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REFERENCE MATERIALS FOR TRACE ANALYSIS BY RADIOANALYTICAL METHODS: U.S. GEOLOGICAL SURVEY ROCK STANDARDS

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REFERENCE MATERIALS FOR TRACE ANALYSIS BY RADIOANALYTICAL METHODS: U.S. GEOLOGICAL SURVEY ROCK STANDARDS

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Eight geological reference materials from the U.S. Geological Survey covering a wide range of chemical compositions have been examined on the basis of available analytical data. The estimated concentrations of 51 trace elements are listed together with indications as to their levels of uncertainty. The use of these samples in the radioanalytical field is encouraged.

Standard materials are of great inportance in the development and quality control of methods used in the analysis of such complex samples as silicate rocks. Since the introduction of the first two U.S. Geological Survey standard rocks granite G-1 and diabase W-1 about 1950, the list of international reference samples for the earth sciences has been rapidly expanding, and includes at present more than 200 materials (1). Only a few of these reference materials however have so far been of general use in trace element analysis.

Radioanalytical techniques play a significant role in the determination of trace elements in geological materials. In particular neutron activation analysis has shown to be a very helpful tool in the analysis of terrestrial as well as extraterrestrial rocks and minarals. Rock standards from the U.S. Geological Survey have been extensively used in the development of radioanalytical methods for geological materials. On the other hand these methods have provided a significant contribution to the establishment of recommended values for a great number of elements in these standard rocks.

Up to about 1965, G-1 and W-1 were the most extensively used geological standards in trace element analysis. At that time the supply of these two rocks was very limited. A new series of six U.S.G.S. standard rocks issued in 1964 therefore became increasingly important. The members of that series were an andesite (AGV-1), a basalt (BCR-1), a granite (G-2), a granodiorite (GSP-1), a dunite (DTS-1) and a periodotite (PCC-1). These rocks have become very popular in trace element analysis in recent years, and recommended values have been issued for a considerable number of elements (2). Unfortunately the supply of even the 1964 series is now very limited (F.J. Flanagan, personal communication).

Note a: <u>Titular Members</u>: M. Sankar Das, Chairman (India), F. Lux, Secretary (FRG), M. de Bruin (Netherlands), M.B.A. Crespi (Argentina), T.A. Rafter (New Zealand), E.A. Schweikert (USA), E. Steinnes (Norway. <u>Associate Members</u>: D. Comar (France), G.B. Cook (Austria), P. Franchimont (Belgium), L. Gorski (Poland), J. Hislop (UK), L. Kosta (Yugoslavia), K.H. Lieser (FRG), B.F. Myasoedov (USSR), M. Sakanoue (Japan), E. Szabo (Hungary), N.E. Whitehead (New Zealand). <u>National Representatives</u>: A.C. Docherty (UK), N. Saito (Japan). A new series of eight rock standards was recently issued by the U.S.G.S. These materials were prepared in much larger quantities than the previous standard rocks, and will presumably be available for a considerable number of years. A description of the various materials and results from analysis of homogeneity, mineralogy and chemical composition are given in a report from the U.S.G.S. (3). The following materials are included in the new series:

<u>BHVO-1</u> is prepared from a sample of basaltic lava originating from the Kilauea volcano, Hawaii. This sample has a quite similar elemental composition to that of W-1, and should be a useful reference material for basaltic rocks.

<u>MAG-1</u> is a sample of fine-grained clayey mud from the gulf of Maine, which may be a suitable reference material for marine sediment analyses.

<u>QLO-1</u> consists of quartz latite, a black volcanic rock, collected in Lake County, Oregon. For most elements its composition is somewhere in between BHVO-1 and RGM-1, and it should be a generally useful standard with special reference to intermediate rocks.

<u>RGM-1</u> was prepared from a rhyolite glass from Glass Mountain, California. Its major element composition is very similar to that of G-1, and it is considered to be a suitable reference material for rocks of granitic composition.

SCo-1 was collected from a silty marine shale in Natrena County, Wyoming.

SDC-1 is a sample of mica schist from Rock Creek Park, Washington, D.C.

 $\underline{SGR-1}$ is a sample of oil shale from the Green River formation. In addition to the inorganic constituents shown in Table 1, this sample contains about 40 % of organic material. In view of the current interest for oil production from shale this sample may be an interesting reference material.

<u>STM-1</u> is a sample of peralkaline nepheline syenite from Table Mountain, Oregon. Among the characteristic compositional features of this rock are high contents of Na and most of the incompatible trace elements such as Zr, Nb, Th and the rare earths. On the other hand several elements such as Sc, Cr, V and Cu show quite low concentrations. STM-1 may therefore in many cases be considered to be a difficult material for analysis, and should as such be a valuable sample for the testing of new methods.

The major element composition of the eight samples, as estimated from available analytical data (3-9), is given in Table 1. As far as these elements are concerned, the composition is already fairly well established in most cases.

A corresponding list for trace elements is presented in Table 2. The basis of each value in the table is indicated in the following manner:

- === Good agreement (Note b) between three different analytical techniques, or by at least two independent values from each of two different analytical techniques.
- Good agreement between two different analytical techniques, or at least three values from the same technique obtained in different laboratories.
- No sign: Good agreement between two different laboratories using the same technique.
- () Only single values available, or poor agreement between different laboratories.

From Table 2 it appears that rather well-established data are already available for some trace elements in these samples. In general, however, there is still much work to do before a set of recommended values can be established

Note b: Agreement within $\frac{1}{2}$ 10 % for concentrations above 10 ppm and $\frac{1}{2}$ 20 % for concentrations below 10 ppm.

for a greater number of elements. In view of the extensive distribution these samples are most probably going to obtain among workers in the earth sciences, the establishment of reliable reference values for a great number of elements as soon as possible appears to be an important task. Radioanalytical methods could make a significant contribution in that respect. The use of the eight new U.S.G.S. rock reference materials in the radioanalytical field is encouraged.

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TABLE 1. Estimated major element composition of eight new U.S. Geological Survey reference materials (%). +)

	BHVO-1	MAG-1	QLO-1	RGM-1	SCo-1	SDC-1	SGR-1	STM-1
Si02	50.1	49.8	65.6	73.0	62.2	65.8	28.3	59.8
-	14.0	16.6	16.3	13.8	13.6	16.3	7.2	18.7
$Fe_{2}^{0}O_{3}^{2}x)$	12.0	6.7	4.4	1.87	5.1	7.1	3.0	5.1
MgŐ	7.1	2.9	1.00	0.27	2.6	1.66	4.4	0.09
Ca0	11.4	1.48	3.2	1.20	2.6	1.41	8.9	1.10
Na ₂ 0	2.2	3.8	4.2	4.1	0.95	2.0	2.9	8.8
_	0.52	3.6	3.6	4.3	2.7	3.2	1.7	4.3
	0.25	5.2	0.27	0.34	3.9	1.4	-	1.4
н20	0.06	2.6	0.19	0.12	2.5	0.17	-	0.19
TiO ₂	2.7	0.73	0.62	0.27	0.75	1.01	0.33	0.15
P205	0.28	0.19	0.26	0.049	0.22	0.18	0.36	0.17
MnO	0.17	0.10	0.092	0.038	0.054	0.12	0.038	0.22

x) Total Fe expressed as Fe₂0₃.

+) The figures in this table are given only to indicate the elemental composition of the samples, and are not to be considered as recommended values.

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TABLE 2. Estimated trace element composition of eight new U.S. Geological Survey reference materials (ppm) +)

	BHVO-1	MAG-1	QLO-1	RGM-1	SCo-1	SDC-1	SGR-1	STM-1
Li	(4)	75	24	51	43	34	130	29
Be		2.8	<u>1.9</u>	2.2	1.7	3.2	(0.9)	10
в		140	40	31	75	(30)	(45)	
F		(1200)	280	370	(1100)	(600)		950
s		5200			(600)	(500)	(19000)	
Cl	(90)	30000	220	500	(70)	(40)	(40)	430
Sc	<u>30</u>	17	<u>10</u>	4.8	10	<u>17</u>	4.6	0.7
v	310	140	60	12	115	105	125	(2)
Cr	310	110	(5)	(3)	67	70	29	2
Co	45	20	7.3	<u>2.1</u>	10.5	18	12	1
Ni	120	55	3	(3)	25	40	32	2
Cu	135	<u>32</u>	<u>30</u>	12	<u>30</u>	<u>30</u>	65	4
Zn	100	<u>130</u>	<u>59</u>	32	<u>105</u>	104	78	<u>230</u>
Ga	22	22	== 18	15	=== 15	<u>===</u> 22	10	<u>35</u>
As	<u></u> (0.7)	(10)	(3)	(3)	12	(0.3)	70	(4)
Se	(007)	1.2	(-)	(-)	(0.9)		3.5	(0.01)
Rb	<u>9</u>	170	70	160	120	130	87	115
Sr	<u> </u>	<u>160</u>	350	115	190	200	420	<u>720</u>
Y	28	<u>≞≌</u> (40)	29	≛≟⊒ 25	<u>≞⊇</u> ⊆ 26	<u>∡⊴⊴</u> (50)	<u>≇≝</u> ≌ (13)	<u>∡</u> ≝≌ 53
Zr	<u>20</u> 170	130	180	210	160	270	(70)	1230
			10			18	<u>5</u>	250
Nb	<u>17</u>	<u>9</u> 0.6	2.8	<u>8</u> 2.2	<u>8</u> 1.4	(<0.1)	36	<u>5</u>
Mo	0.9			(0.1)	(0.1)	(0.1)	<u> </u>	<u>-</u> (0.1)
Ag	(0.05)	(0.1)	(0.05)	(0.1)	(0.1)	(0.1)		(0.09)
In			2			2	2	
Sn	2	4	3	4	4	3	2	8
Sb	0.2	0.9	2.2	<u>1.3</u>	2.5	0.5	3.2	1.7
Те	(0.006)				_	(0.006)		
Cs	(0.09)	8	1.7	10	7	3.8	5.0 .	1.5
Ba	140	<u>490</u>	<u>1390</u>	<u>800</u>	<u>570</u>	<u>640</u>	310	<u>600</u>
La	24	(50)	(35)	(27)	31	(50)	(32)	160
Ce	<u>40</u>	98	65	<u>55</u>	64	110	44	290
Pr	(6)	(8)	(6)	(4)	(5)	(9)	(7)	(19)
Nd	27	37	31	19	26	40	(26)	75
Sm	6	(8)	(5)	(4)	5.4	(7)	(3)	14
Eu	2.0	1.6	1.5	0.8	1.2	1.8	0.6	3.7
Gđ	(6)	(9)	(6)		5		(5)	
Тb	1.0	1.0	0.8	(0.7)	0.75	1.3	0.35	1.7
Dy	(5)	,		(4)	(4)			(11)
Но					(0.9)			(1.7)
Er	(2)				(2.5)			(4)
Tm	(0.3)	(0.4)	(0.4)	(0.4)	(0.4)	(0.7)	(0.2)	
Yb	2.3	3.0	2.9	2.7	2.4	5.2	1.2	5.0
Lu	2.5	5.0	2	<u> </u>	(0.4)			(0.7)
	1 2	3.7	4.4	6.1	4.4	8.2	1.4	28
Нf	$\frac{4.2}{1.1}$							
Ta	1.1	1.0	0.8	1.0	0.8	1.2	0.5	19

	BHVO-1	MAG-1	QLO-1	RGM-1	SCo-1	SDC-1	SGR-1	STM-1
W	(0.3)	(2)	(1)	(2)	(2)	(1)	(2)	(3)
Au	0.0017	0.0025	(0.0013)	0.0003	0.0024	0.0015	0.010	0.0004
Pb	(5)	(20)	21	21	29	(25)	37	17
Bi	0.015	(0.4)	(0.07)	0.25		(0.3)		(0.3)
Th	1.0	12.6	4.5	16	9.9	12	4.9	32
U	0.42	2.8	1.8	5.8	<u>3.1</u>	3.1	5.5	9.1

+) The figures given in this table are given only to indicate the elemental composition of the samples, and are not to be considered as recommended values.