

Temporal variation in chemical composition of the volcanic plume from Aso volcano, Japan, measured by remote FT-IR spectroscopy

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Remote measurements of chemical compositions of the Aso volcanic plume using an FT-IR spectral radiometer were carried out at the 1st crater of Mt. Nakadake, Aso volcano, Japan, for six times from 1996 to 2003. We have succeeded in detecting 6 volcanic gas species (SO_2 , HCl, HF, CO, CO_2 , COS) using the InSb detector. The equilibrium temperatures estimated from observed CO/ CO_2 ratios have remained high at more than 700°C during the observation period. However, the temporal variation of the ratios between volcanic gas components showed significant scrubbing of HCl compared to other species by hydrothermal interaction in 1998. From the visual and FT-IR observations, we presume that SO_2 flux from the volcano was lower in 1998 than in other years. This decrease in flux was not due to hydrothermal scrubbing of SO_2 but was due to decrease in a total supply rate of gas from depth. This assumption is supported by relatively stable CO_2/SO_2 ratio which is probably reflecting stable gas chemistry at the gas source.

Keywords: volcanic gas, hydrothermal interaction, crater lake, remote FT-IR spectroscopy, Aso volcano

INTRODUCTION

Remote measurements of volcanic gas chemistry using Fourier Transform Infrared spectrometers have been reported for many volcanoes since the early 1990s (Mori *et al.*, 1993; Francis *et al.*, 1995; Oppenheimer *et al.*, 1998). One of the great advantages of the remote FT-IR measurements is chemical monitoring of volcanic gas emitting from inaccessible craters or fumaroles due to safety concerns (Mori and Notsu, 1997; Love *et al.*, 1998). So far, eight volcanic gas species, SO_2 , HCl, HF, CO, SiF_4 , CO_2 , COS and H_2O have been measured with infrared absorption spectroscopy. In last 15 years, this method has been proved to be a promising and useful technique for monitoring of volcanic activities (Duffell *et al.*, 2003; Allard *et al.*, 2005).

Aso volcano, in the central part of Kyushu Island, Japan, is an active volcano with a huge caldera (E–W: 18 km, N–S: 24 km) and has some post caldera cones in the center. Mt. Nakadake is one of the cones, and has a group of craters at its summit. The northern most crater of Mt. Nakadake, named the 1st crater, has been very active, and many eruptions emitting ash and scoria were recorded in last 30 years (JMA, 2005). Recently, only three small scaled eruptions were reported in 1994, 1995 and 2003, and scarce mud and water ejection have been observed

between 1993 and 2003 (JMA, 2005). Since March 1993, bottom part of the 1st crater, of Mt. Nakadake has been filled with hot water as a crater-lake. Compared to 1980s and early 1990s, activity of Mt. Nakadake between 1996 and 2003 had been very quiet.

The summit area of Mt. Nakadake is a touristic area. It is easily accessible by ropeway, car and on foot. An overlook area for tourists is restricted to the southwestern rim of the 2nd crater which is several hundred meters south from the crater rim of the 1st crater (Fig. 1).

The 1st crater of Mt. Nakadake has been filled with water of high acidity with grayish to pale green surface. The pH of the lake water in 2000 was 0.81 (Onda *et al.*, 2003). At the southern wall of the 1st crater near to this crater-lake's surface, fumarolic activity has been continuously observed. This fumarolic area of Mt. Nakadake is surrounded by the lake and steep crater wall and is about 150 m below the crater rim. Thus, the area is inaccessible and there is little gas geochemical information on the volcanic gas of Mt. Nakadake. The surface of this fumarolic area sometimes shows incandescence at night. Between 1996 and 2003, incandescence was observed during two periods, April 1996–June 1996 (JMA, 2005) and November 2000–December 2003 (JMA, 2005). This is one of the evidences for high temperature gas emission at Mt. Nakadake. Mori and Notsu (1997) reported the first FT-IR measurements of Mt. Nakadake, detecting 5 volcanic gas species, SO_2 , HCl, CO_2 , CO and COS, and estimated temperature at depth to be $750 \pm 120^\circ\text{C}$ based on CO/ CO_2 ratios. Ono *et al.* (1999) also reported gas chem-

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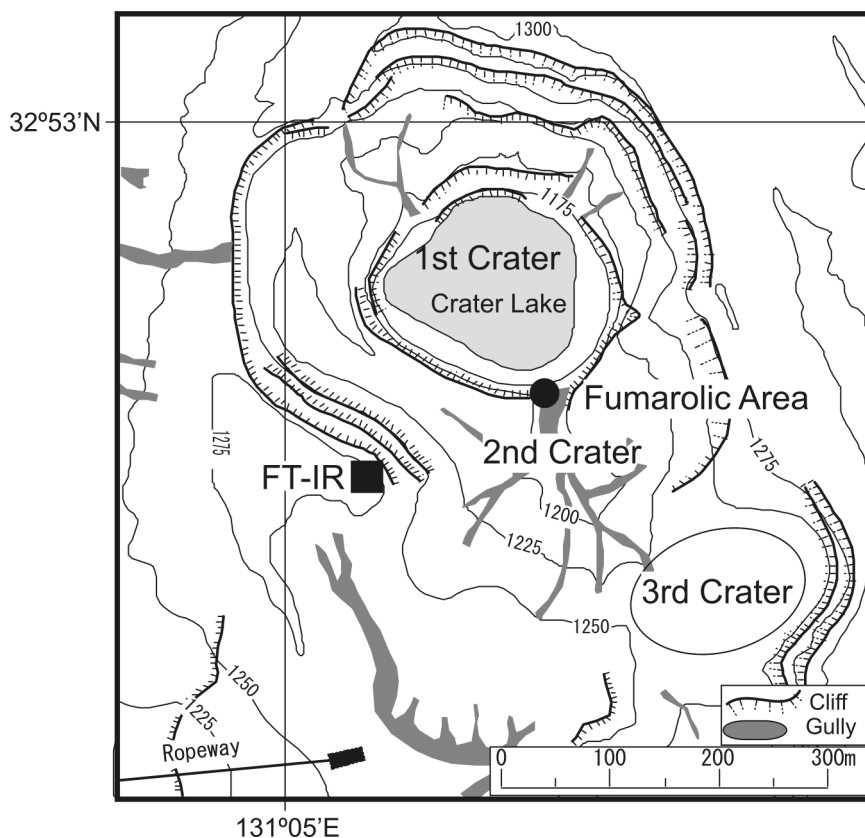


Fig. 1. A map of summit area of Mt. Nakadake, Aso volcano, showing 1st, 2nd and 3rd craters. The solid square shows the location of the FT-IR instrument. The solid circle on the southern part of the crater lake shows the location of the fumarolic area.

istry of Mt. Nakadake observed by remote FT-IR measurements

In this paper, we present chemical data of the plume emitted from Mt. Nakadake, Aso volcano, Japan. We are presenting the data of five newly carried out remote FT-IR surveys between 1997 and 2003 as well as the data of the 1996 survey (Mori and Notsu, 1997). From the changes in observed chemical composition of the plume during 1996–2003, we will discuss the volcanic gas system of Mt. Nakadake, Aso volcano, and its relationship to hydrothermal interaction.

MEASUREMENTS

Between 1996 and 2003, 6 field surveys of remote FT-IR measurements were carried out in; July 1996, May 1997, November 1998, May 2001, March 2002 and October 2003. Infrared spectra were collected with a BOMEM brand Fourier Transform Infrared Spectral Radiometer (MB-100 Series) attached with a Cassegranian telescope (about 30 cm in diameter). An indium antimonide detector (InSb detector) which has sensitivity between 1800 cm^{-1} and 4500 cm^{-1} was used in the meas-

urements. All the spectra retrieval was carried out with a nominal spectral resolution of 1 cm^{-1} . The spectrometer was positioned on the southwestern rim of the 1st crater of Mt. Nakadake, where the fumarolic area on the southern wall is clearly observed (solid square in Figs. 1 and 2). The horizontal and vertical distances between the observation site and the fumarolic area were about 200 m and 150 m, respectively (Mori and Notsu, 1997). The diameter of the view observed by the instrument at the fumarolic area is about 1.3 m. The field configuration of the instrument, volcanic plume and light source (Fig. 2) is same as in previous studies carried out at Aso and Satsuma-Iwojima volcanoes. We used heat of the fumarolic area as an infrared light source (Mori *et al.*, 1995, 2002; Mori and Notsu, 1997).

The raw spectra were recorded as single-beam infrared spectra. To retrieve column amounts of volcanic gas species, a model spectra were generated with LBLRTM (Line-by-Line Radiation Transfer Model) code (e.g., Clough *et al.*, 1992; Clough and Iacono, 1995) using spectral line parameters from the HITRAN database (Rothman *et al.*, 2003) and other parameters (atmospheric pressure, temperature and optical pathlength). In order to obtain

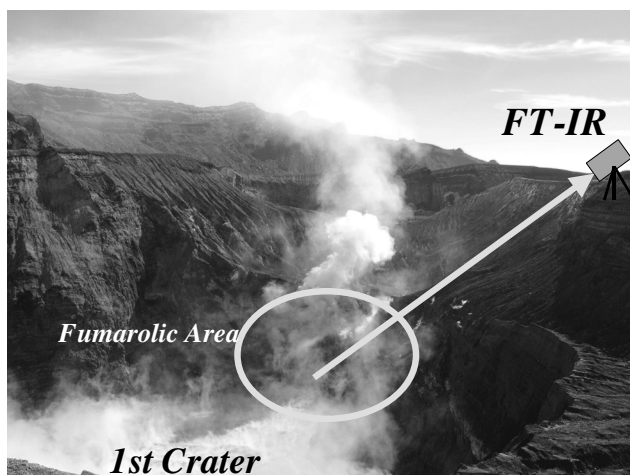


Fig. 2. A photo of the 1st crater and fumarolic area of Mt. Nakadake from the northern crater rim on Nov. 17, 2002. The solid square shows the observation point, and the area inside the circle above the crater-lake indicates the fumarolic area.

optimal column amounts of gas species for a model spectrum, we used nonlinear least-squares algorithm for the following small wavenumber windows of following volcanic gas species; SO_2 ($2420\text{--}2600\text{ cm}^{-1}$), HCl ($2810\text{--}2890\text{ cm}^{-1}$), HF ($4020\text{--}4120\text{ cm}^{-1}$) and CO_2 , CO and COS ($2000\text{--}2140\text{ cm}^{-1}$).

In the 1998 field survey, an apparent volcanic plume from the observation site (Figs. 1 and 2) was very weak compared to those of other field surveys. Some part of the fumarolic area was submerged under the lake water. Both the highest surface temperature of the fumarolic area observed by an infrared thermometer and daily maximum plume height observed by Japan Meteorological Agency (JMA, 2005) were relatively low between the second half of 1998 and the first half of 2000. The maximum daily plume height was usually lower than 200 m during the above period. This height showed gradual increase to average of 500 m from 2001 to 2003. In the eruptive periods, the height often exceeded 1000 m (JMA, 2005). These data support weak fumarolic activity at the time of the 1998 survey.

RESULTS

Figure 3a shows a typical observed single-beam spectrum obtained in the March 2002 field survey. Clear absorption features of SO_2 ($\nu_1 + \nu_3$ band) and HCl (P-branch) are identified in $2420\text{--}2600\text{ cm}^{-1}$ and $2810\text{--}29890\text{ cm}^{-1}$, respectively. Four spectrum windows (Figs. 3b–e) show the observed (dashed lines) and the simulated model (solid lines) spectra for SO_2 (Fig. 3b), HCl (Fig. 3c), CO_2 , CO , and COS (Fig. 3d) and HF (Fig. 3e) analyses, respectively.

Figures 3b–e show that the model spectra calculated for each spectrum windows are in good agreement with the observed spectrum. Most absorption peaks appeared in Figs. 3d and 3e correspond to water vapor, and absorption features of CO_2 , CO , COS in Fig. 3d and HF in Fig. 3e are not as apparent as those of SO_2 in Fig. 3b and HCl in Fig. 3c. In the spectra observed in the 1998 field survey, spectral intensities were low compared to those in other field surveys, and were negligible in the wavenumber range for HF absorption ($4020\text{--}4120\text{ cm}^{-1}$). As stated above, some part of the fumarolic area was submerged under the lake water and fumarolic surface temperature used as the light source was low. Thus, we were not able to analyze HF was not able to be analyzed for the spectra observed in the 1998 field survey.

Corresponding column amounts of 6 gas species for an observed spectrum are retrieved from the model spectra. Figure 4a and 4b show the column amounts plots of SO_2 versus HCl and CO_2 , respectively, for the 2002 survey. Each data points in the figures correspond to respective observed spectra. As seen in the both figures, there are linear trends between the two volcanic gas species. The linear trends seen in the two species' plots show that the gas observed by the instrument is a mixture of air and fumarolic gas with homogeneous chemical composition. In such a case, the gradient of the linear regression lines in the two species' plots yields the average molar ratio of the two gas species of the fumarolic gas. The regression lines for HCl versus SO_2 , HF versus SO_2 and COS versus SO_2 were estimated, assuming the y-intercept to pass through the origin, because amounts of these gases in the air are negligible and purely volcanic origin. In contrast, the regression lines for CO_2 versus SO_2 , and CO versus SO_2 were estimated assuming the intercept to be non-zero, because of atmospheric concentrations of CO_2 and CO species. Comparing two plots, CO_2 versus SO_2 (Fig. 4a) and HCl versus SO_2 (Fig. 4b), latter plot shows greater scattering. This is contrary to the results of Masaya volcano (Burton *et al.*, 2000), where CO_2 versus SO_2 plot has greater scatter than that of HCl versus SO_2 or HF versus HCl plots. This tendency is observed especially for the 2002 and the 2003 field surveys of Aso volcano and is probably reflecting variable mixing of gas and steam rising from the surface of warm crater-lake. Table 1 shows the number of spectra observed and analyzed and the average molar ratios of volcanic gas species determined for Aso volcano for the six field surveys. The X_i/SO_2 molar ratios in Table 1 were obtained using the gradients of the linear regression line in X_i versus SO_2 plot for the respective surveys. X_i is the volcanic gas species other than SO_2 . In the case of CO/CO_2 molar ratios, they were calculated using CO/SO_2 and CO_2/SO_2 ratios. The calculated molar ratios in Table 1 have some errors due to the scattering of the data in two species' plot. The standard er-

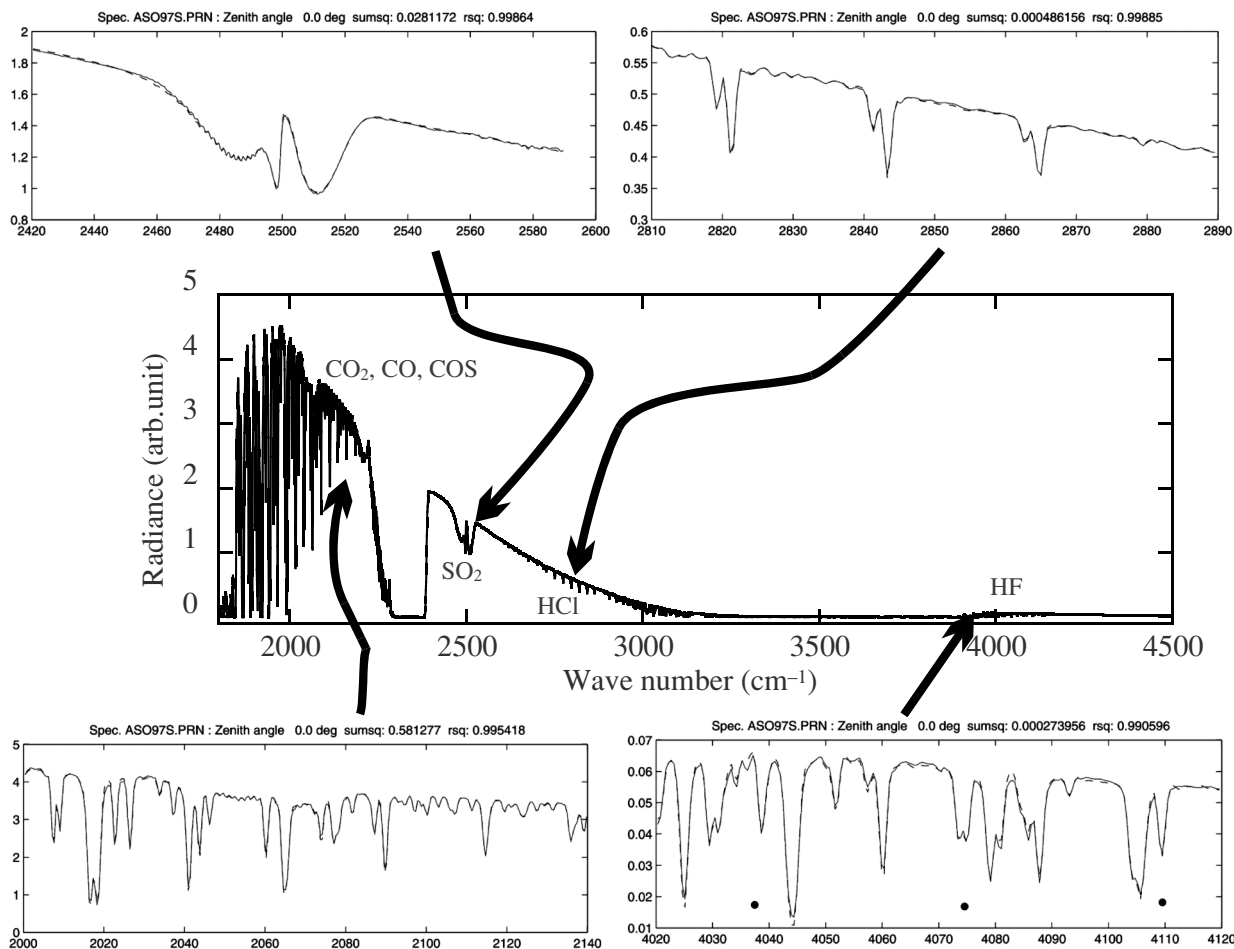


Fig. 3. (a) A typical observed single beam spectrum obtained in the 2002 survey. (b)–(e) The observed (dashed lines) and the simulated model (solid lines) spectra for (b) SO_2 , (c) HCl , (d) CO_2 , CO , and COS , (e) HF analyses windows. Three dots under the spectra in (e) indicate the location of HF absorption peaks.

rors of the average molar ratios are estimated and presented in Table 1. HCl/SO_2 ratio for the 1998 field survey was not obtained, because HCl was not detected in any of the observed spectra. Considering the detection limit of HCl based on $S/N = 3$ (peak-to-peak noise) for an absorption peak of HCl , HCl/SO_2 will be less than 1.4×10^{-2} . Since spectral analysis in this study is carried out using spectral fitting with three HCl absorption peaks, the actual detection limit should be much lower than the above estimation. Figures 5a–e show the temporal variations of molar gas ratios observed by FT-IR for the observation period between 1996 and 2003.

The results of July 1996 field survey have been already reported (Mori and Notsu, 1997). In the spectral analyses of Mori and Notsu (1997), an observed single-beam spectrum which is least influenced by the volcanic plume was used as a background spectrum for calculating absorbance with the other observed spectra. In these calculations, it is assumed that the volcanic plume was a

mere mixture of the air and homogeneous volcanic gas. However, even the least influenced spectrum had small contribution of volcanic gas species, and apparently, the gas composition in the plume is not completely homogeneous as shown in the HCl versus SO_2 plot (Fig. 4a). Thus, the above assumption may not be applied to the spectra analyses. In this paper, we re-analyzed the spectra of the 1996 field survey with the same procedure as other field surveys as explained above. The gas ratios have changed up to double by the new calculation.

Mori and Notsu (1997) compiled CO/CO_2 molar ratios of volcanic gases and its equilibrium temperatures at depth, and obtained empirical equation between the CO/CO_2 ratio and the reciprocal temperature. Figure 5f shows the estimated equilibrium temperature at depth obtained using average CO/CO_2 ratios of our field surveys and equation (1) in Mori and Notsu (1997). The temperature ranges between 670°C and 870°C and they agreed within the error for all (Fig. 5f).

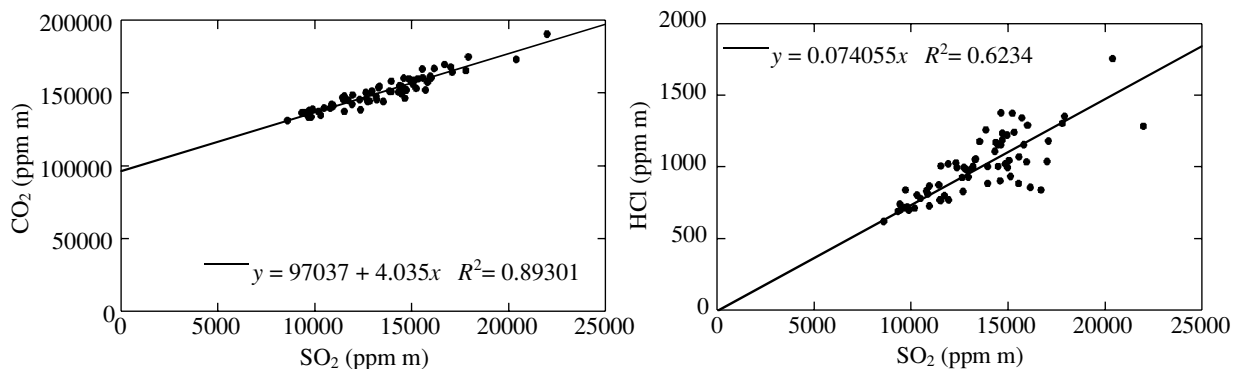


Fig. 4. (a) The column amounts plots of SO_2 versus HCl for the 2002 field survey. (b) The column amounts plots of SO_2 versus CO_2 . Each data points in the figures correspond to respective observed spectra. The thin lines in the plots represents linear regression lines for the plots. The intercepts of the regression line in (b) corresponds to atmospheric CO_2 column amounts value between the FT-IR and the fumarolic area.

Table 1. Average molar ratios of volcanic gas observed at Nakadake, Aso volcano and their standard errors

Date	No. of spec. analyzed	HCl/SO_2 ($\times 10^{-2}$)	CO/CO_2 ($\times 10^{-3}$)	COS/CO_2 ($\times 10^{-4}$)	CO_2/SO_2	HCl/CO_2 ($\times 10^{-2}$)	HF/HCl ($\times 10^{-1}$)
07/26/1996	18	5.9 ± 0.2	3.6 ± 0.3	11 ± 0.9	2.8 ± 0.2	2.1 ± 0.2	2.0 ± 0.3
05/09/1997	13	10 ± 0.4	1.9 ± 0.3	3.5 ± 0.3	5.6 ± 0.4	1.9 ± 0.2	1.1 ± 0.1
11/26/1998	13	n.d.*	1.2 ± 0.5	4.1 ± 0.9	4.2 ± 0.9	n.d.*	n.a.**
05/11/2001	18	10 ± 0.3	4.3 ± 2.0	1.8 ± 0.6	2.8 ± 1.1	3.6 ± 1.4	2.1 ± 0.1
03/09/2002	68	7.4 ± 0.1	1.8 ± 0.2	2.5 ± 0.1	4.0 ± 0.2	1.8 ± 0.1	2.6 ± 0.1
10/15/2003	87	8.5 ± 0.1	8.1 ± 0.6	2.5 ± 0.1	5.3 ± 0.2	1.6 ± 0.1	2.4 ± 0.1

*n.d.: HCl was not detected in the observed spectra.

**n.a.: HF was not able to be analyzed due to low spectroscopic intensity.

CHARACTERISTICS OF FUMAROLIC GAS SYSTEM AT MT. NAKADAKE

The temporal variations of Mt. Nakadake's fumarolic gas chemistry between 1996 and 2003 show following characteristics. 1) HCl was under detection limit for the 1998 field survey. 2) The HCl/SO_2 molar ratio stayed rather stable between $0.6\text{--}1.0 \times 10^{-1}$ except for that in the 1998 survey. 3) The CO_2/SO_2 molar ratio was basically stable for all the time period between 2.8 and 5.6. 4) The equilibrium temperature estimated based on CO/CO_2 molar ratios ranged between 670°C and 870°C and agreed within the error range for the survey period.

These results show that Mt. Nakadake has been emitting fumarolic gas with stable chemical composition at least during the survey period except for low HCl/SO_2 and HCl/CO_2 ratios in 1998. As mentioned earlier, a part of the fumarolic area was submerged under the crater lake in 1998. Hashimoto and Ikebe (2006) and Saito *et al.* (2006) report the temporal variation of the water level of

the 1st crater from 1991 based on angle measuring surveys and/or photo surveys. According to Hashimoto and Ikebe (2006), the water level gradually raised about 20 m between the 1996 and the 1998 survey periods, keeping high level until mid-2000. After then, it declined gradually for about 12 m between mid-2000 and mid-2003 (Saito *et al.*, 2006). These data suggest that the water level was actually in the high period at the time of the 1998 survey. The observed HCl depletion in plume gas chemistry in 1998 may be explained by the hydrothermal interaction with the volcanic gas emission system. The absorption of acidic volcanic gases into a liquid-dominated hydrothermal environment is observed elsewhere (e.g., Fischer *et al.*, 1996, 1997; Giggenbach *et al.*, 1990). Rowe *et al.* (1992b) reported the possibility of lake water invasion to the adjacent fumarolic conduit at Poas volcano, Costa Rica. The effect of volcanic gas and groundwater interaction is intensively studied for various conditions by Symonds *et al.* (2001). According to their model calculations based on equilibrium for closed system, scrub-

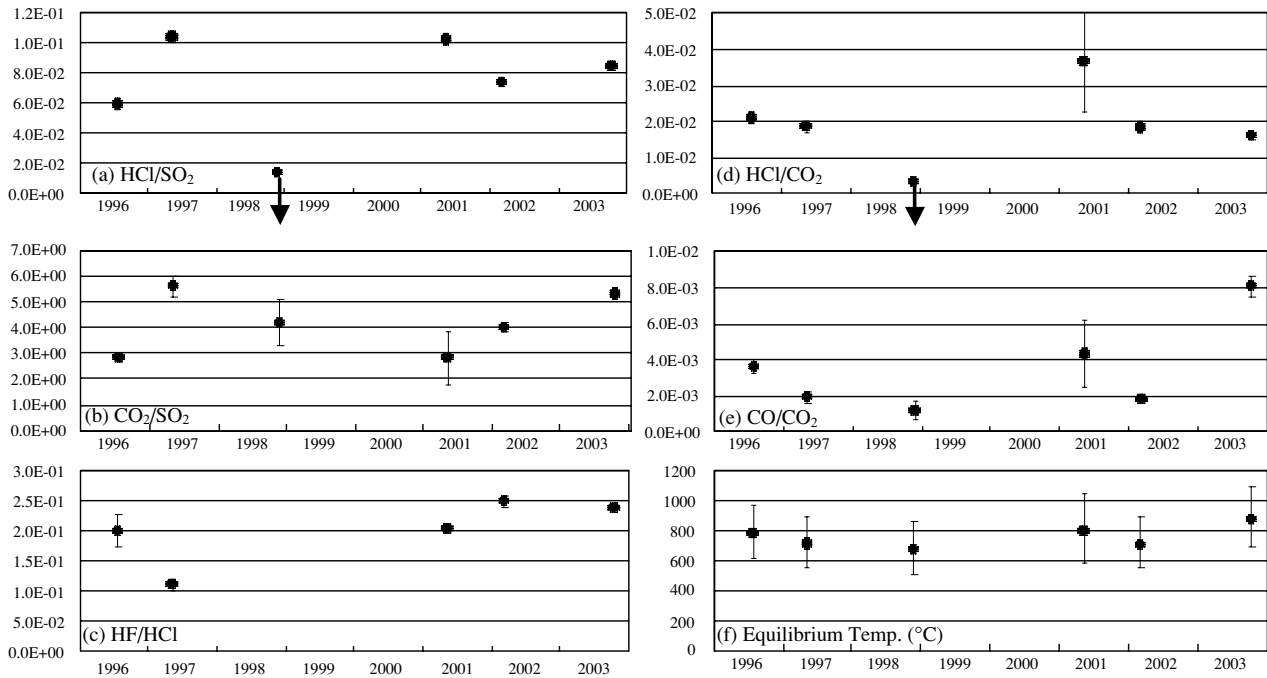


Fig. 5. Temporal variation of molar ratios between volcanic gas species for the six field surveys; (a) HCl/SO₂, (b) HF/HCl, (c) CO₂/SO₂, (d) CO/SO₂ and (e) CO/CO₂. (f) Temporal variation of the estimated equilibrium temperature at depth obtained using average CO/CO₂ ratios in Table 1 and equation (1) in Mori and Notsu (1997). The error bars show the standard error.

bing of gas by water will prevent significant SO₂ and most HCl emissions until dry pathways are established, except for moderate HCl degassing from pH < 0.5 hydrothermal waters (Symonds *et al.*, 2001). Essentially, SO₂ is completely scrubbed from the gas phase in wet condition unless the activity of SO₄²⁻ in the hydrothermal solution is high (Symonds *et al.*, 2001). In our 1998 data, it is not SO₂ but HCl that is significantly scrubbed from the fumarolic gas. Our observation can not be explained by the thermochemical modeling for closed system based on equilibrium. The interaction is probably occurring in an open system and is not attaining equilibrium. In such a case, more soluble HCl is probably preferably scrubbed off compared to SO₂. At Galeras volcano, Columbia, interaction of hydrothermal system to magmatic gas is discussed using HCl/CO₂ and St/CO₂ ratios (Fischer *et al.*, 1996). They used CO₂ as reference because it is a major magmatic gas component which is least influenced by secondary processes. They found minor St/CO₂ temporal changes compared to those of the HCl/CO₂ ratios, and related the significant HCl/CO₂ decline to increased interaction of magmatic gases with a liquid-dominated hydrothermal system (Fischer *et al.*, 1996). Thus, we presume that the interaction may be occurring very near to the surface with crater-lake water or groundwater system incremented by 2nd and 3rd craters of Mt. Nakadake (Fig. 1). The pH of the crater-lake water is very low (Oct. 1993,

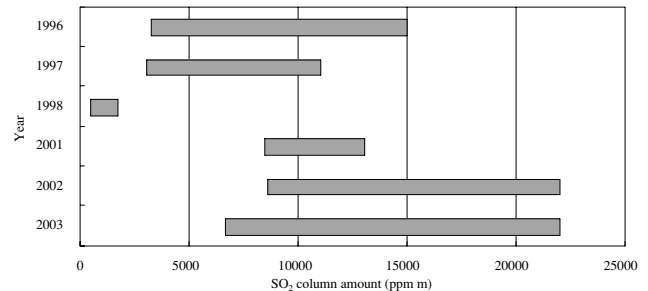


Fig. 6. SO₂ column amounts ranges observed by the remote FT-IR measurements for the six field surveys.

pH = 0.38; Aug. 2000, 0.81; Apr. 2003, -0.72; Onda *et al.*, 2003; Ohsawa *et al.*, 2004). Since volcanic gas interaction with such acidic water will not scrub HCl completely from the gas phase (Symonds *et al.*, 2001; Rowe *et al.*, 1992a), the groundwater system from southern craters with much higher pH are probably responsible for the interaction. In previous and subsequent survey years, considering the stable HCl/SO₂ ratio, the interaction between volcanic gas and the groundwater system was not significant, and a dry pathway for the volcanic gas emission was established even at the shallower depth. Only in 1998, the pathway was invaded by the ground water system.

The CO₂/SO₂ ratio is relatively stable for the whole observation period, even in 1998. This supports the notion that SO₂ was basically not scrubbed by the water interaction in 1998 and the chemical composition of volcanic gas from depth was very stable for the entire observed period, otherwise the CO₂/SO₂ in 1998 happened to have the similar value as those in other years after affected by SO₂ scrubbing. It is more than probable that volcanic gas with very stable chemical composition was supplied to Mt. Nakadake's fumarolic system from depth at least for 8 years during the observation period, and observed HCl depletion in 1998 was caused by the interaction with groundwater, probably, less acidic than the crater lake's water. This HCl depletion continued from the end of 1998 to mid-2000 while the water level of Mt. Nakadake was in the high period.

The SO₂ flux from Mt. Nakadake has been measured with COSPEC since 1970s. The flux increases over 2000 t/d during eruptive periods. Meanwhile, the SO₂ flux is less than 200 t/d for the quiescent period (Institute of Seismology and Volcanology, Faculty of Science, Kyushu University, 2004). At the time of the 1998 survey, volcanic gas emission from the fumarolic area of Mt. Nakadake seemed very weak compared to those in other years by visual observation. Unfortunately, there is no SO₂ flux data by COSPEC between 1998 and 2000, during the high water level period of the 1st crater. Figure 6 shows the ranges of SO₂ column amounts for the six field surveys. SO₂ column amounts ranges over 3000 ppm m and below 22000 ppm m except for that in 1998 (Fig. 6). In contrast, the SO₂ column amount range in 1998 was between 400 ppm m and 1700 ppm m, nearly one magnitude lower than in the other years. The column amount range of SO₂ in our measurements largely depends on the wind conditions in 1st crater of Mt. Nakadake. However, the low column amount range in 1998 can not be simply explained by the wind conditions, considering the ranges in other years. We believe that the SO₂ flux was significantly lower in 1998 compared to other observation periods. The only supporting data for the low SO₂ emission is the relatively low daily maximum plume height observed during this period (JMA, 2005). The low SO₂ emission rate implies scrubbing of SO₂ by hydrothermal system or substantial decrease of deep gas supply. Considering the stable CO₂/SO₂ ratios from 1996 to 2003, and significantly low HCl/CO₂ ratio in 1998, we presume that the lower SO₂ emission rate is due to decrease of gas supply rate from the gas source at depth. This decrease in supply rate of gas may be attributed to both decrease in magmatic gas pressure and plugging of the pathway of the gas. However, detailed discussion on this point is not clear from our observation.

CONCLUDING REMARKS

At Mt. Nakadake, Aso volcano, Japan, we carried out 6 field surveys of remote FT-IR measurements for volcanic plume gas chemistry. In the 1998 field survey, we identified significant HCl scrubbing by hydrothermal interaction. This HCl scrubbing occurred when the water level of the crater-lake was high. Considering the results of the field surveys, the equilibrium temperature deduced from the chemical composition at the gas source under Mt. Nakadake have been keeping high temperature over 700°C and been stable, respectively, for over 8 years. Sulfur dioxide flux from Mt. Nakadake was probably lower in 1998 compared to that of other field surveys. The decrease of the SO₂ flux was due to decrease of total supply rate of gas from depth, not due to the scrubbing of SO₂ by hydrothermal interaction.

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