

Fluorine and Chlorine Contents in the Products of the 1108 (Tennin) Eruption of Asama Volcano

Minoru YOSHIDA^{*,**} and Ryuji AOYAGI^{*,***}

(Received, March 17, 2004; Accepted June 28, 2004)

Fluorine and chlorine have been determined for all kinds of the products of the 1108 activity of Asama volcano. The activity displayed various features that are characteristic of andesitic eruptions, i.e., scoria (pumice) fall (B-scoria L), intermediate-type pyroclastic flow (the Oiwake pyroclastic flow) and lava flow (the Kamino-butai lava flow). Their F-Cl variation patterns are widely varied according to the natures of the eruption in a similar way to those of the 1783 activity of Asama (Yoshida and Tsuchiya, 2004).

The B-scoria L samples show uniform and the highest Cl contents in average. The Kamino-butai lava flow samples have low and uniform Cl contents. These results coincide with those obtained by the study on the 1783 activity and may be explained by the enrichment of volatiles in the uppermost part of the magma column before the eruption.

The F and Cl contents of Oiwake pyroclastic flow samples show very large variances. Some Oiwake samples take almost the same halogen contents as the B-scoria L samples. Whereas, the other samples show the lowest F and Cl contents and the largest variances, and indicate strong release of gas at or after the effusion. The detailed examination of topographical distribution of the F and Cl contents shows that the Oiwake pyroclastic flow is composed of many flow units of high-halogen and of low-halogen contents and may suggest the transition of the mode of the formation of the pyroclastic flow with different degassing conditions. In the low-halogen flow units, volatiles might be mostly released in the early stage of the flow.

Key words: fluorine, chlorine, volatile contents, pyroclastic flow, Asama volcano

1. Introduction

Vesiculation of erupting magma plays an important role in formation and transportation of pyroclastic flows (e.g., Aramaki, 1957; Aramaki and Yamasaki, 1963). Hence it is expected that a study of volatile components in pyroclastic deposits might provide useful information. Fluorine and chlorine are the next, most abundant volatile components after water in volcanic rocks. Yoshida and Tsuchiya (2004) analyzed fluorine and chlorine on the volcanic products of the 1783 eruption of Asama volcano. Comparing with the results of model experiments for the behavior of F and Cl in volcanic process (Yoshida, 1963; 1975; 1990), they reached the following conclusions. The transition of the mode of the eruption from pumice fall to two types of pyroclastic flows followed by lava flow may be intimately related to the volatile contents of the magma at the time of effusion. There might have been a vertical concentration gradient of volatile components in the magma column. The upper part of the magma might

have high volatile contents and vesiculation in the vent brought about pumice eruptions. Volatile contents of the magma, then, decreased until vesiculation took place at the mouth of the vent and the expanding magma overflowed from the crater while continuing to release gas; this could have produced an intermediate-type pyroclastic flow (the Agatsuma pyroclastic flow). At the last stage, the magma flowed out without notable vesiculation as the Oni-oshidashi lava flow. The semi-solid mass formed around the fringe of the vent might plug the vent and be thrown out with violent outburst of compressed gases. The fall of this material would have brought about the Kambara pyroclastic flow. It is the one and only report that discussed on the F and Cl contents of pyroclastic flow deposit as compared with pumice fall deposit and lava flow erupted by the same volcanic activity. In order to ascertain whether or not the proposed mechanism is generally applicable, it is required to examine other examples.

Asama volcano has produced a number of pyroclastic

* Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan.

** Present address: 1-5-16, Mama, Ichikawa-shi, Chiba

272-0826.

*** Present address: 1-11-26, Mita, Meguro-ku, Tokyo 153-0062.

Corresponding author: Minoru Yoshida

flows (Aramaki, 1963; 1968). The Oiwake pyroclastic flow is the largest intermediate-type pyroclastic flow during the activity of Maekake-yama, which is the younger cone of Asama volcano. Total volume of the Oiwake pyroclastic flow is estimated to be 0.6 km^3 and fairly larger than that of the Agatsuma pyroclastic flow (0.1 km^3) (Aramaki, 1963). It was formerly regarded to have erupted in 1281 (Koan) with the B-scoria (pumice) falls (the upper layers: 0.1 km^3 and the lower layers: 0.4 km^3) and the Butai lava flows (the Kamino-butai and the Shimono-butai: $0.1 \sim 0.2 \text{ km}^3$ in all) from descriptions of old documents (Aramaki, 1963). However, the stratigraphic relations between the B-scoria falls and the historic relics of archeologically known age (Arai, 1979), and the ^{14}C -age of carbonized wood-chips buried in the B-scoria falls and in the Oiwake pyroclastic flow deposits (Nakamura and Aramaki, 1966) indicate that they are more reasonably assigned to be the products of the 1108 (Tennin) activity (Arai, 1979; Aramaki, 1980).

Aramaki *et al.* (1989) carried out systematic sampling of rocks presumed to be the products of the 1108 eruption and determined their major components. They found that the major components of the lower layers of the B-scoria (pumice) fall deposits (B-scoria L), the Oiwake pyroclastic flow deposits and the Kamino-butai lava flow ranged very narrowly (59~61% SiO_2). On the other hand, the upper layers of the B-scoria fall deposits (B-scoria U), the Shimono-butai lava flow, the Maru-yama lava flow and the Nishi-maekake-yama ejecta show different trends from the former three groups in variation diagrams. They concluded that the latter groups are the products of the other eruptions.

All the products of the 1108 activity are andesites despite the different nature of the successive effusions. The transition from one type effusion to another is similar to that in the 1783 activity although the 1108 activity lacked an equivalent for the Kambara pyroclastic flow in the 1783 activity. Therefore, we presumed that the transition is also caused by difference in the mode of gas-release from the magma at the effusion. In this study, we determined the F and Cl contents in all kinds of the volcanic products of the 1108 activity and examined their formation mechanism from this viewpoint. Furthermore, Aramaki *et al.* (1989) took so many samples of the Oiwake pyroclastic flow deposits that we expected to be able to obtain more detailed information on the distribution of volatiles in intermediate-type pyroclastic flow.

2. Samples

The analyzed samples are the essential products of the 1108 activity, i.e., 11 samples of the B-scoria L deposits, 81 samples of the Oiwake pyroclastic flow deposits (38

samples from the northern flows: Oiwake N and 43 samples from the southern flows: Oiwake S), and 11 samples of the Kamino-butai lava flow. The samples of the B-scoria U deposits, the Shimono-butai lava flow, the Maru-yama lava flow and the Nishi-maekake-yama ejecta, which were excluded from the volcanic products of the 1108 activity (Aramaki *et al.*, 1989), were also analyzed. All the samples were systematically sampled and analyzed for major components by Aramaki *et al.* (1989). Sample numbers assigned by them are followed in this report. Fig. 1 gives the outline of sampling locations.

3. Analytical method

Fluorine was determined by the method of Tsuchiya *et al.* (1985). A powdered sample is fused with Na_2O_2 in a nickel crucible. The cake is dissolved and F in the solution is distilled as trimethylfluorosilane. The fluoride concentration in the distillate is determined with an ion selective electrode.

Total Cl is determined by the method of Iwasaki *et al.* (1955) improved by Ozawa (Yoshida *et al.*, 1994). A powdered sample is fused with Na_2CO_3 in a platinum crucible. The cake is dissolved and the resulting suspension is centrifuged. Chloride concentration in the solution is determined by the $\text{Hg}(\text{SCN})_2$ spectrophotometry (Tomonari, 1962). Water-soluble Cl is extracted by immersing the rock powder overnight in water and determined by the $\text{Hg}(\text{SCN})_2$ spectrophotometry.

4. Results

Analytical results with various statistical parameters are shown in Tables 1a to 1d for the 1108 products and 2a to 2c for the others. The errors in the determination of both F and Cl are $\pm 10 \mu\text{g/g}$. Water-soluble Cl contents in Japanese volcanic rocks are usually less than $50 \mu\text{g/g}$ and can often be attributed to secondary contamination (Iwasaki *et al.*, 1957; Yoshida *et al.*, 1971). In the present case, most water-soluble Cl contents are less than $50 \mu\text{g/g}$ and the following discussion is based on the water-insoluble Cl contents which is calculated as the difference between the total Cl and water-soluble Cl contents.

Halogen contents of volcanic rocks have approximately lognormal distributions (Iwasaki *et al.*, 1957; Iwasaki *et al.*, 1968; Yoshida *et al.*, 1971), and it is usually appropriate to use logarithmic values for applying statistical analysis to the data for F and Cl contents. Several samples of the Oiwake pyroclastic flow have, however, very low Cl contents, and when we take logarithms of those values, the deviations from the other values are exaggeratedly emphasized. They are regarded as outliers on account of lognormal distribution but not on account of normal distribution as will be

shown later. Those samples are supposed to be strongly degassed samples and cannot be ignored for discussion on the processes of gas-release. Therefore, we do not reject those samples for some discussion and examined also on normal distribution together with lognormal distribution.

5. Discussion

5-1 Statistical examination of the difference of the F and Cl contents with the type of eruption

The F and Cl contents are varied among the B-scoria L deposits, the Oiwake pyroclastic flow deposits, and the Kamino-butai lava samples (Table 1; Fig. 2) in

almost similar manner to the 1783 products (Yoshida and Tsuchiya, 2004). Any significant correlation is not found between SiO_2 (Aramaki *et al.*, 1989) and halogen contents.

Dixon's Q-test (Dixon, 1953) is applied for each group and some outliers are found in the Oiwake pyroclastic flow samples. The F-content of the 1027-13 sample is extremely high at the 1% significance level. The high F contents of this sample and of the 817-10 sample, and possibly of the 817-12 and 817-24 samples, may be attributed to secondary addition of F from gas-phase like the A-5 sample of the Agatsuma pyroclastic flow in the 1783 eruption (Yoshida and

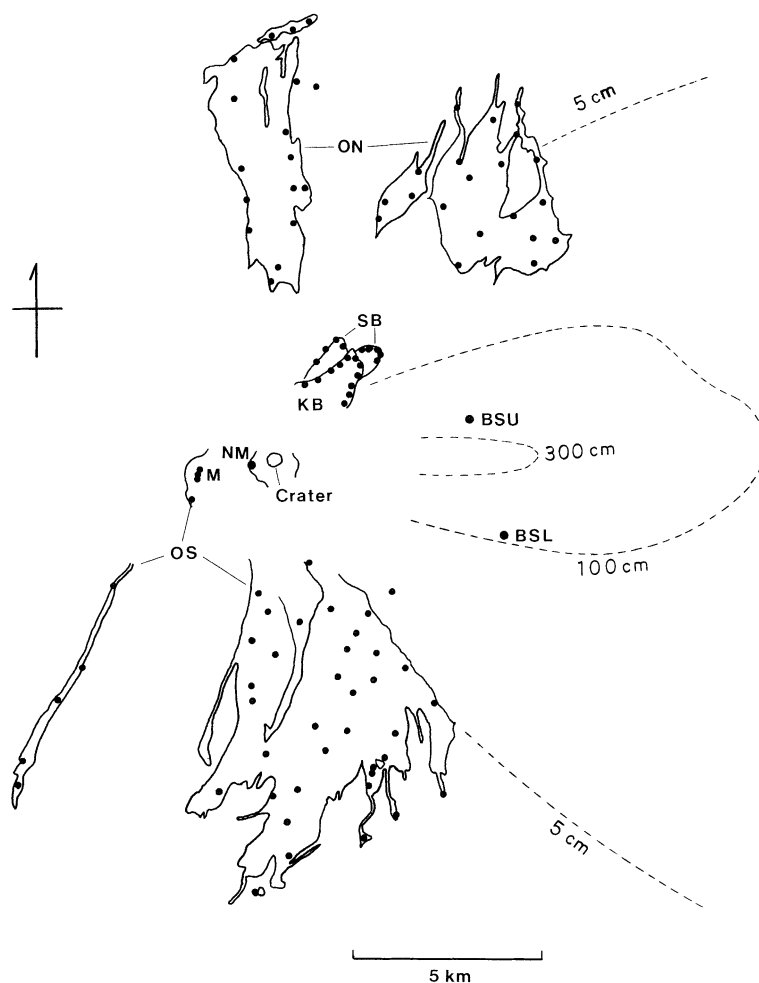


Fig. 1. An outline map showing the sampling locations of the volcanic products of the 1108 and some other Asama eruptions: BSL=B-scoria deposit (lower); BSU=B-scoria deposit (upper); ON=Oiwake northern pyroclastic flow; OS=Oiwake southern pyroclastic flow; KB=Kamino-butai lava flow; SB=Shimono-butai lava flow; M=Maru-yama lava flow; NM=Nishi-maekake-yama ejecta. -----Isopach curves of the B-scoria fall deposit. (5 cm, 100 cm and 300 cm)

Table 1a. F and Cl contents of the lower B-scoria fall samples of the 1108 eruption of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
LP-1-2	268	450	10	1.14
LP-1-3	252	470	10	1.02
LP-1-5	250	480	10	0.99 ₃
LP-1-7	256	440	< 10	1.09
LS-3-2	246	510	30	0.95 ₆
LS-3-4	266	490	20	1.06
LS-3-6	262	520	20	0.97 ₈
LS-5-1	248	440	10	1.08
LS-5-4	252	460	10	1.04
LP-5-5	242	570	30	0.83 ₆
LS-5-7 bomb	266	430	10	1.18
a. m. ^a	255.3	463.6 ^b		1.033
s. d. ^c	8.96	34.43 ^b		0.0936
m (log X) ^d	2.407	2.665 ^b		0.01255
s (log X) ^e	0.0152	0.0314 ^b		0.040553
g. m. ^f	255.1	462.5 ^b		1.029

^a Arithmetic means.^b Calculated for water-insoluble Cl.^c Standard deviations^d Arithmetic means for log X.^e Standard deviations for log X.^f Geometric means.

Table 1b. F and Cl contents of the Oiwake northern pyroclastic flow samples of the 1108 eruption of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
619-4	40	160	20	0.53 ₃
812-7	136	470	20	0.56 ₄
817-1	244	450	20	1.06
817-2	292	550	20	1.03
817-4	124	440	10	0.53 ₈
817-5	214	530	40	0.81 ₅
817-8	108	240	30	0.960
817-9-1	200	470	30	0.84 ₈
817-10	456	250	30	3.87 [§]
817-12	392	550	40	1.43
817-14	114	400	20	0.56 ₀
817-15	106	190	20	1.16
817-16	158	230	20	1.40
817-17	182	220	30	1.79
817-18	130	320	20	0.80 ₉
817-22	330	450	20	1.43
817-24	401	500	30	1.59
818-1	202	370	20	1.08
818-4	250	430	20	1.14
818-5	258	550	20	0.90 ₈
818-7	212	420	20	0.98 ₉
818-9	198	470	20	0.82 ₁
818-10	96	50	50	> 17.9 [§]
818-11	140	160	30	2.01
1026-4	200	490	60	0.86 ₈
1026-5	54	360	10	0.28 ₈
1026-8	84	210	40	0.92 ₂
1026-9	288	380	20	1.49
1026-12	278	470	20	1.15
1026-16	200	450	30	0.88 ₉
1027-3	252	500	20	0.98 ₀
1027-6	150	380	20	0.77 ₈
1027-7	102	360	40	0.59 ₅
1027-9	91	130	40	1.89
1027-10	106	270	80	1.04
1027-11	78	90	30	2.43
1027-13	780 [§]	700	60	2.27
1027-17	298	480	20	1.21
a. m. ^a	209.1	343.4 ^b		1.633 ^h
s. d. ^c	137.52	151.91 ^b		2.7907 ^h
m(log X) ^d	2.243	2.458 ^{b, h}		0.0559 ^h
s(log X) ^e	0.2642	0.3364 ^{b, h}		0.29095 ^h
g. m. ^f	175.0	287.1 ^{b, h}		1.137 ^h

^a ~ ^f Same as in Table 1a.[§] Significantly different from the others with 1% level.^h Calculated on the assumption that Cl_{insol.} in the sample 818-10 is 10 $\mu\text{g/g}$ (lower limit of determination).

Table 1c. F and Cl contents of the Oiwake southern pyroclastic flow samples of the 1108 eruption of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
619-6	204	460	20	0.86 ₅
619-7	266	520	40	1.03
619-8	252	510	30	0.98 ₀
811-1	148	240	20	1.26
811-6	258	480	20	1.05
811-7	250	530	20	0.91 ₅
812-2	258	510	10	0.96 ₃
812-4	250	500	40	1.01
812-5-3	164	90	30	5.10 ^g
813-3	264	470	30	1.12
814-1	204	480	40	0.86 ₅
815-1	262	470	20	1.09
815-3	152	500	10	0.57 ₉
815-6	264	500	30	1.05
815-11	274	500	30	1.09
815-16	254	540	10	0.89 ₄
815-17	122	120	40	2.85
815-20	136	390	30	0.70 ₅
815-21	228	210	20	2.24
816-1	267	550	30	0.95 ₈
816-3	274	480	10	1.09
816-7	264	520	10	0.96 ₆
820-2	166	430	20	0.75 ₆
820-4	261	560	30	0.91 ₉
820-5	246	510	10	0.91 ₈
820-6	220	540	10	0.77 ₅
820-8	268	500	10	1.02
820-10	284	500	10	1.08
821-2	252	230	20	2.24
821-4	260	550	30	0.93 ₃
821-7	256	260	20	1.99
821-10	246	450	30	1.09
821-11	318	560	20	1.10
821-12	276	520	10	1.01
821-17	256	440	20	1.14
821-19	198	350	10	1.09
822-1	226	520	20	0.84 ₃
822-3	244	490	20	0.96 ₉
822-5	236	450	20	1.02
822-7	214	490	20	0.85 ₀
822-8	94	30	20	17.5 ^g
822-10	266	500	10	1.01
822-13	150	480	20	0.60 ₈
a.m. ^a	231.4	418.8 ^b		1.571
s.d. ^c	49.70	133.92 ^b		2.6035
m(log X) ^d	2.352	2.563 ^b		0.0601
s(log X) ^e	0.1126	0.3167 ^b		0.25071
g.m. ^f	224.9	365.4 ^b		1.149

^a ~ ^f Same as in Table 1a.^g Significantly different from the others with 1% level.

Table 1d. F and Cl contents of the Kamino-butai lava flow samples of the 1108 eruption of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
BU-U-2	262	440	20	1.16
BU-U-3	244	320	70	1.82
BU-U-7	260	330	50	1.73
BU-U-8	281	440	40	1.31
BU-U-9	250	330	30	1.56
BU-U-10	280	410	20	1.34
BU-U-11	260	370	20	1.39
BU-U-17	256	380	20	1.33
BU-U-19	262	400	30	1.32
BU-U-20	246	400	20	1.21
BU-U-21	260	410	30	1.28
a.m. ^a	260.1	352.7 ^b		1.404
s.d. ^c	11.90	53.50 ^b		0.2105
m(log X) ^d	2.415	2.542 ^b		0.1432
s(log X) ^e	0.0197	0.0709 ^b		0.06174
g.m. ^f	259.8	348.7 ^b		1.391

^a ~ ^f Same as in Table 1a.

Table 2a. F and Cl contents of the upper B-scoria fall samples of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
US-1-1	258	480	20	1.05
US-1-3	252	450	10	1.07
US-1-5	258	480	20	1.05
US-1-6-b	252	430	20	1.15
US-1-7-w	252	460	20	1.07
US-1-8-b	254	450	< 10	1.05
US-1-10-w	257	490	10	1.00
US-1-10-b	261	500	10	0.99 ₄
US-3-2	240	480	< 10	0.93 ₃
US-3-4	276	480	10	1.10
US-1-12-allw	358 ^g	105 ^g	20	7.86 ^g
a.m. ^{a, h}	256.0	458.0 ^b		1.045
s.d. ^{c, h}	9.08	23.94 ^b		0.0591
m(log X) ^{d, h}	2.408	2.660 ^b		0.0186
s(log X) ^{e, h}	0.0153	0.0231 ^b		0.02480
g.m. ^{f, h}	255.9	457.4 ^b		1.044

^a ~ ^f Same as in Table 1a.^g Significantly different from the others with 1% level.^h The sample US-1-12-allw is excluded as an outlier.

Table 2b. F and Cl contents of the Shimono-butai lava flow samples of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
BU-L-1	294	350	30	1.71
BU-L-5	302	350	30	1.76
BU-L-6	298	420	20	1.39
BU-L-12	310	380	20	1.61
BU-L-13	302	340	20	1.76
BU-L-14	306	360	30	1.73
BU-L-16	308	390	20	1.55
BU-L-18	302	400	10	1.45
BU-L-22	308	480	20	1.25
a.m. ^a	303.3	363.3 ^b		1.579
s.d. ^c	5.20	47.70 ^b		0.1841
m(log X) ^d	2.482	2.557 ^b		0.196
s(log X) ^e	0.00747	0.0548 ^b		0.0528
g.m. ^f	303.3	360.7 ^b		1.569

^a ~ ^f Same as in Table 1a.

Table 2c. F and Cl contents of the Maru-yama lava samples (Maru) and Nishi-maekake-yama samples (MA) of Asama volcano.

Sample	F ($\mu\text{g/g}$)	Cl _{total} ($\mu\text{g/g}$)	Cl _{H₂O-sol.} ($\mu\text{g/g}$)	F/Cl _{insol.} (atom)
Maru-2	66	140	30	1.12
Maru-3	382	460	10	1.58
Maru-4	250	490	20	0.99 ₃
MA-814-2-2w	288	460	20	1.22
MA-814-2-3	240	460	20	1.02
MA-814-2-5b	278	500	10	1.06
MA-814-2-5w	234	520	10	0.85 ₆
MA-814-2-5a	242	490	20	0.96 ₁
MA-814-2-4	120	40	20	11.2
MA-814-2-6	106	10	5	39.6
MA-814-2-7	104	40	10	6.47

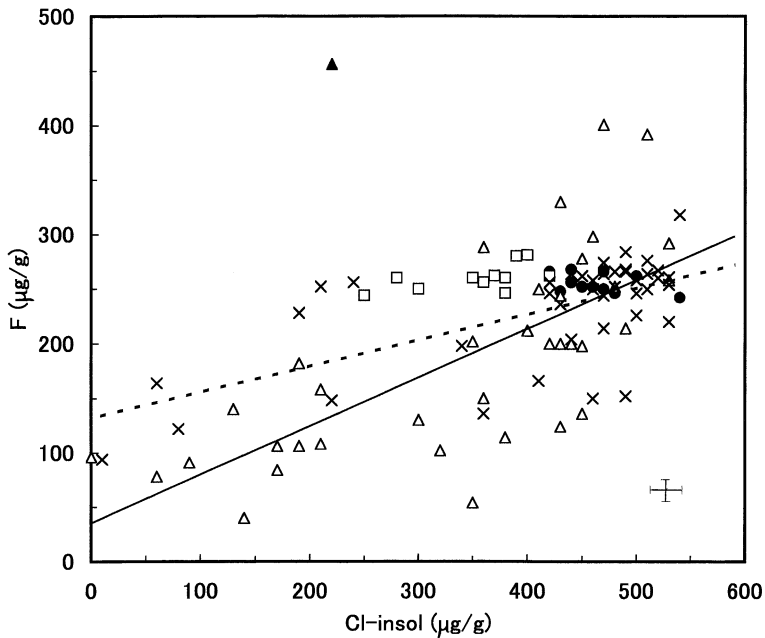


Fig. 2. F-Cl_{insol.} variation patterns for the samples of the 1108 eruption of Asama volcano: ● = B-scoria L samples; △ = Oiwake N pyroclastic flow samples; × = Oiwake S pyroclastic flow samples; □ = Kamino-butai lava samples; ▲ = Oiwake N 817-10 sample. The sample Oiwake N 1027-13 is excluded from the figure. ⊕ Error bars.

Regression lines for

Oiwake N samples, —: $F = 0.4455Cl + 35.50$ ($r = 0.711$)

Oiwake S samples, - - - : $F = 0.2383Cl + 131.64$ ($r = 0.642$)

The sample Oiwake N 817-10 is excluded from the calculation of the regression line.

Tsuchiya, 2004). The log Cl-values of the 812-5-3, 815-17, 822-8 and 818-10 samples, the F/Cl-values of the 812-5-3, 822-8, 817-10 and 818-10 samples, and the log(F/Cl)-values of the 812-5-3, 822-8 and 818-10 samples are regarded to differ at the 1% significance level from the other samples of each group.

The significances of the dissimilarity in the arithmetic mean values m and the mean logarithmic values $m(\log X)$ among the groups were examined by t -test (Table

Table 3. Difference of the arithmetic means and of the mean logarithmic values $m(\log X)$ among the volcanic products of the 1108 eruption and some others examined by t -test^a.

$F^{b, f}$:
Kamino-butai ~ B-scoria L \gg Oiwake S $>$ Oiwake N
B-scoria U ~ B-scoria L
Shimono-butai \gg Kamino-butai
$\log F^f$:
Kamino-butai ~ B-scoria L \gg Oiwake S $>$ Oiwake N
B-scoria U ~ B-scoria L
Shimono-butai \gg Kamino-butai
$Cl_{insol.}^f$:
B-scoria L \geq Oiwake S $>$ Kamino-butai ~ Oiwake N
B-scoria L \gg Kamino-butai
B-scoria L ~ B-scoria U
Shimono-butai ~ Kamino-butai
$\log Cl_{insol.}^{c, f}$:
B-scoria L ~ Oiwake S $>$ Kamino-butai ~ Oiwake N
B-scoria L \gg Kamino-butai
B-scoria L ~ B-scoria U
Shimono-butai ~ Kamino-butai
$F/Cl_{insol.}^{d, f}$:
Kamino-butai $>$ Oiwake N ~ Oiwake S ~ B-scoria L
Kamino-butai \gg Oiwake S
B-scoria U ~ B-scoria L
Shimono-butai \geq Kamino-butai
$\log (F/Cl_{insol.})^{e, f}$:
Kamino-butai \gg Oiwake N ~ Oiwake S ~ B-scoria L
B-scoria U ~ B-scoria L
Shimono-butai \geq Kamino-butai

^a \gg means that the difference is significant at the 1% level; $>$ means that the difference is significant at the 5% level; \geq means that the difference is significant at the 10% level; \sim means that the difference is not significant at the 10% level.

^bThe sample 1027-13 is excluded as an outlier.

^cThe samples 812-5-3, 815-17, 822-8 and 818-10 are excluded as outliers.

^dThe samples 812-5-3, 822-8, 817-10 and 818-10 are excluded as outliers.

^eThe samples 812-5-3, 822-8 and 818-10 are excluded as outliers.

^fThe sample US-1-12-allw is excluded as an outlier.

3). Also differences of the variances s^2 and $\{s(\log X)\}^2$ among the groups were examined by F-test (Table 4). The values distinguished as outliers by Q-test were excluded in these examinations. The results support the deduction from Tables 1a-1d and Fig. 2 that the F and Cl contents of the volcanic products strongly depend upon the type of eruption.

5-2 The F and Cl contents of the scoria and the lava

The Cl contents of the B-scoria L samples are uniform and the arithmetic mean is higher than those of the others. On the other hand, their F contents are almost the same as those of the Kamino-butai lava flow. The Kamino-butai lava samples show lower Cl contents and a little higher variance than those of the B-scoria L samples. This relation coincides with that between the pumice and the Oni-oshidashi lava flow in the 1783 activity. The results support the conclusion of the Yoshida and Tsuchiya's report (2004) that Cl (and perhaps also H₂O) may have been enriched in the uppermost part of the magma column at the beginning of the eruption, and vesiculation in the vent would have

Table 4. Difference of the variances s^2 and of $\{s(\log X)\}^2$ among the volcanic products of the 1108 eruption and some others examined by F-test^a.

$F^{b, f}$:
Oiwake N \gg Oiwake S \gg Kamino-butai ~ B-scoria L
B-scoria U ~ B-scoria L
Kamino-butai $>$ Shimono-butai
$\log F^f$:
Oiwake N \gg Oiwake S \gg Kamino-butai ~ B-scoria L
B-scoria U ~ B-scoria L
Kamino-butai $>$ Shimono-butai
$Cl_{insol.}^f$:
Oiwake S ~ Oiwake N \gg Kamino-butai ~ B-scoria L
B-scoria L ~ B-scoria U
Kamino-butai ~ Shimono-butai
$\log Cl_{insol.}^{c, f}$:
Oiwake N \gg Oiwake S ~ Kamino-butai $>$ B-scoria L
Oiwake S \gg B-scoria L
B-scoria L ~ B-scoria U
Kamino-butai ~ Shimono-butai
$F/Cl_{insol.}^{d, f}$:
Oiwake N ~ Oiwake S $>$ Kamino-butai $>$ B-scoria L
Oiwake N \gg Kamino-butai
B-scoria L ~ B-scoria U
Kamino-butai ~ Shimono-butai
$\log (F/Cl_{insol.})^{e, f}$:
Oiwake N \gg Oiwake S $>$ Kamino-butai ~ B-scoria L
Oiwake S \gg B-scoria L
B-scoria L ~ B-scoria U
Kamino-butai ~ Shimono-butai

^{a-f} Same as in Table 3.

brought about pumice eruption.

5-3 Variation in the F and Cl contents of the pyroclastic flow deposits

The Oiwake pyroclastic deposit samples exhibit the largest variation in the products of the 1108 activity and release of Cl and F after the effusion from intermediate-type pyroclastic flow is indicated. Generally speaking, tendency for the distribution of F and Cl is consistent with that for the Agatsuma pyroclastic flow in the 1783 eruption. Nevertheless, the F and Cl contents of considerable numbers of the Oiwake pyroclastic flow samples are within the range: $m(X) \pm 3s(X)$ of the B-scoria L samples unlike the relation between the Agatsuma pyroclastic flow samples and the pumice fall samples in the 1783 activity. We name these samples high-halogen samples. Aramaki (1963) pointed out that the Oiwake deposits show no welding or induration in many exposures as differ from the Agatsuma deposits. He attributed the difference to the temperature at the time of settling. Then, he concluded that the material of the Oiwake pyroclastic flow might be vertically ejected and cooled, deposited on the flank not far from the crater, and then flowed down. The high-halogen samples, which have the F and Cl contents almost the same as those of the B-scoria L samples, might be produced by this mechanism.

On the other hand, the other Oiwake pyroclastic flow samples have low Cl and F contents. We name them low-halogen samples. Yoshida and Tsuchiya (2004) thought the formation mechanism of the Agatsuma pyroclastic flow in the 1783 eruption as follows. The vertical change of the Cl content in the magma column might be gradual and after the pumice eruption, somewhat less volatile-rich magma would come up to the vent. The magma would have vesiculated near the mouth of the vent and overflowed without being quenched. In this case, volatiles would be released by vesiculation after the effusion, and the F- and Cl-poor, heterogeneous deposits could be produced. The Oiwake low-halogen samples might be resulted by a similar cause and are consistent with the surface flow of high-temperature, gas-releasing, fragmental material. As a whole, the distribution range of the halogen contents of the Oiwake pyroclastic flow became wider than that of the Agatsuma pyroclastic flow.

5-4 Examination on the topographical distribution of the F and Cl contents in the Oiwake pyroclastic flow deposits

The samples of the southern flows (Oiwake S) show higher F and Cl contents than those of the northern flows (Oiwake N) in average. Correlations between F and Cl content both for the Oiwake S and N samples are significant (Fig. 2). The slopes of the regression lines for the two flows are significantly different, but the lines converge at the distribution area of the scoria samples.

This indicates that they were derived from a similar magma but conditions of gas-release were different.

Detailed topographical distribution of the F and Cl contents in the Oiwake pyroclastic flow is illustrated in Figs. 3a and 3b. In these figures, the halogen contents are divided into 8 classes based on the arithmetic means and the standard deviations of the F and Cl contents in the B-scoria L samples. The classes are expressed with the lengths of sides of rectangles, the F contents with the height and the Cl contents with the width. Any relations cannot be recognized between the halogen contents and the distances from the crater to sampling points. The low-halogen and high-halogen groups rather seem to line up roughly parallel with the streamline of the flows. According to Aramaki (1963), the Oiwake pyroclastic flow may be consisted of many small flow units of a few meters thick and a few hundred meters long. Then, these results may suggest that the F and Cl contents will reflect the degassing condition of each flow unit and volatiles might be mostly released at the early stage of the flow. Some flow units indicate very intense gas-release as compared with those of the Agatsuma pyroclastic flow. We cannot clearly explain the condition to cause such a strong degassing, but imagine that addition of external water might play a role as presumed from the experiment by Sugiura (1968). He reported that H₂O vapor accelerates remarkably the volatilization of halogens from volcanic rocks on heating.

Putting all these observations together, we can deduce a transition of the mode of formation of the Oiwake pyroclastic flow. After repetition of the scoria eruptions, volatile contents of the magma decreased. Then, scoriae were not highly ejected, rained mainly over the flank near the crater, and flowed down like pumice flow. They were cooled enough not to release volatiles after the eruption. The flow units of the high-halogen group might be produced in this stage. Further decrease of volatiles led to the next stage in which the magma vesiculated near the mouth of the vent and the gas-releasing magma overflowed without being quenched. This would result in the flow units of the low-halogen group, which are similar to the Agatsuma pyroclastic flow of the 1783 eruption. High-halogen samples were not found in the samples of the Agatsuma pyroclastic flow unlike the Oiwake pyroclastic samples (Yoshida and Tsuchiya, 2004). The difference may indicate that the 1783 eruption lacked the pumice flow stage, perhaps due to the difference in scale of the two eruptions (Aramaki, 1963). Another possibility is that the number of analyzed samples (9) of the Agatsuma flow was not large enough to find high-halogen samples.

5-5 The F and Cl contents of the samples excluded from the 1108 activity

The samples of the groups excluded from the 1108

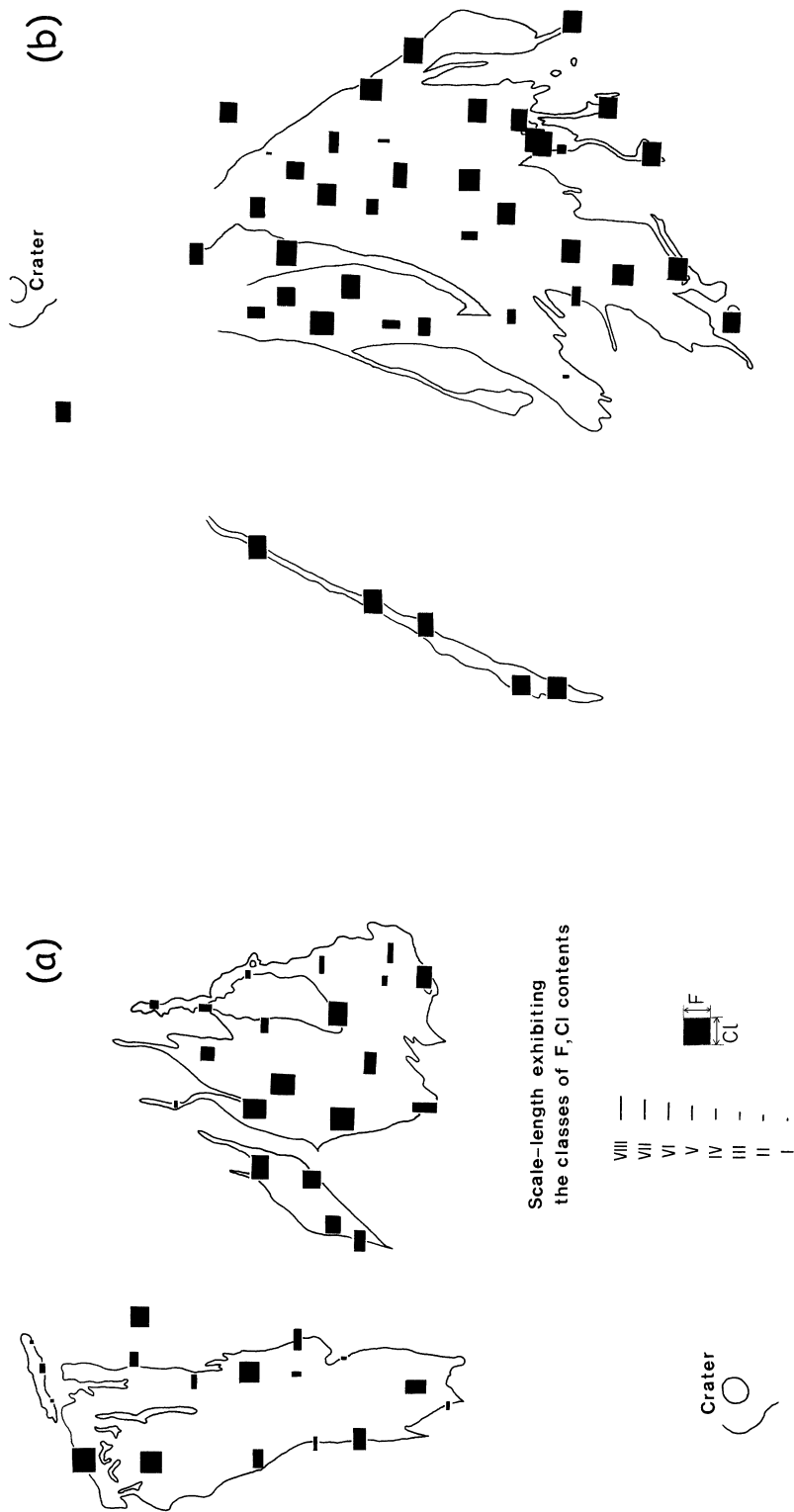


Fig. 3. Topographic distribution of F and Cl contents of the Oiwake pyroclastic flow. a) Northern flows. b) Southern flows. The lengths of sides of rectangles exhibit the class of the halogen contents; m_F and m_{Cl} are the arithmetic means, and s_F and s_{Cl} are the standard deviations of the F and Cl contents in the B-scoria L samples. The height for the F content—I: $< 92 \mu\text{g/g}$ ($< m_F - 14s_F$), II: $92 \sim 127 \mu\text{g/g}$ ($m_F - 14s_F \sim m_F - 10s_F$), III: $128 \sim 163 \mu\text{g/g}$ ($m_F - 10s_F \sim m_F - 6s_F$), IV: $164 \sim 200 \mu\text{g/g}$ ($m_F - 6s_F \sim m_F - 2s_F$), V: $201 \sim 236 \mu\text{g/g}$ ($m_F - 2s_F \sim m_F + 2s_F$), VI: $237 \sim 272 \mu\text{g/g}$ ($m_F + 2s_F \sim m_F + 4s_F$), VII: $273 \sim 309 \mu\text{g/g}$ ($m_F + 4s_F \sim m_F + 6s_F$), VIII: $> 309 \mu\text{g/g}$ ($> m_F + 6s_F$). The width for the Cl content—I: $< 90 \mu\text{g/g}$ ($< m_{Cl} - 11s_{Cl}$), II: $90 \sim 157 \mu\text{g/g}$ ($m_{Cl} - 11s_{Cl} \sim m_{Cl} - 9s_{Cl}$), III: $158 \sim 225 \mu\text{g/g}$ ($m_{Cl} - 9s_{Cl} \sim m_{Cl} - 7s_{Cl}$), IV: $226 \sim 293 \mu\text{g/g}$ ($m_{Cl} - 7s_{Cl} \sim m_{Cl} - 5s_{Cl}$), V: $294 \sim 361 \mu\text{g/g}$ ($m_{Cl} - 5s_{Cl} \sim m_{Cl} - 3s_{Cl}$), VI: $362 \sim 429 \mu\text{g/g}$ ($m_{Cl} - 3s_{Cl} \sim m_{Cl} - s_{Cl}$), VII: $430 \sim 498 \mu\text{g/g}$ ($m_{Cl} - s_{Cl} \sim m_{Cl} + s_{Cl}$), VIII: $> 498 \mu\text{g/g}$ ($> m_{Cl} + s_{Cl}$).

activity by Aramaki *et al.* (1989), i.e., the B-scoria U, the Shimono-butai lava flow, the Maru-yama lava flow, and the Nishi-maekake-yama ejecta, are also analyzed for F and Cl. The Shimono-butai lava flow samples have distinctly higher F contents than the Kamino-butai samples and is consistent with the conclusions from the petrological studies. On the other hand, we cannot find any significant difference in the halogen contents between the B-scoria U and the B-scoria L samples. But, the US-1-12-allw sample has halogen contents very different from the other B-scoria U samples and this sample must be reexamined for its assignment. We cannot make any discussion on the Maru-yama lava flow and the Nishi-maekake-yama ejecta because they show very large variations even within a small number of samples.

6. Conclusion

The F and Cl contents of successive phases of the 1108 eruption of Asama volcano lead to the following conclusions as compared with the 1783 activity.

The transition of the mode of eruption from scoria (pumice) fall to intermediate-type pyroclastic flow and then to lava flow may be intimately related to the volatile contents of the magma at the time of eruption almost similar to that reported for the 1783 eruption. There may have been a vertical concentration gradient of Cl as well as H₂O in the magma column before the eruption. The upper part of the magma had high volatile contents and vesiculated in the vent. The vesiculation in a limited space would have brought about violent explosions ejecting scoriae highly. At the last stage of the scoria eruption, the eruption became weaker to eject the material not so highly and rained over the flank near the crater and piled scoriae flowed down. The volatile contents of the magma decreased further as to vesiculate at the mouth of the vent and the gas-releasing magma overflowed from the crater without being quenched. The volatiles might be mostly released at the early stage of the flow. The Oiwake pyroclastic flow may be consisted of many flow units of these two eruption stages. At the last stage, Cl-poor magma flowed out without notable vesiculation as the Kamino-butai lava flow.

Acknowledgement

We would like to express our hearty thanks to Professor Shigeo Aramaki of Department of Geology and Mineralogy, Hokkaido University (at present, Emeritus Professor of the Earthquake Research Institute, University of Tokyo), Professor Masaki Takahashi of Department of Earth Science, Ibaraki University (at present, Professor of the Department of Applied Earth Sciences, Nihon University) and Dr. Yasuo Ichikawa of the Earthquake Research Institute, University of Tokyo (at

present, Oyo Chisitsu Co.). They generously provided us the systematically collected samples of the 1108 and the other eruptions and also gave us valuable suggestion and discussion from geological and petrological viewpoints.

References

- Arai, F. (1979) Marker tephra layers in the northwestern part of the Kanto districts after the Jomon age. *Kokogaku Journal*, No. 157, 41–52 (in Japanese).
- Aramaki, S. (1957) Classification of pyroclastic flows. *Bull. Volcanol. Soc. Japan*, 1, 47–57 (in Japanese).
- Aramaki, S. (1963) Geology of Asama volcano. *J. Fac. Sci. Univ. Tokyo, sec. II*, 14, 229–443.
- Aramaki, S. (1968) Geology of Asama volcano. *Chigaku Dantai Kenkyukai Senpo*, No. 14, 1–45 (in Japanese).
- Aramaki, S. (1980) Pyroclastic flow disaster of Asama volcano. *Gekkan Chikyu*, 2, 421–429 (in Japanese).
- Aramaki, S. and Yamasaki, M. (1963) Pyroclastic flows in Japan. *Bull. Volcanol.*, 26, 89–99.
- Aramaki, S., Ichikawa, Y. and Takahashi, M. (1989) Major chemical compositions of ejecta of the Tennin eruption of Asama volcano. *Abstracts of the Annual Meeting of the Volcanol. Soc. of Japan*, No. 1, 61A, p. 80 (in Japanese).
- Dixon, W. J. (1953) Processing data for outliers. *Biometrics*, 9, 74–89.
- Iwasaki, I., Katsura, T. and Sakato, N. (1955) Geochemical investigations of the volcanoes in Japan 31, Method for the determination of chlorine in the volcanic rocks. *Nippon Kagaku Zasshi*, 76, 1116–1119 (in Japanese).
- Iwasaki, I., Katsura, T., Sakato, N. and Hirayama, M. (1957) Geochemical investigations of the volcanoes in Japan 41, Chlorine in the volcanic rocks. *Nippon Kagaku Zasshi*, 78, 164–172 (in Japanese).
- Iwasaki, I., Katsura, T., Ozawa, T., Yoshida, M. and Iwasaki, B. (1968). Chlorine content of volcanic rocks and migration of chlorine from the mantle to the surface of the Earth. In *The crust and upper mantle of the Pacific area*. (Knopoff, L., Drake, C. L. and Hart, P. J. eds.), 423–427, *Geophys. Monograph* 12, American Geophys. Union, Washington, D. C.
- Nakamura, K. and Aramaki, S. (1966) 1281(?) eruption of Asama volcano. *Bull. Volcanol. Soc. Japan*, 11, 45 (in Japanese).
- Sugiura, T. (1968) An experimental study on the role of water vapor in the distribution of fluorine and chlorine in volcanic rocks. *Bull. Chem. Soc. Japan*, 41, 1588–1600.
- Tomonari, A. (1962) Improvement of the method for the photometric determination of micro amounts of chloride. *Nippon Kagaku Zasshi*, 83, 693–695 (in Japanese).
- Tsuchiya, K., Imagawa, T., Yamaya, K. and Yoshida, M. (1985) Separation of micro amounts of fluoride coexisting with large amounts of aluminum and silica by improved trimethylsilylating distillation. *Anal. Chim. Acta*, 176, 151–159.
- Yoshida, M. (1963) The volatilization of chlorine and

- fluorine compounds from igneous rocks on heating. *Bull. Chem. Soc. Japan*, **36**, 773–782.
- Yoshida, M. (1975) An experimental study for the fractionation of fluorine and chlorine in volcanic gases through the reaction of them with volcanic rocks. *Nippon Kagaku Kaishi*, **1975**, 449–454 (in Japanese, with English abstract).
- Yoshida, M. (1990) Fractionation of fluorine and chlorine through the volcanic process. In *Geochemistry of gaseous elements and compounds*. (Durrance, E. M., Galimov, E. M., Hinkle, M. E., Reimer, G. M., Sugisaki, R. and Augusthithis, S. S. eds.), 163–184, Theophrastus Publications, S. A., Athens.
- Yoshida, M. and Tsuchiya, K. (2004) Fluorine and chlorine contents in the products of the 1783 (Temmei) eruption of Asama volcano. *Bull. Volcanol. Soc. Japan*, **49**, 65–72.
- Yoshida, M., Uchikawa, K. and Hirabayashi, H. (1994) Fluorine and chlorine contents in the lavas and ejecta of the 1986 eruption of Izu-Oshima volcano. *J. Volcanol. Geotherm. Res.*, **63**, 231–241.
- Yoshida, M., Takahashi, K., Yonehara, N., Ozawa, T. and Iwasaki, I. (1971) The fluorine, chlorine, bromine and iodine contents of volcanic rocks in Japan. *Bull. Chem. Soc. Japan*, **44**, 1844–1850.
- (Editorial handling Kenji Nogami)

浅間火山 1108 年 (天仁) 活動噴出物のフッ素, 塩素含有量

吉田 稔・青柳隆二

浅間山天仁活動は、スコリア (軽石) の噴出に始まり、中間型の追分火砕流の発生を経て、上の舞台溶岩流の流出で終わった。天明活動の鎌原火砕流に相当する噴出物は、天仁噴火では知られていない。これらの噴出物は、同一火口から生じ、いずれも安山岩質で、主成分組成の分布範囲は狭い。著者らは、吉田・土屋 (2004) が、天明 (1783) 活動噴出物につき得た結果と同じく、噴出様式の変化は、噴出時のマグマからのガス放出状況の相違がもたらしたものと考え、各種噴出物中のフッ素、塩素を定量し、これらの成分の揮発に関する吉田の実験結果に基づいて噴出機構を考察した。スコリア試料は、均一で高い塩素含有量を示し、噴火開始時に、マグマ柱の最上部に揮発性成分が濃縮され、火道内部で発泡して激しく放出されるとともに急冷されたとして説明される。追分火砕流試料は、フッ素、塩素含有量の分布範囲が非常に広く、かなりの数の試料がスコリアとほぼ同じ含有量を示す。一方、その他の試料は、フッ素、塩素含有量とも低く、変動幅が著しく大きい。ハロゲン含有量の地理的分布を検討した結果、追分火砕流は、ハロゲン含有量の異なる多くのフローユニットから成るものと見られる。ハロゲンの多いフローユニットは、火口付近に堆積したスコリアが流れ下ったものと推測される。ハロゲンの少ないフローユニットは、天明活動の吾妻火砕流と同様、火口付近で発泡しながら流出したことを示唆する。一方、ハロゲン含量の地理的分布を見ると流出後の脱ガスは主に流下の初期に起きたと思われる。上の舞台溶岩は流出後のガスの放出は少なかったと見られる。これらの結果は、天明噴火噴出物につき得られた結果と調和する。