The Volatilization of Chlorine and Fluorine Compounds from Igneous Rocks on Heating[*]

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It is important for the study of volcanic phenomena to make clear the nature of the volcanic emanation. There are many ways of investigation. Some of the most important information on the problem are provided by analyses of volcanic gases, volcanic sublimates and other products of volcanic activity. An investigation of the chemical composition of volcanic gases from more than 600 fumaroles and hot springs in Japan has, accordingly, been carried out by Iwasaki et al.[1] However, the environmental conditions which affect the chemical composition of volcanic gases are so

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[*] Read at the Symposium on Geochemistry of the Chemical Society of Japan, October, 1961.

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

complicated that it is difficult to understand the nature of volcanic emanations satisfactorily on the basis of this information alone.

The second way to investigate the nature of volcanic emanation is to study the equilibrium between the gas phase and the condensed phase represented by the igneous rocks with which the gas phase is thought to be in contact. Some calculations of these gas-solid equilibria have been made by Ellis[2], Krauskopf[3], Matsuo[4], and others. In some cases, a close approach has been made to the chemical composition of natural volcanic gases by theoretical calculations. There remain, however, many difficult problems concerning the maintenance of equilibrium and the insufficiency of thermochemical data on rock-forming minerals.

The third way is to study the nature of the gases obtained by heating igneous rocks. The components of those gases obtained by heating samples of igneous rocks have been studied by many investigators[5-13]. Little work has, however, been done on the halogen compounds evolved from igneous rocks on heating. Shepherd[9-11] studied the amount of chlorine and fluorine compounds evolved at 1200°C. Brun[8] reported that chlorine compounds were evolved from igneous rocks at temperatures higher than "the explosion temperature". Iwasaki et al.[13] reported that the evolution of hydrogen chloride occured when rocks were heated at temperatures above 800°C. However, the exact relationships between the temperature and the amount of evolved halogen compounds, especially that of fluorine, have not yet been established. The objectives of the present paper are to make clear the volatilization of chlorine and fluorine compounds from igneous rocks at various temperatures ranging from 400 to 1200°C.

Experimental

Materials.—The rock samples used in this study are listed in Table I, together with their chlorine and fluorine contents. The chlorine in the rocks was determined by the method of Iwasaki et al.[13] with some improvements, while the fluorine in the rocks was determined by the method of Kamada et al.[14] The main chemical composition of these rocks is also known.

Reagent grade chemicals and redistilled water were used in the preparation of all reagents and in the procedures.

Methods of Collecting Halogens Evolved from Rock Samples.—The apparatus used in this study is shown in Fig. 1. The maximum temperature attained by electric furnace A is about 1300°C, and the temperature can be controlled with an accuracy of ±20°C. A pyrometer with a platinum-platinum, 10% rhodium thermocouple D was used to measure the temperature of the furnace. A silica-glass tube B (1 m. in length, 25 mm. in inside diameter) was connected to the commercial nitrogen gas cylinder and absorption vessels E by taper joints. Two absorption vessels were connected in a series, each of them containing about 75 ml. of a 0.05 N sodium hydroxide solution.

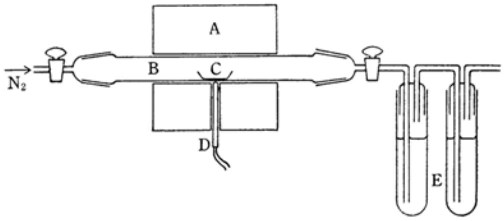

Fig. 1. Apparatus.

A	Electric furnace
B	Silica-glass tube
C	Platinum boat
D	Thermocouple
E	Absorption vessels

One gram of a finely powdered sample was placed in a platinum boat, which was then inserted in silica-glass tube B and placed in the center of the furnace. The flow of nitrogen gas was then started at the rate of 20∼30 l./hr. After the air in the apparatus had been replaced by nitrogen, the sample was heated to a programmed temperature and was maintained at that temperature for one hour. Experiments were carried out at 400, 600, 800, 1000 and 1200°C (in one case, also at 200°C). The acid gas species evolved from the sample in the nitrogen gas were absorbed by the solution in absorption vessels. After the furnace had been cooled, the solutions in each absorption vessel were diluted to 100 ml. in a volumetric flask. An aliquot of the solution was used for the determination of fluoride. Another portion was used for the determination of chloride after oxidizing the sulfide ion by heating the solution with a small amount of sodium peroxide. Sublimates were deposited on the inside surface of the silica-glass tube on outgassing the rocks. These sublimates were dissolved in water by washing the inside of the silica-glass tube three times. All the washings were transferred

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2) A. J. Ellis, *Am. J. Sci.*, **255**, 416 (1957).

3) K. B. Krauskopf, "Researches in Geochemistry", Ed. by P. H. Abelson, John Wiley and Sons, Inc., New York (1959), p. 260.

4) S. Matsuo, *J. Earth Sci. Nagoya Univ.*, **8**, No, 2, 222 (1960); 9, No. 1, 80, 101 (1961).

5) T. Graham, *Proc. Roy. Soc.*, **15**, 502 (1867).

6) A. Gautier, *Compt. rend.*, **132**, 58, 189 (1901).

7) R. T. Chamberlin, "The Gases in Rocks", Carnegie Inst. Wash. Rubl., Washington, D. C. (1908).

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

9) E. S. Shepherd, *J. Geol.*, **33**, (Supplement to No. 3), 289 (1925).

10) E. S. Shepherd and H. E. Merwin, ibid., **35**, 97 (1927).

11) E. S. Shepherd, *Am. J. Sci.*, **35A**, 311 (1938).

12) Lord Rayleigh, *Proc. Roy. Soc.*, **170**, 451 (1939).

13) I. Iwasaki, T. Katsura and N. Sakato, *J. Chem. Soc. Japan, Pure Chem. Sec.*(*Nippon Kagaku Zassi*), **76**, 778, 1116 (1955).

14) The Chemical Society of Japan, "Jikken Kagaku Koza" (Experimental Chemistry), Vol. 14, "Geochemistry" (in Japanese), Maruzen, Tokyo (1958), p. 333.

TABLE I. F AND Cl CONTENTS OF THE ROCK SPECIMENS USED IN THE PRESENT STUDY

No.	Sample	F%	Cl%	F/Cl (atomic ratio)
1	Basalt (lava of 1950 Mt. Mihara Ō-sima volcano, Tokyo Metr.)	0.011	0.031	0.66
2	Basalt (Sakasagawa, Itō, Sizuoka Pref.)	0.025	0.010	4.7
3	Andesite, (Tamagawa hot spring, Akita Pref.)	0.042	0.010	7.9
4	Andesite (lava of 1946 Sakura-zima volcano, Kagoshima Pref.)	0.035	0.033	2.0
5	Dacite (somma lava Akagi volcano, Gumma Pref.)	0.027	0.003	17
6	Liparite (Kōzu-sima volcano, Tkoyo Metr.)	0.025	0.091	0.51
7	Obsidian (Imari, Saga Pref.)	0.049	0.062	1.5
8	Obsidian (Hime-sima, Oita Pref.)	0.049	0.016	5.7
9	Granite (Mt. Tukuba, Ibaragi Pref.)	0.057	0.010	11
10	Granite (Kiuragi, Saga Pref.)	0.028	0.005	10

into a 100 ml.-volumetric flask and diluted to the mark to determine the chlorine and fluorine contents. To minimize the contamination during the procedure, the silica-glass tube and platinum boat were heated and washed in duplicate before being used.

Methods of Determining the Chloride and Fluoride in the Solution.—The chloride was determined by the mercuric thiocyanate method[15] with some improvements. By using this method a difference of 5 μg. of chloride per 100 ml. can be distinguished in the range of 5～200 μg. per 100 ml.

The fluoride was determined by the *p*-dimethylaminoazophenylarsonic acid-zirconium method[16]. A difference of 1 μg. fluoride per 100 ml. can be distinguished in the range of 2～100 μg. per 100 ml. by procedure A, while a difference of 10 μg. of fluoride per 100 ml. can be distinguished in the range of 20～1000 μg. per 100 ml. by procedure B. The accuracy and precision of the methods are enough for the present purposes.

Results and Discussion

Amount of Chlorine and Fluorine Evolved from Igneous Rocks.—To determine the amounts of chloride and fluoride contaminated from reagents, nitrogen gas, or experimental procedures, blank tests were carried out at 1200°C. 10 μg. of chlorine was found from the solutions in each absorption vessel, and 6 μg. of chlorine was found from the solution washed inside the silica-glass tube. However, fluorine was found in neither of them. The data of chloride were corrected for these blank values.

Two absorption vessels connected in a series were used for absorbing the acid gases, but usually both chlorine and fluorine were absorbed almost completely by the solution in the first vessel.

Very small amounts of chlorine and fluorine were evolved from the sample which had once been heated at 1200°C for one hour on reheating at the same temperature for two hours.

The data obtained are shown in Table II. In this table, "Abs." means the amount of chlorine or fluorine determined from the solution in absorption vessels, "Sub." means the amount of chlorine or fluorine determined from the solution washed inside the silica-glass tube, and "Total" is equal to "Abs." plus "Sub.". In the last two columns of the same table, the atomic ratios F/Cl and $(F/Cl)/(F/Cl)_{\text{original rock}}$ are given. In these two columns, ( ) means that the amounts of evolved chlorine and fluorine are fairly small and that the F/Cl ratio might, therefore, contain comparatively a larger error, while > means that the exact value of F/Cl can not be calculated, but only a lower limit of the value given, because the amount of evolved chlorine is smaller than the limit of exact determination.

To examine the reproducibility of the processes, the experiments were duplicated by using basalt from Ō-sima. The results are to be seen in Table II-1. The reproducibility is enough to illustrate the releasing tendency of halogen in rocks at different temperatures.

The percentage of $X_{\max}$ to the amount of halogen originally contained in 1 g. of rock sample is shown in Table III. $X_{\max}$ means the amount of halogen evolved from 1 g. of a certain rock sample at a temperature where the amount reaches its maximum value in each series of experiments. In most cases the temperature was 1200°C. This table shows that, in general, chlorine and fluorine in a rock can not be completely evolved at temperatures at or below 1200°C, as was reported in previous papers[11,13]. As may be seen in Tables II and III, chlorine is generally easier to release by heating than fluorine, so the

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[15] I. Iwasaki, S. Utsumi and T. Ozawa, This Bulletin, **25**, 226 (1952); S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **73**, 835 (1952).

[16] M. Kamada, T. Onishi and M. Ota, This Bulletin, **28**, 148 (1955); M. Kamada and T. Onishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zashhi*), **80**, 275 (1959).

TABLE II. THE AMOUNTS OF Cl AND F RELEASED AT VARIOUS TEMPERATURES

Sample No. 1 Basalt, Ō-sima volcano

Temp., °C		Amounts of evolved halogen, μg.		F/Cl (atomic ratio)	$(F/Cl)/(F/Cl)_{rock}$
		Cl	F		
Abs.	400	10, 0	2	(0.7)	(1)
	600	25, 30	0	(0)	(0)
	800	105, 85	20	0.39	0.59
	1000	185, 155	26	0.29	0.44
	1200	200, 235	25	0.21	0.32
Sub.	400	5, 0	1, 1, 2	(0.7)	(1)
	600	5, 5	3, 2, 5	(1.1)	(2)
	800	5, 5	21, 14, 18	6.7	10
	1000	10, 15	18, 20, 18	2.8	4.2
	1200	25, 25	20, 17, 20	1.4	2.1
Total	400	15, 0	4	(1.0)	(1.5)
	600	30, 35	5	(0.3)	(0.4)
	800	110, 90	38	0.71	1.1
	1000	195, 170	44	0.45	0.68
	1200	220, 260	45	0.35	0.53
		Sample No. 2	Basalt, Itō		
Abs.	400	10	1	(0.2)	(0.04)
	600	15	0	(0)	(0)
	800	30	1	0.1	0.02
	1000	70	50	1.3	0.28
	1200	100	86	1.6	0.34
Sub.	400	0	0	—	—
	600	0	1	(>0.4)	(>0.08)
	800	0	8	>3	>0.6
	1000	0	22	>8	>1.7
	1200	0	38	>14	>3
Total	400	10	1	(0.2)	(0.04)
	600	15	1	(0.1)	(0.02)
	800	30	9	0.6	0.13
	1000	70	72	1.9	0.40
	1200	100	124	2.3	0.49
		Sample No. 3	Andesite, Tamagawa hot spring		
Abs.	400	10	1	(0.2)	(0.02)
	600	10	1	(0.2)	(0.02)
	800	25	52	3.9	0.49
	1000	55	220	7.5	0.95
	1200	65	220	6.3	0.80
Sub.	400	0	2, 4	(>1)	(>0.1)
	600	0	7, 7	>2.5	>0.3
	800	0	24, 31	>9	>1
	1000	0	49, 55	>18	>2
	1200	0	53, 49	>18	>2
Total	400	10	5	(0.9)	(0.1)
	600	10	8	(1.5)	(0.2)
	800	25	83	6.2	0.78
	1000	55	280	9.5	1.2
	1200	65	270	7.8	0.99

TABLE II (Continued)

Sample No. 4 Andesite, Sakura-zima volcano

Temp., °C		Amounts of evolved halogen, μg.		F/Cl (atomic ratio)	$(F/Cl)/(F/Cl)_{rock}$
		Cl	F		
Abs.	400	20	0	(0)	(0)
	600	50	2	0.07	0.04
	800	245	150	1.1	0.55
	1000	350	200	1.1	0.55
	1200	340	180	0.99	0.50
Sub.	400	0	1	(>0.4)	(>0.2)
	600	0	5	>2	>1
	800	0	29	>11	>5.5
	1000	0	41	>15	>7.5
	1200	0	36	>13	>6.5
Total	400	20	1	(0.09)	(0.05)
	600	50	7	0.26	0.13
	800	245	180	1.4	0.70
	1000	350	240	1.3	0.65
	1200	340	220	1.2	0.60
Sample No. 5 Dacite, Akagi volcano					
Abs.	400	10	1	(0.2)	(0.01)
	600	10	1	(0.2)	(0.01)
	800	10	1	(0.2)	(0.01)
	1000	15	9	1.1	0.06
	1200	30	98	6.1	0.36
Sub.	400	0	1	(>0.4)	(>0.02)
	600	0	1	(>0.4)	(>0.02)
	800	0	4	>1	>0.08
	1000	0	14	>5	>0.3
	1200	0	31	>11	>0.6
Total	400	10	2	(0.4)	(0.02)
	600	10	2	(0.4)	(0.02)
	800	10	5	(0.9)	(0.05)
	1000	15	23	2.9	0.17
	1200	30	129	8.0	0.47
Sample No. 6. Liparite, Kōzu-sima					
Abs.	200	10	—	—	—
	400	20	0	0	0
	600	125	0	0	0
	800	465	50	0.20	0.39
	1000	705	91	0.24	0.47
	1200	670	72	0.20	0.39
Sub.	200	0	—	—	—
	400	25	4, 4	0.30	0.59
	600	35	6, 6	0.32	0.63
	800	55	31, 25	0.95	1.9
	1000	45	36, 38	1.5	2.9
	1200	55	29, 35	1.1	2.2
Total	200	10	—	—	—
	400	45	4	0.17	0.33
	600	160	6	0.07	0.14
	800	520	75	0.27	0.53
	1000	750	129	0.32	0.63
	1200	725	107	0.28	0.55

TABLE II (Continued)

Sample No. 7 Obsidian, Imari

Temp., °C		Amounts of evolved halogen, μg.		F/Cl (atomic ratio)	(F/Cl)/(F/Cl)$_{rock}$
		Cl	F		
Abs.	400	15	1	(0.1)	(0.07)
	600	50	2	0.07	0.05
	800	320	130	0.76	0.51
	1000	515	240	0.87	0.58
	1200	525	180	0.64	0.43
Sub.	400	0	1	(>0.4)	(>0.2)
	600	0	4	>1.5	>1
	800	0	24	>9	>6
	1000	5	49	18	12
	1200	10	42	8	5
Total	400	15	2	(0.2)	(0.1)
	600	50	6	0.22	0.15
	800	320	150	0.87	0.58
	1000	520	290	1.0	0.67
	1200	535	220	0.77	0.51
		Sample No. 8 Obsidian, Hime-sima			
Abs.	400	10	0	(0)	(0)
	600	10	0	(0)	(0)
	800	65	190	5.5	0.96
	1000	120	300	4.7	0.82
	1200	115	270	4.4	0.77
Sub.	400	0	2	>0.7	>0.1
	600	0	5	>2	>0.3
	800	0	33	>12	>2
	1000	0	47	>17	>3
	1200	0	36	>13	>2
Total	400	10	2	(0.4)	(0.07)
	600	10	5	(0.9)	(0.16)
	800	65	220	6.3	1.1
	1000	120	350	5.4	0.95
	1200	115	310	4.9	0.86
		Sample No. 9 Granite, Mt. Tukuba			
Abs.	400	10	1	(0.2)	(0.02)
	600	20	0	(0)	(0)
	800	15	1	(0.1)	(0.01)
	1000	45	280	12	1.1
	1200	35	340	18	1.6
Sub.	400	0	0, 1	—	—
	600	0	4, 1	(>1)	(>0.1)
	800	0	22, 15	>7	>0.6
	1000	0	51, 75	>24	>2
	1200	0	80, 74	>29	>2.5
Total	400	10	2	(0.4)	(0.03)
	600	20	1	(0.1)	(0.01)
	800	15	16	2.0	0.18
	1000	45	360	15	1.4
	1200	35	410	22	2.0

Table II (Continued)

Sample No. 10 Granite, Kiuragi

Temp., °C		Amounts of evolved halogen, μg.		F/Cl (atomic ratio)	$(F/Cl)/(F/Cl)_{rock}$
		Cl	F		
Abs.	400	0	0	—	—
	600	10	1	(0.2)	(0.02)
	800	25	1	0.1	0.01
	1000	40	87	4.1	0.41
	1200	50	137	5.1	0.51
Sub.	400	0	1	(>0.4)	(>0.04)
	600	0	1	(>0.4)	(>0.04)
	800	0	7	>2.5	>0.25
	1000	0	33	>12	>1.2
	1200	0	39	>14	>1.4
Total	400	0	1	(>0.4)	(>0.04)
	600	10	2	(0.4)	(0.04)
	800	25	8	(0.6)	0.06
	1000	40	120	5.6	0.56
	1200	50	176	6.6	0.66

Table III

Sample No.	$[X_{max}/(\text{Amount of halogen in the rock})] \times 100$	
	Cl	F
1	84	41
2	100	50
3	65	66
4	106	69
5	100	48
6	82	52
7	86	59
8	75	71
9	45	72
10	100	63

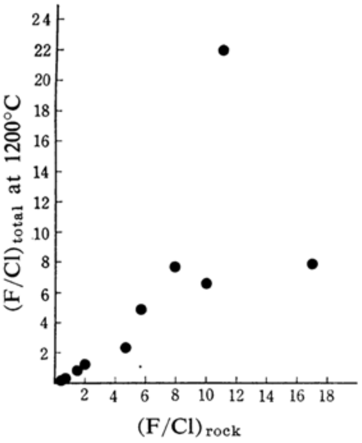

Fig. 2. Relation between $(F/Cl)_{rock}$ and $(F/Cl)_{total}$.

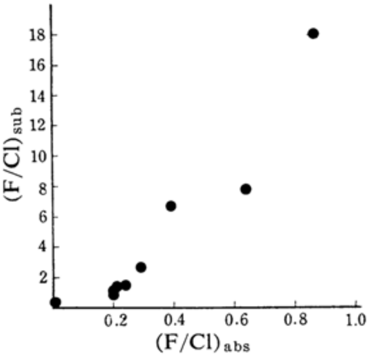

Fig. 3. Relation between $(F/Cl)_{abs}$ and $(F/Cl)_{sub}$.

$(F/Cl)_{evolved,\ total}$ ratio is smaller than the $(F/Cl)_{original\ rock}$ ratio. The $(F/Cl)_{sub}$ ratio is always larger than the corresponding $(F/Cl)_{abs}$ ratio. The results indicate that fluorine is more easily deposited on the surface of the silica-glass tube than chlorine.

$(F/Cl)_{total}$ at 1200°C is plotted against $(F/Cl)_{rock}$ (Fig. 2), and $(F/Cl)_{abs}$ is plotted against $(F/Cl)_{sub}$ (Fig. 3). In these figures, F/Cl values with ( ) or > in Table II are omitted. The almost linear relations, how the F/Cl value of the gas increases as the F/Cl value of the original rock increases, and how the F/Cl value of the sublimate increases as the F/Cl value of the gas from which the sublimate is deposited increases, will be readily seen in these figures.

It has been already stated that 30% or more of the fluorine in the rock is not given off at temperatures at or below 1200°C. However, it can not be decided from the data given in

Table II whether this 30% of the fluorine still remains in the rock or is deposited on the silica-glass tube in a water-insoluble form. In order to make clear the balance of fluorine, rock samples (basalt from Ō-sima and andesite from Tamagawa) which had been heated at 1000°C were analyzed for fluorine and were compared with F_{abs}, F_{sub}, and $F_{original\ rock}$ (Table IV). It may be safely said that the amount of fluorine which deposits on the surface of the silica tube in a water-insoluble form is fairly small compared with that in other forms.

TABLE IV

	F corresponding to 1 g. of original rock (μg.)	
	Basalt Ō-sima	Andesite Tamagawa
Abs.	26± 1	220±10
Sub.	18± 1	55± 1
Residual in the rock	60±20	100±20
Sum	104	375
Original rock	110±20	420±20

The percentage of F_{max} to the amount of fluorine originally contained in the rock sample has a correlation with the fluorine contents of the rock sample, as may be seen in Fig. 4.

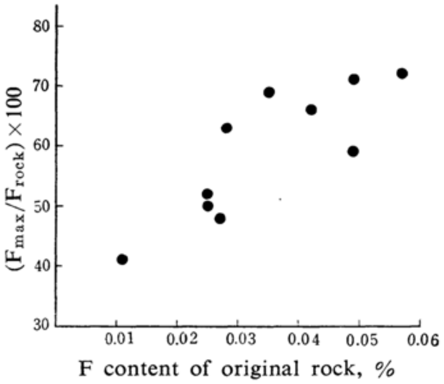

Fig. 4. Relation between F content of original rock and $(F_{max}/F_{rock}) \times 100$.

To see the change in the amounts of evolved fluorine and chlorine at different temperatures, the value [(the amount of chlorine or fluorine evolved from a certain rock sample at a certain temperature)/X_{max}] × 100 is plotted against the temperature (Figs. 5 and 6). Using this value, the results of experiments with various rock samples can be compared with each other in the same diagram. Chlorine compounds are evolved at 600°C (in the experiment with liparite from Kōzu-sima at 400°C), and the amount of evolved chlorine compounds increases gradually with the elevating temperature. On the other hand, although fluorine compounds are evolved scarcely at all at temperatures below 800°C, the amount of evolved fluorine increases suddenly at a certain temperature above 800°C. The temperature above which fluorine compounds are evolved varies from 800 to 1200°C with the kind of rocks.

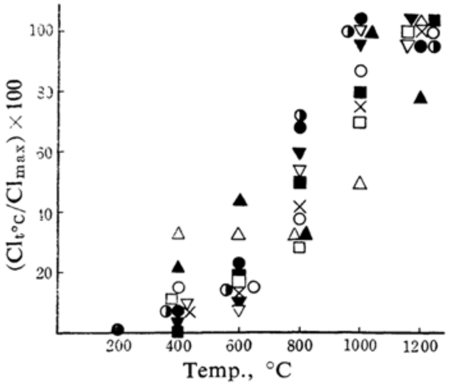

Fig. 5. The change of the amounts of Cl evolved at different temperatures.

× Basalt, Ō-sima
☐ Basalt, Itō
○ Andesite, Tamagawa hot spring
◑ Andesite, Sakura-zima
△ Dacite, Mt. Akagi
● Liparite, Kōzu-sima
▼ Obsidian, Imari
▽ Obsidian, Hime-sima
▲ Granite, Mt. Tukuba
■ Granite, Kiuragi

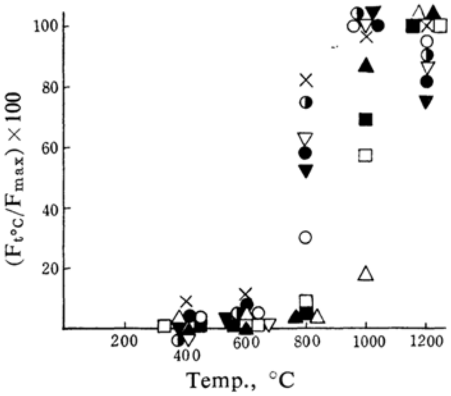

Fig. 6. The change of the amounts of F evolved at different temperatures.

× Basalt, Ō-sima
☐ Basalt, Itō
○ Andesite, Tamagawa hot spring
◑ Andesite, Sakura-zima
△ Dacite, Mt. Akagi
● Liparite, Kōzu-sima
▼ Obsidian, Imari
▽ Obsidian, Hime-sima
▲ Granite, Mt. Tukuba
■ Granite, Kiuragi

From these results, it is obvious that the behavior of fluorine and chlorine in the igneous rocks differs markedly when they are heated at high temperatures.

The temperature above which fluorine compounds are evolved must be related to the state of fluorine in rocks. It is interesting to compare this temperature with the various natures of igneous rocks. For this purpose, it is best to determine this temperature by continuous measurement of the amount of evolved fluorine. It is, however, hard to make such experiments, with various kinds of rocks. In this paper, only the values measured at intervals of 200°C are available. The $1/2\cdot[\{(\text{Amount of F evolved at } 800°\text{C})/F_{\max}\}\times 100 + \{(\text{Amount of F evolved at } 1000°\text{C})/F_{\max}\}\times 100]$ value is used in place of the temperature above which fluorine compounds are evolved. As will be readily understood from the formula mentioned above, the larger the value the lower the temperature above which fluorine compounds are evolved. Comparing this value with the chemical composition of the rocks, it is found that the value has a relation with the fluorine and chlorine contents of the rock. The values mentioned above are plotted against the F/Cl and 1/Cl of the rocks (Figs. 7 and 8). Very good correlations are seen in these figures. The phenomena observed in Figs. 4, 7 and 8 may give interesting suggestions on the distribution of fluorine and chlorine in the igneous rocks.

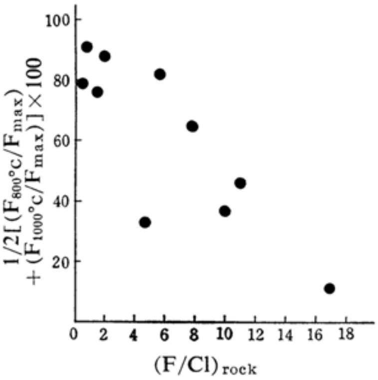

Fig. 7. Relation between $(F/Cl)_{rock}$ and $1/2[(\text{Amount of F evolved at } 800°\text{C}/F_{max})\times 100+(\text{Amount of F evolved at } 1000°\text{C}/F_{max})\times 100]$.

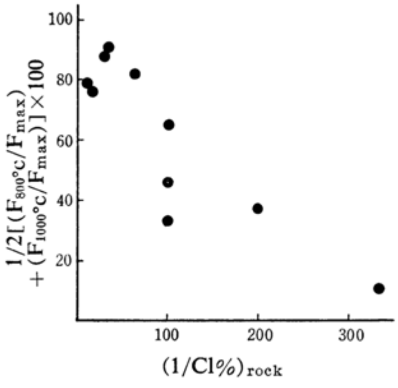

Fig. 8. Relation between $(1/Cl)_{rock}$ and $1/2[(\text{Amount of F evolved at } 800°\text{C}/F_{max})\times 100+(\text{Amount of F evolved at } 1000°\text{C}/F_{max})\times 100]$.

A Comparison with Natural Volcanic Emanation.—Data on the chlorine and fluorine contents of volcanic gases are rather scarce. Day and Shepherd[17] determined the chlorine and fluorine contents of condensed water from magmatic gases which were exhaled directly from a lava lake of Kilauea volcano, Hawaii, thus obtaining 4 g.Cl/l. and 10 g.F/l. data. Iwasaki et al.[18] obtained condensed water from magmatic gas exhaled from a lava lake of Mt. Mihara, Ō-sima volcano; its chlorine content was 67.7 g./l. The present author has determined the chlorine and fluorine contents of many samples of condensed water from active fumarolic gases in Japan*; their maximum values are 42 g.Cl/l. and 3 g.F/l. (Kamanokuti fumarole, Iwo-zima volcano).

The H_2O (+) content of the basalt from Ō-sima volcano used in the laboratory experiments is 0.3% (analyst: B. Iwasaki). Therefore, 3 mg. (3 μl. as liquid water) of water will be obtained from 1 g. of rock sample on heating. The laboratory experiments in this paper show that 240 μg. of Cl and 45 μg. of F are evolved from 1 g. of basalt from Ō-sima volcano at 1200°C. If we made condensed water from the gas evolved from this rock sample, the concentration of halogen in the water would be 80 g.Cl/l. and 15 g.F/l. respectively. It is interesting that these values agree well with the maximum halogen concentrations in water condensed from natural volcanic gases.

The "$F/Cl_{rock} > F/Cl_{gas}$" and "$F/Cl_{sublimate} > F/Cl_{gas}$" relations were obtained in laboratory experiments. To ascertain whether or not these relations are also true in natural volcanic phenomena, comparisons among the data on natural volcanic products were made. Many data on the fluorine and chlorine contents in igneous rocks are reviewed by Correns[19]. The mean value of the F/Cl (atomic ratio) calculated from those data and from data on

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[17] A. L. Day and E. S. Shepherd, *Bull. Geol. Soc. Am.*, **24**, 573 (1913).

[18] I. Iwasaki, T. Katsura, H. Shimojima, T. Ozawa, T. Tarutani and K. Sato, *Bull. Volcanological Soc. Japan*, 2nd Series, **3**, 70 (1958).

* Partly reported in Ref. 1. The details of the study will be reported on in another paper.

[19] C. W. Correns, *Neues Jb. Mineral. Abh.*, **91**, 239 (1957).

Japanese volcanic rocks[20] is 5.3 for igneous rocks. The mean value of F/Cl (atomic ratio) for the volcanic gases in Japan* is about 0.1, and a comparison between the mean values gives the “$F/Cl_{rock} > F/Cl_{gas}$” relation again. It is difficult to find representative data on the F/Cl value of natural volcanic sublimate to be compared with sublimate in laboratory experiments. There are indeed some data on the fluorine and chlorine content of volcanic sublimate. However, in natural conditions, several halogen-bearing minerals are formed by the fractional sublimation from a certain volcanic gas, and the distribution of halogen in these minerals is not uniform. Investigators of the volcanic sublimate usually endeavor to obtain mineral samples of a high purity, but these individual samples represent only a part of the whole sublimate which corresponds to the sublimate in the laboratory experiments. In this paper, the author used the data on the water-soluble component of volcanic ash as a representative of the natural volcanic sublimate, because the volcanic ash is discharged from a volcanic vent with large amounts of volcanic gas and is cooled rather quickly; it is hard, therefore, for fractional separation to occur. The fluorine and chlorine contents of volcanic ash have been studied by Kamada et al.[21] Their study shows that the F/Cl of the water-soluble component of volcanic ash was $0.1\sim7$ (mean value 0.8). The “$F/Cl_{sublimate} > F/Cl_{gas}$” relation is obtained by comparing mean values.

The comparisons of mean values are somewhat ambiguous and may sometimes lead to a wrong conclusion. Therefore, the F/Cl value of the volcanic gas, volcanic rock and water-soluble parts of volcanic ash from the same volcano should be compared with each other. Such data are rather scarce, however; only two sets of data are available, one of Naka-dake Aso volcano[22], and another of Mt. Mihara, Ō-sima volcano. They are shown in Tables V and VI respectively. It may be readily seen in the tables that F/Cl_{rock} is larger than F/Cl_{gas} and that $F/Cl_{sublimate}$ is larger than F/Cl_{gas}.

Table V. F/Cl (atomic ratio) of volcanic products of 1958 activity of Naka-dake Aso volcano (by H. Matsumoto and S. Tanaka)[22]

Fumarolic gas	June (231°C)	0.077
Fumarolic gas	July (139°C)	0.0080*
Water soluble component of volcanic ash		0.18
Old lava		0.55
New scoria		0.80

* Determined by the present author

Table VI. F/Cl (atomic ratio) of volcanic products of Mt. Mihara Ō-sima volcano (by M. Kamada)[1,21],etc.

Fumarolic gas	Aug. 1958 (270°C)	0.37
Water soluble component of volcanic ash	Oct. 1957	0.52
	Aug. 1958	1.35
Lava of 1950		0.66*

* Determined by the present author

Conclusion

From the foregoing results, it may be concluded that chlorine and fluorine behave in different ways in the process of the separation of the gas phase from the solid phase. Fluorine compounds are less volatile than that of chlorine and are more liable to be fixed in solid phases as a sublimate.

A comparison between the results of the laboratory experiments and the data on natural volcanic products suggests that the study of the behavior of halogen compounds during heat treatment would be useful in understanding volcanic phenomena.

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

[21] M. Kamada et al., read at the Symposium on Geochemistry of the Chemical Society of Japan, July, 1957, and at the Meeting of the Volcanological Society of Japan, October, 1957,

[22] H. Matsumoto and S. Tanaka, *Kumamoto J. Sci.*, Series A, **4**, No. 2, 151 (1959).