

RESEARCH LETTER

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Key Points:

- We remotely determined the outlet temperature of fumaroles in Sakurajima volcano based on isotopes in a volcanic plume
- The highest outlet temperature was comparable to the temperature of the magma reservoir
- The present method is the only option available to constrain temperatures of inaccessible fumaroles remotely

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Remote determinations on fumarole outlet temperatures in an eruptive volcano

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Abstract Direct measurement of the fumarole outlet temperature in active volcanoes is impractical. Therefore, we used an aircraft to sample H₂ in the volcanic plume ejected from Sakurajima volcano to remotely estimate the highest fumarolic temperatures of the volcano based on hydrogen isotopic fractionation between H₂ and magmatic H₂O. We successfully estimated that the δD of the fumarolic H₂ in September and December 2014 was $-135 \pm 13\text{‰}$ and $-113 \pm 11\text{‰}$, respectively, and that the corresponding highest outlet temperatures were $1050 \pm 120^\circ\text{C}$ and $1199 \pm 139^\circ\text{C}$. Although the temperatures were higher than those determined by using infrared remote sensing, we concluded that they are more reliable estimates of the highest fumarole outlet temperatures. Combined with plume sampling by using aircraft, remote temperature sensing based on the δD of H₂ in volcanic plumes can be widely applied to active volcanoes to determine the highest fumarole outlet temperatures.

1. Introduction

1.1. Outlet Temperature of Fumaroles

The outlet temperatures of fumaroles in active volcanoes have provided useful information on the magmatic/hydrothermal activity in those volcanoes [e.g., Badrudin, 1994; Botcharnikov et al., 2003; Connor et al., 1993; Matsushima, 2011; Menyailov et al., 1986; Ripepe et al., 2002; Taran et al., 1995; Yokoo, 2009]. In our previous reports, we accurately estimated the outlet temperature of fumaroles remotely by determining the D/H ratios of H₂ in the volcanic plume [Tsunogai et al., 2013, 2011]. This remote temperature sensing technique, known as Hydrogen Isotopes Remote Temperature Sensing (HIReTS), is particularly useful for understanding the magmatic/hydrothermal processes occurring in eruptive volcanoes where direct measurement of the outlet temperatures of fumaroles is impossible.

In previous studies that applied HIReTS to Aso and Satsuma-Iwojima volcanoes (Figure 1a), volcanic plume samples were collected at the rim of each volcanic crater a few hundred meters from the fumaroles located in the bottom of each crater [Tsunogai et al., 2013, 2011]. Direct access to the rims of summit craters, however, is neither practical nor safe in many eruptive volcanoes. Therefore, it is necessary to develop alternative methods and devices for obtaining samples of plumes of eruptive volcanoes and to remotely determine outlet temperatures of fumaroles by using HIReTS.

In general, a volcanic plume spreads laterally at a height close to or slightly higher than the summit of the volcano from which it was ejected so that its height is significantly higher than sea/ground level. As a result, flying devices such as aircraft [e.g., Fiske and Sigurdsson, 1982; Hirabayashi et al., 1982; Saiki and Ohba, 2010; Shinohara et al., 2003] are needed to obtain samples of volcanic plumes when using HIReTS for eruptive volcanoes. Development of devices for sampling the plume air is needed as well.

In this study, we used a manned fixed-wing aircraft to obtain volcanic plume samples ejected from Sakurajima volcano (Figure 1), one of the most active volcanoes in the world, to remotely determine the highest outlet temperature of summit fumaroles by using HIReTS. Because Sakurajima volcano has shown continuous explosive activity at the summit crater since 1955, direct measurement of the outlet temperature has been impractical.

An additional aim of this study is to determine the spatial distribution of fumarolic H₂ in a volcanic plume by using aircraft. To deduce the precise hydrogen isotopic composition (δD) of fumarolic H₂ remotely, samples of volcanic plumes enriched in fumarolic H₂ are needed [Tsunogai et al., 2013, 2011]. In contrast to SO₂

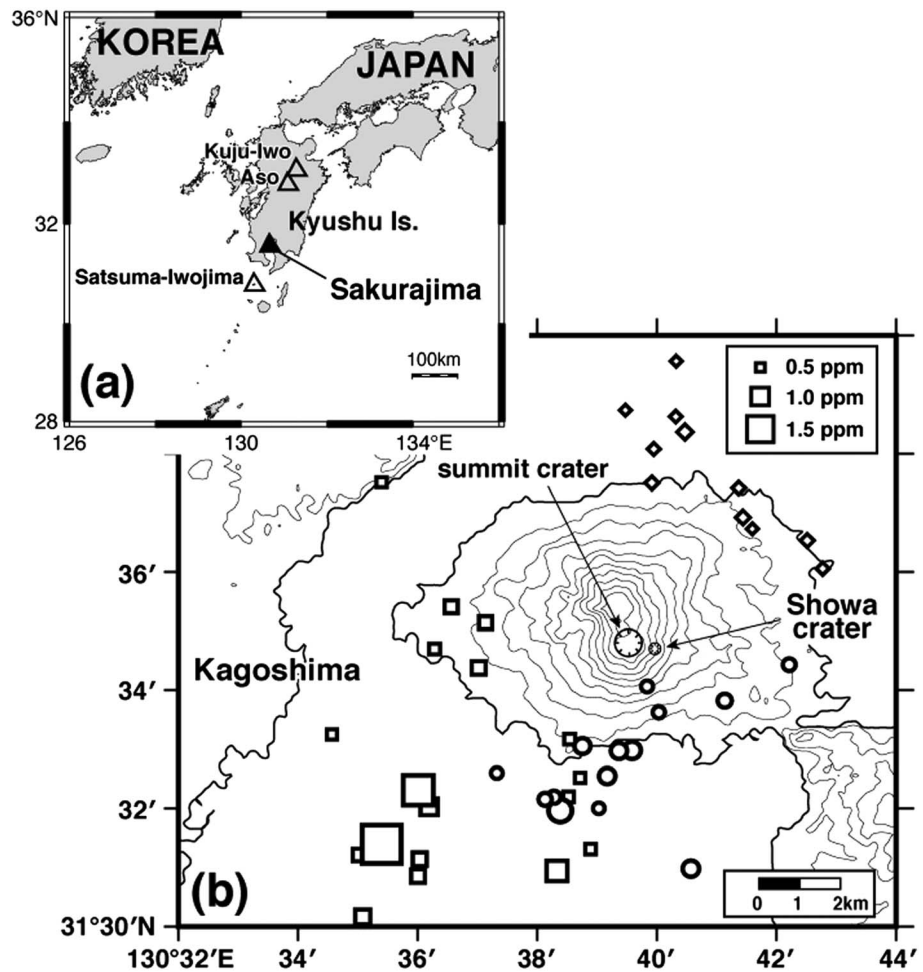


Figure 1. (a) Map showing the location of Sakurajima volcano on Kyushu Island, Japan, including nearby active volcanoes. (b) Topographic map of Sakurajima volcano including the sampling points of the volcanic plume during flights SK14-1, SK14-2, and SK14-3, shown by diamonds, circles, and squares, respectively. The size of each symbol is proportional to the H_2 concentration in each sample.

distributions, little data are available on the spatial distribution of H_2 in a volcanic plume. Although recent advances on in situ direct measurement techniques are remarkable for H_2 [Aiuppa *et al.*, 2011, 2015, 2012; Shinohara *et al.*, 2011], most of the published data have been obtained on ground level. To apply HIRTS to eruptive volcanoes, we must increase our knowledge of the spatial distribution of H_2 in volcanic plumes by using aircrafts.

1.2. Remote Temperature Sensing Using Hydrogen Isotopes in Volcanic Plumes

In volcanic fumaroles showing outlet temperatures exceeding 400°C , H_2 reaches isotope exchange equilibrium with the coexisting H_2O instantaneously [Kiyosu, 1983; Mizutani, 1983; Proskurowski *et al.*, 2006; Tsunogai *et al.*, 2013, 2011; Welhan and Craig, 1983], whereas the isotope exchange reactions do not take place in volcanic plumes at ambient air temperatures. We applied this temperature-dependent isotopic fractionation between fumarolic H_2 and H_2O to remotely determine the outlet temperatures of fumaroles [Tsunogai *et al.*, 2013, 2011]. In this remote sensing, we deduced the δD value of fumarolic H_2 from δD values of H_2 in the volcanic plume. Owing to recent advances in stable isotope measurement, it is possible to determine the δD values of atmospheric H_2 precisely without the need for cumbersome pretreatments [Komatsu *et al.*, 2011; Rahn *et al.*, 2002; Rhee *et al.*, 2004]. We calculated the outlet temperature assuming that fumarolic H_2 had been under hydrogen isotope exchange equilibrium with fumarolic H_2O having δD values of

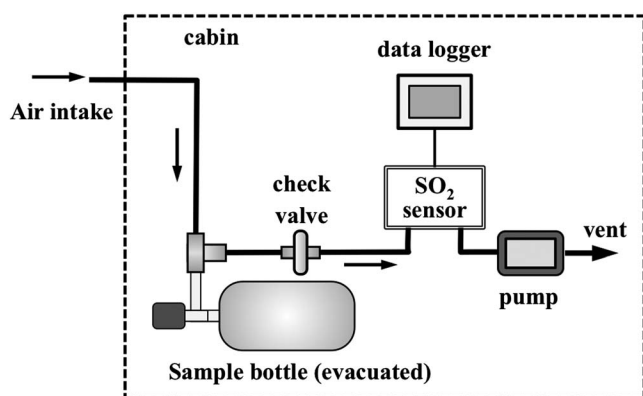


Figure 2. Schematic diagram showing the volcanic plume sampling device installed in the cabin of the aircraft.

temperature within the summit fumaroles showing various temperatures in the volcano [Tsunogai *et al.*, 2013]. Further, we estimated the δD value of the fumarolic H_2 to be $-172 \pm 16\text{‰}$ and the outlet temperature to be $868 \pm 97^\circ\text{C}$ [Tsunogai *et al.*, 2011] in Aso volcano (Figure 1a), where direct temperature measurement in fumaroles is impractical.

2. Materials and Methods

2.1. Sakurajima Volcano

Sakurajima volcano, a postcaldera andesitic stratovolcano in Kyushu Island, Japan (Figure 1), experiences thousands of small eruptions annually. The total emission flux of SO_2 ranges from a few hundred to several thousand tons per day. Because the volcano has been erupting almost constantly since 1955, direct measurement of fumarole outlet temperature is impractical [e.g., Hirabayashi *et al.*, 1982]. Using phase equilibria of phenocryst such as plagioclase and clinopyroxene in a volcanic bomb that erupted in November 1977, Yamamoto *et al.* [1979] estimated the temperature of the magma reservoir to be 950–1040°C.

Among the three major peaks of the volcano, the present volcanic activity is concentrated on the southern peak known as Minami-dake at 1040 m above sea level, particularly at Showa crater located on the eastern upper flank of the Minami-dake peak (Figure 1). Although the summit crater of the Minami-dake peak is also active, the major SO_2 emissions have moved to the Showa crater in recent years [Kazahaya *et al.*, 2013]. Because Kagoshima City is located within a few kilometers of the volcano (Figure 1), monitoring of the outlet temperature of the fumaroles is important for the prevention of volcanic disasters.

2.2. Sampling

The samples of the volcanic plume ejected from the summit craters of Sakurajima volcano were obtained by using a manual sampling device setup in the cabin of a Cessna 172 Skyhawk (Figure 2). During sampling flights SK14-1 on 10 September, SK14-2 on 11 September, and SK14-3 on 9 December 2014, the volcanic plume spread almost laterally from the craters toward the northeast, southeast, and southwest at approximate altitudes of 1200 m, 1500 m, and 1000 m, respectively. Essentially, the aircraft repeated the flights at the same altitudes toward the cross section of the volcanic plume [Wardell *et al.*, 2004]. The aircraft also flew into the plume in the same direction as that of the plume flow.

By using an air pump (GilAir Plus, Sensidyne) at a flow rate exceeding 1 L/min, outside air was introduced continuously into the cabin through a perfluoroalkoxy tube attached to the front of the left wing. To monitor the SO_2 concentration in the introduced stream of air, a constant potential electrolysis-type SO_2 sensor (Komyo Rikagaku Kogyo K.K.) was used. The volcanic plume sample was collected in a preevacuated 1 L glass bottle with a stopcock sealed by O-rings composed of Viton [Tsunogai *et al.*, 2003] connected to the upstream part of the SO_2 sensor in the airflow path. The volcanic plume sample was instantaneously filled to ambient atmospheric pressure in the bottle by opening the stopcock when the SO_2 concentration in the introduced air

$-24.5 \pm 7.3\text{‰}$; the average and the 1σ dispersion range of the magmatic H_2O estimated from high-temperature fumaroles in convergent-plate volcanoes worldwide [Tsunogai *et al.*, 2011]. By applying HIReTS to Satsuma-Iwojima volcano (Figure 1a), we estimated the δD value of the fumarolic H_2 to be $-185.0 \pm 2.5\text{‰}$ and the outlet temperature to be $805 \pm 25^\circ\text{C}$ [Tsunogai *et al.*, 2013]. Moreover, we found that the estimated HIReTS temperature corresponded to the highest outlet

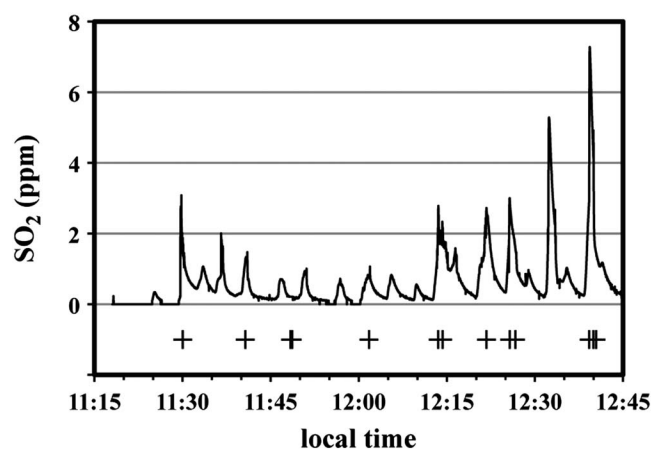


Figure 3. Temporal variation in the concentration of SO_2 during the earlier half of flight SK14-3. The sampling times are indicated by crosses.

(HOBO UX120, Onset Computer Corp.). In addition, we obtained one or two samples of background air during each flight at points outside and upwind of the plume when possible.

2.3. Analysis

The concentrations and δD values of H_2 were determined by using the continuous flow–isotope ratio mass spectrometer system at Nagoya University. Both the analytical system and the analytical procedures are the same as those detailed in our previous research [Komatsu *et al.*, 2011; Tsunogai *et al.*, 2011]. The error in the determined concentrations was $<3\%$, and that in the determined δD values was $<4\%$.

2.4. Temperature Calculation

In this study, apparent equilibrium temperature (AET_D) was estimated from the δD values of fumarolic H_2O and H_2 by using equation (1) [Tsunogai *et al.*, 2011], which we obtained from the relation of $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ and temperature presented in Richet *et al.* [1977]:

$$\text{AET}_\text{D} = \{4.474 \times 10^{-12} \times \Delta^2 + 3.482 \times 10^{-9} \times \Delta + 9.007 \times 10^{-8}\}^{\frac{1}{2}} - 273.15, \quad (1)$$

where Δ represents $10^3 \times \ln(\alpha_{\text{H}_2\text{O}-\text{H}_2})$ and $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ represents the equilibrium fractionation factor of hydrogen isotopes between H_2O and H_2 (i.e., $\alpha_{\text{H}_2\text{O}-\text{H}_2} = (\delta\text{D}(\text{H}_2\text{O}) + 1)/(\delta\text{D}(\text{H}_2) + 1)$).

3. Results and Discussion

3.1. H_2 in the Volcanic Plume

The relationship between the concentrations of SO_2 at the moment of sampling ($[\text{SO}_2]$) and H_2 determined for each bottle ($[\text{H}_2]$) is presented in Figure 4. Most of the volcanic plume samples showed H_2 enrichment compared with the background air samples showing $[\text{SO}_2] = 0$ ppm and $[\text{H}_2] = 0.6 \pm 0.05$ ppm. Moreover, $[\text{H}_2]$ of the background air samples were close to $[\text{H}_2]$ in background tropospheric air in winter, which is about 0.6 ppm [Novelli *et al.*, 1999].

As clearly presented in Figure 4, the plume samples obtained during SO_2 enrichment were also enriched in H_2 . The $\Delta[\text{H}_2]/[\text{SO}_2]$ ratios were approximately 0.2 ± 0.1 , where $\Delta[\text{H}_2]$ corresponds to the excess H_2 in each sample from the most H_2 -depleted background sample. The $\Delta[\text{H}_2]/[\text{SO}_2]$ ratios are typical of high-temperature fumaroles including those in nearby volcanoes, such as 0.5 ± 0.1 in a $>800^\circ\text{C}$ fumarole in Satsuma-Iwojima volcano [Shinohara *et al.*, 2002] and 0.14 in a 400°C fumarole in Kuju-Iwo volcano [Mizutani *et al.*, 1986]. This linear correlation implies that SO_2 and H_2 were ejected from the high-temperature fumaroles in the summit craters of Sakurajima volcano. That is, variations in the mole fractions of volcanic gases within the tropospheric air were responsible for the various H_2 concentrations in the plume samples. The maximum mole fractions of fumarolic H_2 within the total H_2 of the plume were roughly estimated to be 54% in September and 74% in December 2014. This estimation was based on the assumption that the

increased (Figure 3). To prevent sucking cabin air into the bottle from the vent port, a check valve was installed in the flow path (Figure 2).

After closing the stopcock, the glass bottle was replaced with another preevacuated bottle and was prepared for the next sampling. The approximate sampling points for each sample are shown in Figure 1. During flights SK14-1 and SK14-2, the SO_2 concentrations at the moment of sampling were recorded manually. During flight SK14-3, the SO_2 concentrations were recorded continuously by using an analog data logger

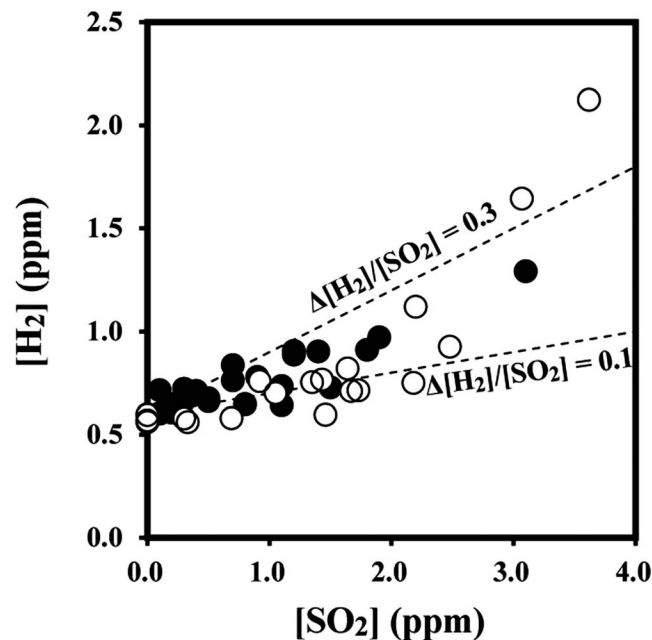


Figure 4. Correlation of $[\text{SO}_2]$ and $[\text{H}_2]$ obtained during flights SK14-1 and SK14-2 (shown by black circles) and SK14-3 (shown by white circles) in addition to hypothetical mixing lines with $\Delta[\text{H}_2]/[\text{SO}_2]$ ratios of 0.3 and 0.1.

volcanic plume. Rather, sampling at the central altitude of the volcanic plume is more important for obtaining volcanic plume samples enriched in H_2 .

3.2. δD Value of Fumarolic H_2

The determined δD values of H_2 in the volcanic plume samples showed large variation, from -47‰ to $+125\text{‰}$, whereas those in the background air samples were almost constant at $+113\text{‰}$. In order to clarify the reason for the large variation in the volcanic plume samples, the δD values of H_2 in the samples were plotted as a function of the reciprocal of the H_2 concentration ($1/[\text{H}_2]$) in Figure 5. As shown in the figure, the δD values showed a strong linear relationship with $1/[\text{H}_2]$. Thus, we concluded that simple mixing between two end-members having different $[\text{H}_2]$ and different δD values of H_2 was responsible for the observed large variation in the δD values of H_2 in the plume samples [e.g., Keeling, 1958; Tsunogai et al., 2013, 1998, 2005, 2011, 2003, 2010]. Similar linear relationships between the $1/[\text{H}_2]$ and δD values of H_2 have been found in the other volcanic plumes such as those in Aso and Satsuma-Iwojima volcanoes [Tsunogai et al., 2013, 2011]. As presented in previous research, the H_2 -depleted end-member showing relatively D-enriched δD values of more than $+110\text{‰}$ must be H_2 in the background air [Rice et al., 2010]. However, the H_2 -enriched end-member showing relatively D-depleted δD values must be fumarolic H_2 , which in past studies always presented lower δD values than those in tropospheric H_2 [Kiyosu, 1983; Mizutani, 1983; Proskurowski et al., 2006; Tsunogai et al., 2013, 2011; Welhan and Craig, 1983]. Furthermore, the strong linear relationship implies that the fumarolic H_2 was stable in the volcanic plume. That is, chemical interactions between H_2 and other coexisting components, such as coexisting H_2O , were minimal in the plume during the mixing with background air. Therefore, we can deduce the δD value of fumarolic H_2 by correcting the contribution of the tropospheric H_2 from the δD values.

By extrapolating each linear relationship shown in Figures 5a and 5b to $1/[\text{H}_2] = 0$ (y axis in the figures) based on the least squares fitting of the straight lines considering the significant differences in errors in the values of $1/[\text{H}_2]$ between the samples, we excluded the contribution of the tropospheric H_2 from the δD value of each sample [Tsunogai et al., 2013, 2011]. Thus, we estimated the average δD value of the fumarolic H_2 to be $-135 \pm 13\text{‰}$ in September and $-113 \pm 11\text{‰}$ in December 2014. The δD value of fumarolic H_2 , which was higher than that of Aso volcano, at $-172 \pm 16\text{‰}$ [Tsunogai et al., 2011], and Satsuma-Iwojima volcano, at $-185.0 \pm 2.5\text{‰}$ [Tsunogai et al., 2013], implies a higher outlet temperature in Sakurajima volcano.

excess H_2 from the most H_2 -depleted sample (=tropospheric air) in each plume sample was derived from the fumaroles [Tsunogai et al., 2000].

The $[\text{H}_2]$ in each sample presented in Figure 1 is shown in proportion to the size of each symbol. As presented in the planar distribution, we were unable to detect a clear correlation between the $[\text{H}_2]$ and the distance toward the craters. Although volcanic gases including fumarolic H_2 are rapidly diluted by the surrounding air just after being ejected from fumaroles and ascending into the air, the mole fraction appears to be almost stable after they stop ascending and begin to spread laterally. Therefore, the distance to the crater was not an essential parameter used to determine the $[\text{H}_2]$ in the

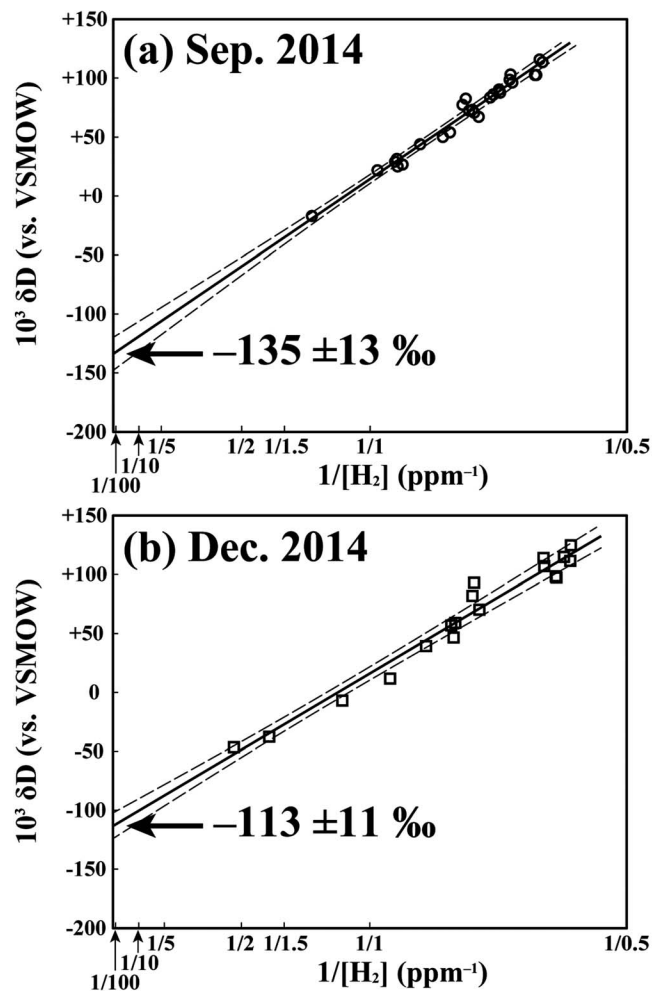


Figure 5. Relationship between δD of H_2 and reciprocal of H_2 concentration ($1/[H_2]$) in the volcanic plume obtained during (a) flights SK14-1 and SK14-2 and (b) flight SK14-3. Each solid line represents the least squares fitting of the samples; each dotted line shows the 2σ variation envelope of the fitting line.

Direct measurement of the outlet temperature of fumaroles is impractical for Sakurajima volcano. Instead, remote measurements of the brightness temperature obtained by using infrared (IR) radiation have been conducted in fumarolic areas several times in the past. Among these past remote measurements, the highest temperature of 854°C was recorded at the bottom of the summit crater in April 2008 by using airborne hyperspectral scanners at an altitude of 5000 m [Jitsufuchi, 2010]. Although the measured temperature in the fumarolic area varied widely in past studies by more than 300°C in each crater, even the highest temperature was lower than that estimated in this study by using HIReTS.

Sakurajima was apparently under an active stage at least during the samplings. Volcanic red glow in and around the craters has been frequently detected at night by visual observation. The number of volcanic tremors often exceeds 1000 times per day. In addition, tiltmeters and strainmeters set in the volcano indicate that Sakurajima volcano has expanded since January 2015 [Japan Meteorological Agency, 2015]. These observations imply that magma had ascended just beneath the fumaroles during our observation in 2014 and that the temperatures determined by using HIReTS are reasonable estimates of the highest outlet temperatures of the fumaroles. The discrepancy between HIReTS and the IR remote sensing can be attributed to insufficient spatial resolution in the IR remote sensing (2 m [Jitsufuchi, 2010]). If the dimension of each high-temperature fumarole at the surface was less than the spatial resolution, the temperature based on the IR remote sensing became lower than the outlet temperature of the fumarole. This hypothesis is also supported by observation

3.3. Estimating the Outlet Temperature of Fumaroles

To calculate the highest outlet temperature of fumaroles from the estimated average δD values of fumarolic H_2 in the Sakurajima volcano, the δD value of coexisting H_2O in the fumaroles should be estimated as well. In this study, we used the average δD value of magmatic H_2O in active volcanoes, $-24.5 \pm 7.3\text{‰}$ [Tsunogai *et al.*, 2011], as the δD value of coexisting H_2O in the fumaroles in Sakurajima volcano. The δD values of high-temperature fumarolic H_2O obtained at nearby volcanoes were also included in the range ($-24.5 \pm 7.3\text{‰}$). These include Satsuma-Iwojima volcano, showing outlet temperatures exceeding 800°C [Shinohara *et al.*, 2002], and Kuju-Iwo volcano, showing those exceeding 400°C [Mizutani *et al.*, 1986].

Applying the average δD value of magmatic H_2O , the maximum outlet temperature was estimated to be $1050 \pm 120^\circ\text{C}$ in September and $1199 \pm 139^\circ\text{C}$ in December 2014 in Sakurajima volcano based on equation (1). The estimated outlet temperatures were comparable to or slightly higher than the temperatures estimated in the magma reservoir in 1977, at $950\text{--}1040^\circ\text{C}$ [Yamamoto *et al.*, 1979].

of the fumarolic area in Satsuma-Iwojima volcano by using an airborne multispectral scanner [Ukawa *et al.*, 2000]. In that case, the highest temperature determined remotely was 311°C, whereas the outlet temperature determined directly was more than 800°C.

In summary, the highest outlet temperature of the fumaroles estimated by HIReTS was comparable to or even slightly higher than the temperatures estimated for the magma reservoir in past research. Further increases in the temperature of the magma reservoir over the old estimate could explain such elevated temperature in the fumaroles. On the basis of petrochemical studies on the historical eruptive products of Sakurajima volcano, Uto *et al.* [2005] detected binary mixing of felsic and mafic magmas beneath the volcano. The elevated fumarolic temperature estimated in this study could imply an increase in the proportion of mafic magma in the reservoir in recent years. A parallel study of HIReTS and petrological studies should be done to verify this hypothesis. Besides, further HIReTS studies should be needed to verify the accuracy of temperature estimation, especially in active volcanoes with high-temperature fumaroles.

4. Conclusions

By combining HIReTS with airborne sampling of a volcanic plume, we estimated the highest outlet temperatures in Sakurajima volcano to be more than 930°C and more than 1060°C in September 2014 and December 2014, respectively. We conclude that HIReTS is more reliable than the IR remote sensing to estimate the highest outlet temperatures of the fumaroles remotely. By combining HIReTS with periodical volcanic plume sampling by aircraft in the future, we can clarify the major factors controlling the outlet temperatures of fumaroles in eruptive volcanoes.

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