

# High SiF<sub>4</sub>/HF ratio detected in Satsuma-Iwojima volcano's plume by remote FT-IR observation

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Remote FT-IR measurements of volcanic plume of Mt. Iwodake, Satsuma-Iwojima volcano, Japan, were carried out in October 1996 to understand plume chemistry of the volcano, especially characteristics of fluorine-bearing species in the plume. The SO<sub>2</sub>/HCl molar ratio in the plume was about 4, that is larger than the ratio in high-temperature gases. The high content of SO<sub>2</sub> is suggested to be caused by sulfur combustion in the crater. An average SiF<sub>4</sub>/HF molar ratio of 0.57 was observed for the plume, which is about one order of magnitude higher than the previously reported ratio. The result shows that SiF<sub>4</sub> is an important species and has similar to even larger contribution for fluorine output from Satsuma-Iwojima volcano than HF. The SiF<sub>4</sub> flux of Satsuma-Iwojima volcano is about 13 t/d, that is the largest SiF<sub>4</sub> flux from volcanoes in the world. The observed SiF<sub>4</sub>/HF ratio cannot be explained only by the high-temperature fumarolic composition of the volcano according to the thermodynamic calculations. The ratio can be explained if contribution of F-rich low-temperature fumaroles to the total gas flux of the volcano is as high as 40%.

## 1. Introduction

Remote infrared absorption spectroscopic measurements revealed that SiF<sub>4</sub> exists in volcanic plumes of Vulcano and Mt. Etna (Francis *et al.*, 1996), although HF is the only F-bearing molecular species that had been reported in chemical analyses of fumarolic gases (e.g., Ozawa, 1966; Giggenbach and Goguel, 1989). The existence of SiF<sub>4</sub> in volcanic gases had been suggested only by thermodynamic calculations in volcanic gas studies (Rosenberg, 1973; Symonds *et al.*, 1992, 1994; White and Hochella, 1992). To determine the fluorine content, volcanic gases discharged from a fumarolic vent are usually absorbed into an alkaline solution in the field, and then analyzed in the laboratory by wet chemical techniques, such as Ion-Specific electrodes (Giggenbach, 1975; Giggenbach and Goguel, 1989) or spectrophotometry (Ozawa, 1966). These techniques measure fluoride in the solution, and the obtained values are reported conventionally as HF. In alkaline solutions, both HF and SiF<sub>4</sub>, which were in volcanic gas, are hydrolyzed to fluoride by decomposition of fluorosilicic ion (Lange, 1950; Colton, 1958). Therefore, distinction between HF and SiF<sub>4</sub> in these samples is impossible. Since analytical procedure of SiF<sub>4</sub> in volcanic gases is not established yet, the remote FT-IR measurement is the only available method to distinctively analyze both SiF<sub>4</sub> and HF in volcanic gases.

The infrared spectroscopic technique for remote and open-path measurements of volcanic gas chemistry has recently been used at nearly a dozen volcanoes. So far seven species, SO<sub>2</sub>, HCl, SiF<sub>4</sub>, CO, COS, HF and CO<sub>2</sub>, in volcanic gases were measured by this technique (Mori *et al.*,

1993, 1995; Mori and Notsu, 1997; Francis *et al.*, 1996, 1998; Love *et al.*, 1998; Oppenheimer *et al.*, 1998). The techniques for field measurements are well documented in Oppenheimer *et al.* (1998). Since the amount of SiF<sub>4</sub> in volcanic gases is considered to be very low based on thermodynamic calculations (Rosenberg, 1973; Symonds *et al.*, 1992, 1994), high sensitivity of the remote FT-IR measurements to the chemical species is one of the great advantages (Francis *et al.*, 1996). Until present, the measurements of SiF<sub>4</sub> and HF in volcanic gases are very few, and the chemical nature of F-bearing species in volcanic gases is not well understood. In order to detect both HF and SiF<sub>4</sub> by this remote technique and to understand the fluorine chemistry of the volcanic plume, a field campaign was performed at Satsuma-Iwojima volcano, Japan, where relatively high HF concentration in volcanic gases is reported by previous investigations (e.g., Yoshida *et al.*, 1966; Matsuo *et al.*, 1974; Shinohara *et al.*, 1993).

## 2. Measurements at Satsuma-Iwojima Volcano, Japan

Satsuma-Iwojima is a small volcanic island (12 km<sup>2</sup>) about 50 km south of Kyushu Island, Japan (Fig. 1). The island is a part of submerged rim of the Kikai Caldera. It has two volcanoes, Mt. Inamuradake and Mt. Iwodake (Fig. 1(a)). Mt. Inamuradake is a basaltic cone, 236 m high with no fumarolic activity. Mt. Iwodake is a rhyolitic dome, 704 m high with fumarolic activity centered at the summit crater. It last erupted about 1200 years ago (Ono *et al.*, 1982) and has probably been intensely degassing since then (Kamada, 1964). An interesting feature of the fumarolic activity at Mt. Iwodake is the high temperature over 880°C (Shinohara *et al.*, 1993). The chemical and isotopic compositions and fluxes of Satsuma-Iwojima's fumarolic gases

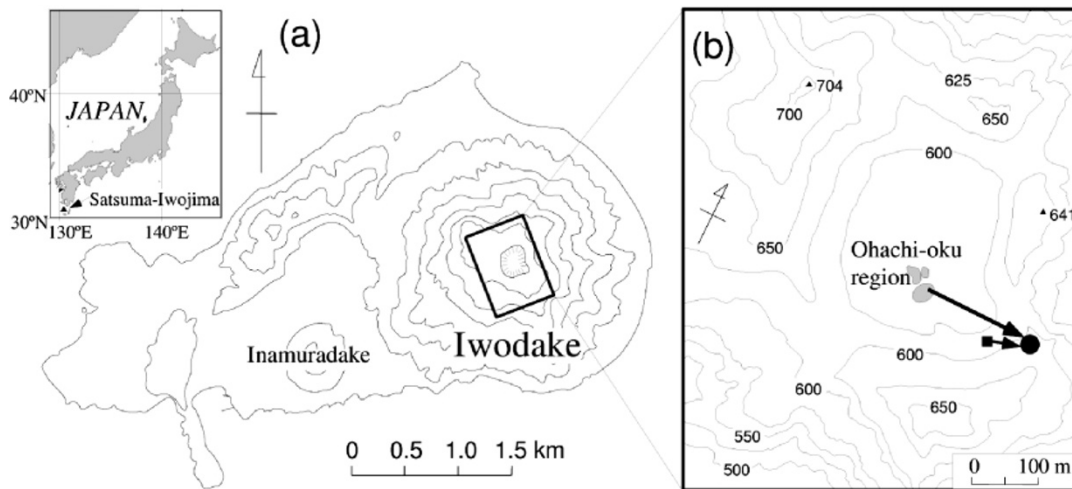


Fig. 1. (a) A map of Satsuma-Iwojima Island and a map of Japan showing location of the island (solid triangle). The contours of the map are at 100 m intervals. The fumarolic activity in this island is mainly concentrated in the summit crater of Iwodake. The box at the summit of Iwodake indicates the area shown in (b). (b) A map of Mt. Iwodake summit. The observation point is on the eastern rim of the crater (solid circle) and target fumarolic area is one of the crater-like structures in the Ohachi-oku region. The shaded areas correspond to crater-like structures. The artificial light source was set on the crater rim about 50 m from the instrument (solid square). The arrows show the optical paths of the measurements.

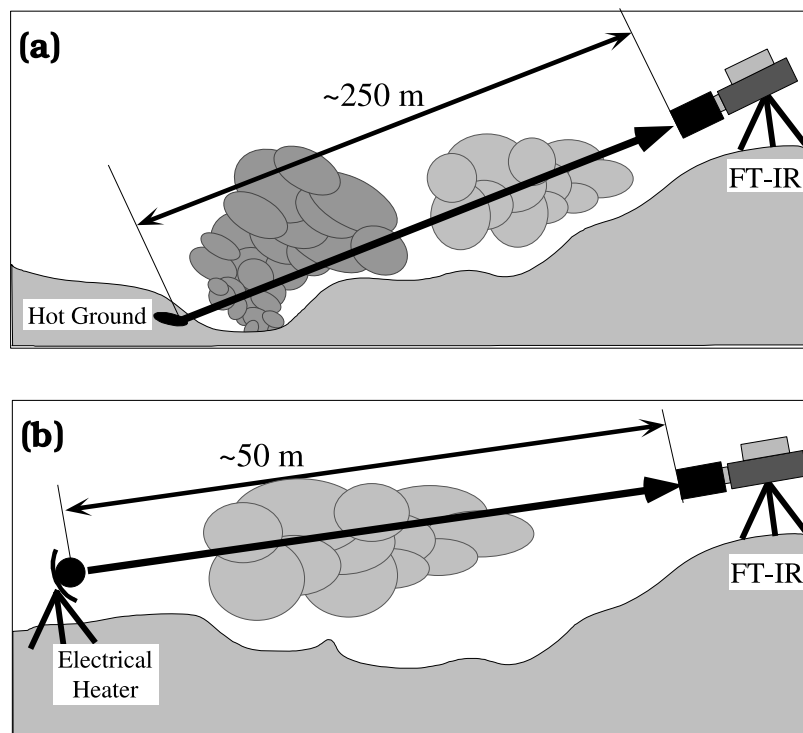


Fig. 2. Arrangement of FT-IR instrument and the light source for the OHO (a) and the ALS (b) measurements.

and hot spring waters have been studied by many researchers (Iwasaki *et al.*, 1962; Kamada, 1964; Matsuo *et al.*, 1974; Shinohara *et al.*, 1993; Hedenquist *et al.*, 1994).

The measurements at Satsuma-Iwojima were carried out on October 16, 1996. A telescope-attached FT-IR instrument, which has a spectral resolution of  $1 \text{ cm}^{-1}$ , was placed on the eastern crater rim of Mt. Iwodake (Fig. 1(b)). On the day of observation, the weather was clear and the wind was blowing from the north. At the time of our field cam-

paign, high-temperature fumaroles of Mt. Iwodake were located mainly in the Ohachi-oku area (Fig. 1(b)) but also at some other places inside and outside of the crater of the Mt. Iwodake cone. There were three small crater-like structures 20–30 m in diameter and 5–10 m in depth in the Ohachi-oku area. Low-temperature fumaroles were found surrounding the high-temperature areas and near the crater wall. As an evidence of the high-temperature emissions, some incandescent areas were observed from the crater rim

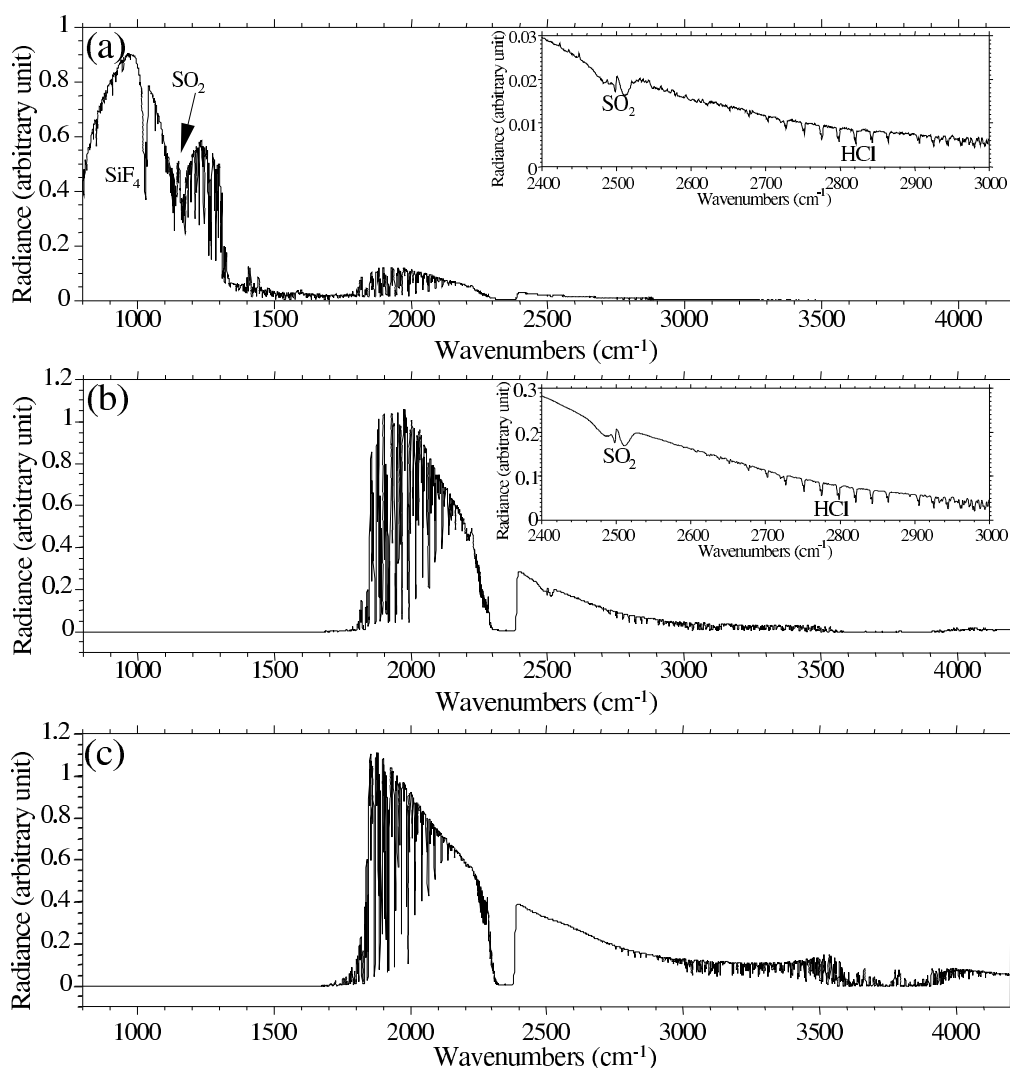


Fig. 3. Typical spectra observed at Mt. Iwodake, Satsuma-Iwojima volcano. The a) and b) are spectra observed by the OHO measurements with the MCT and the InSb detectors, respectively. Insets on the upper right are magnified spectra between 2400 and 3000  $\text{cm}^{-1}$ . The c) is the spectrum observed by the ALS measurements with the InSb detector.

in the nighttime at several locations inside and outside of the summit crater, including the Ohachi-oku fumaroles.

The measurements used hot ground surface at the bottom of one of the crater-like structures in the Ohachi-oku region as the infrared light source (Figs. 1(b) and 2(a)) as in previous studies performed at Vulcano and Aso volcanoes (Mori *et al.*, 1995; Mori and Notsu, 1997). The distance between the light source and the instrument was about 250 m. We also used an artificial infrared light source (a small electrical heater). The light source was placed about 50 m to the WSW of the instrument (Figs. 1(b) and 2(b)). During the Ohachi-oku (OHO) measurements with the natural light source, 17 spectra were obtained with an indium-antimonide (InSb) detector and 18 spectra were obtained with a mercury-cadmium-telluride (MCT) detector. During the artificial light source (ALS) measurements, 19 spectra were measured with the InSb detector. The InSb and MCT detectors are sensitive in the wavenumber ranges of 1800–4500  $\text{cm}^{-1}$  and 800–3000  $\text{cm}^{-1}$ , respectively. The MCT detector was used to measure the absorption of SiF<sub>4</sub>, which is centered at 1032  $\text{cm}^{-1}$ . The InSb detector was used to

measure the absorption of HF, centered around 3960  $\text{cm}^{-1}$ .

### 3. Results

Figure 3 shows typical spectra collected at Satsuma-Iwojima. In the spectra obtained by the OHO measurements with the MCT and InSb detectors (Figs. 3(a) and (b)), the absorption features of SO<sub>2</sub> ( $\nu_1 + \nu_3$  combinational band) and HCl (P-branch) are seen clearly in the wavenumber ranges of 2460–2540  $\text{cm}^{-1}$  and 2700–3000  $\text{cm}^{-1}$ , respectively. The absorption features of SiF<sub>4</sub> centered at 1032  $\text{cm}^{-1}$  and SO<sub>2</sub> ( $\nu_1$  band) at 1100–1200  $\text{cm}^{-1}$  are also identified clearly in the spectrum measured with the MCT detector (Fig. 3(a)). Figure 3(c) is the observed spectra with the ALS measurements, which also shows slight absorption of HCl and SO<sub>2</sub>.

Figure 4 shows a typical observed absorbance spectrum between 950 and 1250  $\text{cm}^{-1}$  with the MCT detector. It may be compared with figure 1 of Francis *et al.* (1996), which was obtained at Vulcano, Italy. The observed absorbance spectrum clearly shows absorption features of SO<sub>2</sub> ( $\nu_1$  band) and SiF<sub>4</sub>. In the spectra collected with both MCT and InSb detectors, the presence of absorption features due to COS,

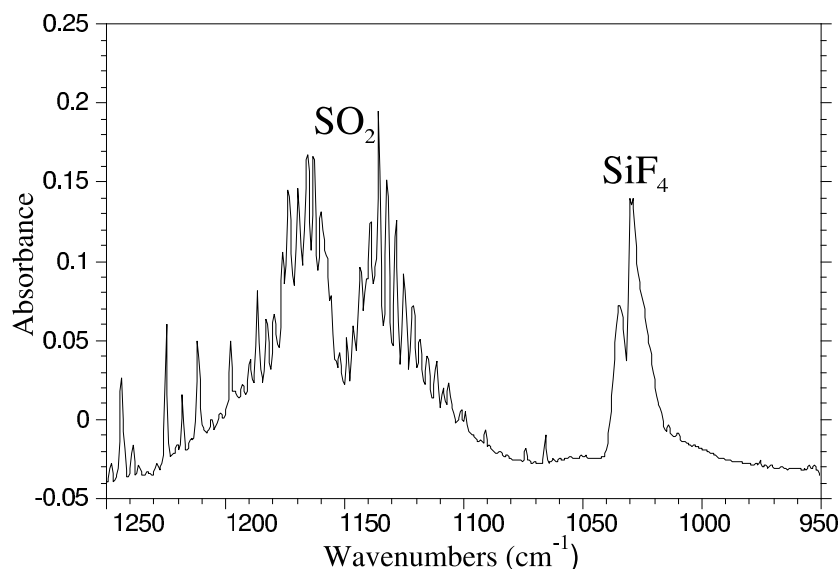


Fig. 4. A typical observed absorbance spectrum at Satsuma-Iwojima volcano with the MCT. The absorption features of SO<sub>2</sub> and SiF<sub>4</sub> appear very clearly, as labeled.

Table 1. Molar ratios of the chemical components of volcanic plume of Mt. Iwodake obtained by remote FT-IR measurements.

Detector	Type* <sup>1</sup>	HCl/SiF <sub>4</sub>	SO <sub>2</sub> /SiF <sub>4</sub>	SO <sub>2</sub> /HCl	SO <sub>2</sub> (ν <sub>1</sub> )/SO <sub>2</sub> (ν <sub>1</sub> + ν <sub>3</sub> )	HF/HCl	SiF <sub>4</sub> /HF* <sup>2</sup>
MCT	OHO	16	71	4.2	1.05	n.a.	5.7 × 10 <sup>-1</sup>
InSb	OHO	n.a.	n.a.	4.0	n.a.	0.11	
InSb	ALS	n.a.	n.a.	1.7	n.a.	8 × 10 <sup>-2</sup>	n.a.

\*<sup>1</sup>OHO and ALS correspond to “Ohachi-oku” and “artificial light source” measurements. See text.

\*<sup>2</sup>Calculated using HCl/SiF<sub>4</sub> and HF/HCl ratios obtained by MCT and InSb detectors, respectively.

n.a.: not analyzed.

CO<sub>2</sub> and CO were searched. However, no absorption features of these species could be identified in the spectra after subtracting the interference from atmospheric CO<sub>2</sub> and water vapor.

To obtain the column amounts of volcanic gas species, the following wavenumber ranges containing absorption bands of the following gases were used: 950–1250 cm<sup>-1</sup> for SiF<sub>4</sub>, SO<sub>2</sub> (ν<sub>1</sub> band), and 2400–2920 cm<sup>-1</sup> for SO<sub>2</sub> (ν<sub>1</sub> + ν<sub>3</sub> band) and HCl (P-branch). The absorbance spectra were obtained by considering a simple background spectrum for each wavenumber range of the observed spectrum. The model absorbance spectrum was then calculated using the standard spectrum of SO<sub>2</sub>, HCl, SiF<sub>4</sub>, H<sub>2</sub>O and the zero level offset of the absorbance spectrum. Then the column amounts of volcanic gases were obtained for each wavenumber ranges using a linear least squares fitting procedure between the observed and model absorbance spectra. Table 1 shows the average molar ratios of HCl/SiF<sub>4</sub>, SO<sub>2</sub>/SiF<sub>4</sub>, SO<sub>2</sub>/HCl and SO<sub>2</sub>(ν<sub>1</sub>)/SO<sub>2</sub>(ν<sub>1</sub> + ν<sub>3</sub>) obtained by the FT-IR measurements. The column amounts of SO<sub>2</sub> estimated from different bands (ν<sub>1</sub> and ν<sub>1</sub> + ν<sub>3</sub> bands) agree well without any significant systematic difference. The corresponding errors at the 95% confidence level are about ±25% for the ratios of HCl/SiF<sub>4</sub>, SO<sub>2</sub>/SiF<sub>4</sub>, SO<sub>2</sub>/HCl and SO<sub>2</sub>(ν<sub>1</sub>)/SO<sub>2</sub>(ν<sub>1</sub> + ν<sub>3</sub>).

Since the interference of atmospheric vapor is quite significant at around the HF absorption wavenumber range, the

observed spectrum that is least influenced by volcanic gas was used as the background spectrum for the case of HF quantification. In the absorbance spectrum of the ALS measurements between 3950 and 4250 cm<sup>-1</sup>, the spectral feature of the HF is clearly identifiable when compared with a reference spectrum of HF (Fig. 5(a)). The absorption feature of HF in the absorbance spectrum of the OHO measurements is also identifiable (Fig. 5(b)), although the noise level is larger in this case due to the lower temperature of the light source. The spectral analyses of HF was done by interactively subtracting the HF standard spectrum from the observed absorbance spectra until the peaks of HF disappeared in the noise. The quantitative analyses of HCl in the same absorbance spectra were done by a linear least squares fitting to calculate HF/HCl ratios. The molar HF/HCl ratios are 0.08 and 0.11 for the ALS and the OHO measurements, respectively (Table 1). The corresponding errors at the 95% confidence level are estimated to be ±35% and ±40% of the HF/HCl molar ratios obtained by the ALS and OHO measurements, respectively (Table 1).

In the present study, molar HCl/SiF<sub>4</sub> and HCl/HF ratios were separately measured with the MCT and InSb detectors, in less than two hour intervals and these ratios were used to calculate the SiF<sub>4</sub>/HF ratio. The average SiF<sub>4</sub>/HF molar ratio in the plume of Satsuma-Iwojima is obtained as 0.57 using the OHO results with the uncertainty of about

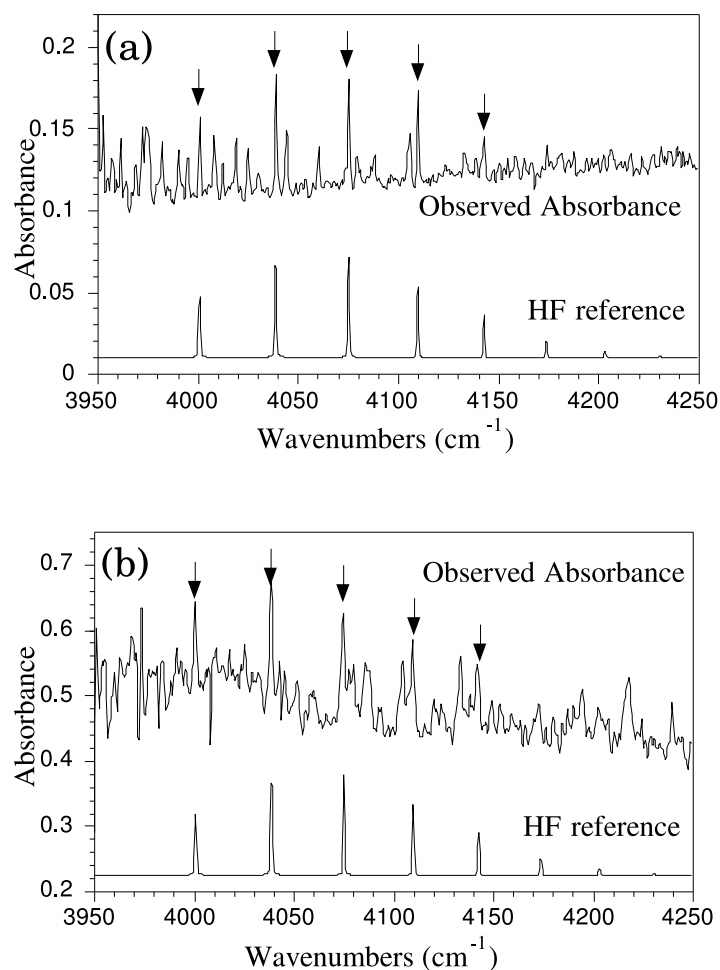


Fig. 5. (a) A typical absorbance spectrum of the ALS measurements between 3950 and 4250  $\text{cm}^{-1}$ . A reference spectrum of HF is shown at the bottom. (b) A typical absorbance spectrum of the OHO measurements in the same wavenumber range. Arrows in the figures indicate locations of the peaks of HF at the observed absorbance.

Table 2. SiF<sub>4</sub> flux from volcanoes.

Volcano	Date for SO <sub>2</sub> /SiF <sub>4</sub> measurements	SO <sub>2</sub> /SiF <sub>4</sub> * <sup>1</sup> molar ratio	SO <sub>2</sub> flux* <sup>2</sup> ton/day	SiF <sub>4</sub> flux ton/day
Satsuma-Iwojima	1996.10.16	71	560±200	13±5
Aso	1996.07 and 1997.05	>3 × 10 <sup>3</sup>	<100	<0.05
Vulcano	1994.09	1.7 × 10 <sup>2</sup>	40±15	0.38±0.14
Etna	1994.09	2.7 × 10 <sup>3</sup>	5600±2500	3.3±1.5
Popocatépetl	1997.02.21–1997.02.24	4.2 × 10 <sup>2</sup> –9.6 × 10 <sup>2</sup>	2000–4100	4.6–7.3
Popocatépetl* <sup>3</sup>	1997.02.26	91–9.6 × 10 <sup>2</sup>	4000–60000	7–1080

\*<sup>1</sup>SO<sub>2</sub>/SiF<sub>4</sub> molar ratios (Satsuma Iwojima, this study; Aso, Unpublished data; Vulcano and Etna, Francis *et al.* (1996); Popocatépetl, Love *et al.* (1998)).

\*<sup>2</sup>The SO<sub>2</sub> fluxes are measured by COSPEC (Satsuma-Iwojima, Shinohara *et al.* (2002) and Shinohara (Personal Communication); Aso, Ohta *et al.* (1988); Vulcano, Allard *et al.* (1993); Etna, Caltabiano *et al.* (1994); Popocatépetl, Love *et al.* (1998)).

\*<sup>3</sup>Series of measurements on Feb. 26, 1997, were carried out immediately after the explosive ash event (Love *et al.* (1998)).

±50% at the 95% confidence level. This value is more than one order of magnitude larger than the molar SiF<sub>4</sub>/HF ratio of  $3.4 \times 10^{-2}$  at Popocatépetl volcano, Mexico (Love *et al.*, 1998; Table 2). The estimated SiF<sub>4</sub>/HF ratio indicates that, contrary to conventional knowledge, SiF<sub>4</sub> is not a minor F-bearing molecular species in some volcanic plumes.

Considering the number of fluorine atoms in SiF<sub>4</sub>, the role of SiF<sub>4</sub> in transporting fluorine into the atmosphere is about twice larger than that of HF at Satsuma-Iwojima volcano. Our result indicates the potential importance of SiF<sub>4</sub> as a fluorine-species in volcanic plumes.

#### 4. The SO<sub>2</sub>/HCl Ratio in the Plume

The average SO<sub>2</sub>/HCl ratios obtained by the ALS and the OHO measurements show more than two fold differences, which are 1.7 and 4.0, respectively. Both ratios are in the range of 0.5 to 5.7 obtained by the conventional gas analyses for each fumaroles, reported by Shinohara *et al.* (1993). The SO<sub>2</sub>/HCl ratios of fumarolic gases analyzed for 1996 sample range between 0.9 and 2.2 for various temperature fumaroles (Shinohara, personal communication). These values are closer to the results from the ALS measurements. According to Shinohara *et al.* (1993), SO<sub>2</sub>/HCl ratio of the common parental gas of the volcano is approximately 1.5.

The plume observed by the ALS measurements originates mainly from fumaroles on the eastern crater wall. In contrast, the plume observed by the OHO measurements are the mixture of gases from fumaroles on the eastern wall and inside the crater. For this plume, the major gas contributions are probably from high-temperature fumaroles of the Ohachi-oku area. This high SO<sub>2</sub>/HCl ratio may be explained by following: (1) Distribution of high SO<sub>2</sub>/HCl (>4) fumaroles in the Ohachi-oku area. (2) Depletion of HCl in the plume during transportation. (3) Addition of SO<sub>2</sub> from burning sulfur crust. The high-temperature fumaroles in the Ohachi-oku area have molar SO<sub>2</sub>/HCl ratio of less than 2.2 in 1996 (Shinohara *et al.*, 2002). We do not have any evidence of high SO<sub>2</sub>/HCl fumaroles with a large flux in 1996. Hydrogen chloride in the plume is usually considered to be more easily absorbed into the mists of the plume compared to SO<sub>2</sub>. This depletion of HCl increases the ratio significantly. The chemical analysis of the plume gas sampled at the crater rim shows slightly lower Cl/S ratio compared to that of the fumaroles, which was explained by the depletion of HCl in the plume (Shinohara and Ohba, 1997). Therefore, we suppose the HCl depletion cannot be the main reason for the two-fold difference.

Sulfur combustion in the atmosphere producing SO<sub>2</sub> can be another reason for the high ratio. At some areas in the crater bottom of Mt. Iwodake, we found 15 to 20 cm thick sulfur crusts covering the area, including the Ohachi-oku area. In those places, we saw molten sulfur flow and also sulfur combustion around high-temperature areas. Such a combustion of a sulfur flow, which produced 2.4 t of SO<sub>2</sub> during a 4-hr-long event, has been documented at Vulcano volcano, Italy (Harris *et al.*, 2000). They also suggest that typical sulfur flow combustion at Vulcano volcano would generate SO<sub>2</sub> flux of 0.6–44 t/hr (Harris *et al.*, 2000). Shinohara *et al.* (2002) report that the crater floor of Mt. Iwodake was heated up in the mid-1990's, and large area of the crater floor became altered zone whose temperature exceeded 500°C at 5 cm depth in October 1996. This temperature is above the sulfur combustion temperature (248–261°C) in air at standard pressure (Harris *et al.*, 2000). The sulfur crust existed was probably combusting, producing SO<sub>2</sub> during our observation in October 1996. Therefore, it is likely that SO<sub>2</sub> produced by the sulfur combustion had caused the increase of SO<sub>2</sub>/HCl ratio in the result of the OHO measurements.

#### 5. SiF<sub>4</sub> Flux

Silicon tetrafluoride has been measured at a several volcanoes by the remote FT-IR measurements (Francis *et al.*,

1996; Love *et al.*, 1998). Table 2 shows SO<sub>2</sub>/SiF<sub>4</sub> ratios and SiF<sub>4</sub> fluxes of several volcanoes estimated from SO<sub>2</sub> flux obtained by COSPEC. The fluxes are measured during passive degassing stages, except for the data from Popocatepetl on Feb. 26, 1997, which was obtained after an ash explosion. The maximum SiF<sub>4</sub> flux of 1080 t/d was recorded soon after the ash explosion at Popocatepetl, but the high flux degassing continued only for a very short period of time (<4 hours). The SiF<sub>4</sub> flux from Satsuma-Iwojima volcano is the largest in the fluxes measured at the five volcanoes during passive degassing. Mt. Etna is known by a huge emission of volcanic gas, whose rates contribute roughly 10%, 30% and 10% of global volcanic fluxes of SO<sub>2</sub>, CO<sub>2</sub> and, HCl (Allard *et al.*, 1991; Williams *et al.*, 1992; Stoiber, 1995; Francis, 1996). The SiF<sub>4</sub> flux from Satsuma-Iwojima is larger than that from Mt. Etna, suggesting that this volcano may be the world's largest source of volcanic SiF<sub>4</sub>.

### 6. Origin of SiF<sub>4</sub> at Satsuma-Iwojima

#### 6.1 Thermodynamic calculations

The thermodynamic calculations of volcanic SiF<sub>4</sub> were made on the basis of chemical equilibrium using following reaction and equation (Rosenberg, 1973; Symonds *et al.*, 1992; White and Hochella, 1992; Symonds and Reed, 1993):



$$\begin{aligned} \log(K(T)) &= \log(P_{\text{H}_2\text{O}}^2 \cdot P_{\text{SiF}_4} \cdot P_{\text{HF}}^{-4} \cdot a_{\text{SiO}_2}^{-1}) \\ &= \log(X_{\text{H}_2\text{O}}^2 \cdot X_{\text{SiF}_4} \cdot X_{\text{HF}}^{-4} \cdot a_{\text{SiO}_2}^{-1}) \\ &\quad - \log(P_t), \end{aligned} \quad (2)$$

where  $K(T)$  is the equilibrium constant for reaction (1) which is a function of temperature,  $T$  in Kelvin. The  $P_i$  and  $X_i$  are partial pressure and mole fraction of gas species  $i$ ,  $a_{\text{SiO}_2}$  is the activity of solid SiO<sub>2</sub>, and  $P_t$  is the total pressures in bar. Variations in the molar HF/SiF<sub>4</sub> ratios with temperature were calculated for given set of partial pressures of HF and H<sub>2</sub>O and total pressure, with an assumption of a silica activity of unity (Rosenberg, 1973; White and Hochella, 1992).

An average logarithmic HF mole fraction in high-temperature volcanic gases (>400°C) is about -3.6 at Satsuma-Iwojima (Kamada, 1964; Matsuo *et al.*, 1974; Shinohara *et al.*, 1993). At this volcano, some low-temperature fumaroles (about 100°C) are rich in HF with an average logarithmic HF mole fraction of about -2.6 (Kamada, 1964; Yoshida *et al.*, 1966). Since these reported mole fractions of HF are obtained by conventional chemical analyses, these values can be considered as the mole fractions of total fluorine ( $X_{\text{Ftotal}}$ ) in the volcanic gas. In order to evaluate possible range of the SiF<sub>4</sub>/HF ratio, we considered the following two extreme cases: (1) High-temperature fumaroles (>400°C) with  $\log X_{\text{Ftotal}} = -3.52$  (the parent gas value in Shinohara *et al.*, 1993); (2) Low-temperature F-rich fumaroles with  $\log X_{\text{Ftotal}} = -2.60$ . For these two  $\log X_{\text{Ftotal}}$  values, the variation in the molar SiF<sub>4</sub>/HF ratios with temperature were calculated assuming chemical equilibrium of reaction (1), logarithm of H<sub>2</sub>O mole fraction of -0.011, a

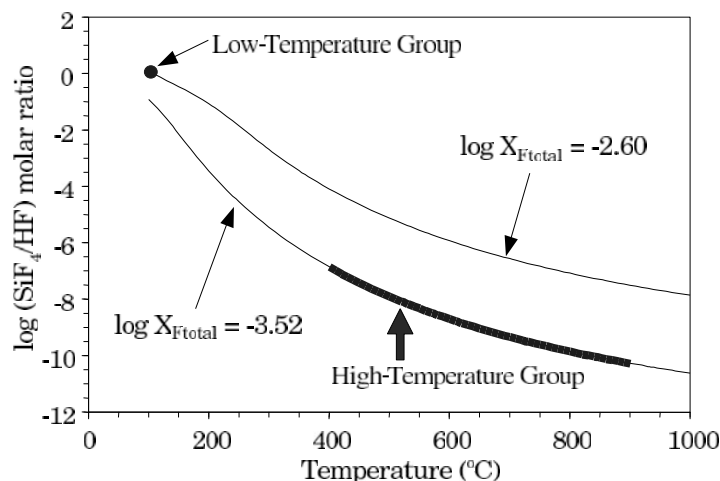


Fig. 6. Variation of molar SiF<sub>4</sub>/HF ratio with temperature for log  $X_{Ftotal}$  values of  $-2.60$  and  $-3.52$ . The variations are calculated based on chemical equilibrium of the reaction (1). A solid circle and a bold line on the curves show low- and high-temperature fumarolic gas groups, respectively.

silica activity of unity and a total pressure of 1 bar. The equilibrium constant for an amorphous silica as a function of temperature for Eq. (2) was obtained from an equation in Symonds and Reed (1993), that was calculated based on the thermodynamic data of Pankratz (1982) and Berman (1988).

In the previous studies, the partial pressure of HF was fixed to the observed partial pressure of HF in volcanic gases (Rosenberg, 1973; White and Hochella, 1992). This causes unrealistically high total fluorine amount in their calculations when temperature is low and the SiF<sub>4</sub>/HF ratio becomes more than unity. In order to keep total fluorine amount in reasonable range, the partial pressure of total fluorine was fixed to satisfy the following equation:

$$4 \times X_{SiF_4} + X_{HF} = X_{Ftotal}, \quad (3)$$

where  $X_{SiF_4}$  and  $X_{HF}$  are mole fractions of SiF<sub>4</sub> and HF, respectively.

Figure 6 shows the variation of molar SiF<sub>4</sub>/HF ratio with temperature for log  $X_{Ftotal}$  values of  $-2.60$  and  $-3.52$  at pressure of 1 bar. By increasing the pressure by one order of magnitude, log(SiF<sub>4</sub>/HF) ratio will increase by 1 at 400°C. At temperature below 400°C, this pressure effect becomes smaller. Figure 6 indicates that SiF<sub>4</sub>/HF ratio is less than  $2 \times 10^{-7}$  for the high-temperature group ( $>400^\circ\text{C}$ , log  $X_{Ftotal} = -3.52$ ), and SiF<sub>4</sub> can be considered as a negligible F-bearing molecular species in the volcanic gas. In contrast, molar SiF<sub>4</sub>/HF ratio of low-temperature gases (about 100°C, log  $X_{Ftotal} = -2.60$ ) is larger than unity and SiF<sub>4</sub> is the major F-bearing molecular species in those fumarolic gases. The graph also implies that it is impossible to form the SiF<sub>4</sub>/HF ratio of 0.57 with log  $X_{Ftotal} = -3.52$ , even if the temperature is as low as 100°C. In order to explain SiF<sub>4</sub>/HF ratio of 0.57, it is necessary to consider contribution of the F-rich low-temperature fumarolic gases to the plume of Satsuma-Iwojima.

Many polymorphs of silica such as tridymite, quartz and cristobalite are also found other than amorphous silica, at the summit area of Mt. Iwodake (Yoshida *et al.*, 1966; Matsubaya *et al.*, 1975). The above calculations were also performed to each polymorphs of silica, using respective

equilibrium constant equation given by Symonds and Reed (1993). The difference of silica species, however, did not alter significantly the calculated SiF<sub>4</sub>/HF ratio.

## 6.2 Contribution of F-rich low-temperature fumaroles

Using the results of FT-IR measurements and the thermodynamic calculations above, contribution of F-rich low-temperature fumaroles to total gas flux of Satsuma-Iwojima volcano can be estimated with following assumptions: 1) All the fumarolic gas of Satsuma-Iwojima is divided into the two groups, that is the low-temperature and high-temperature gases, 2) The SiF<sub>4</sub>/HF ratio and HF mole fraction in the low-T gases are 1.2 and  $2.5 \times 10^{-3}$ , respectively, and those in the high-T gases are 0 and  $3.0 \times 10^{-4}$ , respectively (Fig. 6), 3) The molar SiF<sub>4</sub>/HF ratios in Satsuma-Iwojima's volcanic plume is 0.57, as observed by the remote FT-IR measurements (Table 1). The molar ratio of SiF<sub>4</sub>/HF in the plume can be expressed in terms of total gas fluxes from high-temperature ( $F_H$ ) and low-temperature ( $F_L$ ) groups:

$$\begin{aligned} X_{SiF_4}/X_{HF} &= X_{SiF_4}^L \times F_L / (X_{HF}^L \times F_L + X_{HF}^H \times F_H) \\ &= 0.57, \end{aligned} \quad (4)$$

where superscripts *L* and *H* indicate low- and high-temperature gases. The  $F_L/F_H$  is calculated to be 0.63, which means that the contribution of gas flux from the low-temperature group is about 40% of the total gas flux from the volcano. The contributions of the low-temperature fumaroles were also calculated considering tridymite, cristobalite and quartz as silica-species. The calculated contributions of the low-temperature group for tridymite and cristobalite are essentially as same as the result with amorphous silica. In the case of quartz, the contribution is calculated to be about 30%, which still shows that the F-rich low-temperature fumaroles largely contribute to Mt. Iwodake's plume. The results of the above calculations are consistent with the result by Shinohara and Ohba (1997), who suggested important contributions of low-temperature fumarolic gases to the plume based on the H<sub>2</sub>S/SO<sub>2</sub> ratios in the plume gas collected at the crater rim, although they did not report a quantitative estimate of the contribution.

## 7. Conclusions

Sulfur dioxide, HCl, SiF<sub>4</sub> and HF were detected in the volcanic plume of Mt. Iwodake, Satsuma-Iwojima volcano, Japan, using remote infrared absorption spectroscopy. The SO<sub>2</sub>/HCl in the plume was higher than high-temperature volcanic gases. The higher ratio may be caused by sulfur combustion in the crater of Mt. Iwodake. The observed molar SiF<sub>4</sub>/HF ratio in the plume was 0.57, which is much higher than previously reported values. This high ratio requires contribution of F-rich low-temperature fumaroles as high as 40% to the total gas flux of the volcano.

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