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DETERMINATION OF RARE EARTH ELEMENTS IN GEOLOGICAL STANDARD ROCK SAMPLES BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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Rare earth elements in the standard rock samples such as GSJ JG-1, GSJ JB-1, and USGS AGV-1 have been determined simultaneously by inductively coupled plasma atomic emission spectrometry. It has been found that heavy rare earth elements in JG-1 provide lower values when it is dissolved by the acid digestion method.

The Geological Survey of Japan (GSJ) and the U. S. Geological Survey (USGS) have issued geological standard rock samples such as GSJ JG-1 (granodiorite),[1) GSJ JB-1 (basalt), and USGS AGV-1 (andesite) for the determination of chemical compositions. Analytical data for various elements in those rock samples have been compiled, and certified values have been proposed.[2,3)] Recently, however, it has been pointed out that the proposed values for heavy rare earth elements (REEs) in JG-1 are not consistent, depending on the analytical methods. The values for heavy REEs in JG-1 determined by neutron activation analysis (NAA) are about twice as much as the proposed values which were obtained by isotope dilution mass spectrometry (IDMS).[2-4)] Since the determination of REEs has been receiving more attention in geochemical study,[5)] this problem is serious.

In recent years, the analytical sensitivities of REEs have been improved by inductively coupled plasma atomic emission spectrometry (ICP-AES).[6-8)] Therefore, we have tried to perform simultaneous multielement determination of REEs in some standard rocks, where the sample digestion and chemical separation have been carried out before analysis.

Dissolution of 0.5 g rock sample was made by two methods; HF-HNO_3 acid digestion and Na_2CO_3 alkali fusion. After the decomposition, the samples were dissolved to 50 ml with 1 M HCl. This digested solution was loaded onto a 20 cm x 1 cm column of 100-200 mesh AG50W-X8 cation resin. The

Table 1. Analytical wavelengths and detection limits (in solution)

Element	Wavelength nm	DL[a)] ng/ml
La	398.8	4.4
Ce	418.7	21.2
Pr	422.2	18.7
Nd	430.3	15.0
Sm	442.2	12.4
Eu	381.9	0.8
Gd	303.2	25.6
Tb	367.6	11.6
Dy	340.7	14.2
Ho	345.6	3.4
Er	369.2	3.6
Tm	313.1	11.0
Yb	328.9	0.4
Lu	261.5	28.0

a) DL = detection limit.

Table 2. Analytical results of standard rock samples[a)]

Element	JG-1			JB-1			AGV-1		
	Found[b)]	Found[c)]	Ref. 4	Found[b)]	Found[c)]	Ref. 4	Found[b)]	Found[c)]	Ref. 11
La	20.3	19.9	22	36.7	36.1	36	34.1	35.7	35
Ce	43.6	42.9	43	63.5	63.7	67	71.6	64.9	63
Pr	4.85	4.49	2.3	6.76	6.26	8.7	7.42	7.25	7
Nd	18.8	18.1	20.6	25.3	24.6	27	32.0	30.8	39
Sm	4.36	4.38	4.5	4.90	5.04	5.16	5.63	5.93	5.9
Eu	0.66	0.65	0.69	1.54	1.51	1.5	1.56	1.60	1.7
Gd	3.82	4.42	3.9	4.85	4.73	4.80	4.62	4.64	5.5
Tb	----	----	0.63	----	----	0.47	----	----	----
Dy	3.20	4.45	3.2	3.96	3.75	4.1	3.36	3.23	3.5
Ho	0.55	0.95	0.57	0.73	0.70	0.7	----	0.55	0.6
Er	1.68	2.96	1.60	2.19	2.15	2.23	1.91	1.67	1.2
Tm	----	----	0.51	----	----	0.35	----	----	----
Yb	1.63	3.03	1.5	2.00	2.10	2.1	1.96	1.68	1.7
Lu	----	----	0.23	----	----	0.3	----	----	0.28

a) All values are in μg/g. b) Acid digestion. c) Alkali Fusion.

sample was eluted with 130 ml of 2 M HNO$_3$ solution and these eluent was discarded. The REEs on the resin were then eluted with 50 ml of 6 M HNO$_3$, and the eluent was taken in a Teflon beaker. The entire eluent was then evaporated to dryness on a hot plate. The residue was dissolved in 5 ml of 3 M HCl, in which 10 μg/ml of Cd was added as an internal standard. These procedures were carried out for both acid-digested and alkali-fused samples in the same manner. The solutions were then used for the determination of REEs by ICP-AES. Major elements (Al, Fe, Ca, Mg, Na, and K) and interfering elements (Mn, Ti, V, Be, and Th) could be removed from the sample solutions through the above procedures. If removal of Fe was insufficient, Fe was further removed from the eluted solution by solvent extraction with MIBK. The total yield was 96-98%.

The ICP emission spectrometer used in this study is a Jarrell-Ash model 975 Atom Comp MKII with some laboratory modification. The analytical wavelengths and detection limits for REEs are summarized in Table 1. The detection limits are defined as the REE concentration corresponding to three times of the standard deviation of the background emission at each wavelength. After background correction, blank subtraction and spectral interference correction were required to obtain the analytical values for the standard rock samples. All the analytical results for REEs in JG-1, JB-1, and AGV-1 are summarized in Table 2. Consequently, it has been found that the present method is suitable enough for the simultaneous multielement determination of all REEs except for Tb, Tm, and Lu. The analytical values for Tb, Tm, and Lu are prone to serious interferences with the coexisting other REEs.

The plots of the REE contents normalized to Leedey Chondrite abundance[9)] (REE pattern) for AGV-1 and JB-1 are shown in Fig. 1. Good agreement between the acid digested (black circle) and alkali-fused (black triangle) samples can be seen for both AGV-1 and JB-1, and also the present data are almost consistent with the literature values (open circle [4,11)] and open square[5)]). The REE patterns generally provide smooth curves except for Eu, which can exist as the di- and tri-valent ions.[5)] As can be seen in Fig. 1, smooth curves can be drawn from the present data.

On the other hand, the values of heavy REEs in JG-1 obtained by the different decomposition methods do not agree with each other, as can be seen in Fig. 2. The values obtained by the acid digestion are about two times larger compared to ones by the alkali fusion preparation. The present values of REEs by acid digestion are almost identical with the proposed values[10)] from GSJ, which were mainly obtained by IDMS with acid digestion treatment. On the contrary, the REEs pattern for the alkali fusion is consistent with the values obtained by NAA.[2.3)] These data suggest that heavy REEs are enriched in some minerals which can not be completely decomposed by acid digestion. JG-1 is porphric biotite granodiorite, in which zircon is usually found as an accessory mineral. As is well known, zircon ($ZrSiO_4$), which usually enriches heavy REEs,[5)] is difficult to be decomposed completely by acid digestion.[12)] According to the determination of Zr in JG-1 decomposed by two different methods,[13)] the Zr contents in JG-1 were 38 µg/g in acid digestion and 118 µg/g in alkali fusion. The recommended value of Zr in JG-1 is 111 µg/g.[10)] The difference between the analytical results for heavy REEs in JG-1 obtained by two decomposition methods may be interpreted by that between the Zr values for the corresponding decomposition methods. That is, heavy REEs provide the lower analytical values in acid digestion because of incomplete decomposition of zircon in JG-1. Consequently, it is recommended that alkali fusion should be employed as sample decomposition when a JG-1 type rock sample is analysed.

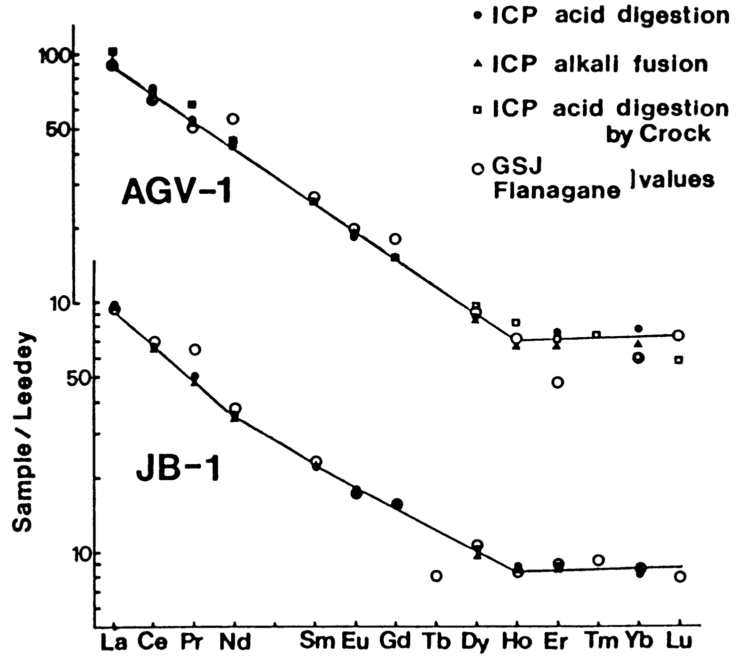

Fig. 1. Leedey-normalized REE pattern for AGV-1 and JB-1.

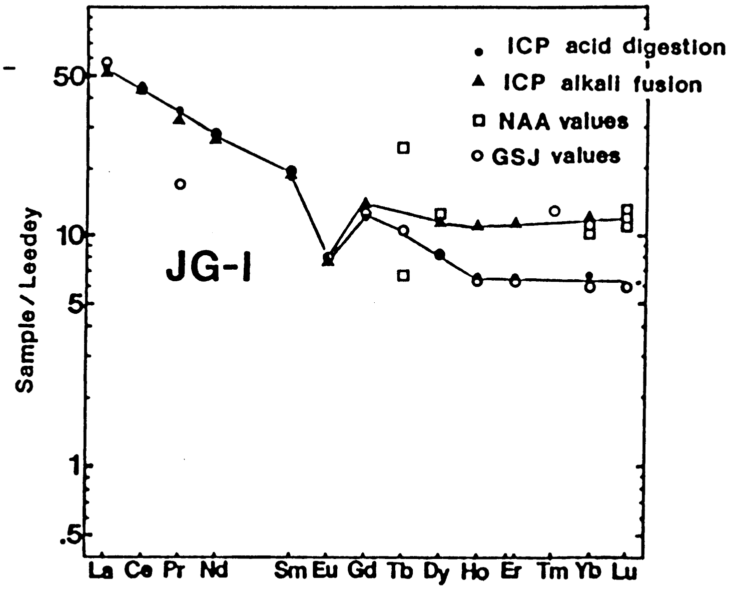

Fig. 2. Leedey-normalized REE patterns for JG-1.

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