Geochemical Investigation of slag samples from Bornish, South Uist

Abstract

Geochemical analyses of two samples of slag and one of unburned sand from Bornish were undertaken, together with macroscopic inspection of the slag samples. The slags comprise a dominantly dark glass, within which are abundant grains relict grains, apparently of quartz. The grain size of the quartz crystals in the slags ranges up to 5 mm, but 100 μm is more typical. There are larger inclusions of up to several centimetres of incompletely fused quartz-rich material within several of the slag specimens. The slags have an enhanced, but still relatively low iron content. The siderophilic element manganese is also enriched in the slags, as are elements commonly enriched in peat such as phosphorus, molybdenum, vanadium and uranium, but there is no enrichment of lead, copper or zinc. The so-called immobile elements (the rare earth elements, yttrium, niobium, titanium and zirconium) are all enriched in the slags, suggesting the inclusion of resistate material. All other elements are within the range of their known occurrence within peat ash. The persistence of quartz in the slags, suggests a low temperature and/or non-equilibrium condition during melt generation. Interpretation of the material is difficult, but modelling of the composition, assuming an admixture of material to the local sand, indicates that the added material was iron-rich. The high iron content seems to be superimposed on material which might represent local sand plus peat ash. This suggests that the slags may be from iron-working. The irregular, low density, low iron slags are not suggestive of primary smelting, but might be compatible with smithing residues.

i. Techniques

All specimens were examined macroscopically and 2 representative slag specimens (Bo A and Bo B) were the subject of further detailed study, together with a single sample of local sand (Bo C). 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

Sand (Bo C): The geochemistry of the sand sample corresponds in composition to a mixture 10-15% calcium carbonate sand (of biological origin) with 85-90% of siliciclastic sand, with a composition only slightly more silicic than the local Lewisian Gneiss (Fettes *et al* .1992) as would be expected from a sorted sand deposit.

Slags (including Bo A and Bo B): The slags mainly comprise a dark green glass within which float sand grains. The slag is highly vesicular, giving a very low bulk density. There are small areas of crystallization of the slag in some specimens, but sections have not yet been prepared for mineral identification. In many specimens there are pale zones around the floating grains, which are probably reaction rims. In several specimens there are regions of pale, grain-rich slags, which are interpreted as wholesale reaction (partial melting) of larger inclusions of pre-existing material. Several specimens show iron-rich areas showing the impression of plant fragments, suggestive of fuel. The slag fragments are generally amorphous in shape, with little indication of “way-up”.

Geochemically the slags show enrichment of many elements besides iron, compared with the sand sample Bo C. Some of this enrichment may be due to the use of more clay-rich material in the hearth, rather than the simple sand, but most is probably due to material introduced in the ash fraction of peat. In particular U, V, Mo and P show major enrichment in the slags (table 4), and these are elements associated with the organic material in peat. The “immobile” elements (the rare earth elements, Y, Nb, Ti and Zr) are also enriched in the slags (e.g. Figure 1), suggesting the involvement of resistate material - perhaps a weathered bedrock component present in peat.

iii. Discussion

Modelling of the slag composition suggests that a sand contribution of 30-60% is numerically possible; in the other 70-40% all elements, apart from iron, are within the range of peat ash compositions recorded by Goodarzi *et al.* (1993) and Shotyk *et al.* (1990). The modelling suggests that the material added to the sand (peat ash?) was relatively light REE enriched compared with the sand. The slag material is, however, sufficiently enriched in iron to make derivation from a simple peat/sand mixture unlikely. The slags are interpreted therefore as associated with iron-working. The high vesicularity, low density, amorphous shape and poor crystallinity are all suggestive of smithing slags, despite their many dissimilarities to conventional smithing slags. The differences are interpreted as reflecting the fuelling of the hearth by peat rather than charcoal (this is suggested by the enrichment of the slags in U, V and Mo) and the sandy, rather than clay-rich hearth lining (suggested by the coarse-grained nature of the larger part-melted inclusions). Modelling of the mass-balance of the process might give some identification of the nature of the iron being worked, but would require additional data from mineralogical studies and from analysis of hearth linings and peat (see below).

iv. Future work

It is our intention to pursue identification and microanalysis of individual phases within the slag, when machine-time permits. In particular the slags will be investigated for the presence of hammer-scale fragments. Modelling of the reactions would be enhanced by the analysis of samples of the local peat. Contacts with archaeometallurgists working in Scotland are being made to try to locate comparative material. Given the volume of metalworking debris, a careful search of collected material should be made to ascertain whether the smithing slags are accompanied by any smelting slags. Careful search of the sediment on the site should be made to look for evidence of slag spherules (< 2mm) which would be suggestive of bloom-smithing, and hammer-scale which would indicate smithing of bar iron or blacksmithing.

References

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Figure Caption

Figure 1. Upper crust normalised (Taylor & McLennan 1981) REE profiles for the Bornish samples. The slags are enriched in REE, and preferentially so in the LREE compared with the sand. LREE depletion and the marked Eu anomaly are tentatively associated with marine influence on the sand composition (e.g. biogenic carbonates).

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)*
Bo A	54.87	9.01	18.66	16.79	0.11	4.23	12.82	2.00	0.99	0.35	1.94	*103.10*
Bo B	53.29	7.63	18.98	17.08	0.14	2.59	7.66	1.56	0.74	0.34	1.35	*92.39*
Bo C	67.03	10.56	1.84	1.66	0.04	0.86	11.88	2.49	0.92	0.15	0.23	*95.82*

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
Bo A	14	8	16	324	161	9	12	<	<	7	<	<
Bo B	<	9	16	168	103	<	10	2	<	4	<	<
Bo C	<	27	17	391	133	<	17	3	<	<	<	8

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
Bo A	74.48	13.72	723.1	11.32	88.47	4.931	4.389	1.621	1.694	9.619	7.849	<	<
Bo B	92.74	14.06	577.1	13.56	74.53	5.093	4.389	1.683	1.917	10.06	8.373	0.365	<
Bo C	21.09	27.84	751.5	5.174	24.21	2.364	0.297	0.321	0.866	10.28	4.313	<	<

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
Bo A	87,600	2415.56	48.97	828.01	89.579	0.2206	255.54	<	2.4887	0.300	112000	18100	8246
Bo B	61,800	2531.93	48.30	1236.24	42.869	0.2215	226.07	<	3.7143	0.323	126000	15000	6598
Bo C	84,900	1041.36	30.44	322.01	62.723	0.3845	276.32	0.2743	5.5185	0.472	11200	4837	1029

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

	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*
Bo A	22.564	47.052	5.4393	18.943	3.4142	0.9293	3.4282	0.4652	2.455	0.4663	1.3156	0.1782	1.1444	0.158	*107.9525*
Bo B	23.52	48.521	5.2241	19.019	3.4401	0.9521	3.5442	0.47	2.5741	0.5269	1.3199	0.1795	1.1766	0.1807	*110.6476*
Bo C	6.5923	13.751	1.7259	6.1442	1.2303	0.4912	1.1753	0.1926	0.9886	0.2017	0.5938	0.0842	0.491	0.078	*33.7405*

Table 3c: Rare earth elements (expressed as ppm) determined by ICP-MS

	Pb	Rb	Cs	Ge	Zn	As	Na	Si	Al	Ba	Ga	Sr	Ca	K	Cu	Cr	Sc	Eu	Th	Lu	Nb
Bo A	0.41	0.45	0.52	0.58	0.69	0.70	0.73	0.75	0.78	0.84	0.85	0.88	0.94	0.98	1.30	1.47	1.66	1.73	1.79	1.85	1.90
Bo B	0.61	0.46	0.53	0.62	0.95	0.46	0.57	0.73	0.66	0.75	0.89	0.70	0.66	0.73	0.62	1.45	1.77	1.77	2.02	2.12	1.97

	Tm	Y	Er	Ho	Ti	Yb	Tb	Dy	Mn	Sm	Gd	Nd	Pr	Ce	La	V	Zr	Mg	U	P	Fe	Mo
Bo A	1.93	2.00	2.02	2.11	2.12	2.13	2.21	2.27	2.35	2.53	2.66	2.81	2.88	3.12	3.13	3.22	3.34	3.42	4.61	7.32	9.13	13.50
Bo B	1.95	2.39	2.03	2.39	2.22	2.19	2.23	2.38	3.51	2.55	2.75	2.83	2.76	3.22	3.26	4.01	2.81	2.83	4.79	5.85	10.27	13.50

Table 4: Enrichment factors for slags over ignited sand.