The Fractionation of Halogen Compounds through the Process of the Volatilization and the Sublimation from Volcanic Rocks on Heating*

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The fractionation of elements through the deposition of the solid phases from magmatic gas is one of the most important processes in the differentiation of the magmatic emanation;[1] the solid phases thus formed appear in nature as volcanic sublimates. The "volcanic sublimates" observed at craters or fumaroles are not, however, always the true sublimates deposited from the magmatic emanation; they also include products of reactions among volcanic gases, surface waters and wall rocks. We can not yet clearly distinguish the true sublimates from others, such as the alteration products of the surrounding rocks.

Brun[2] reported in 1911 that ammonium chloride and some other chlorides sublimed from igneous rocks on heating. One of the present authors (M. Y.) reported in a previous paper[3] that small amounts of fluorine and chlorine were deposited on the surface of a silica-glass tube (or on the surface of a hard glass cap) on out-gassing the igneous rocks by heating them above 800°C, and that sodium and ammonium ions were found as the corresponding cations by qualitative tests. These results suggest that a detailed study of the sublimates formed in the laboratory experiments will give exact information about the sublimates directly derived from the magmatic emanation. The results of the previous study[3] and of the preliminary experiments indicate that the main parts of the sublimates are water-soluble and are composed mainly of chlorine, fluorine, sodium, potassium and ammonium.

To study the fractionation of these chemical species during sublimation, the sublimates deposited on the surface of the silica-glass tube were collected into several fractions, at 100°C intervals, by using a thermal-gradient furnace and silica-glass tubes designed for this purpose. The amounts of the chemical species mentioned above were determined separately in each fraction. Further, the amounts of bromine and iodine volatilized and sublimed from volcanic rocks were determined. Qualitative tests were also run in order to examine if there were some other compounds sublimed from the volcanic rock.

Experimental

Materials.—The rock samples used in the study are listed in Table I, together with their chlorine, fluorine, sodium and potassium contents. The bromine and iodine in these rocks have not yet been determined. The bromine content of basalt from Ō-sima was reported by Sugiura et al.[4] as 0.00003%. The methods used in the determination of fluorine and chlorine in the rocks were the same as those used in the previous study.[3] The main chemical compositions of these rocks are also known.[5,6]

Reagent-grade chemicals and redistilled water were used in the preparation of all reagents and in the procedure described in the following section.

Apparatus and Procedures.—The apparatus used in this study is shown in Fig. 1. A platinum

TABLE I. HALOGEN AND ALKALI CONTENTS OF THE ROCK SPECIMENS USED IN THE PRESENT STUDY

No.	Sample	F%	Cl%	Na%	K%
1	Basalt (lava of 1950 Mt. Mihara, Ō-sima Volcano, Tōkyō Metr.)	0.011	0.031	1.5	0.37
2	Basalt (lava of 1962 Miyake-zima Volcano, Tōkyō Metr.)	0.020	0.060	2.1[6]	0.52[6]
3	Andesite (lava of 1946 Sakura-zima Volcano, Kagosima Pref.)	0.035	0.033	2.1[5]	1.2[5]
4	Glassy andesite (lava of 1934 Shōwa-iwō-zima Volcano, Kagosima Pref.)	0.055	0.060	2.5[5]	1.4[5]
5	Liparite (Kōzu-sima Volcano, Tōkyō Metr.)	0.025	0.091	3.3[5]	1.3[5]
6	Obsidian (Imari, Saga Pref.)	0.049	0.062	2.3[5]	3.9[5]

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[1] I. Iwasaki, T. Ozawa, M. Yoshida, T. Katsura, B. Iwasaki, M. Kamada and M. Hirayama, *Bull. Tokyo Inst. Tech.*, No. **47**, 1 (1962).

[2] A. Brun, "Recherches sur l'Exhalation Volcanique," Libraire Kündig, Genéve (1911).

[3] M. Yoshida, This Bulletin, **36**, 773 (1963).

[4] T. Sugiura, M. Takeuchi, M. Watabe and M. Nagao, Read at the Symposium on Geochemistry of the Geochemical Society of Japan and the Chemical Society of Japan, October, 1963.

[5] Geological Survey of Japan, "Chemical Composition of Volcanic Rocks in Japan" (1962).

[6] T. Matsuda and R. Morimoto, *Science (Kagaku)*, **32**, 578 (1962).

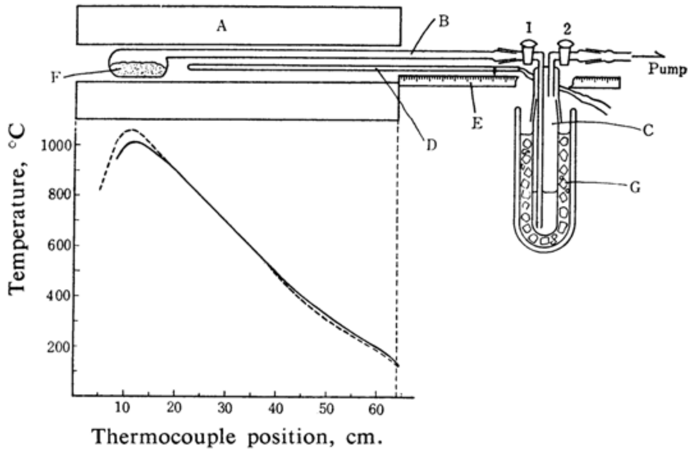

Fig. 1. Apparatus and thermogradient curve in the furnace.

A	Thermal-gradient furnace	B	Silica-glass tube
C	Absorption vessel	D	Thermocouple
E	Stainless steel scale	F	Sample
G	Ice-water	1, 2	Stopcock

—— Curve measured at the inside of the silica-glass tube

---- Curve measured at the outside of the silica-glass tube

TABLE II. METHODS OF ANALYSIS

	Method	Concentration limit of determination	Precision
F^-	*p*-Dimethylaminoazophenylarsonic acid - Zr method[7]	A 0.02—1 p. p. m. B 0.2 —10 p. p. m.	±0.02 p. p. m. ±0.1 p. p. m.
Cl^-	Mercuric thiocyanate method (improved method[8])	0.05—20 p. p. m.	±0.05 p. p. m.
Br^-	Method by its catalytic action on the reaction between I_2 and MnO_4^- [9]	0.01—0.1 p. p. m.	±0.004 p. p. m.
I^-	Method by its catalytic action on the oxidation of $FeSCN^{2+}$ [10]	1 —10 p. p. b.	±0.2 p. p. b.
NH_4^+	Nessler's method	0.1 —20 p. p. m.	±0.05 p. p. m.
Na^+	Flame photometric method	0.05—100 p. p. m.	±5% in relative error
K^+	Flame photometric method	0.05—100 p. p. m.	±5% in relative error

resistance furnace (A) is so made as to obtain an almost linear thermal gradient of 20°C/cm. from 200°C to 1000°C. The temperature distribution is controlled by two transformers; one is connected to a main heater, and the other to an auxiliary heater. The temperature in the furnace is measured by a pyrometer with a movable platinum-platinum, 10% rhodium thermocouple (D); the thermocouple position is read by a stainless steel measure (E) attached to the furnace.

The temperature distribution curves in the furnace measured at the inside and at the outside of the silica-glass tube are also shown in Fig. 1. In the main experiments, the temperature was first measured at the outside and was then corrected to the inside value by means of these curves. The constancy of the distribution of the temperature during an experiment was enough for the present purpose.

The shape of the silica-glass tube used is also shown in Fig. 1 (B). The big end of the tube is 36 mm. in inside diameter and 10 cm. long, while the narrower part is 6 mm. in inside diameter and 65 cm. long. The narrower end of the tube is connected by a taper joint to the absorption vessel (C), which is made of borosilicate glass. To minimize the contamination, the tube was heated and washed twice before use.

Fifty grams of a finely-powdered sample were packed into the big end of the silica-glass tube by using a thistle tube like that used in Penfield's method for the determination of water in rocks. The tube was then connected to the absorption vessel and carefully evacuated to $10^{-1}-10^{-2}$ mmHg. The cock 1 was closed and about 10 ml. of redistilled water was introduced into the vessel. After

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[7] M. Kamada, T. Ōnishi and M. Ōta, This Bulletin, **28**, 148 (1955); M. Kamada and T. Ōnishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 275 (1959).

[8] A. Tomonari, ibid., **83**, 693 (1962).

[9] M. Shiota, S. Utsumi and I. Iwasaki, ibid., **80**, 753 (1959).

[10] S. Utsumi, M. Shiota, N. Yonehara and I. Iwasaki, ibid., **85**, 32 (1964); I. Iwasaki, S. Utsumi and N. Yonehara, ibid., **85**, 36 (1964); N. Yonehara, This Bulletin, **37**, 1101 (1964).

the vessel had been sufficiently evacuated again, cock 1 was opened and cock 2 was closed. Then the silica-glass tube was inserted into the furnace, which had been heated beforehand to obtain the programed temperature distribution, at the sample site temperature of 1000°C. The absorption vessel was cooled by ice water.

About 15 min. were necessary for the stable temperature distribution to be attained. The temperature distribution in the furnace was charefully checked throughout the experiment and was controlled by the transformers if necessary. After 3 hours' heating, cock 1 was closed and the furnace was cooled. Small amounts of liquid water were condensed on the cold part of the tube.

After the furnace had been cooled, a part of the

TABLE III. THE AMOUNTS OF HALOGEN AND ALKALI RELEASED AT 1000°C AND SUBLIMED AT VARIOUS TEMPERATURES

Sample No. 1 Basalt, Ō-sima volcano

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		240	3400	1.1	0.48	100	25	15	0.13	1.4×10^{-4}	3.9×10^{-5}
Sub.	<200°C	26	520	3.8	0.78	280	20	5	0.09_3	3.2×10^{-3}	4.2×10^{-4}
	200–300	2	20	0.0	0.12	0	10	0	0.2	$<2\times10^{-3}$	1.7×10^{-3}
	300–400	1	10	0.0	0.05	0	10	0	(0.2)	$(<4\times10^{-3})$	(1×10^{-3})
	400–500	3	10	0.0	0.00	0	15	5	(0.5)	$(<4\times10^{-3})$	$(<3\times10^{-4})$
	500–600	2	30	0.0	0.00	10	10	10	0.1	$<1\times10^{-3}$	$<1\times10^{-4}$
	600–700	1	20	0.0	0.00	0	5	5	(0.1)	$<2\times10^{-3}$	$<2\times10^{-4}$
	700–800	1	0	0.0	0.00	0	0	0	(>0.2)	—	—
	800–900	1	0	0.0	0.00	0	0	0	(>0.2)	—	—
Total sub.		37	610	3.8	0.95	290	70	25	0.11	2.8×10^{-3}	4.3×10^{-4}
Total evolved		280	4000	4.9	1.43	390	95	40	0.13	5.4×10^{-4}	1.0×10^{-4}

Sample No. 2 Basalt, Miyake-zima volcano

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		340	5100	4.0	0.98	75	0	5	0.12	3.5×10^{-4}	5.4×10^{-5}
Sub.	<200°C	40	350	8.0	0.15	195	5	5	0.21	1.0×10^{-2}	1.2×10^{-4}
	200–300	1	0	0.6	0.06	0	0	0	(>0.2)	$>2\times10^{-2}$	$>2\times10^{-3}$
	300–400	1	0	0.0	0.00	0	0	5	(>0.2)	—	—
	400–500	2	0	0.0	0.00	0	5	5	>0.4	—	—
	500–600	2	30	0.5	0.00	0	20	15	0.12	7×10^{-3}	$<1\times10^{-4}$
	600–700	1	100	0.6	0.00	0	45	20	(0.02)	3×10^{-3}	$<3\times10^{-5}$
	700–800	2	0	0.0	0.00	0	0	0	>0.4	—	—
	800–900	1	0	0.0	0.06	0	0	0	(>0.2)	—	$>2\times10^{-3}$
Total sub.		50	480	9.7	0.27	195	75	50	0.19	9.0×10^{-3}	1.6×10^{-4}
Total evolved		390	5600	14	1.2_5	270	75	55	0.13	1.1×10^{-3}	6.2×10^{-5}

Sample No. 3 Andesite, Sakura-zima volcano

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		380	3200	1.7	0.90	75	10	5	0.22	2.4×10^{-4}	7.8×10^{-5}
Sub.	<200°C	150	550	5.8	0.78	350	5	5	0.51	4.7×10^{-3}	4.0×10^{-4}
	200–300	1	0	0.0	0.08	0	0	5	(>0.2)	—	$>2\times10^{-3}$
	300–400	1	0	0.0	0.20	10	0	0	(>0.2)	—	$>6\times10^{-3}$
	400–500	1	0	0.0	0.00	10	0	0	(>0.2)	—	—
	500–600	1	0	0.0	0.00	0	0	0	(>0.2)	—	—
	600–700	1	20	0.0	0.00	10	15	15	(0.1)	$<2\times10^{-3}$	$<2\times10^{-4}$
	700–800	1	0	0.0	0.00	10	0	0	(>0.2)	—	—
	800–900	0	0	0.0	0.00	0	0	0	—	—	—
Total sub.		156	570	5.8	1.0_6	390	20	25	0.51	4.5×10^{-3}	5.2×10^{-4}
Total evolved		540	3800	7.5	1.9_6	470	30	30	0.27	8.8×10^{-4}	1.5×10^{-4}

TABLE III (Continued)

Sample No. 4 Glassy andesite, Syōwa-iwō-zima volcano

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		1600	11200	6.5	0.26	160	20	5	0.27	2.6×10^{-4}	$6._5\times10^{-6}$
Sub.	<200°C	12	750	$18._6$	0.32	370	0	0	0.030	1.1×10^{-2}	1.2×10^{-4}
	200—300	7	25	0.3	0.03	0	0	0	0.5	5×10^{-3}	3×10^{-4}
	300—400	5	15	0.5	0.02	0	0	0	0.6	$1._5\times10^{-2}$	4×10^{-4}
	400—500	3	35	0.1	0.03	0	15	15	0.2	1×10^{-3}	2×10^{-4}
	500—600	1	10	0.0	0.02	0	5	10	(0.2)	$(<4\times10^{-3})$	(5×10^{-4})
	600—700	0	75	0.2	0.03	0	45	20	<0.03	1×10^{-3}	1×10^{-4}
	700—800	0	0	0.0	0.03	0	0	0	—	—	$>8\times10^{-4}$
	800—900	0	0	0.0	0.02	0	0	0	—	—	$>5\times10^{-4}$
Total sub.		28	910	$19._7$	0.50	370	65	45	0.057	9.6×10^{-3}	1.5×10^{-4}
Total evolved		1630	12100	$26._2$	0.76	530	85	50	0.25	9.6×10^{-4}	1.8×10^{-5}

Sample No. 5 Liparite, Kōzu-sima

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		780	29100	10	0·10	260	5	10	0.050	1.5×10^{-4}	$9._6\times10^{-7}$
Sub.	<200°C	44	1310	57	1.1	660	5	5	0.063	1.9×10^{-2}	2.3×10^{-4}
	200—300	1	80	3.9	0.12	0	0	0	(0.02)	2.2×10^{-2}	4.2×10^{-4}
	300—400	1	15	0.8	0.03	0	0	0	(0.1)	2.4×10^{-2}	6×10^{-4}
	400—500	3	40	0.1	0.03	0	0	5	0.1	1×10^{-3}	2×10^{-4}
	500—600	4	155	0.2	0.03	10	30	35	0.05	6×10^{-4}	5×10^{-5}
	600—700	0	100	0.3	0.03	10	40	10	<0.02	1×10^{-3}	8×10^{-5}
	700—800	0	0	0.0	0.02	0	0	0	—	—	$(>5\times10^{-4})$
	800—900	0	0	0.0	0.03	0	0	0	—	—	$(>8\times10^{-4})$
Total sub.		53	1700	62	1.4	680	75	55	0.058	1.6×10^{-2}	2.3×10^{-4}
Total evolved		830	30800	72	1.5	940	80	65	0.050	1.0×10^{-3}	1.4×10^{-5}

Sample No. 6 Obsidian, Imari

		µg.							Atomic ratio		
		F	Cl	Br	I	NH_4	Na	K	F/Cl	Br/Cl	I/Cl
Abs.		1400	17000	13	0.50	55	5	5	0.15	3.4×10^{-4}	8.2×10^{-6}
Sub.	<200°C	85	560	12	0.30	270	0	5	0.28	9.5×10^{-3}	1.5×10^{-4}
	200—300	0	60	0.7	0.06	0	0	5	<0.03	5×10^{-3}	3×10^{-4}
	300—400	2	15	0.0	0.00	0	0	0	0.2	$<3\times10^{-3}$	$<2\times10^{-4}$
	400—500	3	70	0.0	0.00	0	20	25	0.08	$<6\times10^{-4}$	$<5\times10^{-5}$
	500—600	8	80	0.0	0.00	0	20	25	0.19	$<5\times10^{-4}$	$<4\times10^{-5}$
	600—700	2	5	0.0	0.00	0	0	5	(0.7)	$(<1\times10^{-2})$	$(<6\times10^{-4})$
	700—800	0	0	0.0	0.00	0	0	0	—	—	—
	800—900	1	5	0.0	0.00	10	0	0	(0.4)	$(<1\times10^{-2})$	$(<6\times10^{-4})$
Total sub.		101	800	13	0.36	280	40	65	0.28	7.7×10^{-3}	1.4×10^{-4}
Total evolved		1500	17800	26	0.86	340	45	70	0.16	6.5×10^{-4}	1.4×10^{-5}

silica-glass tube where water was condensed was cut off and washed with water. The washing and the solution in the absorption vessel were combined and made up to 100 ml. in a volumetric flask. The other part of the tube was carefully observed by the naked eyes and by using a magnifying lens. The tube was cut into several pieces of lengths corresponding to the temperature intervals of 100°C. Each piece was washed with water, and the washings were analyzed for halogens and for sodium, potassium and ammonium ions.

The methods for the determination of these chemical species are listed in Table II, together with their precision and the concentration limits of the determination.

The solution in the absorption vessel was made turbid by colloidal sulfur in some experiments. In these cases, an aliquot of the solution was heated by the addition of sodium peroxide to oxidize the sulfur compounds. The halogen content was determined from this solution. Another portion was treated with basic zinc carbonate to remove sulfides, and the ammonium ion content was determined from this. The sodium and potassium contents were determined from the original solution.

Results

Two white spots were observed in the silica-glass tube in all the experiments; one was seen in the 100—200°C range and the other in the 500—700°C range. These two spots were soluble in water. A red or reddish-yellow spot was often found in the 500—700°C range; it was only partly soluble in water, but wholly soluble in 6 N hydrochloric acid. The washings of the pieces of the tube corresponding to the 500—700°C range showed reactions of ferric iron. It has not yet been confirmed what kinds of iron compounds were deposited and how iron was transported. A yellowish-white spot which was insoluble in water was observed in the 100—200°C range in some experiments; this was confirmed to be sulfur by qualitative tests.

The results of the determination of water-soluble halogens and alkalies are shown in Table III, together with the F/Cl, Br/Cl and I/Cl atomic ratios. In this table, "Abs." indicates the amounts of the chemical species found from the solution in the absorption vessel plus the liquid water condensed at the cold part of the silica-glass tube. "Sub." means the amounts of the chemical species found in the washings of each fraction of the tube cut out at 100°C intervals. In the columns of atomic ratios, ( ) means that the amounts of the halogens are fairly small and that the atomic ratio might, therefore, contain a comparatively larger error, while > means that the exact value of the atomic ratio can not be calculated, but only a lower limit of the value given, because the amount of chlorine evolved is smaller than the limit of exact determination.

The amounts of the chemical species contaminated in the experimental procedures were found to be smaller than the lower limit of the determination by means of blank tests.

Discussion

First, comparison between the total amounts of the chemical species evolved from the rocks at 1000°C and those originally contained in the rocks are made. The $(X_{\text{total evolved}}/X_{\text{rock}})\times 100$ values are calculated in Table IV for the elements the contents of which in the rocks are known.

Table IV

Sample No.	$(X_{\text{total evolved}}/X_{\text{rock}})\times 100$ F	Cl	Br	Na	K
1	5.5	26	33	0.0013	0.0021
2	3.9	19	—	0.0007	0.0021
3	3.1	23	—	0.0003	0.0005
4	5.9	40	—	0.0007	0.0007
5	6.7	68	—	0.0005	0.0010
6	6.1	57	—	0.0004	0.0003_5

The amounts of sodium and potassium volatilized from the rocks at 1000°C are very small compared with the amounts in the rocks. Fairly large amounts of chlorine and bromine are evolved from the rock at 1000°C, and the $(\text{Br/Cl})_{\text{total evolved}}$ value is almost equal to the $(\text{Br/Cl})_{\text{rock}}$ value, although there is only one datum on the bromine content in the rock. The $(\text{Cl}_{\text{total evolved}}/\text{Cl}_{\text{rock}})\times 100$ value decreases with an increase in the amounts of the sample; this should be compared with the results of the previous report,[3] in which only 1 g. of the samples was used. The effect is more remarkable in the case of fluorine. The mean value of $(\text{F}_{\text{total evolved}}/\text{F}_{\text{rock}})\times 100$ was about 50% in the previous study, but only about 5% in this study. The "$(\text{F/Cl})_{\text{evolved}} < (\text{F/Cl}_{\text{rock}})$" relation is more clearly recognized in this study than in the previous study.

The second problem to be discussed is the distribution of the chemical species between "Abs." and "Sub." The $(X_{\text{total sub.}}/X_{\text{total evolved}})\times 100$ values are calculated in Table V.

Table V

Sample No.	$(X_{\text{total sub.}}/X_{\text{total evolved}})\times 100$ F	Cl	Br	I	NH_4	Na	K
1	13	15	78	66	74	74	63
2	13	8.6	71	22	72	100	91
3	29	15	77	54	84	67	83
4	1.7	7.5	75	66	70	77	90
5	6.4	5.5	86	93	72	94	85
6	6.7	4.5	49	42	84	89	93

Large percentages of sodium, potassium, ammonium and bromine are deposited on the silica-glass tube. The amounts of chlorine and fluorine deposited are small as compared to those absorbed in water while the amounts of iodine deposited are comparable to those absorbed. The "$(\text{F/Cl})_{\text{abs.}} \fallingdotseq (\text{F/Cl})_{\text{total sub.}}$," "$(\text{Br/Cl})_{\text{abs.}} < (\text{Br/Cl})_{\text{total sub.}}$" and "$(\text{I/Cl})_{\text{abs.}} < (\text{I/Cl})_{\text{total sub.}}$" relations may, therefore, be recognized. On the other hand, Yoshida reported in a previous paper[3] that the $(\text{F/Cl})_{\text{sub.}}$ ratio is always larger than the $(\text{F/Cl})_{\text{abs.}}$ ratio. The discrepancy between the two reports may be ascribed to the difference between the materials on which the halogens were deposited. In the present study, " sublimates " are deposited on the silica-glass surface only. On the other hand, in the previous study " sublimates " might be deposited not only on the silica-glass surface, but also on the hard-glass surface used as a cap for the connection to the absorption vessels. This difference indicates that the main portion of the fluorine determined as " Sub." in the previous study was not a true sublimate, but was deposited by the reaction with the silicate surface.

The third point to be discussed is the problem of how the chemical species are distributed among the sublimates deposited in various temperature regions. To see the general tendency of the distribution, $[X_{(t-t+100^{\circ}C)\,sub.}/X_{total\ sub.}]\times 100$ values were calculated; their mean values are shown in Table VI.

TABLE VI

Mean values of the $[X_{(t-t+100^{\circ}C)sub.}/X_{total\ sub.}]\times 100$ for 6 experiments

Temp., °C	F	Cl	Br	I	NH_4	Na	K
<200	76	80	94	73	97	11	11
200—300	6	3	2	12	0	2	4.5
300—400	4.5	1	0.5	5	0	2	1.5
400—500	5	3	0	1	0	17	18
500—600	5	5	1	1	1	23	32
600—700	1	7	1	1	0.5	44	32
700—800	1	0	0	1	0.5	0	0
800—900	1	0	1	5	0.5	0	0

The following facts may be seen in Table VI:

1) Chlorine and fluorine resemble each other in their distributions. About eighty per cent of each is deposited below 200°C and they show a second maximum in the region between 400°C and 700°C.

2) Almost all ammonium compounds are deposited below 200°C.

3) Large percentages of sodium and potassium are deposited between 400°C and 700°C.

4) Almost all bromine is deposited below 200°C, as in the case of the ammonium compound.

5) Iodine is also largely deposited below 200°C, but it is distributed in higher temperature regions, unlike bromine.

The equivalent relations between the total amounts of cations determined and those of anions are examined for every fraction in Table III. Cations are very deficient in the " Abs." fractions because of the existence of free halogen acids in the solutions. In most " Sub." fractions, the amounts of cations determined are equivalent to those of anions within the range of analytical error. The cations determined are fairly deficient in some fractions, that is, in the 200—300°C fraction and the 500—600°C fraction in the experiment on the obsidian from Imari; in the 200—300°C fraction and the 400—600°C fraction in the experiment on the liparite from Kōzu-sima, and in the 200—300°C fraction in the experiment on the glassy andesite from Syōwa-iwō-zima. Iron is found in the 400—700°C region qualitatively; it may be responsible for the definciency of cations in this temperature region. In the 200—300°C region, some other cations, such as calcium or magnesium must be present, but we have not been able to confirm their existence.

The distribution and equivalent relation of the chemical species determined show that water soluble sublimate deposited below 200°C is mainly composed of ammonium chloride and that that deposited in the 400—700°C region is mainly composed of sodium and potassium chloride.

The F/Cl value has no definite maximum point in any fraction from 100°C to 900°C. The Br/Cl value, in general, reaches its maximum in the 100—300°C region and the I/Cl value, in the 200—400°C region.

A Comparison with Natural Volcanic Emanation.—The Br/Cl (atomic ratio) value of the volcanic gases in Japan has been reported to be $(1—10)\times 10^{-4}$, and the I/Cl value, to be $(1—20)\times 10^{-5}$.[4,11,12] These value agree with the $(Br/Cl)_{abs.}$ and $(I/Cl)_{abs.}$ values obtained in the laboratory experiments. Bromine and iodine in the volcanic gases are, therefore, thought to be supplied from the magma; it is, in general, unnecessary to postulate any other sources.

The water-soluble component of volcanic ash was chosen as a representative of the natural volcanic sublimates in a previous paper,[3] and the "$(F/Cl)_{sublimate}>(F/Cl)_{gas}$" relation was obtained by comparison with natural volcanic gases. As has already been stated, fluorine is not enriched relative to chlorine in the " true sublimate " as compared with the gas phase, but it is enriched in the " so-called sublimate," probably by the reaction with silicates. The enrichment of fluorine in the natural " volcanic sublimates " may be caused by the reaction with silicates or other substances.

Iwasaki, Kamada and Miyaji[13] determined

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[11] T. Sugiura, Y. Mizutani and S. Oana, Read at the Symposium on Geochemistry of the Chemical Society of Japan, October, 1960.

[12] K. Noguchi, T. Gotō, S. Ueno and M. Ichikuni, *Bull. Volcanolog. Soc. Japan* (*Kazan*), 2nd Series, 5, 163 (1961).

[13] I. Iwasaki, M. Kamada and J. Miyaji, Read at the 11th Annual Meeting of the Chemical Society of Japan, April, 1958.

TABLE VII. ATOMIC RATIO AMONG HALOGENS IN NATURAL AMMONIUM CHLORIDE

	Locality	F/Cl	Br/Cl	I/Cl
1	Syōwa-sinzan (Hokkaidō)*,[14]	0.045	0.014	0.5×10^{-5}
	(two analyses)	0.092	0.016	0.6×10^{-5}
2	Mt. Iwate (Iwate Pref.)[12] (three analyses)	—	$(0.9\text{—}1.4)\times10^{-3}$	1×10^{-6}
3	Miyake-zima volcano (Tōkyō Metr.)[16]			
	Group A	—	$(0.4\text{—}1.7)\times10^{-2}$	$(0.0\text{—}1)\times10^{-5}$
	Group B	—	$(0.8\text{—}2.3)\times10^{-2}$	$(0.1\text{—}5.6)\times10^{-4}$
4	Miyake-zima volcano (Tōkyō Metr.)[15]	0.5×10^{-3}	1.1×10^{-3}	1×10^{-6}
5	Tokati-dake (Hokkaidō)[15]	0.5×10^{-3}	1.3×10^{-2}	4.4×10^{-6}

* These samples are contaminated with about 15% sassolite.

TABLE VIII. ATOMIC RATIO AMONG HALOGENS AND ALKALIES IN NATURAL SODIUM AND POTASSIUM CHLORIDE[15]

	Locality	F/Cl	Br/Cl	I/Cl	K/Na
1	Miyake-zima volcano (Tōkyō Metr.)	1.2×10^{-3}	0.45×10^{-3}	1×10^{-6}	0.032
2	Iwō-zima volcano (Kagosima Pref.)	0.3×10^{-3}	2.7×10^{-3}	2×10^{-6}	0.16
	(two analyses)	0.7×10^{-3}	2.8×10^{-3}	1×10^{-6}	0.12

the iodine content in the water-soluble component of volcanic ash. Their study shows that the I/Cl value of the water-soluble component of volcanic ash was $(6\text{—}430)\times10^{-5}$, larger than that of volcanic gases. This relation coincides with that obtained in the laboratory experiment.

Ammonium chloride is widely distributed in active volcanoes. In Japan, it has been found in Syōwa-sinzan,[14] Tokati-dake,[15] Mt. Iwate,[12] Miyake-zima,[15,16] etc.[17] It has not, however, been clearly decided whether ammonia was derived from the magma as an essential component or was the result of contamination from other sources. The results of this study show that ammonia is a common constituent of volatiles from volcanic rocks when they are heated at 1000°C, and that it is deposited below 200°C as ammonium chloride. Mizutani[14] and Noguchi et al.[12,16] analyzed natural ammonium chloride. The atomic ratios among halogens calculated from their data and from our new data[15] are shown in Table VII.

Bromine is strongly enriched and fluorine is not enriched in natural ammonium chloride as compared with the gas phase, in good accordance with the results of the laboratory experiments. Iodine is not enriched in natural ammonium chloride. Mizutani[14] explained the enrichment of bromine in terms of the difference in volatility between ammonium chloride and ammonium bromide. According to this explanation, iodine must also be enriched; he stated that the unstable nature of iodide under fomarolic conditions might be the primary cause of the paucity.

From the results of the present study, the problem may be explained as follows: There is a tendency for iodine to be deposited in higher temperature regions than the region where ammonium chloride is deposited. The temperature gradient may be not so steep at orifice of the natural fumarole as in the furnace used in this study, and so iodine will be more effectively separated from chlorine and bromine.

Sodium chloride has been found as volcanic sublimates in Mt. Mihara, Ō-sima volcano,[18] Miyake-zima volcano[19] and Iwō-zima volcano[15],*; these volcanoes are the most active volcanoes in Japan. Potassium chloride is less common than ammonium and sodium chlorides. It was recently found with sodium chloride at the Kuromoe fumarole (where the orifice temperature is about 600°C) *at Iwō-zima volcano.

Chemical analysis shows that a small amount of potassium is also present in the sodium chloride found in Miyake-zima. The atomic ratios among halogens and alkalies are shown in Table VIII.

Bromine is not so highly enriched in sodium and potassium chloride as in ammonium chloride. Fluorine and iodine are also not enriched.

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[14] Y. Mizutani, *J. Earth Sci. Nagoya Univ.*, **10**, 149 (1962).

[15] Unpublished data by M. Yoshida et al.

[16] K. Noguchi, S. Ueno and H. Kamiya, Read at the Meeting of the Volcanological Society of Japan, October, 1963.

[17] I. Iwasaki "Chemistry of the Volcano" (in Japanese), Kawade Shobō, Tokyo (1948), p. 105.

[18] J. Ossaka, private communication.

[19] J. Ossaka and T. Ozawa, private communication.

* The specimen was collected by Minoru Yoshida as sodium chloride (March 1964). The existence of the sylvine phase was found by Jōyo Ossaka by X-ray analysis. The formula percentage of potassium chloride was found to be 12—16% by chemical analysis. A detailed description of alkali halides found as volcanic sublimates will be given in another paper.

Conclusion

Ammonium chloride, sodium chloride, potassium chloride, iron compounds and sulfur, which have often been found in active volcanoes, have been proved to be capable of forming directly from the magmatic emanation. By comparing the ratio among halogens in natural volcanic products and in products from the laboratory experiments, the following conclusions have been obtained. Bromine is more enriched in the ammonium chloride fraction as compared with the gas phase. Fluorine and iodine behave fairly differently from chlorine in volcanic phenomena. The mechanisms of the fractionation of fluorine and iodine from chlorine are essentially different from one another. The behavior of fluorine in volcanic phenomena is strongly affected by its reaction with silicates.

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