Analytical procedures in the Rock Geochemical Laboratory of the Geological Survey of Denmark and Greenland

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The analytical procedures for analysis of whole rocks for major and selected trace elements, mainly by X-ray fluorescence spectrometry (XRF), are described in detail. The quality of the results is evaluated and results for international standards are given.

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The Rock Geochemical Laboratory of the Geological Survey of Denmark and Greenland (GEUS), formerly of the Geological Survey of Greenland (GGU), produces high-precision analyses for major elements together with reconnaissance data for selected trace elements, mostly on geological materials. The present analytical equipment is centred around a multichannel X-ray fluorescence spectrometer from 1985. A gradual development in the analytical and computational technique has taken place, but since 1993 the procedures have been essentially unchanged. In this period, the laboratory has analysed *c.* 14 000 samples for a variety of purposes, and the results are appearing in scientific papers, geochemical maps, technical reports, and students' theses. The aim of the present note is to provide an accessible and referable account of the analytical procedures in the laboratory.

Analytical procedures

Samples are routinely ground in a tungsten carbide ball mill. Alternatively, samples can be ground in a swing mill of tungsten carbide or agate.

Most elements are determined by X-ray fluorescence spectrometry (XRF) on fused glass discs. The rock powders are dried at 110°C for 2 hours and ignited in an electric furnace at 1000°C for 1 hour, with subsequent determination of the loss on ignition. The ignited samples are mixed with sodium tetraborate in the ratio 0.7500 g sample to 5.2500 g borate, and fused in Pt/Au crucibles over gas burners under continuous agitation for 1–1½ hours. After inspection for homogeneity the melts are poured into a Pt/Au mold, creating glass discs with 32 mm diameter. The X-ray fluorescence spectrometer is a Philips PW1606 multichannel instrument for simultaneous determination of a number of specific elements, equipped with a Rh-anode X-ray tube operated at 50 kV and 50 mA. Calibration and correction for background and line overlaps are calculated from measurements on synthetic mono-element glass discs, and corrections for matrix effects are calculated either from measurements on synthetic glass discs or from Heinrich's (1966) absorption coefficients (Sørensen 1975, 1976, 1981).

Na_2O and Cu are determined by atomic absorption spectrometry (AAS). Each dried sample (0.25–0.5 g) is treated with hydrofluoric acid in a PTFE beaker on a heating plate. After evaporation to dryness the residue is dissolved in a hydrochloric acid – potassium chloride solution, made up to 50 ml, and Na and Cu measured on a Perkin Elmer PE2280 AAS instrument.

For FeO determination each dried sample (0.1 g) is treated with ammonium vanadate – hydrofluoric acid overnight. Boric acid and a measured amount of iron(II) is added and surplus iron(II) is determined by automatic potentiometric titration using Cr(VII) as titrant. The method is a modification of that of Wilson (1955).

'Volatiles' is calculated as the loss on ignition corrected for the calculated gain of weight due to oxidation of iron(II) to iron(III) during ignition.

To give an indication of concentration levels in large

Table 1. Evaluation of analytical results from the Rock Geochemical Laboratory

Element	Line	Precision	LLD rec.	LLD theo.	Accuracy* std. error	Basalts* rel. error	Granites* rel. error	Quality
Major elements		wt%	wt%	wt%	wt%	% of amount present	% of amount present	
SiO_2	Kα	0.15	0.3	0.01	0.24	0.25	0.31	high
TiO_2	Kα	0.015	0.03	0.002	0.033	2.19	19.51	high
Al_2O_3	Kα	0.05	0.1	0.05	0.24	0.59	0.62	high
Fe_2O_3,T	Kα	0.1	0.2	0.0015	0.21	1.19	10.56	high
FeO	–	0.1	0.2	–	0.13	2.25	4.12	high
MnO	Kα	0.003	0.005	0.001	0.005	2.20	10.48	high
MgO	Kα	0.05	0.1	0.05	0.09	0.62	2.89[b]	high
CaO	Kα	0.03	0.05	0.0007	0.07	0.77	2.34	high
Na_2O	–	0.05	0.08	–	0.06	3.93	2.87	high
K_2O	Kα	0.005	0.01	0.003	0.038	1.26	0.28	high
P_2O_5	Kα	0.005	0.01	0.002	0.014	1.62	3.04[b]	good
Volat	–	0.10	–	–	–	–	–	good
Trace elements		ppm	ppm	ppm	ppm	% of amount present	% of amount present	
V	Kα	20	50	10	10.9	4.26	b.d.	good
Cr	Kα	40	50	10	12.0	2.02[a]	b.d.	good
Ni	Kα	15	50	5	12.0	14.3[a]	b.d.	good
Cu	–	2	5	3	5.3	10.1	21.0	good
Zn	Kα	10	50	3	14.0	10.6	8.76[a]	good
Rb	Kα	20	50	3	21.0	55[c]	12.9	moderate
Sr	Kα	20	50	2	38.8	6.35	1.32[b]	good
Y	Kα	20	100	2	32.8	b.d.	b.d.	poor
Zr	Kα	30	50	2	42.6	14.5	11.4	good
Nb	Kα	20	50	2	28.5	b.d.	39[c]	poor
Ba	Lα	60	100	80	47.7	11.2	16.2	moderate

Analyses by XRF except FeO (titration), volatiles (corrected loss on ignition), Na_2O and Cu (AAS).

Fe_2O_3,T: Total iron as Fe_2O_3.

Precision: One standard deviation based on experimental data (repeated analysis over time of a set of internal standards).

LLD rec.: Recommended lower limit of detection. These values (*c.* 1 standard deviation) are based on user experience with the analytical results and are not calculated figures. They include the facts that the matrix and background corrections are not always adequate for samples with strongly contrasting matrices and that there may be variations between different calibrations. For sets of samples with similar matrices run under the same calibration, the effective LLD will normally be somewhat lower.

LLD theo.: Theoretical lower limit of detection: 3 times counting statistical error.

**Results from analysis of 26 international standards*

Std. error: Standard error. Average distance of points from regression line.

Rel. error: The difference between measured and reference values as percentage of the reference value. See text for details.

Basalts: Average relative errors for the five basalt standards BCR-1, BHVO-1, BR, JB-1A and W-2.

Granites: Average relative errors for the four granite standards G-2, GA, GH and NIM-G.

[a-b-c] 1, 2, or 3 reference values are below the recommended lower limit of detection and have not been included in the average.

b.d.: all reference values are below the recommended lower limit of detection.

Quality is a subjective estimate of the reliability of results for concentrations significantly above the recommended LLD.

Table 2. Analytical results obtained for international standards, June 1999

Standard	AGV-1		BCR-1		BHVO-1		BIR-1		DNC-1		DT-N	
	measured	reference	measured	reference	measured	reference	measured	reference	measured	reference	measured	reference
SiO_2	59.91	59.43	54.70	54.55	49.79	49.97	47.83	47.80	47.03	47.20	37.14	36.51
TiO_2	1.08	1.06	2.26	2.26	2.78	2.71	0.96	0.96	0.51	0.48	1.34	1.40
Al_2O_3	17.40	17.32	13.68	13.75	13.76	13.82	15.70	15.36	18.69	18.36	58.97	59.29
Fe_2O_3,T	6.49	6.84	13.43	13.52	12.25	12.24	11.50	11.27	9.84	9.96	0.40	0.66
FeO	2.15	2.08	8.78	8.95	8.38	8.58	8.54	8.39	7.42	7.41	0.09	0.10
MnO	0.098	0.091	0.187	0.181	0.171	0.168	0.177	0.171	0.150	0.149	0.001	0.008
MgO	1.55	1.55	3.48	3.51	7.22	7.23	9.69	9.69	10.15	10.08	0.06	0.04
CaO	4.89	4.99	6.95	7.01	11.34	11.41	13.27	13.25	11.25	11.31	0.02	0.04
Na_2O	4.52	4.30	3.43	3.30	2.40	2.26	1.90	1.75	1.95	1.88	0.03	0.04
K_2O	2.960	2.950	1.750	1.700	0.528	0.520	0.022	0.027	0.230	0.230	0.125	0.120
P_2O_5	0.508	0.495	0.367	0.363	0.277	0.273	0.024	0.046	0.070	0.085	0.072	0.090
V	113	122	399	410	314	317	316	313	149	148	127	150
Cr	19	10	30	16	284	289	403	382	299	286	248	260
Ni	0	16	0	13	99	121	147	166	240	248	0	14
Cu	63	61	21	19	147	136	130	126	104	96	13	7
Zn	86	89	125	131	89	105	50	71	42	66	0	28
Rb	45	68	64	48	32	11	23	1	6	5	0	6
Sr	635	669	339	333	369	403	82	108	117	145	55	30
Y	0	20	66	38	65	27	50	16	28	18	0	7
Zr	199	229	220	192	203	179	69	16	60	41	320	371
Nb	0	15	40	14	55	19	21	1	22	3	0	34
Ba	1200	1238	743	687	108	139	0	7	14	114	97	130

Standard	G-2		MICA-FE		NIM-G		PCC-1		S-7		W-2	
	measured	reference	measured	reference	measured	reference	measured	reference	measured	reference	measured	reference
SiO_2	69.74	69.22	34.31	34.55	75.88	75.70	41.60	41.89	33.24	33.45	52.31	52.56
TiO_2	0.48	0.48	2.55	2.51	0.12	0.09	0.00	0.01	1.59	1.57	1.10	1.06
Al_2O_3	15.43	15.41	19.59	19.58	12.10	12.08	0.55	0.68	4.22	4.27	15.39	15.39
Fe_2O_3,T	2.46	2.66	25.44	25.76	1.70	2.03	8.12	8.29	9.40	9.31	10.70	10.76
FeO	1.43	1.46	18.63	18.99	1.26	1.30	5.32	5.08	4.45	n.a.	8.26	8.33
MnO	0.034	0.030	0.364	0.352	0.017	0.021	0.116	0.121	0.173	0.170	0.168	0.163
MgO	0.75	0.75	4.65	4.57	0.05	0.06	43.22	43.62	26.32	26.21	6.35	6.39
CaO	1.89	1.96	0.39	0.43	0.75	0.78	0.53	0.52	9.63	9.70	10.82	10.90
Na_2O	4.18	4.08	0.25	0.30	3.49	3.36	0.02	0.03	0.63	0.50	2.28	2.15
K_2O	4.500	4.490	9.010	8.790	4.990	4.990	0.003	0.007	1.040	1.040	0.635	0.628
P_2O_5	0.135	0.140	0.418	0.452	0.009	0.010	0.009	0.002	1.440	1.490	0.128	0.131
V	33	36	131	136	7	2	33	31	120	110	254	263
Cr	21	9	97	90	34	12	2749	2742	1301	1370	95	93
Ni	0	5	0	35	0	8	2395	2391	992	1032	57	70
Cu	13	11	31	5	12	12	13	10	68	55	113	103
Zn	82	86	1272	1306	43	50	35	42	54	66	62	77
Rb	143	170	2201	2209	280	320	0	0	68	54	28	20
Sr	487	479	104	5	33	10	28	0	1454	1700	171	194
Y	0	11	141	50	80	143	0	0	39	17	36	24
Zr	295	309	933	803	237	300	0	10	263	240	117	94
Nb	0	12	312	271	4	53	0	1	93	104	25	8
Ba	1953	1884	64	151	169	120	0	1	1627	1700	202	182

Major elements in wt%, trace elements in ppm, n.a.: not available.
Fe_2O_3,T: Total iron as Fe_2O_3.
Reference values for samples NIM-G and S-7 from Govindaraju (1989), others from Govindaraju (1994).
All reference values have been recalculated on dry basis (as dried but not ignited powders).

regional sample sets and samples of economic interest, a number of trace elements are measured simultaneously with the major elements. Calibration and correction for background, line overlaps and matrix effects are carried out as described above for the major elements. The use of glass discs for trace element analysis, in contrast to the normally used pressed powder pellets, poses some problems. Firstly, the weaker signal due to the flux dilution gives higher theoretical lower limits of detection (LLD). Secondly, the calculated corrections for backgrounds and spectral overlaps are not always adequate. The method works satisfactorily for the elements V, Cr, Ni, Zn, Sr and Zr, and less so for Rb, Y, Nb and Ba. Other elements measured are Mo, Sn, La and Ce, but these give poor results and are not used. Because of the high LLDs, concentrations of Nb and Y in most geological materials, and Rb in some, are beyond the limitation of the method.

Quality of results

The major element analyses from the laboratory, obtained by XRF analysis on a routine basis since 1977, have a long-standing record of being highly reproducible. On the other hand, the trace element results have been more variable. The determination of trace element concentrations commenced in 1986, and in the beginning there were problems with reproducibility for a number of the elements. In particular, significant absolute variations between different calibrations were observed. The variability of the results has been monitored with internal standards since 1990, as presented by Steenfelt (1999a, b, this volume). This work confirms the high and uniform quality over time of the major element analyses, with some variations in P_2O_5 at levels below 0.1%. It also illustrates the variations in the early trace element analyses, and, in particular, that the trace element results have been fairly stable since 1993. Table 1 presents estimates of the precision and LLD for both major and trace element determinations, applicable for analyses from 1993 and later.

Analytical results for a set of 26 international standards have been used to evaluate the accuracy of the data. For this exercise, Table 1 includes for each element the *standard error*, which is the average distance of the data points from the regression line for reference values versus measured values. The *relative error* for an element in a sample is the difference between the measured and the reference values, expressed as percentage of the reference value. The relative errors are much larger at low concentrations than at high. Table 1 includes average relative errors for groups of international standards of comparable composition, viz. basaltic and granitic. For some elements in low concentrations, e.g. TiO_2, MnO and Cu in granites, the relative errors in Table 1 may be at least as dependent on the quality of the reference values as on the quality of the measured values. Table 2 shows the analytical results compared to the reference values for 12 of the international standards, selected to illustrate the large compositional range covered by the method.

Conclusions

The Rock Geochemical Laboratory produces major element analyses of high quality and long-term consistency. The reconnaissance trace element analyses obtained on the glass discs have high detection limits, but above these limits the data are of good quality for V, Cr, Ni, Cu, Zn, Sr and Zr, of moderate quality for Rb and Ba, and of poor quality for Y and Nb.

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