Instrumental Neutron Activation Analysis of 13 Trace Elements in Volcanic Rocks

Instrumental Neutron Activation Analysis of
13 Trace Elements in Volcanic Rocks*

Yasuyuki MASUDA**, Shinjiro YAGI** and Tetsuji ASAYAMA**

13 trace elements; Co, Cr, Sc, Ba, Th, Hf, La, Ce, Sm, Eu, Tb, Yb and Lu in some volcanic rocks from an island arc, an oceanic island and a mid-oceanic ridge areas were detemined by a simple method of non-destructive neutron activation analysis. The abundances of Cr, Ba, Hf and rare-earth elements (REE) seem to be able to give the significant informations on the mechanism of magma generation at the above areas.

1. Introduction

Neutron activation analysis is considered to be very effective in general to analyze many metallic trace elements. Especially, the recent development of high resolution lithium-drifted germanium [Ge(Li)] γ-ray detectors and the automatic γ-ray spectrum analysis with an electronic computer have made possible to determine a number of elements simultaneously without any chemical separations, even with a small quantity of a sample[1]. Consequently, the non-destructive instrumental neutron activation analysis (INAA) with a Ge(Li) detector has been actively used for the determination of trace elements in rocks and minerals. Cobb[2] showed that the abundances of several rare-earth elements in a variety of rock types could be determined by neutron irradiation followed by Ge(Li) γ-ray spectrometry, and Gordon et al.[3] analyzed 26 elements in several standard rock samples by INAA with high volume and high resolution Ge(Li) detectors.

In this paper, it is intended to report on the simple determinations of 13 trace elements including 7 rare-earth elements in volcanic rocks, and to discuss the geochemical characteristics of some volcanic rocks from Japan, Hawaii and Mid-Atlantic Ridge.

2. Analytical Methods

About 0.1 gr of powdered rock sample, which was crushed with a tungsten carbide mortar in order to prevent contaminations, was weighed into a polyethylene vial. Neutron irradiation of samples was carried out for 1 hr or 30 min at a thermal neutron flux of about 2×10^{13} n/cm²/sec with a reference sample using the research reactor (KUR—1) of Kyoto University. Gamma-ray spectrum was measured after a suitable cooling time with a 47.3 cc Ge(Li) detector (Ortec 8011—0727) in a 20 cm thick iron-shield cave and a 4096 channel pulse height analyzer at the Radiation
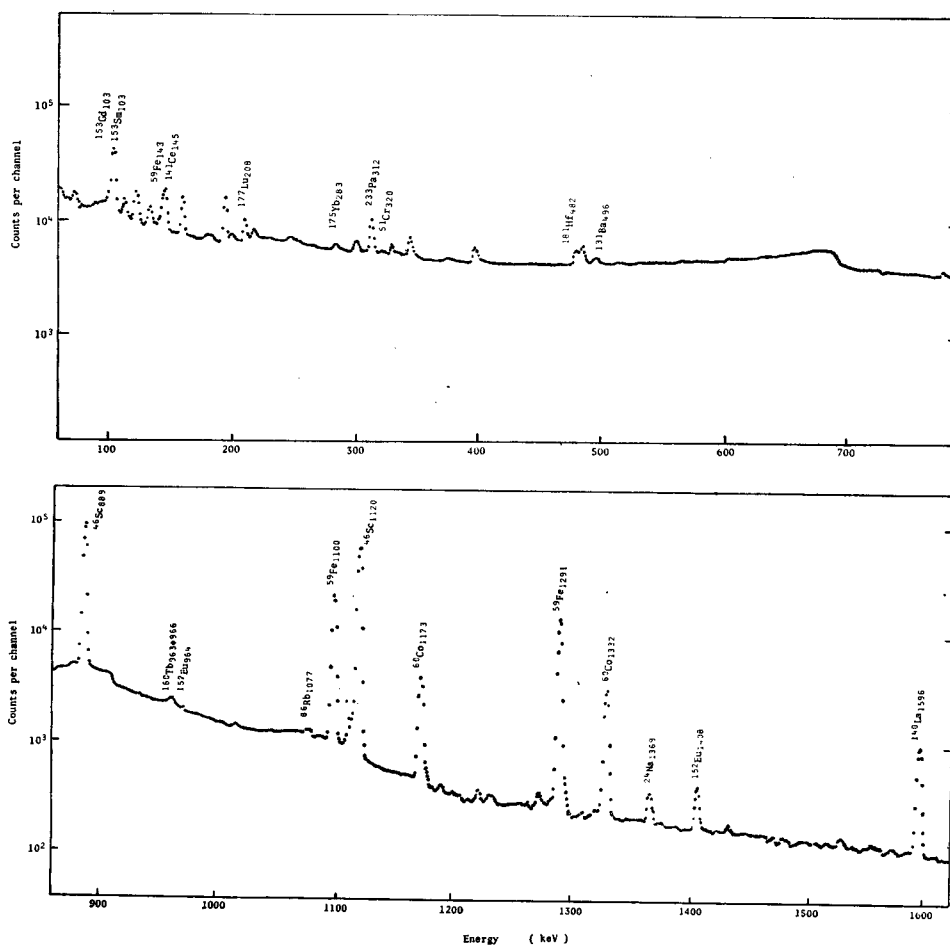
Fig. 1. Gamma-ray spectum of BCR-1. Cooling time is 15 days after irradiation.

Center of Osaka Prefecture. An example of the observed γ-ray spectrum was shown
in Fig. 1. The good resolution of the detector and the use of an electronic computer
program by Mizohata and Mamuro[4] on the calculation of photopeak areas has made
possible to determine 13 trace elements, including 7 rare-earth elements Co, Cr, Sc,
Ba, Hf, Th, La, Ce, Sm, Eu, Tb, Yb and Lu by simple procedures. The elements
analyzed are shown in Table 1, together with their nuclear properties. In the calculation
of photopeak areas, we paid attention to the following points in particular. Since the
103 keV peak of ^{153}Sm changes to that of ^{153}Gd with the lapse of time, the γ-ray
spectrum of short cooling time was used for the analysis of Sm. The peaks of 145. 4
keV of ^{141}Ce and 298. 5 keV of ^{160}Tb are overlapped by those of 142. 5 keV of ^{59}Fe
and 300. 2 keV of ^{233}Pa respectively. The influences of ^{59}Fe and ^{233}Pa for the analyses
of Ce and Tb were removed by calculating the contributions of ^{59}Fe and ^{233}Pa to the
two peaks of ^{141}Ce and ^{160}Tb from the previously measured relative intensity of the
142. 5 keV peak to the 1099. 85 keV peak of ^{59}Fe and that of the 300. 2 keV peak to

Table 1. The analyzed elements and related physical constants.

Target isotope	Isotopic abundance	Product nuclide	Cross section (barns)	Half life	Photopeak used in determination (kev)	Cooling time
[59]Co	1.0000	[60]Co	20.0	5.26y	1332.48	45d
[50]Cr	0.0431	[51]Cr	13.5	27.8d	320.07	15d
[45]Sc	1.0000	[46]Sc	12.0	83.9d	889.27	45d
[130]Ba	0.001	[131]Ba	8.8	12d	496.3	15d
[232]Th	1.0000	[233]Pa	7.4	27.0d	311.9	15d
[180]Hf	0.352	[181]Hf	10	42.5d	482.17	15d
[139]La	0.9991	[140]La	8.2	40.22h	1596.49	15d
[140]Ce	0.8848	[141]Ce	0.31	33d	145.43	15d
[152]Sm	0.2663	[153]Sm	140	47h	103.18	3–5d
[151]Eu	0.4777	[152]Eu	5900	12y	1407.9	45d
[159]Tb	1.0000	[160]Tb	22.0	72.1d	298.5	45d
[174]Yb	0.3184	[175]Yb	60	4.21d	282.6	15d
[176]Lu	0.026	[177]Lu	2100	6.7d	208.36	15d

y : years,   h : hours,   d : days

the 311.9 keV peak of [233]Pa respectively.

The elemental abundances were determined by comparison with those of the reference sample. The BCR—1 (U. S. G. S. standard rock sample) was used for the reference, thus reducing the analytical problems of the activation analysis such as the self-shielding and γ-ray self-absorption. The BCR—1 was analyzed by means of INAA combined with the standard addition method. The results are shown in Table 2. These analytical procedures were checked by analyzing the other standard rock sample (Table 2). The results seem to be reasonable comparing with the data compiled by Flanagan[5].

Table 2. Abundances of trace elements in some standard rock samples (ppm)

	BCR-1	G-2	GSP-1	AGV-1	PCC-1	JG-1	JB-1
Co	37.9	4.9	—	15.8	114	4.0	38.0
Cr	12.2	7.1	13.4	10.0	1800	58.8	420
Sc	32.1	3.4	5.6	11.4	8.0	6.3	27.4
Ba	700	1840	1220	1040	—	470	550
Hf	4.4	7.4	13.3	4.5	—	3.3	3.2
Th	6.43	25.6	112	6.5	—	13.1	9.8
La	24.1	88.6	181	38.3	—	21.0	39.1
Ce	57.7	155	419	70.2	—	43.5	67.8
Sm	6.9	6.8	24.5	5.5	—	5.1	4.5
Eu	2.17	1.44	2.54	1.62	—	0.77	1.43
Tb	1.1	0.46	1.29	0.75	—	0.82	0.71
Yb	3.4	0.72	1.3	1.5	—	2.6	1.6
Lu	0.52	0.11	0.22	0.24	—	0.40	0.33

The used reference sample must be constant in elemental abundances for any irradiations. But the elemental abundances may be different from portion to portion, even in one split of BCR—1. If it is so, the BCR—1 could not be used for the reference sample in the INAA. Table 3 shows the relative intensity of photopeak of each

Table 3. The relative intensities of γ-ray photopeaks at the irradiation times.

Nuclide	^{46}Sc	^{51}Cr	^{60}Co	^{131}Ba	^{140}La	^{141}Ce	^{153}Sm	^{152}Eu	^{160}Tb	^{175}Yb	^{177}Lu	^{181}Hf	^{233}Pa
Energy of photopeak (kev)	889.27	320.07	1173.2	496.3	1596.5	145.4	103.2	1407.9	298.5	282.6	208.4	482.2	311.9
1	3.31	0.0408	0.121	0.0718	7.661	0.395	72.45	0.0133	0.0464	0.208	0.422	0.0799	0.201
2	3.34	0.0380	0.124	0.0607	7.591	0.406	75.19	0.0118	0.0480	0.287	0.430	0.0787	0.187
3	3.29	—	0.121	0.0677	6.881	0.359	75.64	0.0090	0.0457	0.269	0.382	0.0769	0.180
4	3.26	0.0306	0.123	0.0592	7.438	0.373	76.37	0.0116	0.0412	0.309	0.419	0.0749	0.203
5	3.30	0.0397	0.129	0.0657	8.996	0.380	73.87	0.0110	0.0476	0.259	0.429	0.0775	0.207
6	3.23	0.0399	0.123	0.0639	7.447	0.427	80.50	0.0117	0.0479	0.257	0.440	0.0749	0.266
7	3.22	—	0.125	0.0662	7.495	0.439	77.52	0.0112	0.0434	0.287	0.484	0.0666	0.212
8	3.29	0.0370	0.124	0.0764	8.226	0.397	82.12	0.0122	0.0381	0.258	0.418	0.0797	0.199
9	3.35	—	0.131	0.0554	7.847	0.423	69.56	—	0.0333	0.222	0.423	0.0766	0.190
Mean	3.29	0.0377	0.125	0.0651	7.731	0.400	75.91	0.0115	0.0435	0.262	0.427	0.0762	0.205
Standard deviation	0.04	0.0034	0.003	0.0061	0.561	0.025	3.64	0.0011	0.0048	0.030	0.025	0.0038	0.023

radioactive nuclide to the 1099.85 keV peak of ^{59}Fe at the irradiation time. The intensity of photopeak at the irradiation time was calculated from the observed intensity according to the decay factor of each nuclide. If the abundance of ^{58}Fe in the BCR—1 and the efficiency of the detector are constant for every irradiation and γ-ray measurment, the relative photopeak intensity may be expected to be constant for every irradiation and measurment. As shown in Table 3, the elemental abundances of the BCR—1 were considered to be constant in the limits of error for every time of irradiation. The analytical error was about 5% for Sc and Co, and about 10% for the other elements, judging from the standard deviations shown at the bottom of Table 3.

3. Samples

26 representative basaltic rocks from an island arc area (Izu-Bonin arc, Japan), an oceanic island (Hawaii) and a mid-oceanic ridge (Mid-Atlantic Ridge) were analyzed. They are as follows.

    A.   Tholeiite, 1912, Central crater, Izu-Oshima.   OS—1.
    B.   Tholeiite, 1951, Caldera, Izu-Oshima.   OS—4.
    C.   Tholeiite, 1950, Caldera, Izu-Oshima.   OS—5.
    D.   Tholeiite, 1684, Benkene, Izu-Oshima.   OS—9.

E.   Tholeiite, 1962, Sanshichi-yama, Miyakejima.   MY—1.

F.   Tholeiite, 1835, Kasaji, Miyakejima.   MY—4.

G.   Tholeiite, 1643 or 1712, Imazaki, Miyakejima.   MY—8.

H.   Tholeiite, 1643, Shimbana, Miyakejima.   MY—9.

I.   Alkali basalt, Genbudo, Hyogo Pref.   GBS—1.

J.   Alkali basalt, Kozu-ike, Okayama Pref.   KZI—1.

K.   Alkali basalt, Une, Okayama Pref.   UNE—1.

L.   Alkali basalt, Oki-dogo, Shimane Pref.   OKI—1.

M.   Alkali basalt, Takashima, Karatsu, Saga Pref.   TSM—1.

N.   Alkali basalt, Iki island, Nagasaki Pref.   IKI—4.

O.   Tholeiite, 1868, Mauna Loa, Hawaii.   ML1868.

P.   Tholeiite, 1881, Mauna Loa, Hawaii.   ML1881.

Q.   Tholeiite, 1887, Mauna Loa, Hawaii.   ML1887.

R.   Tholeiite, 1926, Mauna Loa, Hawaii.   ML1926.

S.   Tholeiite, 1942, Mauna Loa, Hawaii.   ML1942.

T.   Tholeiite, 1950, Mauna Loa, Hawaii.   ML1950.

U.   Alkali basalt, 1800—1, Hualalai, Hawaii.   HU1800.

V.   Tholeiite, 1840, Kilauea, Hawaii.   KL1840.

W.   Tholeiite, 1921, Kilauea, Hawaii.   KL1921.

X.   Tholeiite, 1955, Kilauea, Hawaii.   KL1955.

Y.   Tholeiite, 1959, Kilauea, Hawaii.   KL1959.

Z.   Abyssal tholeiite, the Mid-Atlantic Ridge near 30°N Latitude, A150—RD7—II (Miyashiro et al.[6]).

4. Results and Discussion

The analytical results are presented in Table 4 and the abundances of rare-earth elements (REE) are shown in Fig. 2, normalizing to those of chondrites. The characteristics of the trace element concentrations in the volcanic rocks are summarized as follows.

(1)   Cr content in the island arc tholeiites from Izu-Oshima and Miyakejima is lower than that of Hawaiian tholeiites, abyssal tholeiite and alkali basalts.

(2)   Ba, Th and Hf contents in the abyssal tholeiite from Mid-Atlantic Ridge and Hawaiian tholeiites are fairly low, while those of alkali basalts from southwest Japan and a Hawaiian alkali basalt are high. The island arc tholeiites are higher in Ba, Th and Hf contents than the abyssal tholeiite.

(3)   La content in the island arc tholeiites and the abyssal tholeiite is considerably low, while that in the alkali basalts is very high and the Hawaiian tholeiites have intermediate content of La. It may be of significance that the abundances of La vary by more than the order of magnitude in the class of rocks designated as tholeiite.

(4)   As shown in Fig. 2, the abyssal tholeiite and the island arc tholeiites are characterized by a depletion of lighter REE (La to Eu) and by no or small Eu

anomalies. Hawaiian tholeiites are characterized by an increasing enrichment of REE with decreasing atomic number and by no Eu anomalies. While the alkali basalts from southwest Japan are characterized by the extreme enrichment of lighter REE and the decrease of REE abundances with increasing atomic number.

Table 4-1. Analytical data of 13 trace elememts in the tholeiites from
Oshima and Miyakejima islands of Izu-Bonin arc.

Sample	A	B Izu-Oshima Tholeiite	C	D		E	F Miyakejima Tholeiite	G	H	
	OS-1	OS-4	OS-5	OS-9	Mean	MY-1	MY-4	MY-8	MY-9	Mean
Co	38.3	41.9	38.7	41.2	40.0	37.9	31.0	33.8	35.7	34.6
Cr	24.0	27.1	30.1	19.9	25.3	41.6	106	27.0	80.9	63.9
Sc	53.2	54.9	54.1	54.8	54.3	43.9	42.2	43.5	47.8	44.4
Ba	236	274	208	220	—	165	390	242	253	—
Th	0.41	0.47	0.37	—	0.43	—	—	0.48	—	—
Hf	1.4	—	1.2	1.0	1.2	—	1.3	1.9	1.6	1.6
La	1.9	2.5	2.4	3.3	2.5	2.6	2.7	3.3	2.7	2.8
Ce	9.0	8.8	7.5	9.4	8.7	14.4	11.9	11.5	13.4	12.8
Sm	2.4	2.5	2.6	2.2	2.4	2.9	3.4	3.5	3.1	3.2
Eu	0.90	1.11	0.87	1.03	0.98	1.23	1.24	1.12	1.09	1.17
Tb	0.62	0.86	0.70	—	0.73	0.77	—	0.84	—	—
Yb	2.97	3.59	3.33	3.61	3.38	3.34	3.26	3.51	3.52	3.41
Lu	0.56	0.44	0.43	0.43	0.47	0.53	0.54	0.61	0.46	0.54
La/Yb	0.64	0.70	0.72	0.91	0.74	0.78	0.83	0.94	0.77	0.83

Table 4-2. Analytical data of 13 trace elements in the alkali basalts
from southwest Japan.

Sample	I	J	K Southwest Japan Alkali basalt	L	M	N	
	GBS-1	KZI-1	UNE-1	OKI-1	TSM-1	IKI-4	Mean
Co	34.5	52.1	53.2	53.8	39.5	36.2	44.9
Cr	99	253	303	430	192	25	217
Sc	22.0	27.8	29.6	17.6	21.2	24.5	23.8
Ba	830	409	600	444	566	628	579
Th	5.3	5.3	8.4	3.5	4.8	6.5	5.6
Hf	4.6	3.3	3.9	3.0	4.0	5.7	4.1
La	44.6	35.0	40.5	24.7	27.1	38.0	35.0
Ce	118	91.4	96.4	46.1	73.7	61.9	81.3
Sm	7.8	7.6	6.4	5.0	5.9	7.8	6.8
Eu	2.48	2.54	2.70	1.77	1.72	2.80	2.34
Tb	1.03	1.00	1.30	0.89	0.36	0.85	0.91
Yb	2.89	2.39	2.96	0.91	0.96	2.53	2.11
Lu	0.33	0.37	0.38	0.23	0.32	0.41	0.34
La/Yb	15.4	14.6	13.7	27.1	28.2	15.0	19.0

Table 4-3. Analytical data of 13 trace elements in the tholeiites from
Mauna Loa volcano, Hawaii.

Sample	O ML1868	P ML1881	Q ML1887	R ML1926	S ML1942	T ML1950	Mean
			Mauna Loa, Hawaii Tholeiite				
Co	59. 3	49. 9	105	51. 1	48. 5	54. 6	61. 4
Cr	397	275	1122	287	234	314	438
Sc	31. 3	33. 6	23. 5	33. 1	33. 9	30. 9	31. 1
Ba	116	98	99	141	166	255	146
Th	0. 44	0. 64	0. 54	0. 54	0. 57	0. 52	0. 54
Hf	1. 80	2. 48	2. 52	3. 69	2. 81	2. 50	2. 63
La	8. 0	9. 1	6. 1	9. 5	8. 2	7. 9	8. 1
Ce	30. 6	28. 8	24. 5	30. 1	27. 8	27. 1	28. 2
Sm	5. 4	5. 6	3. 9	5. 5	5. 7	5. 0	5. 2
Eu	1. 88	1. 89	1. 15	1. 92	1. 89	1. 65	1. 73
Tb	0. 75	0. 85	0. 54	0. 97	0. 96	0. 89	0. 83
Yb	2. 07	2. 26	1. 67	2. 74	2. 62	2. 60	2. 33
Lu	0. 35	0. 35	0. 23	0. 31	0. 34	0. 31	0. 32
La/Yb	3. 86	4. 03	3. 65	3. 47	3. 13	3. 04	3. 53

Table 4-4. Analytical data of 13 trace elements in the alkali basalt and
tholeiites from Hualalai and Kilauea volcanoes, Hawaii and
in the abyssal basalt from Mid-Atlantic Ridge.

Sample	U Hualalai, Alkali basalt HL1800	V KL1840	W KL1921	X KL1955	Y KL1959	Mean	Z Mid-Atlantic Ridge Abyssal basalt A150-RD7-II
			Kilauea, Hawaii Tholeiite				
Co	68. 0	99. 5	56. 7	47. 0	76. 9	70. 0	41. 7
Cr	284	931	406	56	766	540	282
Sc	30. 3	25. 3	37. 8	33. 0	32. 3	32. 1	36. 7
Ba	396	145	198	309	111	191	50
Th	2. 35	0. 52	1. 24	2. 27	1. 26	1. 32	0. 52
Hf	4. 6	2. 8	4. 3	7. 8	4. 1	4. 8	2. 7
La	21. 3	7. 8	15. 5	27. 6	14. 6	16. 4	2. 6
Ce	63. 3	31. 1	45. 5	72. 7	49. 8	49. 8	9. 7
Sm	7. 3	4. 6	7. 1	11. 8	6. 8	7. 6	4. 0
Eu	2. 42	1. 50	2. 67	3. 73	2. 20	2. 53	1. 35
Tb	0. 93	0. 72	1. 1	1. 7	0. 8	1. 1	1. 0
Yb	2. 64	1. 65	2. 39	5. 30	2. 01	2. 84	4. 77
Lu	0. 44	0. 24	0. 36	0. 62	0. 29	0. 38	0. 63
La/Yb	8. 1	4. 7	6. 5	5. 2	7. 3	5. 9	0. 55

The above features of trace element concentrations coincide as a whole with the
data reported by Jakes and Gill[7], Jakes and White[8] and others, except that the Ba
content in the island arc tholeiites (208 to 390 ppm) is higher than the values (50 to

150 ppm) reported by Jakes and Gill.[7]

The chemical properties of REE are similar to each other, but vary quite systematically with atomic number. Therefore, the differences in relative distributions of REE in rocks and minerals may serve as indicators of differences in the conditions of the generation of the rocks and minerals. Accordingly, the degree of fractionation
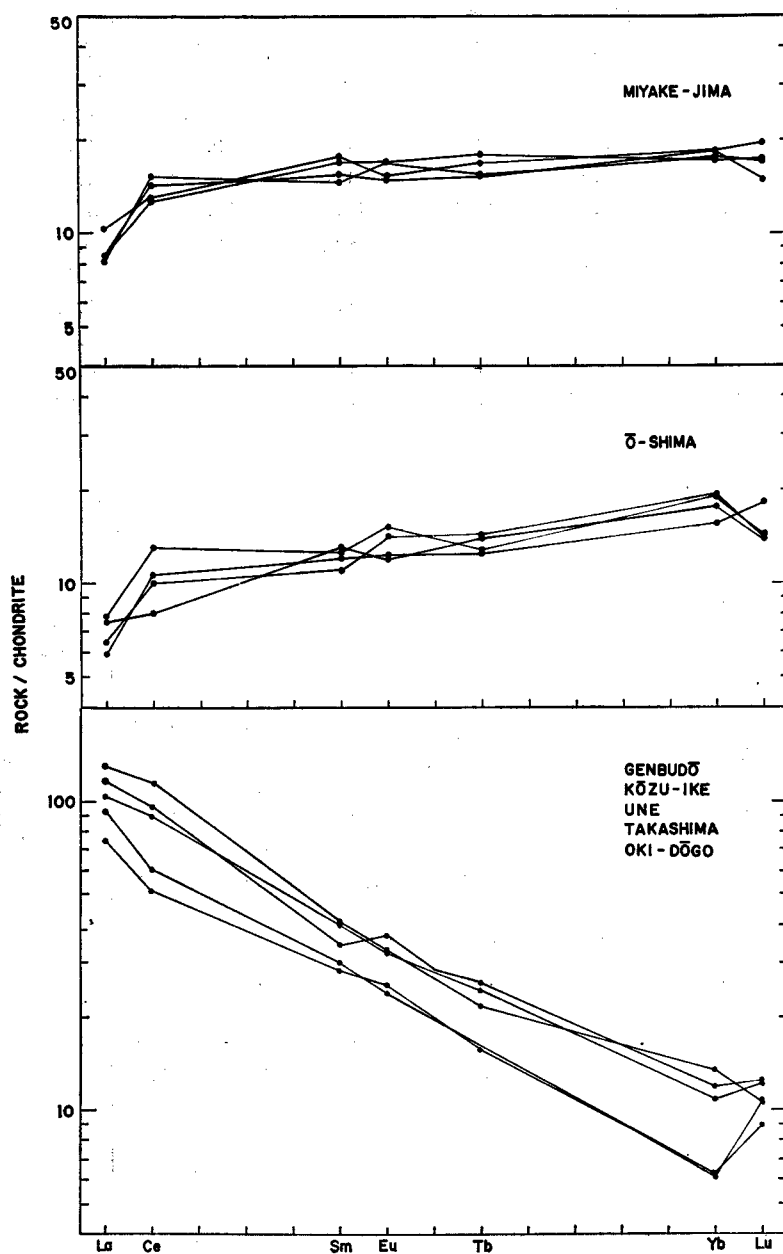

Fig. 2-1. Chondrite-normalized pattern of REE for the tholeiites from Oshima
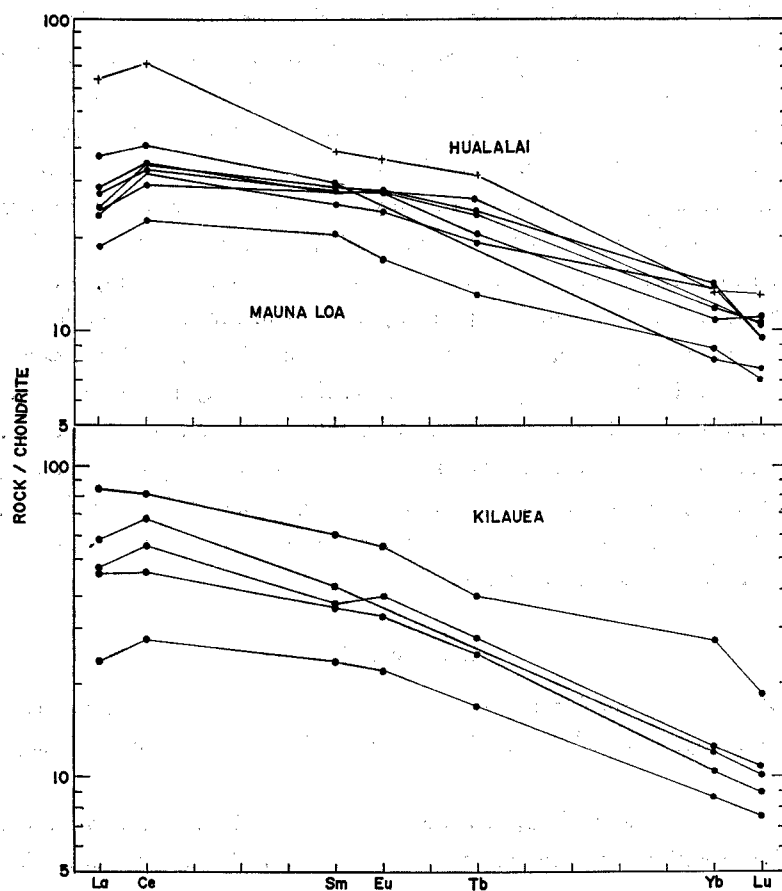and Miyakejima islands and the alkali basalts from southwest Japan.

Fig. 2-2. Chondrite-normalized pattern of REE for the rocks from Hawaii.
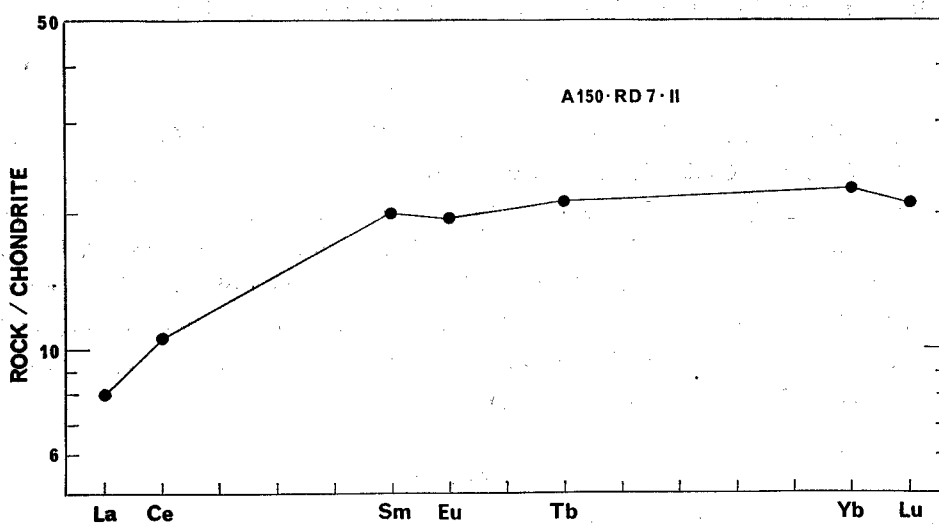
Fig. 2-3. Chondrite-normalized pattern of REE for the abyssal tholeiite from Mid-Atlantic Ridge.

of lighter REE relative to heavier ones and the occurrence of Eu anomalies are essentially important for the geochemistry of REE. The concentrations of REE in volcanic rocks are considered to relate to (1) the degree of partial melting, (2) the phase equilibrium relations between liquid and solid residue and (3) the composition of the upper mantle. Assuming that the concentrations of REE are largely due to the degree of partial melting, the abyssal tholeiite and the island arc tholeiites become to be formed by a higher degree of partial melting than the Hawaiian tholeiites, because the lighter REE tend to concentrate easily to liquid.

Though the abyssal tholeiite is probably formed under the extensional conditions in the mid-oceanic ridge area, and the island arc tholeiite is under the compressional conditions in the island arc area, the both tholeiites may be formed in the similar conditions with each other from the view point of the low concentrations of REE. Miyashiro[9] indicated that the island arc tholeiite occurred characteristically in the high rate area of plate convergence, such as Tonga, Izu-Bonin, Northeast Japan and Kurile-Kamchatka arcs. This fact may be greatly concerned to the conditions of the magma generation in island arc areas.

5. Conclusion

(1) The non-destructive instrumental neutron activation analysis (INAA) can be used for the analyses of 13 trace elements in volcanic rocks only through a simple procedure.

(2) The abundances of Cr, Ba, Th, Hf and REE in volcanic rocks can give the significant informations concerning to the mechanism of magma generation in island arc areas, mid-oceanic ridges and the other orogenic areas.

(3) The tholeiite occurred in island arc areas may be formed under similar conditions to the abyssal tholeiite by high degree of partial melting.

Acknowledgements

References

1) J. R. Devoe (ed.), Modern Trend in Activation Analysis, vol.1 and2, Nat. Bur. Stand. (U. S.), Spec. Publ. 312 (1969).
2) J. C. Cobb, Anal. Chem., **39**, 127 (1967).

3) G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley, Geochim. Cosmochim. Acta, **32**, 369 (1968).
4) A. Mizohata and T. Mamuro, Ann. Rept. Rad. Cent. Osaka Pref., **11**, 29 (1970).
5) F. J. Flanagan, Geochim. Cosmochim. Acta, **33**, 81 (1969).
6) A. Miyashiro, F. Shido and M. Ewing, Contr. Mineral. Petrol., **23**, 38 (1969).
7) P. Jakes and J. Gill, Earth Planet. Sci. Lett., **9**, 17 (1970)
8) P. Jakes and A. J. R. White Geol. Soc. Amer. Bull., **83**, 29 (1972).
9) A. Miyashiro, Amer. J. Sci., **272**, 629 (1972).