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Trace Elements in the Ibaragi Granitic Complex, Osaka Prefecture, Japan - II.

Yasuyuki MASUDA*, Shinjiro YAGI* and Tetsuji ASAYAMA*

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Abstract

10 trace elements; Co, Cr, Sc, Rb, Cs, Ba, Hf, Th, U and Ra, have been determined on the rocks and the separated minerals from the Ibaragi granitic complex. The distribution of these elements in the complex is qualitatively understood by fractional crystallization. Cs is deficient in amount at the later stage of the fractionation, and is supposed to be removed from the rocks to a gaseous phase or hydrothermal water. U is in radioactive equilibrium with Ra in the complex.

1. Introduction

The Ibaragi granitic complex is a 96–76 million years old granitic body[1] located in the northern part of Osaka Prefecture, Japan, and is intruded into the Palaeozoic formations of Tanba zone. Petrography, petrochemistry, K-Ar dating, Rb-Sr isotopic study, rare-earth geochemistry and oxygen isotopic study of the complex have been reported by Tainosho[2], Shibata[3], Ishizaka[1], Masuda et al.[4] and Matsuhisa et al.[5] The granitic complex is principally composed of granodiorite with a smaller amount of quartz diorite and adamellite. The petrographical and the geochemical data suggest that the complex was derived sequentially by fractional crystallization of a parental dioritic magma. It is the purpose of this study to present and discuss the distribution of certain trace elements in the complex in order to understand more adequately the geochemical processes in the granitic complex.

The same fresh 11 whole rock samples and 12 mineral separates as those analyzed for 7 rare-earth elements by Masuda et al.[4] were used for the analyses of 10 trace elements in this work. The sample locations and descriptions have already been described by Masuda et al.[4].

2. Analytical

Na and K were determined by flame photometry, Mg, Ca and ΣFe by EDTA titration method, and U and Ra were analyzed by fluorometric spectrometry (Yagi and Asayama[6]) and Radon method (Nishimura[7]), respectively. Instrumental neutron activation analysis (INAA) was utilized for the determination of the other trace elements (Masuda et al.[8]). Neutron irradiation was carried out for 1 hr or

* Department of Geological Sciences, Faculty of Liberal Arts and Sciences.

30 min in the KUR reactor of Kyoto University at a thermal neutron flux of $2 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot sec^{-1}$. A modified point of the INAA for Rb and Cs analyses is the use of JG–1 instead of BCR–1 as a reference sample, although BCR–1 was used as a reference for the other elements as usual. The produced ^{86}Rb by irradiation was counted 7–10 days after irradiation along with the other produced nuclides, and ^{134}Cs one month after by Ge(Li) detector system using a 4096 channel analyzer at the Radiation Center of Osaka Prefecture. The photopeak energies used for analyses of Rb and Cs are 1077 keV and 796 keV, respectively. 186 ppm and 10.1 ppm were adopted as contents of Rb and Cs in JG–1, respectively (Ando et al.[9]). The analytical procedure for Rb was interchecked by isotope dilution method on the other samples of Nohi rhyolite reported by Okamoto et al.[10] (Fig. 1). The homogeneity of Cs content in the sample powder of JG–1 was verified by calculating the relative

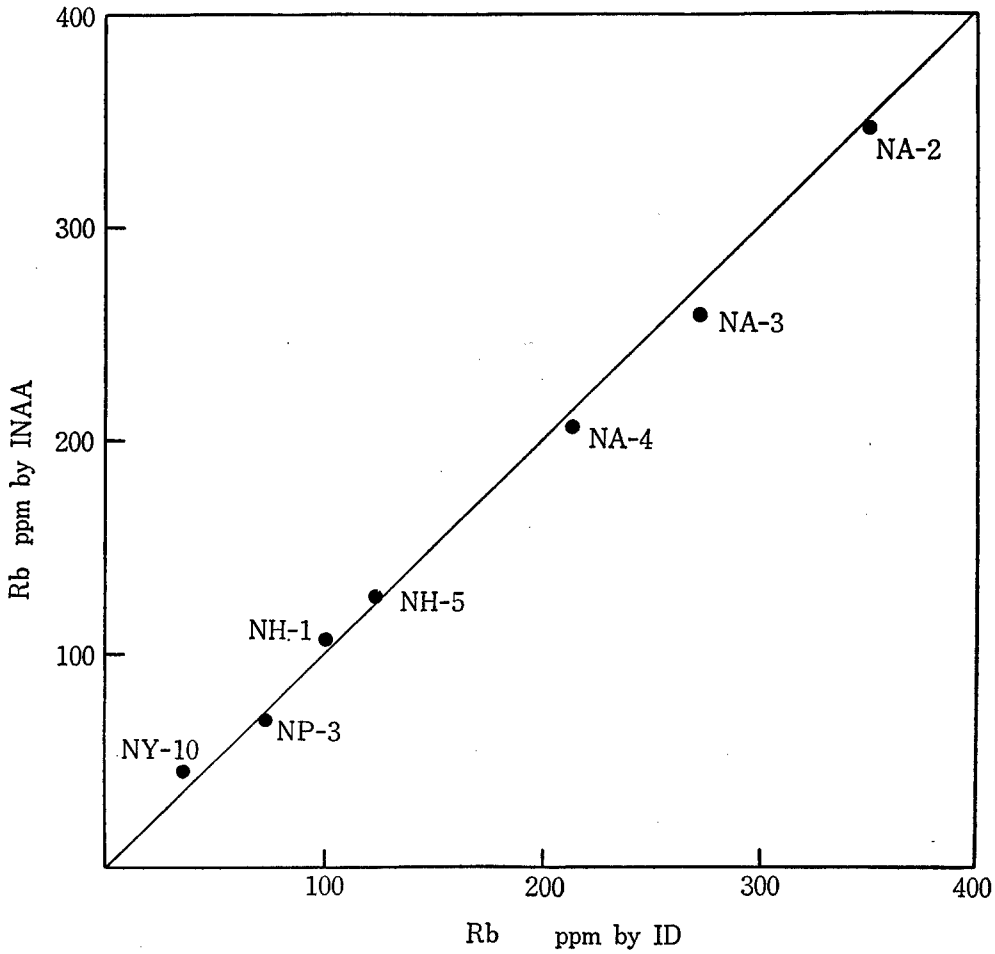

Fig. 1. Relation between the results of Rb content determined by isotope dilution method (ID) and instrumental neutron activation analysis (INAA) on the Nohi rhyolites.

Table 1. The relative intensity of ^{134}Cs to ^{59}Fe at the irradiation time.

Nuclide	^{134}Cs
Energy of Photopeak	795.8 keV
Irradiation 1	0.386
2	0.398
3	0.417
4	0.389
5	0.407
Mean	0.400
σ	0.011

σ: standard deviation.

intensity of ^{134}Cs to ^{59}Fe at the irradiation time, by the same way as reported by Masuda et al.[8] (Table 1). The analytical method of Cs was also checked by analyzing the standard samples. The results are as follows; G–2 : 1.2 ppm, BCR–1: 1.0 ppm, AGV–1 : 1.1 ppm. The analytical error may be less than 5% for major elements, Co and Sc, and 10% for the other elements.

3. Results and Discussion

The analytical results of all samples are tabulated in Tables 2 and 3. Average contents of the trace elements in the six quartz diorites are also shown in Table 3, and they are nearly equal to or a little higher than those of the andesites from the Quaternary volcanoes of Hokkaido (Masuda et al.[11]). Content of each trace element in whole rock samples is plotted as a function of SI in Fig. 2. The SI in the figure is conveniently used as an index of degree of fractionation of the magma. In granitic rocks, whole rock samples are generally mixtures of the minerals crystallized at an earlier stage (cumulative phase) and the materials filling up the space

Table 2. Chemical composition of major elements in whole rock samples from the Ibaragi granitic complex. (weight %)

	NSP–1	NSP–2	NSP–3	KI–4	NSP–4	NSP–5	NSP–6	NSP–7	NSP–8	KI–5	NSP–10
SiO_2	52.59	52.80	53.80	55.09	55.60	55.73	66.00	66.67	66.73	71.62	76.83
Na	2.09	1.82	2.05	2.10	2.09	2.08	2.08	1.99	2.03	1.93	1.89
K	1.18	1.94	0.83	1.59	1.63	1.50	3.25	3.60	2.88	4.77	4.88
Mg	3.24	3.26	2.83	2.50	2.39	2.59	1.02	1.00	0.94	0.43	0.03
Ca	4.71	4.40	5.24	—	5.39	4.79	2.61	2.35	2.67	—	1.89
ΣFe	6.22	6.46	6.49	6.56	6.20	5.78	3.20	3.17	3.05	2.06	0.97
SI	25.5	24.2	23.2	19.6	19.4	21.7	10.7	10.2	10.6	4.7	0.4

$$SI = \frac{Mg}{Mg+\Sigma Fe+Na+K}$$

— : not determined

Table 3. Trace element concentrations in whole rock and mineral samples from the Ibaragi granitic complex.

		Co	Cr	Sc	Rb	Cs	Ba	Hf	Th	U	Ra	eqU	Th/U
Quartz diorite													
NSP-1	WR	27.7	58	29.3	60	3.9	525	2.9	7.6	1.4	0.54	1.5	5.5
NSP-2	WR	27.0	92	28.0	104	3.6	462	2.2	5.7	1.4	0.61	1.7	4.1
NSP-3	WR	24.8	65	28.5	37	2.0	—	1.9	7.2	2.0	0.64	1.8	3.6
KI-4	WR	24.8	75	29.5	69	3.6	469	4.2	6.4	—	—		
NSP-4	WR	22.7	56	28.7	77	3.8	537	4.7	7.3	1.7	0.72	2.0	4.2
	Ho	46.3	159	130	49	1.1	198	1.8	16.2	—	—		
	Bi	53.7	204	25.6	792	10.8	1230	2.4	5.0	—	—		
NSP-5	WR	21.4	60	26.1	78	4.6	387	3.8	10.9	2.4	0.95	2.7	4.6
	Bi	66.8	252	24.1	1300	23.3	1060	0.6	1.9	—	—		
Average of quartz diorite WR		24.7	68	28.4	71	3.6	476	3.3	7.5	1.8	0.69	2.0	4.4
Granodiorite													
NSP-6	WR	8.8	24	12.7	196	7.8	510	5.8	20.1	6.1	1.93	5.5	3.3
	Ho	10.5	50	43.4	67	0.7	163	0.5	76.2	6.7	—		11.4
	Bi	61.2	135	18.4	3200	24.2	500	17.9	16.5	2.8	—		5.9
	Kf	2.5	5	0.1	1050	1.3	550	0.2	3.5	—	—		
NSP-7	WR	5.8	15	8.0	242	7.6	649	5.8	24.9	7.9	3.19	9.1	3.1
	Ho	37.0	161	226	159	1.8	258	6.2	33.7	4.4	—		7.7
	Bi	59.3	130	23.0	3580	35.3	449	8.8	5.0	3.2	—		1.7
	Kf	3.1	3	0.2	1470	2.0	1071	0.3	1.1	—	—		
NSP-8	WR	9.0	22	12.0	167	6.1	525	5.9	26.9	4.9	1.91	5.4	5.5
	Ho	37.6	196	163	100	1.6	401	8.9	14.5	4.3	—		3.4
	Bi	57.9	133	20.7	2688	18.4	354	17.6	5.2	3.3	—		1.6
	Kf	3.3	3	0.2	980	3.2	749	0.7	2.9	—	—		
Adamellite													
KI-5	WR	4.9	10	6.1	316	13.2	715	7.3	38.7	10.0	—		3.9
Aplite													
NSP-10	WR	1.8	3	1.4	255	5.7	180	5.1	47.0	10.1	3.30	9.4	4.7

Ra is expressed in $\mu\mu$g/g, other elements are in ppm. WR=whole rock, Ho=hornblende, Bi=biotite, Kf=potassium feldspar. eqU=equivalent content of uranium calculated from Ra content. —=not determined.

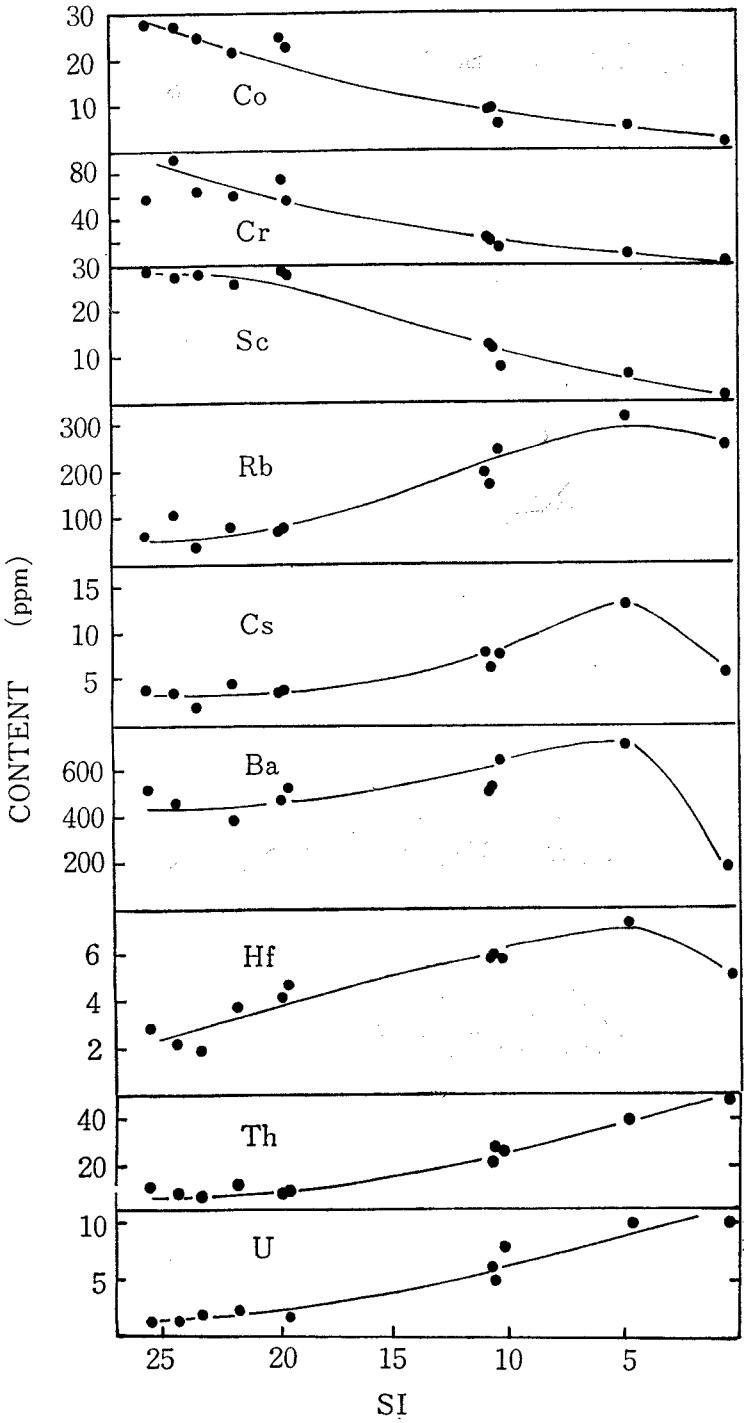

Fig. 2. Variation diagram of 9 trace elements in the Ibaragi granitic complex. SI: solidification index.

between the minerals (intercumulus liquid), and therefore they are not so supposed to represent the residual liquid like as groundmasses of volcanic rocks are. Nevertheless, we take no account of crystal settling and floating as well as contamination and autometasomatism of granitic rocks in this paper, assuming that the various rock types in the granitic complex were derived by a simple equilibrium fractionation during crystallization differentiation.

Cobalt, Chromium and Scandium

As shown in Fig. 2, the contents of Co, Cr and Sc tend to gradually decrease as the rocks become more acid. It may be caused by precipitation of mafic minerals of hornblende and biotite mainly, which have generally higher contents of these elements. The distribution of these trace elements between coexisting biotite and hornblende is shown in Fig. 3 for 4 pairs of samples from the complex. Although the number of data is few, Sc seems clearly to be more concentrated into hornblende preferentially than biotite as reported by Tilling et al.[12]. This is possibly due to the fact that Sc is substituted mainly for Ca in these minerals, considering that the Ca content in biotite is smaller than in hornblende. From these facts a somewhat slow decrease of Sc ,compared with Co and Cr, found in the early stage of fractionation is considered to be an effect of crystallization of biotite. The distribution of Sc in igneous rocks has been studied and discussed by numerous investigaters (Wager and Mitchell[13]; Wilkinson[14]; Greenland and Lovering[15]; Snyder[16]; Sen et al.[17]; Fryklund and Fleischer[18]; Norman and Haskin[19]). However, still controversy exists on a relationship between Sc and some major elements such as Fe^{++}, Mg and Ca in igneous rocks. For the Ibaragi granitic complex a linear relation of Sc content to ΣFe content is observed and seems to support the suggestions by

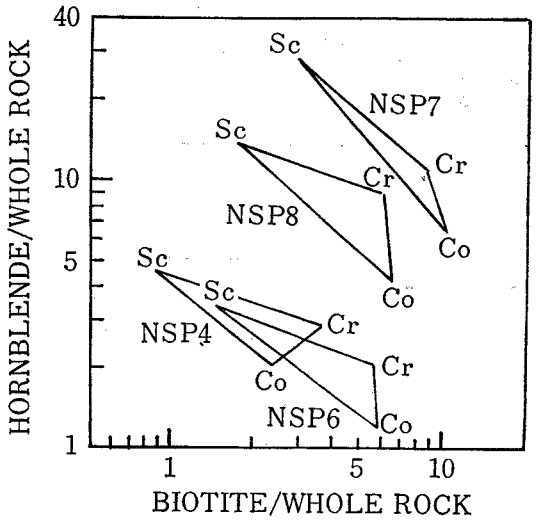

Fig. 3. Distribution of Co, Cr and Sc between coexisting biotite and hornblende from the Ibaragi granitic complex.

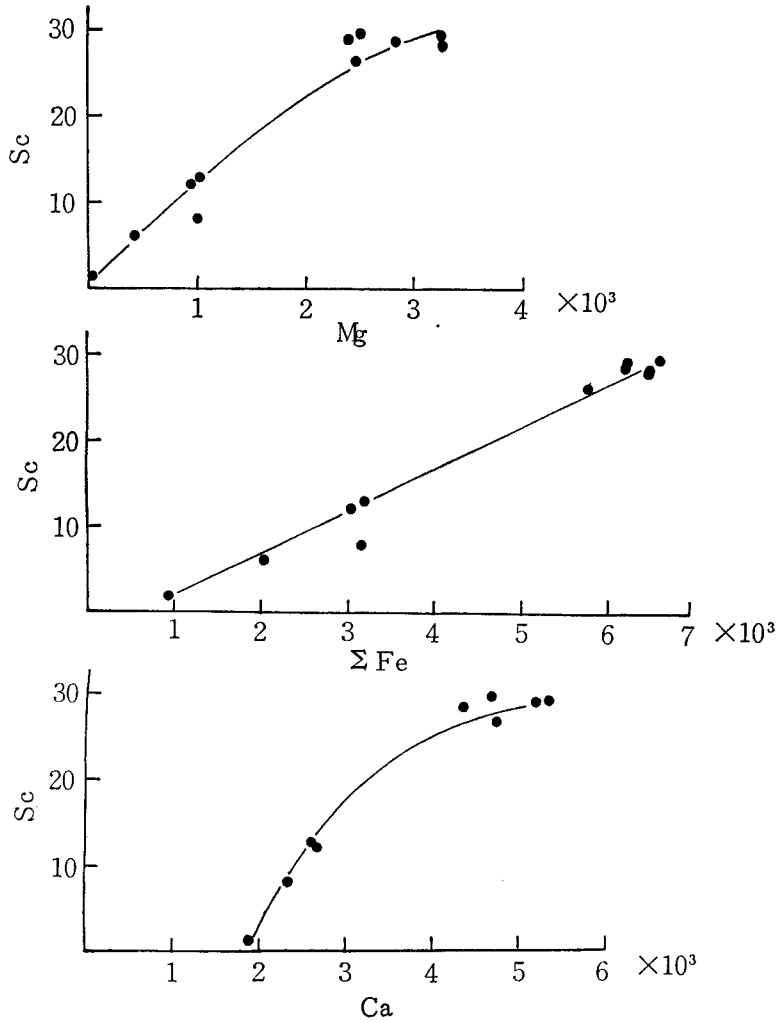

Fig. 4. Relation between Sc content and Mg, ΣFe and Ca contents in ppm.

Wilkinson[14] that Sc is captured by Fe^{++} as a whole as shown in Fig. 4.

Rubidium, Cesium, Barium, Hafnium, Thorium, Uranium and Radium

The other trace elements tend to generally increase in content with proceeding of the fractionation. However, Rb, Cs, Ba, Th and U seem not to increase so much at the early stage of fractionation, while Hf shows only a rapid increase in content. Such a difference between the behaviors of these elements is possibly caused by the fact that Hf dose not enter particularly into any minerals in comparison with the other elements. At the latest stage of fractionation, Rb, Cs, Ba and Hf contents suddenly decrease as seen in the aplite (NSP–10). This is as well probably due to a decrease of modal abundance of biotite, in which these elements concentrate with a large quantity. Hf has become also to be fairly contained in biotite at the later stage as shown in Table 3.

K/Rb and Rb/Cs ratios

The K/Rb ratio of quartz diorite is 207 in average, and tends to decrease with fractionation as reported by Ishizaka[1], although he reported a value of 217 as an average ratio. Rb/Cs ratio of the same rock is 19.9 in average, and tends to increase in contrast with the K/Rb ratio during fractionation as shown in Fig. 5. This is opposite to the predicted trend for Cs (Heier and Adams[20]). Cs ($r = 1.67$ Å) with ionic radius larger than Rb ($r = 1.47$ A) is to be more enriched than Rb in the late-stage differentiates. This is also expected from the fact that every Rb/Cs ratio in the major constituent minerals such as hornblende, biotite and K-feldspar is higher than the ratio in the whole rock as shown in Fig. 5. Consequently, the Rb/Cs ratio is to decrease in the residual melt with fractional crystallization of the minerals. Therefore, the deficiency of Cs observed in granodiorite, adamelite and aplite of the complex must be concluded to be attributable to any other mechanisms, such as the migration of the element along with a gaseous phase or hydrothermal water, than fractional crystallization. The possibility of migration or exchange of trace elements has been suggested on the rare-earth elements[4] and the oxygen isotopic ratio[5] in the present complex. Cs is possibly leached away from the rocks by hydrothermal water or meteoric water, judging from the higher solubility of Cs in water and the considerable deficiency of the element observed in the Precambrian granitic rocks reported by Condie and Lo[21] on Louis Lake batholith. Thus, an abnormal distribution of Rb and Cs is a very important problem in geochemistry, because the behavior of these elements is often used as an indicator of the degree

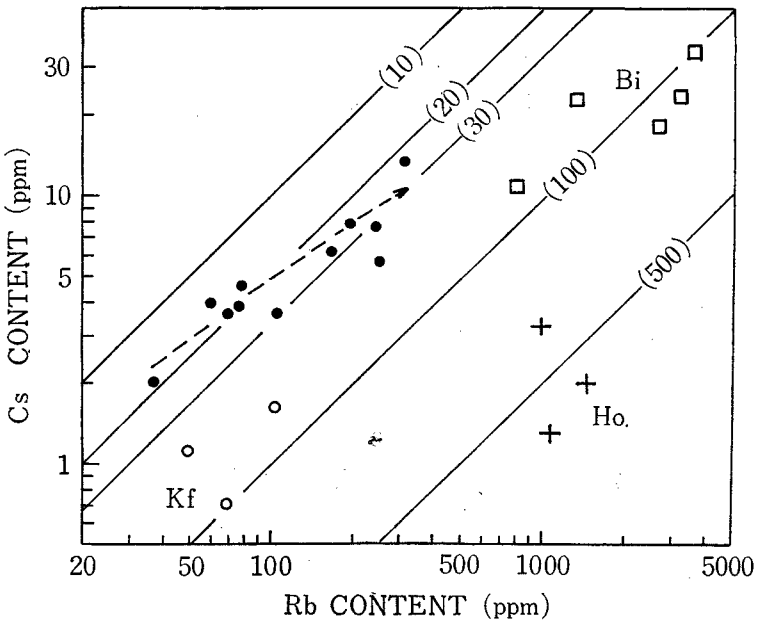

Fig. 5. Log—log plot of Rb and Cs contents in the whole rocks (●), biotite (□), hornblende (+) and potassium feldspar (○) from the Ibaragi granitic complex.

of fractionation of a magma[10].

Th/U ratio

The Th/U ratio seems to increase slightly from quartz diorite to adamellite as the contents of U and Th increase. A number of discussions have been made on the variations of Th/U ratio in igneous rocks for differentiated sequences such as Tasmanian dolerites and Duluth intrusive rocks (Heier and Rogers[22] and Heier et al.[23]), and the variation of Th/U ratio is suggested to be concerned with an oxygen partial pressure of a magma during magmatic differentiation. If the segregated minerals in fractionation have a very low partition coefficient for Th or U to the silicate melt from which the minerals crystallize, the Th/U ratio may be kept constant in the residual magma during fractional crystallization by the same reason as discussed on Rb/Cs ratio by Okamoto et al.[10], and under this condition a change in the ratio may be owing to the variation of physical conditions of the magma such as an oxygen pressure of the magma. In the present granitic complex, however, the change of the Th/U ratio is caused not only by such a physical condition but also by the mineral assemblage segregated, since the hornblende and biotite, which have higher partition coefficients for U and Th as expected from the present analytical data, were crystallyzed in the complex.

Radioactive equilibrium between Uranium and Thorium

Ra and U are expected to be in radioactive equilibrium, if they are in a closed system for 10^4 yr at least, since ^{226}Ra, whose half life is 1622 yr, is a daughter element of ^{238}U, and in this case the equivalent quantity of U (^{eq}U) calculated from the Ra

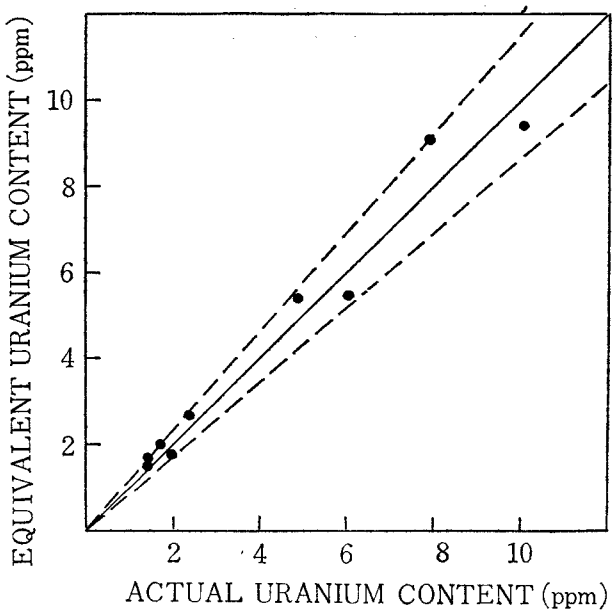

Fig. 6. Relation between the actual uranium content and the equivalent uranium content for the whole rock samples from the Ibaragi granitic complex.

content must be equal to the actual U content in rocks. The relationship between ^{eq}U and U in the present whole rocks is illustlated in Fig. 6, where the solid straight line represents the equilibrium line and the broken lines enclose all the points deviating less than ± 15 percent from the solid straight line. In the figure, the plotted points based on the data seem to somewhat deviate from the equilibrium line. However, taking it into consideration the fact that a deviation of 15% or so from equilibrium is often observed even in rocks which are in radioactive equilibrium as pointed out by Yagi and Asayama[6], U and Ra in the complex may be conceivable to be in radioactive euilibrium from the present results. Ra is not so movable in rocks under the usual geochemical conditions.

4. Conclusion

1. 10 trace elements: Co, Cr, Sc, Rb, Cs, Ba, Hf, Th, U and Ra have been determined on the rocks and the separated minerals from the Ibaragi granitic complex. The behavior and the distribution of these elements are understood by fractional crystallization.

2. Cs is deficient in amount at the late-stage differentiates, and supposed to be removed from the rocks with gaseous phase and/or hydrothermal water or meteoric ground water. Such a migration of trace elements in granitic rocks is a very important phenomenon in geochemistry, when we use the trace elements as an indicator of various magmatic processes.

3. U is in radioactive equilibrium with Ra in the complex.

5. Acknowledgment

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