The Relation between the Volatilization Rates of Chlorine and Bromine Compounds from Volcanic Rocks on Heating

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Experiments on the volatilization rate of chlorine and bromine compounds from volcanic rocks were made at temperatures above 770°C in a stream of nitrogen, both in the presence of water vapor and without it. The rate of volatilization have been studied by following the change in the retained chlorine and bromine contents as a function of the heating time. Their contents retained in rocks during heating were estimated indirectly by determining their amounts evolved from rocks. The chlorine compounds are more volatile than those of bromine, regardless of the rock type. However, the difference in their volatility becomes quite small in the presence of water vapor. This fact suggests that there is little difference in the volatility between chlorine and bromine compounds in the presence of much water vapor, so the Br/Cl ratio in magma does not change very much during the crystallization process.

Sugiura[1] reported that the bromine and chlorine contents of volcanic rocks ranged widely, but that the Br/Cl ratios were to be found in a relatively narrow range, mostly from 1×10^{-3} to 6×10^{-3} by weight, regardless of the rock type. The present author and his co-workers determined the halogen contents of volcanic rocks.[2] Their Br/Cl ratios also fell in a narrow range, regardless of their contents in the rocks and of the rock type. These findings may show the close similarity between the volatilization rates of chlorine and bromine compounds, because the distribution of halogens in volcanic rocks is largely determined by their volatilization. Several studies of the volatilization of halogen compounds were carried out by heating volcanic rocks. Yoshida[3] and Yoshida *et al.*[4,5] studied the fractionation of halogen compounds through the process of volatilization and sublimation by determining their contents in the gases and sublimates obtained by heating rocks. Iwasaki and Katsura[6] carried out an experimental study of the volatilization rate of chlorine compounds from basaltic rock melts, neglecting the effect of water vapor. From the experimental results on the liberation of chlorine and fluorine compounds in the presence of water vapor, Sugiura[7] suggested that the distillation process of halogens with water vapor determines the distribution of halogens in volcanic rocks more than does the chemical and mineralogical nature of the rocks.

No attempt has, however, yet been made to study the rates of volatilization of bromine compounds from volcanic rocks on heating; this has been because of the lack of a suitable analytical method for the determination of bromine. The objective of the present paper is to make clear the relation between the rates of volatilization of chlorine and bromine compounds from volcanic rocks on heating. The experiments on the liberation of their compounds from volcanic rocks were made by heating rocks in a stream of nitrogen, both in the presence of water vapor and without it.

Experimental

Materials. The rock samples used in this study are listed in Table 1, together with their chlorine and bromine contents. The chlorine in rocks was determined by the method of Iwasaki *et al.*[8] with some improvements, while the bromine in the rocks was determined by the method of Takahashi *et al.*[9] Reagent-grade chemicals and redistilled water were used throughout this work.

Apparatus and Procedure. The apparatus used in this study is shown in Fig. 1. The method of generation of the water vapor was the same as that described by Sugiura.[7] The temperature of the furnace was kept constant within ±10°C and measured by a pyrometer with a platinum-platinum, 10% rhodium thermocouple. Two absorption vessels were connected to the three-way cock separately, each containing about 40 m*l* of water and 5 g of potassium hydrox-

TABLE 1. CHLORINE AND BROMINE CONTENTS OF THE ROCK SPECIMENS USED

No.	Sample	Cl ppm	Br ppm	$\mathrm{Br/Cl}\times10^{-3}$ (weight ratio)
1	Basalt (lava of 1962 Miyake-jima Volcano, Tokyo Metr.)	600	1.66	2.8
2	Basalt (Takashima, Saga Pref.)	420	1.31	3.1
3	Andesite (lava of 1946 Sakura-jima Volcano, Kagoshima Pref.)	360	1.45	4.0
4	Liparite (Kozu-shima Volcano, Tokyo Metr.)	910	2.52	2.8
5	Obsidian (Shirataki, Hokkaido)	800	1.20	1.5

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1) T. Sugiura, This Bulletin, **41**, 1133 (1968).

2) M. Yoshida, K. Takahashi, N. Yonehara, T. Ozawa, and I. Iwasaki, *ibid.*, **44**, 1844 (1971).

3) M. Yoshida, *ibid.*, **36**, 773 (1963).

4) M. Yoshida, I. Makino, N. Yonehara, and I. Iwasaki, *ibid.*, **38**, 1436 (1965).

5) I. Iwasaki, M. Yoshida, I. Makino, and N. Yonehara, *Bull. Volcanol. Soc. Japan*, **9**, 1 (1964).

6) B. Iwasaki and T. Katsura, This Bulletin, **40**, 1167 (1967).

7) T. Sugiura, *ibid.*, **41**, 1588 (1968).

8) I. Iwasaki, T. Katsura, and N. Sakato, *Nippon Kagaku Zasshi*, **76**, 1116 (1955).

9) K. Takahashi, M. Yoshida, T. Ozawa, and I. Iwasaki, This Bulletin, **43**, 3159 (1970).

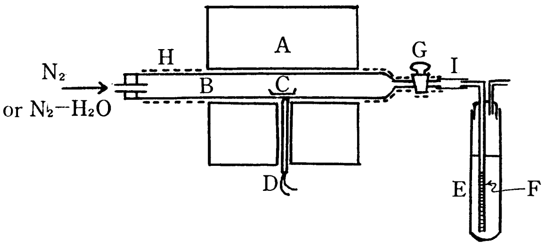

Fig. 1. Apparatus.
A Electric furnace B Silica-glass tube
C Platinum boat D Thermocouple
E Absorption vessel F Silica-glass wool
G Three-way cock H Glass heater
I Silicone rubber tube

ide. From 3 to 4 g of a finely-powdered sample, placed in a platinum boat, was inserted in the silica glass tube and then placed in the center of the furnace at a given temperature. Nitrogen gas freed of halogens by sodium hydroxide pellets was then allowed to flow through at a fixed flow rate of about 360 m*l*/min. The halogen compounds which were liberated from the sample were absorbed by the solution in the absorption vessel. After various periods of heating, the three-way cock was turned in order to trace the change in the amounts of chlorine and bromine evolved as a function of the heating time. After the solution in each absorption vessel has been adequately diluted, an aliquot of the solution was used for the determination of bromine. Another portion was used for the determination of chlorine after oxidizing the sulfide by heating the solution with a small amount of hydrogen peroxide. The chlorine was determined by the mercuric thiocyanate method[10] with some improvements, while the bromine was determined by a modification of the method reported in a previous paper.[9] The amounts of chlorine and bromine deposited on the inside surface of the silica-glass tube and the cock on the outgassing of the rocks were small enough to be neglected; the bromine was less than 5% of the total amount of bromine evolved from rocks, and the chlorine, less than 2% of the total amount of chlorine evolved.

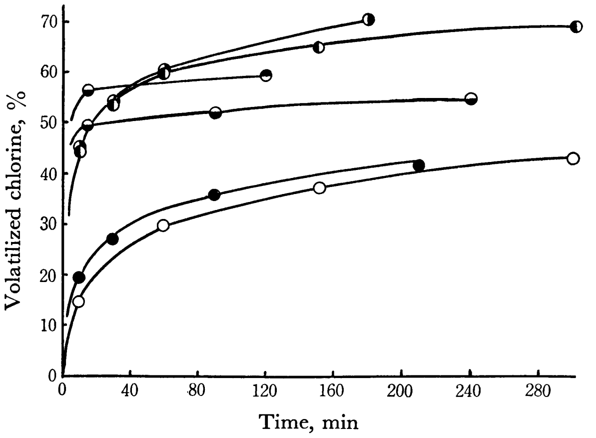

Fig. 2. Change in the percentage ratio of the volatilized chlorine content to the original chlorine content with heating time at different temperatures in N_2 and N_2-H_2O mixture.
Sample: Basalt from Miyake-jima, 4 g
○ 770°C ● 770°C
◐ 950°C } in N_2 ◑ 950°C } in N_2-H_2O
◒ 1170°C ◓ 1170°C

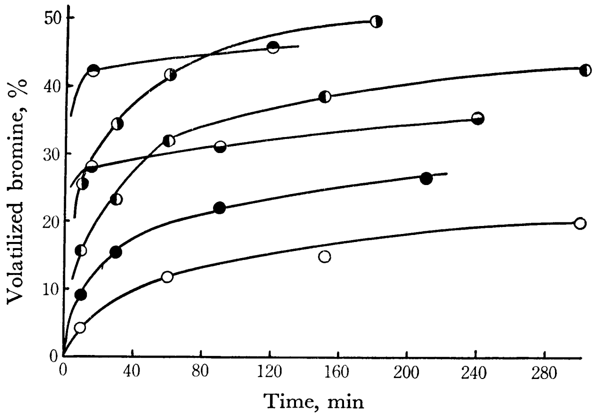

Fig. 3. Change in the percentage ratio of the volatilized bromine content to the original bromine content with heating time at different temperatures in N_2 and N_2-H_2O mixture.
Sample: Basalt from Miyake-jima, 4 g
○ 770°C ● 770°C
◐ 950°C } in N_2 ◑ 950°C } in N_2-H_2O
◒ 1170°C ◓ 1170°C

Results and Discussion

The Rates of Volatilization of Chlorine and Bromine Compounds from Volcanic Rocks on Heating. The results of experiments conducted at different temperatures and at various heating times are shown in Figs. 2 and 3. In Figs. 2 and 3, only the results for basalt from Miyake-jima are presented, because the shapes of the curves for this basalt are very similar to those for all the other rocks used in this study. Figure 2 shows the change in the ratio (%) of the volatilized chlorine content to the original chlorine content with the heating time at different temperatures, both in the presence and absence of water vapor. Figure 3 shows the change in the ratio of the volatilized bromine content to the original bromine content, as in the case of chlorine. From the results shown in Figs. 2 and 3, it is evident that the rates of volatilization of chlorine and bromine compounds are remarkably fast in the initial heating

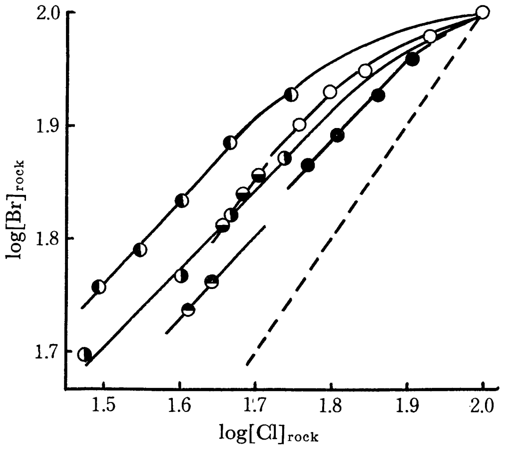

Fig. 4. The log-log relation between the percentage fractions of retained chlorine and bromine in rocks during heating.
Sample: Basalt, Miyake-jima, 4 g
○ 770°C ● 770°C
◐ 950°C } in N_2 ◑ 950°C } in N_2-H_2O
◒ 1170°C ◓ 1170°C

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[10] T. Ozawa, *Bunseki Kagaku*, **17**, 395 (1968).

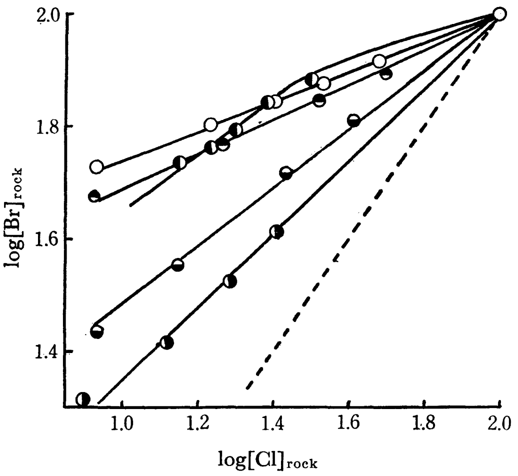

Fig. 5. The log-log relation between the percentage of retained chlorine and bromine in rocks during heating.
○ Andesite, Sakura-jima, 4 g: 950°C, N_2
◐ Basalt, Takashima, 4 g: 950°C, N_2
◑ Basalt, Takashima, 4 g: 950°C, N_2-H_2O
◓ Obsidian, Shirataki, 4 g: 950°C, N_2
◒ Obsidian, Shirataki, 4 g: 950°C, N_2-H_2O

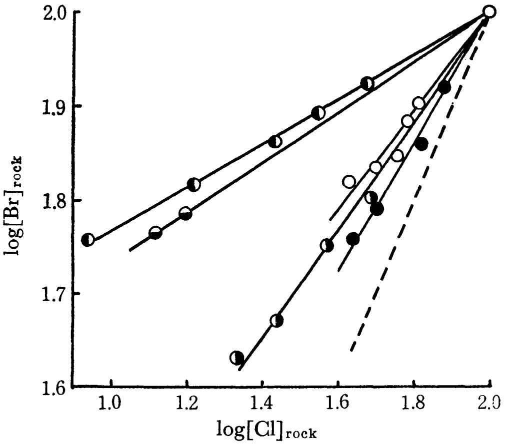

Fig. 6. The log-log relation between the percentage of retained chlorine and bromine in rocks during heating.
Sample: Liparite, Kozu-shima, 3 g
○ 770°C, ◐ 950°C, ◒ 1170°C in N_2
● 770°C, ◑ 950°C in N_2-H_2O

period, and that then the rates become slow. The liberation of their compounds from the rocks becomes remarkably difficult as soon as they begin to melt. The basaltic sample from Miyake-jima begins to melt after several minutes in the furnace at 1170°C. The chlorine and bromine compounds tend to volatilize more easily in the presence of water vapor than without it. There is an especially striking difference in the rate curves of the liberation of bromine compounds in nitrogen and in a N_2-H_2O mixture. Figure 3 shows that the bromine compounds are much more easily liberated in the N_2-H_2O mixture.

The kinetics of the volatilization of the chlorine and bromine compounds is very complex because a rock is a multicomponent and inhomogeneous system. According to Iwasaki *et al.*[11] and the results of the pH measurements, which are not listed in this paper, the chemical form of the chlorine evolved is mostly hydrogen chloride. This would be the case for bromine, also. For this reason, it is evident that water in rocks plays an important role in the kinetics of the volatilization of their compounds.

The Relation between the Rates of Volatilization of Chlorine and Bromine Compounds from Rocks on Heating. Figures 4, 5, and 6 show the relation between the percentage fractions of retained chlorine and bromine in rocks during heating, both in the presence of water vapor and in its absence. $[Cl]_{rock}$ and $[Br]_{rock}$ represent the percentage of the retained chlorine and bromine contents respectively in relation to their original contents. The chlorine compounds are remarkably easier to release than those of bromine on heating in the absence of water vapor, regardless of the rock type. The plots of log $[Br]_{rock}$ *vs.* log $[Cl]_{rock}$ all yield approximately straight lines except for basalt. The ratio of the volatility of chlorine compounds to that of bromine compounds, k, was defined by the equation:

$$(-d[Cl]_{rock}/[Cl]_{rock}dt)/(-d[Br]_{rock}/[Br]_{rock}dt) = k.$$

From the slopes of the straight lines, the volatility ratios obtained for andesite from Sakura-jima, liparite from Kozu-shima, and obsidian from Imari on heating at 950°C in N_2 are 3.9, 4.3, and 3.4 respectively.

The Br/Cl ratio in rocks increases with an increase in the duration of heating because of the higher volatility of chlorine compounds. In other words, the lower the chlorine content retained in rocks on heating, the larger the $(Br/Cl)_{retained}$ ratio. It is interesting to note that these observations are similar to the relation between the Br/Cl ratio and the chlorine content of ordinary chondrites reported by Goles *et al.*[12] The Cl/Br ratio in ordinary chondrites increases rapidly with an increase in the chlorine content. The thermal history of meteorites seems to have a large influence on the abundance of chlorine and bromine in them.

On the other hand, the difference in volatility between chlorine and bromine compounds becomes remarkably small in the presence of water vapor. The effect becomes even stronger with an increase in the water-vapor pressure, and each curve in the log-log relation in Figs. 4, 5, and 6 gradually approaches the broken line which shows the case in which there is no difference in volatility between chlorine and bromine compounds.

The chlorine and bromine contents of magma are considered to decrease rapidly during cooling because of the volatilization of their compounds. Provided that the Br/Cl ratio in any magma is approximately constant and that chlorine and bromine do not enter into the rock-forming minerals in volcanic rocks, the ratio of the retained bromine to the retained chlorine in magmas can be determined by means of the difference in volatility between their compounds. If the chlorine compounds are more volatile than that of bromine under natural conditions, the Br/Cl ratio in rocks will increase as their contents decrease. As can be seen in Fig. 7, the Br/Cl ratios in volcanic rocks fall in a narrow range,

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[11] I. Iwasaki, T. Katsura, and N. Sakato, *Nippon Kagaku Zasshi*, **76**, 778 (1955).

[12] G. G. Goles, L. P. Greenland, and D. Y. Jerome, *Geochim. Cosmochim. Acta*, **31**, 1771 (1967).

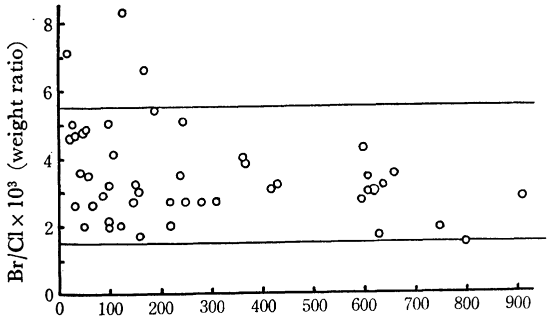

Fig. 7. Relationship between Br/Cl ratio and Cl content in volcanic rocks.

mostly from 1.5×10^{-3} to 5.5×10^{-3} by weight, regardless of the chlorine content and the rock type. This fact seems to result from the close similarity between the volatilities of chlorine and bromine compounds during the cooling process of magma under hydrous conditions.

In order to obtain information on the volatilities of chlorine and bromine compounds from magma, the data on the Br/Cl ratio in volcanic gases may be important. The data in high-temperature volcanic gases are especially required because the chlorine and bromine compounds in low temperature volcanic gases are fractionated by means of the process of sublimation and by other phenomena. For example, Mizutani[13)] and Yoshida *et al.*[4)] pointed out that bromine is strongly enriched in ammonium chloride as volcanic sublimate. From the results of heating experiments on the rocks, Yoshida *et al.*[4)] showed also that bromine is deposited more easily than chlorine. The data on the chlorine and bromine contents in volcanic gases are insufficient. Sugiura *et al.*[14)] and Honda[15)] determined the Br/Cl ratios in volcanic gases from several active volcanoes in Japan. The Br/Cl ratios in gases with temperatures above 300°C are $(1-2)\times10^{-3}$ by weight. This value is a little smaller than that in volcanic rocks. According to Sugiura,[1)] however, the Br/Cl ratios in the volcanic gases are nearly the same as those in volcanic rocks at each volcano studied. From these facts, it seems likely that there is little difference in volatility between chlorine and bromine compounds under magmatic conditions.

As has often been pointed out, water vapor which is believed to be ubiquitous in magma plays an important role in the volatilization of halogen compounds.[7,16,17)] According to the very simple thermodynamic calculations of Kogarko and Ryabchikov,[17)] reactions between water vapor and metal halides at high temperature yield volatile hydrogen halides. In the present study, the addition of water vapor slightly affected the volatilization of chlorine compounds, while it greatly affected that of bromine compounds. This suggests that water vapor formed in rocks on heating reacts with chlorine compounds more effectively than with bromine compounds through the process of the rapid escape of water vapor.

Conclusion

The chlorine compounds are more volatile than those of bromine on heating without water vapor, regardless of the rock type, so the lower the content of retained chlorine during heating, the larger the Br/Cl ratio in rocks. This relation is consistent with the correlation of the Br/Cl ratio with the chlorine content in ordinary chondrites. The difference in volatility between their compounds tend to become noticeably smaller in the presence of water vapor. This fact, and the close relation between the abundance of chlorine and that of bromine in volcanic rocks, show that the ratio of the volatilization loss of chlorine to that of bromine is nearly constant during the cooling process of hydrous magma.

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13) Y. Mizutani, *J. Earth Sci., Nagoya Univ.*, **10**, 149 (1962).

14) T. Sugiura, Y. Mizutani, and S. Oana, *ibid.*, **11**, 272 (1963).

15) F. Honda, *Geochem. J.*, **3** 187 (1970).

16) P. K. Kuroda and E. B. Sandell, *Bull. Geol. Soc. Am.*, **64**, 879 (1953).

17) L. N. Kogarko and I. D. Ryabchikov, *Geochemistry*, **1961**, 1192.