF

element	Sn	Zn	Ni	S	Cl	As	Te	Sb	Ag	Cd	Se	Bi
det. limit	11	3	2	13	17	5	5	2	2	3	2	5
Cl 1	14	8	16	324	161	9	12	<	<	7	<	<
Cl 2	<	9	16	168	103	5	10	2	<	4	<	<

Table 2: Minor and trace elements (expressed as ppm) determined by XRF

element	V	Rb	Sr	Y	Zr	Nb	Mo	U	Th	Ga	Sc	Cd	Be
Cl 1	74.48	13.72	723.1	11.32	88.47	4.931	4.389	1.621	1.694	9.619	7.849	<	<
Cl 2	92.74	14.06	577.1	13.56	74.53	5.093	4.389	1.683	1.917	10.06	8.373	0.365	<

Table 3a: Trace elements (expressed as ppm) determined by ICP-MS

element	Ca	Ti	Cr	Mn	Cu	Cs	Ba	Tl	Pb	Ge	Fe	Mg	P
Cl 1	87,600	2415.56	48.97	828.01	89.579	0.2206	255.54	<	2.4887	0.300	112000	18100	8246
Cl 2	61,800	2531.93	48.30	1236.24	42.869	0.2215	226.07	<	3.7143	0.323	126000	15000	6598

Table 3b: Major and trace elements (expressed as ppm) determined by ICP-MS

element	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	S REE
Cl 1	24.57	54.464	7.0194	27.404	5.9865	1.398	6.3563	1.0051	5.6703	1.08	2.9619	0.4507	2.9622	0.4099	141.737
Cl 2	14.096	30.31	3.9528	15.971	3.7703	0.8976	3.7145	0.5876	3.267	0.5776	1.5396	0.2375	1.4625	0.1931	80.5767
Cl 1/Cl 2**	*1.38*	*1.42*	*1.40*	*1.35*	*1.25*	*1.23*	*1.35*	*1.35*	*1.37*	*1.49*	*1.52*	*1.50*	*1.608*	*1.68*	

Table 3c: Rare earth elements (expressed as ppm) determined by ICP-MS. Cl 1*/Cl 2* is ratio of two samples on iron-free basis.