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Bromine to Chlorine Ratios in Igneous Rocks

Tsutomu SUGIURA[*1]

Department of Earth Sciences, Nagoya University, Chikusa, Nagoya

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Samples were decomposed by fusion with Na_2O_2 and benzoic acid in a Parr-bomb, then halogens were separated from other elements by distillation and determined colorimetrically; chlorine by the thiocyanate method and bromine by the rosaniline method. The chlorine and bromine contents of rocks cover a very wide range with no relation to the type of rock. The Br/Cl ratio, however, is in a relatively narrow range from 1×10^{-3} to 16×10^{-3} by weight, mostly from 1×10^{-3} to 6×10^{-3}, and evidently lower than those reported by previous investigators. The average Br/Cl ratio is $(3\pm2)\times10^{-3}$, about one-seventh of the value generally accepted for igneous rocks. The halogen content of quartz and feldspar is usually so small that it was not usually determined. The Br/Cl ratio in biotite seems to be rather small and certainly is smaller than 3×10^{-3} on the average. The Br/Cl ratios in volcanic rocks are similar to those in volcanic gases for any one volcano studied.

Sugiura *et al.*[1] (1963) reported that the Br/Cl ratio in volcanic gases is very alike at every volcano, and evidently smaller than the Br/Cl ratio in igneous rocks reported by Behne[2] (1953). This fact seemed interesting for the consideration of their behavior in volcanic emanations.

The bromine content of igneous rocks was first determined by Fellenberg and Lunde in 1926 (Behne,[2] 1953), and again by Selivanow[3] in 1940 and Behne in 1953. Behne's data had been accepted until Filby[4] (1964) reported the bromine contents of the standard rocks, granite G-1 and diabase W-1. His values are appreciably lower than the average values given by Behne.

Krasitseva[5] (1964) postulated that the Br/Cl ratio in ocean water has been decreasing through geologic time. One important fact supporting his hyporthesis is that the average Br/Cl ratio in igneous rocks seems to be far higher than that in present-day ocean water.

From the above, it seems to be very important and urgent to obtain true average Br/Cl ratio for igneous rocks. In the present study, the author has determined the chlorine and bromine contents of volcanic and plutonic rocks. In order to examine the average Br/Cl ratio obtained the relations between the Br/Cl ratio in biotite and in coexisting quartz and feldspar, and also the ratios in volcanic rocks and volcanic gases from one volcano were investigated.

Experimental

Total Chlorine and Total Bromine. About 1 kg of rock sample was taken at each locality, and 50 to 100 g of sample crushed in a steel mortar and ground to approximately 200 mesh in an agate mortar, taking special precaution against any possibility of chlorine or bromine contamination. The powdered sample was decomposed by fusion with sodium peroxide, and chlorine and bromine separated from other elements by distillation. Chlorine was determined by the method of Iwasaki *et al.*[6] (1957), and bromine by a modification of the method of Hunter and Goldspink[7] (1954).

Separation of Chlorine and Bromine. The sample (1 to 3 g) was decomposed by fusion with 15 g of sodium peroxide and 0.5 g of benzoic acid in a Parr-bomb.[*2] The cake was put into 100 m*l* of distilled water. The solution was condensed to about 50 m*l* on an electric heater, and transferred into a 150 m*l* distilling flask. Two milliliters and 50 m*l* of 2 N potassium hydroxide solution were added to trap A and trap B, respectively (Fig. 1). Forty milliliters of 14 N sulfuric acid and 10 *l* of 10% potassium permanganate solution were added to the distilling flask. The solution was heated to boiling and air bubbled in at the rate of 100 m*l*/min. Distillation was continued to obtain 50 m*l* of distillate. A half milliliter of 30% hydrogen peroxide was added to the distillate. The solution was boiled on a water-bath to decompose the surplus hydrogen peroxide, and made up to 5.0 m*l*.

Chlorine. One milliliter of the solution of chlorine

[*1] Present address: Department of Chemistry, Aichi Kyoiku University, Higashi, Nagoya, Japan.

[1] T. Sugiura, Y. Mizutani and S. Oana, *Earth. Sci. Nagoya Univ.*, **11**, 272 (1963).

[2] W. Behne, *Geochim. et Cosmochim. Acta*, **3**, 186 (1953).

[3] L. S. Selivanov, *Dokl. Akad. Nauk SSSR*, **28**, 809 (1940).

[4] R. H. Filby, *Anal. Chim. Acta*, **31**, 434 (1964).

[5] U. U. Krasitseva, *Geokhimiya*, No. 2, 171 (1964).

[*2] "Peroxide Bomb Apparatus and Methods" published by Parr Instrument Company, 211 Fifty-third Street, Moline, illinois, U.S.A.

[6] I. Iwasaki, T. Katsura, N. Sakato and M. Hirayama, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 164 (1957).

[7] G. Hunter and A. A. Goldspink, *Analyst*, **79**, 467 (1954).

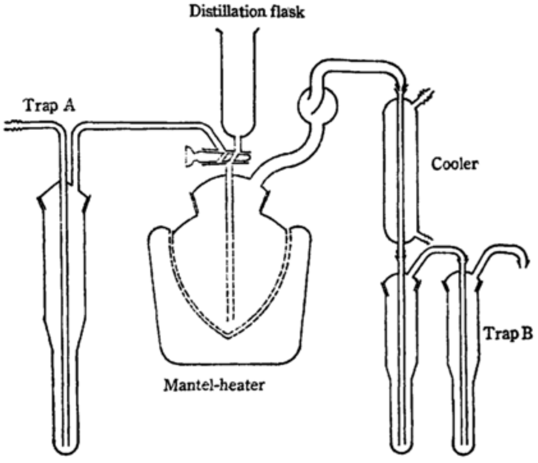

Fig. 1. Apparatus for distillation of chlorine and bromine.

and bromine, 1 m*l* of mercuric thiocyanate solution (0.3 g of $Hg(SCN)_2$ in 100 m*l* of C_2H_5OH) and 2 m*l* of ferric ammonium sulfate solution (6 g of $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$ in 100 m*l* of 6 N NHO_3) were added to a 20 m*l* testtube, in that order. The volume of the solution was made up to 20 m*l* with distilled water and mixed well. The absorbance of this colored solution was measured at 460 $m\mu$. Ten μg of chlorine in the colored solution can be determined within 10% by this colorimetric method, and chlorine in samples with more than 0.01% (100 ppm) chlorine can also be determined within 10%, by taking one-fifth of the distillate. The precision of this distillation method, which actually was examined in detail on the determination of bromine, is presented in Table 2.

Bromine. Four milliliters of the solution of chlorine and bromine, 1.0 m*l* of 1 N dihydrogen sodium phosphate solution (to adjust pH to about 6.3) and 0.5 m*l* of 1 N sodium hypochlorite solution (1 N NaClO in 0.1 N NaOH sol.) were added to a testtube which was kept in the boiling water for 15 min, and cooled with tap water for a few minutes. A half m*l* of 50% sodium formate solution was added. The testtube was again warmed in boiling water for 15 min, and cooled with tap water for 30 min. On the other hand, 0.5 m*l* of bromide-molybdate solution (0.15 g of KBr and 3.0 g of $(NH_4)_6 7Mo_7O_{24} \cdot 4H_2O$ in 100 m*l* of H_2O), 0.5 m*l* of rosaniline solution (0.006 g of $C_{20}H_{20}N_3OH$ in 100 m*l* of 2 N H_2SO_4 sol.) and 1 m*l* of 14 N sulfuric acid were put into a 20 m*l* flask in this order and mixed well. The above prepared solution was added slowly to this flask and stirred. After precisely 5 min, 10 m*l* of *t*-butyl alcohol ($(CH_3)_3COH$ containing 5% C_2H_5OH) was added and mixed well. After 5 min, 1 m*l* of 14 N sulfuric acid was added. The volume of the solution was made up to 20.0 m*l* with distilled water and mixed well. The absorbance of the colored solution was measured at 570 $m\mu$. The smallest detectable amount of bromine in specimens is 0.5 μg, and the error in determination less than 0.5 μg. Hence, as 3 g of sample can be treated at a distillation, bromine in samples with more than 0.00002% (0.2 ppm) bromine can be determined with an error of less than 0.2 ppm. The relationship between the recovery of bromine and the volume of the distillate and precision of the determination are presented in Tables 1 and 2, respectively.

TABLE 1. RELATIONSHIP BETWEEN THE RECOVERY OF BROMINE AND THE WATER VOLUME DISTILLED

Analysis number	Watere volume distilled (m*l*)	Amount of bromine (μg) Added	Amount of bromine (μg) Found	Recovery (%)
1	5	2	0.8	40
2	10	2	1.6	80
3	10	2	1.0	50
4	20	2	1.6	80
5	20	10	9.5	95
6	30	2	1.8	90
7	30	2	1.4	70
8	40	2	1.6	80
9	40	2	1.9	95
10	50	2	2.0	100
11	50	2	1.7	85
12	50	1	0.8	80
13	50	1	1.1	110

TABLE 2. PRECISION OF THE ANALYTICAL METHOD

Analysis number	Amount of sample used (g)	Amount of chlorine and bromine determined (μg) Chlorine	Amount of chlorine and bromine determined (μg) Bromine
14	2 g of No. 3	850	0.6
15	2 g of No. 3	880	0.8
16	3 g of No. 3	1310	1.0
17	3 g of No. 3	1240	0.8
18	3 g of No. 18	270	0.9
19	3 g of No. 18	340	1.2
20	3 g of No. 18	300	1.0
21	3 g of No. 18	280	0.7
22	2 g of No. 22	580	1.9
23	2 g of No. 22	580	1.4
24	3 g of No. 19	230	1.1
25	3 g of No. 19	240	0.7

Soluble Chlorine and Bromine. Two grams of sample per determination were soaked in 50 m*l* of water for 24 hr at room temperature, and stirred occasionally. One drop of concentrated nitric acid was added to the solution, and it centrifuged. The precipitate was soaked again in 50 m*l* of water containing one drop of concentrated nitric acid for 24 hr, and centrifuged. This procedure was repeated till the amount of leached chlorine in the water becomes negligibly small. The process usually was repeated two or three times. The amounts of chlorine and bromine leached in water were determined separately by the method described above.

Samples

Samples for the present study consist of 28 volcanic and 14 plutonic rocks collected from various parts of Japan. Rock species and localities of specimens are briefly described in Tables 3 and 4, to-

TABLE 3. CHLORINE AND BROMINE CONTENTS OF VOLCANIC ROCKS

Specimen number	Rock species	Locality	Total-Cl g/t	Soluble-Cl g/t	Total-Br g/t	Soluble-Br g/t	$\frac{\text{Total-Br}}{\text{Total-Cr}}\times 10^3$ (wt)	$\frac{\text{Soluble-Br}}{\text{Soluble-Cl}}\times 10^3$ (wt)
1	Basalt	Notoiida, Ishikawa Pref.	120	30	<0.2	—*	<2	—
2	Basalt	Tojinbo, Fukui Pref.	450	0	2.0	—	4	—
3	Basalt	Miharayama, Oshima, Tokyo Metropolitan	430	45	0.3	—	1	—
4	Basalt	Okada, Oshima, Tokyo Metropolitan	100	100	0.2	0.3	2	3
5	Basalt	Shidara, Okuwa, Aichi Pref.	150	40	0.5	—	4	—
6	Basalt	Shidara, Oidaira, Aichi Pref.	160	60	0.5	0.2	3	3
7	Sanukite	Shiraminezan, Kagawa Pref.	210	5	0.7	—	3	—
8	Andesite	Daisen, Tottori Pref.	200	30	0.5	—	3	—
9	Andesite	Yakeyame, Akita Pref.	180	10	<0.2	—	<2	—
10	Andesite	Usuzan, Hokkaido	200	40	0.8	—	4	—
11	Andesite	Issaikyoyama, Fukushima Pref.	140	45	0.8	—	6	—
12	Andesite	Chausudake, Tochigi Pref.	260	5	0.3	—	1	—
13	Andesite	Asahidake, Tochigi Pref.	80	5	0.2	—	3	—
14	Andesite	Kujyu-Ioyama, Oita Pref.	120	30	0.4	—	3	—
15	Andesite	Asosan, Kumamoto Pref.	430	35	1.3	—	3	—
16	Dacite	Tojinbo, Fukui Pref.	190	0	<0.2	—	<1	—
17	Dacite	Sanbeizan, Shimane Pref.	110	20	0.2	—	2	—
18	Dacite	Showashinzan, Hokkaido	100	20	0.3	—	3	—
19	Dacite	Ousu, Hokkaido	120	15	0.3	—	3	—
20	Dacite	Ogariyama, Usu, Hokkaido	50	10	<0.2	—	<4	—
21	Dacite	Kousu, Usu, Hokkaido	30	10	0.2	—	7	—
22	Pearlite	Horaiji, Aichi Pref.	290	50	0.8	—	3	—
23	Obsidian	Shirataki, Hokkaido	690	—	2.0	—	3	—
24	Pitch stone	Horaiji, Aichi Pref.	100	25	0.3	—	3	—
25	Pitch stone	Sosogi, Ishikawa Pref.	1020	40	5.5	—	5	—
26	Hyalolipalite	Kumano, Mie Pref.	90	—	1.4	—	16	—
27	Pyroclastic rock	Noto, Fukui Pref.	790	40	1.5	—	2	—
28	Pyroclastic rock	Shirataki Hokkaido	640	—	4.0	—	6	—

* Not detected

TABLE 4. CHLORINE AND BROMINE CONTENTS OF PLUTONIC ROCKS AND THEIR MINERALS

Specimen number	Rock species	Locality	Total-Cl g/t	Soluble-Cl g/t	Total-Br g/t	Soluble-Br g/t	$\frac{\text{Total-Br}}{\text{Total-Cl}} \times 10^3$ (wt)
29	Pegmatite	Ishikawa, Fukushima Pref.	40	0	0.2	—	5
	Biotite		100	30	0.2	—	2
	Quartz		10	—	—	—	—
	Feldspar		10	—	—	—	—
30	Pegmatite	Naegi, Gifu Pref.	—	—	—	—	—
	Biotite		2400	20	0.5	—	0.2
	Quartz		30	25	≦0.2	—	≦4
	Feldspar		50	30	≦0.2	—	≦7
31	Pegmatite	Ishikawa, Fukushima Pref.	20	—	—	—	—
	Muscovite		10	—	—	—	—
	Quartz+Feldspar		30	—	—	—	—
32	Granite	Ishikawa, Fukushima Pref.	10	—	—	—	—
	Biotite		20	—	—	—	—
	Quartz		10	—	—	—	—
	Feldspar		10	—	—	—	—
33	Granite	Naegi, Gifu Pref.	70	0	0.3	—	4
	Biotite		250	25	0.4	—	2
	Quartz+Feldspar		50	10	0.3	—	6
34	Granite	Yashirojima, Yamaguchi Pref.	100	10	≦0.2	—	≦2
	Biotite		200	5	≦0.2	—	≦1
	Quartz+Feldspar		80	20	≦0.2	—	≦3
35	Granodiorite	Taguchi, Aichi Pref.	90	—	—	—	—
	Biotite		700	—	—	—	—
	Quartz+Feldspar		10	—	—	—	—
36	Granite	Okazake, Aich Pref.	10	—	—	—	—
	Biotite		210	—	0.3	—	1
	Quartz+Feldspar		5	—	—	—	—
37	Granite	Tsunogawa, Yoshikigun, Gifu Pref.	40	—	≦0.2	—	≦5
	Biotite		1020	10	≦0.5	—	≦0.5
38	Quartzdiorite	Nakagawa, Shimoashikagara-gun Kanagawa Pref.	70	—	0.3	—	4
	Hornblende		200	—	0.4	—	2
	Quartz+Feldspar		5	—	—	—	—
39	Granite	Kadoshima, Yasuoka-mura, Nagano Pref.	30	10	0.3	—	10
	Biotite		280	10	≦0.5	—	≦2
40	Eclogite	Higashiakaishi, Ehime Pref.	20	—	—	—	—
	Pyroxene		70	—	≦0.5	—	≦7
	Garnet		10	—	—	—	—
41	Gabro	Murotozaki, Kochi Pref.	70	—	0.2	—	3
	Pyroxene		60	—	<0.5	—	<8
	Magnetite		90	—	0.2	—	2
	Plagioclase		80	—	<0.5	—	<6
42	Peridotite	Higashiakaishi, Ehime Pref.	40	—	0.2	—	5
	Pyroxene		70	—	<0.5	—	<7
	Olivine		10	—	—	—	—
	Spinel		75	—	<0.5	—	<7

gether with the chlorine and bromine contents. The analyzed minerals were roughly separated first with a magnetic separater, and then hand-picked under a microscope.

Result and Discussion

1) Br/Cl Ratios in Volcanic Rocks. Results of the determinations of chlorine and bromine in volcanic rocks are given in Table 3.

Kuroda and Sandell[8] (1953) and Iwasaki *et al*[6] (1957) have stated that the amount of water-soluble chlorine is generally very small compared with the total amount of chlorine in rocks which are fresh and not contaminated by sea-water. Also Iwasaki and Katsura[9] (1964) stated that the amount of water soluble chlorine in Hawaiian lavas is small and almost constant, and a rather large amount of the water-soluble chlorine found in rock specimens is supplied by sea-water. The present author determined the amount of water-soluble chlorine to see if the chlorine in rocks is due to secondary contamination. The results showed that the amount of water-soluble chlorine in rocks was within 30% of the total chlorine content, except in specimens Nos. 4 and 6. This percentage is normal for previously reported fresh rocks. Moreover, in the discussion of the Br/Cl ratio, such an amount of water-soluble chlorine does not seriously affect the ratio, even if almost all of this water-soluble chlorine is secondary. Most of the water-soluble chlorine in specimens No. 4 and No. 6 might be secondary, however, the Br/Cl ratio in them falls in the range for ordinary rocks. In Table 3, it is noticed that both chlorine and bromine contents are scattered over a wide range, from 30 to 1020 ppm for chlorine, and from 0 to 5.5 ppm for bromine. The abundance of these lements, however, does not show any marked relationship to the type of rock, as shown in Figs. 2 and 3. Some glassy rocks show much higher chlorine and bromine contents. These results coincide with what has been given by Iwasaki *et al.*[6] (1957) on the chlorine content of volcanic rocks in Japan, and by Kokubu[10] (1956) on fluorine. Figure 4 shows the relationship between chlorine and bromine contents. No distinct linear relationship is seen between them. Br/Cl ratios, however, are mostly involved in the range from 1×10^{-3} to 6×10^{-3}, apparently lower than those reported by Behne. On the average: 200±100 ppm for chlorine, 0.3±0.2 ppm for bromine and $(3\pm2)\times10^{-3}$ for Br/Cl ratio. A comparison of the values of Behne and those of the present author gives about the same value for chlorine, about one-tenth for bromine and about one-seventh for the Br/Cl ratio. This discrepancy for bromine is too large to be accounted for only by the difference in methods of determintion.

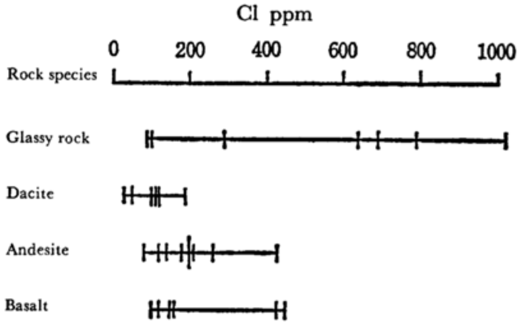

Fig. 2. Relationship between chlorine content of rocks and rock species.

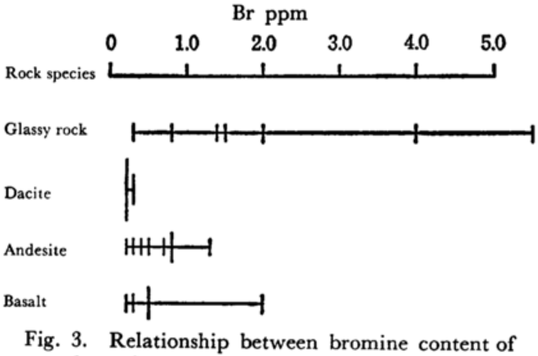

Fig. 3. Relationship between bromine content of rocks and rock species.

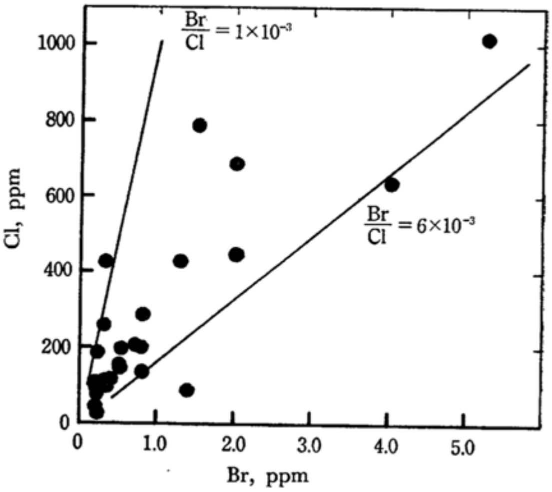

Fig. 4. Relationship between chlorine contents and bromine contents.

2) Br/Cl Ratios in Plutonic Rocks. The results are presented in Table 4, together with the chlorine and bromine contents of minerals in the rocks. Of plutonic rocks, only pegmatite, granite and a few other types of rocks have been analyzed, since it became clear in an early stage of this study

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8) P. K. Kuroda and E. B. Sandell, *Anal. Chem.*, **22**, 1144 (1950).

9) B. Iwasaki and T. Katsura, This Bulletin, **37**, 1827 (1964).

10) N. Kokubu, *Kyushu Univ. Ser. C., Chemistry*, **2**, 95 (1956).

that the abundance of bromine in plutonic rocks is generally very small and the exact determination of bromine impossible for most specimens by the method employed. The chlorine content of the rocks analyzed, which contained negligibly small amounts of water-soluble chlorine and were believed to be uncontaminated by sea-water or other sources of contamination, is ordinarily 10—40 ppm, and a maximum of 100 ppm. The amount of chlorine in most rocks in this study is too small to be accurately determined. The situation is the same for bromine. The calculated Br/Cl ratios for these rocks are, of course, uncertain. However, the average Br/Cl ratio in plutonic rocks certainly is not as high as 21×10^{-3}, which was given by Behne. The highest value in any determination was 10×10^{-3}. The average Br/Cl ratio would then be the same as the average in volcanic rocks, $(3\pm2)\times10^{-3}$ or less.

3) Br/Cl Ratios in Biotite and Coexisting Quartz and/or Feldspar. Br/Cl ratios in plutonic rocks are still uncertain for most specimens. In order to examine the ratios obtained for these rocks, the author determined the Br/Cl ratios in biotite, and in quartz and feldspar coexisting with biotite. Biotite is considered to contain the greatest amount of chlorine in plutonic rocks, and is said to contain an appreciable amount of halogen in its crystal lattice. Chlorine and bromine in quartz and feldspar occur in quite a different manner from biotite. However, as shown in Table 4, bromine could not be determined accurately for most specimens, even for biotite containing a considerably high amount of chlorine. Yet, from these values, it was found that the Br/Cl ratio in these plutonic rocks is considerably smaller than the value reported by Behne, because the Br/Cl ratio in biotite, which seems to contain most of the chlorine found in these rocks, is certainly very small, 2×10^{-3} at maximum.

4) Relationship between the Br/Cl Ratios in Volcanic Rocks and in Volcanic Gases. Table 5 shows the chlorine and bromine contents and also the Br/Cl ratios in volcanic rocks and gases from a few volcanoes in Japan. For the Br/Cl ratio in volcanic gases, as mentioned above, it was confirmed in an earlier study1) (1963) that they are more or less affected by many factors, and are usually in the range from 1×10^{-3} to 3×10^{-3} in weight ratio. The Br/Cl ratios in volcanic gases presented here are representative of the values obtained for each volcano in an earlier study1) (1963). The Br/Cl ratio in rocks is somewhat larger than that in gases at Showashinzan, Fujusan and Issaikyoyama, while it is a little smaller than that at Chausuyama and Miharayama.

TABLE 5. THE CHLORINE AND BROMINE CONTENTS OF VOLCANIC ROCKS AND VOLCANIC GASES FOR 5 VOLCANOES IN JAPAN

Volcano		Cl, ppm	Br, ppm	$Br/Cl\times10^3$ (weigt)
Showashinzan	rock	90	0.3	3
	gas	856	1.1	1.2
Kujusan	rock	120	0.4	3
	gas	6250	7.6	1.2
Chausuyama	rock	260	0.3	1
	gas	429	0.6	1.4
Miharayama	rock	430	0.3	1
	gas	1640	2.8	1.7
Issaikyoyama	rock	140	0.8	6
	gas	239	0.5	2.4

5) Average Br/Cl Ratio in Igneous Rocks. Concerning the Br/Cl ratio in volcanic rocks, Kogarko and Gulyayeva11) (1965) studied the halogen contents of the alkaline rocks of the Lovozero massif, and revealed that the chlorine and bromine contents of these rocks are normally in a linear log relationship independent of the rock species, and that the average Br/Cl ratio in the Lovozero rocks is about 1×10^{-3}. There are few determinations of the Br/Cl ratio in plutonic rocks. Filby4) (1964) determined the bromine contents of standard rocks, granite G-1 and diabase W-1, by a neutron activation analysis developed by himself, and obtained values of 0.484 and 0.496 ppm for bromine of G-1 and W-1, respectively. These values are considerably lower than the averages for granites and basalts previously reported by Behne. The Br/Cl ratios of the standard rocks calculated with the chlorine contents determined by Kuroda *et al.*12,13) (1950, 1951) are 5.7×10^{-3} for G-1, and 2.3×10^{-3} for W-1.

Most of the fluorine and chlorine in plutonic rocks is generally thought to exist in apatite or in minerals which contain OH^- in their crystal structure, replacing OH^-. This would be the case for bromine in rocks, also. The bromine to chlorine ratio, however, would be smaller in such minerals than in the liquid phase. The reason for this would be that the ionic radius of chlorine (1.81 Å) is closer to that of OH^- (1.40 Å) than that of bromine (1.96 Å), and the electron affinity of chlorine (3.82) is also stronger than that of bromine (3.54). It is realized that the Br/Cl ratio in biotite was very small in this study.

The Br/Cl ratio in volcanic rocks was roughly the same as that in volcanic gases at each volcano studied. However, as the Br/Cl ratio in volcanic gases has been reported to be $(1-3)\times10^{-3}$ in general, the average ratio obtained for volcanic rocks, $(3\pm2)\times10^{-3}$, is in rather good agreement with these values.

From the above, the average Br/Cl ratio obtained in this study is thought to be more reliable than previous values.

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11) L. N. Kogaruko and L. A. Gulyayeva, *Geokhimiya*, No. 8, 1011 (1965).

12) P. K. Kuroda and E. B. Sandell, *Anal. Chem.*, **22**, 1144 (1950).

13) P. K. Kuroda and E. B. Sandell, *ibid.*, **22**, 1304 (1951).

Summary

1) Both chlorine and bromine contents of volcanic rocks are distributed over a wide range with no relation to rock types. The Br/Cl ratios, however, are restricted within a rather narrow range independent of their amounts in rocks, and the average value is $(3\pm2)\times10^{-3}$ by weight.

2) The average Br/Cl ratio in plutonic rocks is not so large as previously reported, but is the same as or less than the average in volcanic rocks.

3) The bromine contents of biotite, quartz and feldspar have not been determined accurately for most specimens, but it is certain that the Br/Cl ratio in biotite which contains most of chlorine in the rocks is very small.

4) The Br/Cl ratio in volcanic rocks and in volcanic gases at each volcano are nearly same in all volcanoes studied.

5) Taking account of these results together with the reports of Kogaruko and Gulyayeva[11] (1965), and others, the average Br/Cl ratio, $(3\pm2)\times10^{-3}$ in volcanic rocks seems to be more acceptable than the previous one, 21×10^{-3}.

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