The Fluorine, Chlorine, Bromine, and Iodine Contents of Volcanic Rocks in Japan[1)]

Minoru YOSHIDA, Kazuyoshi TAKAHASHI, Norinobu YONEHARA,* Takejiro OZAWA, and Iwaji IWASAKI[2)]

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

* *Department of Chemistry, Faculty of Science, Kagoshima University, Kamoike-cho, Kagoshima-shi*

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The halogen contents of 49 Japanese volcanic rocks are; F: 50—1700 (average 410), Cl: 17—1220 (av. 270), Br: 0.09—8.10 (av. 0.85), I: 0.011—0.32 (av. 0.088) μg/g. The fluorine and chlorine were determined by usual photometric methods, and the bromine and iodine, by photometric methods based on their catalytic action, after decomposition and separation procedures suitable for each case. The bromine and iodine contents are appreciably lower than the values generally accepted for igneous rocks. The bromine content agrees with Sugiura's value. The frequency distribution of each halogen content shows an approximate lognormality. The chlorine and bromine contents are strongly correlated, and the Br/Cl atomic ratio is in a narrow range $(0.66—3.7)\times10^{-3}$ (av. 1.5×10^{-3}). No other correlation is observed among the halogen contents at all. Each halogen content has no marked relation to the type of rock. A regional difference is seen in the F/Cl and I/Br ratios. Three ultrabasic rocks have very low fluorine ($\leq$20) and chlorine contents ($\leq$50 μg/g). On the other hand, they have a slightly lower bromine content (0.15—0.34 μg/g) than, and almost the same iodine content (0.07—0.13 μg/g) as, the volcanic rocks.

Data on the halogen contents of igneous rocks are important in discussing the relation between igneous rocks and magmatic emanations. The investigation of the halogens is also interesting in connection with the "geochemical balance" of the elements. The origin of the oceans has often been discussed on the basis of the volatilization of the halogens and some other elements.[3—8)] Since Correns[9)] reviewed "the geochemistry of the halogens" in 1956, the fluorine and chlorine contents of igneous rocks have been reported by many investigators. The data on fluorine were compiled by Fleischer and Robinson (1963),[10)] and those on chlorine, by Johns and Huang (1967),[11)] although the latter authors did not quote the results of the studies by Japanese investigators.[12,13)] On the other hand, data on bromine and iodine, especially those on iodine, are scarce.

Behne's results[14)] of a systematic investigation of bromine in rocks were long accepted as reliable. In 1964, however, Filby[15)] reported that the bromine content of two standard rock samples, G1 and W1, prepared by the U. S. Geological Survey, as determined by neutron activation analysis, was appreciably lower than Behne's average value. He confirmed this conclusion by analyzing some other standard rock samples.[16)] The results of the recent determinations[17—19)] of the bromine content of meteorites also show that Behne's values are too high. Recently, Sugiura[20)] determined the bromine content of igneous rocks by a photometric method. His values were also lower than those of Behne; indeed, some rocks have a bromine content lower than the limits of determination of the method (0.2 ppm).

The iodine contents of igneous rocks have not yet been studied systematically so far as is known. The classical values determined titrimetrically by Fellenberg and Lunde[21)] are widely used for many discussions, even at present,[7,22)] in spite of doubts raised by several investigators. Noddacks' value[23)] on the iodine in the earth's surface material is appreciably lower than Fellenberg's value; Urey[5)] used the former value in his discussion of the concentration of certain elements at the earth's surface. Goles and Anders[24)] determined

1) A part of this study was presented at the Meeting of the Volcanological Society of Japan, Fukuoka, Oct., 1968.

2) Present address: Department of Chemistry, Faculty of Science, Tōhō University, Izumi-chō, Narashino-shi.

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the iodine content of several meteorites by the neutron activation method and concluded that most of the iodine data in Fellenberg's study are systematically too high by factors of 5 to 30. Brown and Wolstenholme[25] could not detect iodine in their attempt to determine the minor components in G1 and W1 by spark-source mass spectrometry (limit of detection: 0.05 ppm). Crouch[26] investigated the applicability of a spectrophotometric method for the determination of iodine in silicate rocks and gave some data somewhat lower than Fellenberg's value, but his work has not been continued.

In our opinion, ordinary photometric methods, to say nothing of titrimetric methods, have too low sensitivities to be used in the determination of bromine and iodine in igneous rocks. The neutron activation method has, indeed, a very high sensitivity, but it requires special equipment and time-consuming procedures. The present authors have previously established photometric methods for the determination of bromine[27] and iodine[28] in silicate rocks based upon their catalytic effects on certain redox reactions. The bromine and iodine contents of about fifty volcanic rocks are here determined using these methods. Their fluorine and chlorine contents are also determined. The relations among the abundances of halogens themselves and those between the halogen contents and the other properties of rocks are discussed. The only report which has dealt with the contents of our halogens in the same rock is that of Kogarko and Gulyayeva[29] on the rocks in Lovozero alkalic massif. These rocks are, however, of a specific type and have unusually high halogen contents.

Experimental

The samples used for the present study cover various types of Japanese volcanic rocks. Three ultramafic rocks obtained from New Zealand and New Guinea were also analysed. All the samples were crushed in a steel Ellis mortar and finely pulverized in an agate mortar, with special caution taken against the contamination of the halogens.

The method of analysis will be described only briefly here; the details are given in the papers cited. The fluorine was determined as follows:[30] About 1 g of a sample was fused with sodium peroxide in a nickel crucible. After cooling, the cake was treated with a small amount of water, taking precautions against a violent reaction. The resultant solution and residue were transferred into a distillation flask. After the addition of about 30 m*l* of conc. sulfuric acid and a small amount of hydrazine sulfate, the fluorine was steam-distilled at about 140°C. The fluorine in the distillate (1 *l*) was determined by the photometric method, using zirconium and *p*-dimethylaminoazophenylarsonic acid.[31] The fluorine content of rocks can be determined with a precision of about ± 20 μg/g by this method.

The chlorine was determined by the method of Iwasaki *et al.*,[32] with some improvements.[33] About 0.2 g of a sample was fused with anhydrous sodium carbonate in a platinum crucible. After cooling, the chlorine was extracted with hot water and was determined by the photometric method, using mercuric thiocyanate. The chlorine content of rocks can be determined with a precision of about ± 10 μg/g by this method.

The bromine was determined by the method of Takahashi *et al.*[27] After 0.25—0.5 g of a sample had been fused with potassium hydroxide in a nickel crucible, the resulting cake was leached with water. The bromine in the solution was converted to the elementary form and extracted with benzene. Then, it was back-extracted into the aqueous phase by shaking it with a sodium hydroxide solution; it was determined by the photometric method on the basis of its catalytic action on the oxidation of iodine to iodate by potassium permanganate. The error in this method is about ± 0.03 μg at bromine of 0.50 μg and less at lower amounts.

The iodine was determined by the method of Yonehara *et al.*[28] After 0.5—1 g of a sample had been fused with potassium hydroxide in a nickel crucible, the resulting cake was treated with water and sulfuric acid. The iodine in the solution was converted to the elementary form and extracted with carbon tetrachloride. Then it was back-extracted into the aqueous phase by shaking it with a sodium hydroxide solution and determined by the photometric method on the basis of its catalytic action on the color-fading of a ferric thiocyanate complex. The iodine content of rocks can be determined with a precision of about ± 0.005 μg/g.

The water-soluble halogens in some rocks were determined by methods similar to that described by Iwasaki and Katsura.[13]

All the chemicals used were of analytical-reagent quality or were specially purified. Redistilled water was used throughout the analytical procedures. Blank tests were made on all the procedures of each analytical method.

Results and Discussion

Table 1 gives the results of the determination and some atomic ratios among halogens. The fluorine contents of these volcanic rocks range from 50 to 1700 μg/g; the arithmetic mean is 410 μg/g. The chlorine contents range from 17 to 1220 μg/g; the arithmetic mean is 270 μg/g. The F/Cl ratio is scattered over a wide range, from 0.43 to 45 (average 7.8). These results are consistent with those of the previous reports summarized in Table 2. The bromine contents range from 0.09 to 8.10 μg/g; the arithmetic mean is 0.85 μg/g. The Br/Cl ratio falls within a narrow range from 0.66×10^{-3} to 3.7×10^{-3} (average 1.5×10^{-3}). These values agree with those of Sugiura[20] and are lower than Behne's value.[14] The iodine contents range from 0.011 to 0.32 μg/g; the arithmetic mean is 0.088 μg/g. The

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TABLE 1. HALOGEN CONTENTS AND RATIO AMONG THEM

No.	Sample	Content (μg/g)[a) F	Cl	Br	I	F/Cl	Atomic Ratio Br/Cl ($\times 10^{-3}$)	I/Cl ($\times 10^{-5}$)	I/Br
1	Basalt; Lava of 1950, Mihara-yama, Ô-shima, Tôkyô Metr.	110 (1.6)	310 (12)	0.83 (0.1)	0.082 (0.03)	0.66	1.2	7.4	0.062
2	Basalt; Okada, Ô-shima, Tôkyô Metr.	50	220	0.44	0.029	0.43	0.88	3.7	0.042
3	Basalt; Lava of 1962, Miyake-jima, Tôkyô Metr.	200 (3.0)	600 (14)	1.66	0.086 (0.00)	0.62	1.2	4.0	0.033
4	Basalt; Nishi-yama, Hachijô-jima, Tôkyô Metr.	70	245	1.24	0.13	0.53	2.2	15	0.066
5	Basalt; Sakasagawa, Itô, Shizuoka Pref.	250	100	0.32	0.084	4.7	1.4	24	0.17
6	Basalt; Lava of 864, Aokigahara, Fuji-san, Yamanashi Pref.	250 (40)	250 (50)	0.68	0.032	1.9	1.2	3.6	0.030
7	Basalt; Shirogane Lava, Tokachi-dake, Hokkaidô	300	430	1.38	0.072	1.3	1.4	4.7	0.033
8	Basalt; Orimoto-tôge, Shidara, Aichi Pref.	250	110	0.45	0.095	4.3	1.8	24	0.13
9	Basalt; Ôkuwa, Shidara, Aichi Pref.	400	150	0.41	0.14	5.0	1.2	26	0.20
10	Basalt; Yuto, Shidara, Aichi Pref.	210	155	0.50	0.10	2.5	1.4	18	0.13
11	Basalt; Iwano, Karatsu, Saga Pref.	370 (10)	45 (20)	0.16	0.029	15	1.6	18	0.11
12	Basalt; Taka-shima, Karatsu, Saga Pref.	420 (30)	420 (380)	1.31 (1.04)	0.046	—	—	—	—
13	Basalt; Kuniga, Nishino-shima, Oki, Shimane Pref.	1200	50	0.24	0.042	45	2.1	24	0.11
14	Basalt; Imazu, Saigô, Oki-Dôgo, Shimane Pref.	520	280	0.75	0.018	3.5	1.2	1.8	0.015
15	Basalt; Inamura-dake, Satsuma-iwô-jima, Kagoshima Pref.	190	190	1.03	0.12	1.9	2.4	18	0.073
16	Trachyandesitic Basalt; South of Ôkuwa, Shidara, Aichi Pref.	370	35	0.09	0.070	20	1.1	56	0.49
17	Nepheline basalt; Nagahama, Hamada, Shimane Pref.	1700 (10)	90 (30)	0.26	0.045	35	1.3	14	0.11
18	Dolerite; Kawai, Shidara, Aichi Pref.	330	32	0.15	0.096	19	2.1	84	0.40
19	Andesite; Lava of 1914, Sakura-jima, Kagoshima Pref.	300	n.d.	n.d.	0.082	—	—	—	—
20	Andesite; Lava of 1946, Sakura-jima, Kagoshima Pref.	350 (9.8)	330 (17)	1.45 (0.05)	0.042 (0.01)	2.0	1.9	3.6	0.018
21	Andesite; Iwô-dake, Satsuma-iwô-jima, Kagoshima Pref.	430	130	1.08	0.052	6.2	3.7	11	0.030
22	Andesite; Haha-jima, Bonin Islands, Tôkyô Metr.	200	640	2.02	0.23	0.58	1.4	10	0.072
23	Andesite; Kami-futago-yama, Hakone, Kanagawa Pref.	180	240	0.83	0.091	1.4	1.5	11	0.069
24	Andesite; Lava of 1783, Asama-yama, Gumma Pref.	240	360	1.40	0.25	1.3	1.7	19	0.11
25	Andesite; Sasshô-gawara, Kusatsu-shirane-san, Gumma Pref.	110	150	1.12	0.26	1.4	3.3	49	0.15
26	Andesite; Bomb ejected in 1962, Tokachi-dake, Hokkaidô	370	620	1.89	0.15	1.1	1.3	6.8	0.050
27	Andesite; Lava of parasitic crater (Minami Kakô), Yôtei-zan, Hokkaidô	620	220	0.60	0.022	5.3	1.2	2.8	0.023
28	Andesite; Lava of Yake-yama, Tamagawa-hotspring, Akita Pref.	420 (12)	100 (16)	0.20 (0.1)	n.d.	7.9	0.88	—	—
29	Andesite; Kuniga, Nishino-shima, Oki, Shimane Pref.	1200	90	0.18	0.064	25	0.88	20	0.22
30	Glassy andesite; Shôwa-iwô-jima, Satsuma-iwô-jima, Kagoshima Pref.	550	600	2.60	0.13	1.7	1.9	6.1	0.032
31	Dacitic andesite; Lava of young somma, Sukomogawa, Hakone, Kanagawa Pref.	230	70	0.18	0.070	6.1	1.1	28	0.25
32	Dacitic andestite; Sambe-yama, Shimane Pref.	250	160	0.48	0.032	2.9	1.3	5.6	0.042
33	Trachyandesite; Iwô-jima, Sulfur Islands, Tôkyô Metr.	750	100	0.50	0.26	14	2.2	73	0.33

TABLE 1. Continued

No.	Sample	Content ($\mu g/g$)[a] F	Cl	Br	I	F/Cl	Atomic Ratio Br/Cl ($\times 10^{-3}$)	I/Cl ($\times 10^{-5}$)	I/Br
34	Trachyte; Funakoshi, Nishino-shima, Oki, Shimane Pref.	370	100	0.20	0.036	6.9	0.88	10	0.11
35	Phonolitic trachyte; Tokage-iwa, Tsuzurao-yama, Fuse, Oki-Dôgo, Shimane Pref.	240	17	0.12	0.080	26	3.1	130	0.42
36	Dacite; Shôwa-shinzan, Usu, Hokkaidô	80	50	0.24	0.051	3.0	2.1	29	0.13
37	Dacite; Ôusu-dake, Usu, Hokkaidô	260	60	0.21	0.034	8.1	1.5	16	0.10
38	Dacite; Onigashiro, Yake-yama, Akita Pref.	530	610	2.10	0.22	1.6	1.5	10	0.066
39	Dacite; Lava of somma, Numajirigawa, Akagi-yama, Gumma Pref.	270 (3.8)	30 (7)	0.14 (0.0)	0.066 (0.01)	17	2.1	62	0.30
40	Liparite; Kôzu-shima, Tôkyô Metr.	250 (2.8)	910 (320)	2.52 (1.10)	0.073 (0.01)	0.51	1.2	2.3	0.018
41	Liparite; Nii-jima, Tôkyô Metr.	230 (20)	750	1.42	0.011	0.57	0.83	0.41	0.0049
42	Liparite; Shikine-jima, Tôkyô Metr.	220	630	1.05	0.062	0.65	0.73	2.8	0.037
43	Rhyolitic rock; Nishida, Saigô, Oki-Dôgo, Shimane Pref.	1100	50	0.10	0.026	41	0.88	15	0.16
44	Potash liparite; Manzô-yama, Shimoda, Shizuoka Pref.	50	30	0.15	0.14	3.1	2.2	130	0.59
45	Alkali rhyolite; Madara-jima, Saga Pref.	640 (40)	1220 (1150)	8.10 (7.80)	0.32	—	—	—	—
46	Obsidian; Shirataki, Hokkaidô	440 (3.4)	800 (6)	1.20 (0.00)	0.020 (0.01)	1.0	0.66	0.70	0.011
47	Obsidian; Koshi-dake, Imari, Saga Pref.	490 (6.6)	620 (7)	1.84 (0.1)	0.057 (0.01)	1.5	1.3	2.6	0.020
48	Obsidian; Hime-shima, Ôita Pref.	490 (48)	160 (3)	0.27 (0.0)	0.065 (0.04)	5.7	0.74	11	0.15
49	Glassy rock; Igo, Nakamura, Oki-Dôgo, Shimane Pref.	1000	660	2.28	0.11	2.8	1.5	4.7	0.030
50	Dunite; Dun Mountain, New Zealand	20	50	0.34	0.13	0.8	3.0	73	0.24
51	Harzburgite; Red-Hill, New Zealand	20	<10	0.15	0.078	>3.7	>6.6	>210	0.33
52	Peridotite; New Guinea	10	<10	0.24	0.070	>1.9	>10	>190	0.18

a) Numerical values in parentheses are contents of the water-soluble halogens

I/Cl ratio is scattered over a wide range, from 0.41×10^{-5} to 130×10^{-5} (average 23×10^{-5}). These values are appreciably lower than Fellenberg's value,[21] which is generally accepted. The rocks in Lovozero alkalic massif have very high halogen contents, as is shown in Table 2d.[29] The ratios among halogens are, however, in good agreement with those of the present study.

The amounts of the water-soluble halogens are usually small as compared with those of the total halogens. Some specimens (No. 12, No. 45) contain unusually large amounts of the water-soluble chlorine and bromine. They were obtained at localities near the sea and are possibly contaminated. The data on these specimens are excluded from the calculation of the ratios and the mean values. However, we do not think that all the water-soluble halogens have their origin in contamination.

The abundance of each halogen does not show any marked relationship to the type of rock, as many authors

TABLE 2. HALOGEN CONTENTS OF IGNEOUS ROCKS IN THE LITERATURE

a) F in Volcanic Rocks (mainly from Fleischer and Robinson[10])

Rock Name	No. of Samples	F ($\mu g/g$) Range	Average
Basalt	268	20—2400	380
Andesite	83	0— 780	230
Rhyolitic Rocks[a]	145	0—6850	700
Phonolite, Trachyte	51	830—1490	920

a) Rhyolite, Liparite, Obsidian

b) Cl in Volcanic Rocks

Rock Name	No. of Samples	Cl ($\mu g/g$) Range	Average
Basaltic Rocks[a,b]	279	30—890	160
Basalt[c] (Japan & North-eastern China)	84	80—890	230
Basalt[d] (Hawaii)	110	60—300	100
Andesite, Dacite[b]	109	20—3900	230
Andesite, Dacite[c] (Japan)	82	30—3900	250
Rhyolitic Rocks[b,e]	94	20—7900	550
Rhyolitic Rocks[c] (Japan)	6	240—690	550

a) Basalt, Diabase
b) All the data available including c), d); others are from Johns and Huang[11]
c) from I. Iwasaki, *et al.*[12]
d) from B. Iwasaki and Katsura[13]
e) Rhyolite, Liparite, Obsidian

c) Br in Volcanic Rocks (from Sugiura[20])

Rock Name	No. of Samples	Br (μg/g) Range	Average
Basalt	6	<0.2—2.0	0.6
Andesite[a)]	9	<0.2—1.3	0.6
Dacite	6	<0.2—0.3	0.2
Glassy Rock[b)]	7	0.3—5.5	2.2
Br/Cl (atomic), all		$(<0.5—8)\times10^{-3}$	average 1.5×10^{-3}

a) including one sample of Sanukite
b) Hyaloliparite, Obsidian, Pearlite, Pitchstone and Pyroclastic rock

d) Halogen in Lovozero Alkalic Rocks (from Kogarko and Gulyayeva[29])

	No. of Samples	Content or Ratio (atomic) Range	Average
F	21	$n\times10^{-3}$—1.05%	0.21%
Cl	23	trace-2.75%	0.49%
Br	24	$(0.02—3.28)\times10^{-3}$%	0.60×10^{-3}%
I	24	trace-0.13×10^{-3}%	0.06×10^{-3}%
F/Cl	21	0.02—98	8.4
Br/Cl	22	$(0.09—1.8)\times10^{-3}$	0.60×10^{-3}
I/Cl	21	$(0.2—7.0)\times10^{-4}$	1.4×10^{-4}

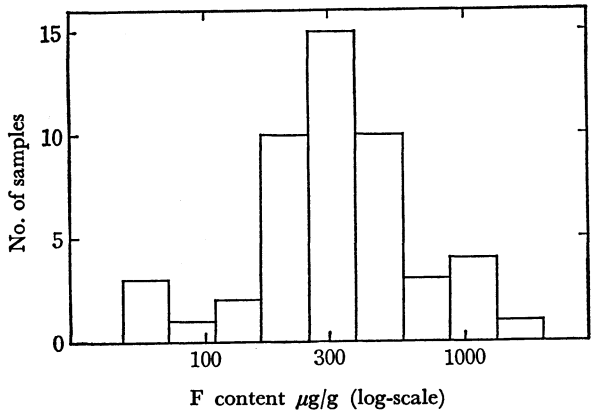

Fig. 1. Frequency distribution of fluorine content in volcanic rocks.

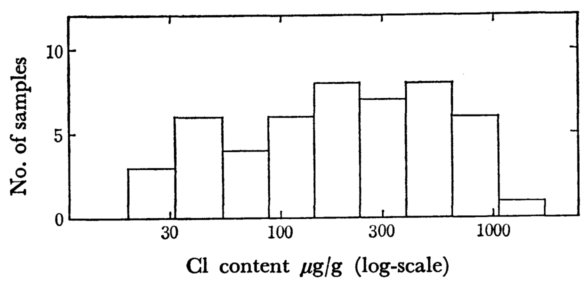

Fig. 2. Frequency Distribution of chlorine content in volcanic rocks.

have pointed out.[8–12,20] All we can say is that some glassy rocks have high chlorine and bromine contents, and that some rocks from alkaline rock provinces have high fluorine contents.

Figures 1—4 give the frequency distribution of each halogen content of the volcanic rocks analysed in this study. They show approximate lognormalities.

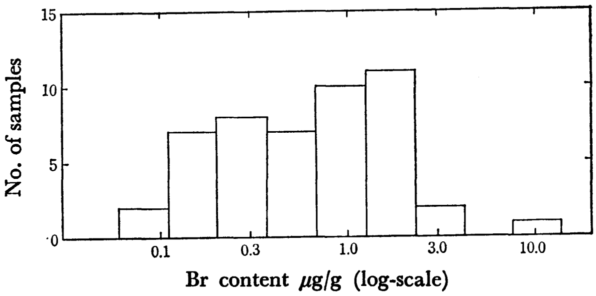

Fig. 3. Frequency distribution of bromine content in volcanic rocks.

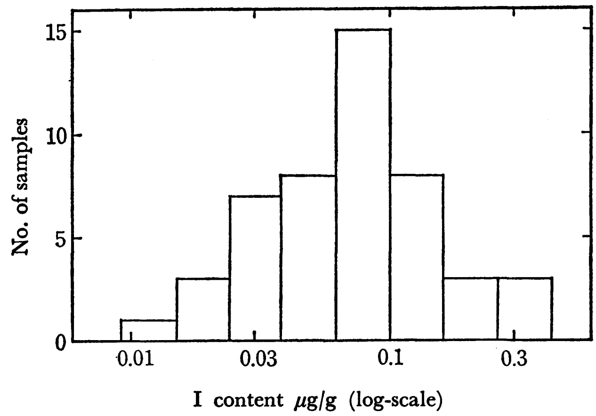

Fig. 4. Frequency distibution of iodine content in volcanic rocks.

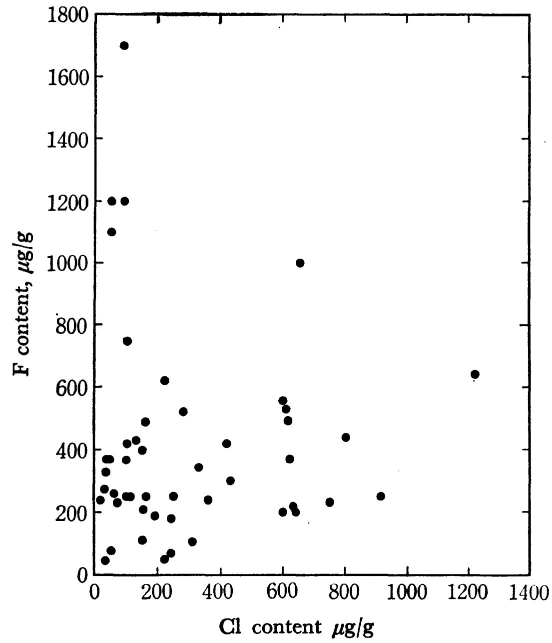

Fig. 5. Relation between chlorine content and fluorine content.

Strictly speaking, the fluorine and chlorine contents show deviations from the log-normal type distribution when they are plotted on cumulative frequency diagrams. The number of samples are, however, insufficient for a further discussion of the distribution of the halogens.

The correlations among halogens are shown in Figs. 5—9: F—Cl in Fig. 5, Br—Cl in Fig. 6, I—Cl in

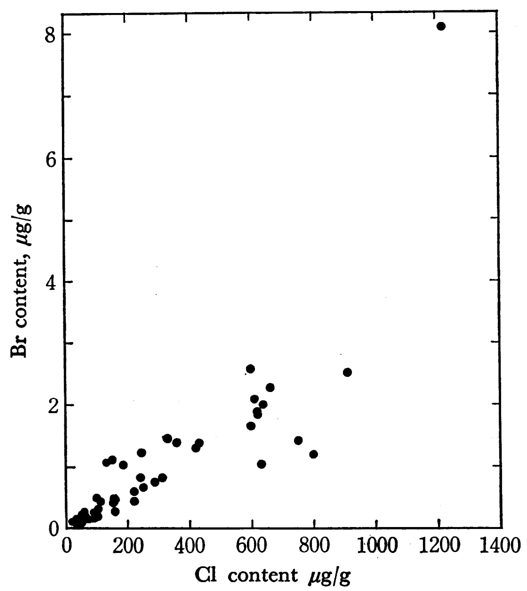

Fig. 6. Relation between chlorine content and bromine content.

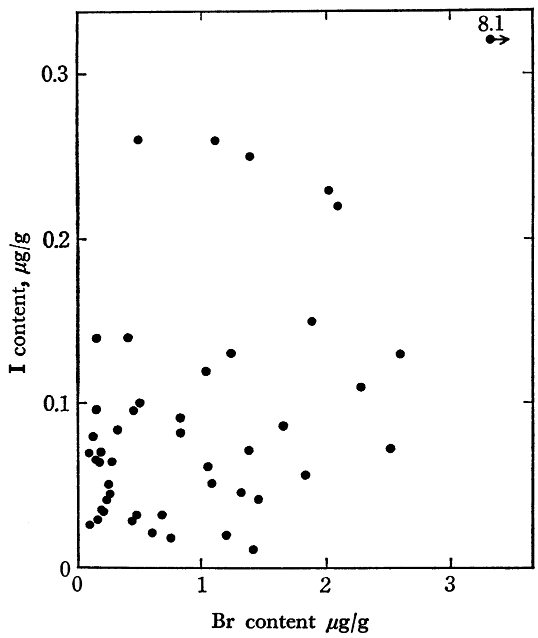

Fig. 8. Relation between bromine content and iodine content.

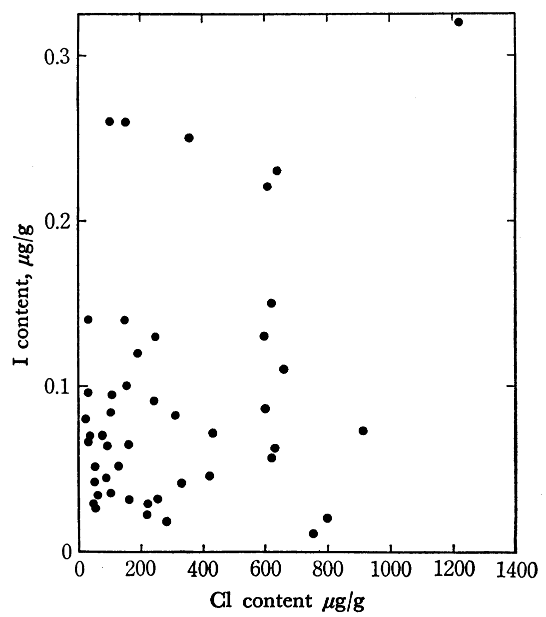

Fig. 7. Relation between chlorine content and iodine content.

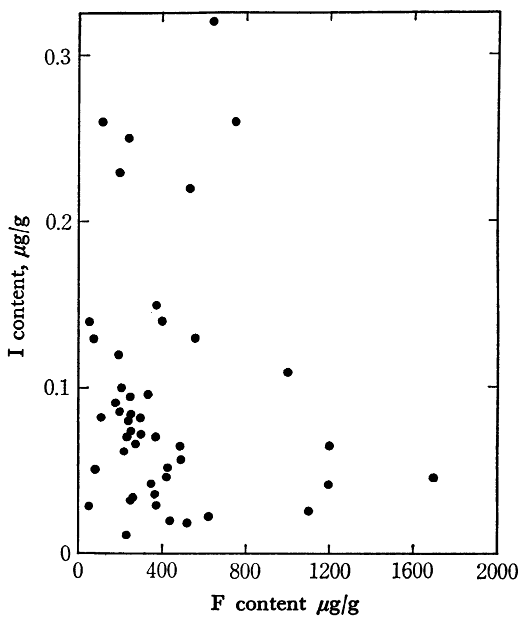

Fig. 9. Relation between fluorine content and iodine content.

Fig. 7, I—Br in Fig. 8, and I—F in Fig. 9. The chlorine and bromine contents are strongly correlated, as may be seen in Fig. 6. On the contrary, the other figures show no correlation at all. These findings indicate that in the process of the formation of volcanic rocks halogen behave in markedly different ways except for the similarity between chlorine and bromine. According to recent investigations, a primary factor governing their halogen contents is thought to be the distribution of volatile halogen compounds between the molten silicate phase and the gas phase. Kuroda and Sandell[34] stated that much of the chlorine escapes as hydrogen chloride formed by the reaction: $Cl^- + H_2O \rightleftharpoons HCl + OH^-$. Kogarko and Ryabchikov[35] discussed the relation between the fluorine and chlorine contents in gas and the chemical composition of the condensed phases in equilibrium with the gas on the basis of this reaction: $2X^-_{melt} + H_2O_{gas} = O^{2-}_{melt} + 2HX_{gas}$. Iwasaki and Katsura[36] discussed the chlorine content of volcanic rocks on the basis of the solubility of hydrogen chloride in rock melts. All the volatile components in the igneous rock have usually been regarded in the same light despite the distinctive chemical property of each of them. If the distribution of the four halogens was controlled mainly by the same mechanism

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TABLE 3. RATIOS AMONG HALOGENS IN VOLCANIC GASES

Locality	Temperature °C	No. of samples	Ratio	
			Range	Average
F/Cl				
Eleven Volcanoes in Japan[40]	95—760	23	$<$0.001—0.65	0.14
Satsuma-iwô-jima[39] A	350—745	23	0.050—0.44	0.14
Satsuma-iwô-jima[39] B	150—350	7	0.023—0.24	0.12
Satsuma-iwô-jima[39] C	$<$150	20	$<$0.005—13	0.99
Five Volcanoes in Japan[37]	141—813	27	$<$0.001—0.64	0.32
Br/Cl				
Five Volcanoes in Japan[37]	141—813	27	$(0.2—1.1)\times 10^{-3}$	$0.6_2\times 10^{-3}$
I/Cl				
Eight Volcanoes in Japan[38]	96—759	69	$(0.047—3.6)\times 10^{-4}$	1.1×10^{-4}

the halogen contents of volcanic rocks should be intimately correlated with each other. From our results, chlorine and bromine may be taken as an illustration of this. On the other hand, the behavior of fluorine and iodine must be controlled by other factors. The ratios among halogens in natural volcanic gases are listed in Table 3.[37–40] A comparison between the data in Table 3 and the data of the present study shows that the F/Cl ratio in the gases is appreciably lower than that of volcanic rocks, as was stated in our previous reports.[39–42] The Br/Cl and I/Cl ratios in the gases are nearly equal to, or a little smaller than, those of the volcanic rocks. The same relations concerning F/Cl, Br/Cl, and I/Cl can be observed between gases evolved from volcanic rocks on heating and the original rocks used in the experiments.[40–43] The difference in behavior between fluorine and chlorine may be attributed to the formation of stable metal-fluorine complexes in rock melts, as was suggested by Kogarko *et al.*[35] Several factors which may control the distribution of iodine have been suggested: its large ionic size, its possible occurence as an elemental form, its chalcophile properties, *etc.* At present, we have no way to decide which of them is the main factor.

A regional difference is observed with regard to some ratios among halogens. The rocks from the Izu Seven Islands have low F/Cl and I/Br ratios; on the contrary, the rocks from the Circum-Japan Sea Province have high F/Cl and I/Br ratios, with a few exceptions. These two petrographic provinces have already been said to be in marked contrast to one another.[44]

The ultra-basic rocks analysed have very low chlorine and fluorine contents as compared with volcanic rocks. The results agreed with those of Stueber *et al.*[45] The bromine content is slightly lower than those of volcanic rocks, while the iodine content is almost the same as those of volcanic rocks. As a result, their Br/Cl and I/Cl ratios are appreciably higher than those of the volcanic rocks. This fact is interesting for showing the difference in the behavior of bromine and iodine from that of fluorine and chlorine during the formation of magma in the mantle.

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