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Determination of Major and Trace Elements in Nine Japanese Geochemical Standard Rock Samples by Instrumental Neutron Activation Analysis

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Abstract

Non-destructive instrumental neutron activation analyses were carried out for determining four major and twelve trace elements in Japanese standard rock samples, JG-2, JG-3, JR-2, JA-2, JA-3, JP-1, JB-2, JB-3 and JF-2, which were issued from the Geological Survey of Japan (GSJ). Among those elements, the values for Eu, Lu and Tb in JG-3 and JA-3, and Eu in JG-2, JP-1 and JF-2 are given for the first time in this report.

1. Introduction

The Geological Survery of Japan (GSJ) has been issuing standard rock samples since 1967 (ANDO, 1986). The first two rock samples, JG-1 (granodiorite, issued in 1967) and JB-1 (basalt, 1968) have been analyzed in many laboratories and are well established as reference materials. Other rock samples, which were issued after 1981, have also been analyzed by many researchers using various techniques. These data have been compiled and were recently published as "1986 consensus values for GSJ rock reference samples, "Igneous rock series" by ANDO *et al.* (1987). However some of them are far from certified ones, and further, values for some elements of several samples are still lacking. It is necessary to obtain additional data to establish these samples as reference materials.

Instrumental neutron activation analysis (INAA) has been applied to the present work, because this method has the advantage that while it is rather simple, various elements are determined simultaneously with high sensitivity and no contamination problem.

In this report, analytical results, including some new data for Eu, Lu and Tb, of nine GSJ standard rocks JG-2, JG-3, JR-2, JA-2, JA-3, JP-1, JB-2, JB-3 and JF-2 which had been issued between 1982 and 1986 are reported, and compared with 1986 values.

Table 1. Published best values for W-1 and JB-1 using as the standards for the analyses.

Element	W-1*	JB-1**	Element	W-1*	JB-1**
Major elements (%)					
Fe	7.76	6.27	K	0.53	1.18
Na	1.59	2.07	Mn	0.13	0.12
Trace elements (ppm)					
Ce	23	67	Sc	35.1	27.4
Co	47	38.7	Sm	3.6	5.0
Eu	1.11	1.52	Ta	0.50	3.6
Ga	16	18.1	Tb	0.65	1.2
La	9.8	38	Th	2.42	9.2
Lu	0.35	0.31	Zn	86	83

* F. J. FLANAGAN, *Geochim. Cosmochim. Acta*, **37**, 1189 (1973).
** A. ANDO *et al.*, *Geostand. Newslet.*, **11**, 159 (1987).

Table 2. Nuclear data used in this work-1—Target nuclides.

Element	Nuclide	Isotopic abundance* (%)	Cross section** (burns)	Produced nuclide (decay scheme & half life***)
Fe	^{58}Fe	0.28	1.14	^{59}Fe
Na	^{23}Na	100	0.10	^{24}Na
			0.43	^{24m}Na (IT, β^-, 20.21 ms)
K	^{41}K	6.7302	1.46	^{42}K
Mn	^{55}Mn	100	13.3	^{56}Mn
Ce	^{140}Ce	88.48	0.56	^{141}Ce
	^{142}Ce	11.08	0.95	^{143}Ce
Co	^{59}Co	100	18.2	^{60}Co
			19.1	^{60m}Co (IT, β^-, 10.47 m)
Eu	^{151}Eu	47.8	5.8×10^3	^{152}Eu
			3.2×10^3	^{152m_1}Eu
			4	^{152m_2}Eu (IT, 96.1 m)
Ga	^{71}Ga	39.9	4.6	^{72}Ga
La	^{139}La	99.91	9.2	^{140}La
Lu	^{176}Lu	2.59	2.0×10^3	^{177}Lu
Sc	^{45}Sc	100	17	^{46}Sc
			9	^{46m}Sc (IT, 18.71 s)
Sm	^{152}Sm	26.7	205	^{153}Sm
Ta	^{181}Ta	98.988	21.1	^{182}Ta
Tb	^{159}Tb	100	23	^{160}Tb
Th	^{232}Th	100	7.4	^{233}Th (β^-, 22.3 m) → ^{233}Pa
Zn	^{64}Zn	48.6	0.78	^{65}Zn

* after IUPAC-CAWIA report, *Pure Appl. Chem.*, **56**, 675 (1984).
** C. M. LEDERER and V. S. SHIRLEY ed. "Table of Isotopes" 7th ed., Wiley & Sons (1978).
*** Nuclides which were measured through their decay product only.

2. Experimental

About 10 mg of each rock sample was weighed accurately, sealed in a small polyethylene bag and irradiated for 10 minutes in JRR-4 reactor at a flux of 8×10^{13} neutrons/cm^2·sec in the Japan Atomic Energy Research Institute at Tokai. Two rock samples W-1 (diabase, issued from U.S. Geological Survey in 1951) and JB-1, which have well-established analytical values, were used as standards. Their published best values used as standards in this work are summarized in Table 1. They were treated in the same way as used with above rock samples. A standard monitor prepared from $Th(NO_3)_4$ solution was also used as Th standard except for JG-3, JA-3 and JB-3.

Irradiated samples were cooled for about 20 hours, and then produced γ-ray

Table 3. Nuclear data* used in this work-2—Measured nuclides.

Element	Nuclide	Half life	γ-ray energy used (keV)	γ-ray intensity (%)
Fe	^{59}Fe	44.497 d	1099.252	56.5
			1291.597	43.2
Na	^{24}Na	14.659 h	1368.599	100
K	^{42}K	12.360 h	1524.59	18.8
Mn	^{56}Mn	2.5786 h	846.812	98.9
			1810.80	27.3
Ce	^{141}Ce	32.50 d	145.440	48.4
	^{143}Ce	1.376 d	293.273	42
Co	^{60}Co	5.271 y	1173.237	99.90
			1332.502	99.9825
Eu	^{152}Eu	13.33 y	121.7758	28.5
			344.286	26.7
	$^{152m_1}Eu$	9.32 h	121.7758	7.2
			841.586	14.6
			963.360	12.0
Ga	^{72}Ga	14.10 h	630.017	24.9
			834.088	95.63
La	^{140}La	1.6780 d	328.759	20.7
			487.026	46.0
			1596.54	95.4
Lu	^{177}Lu	6.71 d	208.364	11.0
Sc	^{46}Sc	83.83 d	889.25	99.984
			1120.52	99.987
Sm	^{153}Sm	1.946 d	103.1806	28.4
Ta	^{182}Ta	115.0 d	67.7485	41.2
Tb	^{160}Tb	72.3 d	86.788	13.3
			298.576	26.9
Th	^{233}Pa	27.0 d	312.012	36
Zn	^{65}Zn	244.1 d	1115.518	50.75

* E. Browne, R. B. Firestone and V. S. Shirley, "Table of Radioactive Isotopes" Wiley & Sons (1986).

activities were measured by a Ge(Li) γ-ray spectrometer without any chemical treatment.

For long-lived nuclides, measuring time intervals were sometimes extended to 3 or more weeks.

Nuclear data for each nuclide selected for the determination of the respective elements are listed in Tables 2 and 3.

3. Results and discussion

Results are tabulated in Tables 4, 5 and 6 together with 1986 consensus values reported by ANDO *et al.* (1987). Each value in the tables was obtained through averaging at least three data which had been measured at different times. This procedure is necessary not only to check the reproducibility of data, but also to confirm the present measured nuclides with their half-lives. The quoted errors in the tables are the 50% confidence limits of the reproducibities. The values for Eu, Lu and Tb in JG-3 and JA-3, and Eu in JG-2, JP-1 and JF-2 are determined for the first time in this work,

Table 4. Rerults of neutron activation analyses of standard rock samples JG-2, JG-3 and JR-2.

Element	JG-2		JG-3		JR-2	
	'86 value*	This work	'86 value*	This work	'86 value*	This work
Major elements (%)						
Fe	0.64	0.71±0.03	2.61	2.54±0.06	0.60	0.60±0.04
Na	2.63	2.54±0.03	2.99	3.09±0.06	2.99	3.08±0.03
K	3.95	3.72±0.05	2.18	2.31±0.07	3.72	3.77±0.07
Mn	0.012	—	0.056	0.063±0.003	0.085	0.096±0.009
Trace elements (ppm)						
Ce	46	52±4	42	34±2	38	39±4
Co	4.5	4.2±0.1	11.4	12.4±0.3	0.4	—
Eu	—	0.093±0.009	—	0.87±0.02	0.13	0.18±0.03
Ga	19	19±2	17	20±2	18.2	22±3
La	18	21±1	22	21±1	17.5	17±1
Lu	—	—	—	0.16±0.02	0.92	—
Sc	2.0	2.64±0.03	2.1	8.93±0.09	5.4	5.61±0.07
Sm	7.1	8.4±0.2	3.8	3.6±0.2	6.2	5.9±0.2
Ta	1.9	3.6±0.2	—	—	2.4	2.7±0.1
Tb	—	—	—	0.5±0.1	1.2	—
Th	29.7	31±1	8	6.7±0.3	32.2	31±1
Zn	12.7	—	44.8	42±3	27.2	28±4

JG-2 Granite. Naegi granite (Biotite granite) Cretaceous, Hirukawa-mura, Gifu Prefecture. split 5, position 7.

JG-3 Granodiorite. Mitoya granodiorite (Hornblende-biotite granodiorite) Cretaceous-Paleogene, Mitoya-cho, Shimane Prefecture. split 3, position 11.

JR-2 Rhyolite. Wada Toge obsidian, South of Wada Toge, Shimosuwa-machi, Nagano Prefecture. split 7, position 68.

* A. ANDO *et al.*, *Geostand. Newslett.*, **11**, 159 (1987).

Table 5. Rerults of neutron activation analyses of standard rock samples JA-2, JA-3 and JP-1.

Element	JA-2		JA-3		JP-1	
	'86 value*	This work	'86 value*	This work	'86 value*	This work
Major elements (%)						
Fe	4.29	4.2±0.1	4.61	4.60±0.07	5.83	6.0±0.1
Na	2.28	2.31±0.03	2.35	2.32±0.03	0.016	—
K	1.48	1.48±0.02	1.19	1.17±0.02	0.002	—
Mn	0.085	0.083±0.007	0.0821	0.083±0.002	0.093	0.097±0.002
Trace elements (ppm)						
Ce	29	34±3	23	23±2	13	—
Co	30	28.9±0.7	21	23±1	116	125±2
Eu	0.91	0.95±0.02	—	0.88±0.02	—	0.0368±0.0005
Ga	16.4	17±3	17	17±1	0.5	—
La	16	16.6±0.9	14	9.2±0.3	3.6	6.1±0.1
Lu	0.27	—	—	0.22±0.03	—	—
Sc	19	17.8±0.2	15	20.9±0.9	7.7	7.44±0.09
Sm	3.1	3.25±0.09	3.2	3.4±0.2	—	—
Ta	0.61	0.89±0.05	—	—	<1	—
Tb	0.48	—	—	0.42±0.05	—	—
Th	4.7	5.1±0.5	5	3.4±0.1	0.18	—
Zn	62.7	62±7	67.5	66±7	29.5	47±5

JA-2 Andesite. Goshikidai sanukitoid (Olivine andesite) 13 Ma, Sakaide, Kagawa Prefecture. split 10, position 14.

JA-3 Andesite, Asama Volcano (Olivine-bearing augite-hypersthene andesite) erupted in 1783, Oni-Oshidashi, Tsumagoi-mura, Gumma Prefecture. split 10, position 3.

JP-1 Peridotite. Horoman peridotite (Dunite), Horoman, Hokkaido. split 2, position 65.

* A. Ando *et al.*, *Geostand. Newslett.*, 11, 159 (1987).

that is, they are not given in 1986 values.

The results are generally in good agreement with 1986 values, which could certify the reliability of our method.

A slight differences between our results and 1986 values which are slightly beyond our errors may be explained as follows. Each consensus value has its own error, some of which may be a quite large, while it was only written in their report that consensus values had been evaluated by calculating the mean, after eliminating results beyond $\pm 2\sigma$. Considering these facts, slight differences could be covered by their errors.

On the other hand, large differences between our data and 1986 values in Ta in JG-2, Sc in JG-3, La and Sc in JA-3, La and Zn in JP-1, and Ce, Co, Sc, Sm and Th in JF-2 cannot be attributed to the quoted errors. One possible reason for them is that γ-rays from unknown impurity nuclides in the sample could be miscounted, or the background from those impurity nuclides was not properly subtracted. The second is the inhomogeneity of the sample, especially in the case of Sc, it could be considered as a reason. A third possibility is that the consensus values may still remain preliminary

Table 6. Results of neutron activation analyses of standard rock samples JB-2, JB-3 and JF-2.

Element	JB-2		JB-3		JF-2	
	'86 value*	This work	'86 value*	This work	'86 value*	This work
Major elements (%)						
Fe	10.03	9.9±0.2	8.31	8.2±0.1	0.04	0.052±0.03
Na	1.51	1.57±0.01	2.09	2.01±0.04	1.82	1.78±0.01
K	0.36	0.368±0.006	0.66	0.66±0.03	10.87	10.4±0.1
Mn	0.15	0.17±0.01	0.12	0.14±0.01	0.0008	—
Trace elements (ppm)						
Ce	6.5	—	20.5	25±1	0.5	2.2±0.5
Co	39.8	37.5±0.7	36.3	37±1	0.4	0.81±0.03
Eu	0.85	0.90±0.03	1.3	1.35±0.03	—	0.61±0.01
Ga	17.0	19±2	20.7	21±2	18	18±2
La	2.4	—	9.1	7.9±0.3	2.6	—
Lu	0.40	—	0.38	0.27±0.03	—	—
Sc	54	54.6±0.6	35	32±2	1.0	0.11±0.02
Sm	2.3	2.0±0.4	4.3	4.3±0.2	0.2	0.47±0.08
Ta	0.2	—	0.15	—	—	—
Tb	0.62	—	0.82	0.66±0.09	—	—
Th	0.33	—	1.3	1.9±0.2	1	0.20±0.06
Zn	110	125±14	106	107±7	0.8	—

JB-2 Basalt. O-Shima Volcano (Tholeiitic basalt, Augite-bronzite basalt) erupted in 1950–1951 northern rim of Mihara crater, O-Shima, Tokyo. split 6, position 45.

JB-3 Basalt. Fuji Volcano (High alumina basalt, Hypersthene-augite-olivine basalt) erupted in 864, Aokigahara lava flow, Narusawa-mura, Yamanashi Prefecture. split 4, position 104.

JF-2 Feldspar. Kurosaka feldspar (Orthoclase), Kurosaka, Ibaraki Prefecture. split 2, position 4.

* A. ANDO *et al.*, *Geostand. Newslett.*, 11, 159 (1987).

and require further corrections.

KAMIOKA and TANAKA (1987) have very recently analyzed the content of Sc in JG-3, JA-3 and JF-2 by INAA, and obtained 8.66, 21.7 and 0.08 ppm, respectively. These results are in good agreement with ours (8.93, 20.9, and 0.11 ppm, respectively), which may certify the reliableness of mutual results. 1986 values for Sc in above rocks were obtained from the means of X-ray fluorescence (XRF) (ANDO, 1987), which may not reflect representive values of the sample. It indicates that it is necessary to collect additional data using various methods to establish these rocks as reference materials.

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References

ANDO, A., 1986. GSJ rock reference materials "Igneous rock series". *Bunseki*, **1986**: 593–594 (in Japanese).

ANDO, A., N. MITA, and S. TERASHIMA, 1987. 1986 values for fifteen GSJ rock reference samples, "Igneous rock series". *Geostandards Newslett.*, **11**: 159–166.

ANDO, A., 1987. private communication.

BROWNE, E. and R. B. FIRESTONE, and V. S. SHIRLEY, 1986. Table of radioactive isotopes, John Wiley & Sons, Inc., New York.

FLANAGAN, F. J., 1973. 1972 values for international geochemical reference samples. *Geochim. Cosmochim. Acta*, **37**: 1189–1200.

HOLDEN, N. E., R. L. MARTIN, and I. L. BARNES, 1984. Isotopic composition of the elements 1983. *Pure Appl. Chem.*, **56**: 675–694.

KAMIOKA, H. and T. TANAKA, 1987. private communication.

LEDERER, C. M. and V. S. SHIRLEY, 1978. Table of isotopes, 7th ed., John Wiley & Sons, Inc., New York.