Analyses of the Swedish ancient iron reference slag W-25:R

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ABSTRACT: *The increasing importance of chemical analyses for the interpretation of slags found at archaeometallurgical sites has increased the need for a reference material for ancient iron slags. Several sets of analytical data on the Swedish reference slag W-25:R are presented and discussed.*

Introduction

Chemical compositions of ancient iron slags derived from bloomery processes are characterized by high iron contents, the presence of metallic iron, variable but generally high manganese contents, and fairly low silica contents. Thus, these compositions are often outside the calibration range of commercial analytical laboratories.

Chemical analyses of ancient slags have increasingly grown in importance for the interpretation of both ores and techniques used (*eg*, Kresten *et al* 1998). Therefore, the need for a reference material has increased. To meet that demand, we now present the first compilation of data on the Swedish ancient iron reference slag W-25:R.

The material

The Viking Age iron production site Gryssen in Dalecarlia has been described by Serning (1973). The site is situated on a small point of land protruding into lake Gryssen, which apparently supplied lake ore for the process. The slags sampled are composed of wüstite (93-96% FeO, minor amounts of TiO_2, Al_2O_3, MnO and MgO) and fayalitic olivine (~29% SiO_2, ~66% FeO, ~1.5% MnO, 0.6-1.5% MgO) set in a glassy matrix (38-44% SiO_2, 12-21% FeO, <0.5% MnO, 8-10% CaO, ~4% Na_2O, ~6% K_2O). In addition, occasional droplets of metallic iron occur.

The melting temperature of the homogenized sample was determined by differential thermal analysis (DTA) to be 1115°C. The compositions of co-existing olivine-glass pairs indicate olivine crystallization temperatures in the range 1050-1090°C (for details on the method, see Kresten *et al* 1998).

Thirty-two kilograms of slag were collected and crushed in a jaw crusher. The crushed sample was split into two parts, A and B, which were each subdivided into four parts, A1 to A4, and B1 to B4, respectively. Each one of these was ground in a rotating mill with Widia grinding vessels and split into four parts, labelled A11, A12, A21, A22, etc, each of which was divided into six sub-sets, A111-A116, A121-A126 etc, weighing about 170g each.

Participating laboratories

The following laboratories have participated:

- VOEST, Linz, Austria. Conventional methods (wet-chemical, atomic absorption).
- MinPro, Swedish Mineral Processes AB, Stråssa, Sweden. Conventional methods (wet-chemical, atomic absorption).
- Sandvik steel research laboratory, Sandviken, Sweden. Conventional methods (wet-chemical, atomic absorption).
- Studsvik Energiteknik AB, Studsvik, Sweden. Instrumental neutron activation analysis (INAA).
- LKAB Prospektering, Håksberg, Sweden. Inductively coupled plasma spectroscopy (ICP-AES).
- SGAB1, Swedish Geological Company, Luleå, Sweden. Inductively coupled plasma spectroscopy (ICP-AES).
- SGU (Swedish Geological Survey), Uppsala, Sweden. Conventional methods (atomic absorption, titration, gravimetry).

- Analytica AB, Täby, Sweden. X-ray fluorescence (XRF).
- SGAB2, Svensk Grundämnesanalys AB, Luleå, Sweden. Inductively coupled plasma spectroscopy (ICP-AES, ICP-MS).

For analyses 1-9 (Tables 1-2), the laboratories were requested to analyse a reference material that had been analysed previously. Analyses 10-11, by contrast, were sent in on two occasions together with several other slag samples as monitors of routine analytical procedures.

Results

The results are given in Tables 1 and 2, listing the analytical results of the individual laboratories, the mean values, standard deviation, and the relative standard deviation in per cent.

Available data suggest that the sample is homogeneous and suitable as reference material for analytical purposes. The relative standard deviation for values reported for most major and minor elements is low (Table 1), with the notable exception of phosphorous which shows a spread between 0.08 and 0.51% P_2O_5. Most likely, the two lowest values as well as the highest one are erroneous as the glass phase that makes up about 30% of the sample and would contain most of the phosphorous was by microprobe analyses found to contain about 0.8% P_2O_5.

Ferric iron, ferrous iron and metallic iron all show major variations in determined contents, although only two data sets are available at present (Table 1). We have recommended reporting analytical results as total iron only (Hjärthner-Holdar 1993), not only because of the apparent analytical difficulties, but also due to the introduction of ferric iron by weathering processes, bearing no relation on the original compositions. Total iron contents also show much better statistics (Table 1).

Analytical data for trace elements (Table 2) in some

Table 1: Analyses of reference sample W-25:R. Major and minor elements in wt%.

Analysis No.	1	2	3	4	5	6	7	8	9	10	11	mean	st dev	rel st dev (%)
Laboratory	VOEST	MinPro	Sandvik	Studsvik	LKAB	SGAB1	SGU	Analytica	SGAB2	SGAB2	SGAB2			
Method	conv	conv	conv	INAA	ICP	ICP	conv	XRF	ICP	ICP	ICP			
Sample	A113	A122	A123	A125	A112	A111	A111	A101	A226	A226	A226			
SiO_2	25.26	24.10	25.40	-	-	-	24.40	25.00	24.10	24.10	25.50	24.73	0.58	2
TiO_2	0.28	0.33	0.31	-	0.33	0.30	0.33	0.31	0.31	0.32	0.42	0.32	0.04	11
Al_2O_3	7.20	7.40	7.30	5.30	7.60	6.44	7.63	7.70	7.37	7.08	7.56	7.14	0.67	9
FeO total	48.98	61.87	59.70	60.00	54.80	63.60	56.00	53.14	55.88	56.15	57.95	57.10	3.95	7
MnO	3.22	3.10	3.10	2.70	3.08	3.25	2.30	3.14	3.03	3.14	3.10	3.01	0.26	9
MgO	0.23	0.30	0.40	-	0.41	0.38	0.34	0.50	0.44	0.41	0.38	0.38	0.07	19
CaO	1.49	1.00	1.40	-	1.44	1.47	1.33	1.40	1.65	1.49	1.55	1.42	0.16	12
Na_2O	0.79	0.67	0.70	0.57	-	0.59	0.60	0.70	0.43	0.53	0.55	0.61	0.10	16
K_2O	1.12	1.10	1.00	1.00	-	0.92	0.93	0.99	1.01	1.04	1.05	1.02	0.06	6
P_2O_5	0.36	0.26	0.26	0.26	0.26	0.24	0.13	0.23	0.29	0.24	0.51	0.26	0.11	43
LOI	-	-	-	-	-	-	5.92	-	-	-	-	5.92	-	-
GOI	5.45	-	5.60	-	-	-	6.14	-	-	-	5.90	5.77	0.27	5
S	0.04	0.03	-	-	-	-	-	0.04	-	-	-	0.04	0.00	11
C	0.07	-	-	-	-	-	-	-	-	-	-	0.07	-	-
Sum	89.04	99.99	99.57	-	-	-	99.91	93.15	94.52	94.50	98.57	-	-	-
Fe_2O_3	13.87	7.00	-	-	-	-	-	-	-	-	-	10.44	3.44	33
FeO	36.50	53.00	-	-	-	-	-	-	-	-	-	44.75	8.25	18
Fe metal	0.00	2.00	-	-	-	-	-	-	-	-	-	1.00	1.00	100

Note: LOI = loss on ignition; GOI = gain on ignition

Table 2: Analyses of reference sample W-25:R. Trace elements part per million.

Analysis No.	1	2	4	5	6	8	9	10	11	mean	st dev	rel st dev (%)
Laboratory	VOEST	MinPro	Studsvik	LKAB	SGAB1	Analytica	SGAB2	SGAB2	SGAB2			
Method	conv	conv	INAA	ICP	ICP	XRF	ICP	ICP	ICP			
Sample	A113	A122	A125	A112	A111	A101	A226	A226	A226			
Li	-	-	-	5	5.1	-	-	-	-	5.05	0.05	1
Be	-	-	-	13	<4.9	-	15.4	14.6	15.1	14.53	0.93	6
B	-	-	-	685	-	-	-	-	-	-	-	-
Sc	-	-	5.9	-	5.2	-	3.69	4.32	4.09	4.64	0.80	17
V	168	230	93	142	133	-	131	183	155	154.38	38.16	25
Cr	<15	55	49	3	47	-	61.6	37	78.8	47.34	21.80	46
Co	-	-	6.8	16	<4.9	-	61.9	<6.16	<8.90	28.23	24.10	85
Ni	8	157	-	-	<4.9	-	<6.3	<12.3	44.2	69.73	63.45	91
Cu	<4	70	-	-	12	-	36.2	6.41	19.5	28.82	22.90	79
Zn	-	-	-	88	<4.9	-	<6.3	25.5	30.8	48.10	28.30	59
Ga	-	-	-	-	-	-	-	-	72.2	-	-	-
As	-	-	-	805	-	-	-	-	-	-	-	-
Rb	-	-	<50	-	-	-	-	-	39.9	-	-	-
Sr	-	-	-	99	91	-	91	93.4	93.9	93.66	2.93	3
Y	-	-	-	111	94	-	92.1	90.7	89.3	95.42	7.94	8
Zr	-	-	-	76	92	-	97.4	97.5	96.2	91.82	8.16	9
Nb	-	-	-	32	<24	-	27.6	8.87	7.02	18.87	11.06	59
Mo	-	-	-	15	<24	-	<6.3	<6.16	3.87	9.44	5.57	59
Sn	-	-	-	75	<24	-	29.8	<24.7	5.38	36.78	28.84	79
Sb	-	-	<0.9	9	-	-	-	-	-	-	-	-
Cs	-	-	<2.5	-	-	-	-	-	-	-	-	-
Ba	-	-	600	847	769	806	818	835	964	805.58	101.02	13
La	-	-	87	81	63	-	83.4	-	80.7	79.02	8.32	11
Ce	-	-	270	327	-	-	264	-	235	274.00	33.34	12
Pr	-	-	-	-	-	-	25.5	-	20.7	23.10	2.40	10
Nd	-	-	160	-	-	-	107	-	88.7	118.57	30.24	26
Sm	-	-	16	-	-	-	18.9	-	14.3	16.40	1.90	12
Eu	-	-	1.9	-	-	-	2.29	-	1.59	1.93	0.29	15
Gd	-	-	-	-	-	-	20.2	-	19.1	19.65	0.55	3
Tb	-	-	<1.5	-	-	-	2.57	-	2.49	2.53	0.04	2
Dy	-	-	-	-	-	-	16.6	-	13.6	15.10	1.50	10
Ho	-	-	-	-	-	-	3.87	-	3.06	3.47	0.41	12
Er	-	-	-	-	-	-	13.2	-	11.2	12.20	1.00	8
Tm	-	-	-	-	-	-	2.16	-	1.87	2.02	0.14	7
Yb	-	-	15	-	-	-	15.9	-	12.7	14.53	1.35	9
Lu	-	-	2	-	-	-	2.69	-	2.09	2.26	0.31	14
Hf	-	-	3.3	-	-	-	3.3	-	4.2	3.60	0.42	12
Ta	-	-	-	10	-	-	10	-	0.592	6.86	4.43	65
W	-	-	<35	2	<24	-	-	<24.7	1.47	1.74	0.27	15
Au	-	-	<0.03	-	-	-	-	-	-	-	-	-
Pb	-	-	-	-	<49	-	-	-	-	-	-	-
Bi	-	-	-	41	-	-	-	-	-	-	-	-
Th	-	-	14	-	-	-	14	-	14.4	14.13	0.19	1
U	-	-	13	-	-	-	13	-	14	13.33	0.47	4

Note: Data 'less than' have been omitted in calculating the means and standard deviations.

cases show good agreement between different laboratories, often using different methods. This seems to be the case for scandium (Sc), strontium (Sr), yttrium (Y), zirconium (Zr), many of the rare earth elements (La-Lu), hafnium (Hf), thorium (Th) and uranium (U). Other elements such as chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) show apparently conflicting data sets. However, it has to be born in mind that many trace elements may occur in discrete minerals found in very small amounts in the slag, thus posing particular difficulties in homogenizing the sample. For several trace elements, available data are few and further analyses are required.

The differences occurring when analysing a reference sample (analysis 9) and routine samples (analyses 10 and 11) at Svensk Grundämnesanalys AB are in most cases not significant (Tables 1-2).

Availability

Laboratories that are prepared to contribute with analytical data can receive a sample free of charge. Other parties will be charged a fee. Both will receive updated information on analytical results. All requests should be made to the authors.

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References

Hjärthner-Holdar E 1993, *Järnets och järnmetallurgins introduction i Sverige* [The introduction of iron and iron metallurgy to Sweden] (Uppsala: Aun 16).

Kresten P, Hjärthner-Holdar E and Larsson L 1998, 'Geochemistry in archaeometallurgy', in *Proceedings of the fourth international conference on the beginning of the use of metals and alloys (BUMA-IV)*, 139-44.

Serning I 1973, *Förhistorisk järnhantering i Dalarna* (Stockholm: Jernkontorets Forskning H29).

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