

Temporal variations in the constituents of volcanic ash and adherent water-soluble components in the Unzen Fugendake eruption during 1990–1991

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(Received August 28, 2000; Revised March 9, 2001; Accepted March 12, 2001)

A change in the chemical compositions of volcanic gases is one of the noticeable phenomena that frequently occurs prior to an eruption. Analysis of the water-soluble components adhering to volcanic ash is available for remote monitoring of volcanic gases from inaccessible volcanoes. It is a secure method for monitoring volcanic activity without using particular devices. Prolonged volcanic eruption at the Unzen Fugendake volcano from 1990 to 1995 started with a phreatic eruption after 198 years of dormancy. Volcanic activity changed from a phreatic and phreatomagmatic eruption to a magmatic eruption with pyroclastic flows in May 1991. The relationship between the chemical composition of volcanic ash and the contents of the water-soluble components adhering to it are discussed in relation to the early stage of the long-term eruption. Volcanic ash ejected by phreatic and phreatomagmatic eruption before dome formation was the product of the alteration in the volcanoclastic materials beneath the surface. The ash had a high content of water-soluble components, which was caused by the absorption of hydrogen chloride and sulfur dioxide gases from magma into wet debris before dome formation. Volcanic ashes which were generated by pyroclastic flows after dome formation were fresh lava fragments. While the contents of water-soluble sulfate adhering to the ash noticeably decreased, those of water-soluble chloride adhering to the ash hardly decreased. The considerable decrease in the contents of water-soluble sulfate was caused by the reaction of volcanic gases with dry lava fragments. Contrary to this, the concentration of hydrogen chloride gas in ash clouds was extremely high, which obstructed the decrease in the water-soluble chloride content in the ash. Volatility of chlorine and sulfur from volcanic rock suggests that the inner temperature of pyroclastic flows was higher than 600~700°C at least.

1. Introduction

Activation of volcanic activity is accompanied by noticeable volcanic phenomena such as earthquake swarm, thermal anomaly, and diastrophism. Change in chemical compositions and flux of fumarolic gases is one of the most remarkable phenomena which is frequently observed prior to an eruption. Monitoring volcanic gases can provide information on subsurface conditions and continual observation of volcanic gases will contribute towards the prediction of eruptions (e.g. Hirabayashi *et al.*, 1999; Nogami *et al.*, 2000).

Observation of eruptions near active craters will provide us with authentic information on volcanic activity, although, approaching an erupting volcano involves great danger. Remote monitoring devices can reduce the inherent hazards involved in investigating active volcanoes. COSPEC (CORrelation SPECTrometer) is a spectrometric instrument, which was contrived for SO₂ measurement and has been widely utilized in the observation of flux at several volcanoes (e.g.

Okita and Shimozuru, 1975; Ohta, 1988). Hirabayashi *et al.* (1995) showed that the discharge rate of SO₂ from Unzen Fugendake correlates with the extrusion rate of magma. Recently, chemical species in volcanic gases have been measured synchronously by FT-IR (Fourier-Transform InfraRed Spectroscopy) at active volcanoes (Mori *et al.*, 1993, 1995; Mori and Notsu, 1997; Ono *et al.*, 1997).

Water-soluble matter adhering to volcanic ash has been studied through analysis of water leachates of volcanic ash. They can be ascribed to the adhesion of volcanic gases, aerosols, and alteration products of rocks to the surface of ash particles during eruptions (Taylor and Stoiber, 1973). Analysis of water leachates of pristine ash enables the estimation of volcanic gas compositions without using particular equipment. It is a kind of remote monitoring method which is available for observation of volcanic activity (e.g. Taylor and Stoiber, 1973; Ossaka and Ozawa, 1975; Ossaka *et al.*, 1998; Nogami *et al.*, 2000).

The Unzen Fugendake volcano is located in the center of the Shimabara Peninsula, Kyushu, Japan (Fig. 1). Phreatic eruptions at the Kujukushima and Jigokuato craters on 17 November 1990, after 198 years of dormancy, were the beginning of long-term volcanic activity between 1990 and

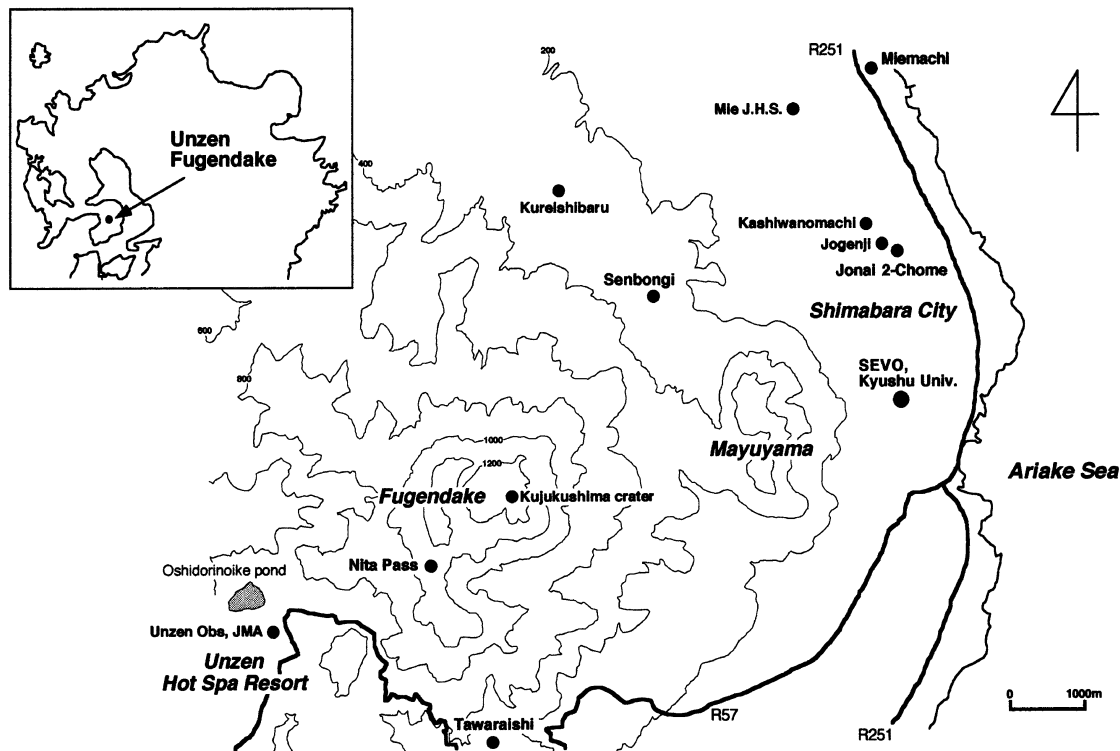


Fig. 1. Map showing localities of volcanic ash and volcanic gas samples collected at and around the Unzen Fugendake volcano.

Table 1. Major components compositions of volcanic ejecta and lava from the Unzen Fugendake volcano.

Date	Locality	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Ig.loss
18-Nov-90	Kujikushima-U	60.87	0.71	15.54	4.89	0.08	1.83	3.76	2.69	2.08	0.20	4.31
18-Nov-90	Kujukushima-M	62.14	0.68	15.95	4.75	0.07	1.71	4.28	2.69	1.93	0.16	4.64
18-Nov-90	Kujukushima-L	61.71	0.71	16.01	4.62	0.08	1.82	4.03	2.66	2.05	0.16	4.79
12-Feb-91	Shimabara City	60.87	0.67	16.35	4.50	0.10	2.31	5.22	3.30	2.05	0.16	
18-Mar-91	Fugendake	61.19	0.70	16.04	4.56	0.10	2.30	4.92	3.10	2.08	0.17	2.44
20-Apr-91	Muhyozawa	60.83	0.70	16.15	4.62	0.10	2.31	5.01	3.12	2.07	0.17	3.09
30-Apr-91	Kujukushima	61.66	0.70	16.54	4.43	0.09	2.21	4.95	3.26	2.10	0.17	2.62
8-Jun-91	Kashiwanomachi	63.64	0.64	16.21	4.19	0.09	2.12	4.60	3.20	2.40	0.19	
19-Jun-91	Nita Pass	65.35	0.57	15.96	3.71	0.09	1.99	4.30	3.46	2.54	0.16	0.70
25-Jun-91	Mie J. H. School	65.43	0.60	16.82	3.98	0.09	2.02	4.51	3.41	2.40	0.16	
27-Jun-91	Jogenji Temple	65.49	0.59	16.38	3.95	0.09	2.03	4.57	3.29	2.42	0.16	
22-Jul-91	Jonai 2-Chome	64.28	0.59	16.36	3.83	0.08	1.97	4.48	3.30	2.39	0.16	
25-Jul-91	Mie J. H. School	64.51	0.61	16.47	3.83	0.08	1.93	4.63	3.31	2.37	0.16	
7-Aug-91	Fukae Town	63.24	0.64	17.01	4.03	0.09	2.12	4.75	3.25	2.24	0.17	
8-Aug-91	JMA Unzen Obs	63.63	0.56	15.94	3.74	0.09	2.08	4.42	3.42	2.39	0.15	
12-Aug-91	Senbongi	64.34	0.64	16.66	4.08	0.09	2.17	4.90	3.56	2.11	0.16	0.67
13-Aug-91	JMA Unzen Obs	64.63	0.61	16.67	3.85	0.09	2.17	4.50	3.50	2.40	0.16	
26-Aug-91	JMA Unzen Obs	63.91	0.60	16.49	3.91	0.09	2.15	4.54	3.43	2.36	0.16	
27-Aug-91	JMA Unzen Obs	65.49	0.61	16.83	4.01	0.09	2.12	4.53	3.52	2.44	0.17	
	Dome 1	64.90	0.64	16.53	4.22	0.10	2.20	4.83	3.57	2.31	0.16	
	Dome 3	64.51	0.66	16.38	4.39	0.10	2.31	4.89	3.54	2.30	0.16	
	Old lava**	62.60	0.85	15.80	4.99	0.09	2.91	5.33	3.70	2.17	0.24	0.58***

FeO*: Total Fe as FeO, Old lava**: Yamamoto (1960), ***: H₂O (±).

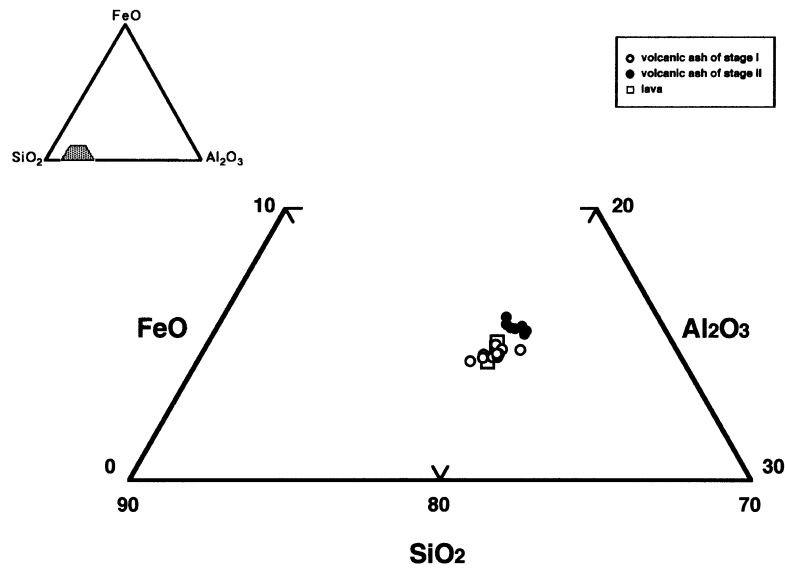


Fig. 2. Relative SiO_2 , Al_2O_3 and FeO ratios of the volcanic ash and the dome lava.

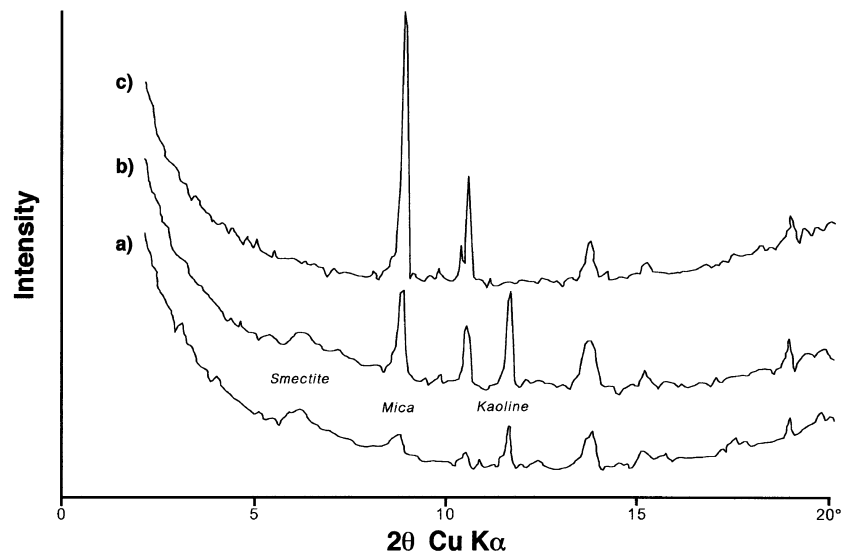


Fig. 3. XRD patterns of volcanic ash collected at Kujukushima crater (a), Fugen Shrine (b) in stage I and Shimabara City (c) in stage II.

1995. Emission of ash from the new craters ceased after a few days and only fumarolic activity at the Kujukushima crater continued until February 1991 with a gradual decrease of temperature and gas flux.

On 12 February 1991, eruption suddenly resumed, resulting in the formation of the craters Byobuiwa. Violent phreatomagmatic eruptions took place intermittently at the craters until early May 1991. A reddish new lava spine appeared at the Jigokuato crater on 20 May and grew into a lava dome within a few days. Lava blocks filled the crater and the collapse of these blocks into the eastern outer slope of the crater generated the first pyroclastic flows on 24 May (Geological party, Joint University Research Group, 1992; Nakada *et al.*, 1999).

In this paper, we focus on the volcanic activity between November 1990 and August 1991 because the type of erup-

tion drastically changed during this period. We discuss the relationship between chemical composition of volcanic ash and the contents of water-soluble components adhering to it during the early stage of the prolonged volcanic activity.

2. Sampling and Analysis

The period from 17 November 1990 to 31 August 1991 are divided into two stages according to the type of eruption. Stage I is the period from 17 November 1990 to 24 May 1991 in which phreatic and phreatomagmatic eruptions occurred at the summit craters of this volcano. Stage II is the following period from 24 May to 31 August 1991 in which lava domes formed and pyroclastic flows due to the collapse of lava blocks were frequently generated.

Figure 1 shows the ash sampling sites near Unzen Fugendake. Volcanic ash which was contaminated by soil and

Table 2. Water-soluble components adhering to volcanic ash from the Unzen Fugendake volcano.

No.	Date	Locality	pH	Fluoride*	Chloride*	Sulfate*	Cl/SO ₄ **
1	18-Nov-90	Kujukushima ejecta Upper		—	293	3580	0.22
2	18-Nov-90	Kujukushima ejecta Middle		—	250	3760	0.18
3	18-Nov-90	Kujukushima ejecta Lower	4.36	—	167	3470	0.13
4	18-Nov-90	Fugen Shrine		—	510	5160	0.26
5	18-Nov-90	Nita Pass		—	321	3480	0.25
6	12-Feb-91	Nita Pass		—	510	3860	0.36
7	12-Feb-91	Nita Pass	7.57	—	529	4340	0.33
8	12-Feb-91	Fugen Shrine	7.22	—	424	3800	0.30
9	12-Feb-91	Shimabara City		—	510	3860	0.36
10	18-Feb-91	1.2 km SE of Nita Pass		—	358	3490	0.28
11	18-Feb-91	200 m East of summit crater	7.24	—	367	3580	0.28
12	18-Mar-91	Fugendake	5.71	—	547	4240	0.35
13	31-Mar-91	Fugendake	4.05	—	37.5	3800	0.03
14	09-Apr-91	Kazaana	4.32	4.6	381	3860	0.27
15	12-Apr-91	Kazaana	4.61	—	433	4960	0.24
16	20-Apr-91	Muhyozawa	4.96	—	576	5820	0.27
17	30-Apr-91	Kujukushima crater	4.25	—	504	5020	0.27
18	11-May-91	Fugendake	4.74	—	388	6000	0.18
19	27-May-91	Fukae Town	5.43	8.1	77.8	450	0.47
20	27-May-91	Kureishibaru	5.15	5.9	128	682	0.51
21	27-May-91	Fukae Town Kami-Ohnokoba		72.8	785	0.25	
22	30-May-91	Tawaraihi	4.64	15.4	184	646	0.77
23	02-Jun-91	Yakeyama	5.50	2.2	54.4	125	1.18
24	03-Jun-91	Shimabara Castle		40.8	71.4	242	0.80
25	05-Jun-91	Shimabara City	4.63	11.1	105	317	0.90
26	08-Jun-91	Shimabara, Mie machi	4.73	11	137	668	0.56
27	08-Jun-91	Shimabara City	4.36	6.7	232	770	0.82
28	08-Jun-91	Shimabara, Kashiwanomachi	6.13	4.9	231	532	1.18
29	16-Jun-91	Nita Pass	4.56	7.9	60	127	1.28
30	17-Jun-91	Unzen Spa	4.50	7.9	167	160	2.83
31	17-Jun-91	Unzen P and J. H. School	6.01	5.3	74.3	100	2.01
32	18-Jun-91	Nita Pass	4.88	20.5	165	268	1.67

exposed to rain was not available for chemical analysis. Dry ash was gathered from leaves and windscreens of parked cars to avoid soil contamination. Falling ash was also collected on plastic sheets.

At stage II, pyroclastic flows with ash fall occurred with some frequency. As we could not follow all of them, we asked some residents of Shimabara City to collect volcanic ash in plastic vessels. Immediately after the volcanic ash was collected, the samples were sent to our laboratory. The fresh samples were used in the analysis of water-soluble components and rock-forming components. The number of ash samples collected near the volcano amounted to 64 in the two stages.

Each ash sample was correctly weighed and warmed in about 60 ml of pure water on a hot plate at about 80°C for 12 hours. The solution containing the ash was transferred

to a 100-ml measuring flask through a filter and then diluted with distilled water. Concentrations of fluoride, chloride, and sulfate ions in the water leachates were determined by ion chromatography. The contents of water-soluble component x in mg per 1 kg of ash was calculated by the simple equation

$$W_x = 100 \times C_x \times A^{-1},$$

where W_x , C_x , and A are the contents of water-soluble component x adhering to the ash (in mg/1 kg), the concentration of component x in water leachates of ashes (in ppm), and the weight of the ash sample (in grams), respectively.

The major elements of ash and dome lava were analyzed by X-Ray fluorescence (XRF) at the Kusatsu-Shirane Volcano Observatory of the Tokyo Institute of Technology. X-Ray Diffraction (XRD) patterns of constituent minerals of the ash were obtained with Ni-filtered Cu-K α radiation and

Table 2. (continued).

No.	Date	Locality	pH	Fluoride*	Chloride*	Sulfate*	Cl/SO ₄ **
33	25-Jun-91	Mie J. H. School	5.89	2.1	110	262	1.14
34	26-Jun-91	Yakeyama	4.66	10.5	254	267	2.58
35	27-Jun-91	Shimabara City	4.66	8.2	137	257	1.44
36	27-Jun-91	Mie J. H. School	5.34	22.1	257	194	3.59
37	27-Jun-91	Jogenji Temple		8.0	118	266	1.20
38	27-Jun-91	Jogenji Temple		8.9	149	283	1.43
39	27-Jun-91	Shimabara, Jonai 2-Chome	5.66	13.9	449	262	5.16
40	05-Jul-91	Shimabara City	4.53	35.7	219	459	1.29
41	13-Jul-91	SEVO, Kyushu Univ.	4.70	14.1	158	68	6.30
42	16-Jul-91	Shimabara City	4.54	6.8	252	101	6.76
43	18-Jul-91	Shimabara City	4.53	11	129	51.8	6.75
44	19-Jul-91	Shimabara City	4.31	20.5	595	144	11.2
45	22-Jul-91	Shimabara, Jonai 2-Chome	5.35	7.0	110	159	1.87
46	22-Jul-91	Shimabara, Jonai 2-Chome	5.45	6.5	593	261	6.16
47	25-Jul-91	Mie J. H. School	5.47	7.7	461	391	3.19
48	01-Aug-91	Shimabara, Jonai 2-Chome	5.27	18	329	162	5.50
49	02-Aug-91	SEVO, Kyushu Univ.	4.54	18.9	327	126	7.03
50	05-Aug-91	SEVO, Kyushu Univ.	4.32	27.4	478	79.8	16.2
51	05-Aug-91	SEVO, Kyushu Univ.	4.38	56.2	708	166	11.6
52	05-Aug-91	SEVO, Kyushu Univ.	4.39	102	458	86	14.4
53	07-Aug-91	Fukae Town	4.35	16	402	130	8.38
54	07-Aug-91	Fukae Town	4.40	6.2	239	76	8.52
55	11-Aug-91	Shimabara, Jonai 2-Chome	5.49	49.2	1630	344	12.8
56	12-Aug-91	Senbongi	4.57	40.2	1240	274	12.3
57	12-Aug-91	Minami Shimabara station	5.13	54.2	924	410	6.11
58	12-Aug-91	Jogenji Temple	6.08	44.6	710	375	5.13
59	13-Aug-91	Nita Pass	5.22	9.8	336	273	3.34
60	26-Aug-91	Unzen P and J. H. School	5.38	26.6	347	218	4.31
61	30-Aug-91	Mie J. H. School	5.29	9.4	574	163	9.54
62	31-Aug-91	SEVO, Kyushu Univ.	4.96	7.3	578	315	4.97
63	31-Aug-91	Mie J. H. School	5.70	7.5	255	333	2.08
64	31-Aug-91	Mie J. H. School	5.69	8.2	223	218	2.77

*: in mg/1 kg of ash, **: in molar ratio.

at a scanning speed of 0.02°/sec over a range of 2° to 20° 2 θ .

3. Results and Discussion

3.1 Chemical composition of the ash

The chemical composition of ash and lava are listed in Table 1. Volcanic ash collected at each stage showed little change in composition. "Ig.loss" given in Table 1 is a percentage of weight loss on ignition without correction of weight gain by oxidation of FeO to Fe₂O₃. This indicates that the degrees of hydration of all ash collected at stage I are higher than those of ash collected at stage II.

The relative SiO₂, Al₂O₃, and FeO ratios of ashes and dome lava are shown in Fig. 2. The relative ratios of ash from stage II fall within a limited field and are very similar to those of old Fugendake lava and new dome lava. On the

other hand, the ratios of ash at stage I are enriched in FeO.

XRD patterns of representative ash samples at each stage are illustrated in Fig. 3. Smectite and kaoline are identified in all the ash from stage I, while no clay minerals are detected in the ash at stage II. Kaolinite, which is formed by weathering of rock-forming silicates, is stable in the Earth's surface environment. Smectite, which is formed by a change in alkaline conditions is stable in the subsurface environment.

It is generally acknowledged that rocks are depleted in SiO₂ and enriched in FeO through changes beneath the Earth's surface (e.g. Osaka, 1968). Though ash from stage I contained vitreous fragments after resumption of eruptions in February 1991 (e.g. Nakada *et al.*, 1995), they are regarded as alteration products of old Fugendake lava and vol-

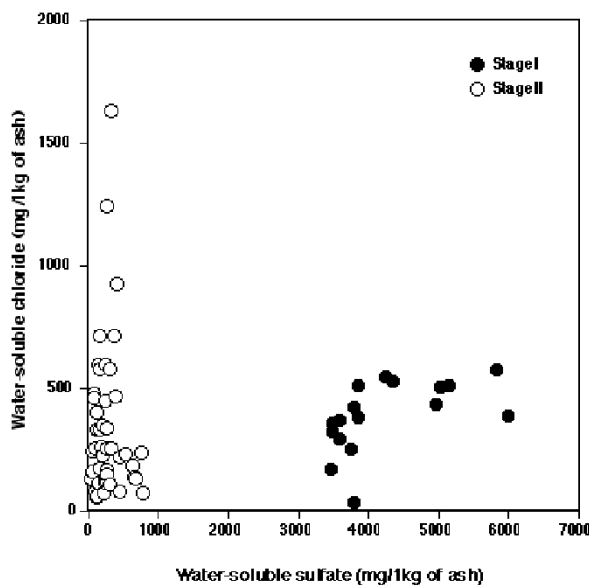


Fig. 4. Change of the contents of water-soluble chloride and sulfate adhering to the volcanic ash.

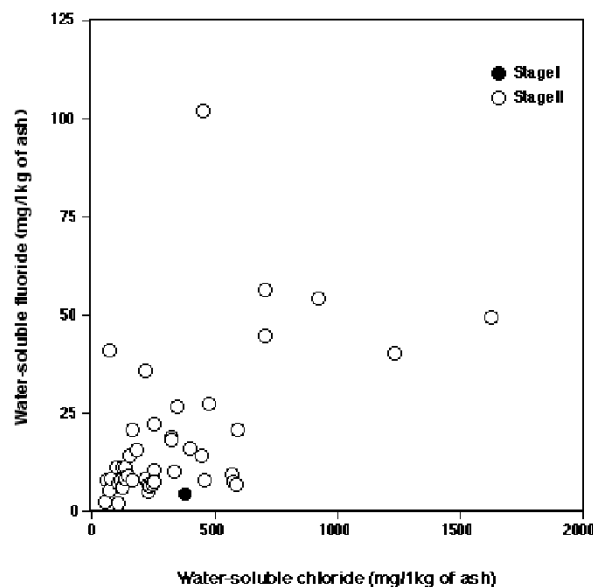


Fig. 5. The contents of water-soluble fluoride and chloride adhering to the volcanic ash.

canoclastic materials beneath the Earth's surface. Contrary to this, ash generated by pyroclastic flows at stage II are fine fragments of new lava. The composition of ash shown in Fig. 2 indicates that segregation of constituent minerals of dome lava rarely occurred during drifting of pyroclastic flows in ash clouds. Watanabe *et al.* (1999) pointed out through microscopic observation that the dominant constituents of volcanic ash changed from light minerals and lithic fragment to non-vesiculated glass after dome formation.

3.2 Water-soluble components adhering to ash

The contents of water-soluble components are listed, with pH values of water leachates, in Table 2. Figure 4 shows the relationship between the contents of water-soluble chloride and sulfate. Ash from stage II is distinguished from that of stage I in the $\text{Cl}^-/\text{SO}_4^{2-}$ diagram by its sulfate content. The contents of water-soluble fluoride and chloride in the ash are shown in Fig. 5. The data are scattered in the F-Cl diagram and no clear correlation between the two components was found.

Temporal change in $\text{Cl}^-/\text{SO}_4^{2-}$ molar ratios is shown in Fig. 6. The Cl/S ratios become higher than 5 during early July 1991. Although equivalence between the $\text{Cl}^-/\text{SO}_4^{2-}$ molar ratios of water leachates of ash and HCl/SO_2 molar ratios of volcanic gases diffusing in the atmosphere has been confirmed at the Sakurajima volcano (Ossaka and Ozawa, 1975), we never obtained such high values of water leachates of volcanic ash before. Thus, volcanic gases diffusing in the atmosphere were collected near lava domes on 22 July 1991 to examine the HCl/SO_2 molar ratios of volcanic gases. A radio-controlled aircraft equipped with vacuum bottles was used for collecting volcanic gas samples. The molar ratios of HCl/SO_2 in diffusing gases were 6, which is equal to the $\text{Cl}^-/\text{SO}_4^{2-}$ molar ratios in water leachates of the ash collected on that day. This proved that the Cl/S molar ratio of volcanic gases was equivalent to the

ratio of water leachates and that the concentration of HCl gas was much higher than that of SO_2 gas in ash clouds.

The equilibrium temperature calculated from the chemical composition of fumarolic gases was between 850 and 911°C (Ohba *et al.*, 1994) and the temperature of the dome lava was estimated by Fe-Ti oxide geothermometers to be between 780 and 880°C (Nakada and Motomura, 1999). The contents of volatile components in magma controls the chemical composition of volcanic gases and the type of eruption. Quantification of the contents of volatile components in dome lava are indispensable in understanding the degassing processes of volatile components from dome lava. The contents of fluorine, chlorine, and sulfur in new dome lava collected in June 1991 ranged from 230 to 275 ppm, from 197 to 322 ppm, and from 50 to 100 ppm, respectively (Hirabayashi *et al.*, 1992). Yoshida (1962) experimentally investigated the behavior of F, Cl, and S in the degassing processes from volcanic rocks. He concluded that F was the least volatile below 800°C and that S and Cl volatilized above 400 and 600°C, respectively. At 800°C, about 75 percent of the chlorine content and about 90 percent of the sulfur content volatilized from the rock. This result indicated that the Cl/S molar ratio in volcanic gases at high temperatures was approximately equivalent to the ratio in the rock. The molar ratio of Cl/S of the dome lava was higher than 3, which caused a high Cl/S ratio of volcanic gases in ash clouds. The volatility of chlorine and sulfur from the rock suggests that the inner temperature of pyroclastic flows was higher than 600~700°C.

At stage I, the volcanic ash which was ejected with the volcanic gases from the Jigokuato and Kujukushima craters was altered volcanoclastic materials containing clay minerals. Kagiya *et al.* (1999) revealed an electrical resistivity structure beneath the Unzen volcano by extensive magnetotelluric surveys. A low resistivity layer, which was interpreted to be a water-saturated layer, was found at 400 to

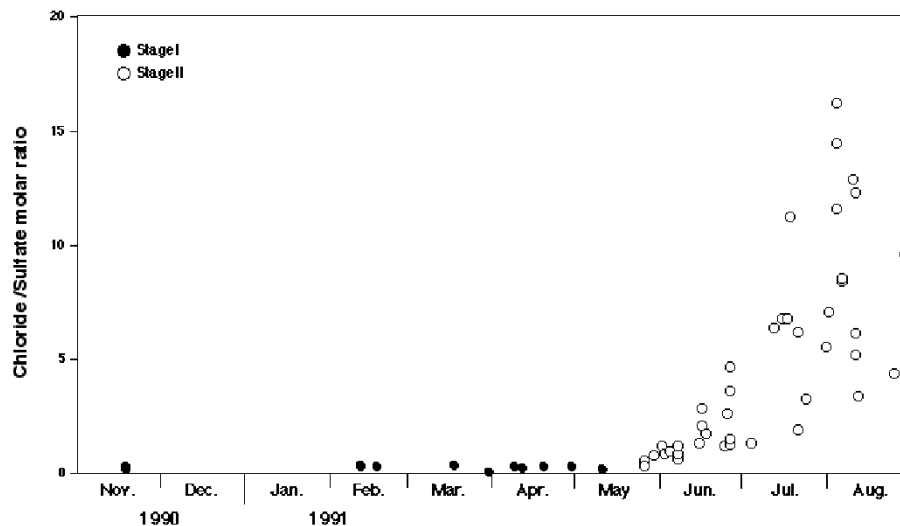


Fig. 6. Variation of Cl/S molar values in the ash leachates.

Table 3. Chemical composition of volcanic gases from the Kujukushima crater of the Unzen Fugendake.

Date	Temp (°C)	H ₂ O (vol. %)	composition of gases exclusive of water (vol. %)				composition of R-gas (vol. %)				
			SO ₂	H ₂ S	CO ₂	R	He	H ₂	N ₂	CH ₄	Ar
Nov. 18, 1990	115	99.7	n.d.*	11.8	82.6	5.6	0.029	34.4	65.4	0.21	n.a.**
Nov. 19, 1990	116	99.7	n.d.	14.9	80.1	5.0	0.018	27.8	71.7	0.47	n.a.**
Dec. 3, 1990	96.8	96.8	0.06	4.4	93.8	1.7	0.064	79.8	19.5	0.67	n.a.**
Dec. 20, 1990	98	97.7	<0.0	5.6	92.0	2.4	0.045	58.3	41.4	0.26	0.27

n.d.*: not detected, n.a.**: not analyzed.

500 m above sea level throughout the Fugendake area. The aquifer beneath the Jigokuato crater was only a few hundred meters deep. They considered that the occurrence of phreatomagmatic eruptions was due to the interaction of ascending magma with the shallow aquifer beneath the Jigokuato crater.

There was a high water-soluble chloride and sulfate content in the ash from stage I. Volcanic gases collected at the Kujukushima crater on 18 November 1990 were mainly composed of CO₂ exclusive of H₂O. Hydrogen chloride and sulfur dioxide gases were negligible (Table 3). These results indicate that the hydrogen chloride and sulfur dioxide in the volcanic gases were absorbed in "wet" debris in the shallow aquifer beneath the Jigokuato crater.

At stage II, the volcanic ash was very fine fragments of new lava. Ash rose with the volcanic gases forming ash clouds when pyroclastic flows descended along the valley. Water-soluble matter formed on the surface of the ash through the reaction of fresh lava fragments with the volcanic gases. The reaction of dry rock fragments with high-temperature volcanic gases led us to expect a decrease in the content of water-soluble components in the ash. The content of water-soluble sulfate in the ash at this stage decreased considerably, as we expected. However, the concentration of hydrogen chloride in the ash clouds was much higher than

that of sulfur dioxide, which obstructed the decrease in the water-soluble chloride content in ashes.

4. Conclusions

Observation of live volcanic phenomena at the Unzen Fugendake volcano during the long-term eruption from 1990 to 1995 provided us with some important new data on volcanology. The change of volcanic activity from a phreatic and phreatomagmatic eruptions to a magmatic eruption with pyroclastic flows in May 1991 was one of the big volcanic events of this long-term eruption.

Volcanic ash ejected by phreatic and phreatomagmatic eruptions at stage I were products of the alteration of old Fugendake lava and volcanoclastic materials beneath the Earth's surface. At this stage, the volcanic ash had a high content of water-soluble components. Dissolution of hydrogen chloride and sulfur dioxide gases into wet debris beneath the summit crater caused great adhesion of water-soluble components to the ash.

On the other hand, the ash which was generated by pyroclastic flows during stage II were fine fragments of new dome lava. Water-soluble matter was formed on the surface of the ash through the reaction of volcanic gases with dry lava fragments in ash clouds. The considerable decrease in the water-soluble sulfate content in the ash was due to the re-

action of dry lava fragments and high temperature volcanic gases in the ash clouds. Molar ratio of $\text{Cl}^-/\text{SO}_4^{2-}$ in water leachates drastically increased at this stage, which indicates a high HCl/SO_2 molar ratio in ash clouds. The extremely high concentration of HCl in ash clouds prevents the water-soluble chloride content from decreasing. The high ratio in leachates also suggests that the inner temperature of pyroclastic flows was greater than $600\sim 700^\circ\text{C}$.

Acknowledgments. We are grateful to Prof. Emeritus Kazuya Ohta and to all the staff of the Shimabara Earthquake and Volcano Observatory (SEVO), Kyushu University, for their support and hospitality. We are deeply indebted to Mr. Kazumasa Miura, a member of Shimabara Group No. 2, Nagasaki Scout Council, BSN, and other residents in Shimabara City for their dedicated cooperation. We also thank Mr. Hideo Ito for his dedication to gas sampling through his superhuman technique in handling a radio-controlled airplane. This paper benefited from the helpful and constructive reviews by Drs. Kenji Notsu and Setsuya Nakada.

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