Hydrogen isotopes in volcanic plumes: tracers for remote temperature sensing of fumaroles

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[8928 words of text with 352-word abstract and 892-word Appendix, 2 tables, 5 figures, and 74 references]
Abstract
In high-temperature volcanic fumaroles (>400°C), the isotopic composition of molecular hydrogen (H₂) reaches equilibrium with that of the fumarolic H₂O. In this study, we used this hydrogen isotope exchange equilibrium of fumarolic H₂ as a tracer for the remote temperature at volcanic fumaroles. In this remote sensing, we deduced the hydrogen isotopic composition (δD value) of fumarolic H₂ from those in the volcanic plume. To ascertain that we can estimate the δD value of fumarolic H₂ from those in a volcanic plume, we estimated the values in three fumaroles with outlet temperatures of 630°C (Tarumae), 203°C (Kuju), and 107°C (E-san). For this we measured the concentration and δD value of H₂ in each volcanic plume, along with those determined directly at each fumarole. The average and maximum mixing ratios of fumarolic H₂ within a plume’s total H₂ were 97 % and 99 % (at Tarumae), 89 % and 96 % (at Kuju), and 97 % and 99 % (at E-san). We found a linear relationship between the depletion in the δD values of H₂, with the reciprocal of H₂ concentration. Furthermore, the estimated end-member δD value for each H₂-enriched component (−260±30‰ vs. VSMOW in Tarumae, −509±23‰ in Kuju, and −437±14‰ in E-san) coincided well with those observed at each fumarole (−247.0±0.6‰ in Tarumae, −527.7±10.1‰ in Kuju, and −432.1±2.5‰ in E-san). Moreover, the calculated isotopic temperatures at the fumaroles agreed to within 20°C with the observed outlet temperature at Tarumae and Kuju. We deduced that the δD value of the fumarolic H₂ was quenched within the volcanic plume. This enabled us to remotely estimate these in the fumarole, and thus the outlet temperature of fumaroles, at least for those having the outlet temperatures more than 400°C. By applying this methodology to the volcanic plume emitted from the Crater 1 of Mt. Naka-dake (the volcano Aso) where direct measurement on fumaroles was impractical, we estimated that the δD value of the fumarolic H₂ to be −172±16‰ and the outlet temperature to be 868±97°C. The remote temperature sensing using hydrogen isotopes developed in this study is widely applicable to many volcanic systems.
1. INTRODUCTION

The temperature of fumarolic gases provides important information about the magmatic/hydrothermal systems under the volcanoes (e.g. Giberti et al., 1992; Connor et al., 1993; Stevenson, 1993; Taran et al., 1995; Ripepe et al., 2002; Botcharnikov et al., 2003). The temperature often increases prior to eruptions or during shallow intrusions of magma (e.g. Menyailov et al., 1986). Thus, measurements of fumarole outlet temperature have been carried out extensively to understand magmatic processes and to detect the precursors of eruptions.

However, direct measurements on fumaroles are often neither practical nor safe. Remote sensing using infra-red (IR) wavelengths of surface temperatures offers an alternative to direct measurement. This technique has been applied to a variety of volcanoes since the early 1960s (e.g. Fischer et al., 1964; Shimozuru and Kagiyama, 1976; Saito et al., 2005; Harris et al., 2009).

Thermometers using IR remote sensing, however, have several problems when applied to the determination of outlet temperatures of active volcanic fumaroles: (1) IR remote sensing determines the average temperature for each pixel. When a fumarole has surface dimensions smaller than the pixel, the measured temperature becomes the average temperature of an area including low temperature ground surrounding the fumarole. As a result, the measured temperature is inaccurate for that of the fumarole; (2) Line-of-sight is necessary for these thermometers, this is difficult when the fumarole is obscured, e.g. by fogs, rocks, and ejecta (volcanic clouds and ash), (3) absorption of the IR radiation by gases emitted from fumaroles (e.g. H$_2$O and CO$_2$) gives low accuracy and precision of measured temperatures; (4) non-measurement IR radiation (solar, or ground radiation) can also give low accuracy and precision of the measured temperature. Thus, we developed an alternative method to determine the temperature of distant volcanic fumaroles using geochemical tracers in the volcanic plume.
Because of rapid reactions between fumarolic components at high temperatures, fumarolic gases often attain chemical and isotopic equilibrium close to the outlet (e.g. Ellis, 1957; Matsuo, 1961; Giggenbach, 1987; Shinohara et al., 1993; Ohba et al., 1994; Symonds et al., 1994). In particular, for the hydrogen isotope exchange reaction between H$_2$O and H$_2$ in fumaroles at outlet temperatures greater than 400°C, the calculated isotope temperatures (assuming hydrogen isotope exchange equilibrium between H$_2$O and H$_2$; see section 3.3 for the details of the calculation) were close to the actual outlet temperatures (e.g. Bottinga, 1969; Mizutani, 1983; Kiyosu and Okamoto, 1998; Taran et al., 2010).

\[ \text{H}_2\text{O} + \text{HD} \leftrightarrow \text{HDO} + \text{H}_2 \]  

(1.1)

For example, the fumarole outlet temperatures of both the Showashinzan and Nasudake volcanoes have declined, from 800°C in 1954 to 617°C in 1977, and from 489°C in 1960 to 277°C in 1969, respectively. Consistent with these declines, the calculated isotope temperatures also declined, from 750°C to 630°C at Showashinzan and from 470°C to 290°C at Nasudake (Mizutani, 1983). A similar agreement between the calculated isotope temperatures and the outlet was found in subaerial/submarine hydrothermal fluids showing the temperatures more than 200–300 °C (e.g. Kiyosu, 1983; Welhan and Craig, 1983; Proskurowski et al., 2006; Kawagucci et al., 2010). These past observations of fumarolic H$_2$ suggest that the isotope exchange reaction is rapid enough at the outlet temperature to re-equilibrate the calculated isotope temperature to the outlet temperature of the volcanic fumarole, irrespective of the origin of H$_2$O and H$_2$ in the fumarole. Furthermore, the isotope exchange reactions slow down sufficiently after cooling that the D/H ratio is effectively “frozen” at the D/H ratio just before sampling.

Similar processes that result in the re-equilibration of the hydrogen isotopes and subsequent “freezing” of that re-equilibration can also be anticipated in volcanic plumes. If we could estimate the hydrogen isotopic compositions of both the H$_2$O and H$_2$ in the fumaroles from those in the volcanic plume, it would be possible, by assuming the isotope
exchange equilibrium in fumarolic H₂O and H₂, to remotely deduce the temperature of the fumaroles. Within the possible isotope fractionations among the major components in fumarolic gases, the hydrogen isotope fractionation between H₂O and H₂ has the largest fractionation factor under the isotope exchange equilibrium, as well as the largest temperature-dependent variation (Richet et al., 1977), so that the temperature estimation using hydrogen isotopes can be precise.

While H₂ is one of the major components in high-temperature fumarolic gases (0.1 to 3% by volume (including H₂O), Symonds et al., 1994), H₂ is depleted in atmosphere, present at concentrations of ca. 0.5 ppm in tropospheric air (Novelli et al., 1999). Hence, the volcanic plume has an excess of H₂ relative to the troposphere (McGee, 1992; Symonds et al., 1994). Consequently, we can estimate the D/H ratio of fumarolic H₂ from the concentrations and D/H ratios of the H₂ in the volcanic plume, by subtracting atmospheric contributions to the D/H ratios of the H₂ in the volcanic plume (see section 4.2 for the detail). It is more difficult to estimate D/H ratios of fumarolic H₂O from those in plume because of possible enrichment of H₂O in tropospheric air. However, it turns out that we can assume the D/H ratios without actual measurements (see sections 4.3 and 4.4 for the detail). As a result, we can estimate the outlet temperature of fumaroles, from the D/H ratios of the fumarolic H₂ (determined) and the fumarolic H₂O (assumed).

In this study we determined both the concentrations and D/H ratios of H₂ in volcanic plumes emitted from fumarolic areas in active volcanoes in Japan, together with those from high-temperature fumaroles wherefrom the plumes are derived, to verify that:

1. H₂ from high-temperature fumaroles attain isotope exchange equilibrium with co-existing fumarolic H₂O, and,
2. the D/H ratios of fumarolic H₂ are “frozen” in the plume, and, that we can deduce them from those in volcanic plume.
Furthermore, we applied this new methodology to a volcanic plume emitted from a fumarolic area where direct temperature measurements were difficult, to estimate the D/H ratio of fumarolic H₂ and thus the outlet temperature of fumaroles remotely. As far as we are aware, this is the first report of a D/H ratio from H₂ in a volcanic plume. This work has been made possible by recent advances in stable isotope measurements using Continuous-Flow Isotope Ratio Mass-Spectrometry (CF-IRMS), which enabled us to make such highly sensitive measurements on the D/H ratios of H₂ close to the atmospheric levels without any cumbersome and time-consuming pretreatments (Rahn et al., 2002; Rhee et al., 2004; Rice et al., 2010).

2. GEOLOGICAL BACKGROUND

In this study, samples of high-temperature fumarolic gases were taken from 3 surface volcanic fumaroles, together with the samples of volcanic plumes derived apparently from the fumaroles, in the active volcanoes of Tarumae, Kuju, and E-san. Additionally, plume samples emitted from the Crater 1 of the volcano Mt. Naka-dake in Aso were taken, where neither direct sampling of fumarolic gases nor direct measurement of the outlet temperature at the fumaroles on the floor of the crater were possible. The locations of the studied volcanoes are presented in Figure 1.

Tarumae volcano

The Shikotsu caldera (13 × 15 km), largely filled by the waters of Lake Shikotsu, was formed during one of the largest Quaternary eruptions about 31 to 34 KY BP in Hokkaido Island, Japan (Fig. 1). The small andesitic Tarumae stratovolcano was then constructed on the south-eastern rim and has been Hokkaido's most active volcano since. The Tarumae volcano is now capped by an andesitic flat-topped summit lava dome that formed in 1909, having the diameter of 450 m and the height of 130 m. There are 7 major fumarolic vents in and around the summit lava dome, named A, B, C, D, E, F, and G. Vent A is located on the south-eastern
flank of the lava dome and is presently one of the most active fumarolic areas on the Tarumae
volcano. Previously, this had been a huge vent having a inner diameter of more than a meter,
so that no data had been reported for the chemical composition of exiting gases, except for
estimations from the volcanic plume (Shinohara, 2005). However, the inner wall of Vent A
collapsed in 2004 so that most of the main vent has been buried by the debris. Now, an
intense gas emission occurs from many tiny fumaroles at the bottom of a crater about 5 m
deep with a 10 m diameter. In this study, the samples for analysis were taken in and around a
fumarole in Vent A.

Kuju volcano

Kuju volcano consists of 20 lava domes and cones, located in the central part of Kyushu
Island, Japan (Fig. 1). One of the most active fumarolic areas in the volcano is Mt. Iwoyama,
situated on the north-eastern flank of Mt. Hossho, where sulfur used to be mined. The
fumarolic area consists of 4 fields named A, B, C, and D. The fields A, B and C were
pre-existent, and in older literature named “KX”, “KO”, and “KH”, respectively. (e.g.
Mizutani et al., 1986). Field D on the other hand is a group of new vents (named a, b, c, d and
e) that were opened by the phreatic eruption of 1995.

Temporal variations were observed in the chemical and isotopic compositions of the
fumarolic gases in Field C (the KH field) between 1959 and 1984 and were attributed to the
increase in the mixing ratios of meteoric water with magmatic gases (Mizutani et al., 1986).
On the other hand, temporal variations were small for Fields A and B (Mizutani et al., 1986;
Amita and Ohsawa, 2003). All the samples for analysis from the Kuju volcano were taken in
and around a fumarole in Field A.

E-san volcano

The E-san volcano, a small andesitic stratovolcano capped by a 618-m-high lava dome,
is located in southernmost part of Hokkaido Island, Japan (see Fig. 1). The E-san volcano
occupies the eastern tip of the double-pronged Oshima Peninsula across the Tsugaru Strait
The lava dome of the E-san volcano, which formed about 9 KY BP, and the volcano has been active during the Holocene. A minor phreatic eruption in 1846 produced a mudflow that caused many fatalities. The most recent activity at E-san was a small eruption in 1874. Active fumaroles at temperatures of up to 225°C occur in fumarolic areas on the upper northwestern flank (Y field) and the middle western flank (X field). These are located about 400 m apart. Past studies on the fumarolic gases revealed that discharges were dominated by magmatic water and gases (Matsubaya et al., 1978; Hedenquist and Aoki, 1991).

All the samples for analyzing fumarolic gases from the E-san volcano were taken at one of the active fumaroles in the X field. The plume samples were taken around the fumarole.

Aso volcano

The Aso volcano is a volcanic caldera located in the central part of Kyushu Island, Japan (see Fig. 1). It was formed during the major explosive eruptions between 300 KY BP and 90 KY BP. A group of 17 central cones formed in the middle of the caldera, one of which, Mt. Naka-dake, is one of the most active volcanoes in Japan. It was the location of Japan's first documented historical eruption in 553 AD.

The active crater located in the Mt. Naka-dake, named as the Crater 1 of Mt. Naka-dake, is about 400 m in diameter, (see Fig. 2). The active fumarolic area is located at the bottom of the Crater 1, about 80 m below the crater edge, (see Fig. 2). Neither direct sampling of fumarolic gases nor direct measurements of fumarolic temperature were practical in this deep crater. In this study, the samples of volcanic plume were taken at the points A to F (see Figure 2).

3. METHODS

3.1 Sampling
The samples were taken at Tarumae on 6 October, 2010, Kuju on 11 November, 2010, E-san on 19 June, 2010, and Aso on 10 November, 2010. Prior to sampling the fumarolic gases, we measured the temperature of fumaroles as many fumaroles as possible to choose the fumarole that exhibited the highest outlet temperature within each fumarolic area. The highest temperature of the fumaroles in each fumarolic area, where the fumarolic gas samples were taken, were 609°C at Tarumae, 203°C at Kuju, 107°C at E-san (Table 1).

A quartz pipe and silicone rubber tubing were used to introduce the fumarolic gases into sampling bottles, after flushing them with sample for more than 15 minutes. Then, the fumarolic gases were introduced into a 100 mL glass syringe with two mouths via condensation traps made of Pyrex glass (ca. 300 mL) cooled to 0°C. The gases were sucked into the trap by syringe. The water content of the sample was determined from the difference in weight of the trap before and after sample collection. The volume of dried fumarolic gases relative to the water content was determined from both inner volume of the syringe (100 mL) and the number of strokes. The water sample in the condensation traps was stored in polypropylene bottles for later analysis on D/H ratios. The dried fumarolic gases in the glass syringe were introduced via the needle into a pre-evacuated glass vial with a butyl rubber septum stopper (20 to 65 mL). These samples were analyzed for both H$_2$ concentrations and D/H ratios. This method was found to preserve fumarolic H$_2$ samples for more than a month, without detectable changes in either the concentrations or D/H ratios.

Additional to the description above, samples of fumarolic gases were introduced into pre-evacuated 140 mL glass bottles containing 10 mL of 5 mol/L NaOH solution (ultra pure grade) (Giggenbach and Goguel, 1989). These samples were used to determine concentrations of H$_2$O and H$_2$ in fumarolic gases. Acidic components of the fumarolic gases dissolved in the NaOH solution, whereas the other non-acidic gases such as H$_2$ remained in the head space. H$_2$ concentrations in the fumarolic gases were determined from those in head space. H$_2$O concentrations in the fumarolic gases were determined from the increase in the volume of the
NaOH solution. D/H ratios of H\textsubscript{2} in the head space were measured as well. However, these changed toward D enrichment with storage beyond the analytical precision (a few ‰ per day). Hence, we did not include the D/H ratios of H\textsubscript{2} obtained through this method in the final results.

The samples of each volcanic plume were taken into pre-evacuated 300 mL glass bottles with two stopcocks (sealed by o-rings made of Viton) at both ends. These were filled to atmospheric pressure (Tsunogai et al., 2003). Samples were taken by moving away from each targeted fumarole, along the line of the plume. Approximate distances to each targeted fumarole for each sampling point are shown in Table 2. We also took samples of background air at each site, at a point distant from the fumarolic area and if possible upwind (Table 2). The wind speed during sampling was always less than 2 m/s.

3.2 Analysis

Concentrations and D/H ratios of H\textsubscript{2} were determined using the CF-IRMS system at Hokkaido University (e.g. Tsunogai et al., 2002; Ishimura et al., 2004; Kawagucci et al., 2005; Komatsu et al., 2005; Komatsu et al., 2008; Hirota et al., 2010). This system consists of an original helium-purged pre-concentration system for H\textsubscript{2} and a Delta V Advantage (Thermo Fisher Scientific, Waltham, MA, USA) with a modified GC-C/TC III interface and Thermo Trace GC ULTRA gas chromatograph. The analytical procedures are outlined below, details will be presented elsewhere.

For each measurement, a gas sample of appropriate volume (250 mL at STP for a 0.5 ppm plume sample, and 0.25 mL at STP for a 5,000 ppm fumarolic gas sample, where ppm means parts per million by volume), was introduced into our original stainless steel line (pre-flushed with carrier gas stream of ultra pure helium). In this line, H\textsubscript{2} in each sample was purified from the other coexisting components, such as O\textsubscript{2}, Ar, N\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}, SO\textsubscript{2}, H\textsubscript{2}S, and H\textsubscript{2}O, by passing the sample through a cold condensation trap (4 mm ID) held at −197°C and a
column (4 mm ID) packed with Molecular sieve 5A held at –110°C. The H₂ was gathered onto the head of a column (2 mm ID) packed with Molecular sieve 5A held at –197°C and where the carrier pressure was greater than 3,000 Torr. The temperature of the column was then ramped up to room temperature, and the eluted H₂ portion was concentrated again at the head of an HP-PLOT Molsieve capillary column (30 m, 0.32 mm ID) held at –197°C (Tsunogai et al., 2002). The column head was then quickly heated to room temperature under a continuous helium flow rate of 0.4 mL/min and the column-separated H₂ was passed into a mass spectrometer to determine both content and D/H ratios by simultaneous monitoring of the masses of H₂⁺ (m/z=2) and HD⁺ (m/z=3). We introduced pure H₂ before and after the sample H₂ peak, as a calibration standard for the D/H ratios (Tsunogai et al., 2002).

Following provisional IUPAC recommendations (Coplen, 2008), the δ-notation is used in this paper to denote D/H ratios (δD) as defined by the following equation:

\[
\delta D = \frac{R_X}{R_{STD}} - 1
\]  

(3.1)

where \(R_X\) denotes the D/H ratio of a sample and \(R_{STD}\) denotes the D/H ratio of standard material. Unless otherwise noted, we used VSMOW (Coplen and Hopple, 1995) as for the standard material to present δD values in this paper. Within the text, usual δD values are presented using the traditional ‰ (\(i.e. 10^{-3}\)). Please therefore note that a δD value of +5‰, for instance, means +0.005.

Whilst quantifying samples, as a quality control measure we also analyzed a working-standard gas mixture containing H₂ of known concentration (221 ppm) and known δD(H₂) values at least once a day in the same manner as the samples themselves. The δD values of H₂ in the working-standard gas mixture were precisely calibrated by using commercial standards of pure H₂. By using the peak area ratios of m/z 2 vs. 3, we calculated the δ value between the sample and the running standard during sample analysis. For normalization to the international standard, the following relation was applied:
where $\delta_{\text{rs-std}}$ is the $\delta D$ value for the running standard against the international standard, which was determined from the measurement of the working-standard gas mixture that contains $H_2$ of known $\delta D$ compositions ($\delta_{\text{ws-std}}$) via the following calculation:

$$
\delta_{\text{rs-std}} = \delta_{\text{ws-std}} + \delta_{\text{rs-ws-std}} + \left( \delta_{\text{ws-std}} \times \delta_{\text{rs-std}} \right)
$$

(3.2)

The concentration of $H_2$ in a sample was calculated by comparing each $H_2$ peak area with that of the working standard gas mixture. The error of the determined concentrations was estimated to be <3%. An analytical precision of 4‰ for $\delta D$ was achieved for samples containing as little as 5 nmol $H_2$ within the one hour required for a single sample analysis. Total analytical blank associated with the method was estimated to be ca. 50 pmol for $H_2$ having the $\delta D$ value of +1300‰ using the method described in Gelwicks and Hayes (1990). These were subtracted from the final concentrations and $\delta D$ values of $H_2$.

The stable hydrogen isotopic compositions of $H_2O$ ($\delta D(H_2O)$) were determined using the same CF-IRMS system in Hokkaido University, after converting 0.5 µl of sample $H_2O$ to $H_2$ using chromium at 880°C under vacuum condition (Itai and Kusakabe, 2004). A portion (about 2%) of $H_2$ was sub-sampled and introduced into the stainless steel line while flushing with the carrier gas stream of ultra pure helium. It was pre-concentrated on the head of a column (2 mm ID) packed with Molecular sieve 5A held at −197°C. Subsequent procedures were the same with the $\delta D(H_2)$ analysis. In addition to analyzing the samples, we also analyzed our internal working-standards (filtered deep-sea water, filtered tap water, and filtered Antarctic ice water, each having known $\delta D(H_2O)$ values). We did these measurements at least twice every day in the same manner as the samples themselves to calibrate the $\delta D(H_2O)$ values of sample to the international scale. The $\delta D$ values of the working-standards had been precisely calibrated by using international standards of VSMOW and VSLAP.
(Coplen and Hopple, 1995). An analytical precision of 0.8‰ for δD can be achieved for a single sample analysis within the 20 minutes required for analysis.

3.3 Calculation of apparent equilibrium temperature

By using the temperature-dependent variation in the equilibrium fractionation factor of hydrogen isotopes between H₂O and H₂ (α_{H₂O-H₂}), we can estimate the apparent equilibrium temperature (isotope temperature) for δD (AET_D) from the values of δD(H₂O) and δD(H₂), assuming hydrogen isotope exchange equilibrium between H₂O and H₂ (i.e. α_{H₂O-H₂} = (δD_{H₂O}+1)/(δD_{H₂}+1)). In this study, AET_D less than 1,000 °C is estimated from α_{H₂O-H₂} using the following equation (3.4), which we obtained through least squares fitting to the relationship between AET_D (°C) and 10^3×ln(α_{H₂O-H₂}) as presented in Richet et al. (1977):

\[
AET_D = \left\{ \frac{4.474 \times 10^{-12} × \Delta^2 + 3.482 \times 10^{-9} × \Delta + 9.007 \times 10^{-8}}{273.15} \right\}^{\frac{1}{2}} - 273.15 \tag{3.4}
\]

where Δ represents 10^3×ln(α_{H₂O-H₂}). The relationship between AET_D and 10^3×ln(α_{H₂O-H₂}) is schematically shown in Fig. 3.

4. RESULTS & DISCUSSION

4.1 H₂ in Fumaroles

The chemical and isotopic compositions of the fumarolic gases are presented in Table 1. The concentrations of H₂ were expressed relative to H₂O concentration in µmol/mol. Both H₂/H₂O ratios and δD(H₂O) values agreed well with those reported for each volcano in past studies. For example, Mambo and Yoshida (1993) reported H₂/H₂O ratios of 430±340 µmol/mol for a 232°C fumarole at Vent B (Tarumae) (recalculated from their data assuming the mixing ratio of H₂ within the total non-acidic gases, such as H₂, N₂, He, CH₄, CO and Ar, to be 50±40%, in which most of high-temperature fumarolic gas data are included; Symonds et al., 1994). For Kuju, Amita and Ohsawa (2003) reported H₂/H₂O ratio of 41.8 µmol/mol.
and $\delta D(H_2O)$ value of $-49.9\%$ for a 157°C fumarole in Field A, Saito et al. (2002) reported H$_2$/H$_2$O ratios of ca. 70 µmol/mol and $\delta D(H_2O)$ values of ca. $-50\%$ for a 351°C fumarole in Field C, and Mizutani et al. (1986) reported H$_2$/H$_2$O ratio of 5 (µmol/mol) and $\delta D(H_2O)$ value of $-37\%$ for a 165°C fumarole in Field A. At E-san, Mambo and Yoshida (1993) reported $\delta D(H_2O)$ values of $-32\%$ and $-36\%$ for fumaroles showing temperatures of 157 and 185°C, respectively, and Hedenquist and Aoki (1991) reported $\delta D(H_2O)$ values from $-50$ to $-30\%$ for fumaroles at 100 to 225°C. Taking into account that both H$_2$/H$_2$O ratios and $\delta D(H_2O)$ values tend to increase with both outlet temperatures (e.g. Matsuo, 1961; Symonds et al., 1994; Goff and McMurtry, 2000; Botcharnikov et al., 2003) and mixing ratios of magmatic water relative to meteoric water (e.g. Mizutani et al., 1986; Goff and McMurtry, 2000; Botcharnikov et al., 2003), our data on the H$_2$/H$_2$O ratios and the $\delta D(H_2O)$ values (see Table 2) are not unreasonable for those of fumarolic discharges from these volcanoes. The $\delta D(H_2O)$ values imply that local meteoric water also contributed to fumarolic H$_2$O, especially at Kuju. The mixing ratios, however, were always less than 50 %. That is to say, the major portion of fumarolic H$_2$O was magmatic in these fumaroles.

The $\delta D(H_2)$ values in Table 2 were reasonable for those of high-temperature fumarolic discharges. Past studies show that the H$_2$ in fumarolic discharges re-equilibrated with coexisting fumarolic H$_2$O at outlet temperature greater than 400°C (e.g. Bottinga, 1969; Mizutani, 1983). The observed outlet temperatures are presented in Table 1, together with the AET$_D$ calculated from the values of $\delta D(H_2O)$ and $\delta D(H_2)$ in each fumarolic gas sample. Besides, the relation between $10^3\times \ln(a_{H_2O:H_2})$ and AET$_D$ in each fumarolic area is plotted in Fig. 3.

At Tarumae, where the highest outlet temperature of 609°C was recorded in this study, the calculated AET$_D$ was 626°C. These values agree well with each other (Table 1). We
conclude that the re-equilibration via reaction (1.1), almost reached the isotope exchange equilibrium under the outlet temperature of 609°C at this fumarole.

On the other hand, the calculated AET_D (287°C) at E-san was rather different from the observed highest outlet temperature (107°C) in Field X of E-san. This overestimation when fumarole outlet temperatures are <400°C is not inconsistent with the results of other work (see Figure 4). The most probable reason for this overestimation is that the fumarolic gases had been at the AET_D temperature near the surface but were then quenched by some sudden cooling event (such as mixing with meteoric water etc.) just prior to venting from the fumarole (Mizutani, 1983). The highest outlet temperature of 225°C observed in Field Y of E-san (Mambo and Yoshida, 1993) also suggests that the fumarolic gases had been at a temperature of about the AET_D (287°C) near the surface. The reaction rate of equation (1.1) at the lower temperature (107°C) would be too slow to allow re-equilibration.

In case of Kuju, where an outlet temperature of 203°C was recorded in this study, the calculated AET_D (185°C) was similar to the observed outlet temperature (Table 1). We conclude that the reaction (1.1) almost reached the isotope exchange equilibrium at 203°C, even though this temperature is lower than 400°C. With the exception of results from the Showashinzan volcano, previous work shows that for fumarole outlet temperatures of 200 - 400°C there is usually reasonably close agreement of temperature and δD(H_2) values close to the isotope exchange equilibrium with coexisting fumarolic H_2O at the temperatures of outlet (Fig. 4). While the reaction rate of equation (1.1) would be slow below 400°C, the key is probably whether there is sufficient time for re-equilibration before emission, and these results seem to indicate that for this fumarole, there was indeed sufficient time.

In conclusion, we can apply the AET_D as a tracer of temperature to fumaroles with outlet temperatures greater than 200°C. We are able to estimate accurate outlet temperatures for fumaroles having outlet temperatures of more than 400°C from their AET_D. On the other hand, for fumaroles having outlet temperatures of between 200 and 400°C, the quality of the
estimates are dependent on the residence time of the fumarolic fluids/gases within volcano, since the final reduction of temperature at depths until emission from fumaroles. For the fumaroles for which the outlet temperatures is as low as 200°C, for instance, the potential errors of up to 150°C on the calculated AET$_D$ are possible (Fig. 4). For fumaroles having outlet temperatures of less than 200°C, significant deviations from the outlet can be expected. Even for the fumaroles for which the outlet temperatures are less than 200°C, the absolute δD values of fumarolic H$_2$ and their temporal variation can provide important information about the magmatic/hydrothermal system under the volcano. For instance, we can estimate the temperature of fumarolic gases at depths just prior to cooling, from the δD(H$_2$) value (e.g. Mizutani, 1983; Taran et al., 2010). Furthermore, we can detect variations in the temperature of fumarolic gases prior to the cooling by continuous monitoring the δD values of fumarolic H$_2$.

The difference of AET$_D$ from the actual temperatures of the outlets (200–400°C) of fumaroles of Showashinzan volcano reported in the literature may have a different explanation. It is possible that contamination of the δD value by δD(CH$_4$) could be an alternative possible cause. Under this scenario, while H$_2$ attained isotope exchange equilibrium with fumarolic H$_2$O at temperatures as low as 200°C, the contribution of fumarolic CH$_4$ to H$_2$ during δD analysis could have increased the observed δD(H$_2$) values of the 200–400°C fumaroles and thus AET$_D$ (see Appendix for the detail). If so, we could extend our application of AET$_D$ as a tracer of temperature to the fumaroles to reliably predict temperatures at outlet temperatures as low as 200°C, e.g. the Kuju volcano, see above. To verify this possibility, further studies on fumarolic H$_2$ are needed, especially for those in fumaroles showing the outlet temperatures between 200 and 400°C.

4.2 H$_2$ in the Volcanic Plumes
Both concentrations and δD values of H₂ in the plume samples were presented in Table 2, together with the approximate distance to the fumarole from which each plume cloud apparently derived. All the plume samples can be characterized by significant enrichment in H₂. The average H₂ concentration of the plume samples taken apparently within the volcanic plume in each volcano were for Tarumae, 17 ppm (from 0.65 ppm to 47.6 ppm, n = 7), for Kuju 4.6 ppm (from 0.62 ppm to 13.0 ppm, n = 5), for E-san 16 ppm (from 0.49 ppm to 82.9 ppm, n = 7), and 1.2 ppm (from 0.54 ppm to 2.3 ppm, n = 12) for Aso. Those samples taken apparently outside the volcanic plume were 0.51 ppm, 0.53 ppm, 0.53 ppm, and 0.53 ppm respectively. The highest H₂ concentration in each area was always obtained at the sampling points closest to the targeted fumarole, usually at distances less than 1 m. While most of the samples showed significant H₂ enrichment, the air samples taken outside the volcanic plume exhibited H₂ concentrations close to the minimum in each area, indeed close to those in background tropospheric air (ca. 0.5 ppm; Novelli et al., 1999). We concluded that fumarolic H₂ was the source of the excess H₂ in the plume samples. That is to say, variations in the mixing ratios of fumarolic gases within ambient air resulted in the variable H₂ concentrations in the plume samples. The average (maximum) mixing ratios of fumarolic H₂ within the total H₂ of the plume were roughly estimated to be 97 (99)% at Tarumae, 89 (96)% at Kuju, 97 (99)% at E-san, and 59 (78)% at Aso, assuming that the excess H₂ corresponds to fumarolic H₂ in each plume sample.

This conclusion was also supported by the δD values of the H₂ in the plume samples. As shown in Figure 5, the reciprocal of the H₂ concentration in the plume samples showed a good linear relationship with the δD values. Similar linear relationships between the reciprocal of concentrations and their isotopic compositions were recognized in H₂ from urban atmospheres (Gerst and Quay, 2001). The linear relationships suggested that both the concentrations and the δD values of H₂ in the samples from each site can be explained by simple mixing between two end-members, both of which can be classified to a single category at least for the δD
values of H₂ (e.g. Keeling, 1958; Tsunogai et al., 1998; Tsunogai et al., 2003; Tsunogai et al., 2005; Tsunogai et al., 2010). Furthermore, the H₂-depleted end-member seems to be almost common irrespective of the volcano under study, showing an H₂ concentration of ca. 0.5 ppm and D-enriched δD values of around +100 ‰. The H₂-depleted end-member must be H₂ in background tropospheric air, certainly both compare well with literature values (Gerst and Quay, 2001; Rice et al., 2010). On the other hand, the H₂-enriched end-member containing highly D-depleted H₂ (compared to background tropospheric H₂) must be the fumarolic H₂, because fumarolic H₂ are always characterized by lower δD values than those in the tropospheric H₂ (Table 1).

By extrapolating the linear relationship between 1/H₂ and δD to 1/H₂ = 0 to exclude the contribution of the tropospheric H₂ (the H₂-depleted end-member) from the δD value of each sample (e.g. Keeling, 1958; Tsunogai et al., 2003), we estimated the δD values of fumarolic H₂ (the H₂-enriched end-member) to be −260 ± 30‰ at Tarumae, −509 ± 23‰ at Kuju, and −437 ± 14‰ at E-san (Fig. 5) through the least squares fitting of strait lines. Because the data errors were variable especially in 1/[H₂], we fitted each line taking into account the differences in the errors (York, 1966).

The 1/H₂ values of the fumarolic H₂ were larger than 0, which means that the δD values of the H₂-enriched end-members must be larger than the δD values estimated. The 1/H₂ values of the fumarolic H₂ were around 10⁻¹ (ppm⁻¹) and the slopes of the linear fitted relationships (Fig. 5) were always less than +500‰ per ppm⁻¹ so that the differences were less than 0.05‰. As a result, we disregarded this difference and used 0 for the 1/H₂ value of the H₂-enriched end-members.

The estimated δD values of Tarumae, Kuju, and E-san corresponded to those in each fumarolic H₂ within the error of the fitting (Fig. 5). We concluded that each fumarolic H₂ was the only source of the excess H₂ in each volcanic plume. Furthermore, δD values of fumarolic H₂ were always quenched in volcanic plume without interactions with the other components,
including H$_2$O in volcanic plume, during mixing with ambient air, hence holding the same $\delta$D values as those at the fumarole. As a result, we can deduce the $\delta$D value of fumarolic H$_2$ without sampling of fumarolic gases directly, by determining both the concentrations and the $\delta$D values of H$_2$ in its volcanic plume and correcting the contribution of the tropospheric H$_2$ from the $\delta$D values as we did in Tarumae, Kuju, and E-san.

It is possible that each volcanic plume cloud derived from not one (targeted) fumarole, but from many fumaroles located in each fumarolic area. That is to say, the excess H$_2$ in the plume samples could comprise most of the fumarolic H$_2$ from nearby fumaroles. This could lead to heterogeneities in the outlet temperatures in a fumarolic area, which could change the $\delta$D values of fumarolic H$_2$ estimated from the plume.

However, as shown above, each end-member $\delta$D value estimated from the plume H$_2$ corresponded to those of the targeted fumarole (Fig. 5). Furthermore, all the plume samples showed good linear correlation on the mixing line (Fig. 5). As a result, contribution of fumarolic H$_2$ from the nearby low temperature fumaroles seems to be minimal. This is especially true at Kuju and E-san, probably because of the depletion of H$_2$ in the low temperature fumaroles (e.g. Giggenbach, 1987; Symonds et al., 1994; Taran et al., 1995). It is also possible that the emission fluxes might be smaller from the low temperature fumaroles than the targeted ones. In conclusion, we have shown that the end-member $\delta$D value deduced from the plume H$_2$ is close to the $\delta$D value of H$_2$ in the fumarole showing highest outlet temperature in each fumarolic area.

4.3 Application to Remote Temperature Sensing on the Aso Volcano

By extrapolating the linear relationship between 1/H$_2$ and $\delta$D in the plume samples taken at Aso to 1/H$_2$ = 0, we estimated the average $\delta$D value of fumarolic H$_2$ to be $-172 \pm 16\%$ (Fig. 5). The $\delta$D value of fumarolic H$_2$ was much higher than that of the 609°C fumarole at Tarumae ($-247 \%$), but much lower than that of the tropospheric H$_2$. We concluded that the
major source of the excess H$_2$ in the volcanic plume were the fumaroles at the bottom of the crater. By applying the average $\delta$D value of magmatic H$_2$O obtained from the active volcanoes in convergent margins (−24.5 ± 7.3‰) (the average and the 1 σ dispersion range of the fumarolic H$_2$O in high temperature fumaroles on convergent-plate volcanoes; Giggenbach, 1992), we estimated the AET$_D$ of the Aso fumaroles to be 868 ± 97°C. While the range of $\delta$D value applied to the fumarolic H$_2$O in Aso was assumed from the high-temperature fumaroles in the volcanoes on convergent margins worldwide, the value is reasonable for H$_2$O in such locally occurring high-temperature fumaroles as well. This includes those in high-temperature fumaroles of nearby volcanoes within the possible variation range, such as those at the Satsuma-Iwojima volcano showing an outlet temperature more than 800°C (from −31 to −23‰; Shinohara et al., 2002), and at the Kuju volcano, showing the outlet temperatures of more than 480°C (−18.9 ‰ and −17.0‰; Mizutani et al., 1986).

Neither direct sampling of fumarolic gases nor direct measurement of fumarolic temperatures have been practical in the deep crater of Aso. Instead, remote sensing has been employed at the crater edge in past studies, at distances of about 200 m from the fumarolic area (Mori and Notsu, 1997; Saito et al., 2005; Furukawa, 2010; Shinohara et al., 2010). The highest temperature of the fumarolic area at Aso (Fig. 2), has been monitored periodically (at least monthly) by the Japan Metrological Agency (JMA) since 1993 using a dedicated IR thermometer (operating at wavelengths of 8–13 µm). That work reported that the outlet temperature was ca. 300°C in Nov., 2010 when we took our plume samples (Japan Meteorological Agency, 2010). Although the highest temperature of the fumarolic area at the Aso volcano as determined by JMA has varied widely in past, showing the maximum of ca. 500°C in 2003 and 2009, and a minimum of less than 100°C in 1999 and 2006. It is true though, that the highest temperature determined by JMA was much lower than the AET$_D$ we estimated from the fumarolic area.
On the other hand, some glowing spots (red glow) have been observed with the unaided human eye at night in the fumarolic area at times since November 2000. Given this, the temperature of the red glow must be more than 500°C (Saito et al., 2005). The latest observation of red glow prior to our sampling was in May, 2010. Therefore, that the temperatures determined by JMA (e.g. 350°C in May, 2010) must be lower than the actual outlet, by at least 150°C. Furthermore, Mori and Notsu (2008) determined CO/CO₂ ratios of the fumarolic gases at the Aso volcano remotely using FT-IR on six occasions from 1996 to 2003, and estimated the equilibrium temperature of fumarolic gases was almost stable at 670°C to 870°C, using the empirical relation between the equilibrium temperatures and CO/CO₂ ratios in the fumarolic gases. Shinohara et al. (2010) also obtained similar equilibrium temperatures from 750°C to 950°C for the fumarolic gases during the observations from 2006 and 2009 using both H₂/H₂O ratios and SO₂/H₂S ratios in the volcanic plume determined by using a portable multi-sensor system (Shinohara, 2005). Although the equilibrium temperatures could be higher than the outlet to some extent (e.g. Symonds et al., 1994), both the presence of the red glow only 5 months before and the equilibrium temperatures close to the AET_D suggest that the calculated AET_D was a reasonable estimate of the fumarole outlet temperatures.

The azimuthal resolution of the IR thermometer of JMA is 1°, and this corresponds to a spatial resolution of more than 1 m at their measurements at the distance of ca. 200 m from the fumarolic area. The dimension of each fumarole at the surface must be much less than 1 m (Furukawa, 2010), so that the lower spatial resolution as compared to the dimension of each fumarole is likely to be responsible for the lower temperatures in the IR thermometer measurements of JMA. This hypothesis is also supported by the observation on the fumarolic area using a high resolution IR thermometer having ca. two order of magnitude better resolution than that of JMA instrument (Saito et al., 2005). The highest temperature of up to 800°C was detected on November 2003 (Saito et al., 2005), when the highest temperature...
determined by JMA was only 350°C. Although the estimated temperatures using the high
resolution IR thermometer decreased to less than 500°C in September 2003, and less than
300°C in March 2005 (Furukawa, 2010), we concluded that the AET<sub>D</sub> (868 ± 97°C in Nov.
2010) represented the highest outlet temperature of the fumaroles at Aso and that further
reduction in the dimensions of the fumaroles at the surface has been responsible for the
declines in the temperatures determined by using the high-resolution IR thermometer since
September 2003. That is to say, temporal variation in the dimensions of fumaroles at surface,
probably because of variation in the emission flux of fumarolic gases, was responsible for the
temporal variation in the temperature determined by the IR thermometers, as well as the
appearance/disappearance of the red glow. Hence we conclude that the actual outlet
temperature of the Aso fumaroles keeps the temperature close to the chemical equilibrium
temperature between H<sub>2</sub>-H<sub>2</sub>O, SO<sub>2</sub>-H<sub>2</sub>S, and CO-CO<sub>2</sub>. These features of the fumarolic area at
the Aso volcano resemble those at the Satsuma-Iwojima volcano, which is characterized by
the continuous, long-term emission of volcanic gases from the fumaroles. The highest outlet
temperatures vary very little being around 850°C (e.g. Shinohara et al., 1993), and also have
the accompanying “red glows” on the fumarolic area.

4.4 Application to Remote Temperature Sensing on Volcanic Fumaroles in general
Our observations on the Aso plume suggest that the average δD value of fumarolic H<sub>2</sub>
for a fumarolic area should be amenable to estimation with a similar precision as that at Aso
(less than ±20‰) from those in the plume, provided the plume is enriched in H<sub>2</sub> to a similar
degree as is the Aso plume (from 0.54 ppm to 2.3 ppm). This means that the excess H<sub>2</sub> (i.e.
the fumarolic H<sub>2</sub>) occupies 59 % (on average) and 78 % (maximum) of total H<sub>2</sub> in the plume.
The observed H<sub>2</sub> enrichment in the Aso plume was not a special characteristic limited to Aso,
but is fairly general. For example, the average excess H<sub>2</sub> in comparison with the ambient
atmospheric H<sub>2</sub> in the July 29, 1980 plume (non-eruptive) of Mount St. Helens, for instance,
was +0.59 ppm at 16 km downwind from the fumarolic area (McGee, 1992), so that the average mixing ratio of fumarolic H\(_2\) within total H\(_2\) in the plume was greater than 50 \% (calculated assuming the H\(_2\) concentration of ambient air to be 0.5 ppm H\(_2\); Novelli et al., 1999). Because the average mixing ratio is very similar to that in the Aso plume samples we obtained in this study, we could estimate the \(\delta D\) values of fumarolic H\(_2\) of Mount St. Helens precisely, with a similar precision to that at Aso (± 16\%), if we had sampled the plume of Mount St. Helens at the distances of 16 km downwind from the fumarolic area and determined both concentrations and \(\delta D\) values of H\(_2\) in the plume in 1980.

Sufficient H\(_2\) enrichment in volcanic plumes derived from high-temperature volcanic fumaroles is a promising way ahead. The H\(_2\)/H\(_2\)O ratio in the fumarolic gases at Aso, estimated from those in the plume to be \(10^3\) to \(10^4\) \(\mu\text{mol/mol}\) (Shinohara et al., 2010), can be classified as having a lower H\(_2\)/H\(_2\)O ratio than most of the high-temperature fumarolic gases in world volcanoes, such as St. Augustine (5,800 \(\mu\text{mol/mol}\)), Etna (11,000 \(\mu\text{mol/mol}\)), Merapi (12,000 \(\mu\text{mol/mol}\)), Momotombo (4,700 \(\mu\text{mol/mol}\)), St. Helens (5,300 \(\mu\text{mol/mol}\)), Poas (5,800 \(\mu\text{mol/mol}\)), Showashinzan (1,900 \(\mu\text{mol/mol}\)), Usu (3,200 \(\mu\text{mol/mol}\)), Ardoukoba (22,000 \(\mu\text{mol/mol}\)), Erta’ Ale (22,000 \(\mu\text{mol/mol}\)), Nyiragongo (34,000 \(\mu\text{mol/mol}\)), Surtsey (27,000 \(\mu\text{mol/mol}\)), Kilauea summit lava lake (15,000 \(\mu\text{mol/mol}\)), and Kilauea East Rift Zone (12,000 \(\mu\text{mol/mol}\)), [mean values of those compiled in Symonds et al. (1994)]. Thus, as far as the extent of dilution by ambient air is the similar, we can anticipate similar H\(_2\) enrichment (more than a 50% contribution of fumarolic H\(_2\) in the plume H\(_2\) on average) in a typical volcanic plume.

In the case of low temperature fumaroles, the concentrations of fumarolic H\(_2\) are small in general (e.g. Giggenbach, 1987; Symonds et al., 1994; Taran et al., 1995). As a result, the estimation on fumarolic \(\delta D(H_2)\) from H\(_2\) in the volcanic plume might be difficult for them because of the small H\(_2\) enrichment in the plume. However, even if the plume is too depleted in H\(_2\) at the point where it is safe enough to sample by hand, recent advances in remote
sampling tools such as manned aerial vehicles (e.g. Fiske and Sigurdsson, 1982; Shinohara et al., 2003; Wardell et al., 2004), unmanned aerial vehicles (e.g. Saiki and Ohba, 2010), balloons (e.g. Belousov and Belousova, 2004), and robots (e.g. Muscato et al., 2003) could be utilized to take more concentrated samples in places where people cannot safely go.

In the case of high temperature fumaroles, care must be taken when the variation in $\delta^D$ values under the isotope exchange equilibrium becomes relatively insensitive to temperature variation, especially for those having temperatures exceed 1,000 °C (Fig. 3). That is to say, variations in $\delta^D(H_2)$ values in response to the same degree of temperature variation becomes relatively smaller at higher temperatures. In the case of Aso, for instance, we estimated the outlet temperature (868 °C) within an error of 97°C. By using both the fumarolic $\delta^D(H_2)$ with an error of 16‰ and the fumarolic $\delta^D(H_2O)$ with an error of 7.3‰ (see section 4.3 for the detail). Even if we determined both $\delta^D(H_2)$ and $\delta^D(H_2O)$ in a fumarole with the same degree of errors as those in the case of Aso ($\pm 16\%$ and $\pm 7.3\%$, respectively), the error accompanied in its estimated temperature would be ca. $\pm 120$ °C when the outlet temperature was 1,000 °C, and ca. $\pm 170$ °C when the outlet temperature was 1,200 °C. As a result, for the fumaroles having elevated outlet temperatures, we have to estimate fumarolic $\delta^D(H_2)$ more precisely from $H_2$ in the volcanic plume, to attain a similar precision to that of with Aso (smaller than $\pm 100$ °C). For instance, precisions smaller than $11\%$ and $6\%$ are needed for 1,000 °C and 1,200 °C fumaroles, respectively, to attain a similar precisions to those of Aso. The concentrations of fumarolic $H_2$ are large in general in the high temperature fumaroles (e.g. Giggenbach, 1987; Symonds et al., 1994; Taran et al., 1995). As a result, precise estimation of fumarolic $\delta^D(H_2)$ from $H_2$ in the volcanic plume might be possible.

In addition to the problem of insensitivity to temperature variation in the high temperature region, care must be taken because no reliable fractionation factors are available at temperatures greater than 1,300 °C (Richet et al., 1977). To apply HIReTS to fumaroles having temperatures greater than 1,300 °C, we must calculate/estimate equilibrium
fractionation factors for the temperatures greater than 1,300 °C. However, 1,300 °C is sufficient as the upper limit to determine the temperature for most of the volcanic fumaroles throughout the world.

The δD value of fumarolic H\textsubscript{2} estimated from plume samples will enable us to estimate the highest outlet temperature of the fumaroles of interest if the temperature exceed 400 °C, assuming the isotope exchange equilibrium between the fumarolic H\textsubscript{2} and fumarolic H\textsubscript{2}O. For the estimation of temperature, however, data on the δD value of fumarolic H\textsubscript{2}O is also essential. In contrast to H\textsubscript{2}, it is rather difficult to estimate δD value of fumarolic H\textsubscript{2}O from the plume because the concentration of H\textsubscript{2}O in background air is much higher than that of H\textsubscript{2}, about 10\textsuperscript{3} to 10\textsuperscript{4} ppm is usual. Furthermore, both concentrations and δD values of H\textsubscript{2}O in air can be quite varied. Based on the knowledge obtained on the fumarolic H\textsubscript{2}O from past studies, however, we can estimate the value precisely in several ways outlined below.

In case of fumarolic H\textsubscript{2}O in high-temperature magmatic discharges on convergent-plate volcanoes, we can assume an approximate δD value from the literature to be –24.5±7.3‰ (the average and the 1 σ variation range of the fumarolic H\textsubscript{2}O in high-temperature fumaroles on convergent-plate volcanoes; Giggenbach, 1992). This is the same data previously applied to Aso in section 4.3. It may be that such a general δD value for H\textsubscript{2}O cannot be applied to the fumarolic H\textsubscript{2}O studied. However, because H\textsubscript{2}O is the major component in most fumarolic fluids and the alternative end-member is local meteoric water, we can restrict the most extreme δD value from the magmatic fluids to that of local meteoric water (Giggenbach, 1992; Goff and McMurtry, 2000). Furthermore, because H\textsubscript{2}O is the major component in fumarolic gases that have fumarolic H\textsubscript{2}/H\textsubscript{2}O ratios less than 0.04 (e.g. Symonds et al., 1994), typical variation range of δD values in fumarolic H\textsubscript{2}O are much narrower than that of fumarolic H\textsubscript{2} (e.g. Bottinga, 1969; Mizutani, 1983; Giggenbach, 1992; Taran et al., 1995; Kiyosu and Okamoto, 1998; Goff and McMurtry, 2000; Taran et al., 2010). As a result, we can approximate the δD values of fumarolic H\textsubscript{2}O to be uniform irrespective of variations in
the temperature of fumaroles. In the case of the decline in temperature over time shown at
Showashinzan and Nasudake, which was discussed in section 1, for example, while $\delta D(H_2)$
decayed at the rates of $-1.9 \pm 1.0\%/yr$ at Showashinzan and $-12.9 \pm 2.5\%/yr$ at Nasudake,
$\delta D(H_2O)$ showed little variation, with values of $-0.4 \pm 0.8 \%/yr$ and $-1.8 \pm 1.0 \%/yr$,
respectively (Mizutani, 1983). Hence, it may be that if some past data on the $\delta D(H_2O)$ were
available for a particular fumarolic area, the values could be applicable to the present as well.
It may also be that we could use the $\delta D$ value of magmatic H$_2$O estimated for the volcano
using alternative methods: such as measuring that found in fresh volcanic rocks (e.g. Newman
et al., 1983; Taylor et al., 1983; Kusakabe et al., 1999). Furthermore, H$_2$ data alone is
sufficient to estimate relative temperature variation. In conclusion, we can remotely estimate
the temperature of the fumaroles (or at least for their temporal variations) at a distance based
only on H$_2$ in the plume.

4.5 Comparison with the Traditional Methods

Our method using Hydrogen Isotopes for Remote Temperature Sensing (HIReTS) has
significant advantages over traditional remote sensing methods, e.g. using IR radiation. The
described method in particular overcomes the problems of remote and accurate temperature
measurement of fumaroles that have small dimensions, or to which there is no direct
line-of-sight, as shown in section 4.3 for Aso. In contrast to some of the IR thermometers,
which cannot determine temperature during daytime (Saito et al., 2005), it is possible to
determine the temperature at any time, day or night, using HIReTS. Furthermore, field work
at volcanoes becomes simpler: one just needs to bring more than a few evacuated 300 mL
glass bottles (200 g for each) to a point downstream of the fumarolic area and open the seal.

Most of the advantages of HIReTS described above are applicable to the other remote
temperature sensing methods that determine the chemical compositions of fumarolic gases
remotely and estimate the equilibrium temperature (e.g. Mori and Notsu, 1997; Shinohara,
In practice, however, it is difficult to deduce accurate and precise fumarolic concentrations for all of the components of the chemical equilibrium from those in the plume. This is especially true when the measurements on the plume are being done at a distance from the fumarolic area (Symonds et al., 1994). As a result, the estimate of equilibrium temperature comes with significant errors (e.g. ±150 to ±200°C; Mori and Notsu (2008)). Furthermore, the equilibrium temperature is the temperature at depth - potentially somewhat higher than that at the outlet (e.g. Symonds et al., 1994). While the information on the equilibrium temperature is useful in many respects, HIReTS is preferable to determine the outlet temperature of fumaroles remotely.

On the other hand, the disadvantage of using HIReTS compared to the traditional methods is the time needed to determine temperature. While most of the IR thermometers can determine the temperature on site, the HIReTS methodology needs more than a few days to estimate temperature for a fumarolic area subsequent to the field and laboratory work. Also, to avoid potentially large errors (see section 4.1), prior to applying HIReTS, we would have to verify the fumarolic temperature to be more than 400°C (or at least more than 200°C), using some alternative method, such as a traditional IR thermometer. Furthermore, ambiguity in the δD values of fumarolic H₂O could reduce the accuracy of the absolute temperature obtained from HIReTS in some volcanoes.

In conclusion, HIReTS can be a better or only choice for remote temperature sensing of fumaroles in many volcanoes, but care must be exercised because each applications is likely to be different. It would be better to combine HIReTS with the other traditional methods during the actual temperature sensing in field. Moreover, to be certain of collecting plume samples enriched in H₂, it might be preferable to measure H₂ concentration real-time during the field work at volcanoes, applying some portable sensors (Shinohara et al., 2010).

5. CONCLUSIONS
For a fumarolic area in a volcano having outlet temperatures of more than 400°C, we can remotely estimate an accurate temperature of the fumaroles by using HIReTS developed in this study. This method estimates the $\delta$D value of fumarolic $H_2$ from those in the plume. It is possible that HIReTS can be expanded to temperatures as low as 200°C in the future, although it will depend on the results of further studies on fumarolic $H_2$. HIReTS can be a better or indeed the only choice for accurate remote temperature sensing of fumaroles at many volcanoes. Furthermore, even for fumaroles showing temperatures lower than the HIReTS lower limit, we can obtain novel information concerning the magmatic/hydrothermal systems under the volcano. However, as we have to presume the $\delta$D value of fumarolic $H_2O$ without actual measurement to obtain absolute temperature of these fumaroles using HIReTS, the accuracy of temperatures estimated by HIReTS could be worse for fumaroles for which we cannot presume accurate $\delta$D values for fumarolic $H_2O$.

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APPENDIX

The data set on \( \text{AET}_D \) in high-temperature volcanic fumaroles used in this study (Fig. 4) was compiled from past work and did not include the \( \text{AET}_D \) data from the Kuju volcano reported by Mizutani (1983), in which the \( \text{AET}_D \) estimated at the Kuju volcano were very different from that at the outlet. The observed outlet temperature was 151°C, but \( \text{AET}_D \) was 790°C, in 1964. While Mizutani (1983) proposed that the \( \text{AET}_D \) represented the elevated temperature in the gas reservoir at depth below the Kuju volcano, we concluded that the values were affected by artifacts and hence removed them from the figures and discussions of this paper. Our reasons for this were:

1. The \( \delta D \) values of fumarolic \( \text{H}_2 \) reported for the same Field A in Mizutani (1983) showed significant deviation from those that we determined in this study (2010).

2. Because of the little apparent variation in Field A of the Kuju volcano since 1964, (highest outlet temperatures were 183°C in 1964, 214°C in 1984, 200°C in 2000, and 203°C in this study; Mizutani et al., 1986; Amita and Ohsawa, 2003), it is difficult to attribute such significant variation in the \( \delta D \) values of fumarolic \( \text{H}_2 \) between Mizutani (1983) and this study to temporal variation in the fumarolic \( \text{H}_2 \).

The most important difference between Mizutani (1983) and this study is the analytical method employed to determine the \( \delta D(\text{H}_2) \) values. While our method did not include gases other than \( \text{H}_2 \) in the determined \( \delta D(\text{H}_2) \) values, the \( \delta D(\text{H}_2) \) values used by Mizutani (1983) was the total \( \delta D \) value of the gases that had not dissolved in NaOH solution during sampling. These gases included \( \text{H}_2, \text{N}_2, \text{CO}, \text{Ar}, \text{He}, \text{and CH}_4 \). As a result, the differences of the \( \delta D(\text{H}_2) \) value produced by the method would be significant if the fumarolic gases contained elevated \( \text{CH}_4 \) relative to \( \text{H}_2 \). While Mizutani (1983) disregarded this possibility based on analytical results from only one fumarolic gas sample taken at a fumarole in Field C of the Kuju volcano in 1961 that showed an outlet temperature of 400°C and a \( \text{CH}_4/\text{H}_2 \) ratio of 0.0014. We
concluded that the actual CH₄/H₂ ratios of the samples, for which Mizutani (1983) determined δD(H₂) values, were much higher than 0.0014 and that the δD(H₂) value was contaminated by CH₄, and this was responsible for the elevated δD(H₂) values reported in that work. Our reasons for thinking this are:

(1) While the sample showing the CH₄/H₂ ratio of 0.0014 was taken at 1961, the samples for which Mizutani (1983) determined the δD values of H₂ were taken during 1964 to 1967. Because the CH₄/H₂ ratios at the fumaroles on the Kuju volcano increased to 0.04–2.0 in their subsequent observation on August 1984 (Mizutani et al., 1986), the CH₄/H₂ ratios during 1964 to 1967 would have been much larger than 0.0014.

(2) While the sample showing the low CH₄/H₂ ratio of 0.0014 was taken at a fumarole with an outlet temperature of 400°C, the samples for which Mizutani (1983) determined the δD values of H₂ were taken at fumaroles with outlet temperatures from 121 to 360°C. Because the CH₄/H₂ ratios at Kuju tended to increase in proportionally with the decrease in the outlet temperatures (the CH₄/H₂ ratio of a fumarole showing an outlet temperature of 170°C in 1984, for example, was 2.0; Mizutani et al., 1986), the samples for which he determined δD(H₂) values could have more elevated CH₄/H₂ ratios.

(3) Because the δD(CH₄) value is much higher than δD(H₂) value under the hydrogen isotope exchange equilibrium (Richet et al., 1977), contamination of fumarolic H₂ by fumarolic CH₄ might enhance observed δD(H₂) values and thus AETₐ.

To test our hypothesis, we recalculated the δD(H₂) value and AETₐ for the 151°C fumarole; using 2 for the actual CH₄/H₂ ratio (that of a 170°C fumarole at Kuju determined in 1984) and −100 ‰ for the δD(CH₄) value (the δD value of CH₄ in deep-sea hydrothermal fluids; Welhan and Craig, 1983). The δD(CH₄) value also corresponds to the δD(CH₄) value that is at isotope exchange equilibrium with coexisting fumarolic H₂O at 600°C. While Mizutani (1983) determined the δD(H₂) value of this fumarole to be −185‰ and the AETₐ
790°C, the recalculated $\delta D(H_2)$ value became $-525\%o$, and the recalculated $AET_D$ became 175°C; almost corresponding to the outlet (151°C). Thus, we concluded that all the $\delta D(H_2)$ values of Kuju in Mizutani (1983) were affected by artifacts, such as contamination of CH$_4$ to the $\delta D(H_2)$ values.

The problems on the CH$_4$ contamination could also have impacted some past $\delta D(H_2)$ data of low temperature fumaroles (< 400°C), such as those in the Showashinzan volcano. The $AET_D$ in the 200–400°C fumaroles correspond to the outlet in most of the volcanoes, except the Showashinzan volcano (see Fig. 4). While the $\delta D(H_2)$ data included fumaroles showing outlet temperatures less than 400°C (Mizutani, 1983), data on the CH$_4$/H$_2$ ratio were from those of more than 500°C in the volcano (Mizutani and Sugiura, 1982). Because $\delta D(CH_4)$ is much higher than the $\delta D(H_2)$ under the isotope exchange equilibrium as stated above, CH$_4$ contamination is likely to be responsible for the overestimated $AET_D$ as well.

Differ from the Kuju volcano, however, it is difficult to verify $\delta D(H_2)$ again in the Showashinzan volcano at present. As a result, further studies on the other volcanoes are needed to compare the $AET_D$ with the outlet temperatures of the fumaroles showing 200–400°C, as presented in section 4.2.
Table 1
Chemical and isotopic compositions of fumarolic gas samples, together with apparent equilibrium temperature calculated for $\delta$D(H$_2$O) and $\delta$D(H$_2$) ($AET_D$).

<table>
<thead>
<tr>
<th></th>
<th>temp. (°C)</th>
<th>H$_2$/H$_2$O (µmol/mol)</th>
<th>$\delta$D(H$_2$O) (%)</th>
<th>$\delta$D(H$_2$) (%)</th>
<th>$AET_D$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tarumae  Vent A</td>
<td>609</td>
<td>811</td>
<td>-33.4</td>
<td>-247.0 ±0.6</td>
<td>626</td>
</tr>
<tr>
<td>Kuju     Field A</td>
<td>203</td>
<td>47</td>
<td>-44.3 ±1.0</td>
<td>-527.7 ±10.1</td>
<td>185</td>
</tr>
<tr>
<td>E-san   X field</td>
<td>107</td>
<td>18</td>
<td>-35.3</td>
<td>-432.1 ±2.5</td>
<td>287</td>
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Table 2
Chemical and isotopic compositions of H$_2$ in volcanic plume samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>distance* (m)</th>
<th>H$_2$ (ppm)</th>
<th>$\delta$D(H$_2$) (%)</th>
<th>Remark</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TA-01</td>
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<td>0.51</td>
<td>+86.2</td>
<td>Background air</td>
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<td>TA-02</td>
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<td>-187.3</td>
<td></td>
</tr>
<tr>
<td>H-16</td>
<td>15</td>
<td>12.5</td>
<td>-244.7</td>
<td></td>
</tr>
<tr>
<td>K-13</td>
<td>8</td>
<td>34.3</td>
<td>-243.3</td>
<td></td>
</tr>
<tr>
<td>H-91</td>
<td>3</td>
<td>19.0</td>
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<td></td>
</tr>
<tr>
<td>H-89</td>
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<td>2.1</td>
<td>-219.1</td>
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</tr>
<tr>
<td>K-07</td>
<td>1</td>
<td>47.6</td>
<td>-226.3</td>
<td></td>
</tr>
<tr>
<td>H-87</td>
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<td>-40.8</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>0.53</td>
<td>+61.9</td>
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</tr>
<tr>
<td>K-10</td>
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<td>0.62</td>
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<td>H-28</td>
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<td>E-san volcano</td>
</tr>
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<td>0.89</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td>-435.1</td>
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<td></td>
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<td>ASO-C07</td>
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</tr>
<tr>
<td>ASO-C08</td>
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<td>-99.5</td>
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<td>-99.6</td>
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<td>0.94</td>
<td>-45.7</td>
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</table>

* approximate distance from the targeted fumarole.
# the sampling point shown in Fig. 2.
Fig. 1
A map showing the location of the study volcanoes.
Fig. 2
A topographic map showing the summit area of Mt. Naka-dake, Aso volcano, together with the sampling points of the volcanic plume samples shown by the solid circles (points A to F) and the major wind direction during sampling. The open circle on the south-eastern part of the Crater 1 shows the location of the major fumarolic area.
Fig. 3
Relationships between the apparent equilibrium temperature assuming hydrogen isotope exchange equilibrium between H$_2$O and H$_2$ (AET$_D$) and the value of 1000 ln\(\{\delta D_{\text{H}_2O}+1\}/(\delta D_{\text{H}_2}+1)\}\), estimated from the fractionation factors in Richet et al. (1977).
Fig. 4
The calculated temperatures assuming isotope exchange equilibrium between $\text{H}_2$ and $\text{H}_2\text{O}$ in fumarolic gases ($\text{AET}_D$) determined in this study (black circle: Tarumae, black square: Kuju, black triangle: E-san) plotted as a function of the outlet temperatures of fumaroles, together with those determined in Mizutani (1983) (open circles: Showashinzan, open squares: Nasudake, open triangles: Yakedake), except for Kuju in the literature (see Appendix for the rationale).
Fig. 5
Relationship between δD of H₂ and the reciprocal of H₂ concentration in the volcanic plume of Tarumae (a), Kuju (b), E-san (c), and Aso (d) (open circles), together with those in each fumarole (solid circles). Each solid line is the least squares fitting of the plume samples, while each dotted line is the 2σ variation envelop of the fitting line.
References:


Mizutani Y. and Sugiura T. (1982) Variations in chemical and isotopic composition of


