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

TOSHIYA MORI* and KENJI NOTSU
Laboratory for Earthquake Chemistry, Graduate School of Science, University of Tokyo, Tokyo 113-0033, Japan
(Received May 28, 2007; Accepted November 12, 2007)

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 (SO₂, HCl, HF, CO, CO₂, COS) using the InSb detector. The equilibrium temperatures estimated from observed CO/CO₂ 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 SO₂ flux from the volcano was lower in 1998 than in other years. This decrease in flux was not due to hydrothermal scrubbing of SO₂ but was due to decrease in a total supply rate of gas from depth. This assumption is supported by relatively stable CO₂/SO₂ 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, SO₂, HCl, HF, CO, SiF₄, CO₂, COS and H₂O 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, SO₂, HCl, CO₂, CO and COS, and estimated temperature at depth to be 750 ± 120 °C based on CO/CO₂ ratios. Ono et al. (1999) also reported gas chem-
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 Cassegranean 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 measurements. 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
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; \( \text{SO}_2 \) (2420–2600 cm\(^{-1}\)), \( \text{HCl} \) (2810–2890 cm\(^{-1}\)), \( \text{HF} \) (4020–4120 cm\(^{-1}\)) and \( \text{CO}_2, \text{CO} \) and \( \text{COS} \) (2000–2140 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 \( \text{SO}_2 \) \( \nu_1 + \nu_3 \) band and \( \text{HCl} \) (P-branch) are identified in 2420–2600 cm\(^{-1}\) and 2810–29890 cm\(^{-1}\), respectively. Four spectrum windows (Figs. 3b–e) show the observed (dashed lines) and the simulated model (solid lines) spectra for \( \text{SO}_2 \) (Fig. 3b), \( \text{HCl} \) (Fig. 3c), \( \text{CO}_2, \text{CO} \) and \( \text{COS} \) (Fig. 3d) and \( \text{HF} \) (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 \( \text{CO}_2, \text{CO} \), \( \text{COS} \) in Fig. 3d and \( \text{HF} \) in Fig. 3e are not as apparent as those of \( \text{SO}_2 \) in Fig. 3b and \( \text{HCl} \) 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 \( \text{HF} \) absorption (4020–4120 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 \( \text{HF} \) 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 \( \text{SO}_2 \) versus \( \text{HCl} \) and \( \text{CO}_2 \), 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 \( \text{HCl} \) versus \( \text{SO}_2 \), \( \text{HF} \) versus \( \text{SO}_2 \) and \( \text{COS} \) versus \( \text{SO}_2 \) 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 \( \text{CO}_2 \) versus \( \text{SO}_2 \), and \( \text{CO} \) versus \( \text{SO}_2 \) were estimated assuming the intercept to be non-zero, because of atmospheric concentrations of \( \text{CO}_2 \) and \( \text{CO} \) species. Comparing two plots, \( \text{CO}_2 \) versus \( \text{SO}_2 \) (Fig. 4a) and \( \text{HCl} \) versus \( \text{SO}_2 \) (Fig. 4b), latter plot shows greater scattering. This is contrary to the results of Masaya volcano (Burton et al., 2000), where \( \text{CO}_2 \) versus \( \text{SO}_2 \) plot has greater scatter than that of \( \text{HCl} \) versus \( \text{SO}_2 \) or \( \text{HF} \) versus \( \text{HCl} \) 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 \( x_i/\text{SO}_2 \) molar ratios in Table 1 were obtained using the gradients of the linear regression line in \( x_i \) versus \( \text{SO}_2 \) plot for the respective surveys. \( x_i \) is the volcanic gas species other than \( \text{SO}_2 \). In the case of \( \text{CO}/\text{CO}_2 \) molar ratios, they were calculated using \( \text{CO}/\text{SO}_2 \) and \( \text{CO}_2/\text{SO}_2 \) 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.

Torres 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).
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/SO2 molar ratio stayed rather stable between 0.6 – 1.0 × 10-1 except for that in the 1998 survey. 3) The CO2/SO2 molar ratio was basically stable for all the time period between 2.8 and 5.6. 4) The equilibrium temperature estimated based on CO/CO2 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/SO2 and HCl/CO2 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-
Bubbling of gas by water will prevent significant SO$_2$ 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, SO$_2$ is completely scrubbed from the gas phase in wet condition unless the activity of SO$_4^{2–}$ in the hydrothermal solution is high (Symonds et al., 2001). In our 1998 data, it is not SO$_2$ but HCl that is significantly scrubbed from the fumarolic gas. Our observation cannot 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 SO$_2$. At Galeras volcano, Columbia, interaction of hydrothermal system to magmatic gas is discussed using HCl/CO$_2$ and St/CO$_2$ ratios (Fischer et al., 1996). They used CO$_2$ as reference because it is a major magmatic gas component which is least influenced by secondary processes. They found minor St/CO$_2$ temporal changes compared to those of the HCl/CO$_2$ ratios, and related the significant HCl/CO$_2$ 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, 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/SO$_2$ 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, considering the ranges of SO₂ in other years by visual observation. Unfortunately, there is no SO₂ column data by COSPEC between 1998 and 2000, during the high water level period of the 1st crater lake.

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.

ACKNOWLEDGMENTS
We would like to thank all the members of Aso Volcanological Laboratory, Kyoto University for their support in the observations at Aso volcano. We are also grateful to Yoichi Shimokawa, Masanori Sato, Junji Yamamoto and Tomoaki Shuto for their assistance in the field surveys. For this study, we have used the computer systems of the Earthquake Information Center of the Earthquake Research Institute, the University of Tokyo. This manuscript was considerably improved by the helpful reviews of Dr. Tobias Fischer and an anonymous reviewer.

REFERENCES


Fischer, T. P., Sturchio, N. C., Stix, J., Arehart, G. B., Counce,


