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An Experimental Study on the Role of Water Vapor in the Distribution of Fluorine and Chlorine in Volcanic Rocks

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Fluorine and chlorine contents of volcanic rocks were examined with respect to the characteristics of the rocks. Fluorine showed rather linear relationships with some chemical components of the rocks and also with stages in the differentiation of magmas. But any universal relationship covering all the rock types was not found. The cause of this fact is expected to be the loss of halogens from rocks resulted from the interaction between rocks and water vapor, which is believed to be ubiquitous in magma and is gradually emanated from it during or after the formation of rocks. So, in order to make clear the role of water vapor in the distribution of halogens in rocks, the author has distilled fluorine and chlorine from rock samples with water vapor at elevated temperatures and studied following relations; (1) the relationship between the amount of distilled halogens and the fluorine and chlorine contents of the rocks, and (2) the relationship between the amount of distilled halogens and the characteristics of the rocks. In distillation of fluorine and chlorine with water vapor, almost all fluorine remained in each rock specimen at low temperatures below 300°C, and at temperatures above 700°C the ratio of the amount of distilled fluorine to the initial amount of fluorine in rocks fluctuated among specimens. However, there was no relation between patterns of the distilled fluorine and the fluorine content of the rocks, and also the characteristics of the rocks. Meanwhile, distillation curve of chlorine showed various patterns without having any relation to chlorine content of the rocks, and indicated that chlorine was retained more in basic rocks than in acidic rocks at higher temperatures, although no relation was observed between the chlorine content of the rocks and the characteristics of the rocks. Generally the ratio of distilled fluorine to initial fluorine in rocks is smaller than the ratio of distilled chlorine to initial chlorine in rocks at low temperatures. The results of the distillation experiments suggest that the distillation process of halogens with water vapor controlls the distribution of halogens in volcanic rocks more than does the chemical and mineralogical nature of the rocks.

Fluorine and chlorine contents of volcanic rocks are known to vary in wide range from nearly zero to a few thousand ppm. The cause of the variation is not yet exactly known. Many investigators have attempted to find relationships between the halogen contents and the characteristics of the rocks. The relationship between chlorine and silica in rocks is controversial. According to Goldschmidt,1) Simonen,2) Behne3) and others, chlorine is generally more abundant in acidic rocks than in basic rocks. Kuroda and Sandell,4) Iwasaki *et al.*5) Correns6) and others, however, reported no marked association of chlorine with silica in rocks. From the mineralogical point of view, all the fluorine seemed to be fixed in apatite in the case of basaltic rocks.7) Neverthless, Koritnig,8) Iwasaki *et al.*9,10) reported that the concentrations of fluorine and chlorine in rocks could not be explained from their amounts in apatite. Iwasaki and Katsura11) experimentally concluded that the solubility of hydrogen chloride in volcanic rock melts was reciprocal to the silica content of the melts. The analytical results in Miyakejima leva flow, however, were inconsistent with the experiments mentioned above12); that is, the

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1) V. M. Goldschmidt, "Geochemistry," Clarendon Press, Oxford (1954).

2) A. Simonen, *Bull. Comm. Geol. Finlande,* **143**, 1 (1948).

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

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

5) I. Iwasaki, K. Katsura, N. Sakato and K. Hirayama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.),* **78**, 164 (1957).

6) C. W. Correns, "The Physics and Chemistry of the Earth," Vol. 1, Pergamon Press, London (1956).

7) T. Barth, *J. Geol.,* **55**, 420 (1947).

8) S. Koritnig, *Geochim. et Cosmochim. Acta,* **1**, 89 (1951).

9) B. Iwasaki, This Bulletin, **38**, 992 (1965).

10) B. Iwasaki and T. Katsura, *ibid.,* **37**, 1827 (1964).

11) B. Iwasaki and T. Katsura, *ibid.,* **40**, 554 (1967).

12) B. Iwasaki, Read at the Meeting of the Geochemical Society of Japan, October, 1967.

chlorine concentration in the lava flow is generally higher in acidic rocks than in basic rocks. According to Yoshida *et al.*,13) the variation in halogen contents of rocks placed in volcanic gases containing much halogens is independent of rock types. Anyway, essential factor affecting halogen contents of volcanic rocks is not decided so far.

Possible factors controlling halogen contents of volcanic rocks may be roughly classified into two groups. One group consists of factors concerning the characteristics of rocks, such as chemical, physical and petrological nature of rocks. The other comprises physico-chemical conditions of environments during or after the formation of rocks.

In the present research, it is aimed to make clear experimentally whether or not the former, the characteristics of the rocks, actually affect the halogen contents of rocks, even in the case where water vapor contained in magma emanates from rocks during or after the formation of rocks. First of all in this study, the distribution of fluorine and chlorine in rocks has been examined with relation to the characteristics of the rocks, such as magma types, rock types, solidification index of rocks and so on. The distribution of halogens in rocks was, thereby, supposed to be more affected by water vapor than the characteristics of the rocks. So, to ascertain the role of water vapor in the distribution of halogens in rocks, the author has heated the rocks in the presence of water vapor at temperatures from 100 to 900°C, and examined the mutual relationships among the amounts of halogens distilled from the rocks with water vapor at elevated temperatures and their concentrations in the rocks and the characteristics of the rocks. For this study, a systematic investigation has necessarily been made for series of rocks differentiated from the same magma; alkaline rocks collected at Okinoshima, Ehime Prefecture, hypersthenic and pigeonitic rocks sampled at Hakone, Kanagawa Prefecture and Oshima, Tokyo Metropolitan, which were already studied chemically and petrologically by Uchimizu14) and Kuno.*2

Nagashima15) reported that fluorine was more enriched in hypersthenic rocks than in pigeonitic rocks. Kokubu,16) on the contrary, mentioned that there is no marked difference in fluorine content of rocks between them. The ranges of fluorine content*3 of rocks studied in the present study were from 40 to 200 ppm for pigeonitic rocks, from 150 to 240 ppm for hypersthenic rocks and from 70 to 980 ppm for alkaline rocks. From these figures, it may be concluded that there is no significant difference in fluorine content between pigeonitic rocks and hypersthenic rocks. Meanwhile, most alkaline rocks contain far much amount of fluorine as compared with other rocks. Chlorine content*4 ranges from 30 to 170 ppm in pigeonitic rocks, from 70 to 180 ppm in hypersthenic rocks and from 10 to 380 ppm in alkaline rocks. The value of 380 ppm chlorine in an alkaline rock is exceedingly larger than the values in other alkaline rocks, and most of the chlorine in this specimen is in water-soluble state. Excluding this value, the range of chlorine in alkaline rocks is from 10 to 175 ppm, which is nearly the same as those in rocks of other types. Although fluorine and chlorine are volatile constituents in rock melts and are expected to behave similarly, no relationship is observed between fluorine and chlorine contents, as shown in Table 1. They are also independent of the values of (+) H_2O and (−) H_2O in rocks. As mentioned above, some authors have claimed that fluorine and chlorine are generally concentrated in acidic rocks rather than in basic rocks. The total chlorine analyzed here, however, has no relation to silica content for any

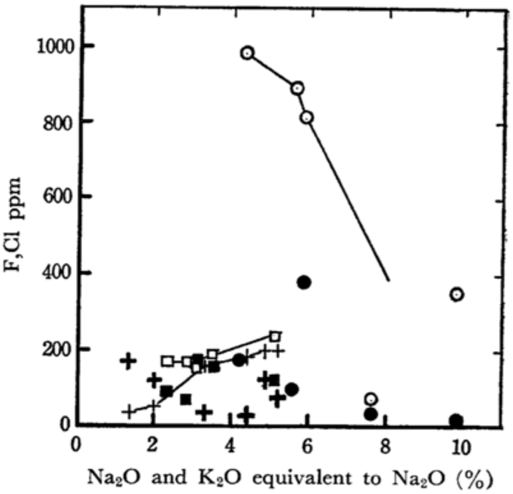

Fig. 1. Relationship between the fluorine and chlorine contents of rocks and alkaline elements (Na and K).

A. R. S. {-○-: F, -●-: Cl} P. R. S. {-+-: F, -+-: Cl}

H. R. S. {-□-: F, -■-: Cl}

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13) M. Yoshida, T. Ozawa and J. Ossaka, Read at the Meeting of the Geochemical Society of Japan, October, 1967.

14) M. Uchimizu, *J. Fac. Sci. Tokyo Univ.*, **16**, 85 (1966).

15) K. Nagashima, *Bull. Fac. Agr., Tokyo Univ. of Agriculture and Technology*, **1**, No. 2, 1 (1953).

16) N. Kokubu, *Memoirs of the Faculty Sci. Ser. C. Chemistry, Kyushu Univ.*, **2**, No. 3, 96 (1956).

*2 References are given in remarks attached to Table 1.

*3 Fluorine was separated from other chemical elements by distillation, and determined colorimetrically by the method of Grimaldi *et al.*20)

*4 Total chlorine and water soluble chlorine were determined by the method reported in a previous paper.21)

TABLE 1. CHEMICAL AND NORMATIVE COMPOSITIONS OF

Specimen number Rock type	A. R. S. 1 basalt	A. R. S. 2 mugearite	A. R. S. 3 andesite	A. R. S. 4 trachyte	A. R. S. 5 rhyolite	P. R. S. 1 basalt	P. R. S. 2 basalt
Chemical composition (%)							
SiO_2	48.90	50.54	60.32	61.57	71.87	51.02	51.25
Al_2O_3	16.73	14.44	15.65	17.95	13.33	14.39	14.73
Fe_2O_3	2.30	3.58	3.79	3.19	1.30	3.17	3.82
FeO	8.26	8.24	2.51	2.39	0.99	9.98	10.22
MgO	7.49	3.08	1.96	0.07	0.05	7.48	5.47
CaO	8.22	6.98	4.82	0.87	0.31	11.35	11.73
Na_2O	3.23	3.75	3.52	6.25	4.03	1.29	1.85
K_2O	1.81	2.91	3.38	5.35	5.44	0.15	0.26
H_2O (+)	0.52	2.38	1.05	1.20	2.00	0.32	0.11
H_2O (−)	0.25	1.15	1.15	0.75	0.30	0.25	0.02
TiO_2	2.54	2.64	1.05	0.37	0.22	0.79	0.81
P_2O_5	0.10	0.34	0.51	0.06	0.06	0.07	0.13
MnO	0.16	0.21	0.10	0.15	0.03	0.23	0.28
SrO	—	—	—	—	—	—	—
Norme (%)							
Q	—	—	16.08	2.28	24.47	5.87	18.36
C	—	—	—	0.41	0.11	—	—
Or	10.62	17.38	19.35	31.58	30.52	0.89	7.23
Ab	25.57	31.70	29.19	52.58	38.88	10.91	25.15
An	25.80	13.98	19.15	4.03	—	33.04	23.35
Ne	0.40	—	—	—	—	—	—
Wo	6.01	7.68	1.10	—	—	9.53	3.60
En	3.75	6.26	4.09	0.17	—	18.62	8.30
Fs	1.89	6.77	—	1.43	1.56	14.81	7.13
Fo	10.39	0.97	—	—	—	—	—
Fa	5.79	1.12	—	—	—	—	—
Mt	3.34	5.20	3.97	4.64	1.79	4.61	4.87
Hm	—	—	1.41	—	—	—	—
Il	4.83	5.02	2.05	0.70	0.43	1.51	1.98
Ap	0.26	0.79	1.18	0.15	1.86	0.17	0.34
Halogen contents (ppm)							
F	980	890	810	350	70	40	50
Cl (total)	175	100	380	10	40	170	120
Cl (soluble)	35	15	295	10	40	155	40
Cl (insoluble)	140	85	85	0	0	15	80
F/Cl (total)	5.6	8.9	2.1	35	2.8	0.2	0.4
F/Cl (insoluble)	7.0	10.5	9.5	—	—	2.7	0.6

A. R. S. 1=no. 10, *J. Fac. Sci., Univ. Tokyo*, **16**, 60 (1966) (by Uchimizu).
A. R. S. 2=no. 11, *ibid.*, 61.
A. R. S. 3=no. 15, *ibid.*, 61.
A. R. S. 4=no. 18, *ibid.*, 61.
A. R. S. 5=no. 30, *ibid.*, 62.
P. R. S. 1=HK 36092301b, *J. Petrol.*, **6**, 304 (1965) (by Kuno).
P. R. S. 2=d, *Bull. Geol. Soc., Am.*, **61**, 1005 (1950) (by Kuno).
P. R. S. 3=21, *ibid.*, 1004.
P. R. S. 4=23, *ibid.*, 1004.

magma type. Meanwhile, fluorine content generally increases with increasing silica in both pigeonitic and hypersthenic rocks; but the trend is reverse in alkaline rocks; namely, fluorine obviously decreases with increasing silica.

Kogaruko and Gulyayeva[17] reported that alkaline elements in rocks make it difficult for halogens to diffuse from rocks. As shown in Fig. 1, the relation between alkali (Na and K) and chlorine

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[17] L. N. Kogaruko and L. A. Gulyayeva, *Geokhimiya*, 1011 (1965).

ROCKS, AND FLUORINE AND CHLORINE CONSTENTS OF ROCKS

P. R. S. 3 andesite	P. R. S. 4 andesite	P. R. S. 5 andesite	P. R. S. 6 tuff br.	H. R. S. 1 basalt	H. R. S. 2 andesite	H. R. S. 3 andesite	H. R. S. 4 andesite	H. R. S. 5 dacite
56.54	65.54	67.37	75.85	49.08	55.62	57.07	62.25	76.05
15.49	15.33	15.28	11.45	17.68	16.91	17.53	15.85	12.79
4.58	1.69	1.13	1.40	2.33	2.02	2.59	2.06	1.47
7.09	4.51	3.86	1.26	8.00	6.24	5.44	5.19	0.31
3.00	1.45	1.20	0.50	8.02	5.87	3.87	2.79	0.08
7.33	4.75	4.46	2.42	10.26	8.63	8.77	7.21	1.60
2.98	3.89	4.67	4.11	2.02	2.98	2.80	2.20	3.89
0.55	0.84	0.92	1.39	0.35	0.72	0.52	0.97	1.82
0.35	0.68	0.14	0.53	—	0.35	0.27	0.21	0.74
0.72	0.50	0.09	0.07	—	0.05	0.12	0.31	0.52
0.96	0.89	0.72	0.46	0.90	0.86	0.77	1.14	0.19
0.08	0.21	0.18	0.19	n. d	0.24	0.08	0.06	tr.
0.22	0.19	0.15	0.11	0.25	0.14	0.14	0.18	0.05
—	—	—	0.26	n. d	—	—	0.09	—
15.45	25.56	24.06	41.52	—	7.32	13.68	24.72	42.96
—	—	—	—	—	—	—	—	—
3.34	5.00	5.56	8.34	2.22	4.23	2.78	5.56	10.56
25.15	33.01	39.30	34.58	16.77	25.22	23.85	18.34	33.01
27.24	21.68	18.07	8.62	38.36	30.66	33.92	30.68	8.06
—	—	—	—	—	—	—	—	—
3.48	0.46	1.39	1.04	5.22	4.48	3.60	2.20	1.43
7.50	3.60	3.00	1.20	18.70	14.62	9.70	6.90	0.20
8.06	5.81	5.28	0.40	11.09	8.62	6.73	6.30	0.00
—	—	—	—	0.98	—	—	—	—
—	—	—	—	0.61	—	—	—	—
6.73	2.55	1.62	2.09	3.25	2.92	3.71	3.02	0.46
—	—	—	—	—	—	—	—	—
1.82	1.67	1.37	0.91	1.67	1.64	1.52	2.13	0.46
0.34	0.11	0.34	0.11	—	0.57	—	—	1.12
160	180	200	200	170	190	150	170	240
30	30	80	125	90	155	180	70	120
20	20	30	60	50	65	30	10	50
10	10	50	65	40	90	150	60	70
5.3	6.0	2.5	1.6	1.9	1.2	0.8	2.4	2.0
16.0	18.0	4.0	3.0	4.2	2.1	1.0	2.8	3.4

P. R. S. 5=banded lava of Hakone volcano, high way between Ashinoyu and Gannosuyama, Hakone, Kanagawa Pref.

P. R. S. 6=11, Catalogue of the Active Volcanoes of the World, Part XI, p. 77 (by Kuno).

H. R. S. 1=2, *J. Fac. Sci. Univ. Tokyo*, **9**, 258 (1955) (by Kuno).

H. R. S. 2=HK 62090502, *J. Petrol.*, **6**, 308 (1965) (by Kuno).

H. R. S. 3=14, *Bull. Geol. Soc. Am.*, **61**, 1000 (1950) (by Kuno).

H. R. S. 4=lava-flow of Hakone volcano, west-side slope of north road of Hatajyuku, Hakone, Kanagawa Pref.

H. R. S. 5=18, *Bull. Geol. Soc. Am.*, **61**, 1001 (1950) (by Kuno).

is not clear for any magma type: On the other hand, fluorine increases with the concentration of the alkaline elements in pigeonitic and hypersthenic rocks, and decreases in alkaline rocks, just like the relationship between fluorine and silica in rocks.

Fluorite is the most stable among simple fluorine compounds and is often found in volcanic rocks. A positive relationship between fluorine and calcium contents, however, is observed only in alkaline rocks.

Mica, amphibole and apatite are generally considered to be important halogen containing minerals in volcanic rocks. Halogens are easily incorporated in their crystal lattices. Unfortunately, the amount of these minerals in the samples used here were not quantitatively measured except for the calculation of normative apatite. The fluorine and chlorine contents were plotted against the phosphate content of rocks in Fig. 2. A line drawn in the figure shows the relationship between fluorine content and the amount of apatite, assuming that all of phosphate exists as apatite. The relationship between apatite and fluorine is not generally observed, although the relation seemingly exists in pigeonitic rocks. Moreover, no correlation is seen between the amount of apatite and chlorine in rocks. Although the halogen contents of mica and amphibole were not determined

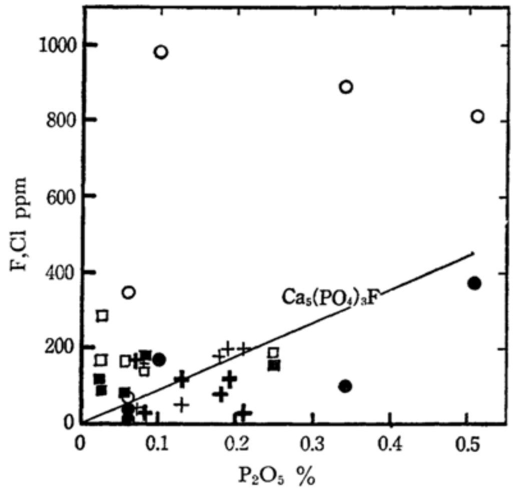


Fig. 2. Relationship between fluorine, chlorine contents and P_2O_5 content of rocks.

A. R. S. -○-: F
-●-: Cl
P. R. S. -+-: F
-✚-: Cl
H. R. S. -□-: F
-■-: Cl

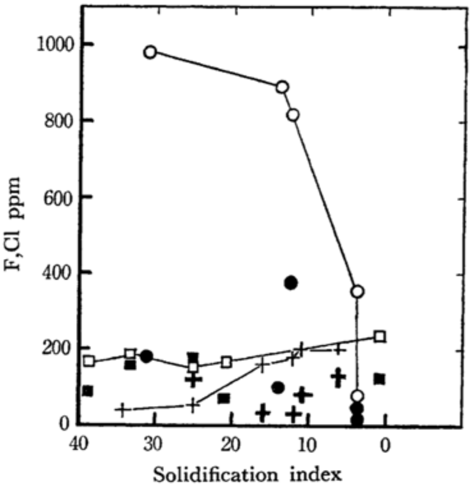


Fig. 3. Relationship between the fluorine and chlorine contents and solidification index of rocks (solidification index=$MgO \times 100/MgO+FeO+Fe_2O_3+Na_2O+K_2O$).

A. R. S. -○-: F
-●-: Cl
P. R. S. -+-: F
-✚-: Cl
H. R. S. -□-: F
-■-: Cl

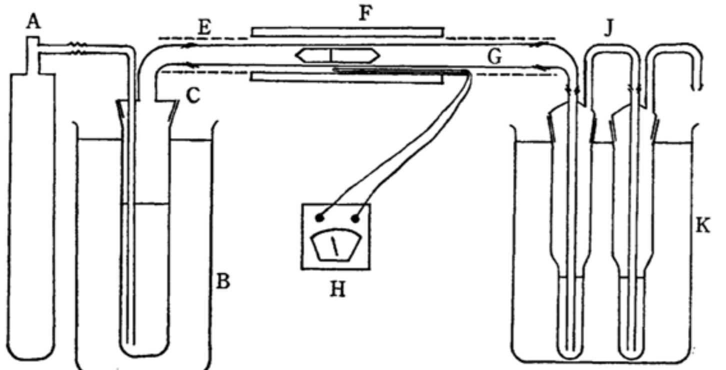


Fig. 4. Apparatus to distill halogens in rocks.

A: Commercial nitrogen gas tank.
B: 1 *l* beaker filled with water boiled with heater D.
C: Glass-vessel containing distilled water.
D: Heater.
E: Glass-heater.
G: Silica-glass-tubing (60 cm in length, 2 cm in inside diameter).
H: Thermocouple.
I: Silica-glass-boat (10 cm in length, 1.4 cm in inside diameter).
J: Absorption vessel.
K: 1 *l* beaker filled with cold water.

TABLE 2. REPRODUCIBILITY OF THE DISTILLATION METHOD
(sample: A. R. S.)

Temp. °C	Experiment 1		Experiment 2		Experiment 3	
	F ppm	Cl ppm	F ppm	Cl ppm	F ppm	Cl ppm
100	0	10	0	10	0	10
200	0	10	0	10	0	10
300	0	10	0	10	5	10
400	27	10	16	10	26	10
500	10	10	20	10	30	10
600	13	10	16	10	24	10
700	22	10	20	10	38	10
800	100	150	60	115	40	105
900	70	30	80	35	30	40
	232	180	212	150	193	145

TABLE 3. THE AMOUNT OF DISTILLED HALOGENS FROM A FEW COMPOUNDS CONTAINING HALOGENS WHEN DISTILLED WITH WATER VAPOR

Temp. °C	KF (0.59 g) and KCl (0.5 g)		CaF_2 (0.59 g) and $CaCl_2$ (0.5 g)		Biotite (1.0 g)	
	F (mg)	Cl (mg)	F (mg)	Cl (mg)	F (mg)	Cl (mg)
100	—	—	—	—	—	—
200	—	—	—	—	—	—
300	40	20	—	—	—	—
400	100	180	10	50	—	—
500	10	100	80	190	—	—
600	5	10	120	70	0.5	0.7
700	—	—	20	—	0.9	0.4
800	—	—	—	—	0.1	—

TABLE 4. THE AMOUNT OF DISTILLED CHLORINE AT HIGH TEMPERATURES ABOVE 500°C
(μg chlorine/1 g of sample)

	500°C	600°C	700°C	800°C	900°C	undistilled*
A. R. S. 1	—	—	—	105	40	30
A. R. S. 2	—	15	—	35	—	50
A. R. S. 3	50	38	—	—	—	−13
A. R. S. 4	—	—	—	—	—	0
A. R. S. 5	—	—	—	—	—	0
P. R. S. 1	22	25	—	10	—	62
P. R. S. 2	11	18	12	23	23	−4
P. R. S. 3	—	—	—	—	—	28
P. R. S. 4	—	—	—	—	—	30
P. R. S. 5	—	—	—	—	—	13
P. R. S. 6	15	10	—	—	—	−15
H. R. S. 1	—	—	—	—	—	70
H. R. S. 2	20	10	40	15	30	0
H. R. S. 3	10	40	70	40	—	−15
H. R. S. 4	—	—	20	—	—	5
H. R. S. 5	10	20	—	—	—	25

* Error can be accumulated to 20 ppm.

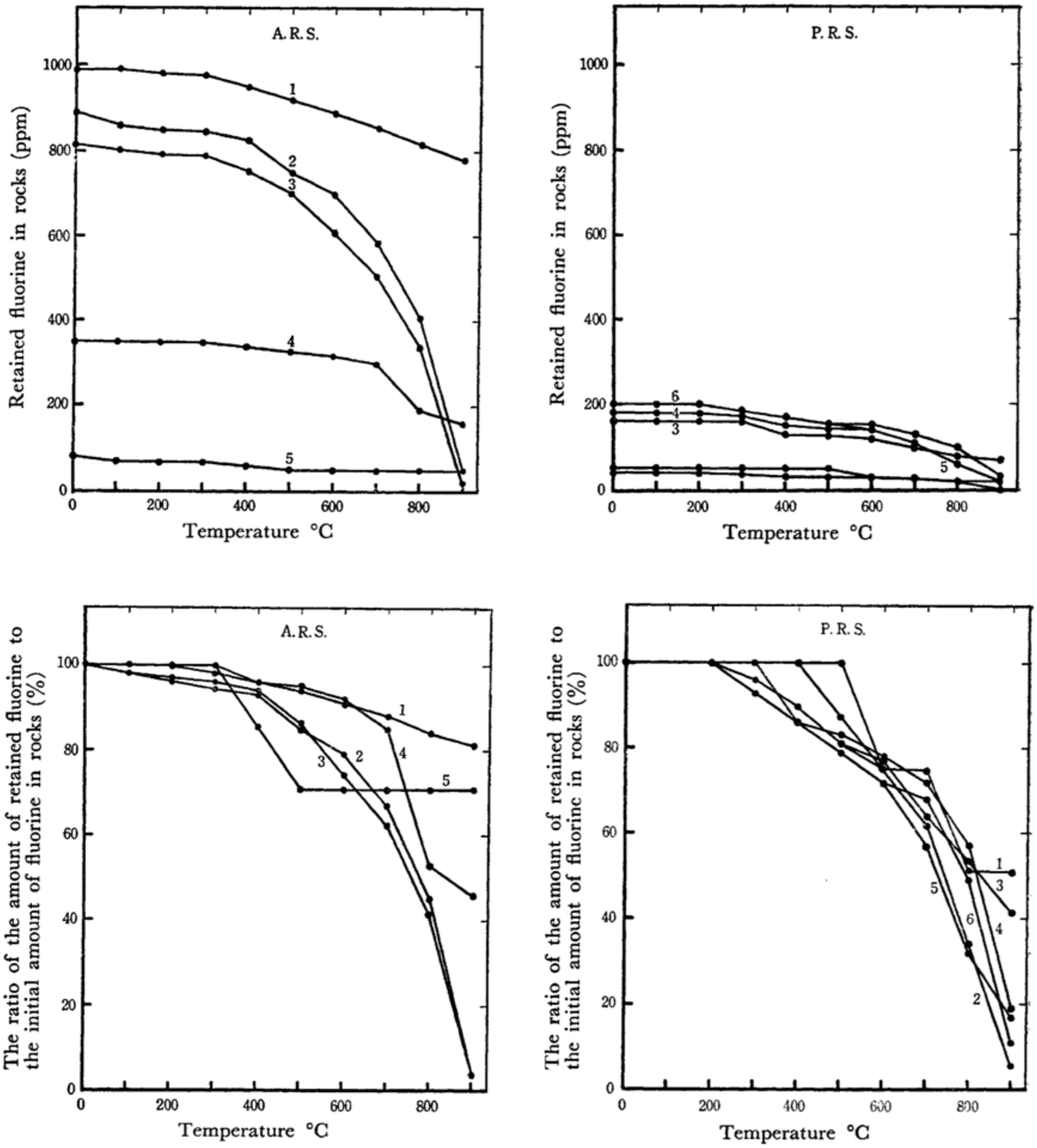
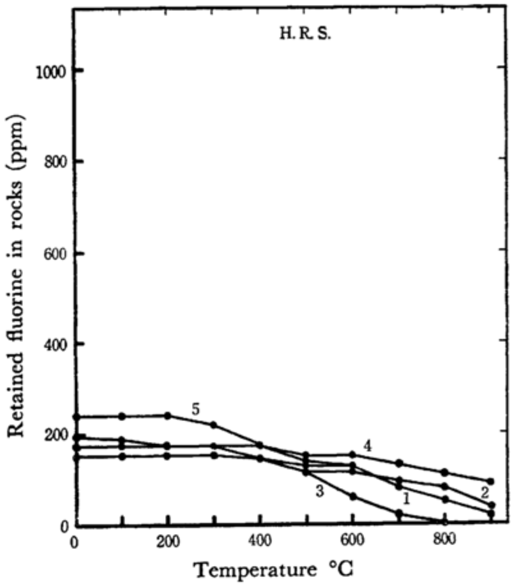
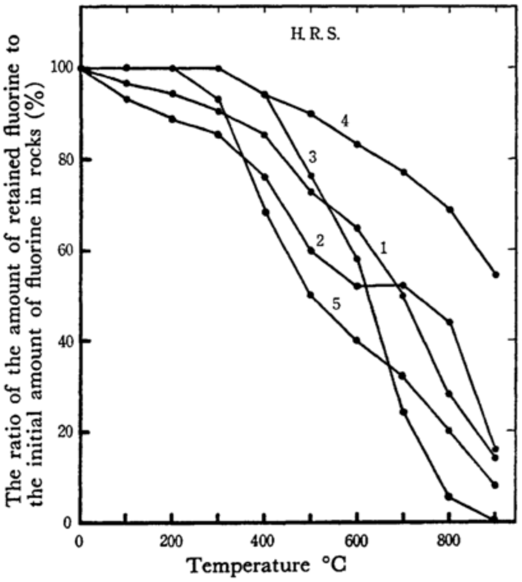


Fig. 5. The relationship between the retained fluorine and





the distillation temperature.

in this study, chlorine in mica is considered to be a small portion of the total amount of chlorine in the rocks.⁽10⁾

As to a series of rocks differentiated from the same magma, Greenland and Lovering⁽18⁾ reported that chlorine is generally more concentrated in differentiates of the later stage than in the earlier one. Figure 3 shows the variations of fluorine and chlorine in each stages expressed in terms of the solidification index given by Kuno *et al.*⁽19⁾ No regularity is seen for chlorine variation. Fluorine is apparently enriched in later stage pigeonitic and hypersthenic rocks; on the contrary, it decreases in later stage alkaline rocks.

Thus, the variations of fluorine in alkaline rocks are always entirely different from those in other rocks: From the petrological point of view, alkaline rocks are clearly distinguished from others; nevertheless, any petrological evidence for the difference in fluorine content is not found.

From the above results concerning the relationship between the halogen contents of rocks and the chemical, mineralogical and petrological nature of the rocks, it is safely said that halogen contents of rocks are not decidedly controlled by the nature of the rocks considered above. The author considered that halogen contents of rocks would be controlled by water vapor rather than by the characteristics of the rocks. Water is ubiquitous in magma and evaporates from rocks reacting with rocks during or after the formation of the rocks. So, he made following experiments to find out the role of water vapor in the distribution of halogens in volcanic rocks.

Experimental

One gram of a rock sample ground finer than 200 mesh is placed in a boat of silica-glass (I), whch is put into a silica-glass-tubing (G) as shown in Fig. 4. Distilled water is heated to boiling in a distillation vessel (C). A mixture of water vapor from the vessel (C) and nitrogen gas, which is bubbled into the vessel (C) from tank (A) at a flow rate of 30 *l*/hr, is passed through the silica-glass-tubing heated in a furnace (F) at fixed temperatures. The distillate is collected in an absorption vessel (J) containing 5 m*l* of 1 N NaOH solution. About 50 m*l* is collected at each temperature. Fluorine and chlorine in distillates are determined by the methods mentioned above. Reproducibility of the determination is presented in Table 2.

Results and Discussion

Before a rock sample was tested, the possibility of distillation of halogens with water vapor had

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18) L. Greenland and J. F. Lovering, *Geochim. et Cosmochim. Acta,* **30**, 963 (1966).

19) H. Kuno, K. Yamasaki, C. Iida and K. Nagashima, *J. Geol. Soc. Japan,* **28**, 179 (1957).

20) F. S. Grimaldi, B. Ingram and F. Cuttita, *Anal. Chem.*, **27**, 918 (1955).

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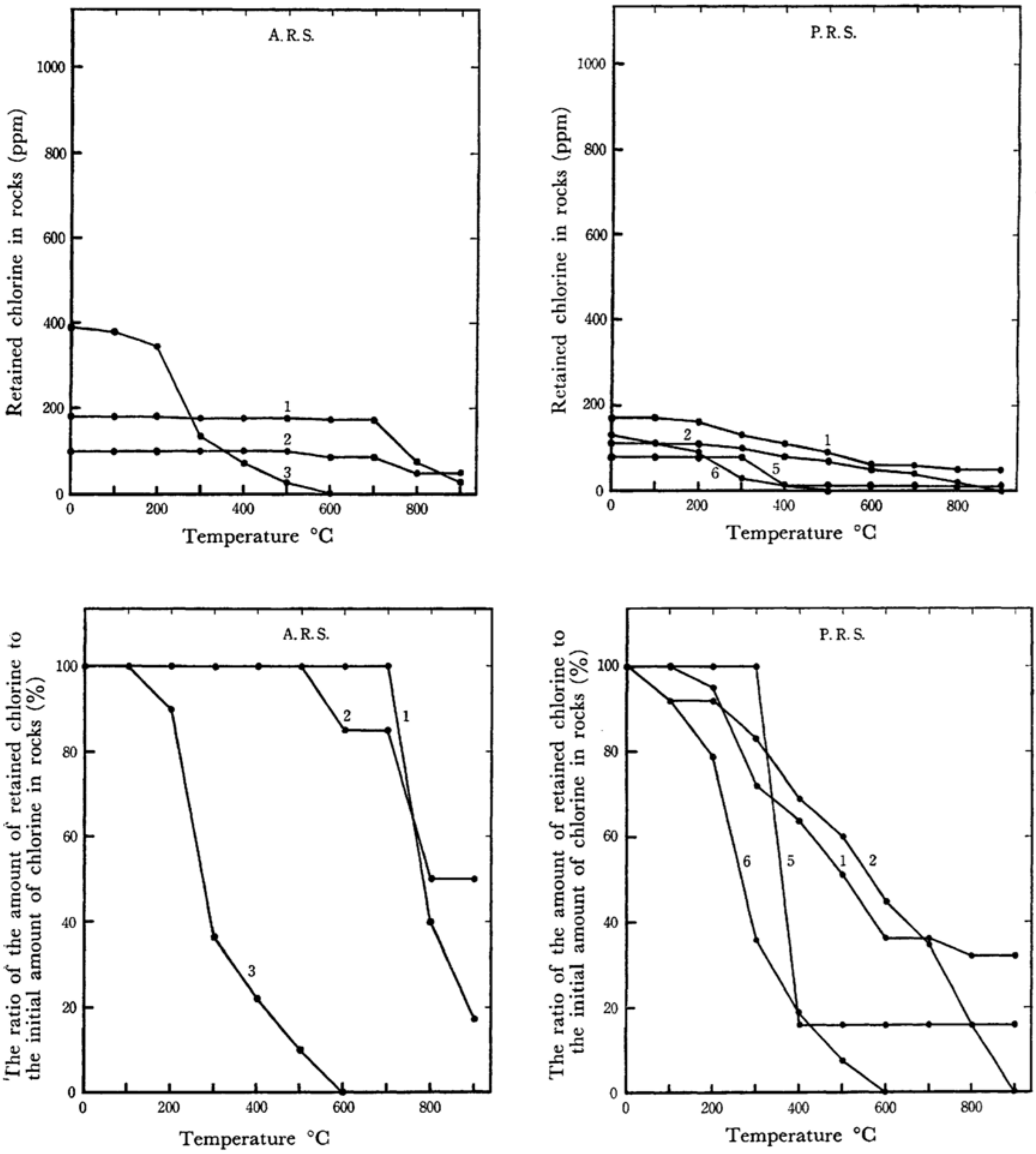
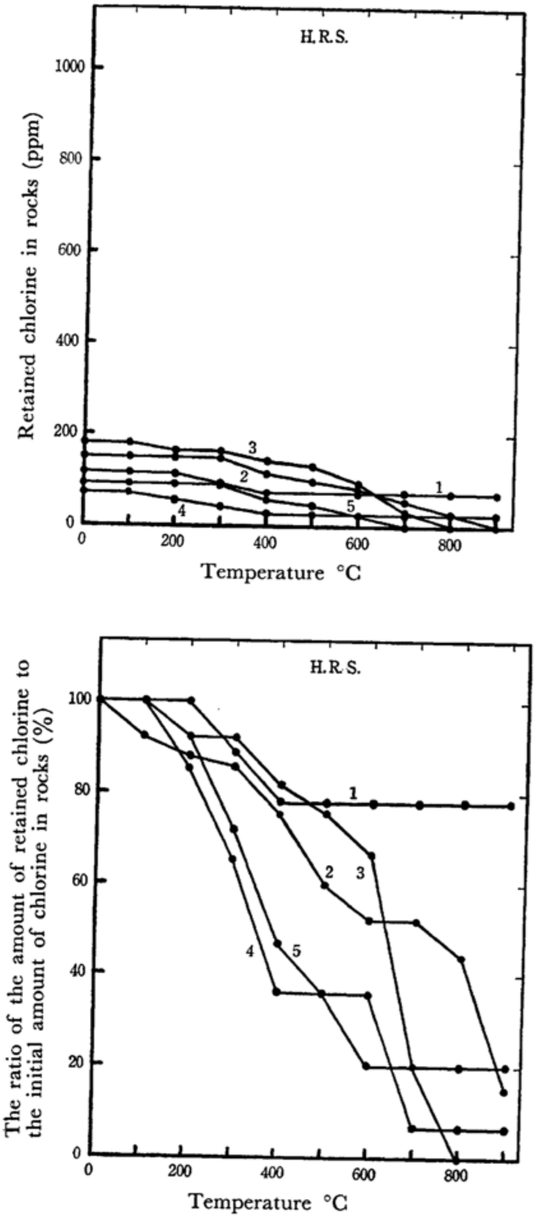


Fig. 6. The relationship between the retained chlorine and



distillation temperature.

been verified for simple compounds containing fluorine or chlorine.

Different patterns of distillation were observed for various compounds containing halogens, as given in Table 3. The initial temperatures at which determinable amount of halogens appeared in distillate were 300°C, 400°C and 600°C for potassium halogenides, calcium halogenides and biotite, respectively. From a mixture of potassium fluoride and potassium chloride, fluorine was more easily distilled than chlorine; in the other materials, the relation was reverse.

The experimental results for rock samples are as follows. The amounts of residual fluorine in rocks at various distillation temperatures are graphically shown in Fig. 5. Almost all fluorine remained in each rock specimen at low temperatures below 300°C, and the lowest temperature at which detectable amount of fluorine appeared was around 400°C. The ratio of the amount of retained fluorine to the initial amount of fluorine in rocks fluctuated among specimens in the temperature range above 700°C. About 70% of fluorine in H. R. S. 1, H. R. S. 3 and H. S. R. 5 was distilled up to 800°C, while most fluorine in A. R. S. 1, A. R. S. 4 and H. R. S. 4 remained in rocks at the temperature. There seemed to be no relation between the pattern of fluorine distillation and rock types. The difficulty of the fluorine distillation was in the order of A. R. S. 1>A. S. R. 4> A. R. S. 2≈A. R. S. 3 for alkaline rocks and H. R. S. 4 > H. R. S. 1 ≈ H. R. S. 2 > H. R. S. 3≈ H. R. S. 5 for hypersthenic rocks, and is not related to silica content of rocks. The smaller the specimen-number, the more basic the rock. The order of the difficulty of distillation was not clearly observed in pigeonitic rocks. The distillation pattern of fluorine was not related to the fluorine content even in rocks differentiated from a given magma; that is, the order of fluorine content in alkaline rocks was A. R. S. 1 > A. R. S. 2 > A. R. S. 3 > A. R. S. 4, and the difficulty of the fluorine distillation was in the order of A. R. S. 1>A. R. S. 4> A. R. S. 2≈A. R. S. 3. The distillation pattern in alkaline rocks containing much fluorine was not essentially different from the patterns in pigeonitic and hypersthenic rocks with low concentration of fluorine.

On the other hand, the distillation pattern of chlorine considerably varied according to specimens as shown in Fig. 6. Chlorine in some specimens was mostly distilled in a lower temperature range, and in some others chlorine was gradually distilled in a higher temperature range. Water-soluble chlorine was naturally expected to be distilled at relatively low temperatures. Nevertheless, there was not a distinct relationship between distillation patterns and the amount of water-soluble chlorine. For instance, A. R. S. 3 contains 295 μg of water-soluble chlorine in one gram of the rock

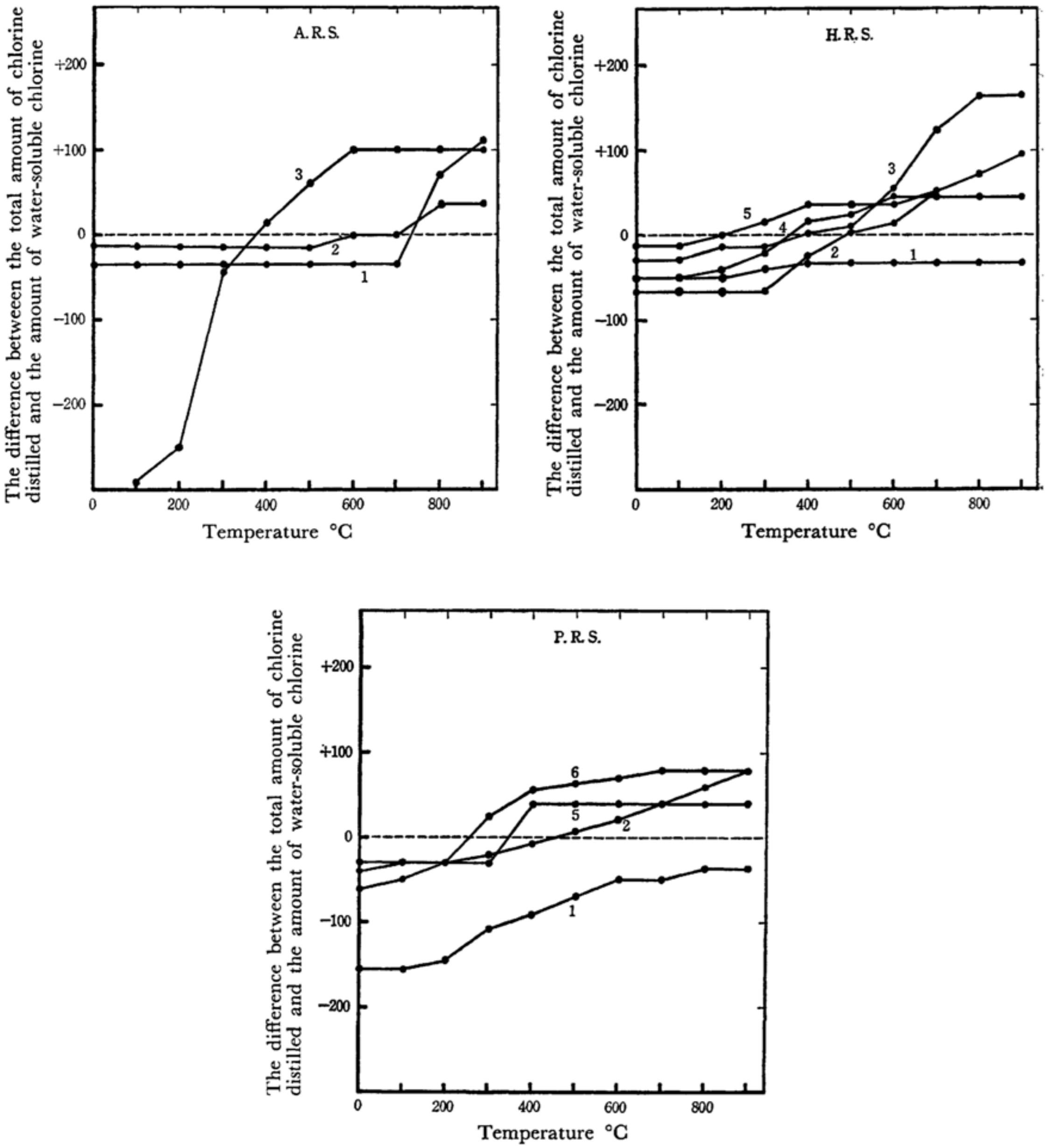


Fig. 7. The difference between the total amount of chlorine distilled and the amount of water-soluble chlorine.

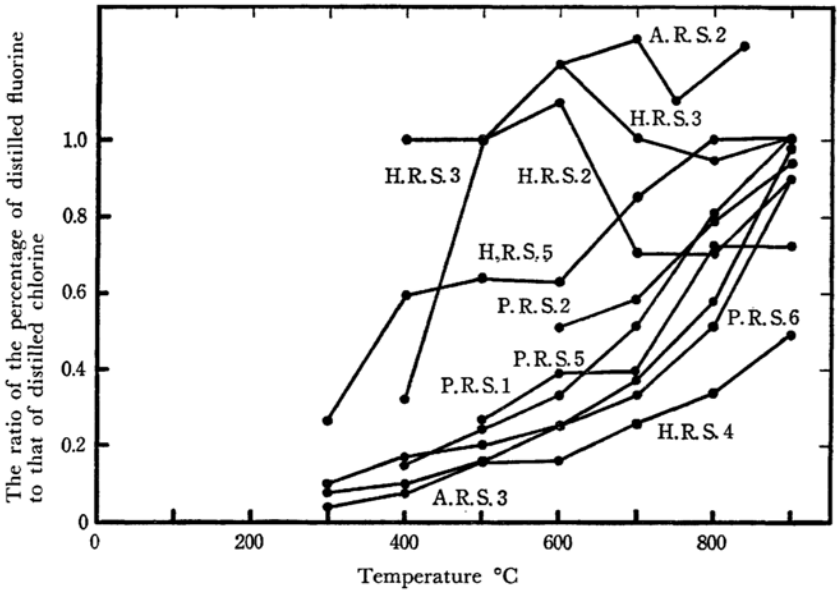


Fig. 8. The ratio of the percentage of distilled fluorine to that of distilled chlorine.

and the amount of chlorine distilled up to 400°C was 305 μg; similarly, from P. R. S. 6 with 60 μg of water-soluble chlorine, 90 μg was distilled, and from H. R. S. 5 with 50 μg, 65 μg was distilled. On the contrary, from P. R. S. 1 with 155 μg of water-soluble chlorine, only 61 μg was distilled up to 400°C; in H. R. S. 1, water-soluble chlorine was 50 μg and distilled chlorine was 20 μg.

The amount of chlorine distilled at temperatures above 500°C and the amount of chlorine remained at 900°C are listed in Table 4. These experiments show that chlorine distilled only at high temperatures and/or remained in rocks at 900°C obviously exists in basic rocks and does not exist in acidic rocks.

The difference between the total amount of chlorine distilled and the amount of water-soluble chlorine was plotted against distillation temperatures as shown in Fig. 7. Negative values in the figure indicate water-soluble chlorine which remains undistilled; the number of the line in the figure corresponds to the order of silica content of rocks. These results suggest that chlorine in basic rocks is generally more resistant to water vapor than in acidic rocks. Although this fact can not be explained reasonably, the chemical nature of rocks might be responsible for this result because it coincides with the experimental result of the chlorine solubility in rock melts reported by Iwasaki *et al.*11)

The ratio of the distilled percentage of fluorine to that of chlorine at various temperatures is graphically shown in Fig. 8: Generally chlorine is distilled more easily than fluorine at low temperatures. The different behaviors of these elements in water vapor are very important for consideration of fluorine and chlorine contents of volcanic rocks. If rocks are placed in water vapor at a high temperature for a long time, both fluorine and chlorine would diffuse out from rocks at an approximately same rate, but at a low temperature, about 300°C, chlorine would diffuse out from rocks more rapidly than fluorine.

This experimental result also could have a geochemical significance to the origin of halogens in volcanic gases; the halogens in volcanic rocks are easily distilled with water vapor and the ratio of fluorine to chlorine increases with temperature. On the other hand, the ratio of fluorine to chlorine in volcanic gases from some volcanoes is known to be smaller for low temperature fumaroles and larger for high temperature fumaroles.22,23)

Summary and Conclusion

There have been various interpretations on the effect of the characteristics of rocks on the abundance of fluorine and chlorine in volcanic rocks. This study has revealed that the chlorine content of rocks does not show any relation to the characteristics of rocks of any magma type, and fluorine content decreases in later stage of magmatic differentiation for alkaline rocks and slightly increases for pigeonitic and hypersthenic rocks. Meanwhile, when fluorine in rocks was distilled with water vapor, the pattern of distilled fluorine fluctuated considerably. The pattern, however, seemed to depend on neither the characteristics of the rocks nor fluorine content of rocks.

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Accordingly, fluorine content of rocks can not be explained by the difference in chemical and mineralogical characteristics of rocks, but should be explained by the cooling histry of magma during the formation of rocks.

Chlorine is often reported to be concentrated rather in acidic rocks than in basic rocks. The present study, however, shows that chlorine concontent is independent of rock types. In the experiments, chlorine in basic rocks is more stable than in acidic rocks. From these evidences, it can be concluded that chlorine content of rocks is also controlled mainly by environmental conditions even if the characteristics of rocks might affect the behavior of chlorine in rocks.

In natural environments, water is much emanated from magma during its cooling, and probably carries out halogens with it as shown in the present experiments. The distillation process can be essentially responsible for halogen contents of rocks.

The distillation experiment with water vapor described here is important in considering the origin of halogens in volcanic gases. In order to study the behavior of halogens in volcanic emanation, Yoshida *et al.*(24,25) analyzed halogen compounds driven from rocks heated in nitrogen gas without water vapor. However, water plays essentially an important role in magmatic emanation. Accordingly, the present experiment with water vapor reproduces more closely natural conditions.

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