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Author(s)	Tsunogai, Urumu; Kamimura, Kanae; Anzai, Saya; Nakagawa, Fumiko; Komatsu, Daisuke D.
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Hydrogen isotopes in volcanic plumes: tracers for remote temperature sensing of fumaroles

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Urumu Tsunogai*, Kanae Kamimura, Saya Anzai, Fumiko Nakagawa, and Daisuke D. Komatsu

Earth and Planetary System Science, Faculty of Science, Hokkaido University
N10 W8, Kita-ku, Sapporo 060-0810, Japan

* Corresponding author. E-mail: urumu@mail.sci.hokudai.ac.jp; Tel: +81-11-706-3586; Fax: +81-11-746-0394

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1 **Abstract**

2 In high-temperature volcanic fumaroles ($>400^{\circ}\text{C}$), the isotopic composition of molecular
3 hydrogen (H_2) reaches equilibrium with that of the fumarolic H_2O . In this study, we used this
4 hydrogen isotope exchange equilibrium of fumarolic H_2 as a tracer for the remote temperature
5 at volcanic fumaroles. In this remote sensing, we deduced the hydrogen isotopic composition
6 (δD value) of fumarolic H_2 from those in the volcanic plume. To ascertain that we can
7 estimate the δD value of fumarolic H_2 from those in a volcanic plume, we estimated the
8 values in three fumaroles with outlet temperatures of 630°C (Tarumae), 203°C (Kuju), and
9 107°C (E-san). For this we measured the concentration and δD value of H_2 in each volcanic
10 plume, along with those determined directly at each fumarole. The average and maximum
11 mixing ratios of fumarolic H_2 within a plume's total H_2 were 97 % and 99 % (at Tarumae),
12 89 % and 96 % (at Kuju), and 97 % and 99 % (at E-san). We found a linear relationship
13 between the depletion in the δD values of H_2 , with the reciprocal of H_2 concentration.
14 Furthermore, the estimated end-member δD value for each H_2 -enriched component
15 ($-260\pm 30\text{‰}$ vs. VSMOW in Tarumae, $-509\pm 23\text{‰}$ in Kuju, and $-437\pm 14\text{‰}$ in E-san)
16 coincided well with those observed at each fumarole ($-247.0\pm 0.6\text{‰}$ in Tarumae,
17 $-527.7\pm 10.1\text{‰}$ in Kuju, and $-432.1\pm 2.5\text{‰}$ in E-san). Moreover, the calculated isotopic
18 temperatures at the fumaroles agreed to within 20°C with the observed outlet temperature at
19 Tarumae and Kuju. We deduced that the δD value of the fumarolic H_2 was quenched within
20 the volcanic plume. This enabled us to remotely estimate these in the fumarole, and thus the
21 outlet temperature of fumaroles, at least for those having the outlet temperatures more than
22 400°C . By applying this methodology to the volcanic plume emitted from the Crater 1 of Mt.
23 Naka-dake (the volcano Aso) where direct measurement on fumaroles was impractical, we
24 estimated that the δD value of the fumarolic H_2 to be $-172\pm 16\text{‰}$ and the outlet temperature to
25 be $868\pm 97^{\circ}\text{C}$. The remote temperature sensing using hydrogen isotopes developed in this
26 study is widely applicable to many volcanic systems.

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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 Kagiya, 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. H₂O and CO₂) 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.

53 Because of rapid reactions between fumarolic components at high temperatures,
 54 fumarolic gases often attain chemical and isotopic equilibrium close to the outlet (*e.g.* Ellis,
 55 1957; Matsuo, 1961; Giggenbach, 1987; Shinohara *et al.*, 1993; Ohba *et al.*, 1994; Symonds
 56 *et al.*, 1994). In particular, for the hydrogen isotope exchange reaction between H₂O and H₂ in
 57 fumaroles at outlet temperatures greater than 400°C, the calculated isotope temperatures
 58 (assuming hydrogen isotope exchange equilibrium between H₂O and H₂; see section 3.3 for
 59 the details of the calculation) were close to the actual outlet temperatures (*e.g.* Bottinga, 1969;
 60 Mizutani, 1983; Kiyosu and Okamoto, 1998; Taran *et al.*, 2010).



62 For example, the fumarole outlet temperatures of both the Showashinzan and Nasudake
 63 volcanoes have declined, from 800°C in 1954 to 617°C in 1977, and from 489°C in 1960 to
 64 277°C in 1969, respectively. Consistent with these declines, the calculated isotope
 65 temperatures also declined, from 750°C to 630°C at Showashinzan and from 470°C to 290°C
 66 at Nasudake (Mizutani, 1983). A similar agreement between the calculated isotope
 67 temperatures and the outlet was found in subaerial/submarine hydrothermal fluids showing
 68 the temperatures more than 200–300 °C (*e.g.* Kiyosu, 1983; Welhan and Craig, 1983;
 69 Proskurowski *et al.*, 2006; Kawagucci *et al.*, 2010). These past observations of fumarolic H₂
 70 suggest that the isotope exchange reaction is rapid enough at the outlet temperature to
 71 re-equilibrate the calculated isotope temperature to the outlet temperature of the volcanic
 72 fumarole, irrespective of the origin of H₂O and H₂ in the fumarole. Furthermore, the isotope
 73 exchange reactions slow down sufficiently after cooling that the D/H ratio is effectively
 74 “frozen” at the D/H ratio just before sampling.

75 Similar processes that result in the re-equilibration of the hydrogen isotopes and
 76 subsequent “freezing” of that re-equilibration can also be anticipated in volcanic plumes. If
 77 we could estimate the hydrogen isotopic compositions of both the H₂O and H₂ in the
 78 fumaroles from those in the volcanic plume, it would be possible, by assuming the isotope

79 exchange equilibrium in fumarolic H₂O and H₂, to remotely deduce the temperature of the
80 fumaroles. Within the possible isotope fractionations among the major components in
81 fumarolic gases, the hydrogen isotope fractionation between H₂O and H₂ has the largest
82 fractionation factor under the isotope exchange equilibrium, as well as the largest
83 temperature-dependent variation (Richet *et al.*, 1977), so that the temperature estimation using
84 hydrogen isotopes can be precise.

85 While H₂ is one of the major components in high-temperature fumarolic gases (0.1 to
86 3% by volume (including H₂O), Symonds *et al.*, 1994), H₂ is depleted in atmosphere, present
87 at concentrations of *ca.* 0.5 ppm in tropospheric air (Novelli *et al.*, 1999). Hence, the volcanic
88 plume has an excess of H₂ relative to the troposphere (McGee, 1992; Symonds *et al.*, 1994).
89 Consequently, we can estimate the D/H ratio of fumarolic H₂ from the concentrations and
90 D/H ratios of the H₂ in the volcanic plume, by subtracting atmospheric contributions to the
91 D/H ratios of the H₂ in the volcanic plume (see section 4.2 for the detail). It is more difficult
92 to estimate D/H ratios of fumarolic H₂O from those in plume because of possible enrichment
93 of H₂O in tropospheric air. However, it turns out that we can assume the D/H ratios without
94 actual measurements (see sections 4.3 and 4.4 for the detail). As a result, we can estimate the
95 outlet temperature of fumaroles, from the D/H ratios of the fumarolic H₂ (determined) and the
96 fumarolic H₂O (assumed).

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

- 100 (1) H₂ from high-temperature fumaroles attain isotope exchange equilibrium with
101 co-existing fumarolic H₂O, and,
102 (2) the D/H ratios of fumarolic H₂ are “frozen” in the plume, and, that we can deduce
103 them from those in volcanic plume.

104 Furthermore, we applied this new methodology to a volcanic plume emitted from a fumarolic
105 area where direct temperature measurements were difficult, to estimate the D/H ratio of
106 fumarolic H₂ and thus the outlet temperature of fumaroles remotely. As far as we are aware,
107 this is the first report of a D/H ratio from H₂ in a volcanic plume. This work has been made
108 possible by recent advances in stable isotope measurements using Continuous-Flow Isotope
109 Ratio Mass-Spectrometry (CF-IRMS), which enabled us to make such highly sensitive
110 measurements on the D/H ratios of H₂ close to the atmospheric levels without any
111 cumbersome and time-consuming pretreatments (Rahn et al., 2002; Rhee et al., 2004; Rice et
112 al., 2010).

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114

2. GEOLOGICAL BACKGROUND

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

122 *Tarumae volcano*

123 The Shikotsu caldera (13 × 15 km), largely filled by the waters of Lake Shikotsu, was
124 formed during one of the largest Quaternary eruptions about 31 to 34 KY BP in Hokkaido
125 Island, Japan (Fig. 1). The small andesitic Tarumae stratovolcano was then constructed on the
126 south-eastern rim and has been Hokkaido's most active volcano since. The Tarumae volcano
127 is now capped by an andesitic flat-topped summit lava dome that formed in 1909, having the
128 diameter of 450 m and the height of 130 m. There are 7 major fumarolic vents in and around
129 the summit lava dome, named A, B, C, D, E, F, and G. Vent A is located on the south-eastern

130 flank of the lava dome and is presently one of the most active fumarolic areas on the Tarumae
131 volcano. Previously, this had been a huge vent having a inner diameter of more than a meter,
132 so that no data had been reported for the chemical composition of exiting gases, except for
133 estimations from the volcanic plume (Shinohara, 2005). However, the inner wall of Vent A
134 collapsed in 2004 so that most of the main vent has been buried by the debris. Now, an
135 intense gas emission occurs from many tiny fumaroles at the bottom of a crater about 5 m
136 deep with a 10 m diameter. In this study, the samples for analysis were taken in and around a
137 fumarole in Vent A.

138 *Kuju volcano*

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

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

152 *E-san volcano*

153 The E-san volcano, a small andesitic stratovolcano capped by a 618-m-high lava dome,
154 is located in southernmost part of Hokkaido Island, Japan (see Fig. 1). The E-san volcano
155 occupies the eastern tip of the double-pronged Oshima Peninsula across the Tsugaru Strait

156 from Honshu. The lava dome of the E-san volcano, which formed about 9 KY BP, and the
157 volcano has been active during the Holocene. A minor phreatic eruption in 1846 produced a
158 mudflow that caused many fatalities. The most recent activity at E-san was a small eruption in
159 1874. Active fumaroles at temperatures of up to 225°C occur in fumarolic areas on the upper
160 northwestern flank (Y field) and the middle western flank (X field). These are located about
161 400 m apart. Past studies on the fumarolic gases revealed that discharges were dominated by
162 magmatic water and gases (Matsubaya *et al.*, 1978; Hedenquist and Aoki, 1991).

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

165 *Aso volcano*

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

171 The active crater located in the Mt. Naka-dake, named as the Crater 1 of Mt. Naka-dake,
172 is about 400 m in diameter, (see Fig. 2). The active fumarolic area is located at the bottom of
173 the Crater 1, about 80 m below the crater edge, (see Fig. 2). Neither direct sampling of
174 fumarolic gases nor direct measurements of fumarolic temperature were practical in this deep
175 crater. In this study, the samples of volcanic plume were taken at the points A to F (see Figure
176 2).

177

178

3. METHODS

179

180 3.1 Sampling

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

187 A quartz pipe and silicone rubber tubing were used to introduce the fumarolic gases into
188 sampling bottles, after flushing them with sample for more than 15 minutes. Then, the
189 fumarolic gases were introduced into a 100 mL glass syringe with two mouths via
190 condensation traps made of Pyrex glass (ca. 300 mL) cooled to 0°C. The gases were sucked
191 into the trap by syringe. The water content of the sample was determined from the difference
192 in weight of the trap before and after sample collection. The volume of dried fumarolic gases
193 relative to the water content was determined from both inner volume of the syringe (100 mL)
194 and the number of strokes. The water sample in the condensation traps was stored in
195 polypropylene bottles for later analysis on D/H ratios. The dried fumarolic gases in the glass
196 syringe were introduced via the needle into a pre-evacuated glass vial with a butyl rubber
197 septum stopper (20 to 65 mL). These samples were analyzed for both H₂ concentrations and
198 D/H ratios. This method was found to preserve fumarolic H₂ samples for more than a month,
199 without detectable changes in either the concentrations or D/H ratios.

200 Additional to the description above, samples of fumarolic gases were introduced into
201 pre-evacuated 140 mL glass bottles containing 10 mL of 5 mol/L NaOH solution (ultra pure
202 grade) (Giggenbach and Goguel, 1989). These samples were used to determine concentrations
203 of H₂O and H₂ in fumarolic gases. Acidic components of the fumarolic gases dissolved in the
204 NaOH solution, whereas the other non-acidic gases such as H₂ remained in the head space. H₂
205 concentrations in the fumarolic gases were determined from those in head space. H₂O
206 concentrations in the fumarolic gases were determined from the increase in the volume of the

207 NaOH solution. D/H ratios of H₂ in the head space were measured as well. However, these
208 changed toward D enrichment with storage beyond the analytical precision (a few ‰ per day).
209 Hence, we did not include the D/H ratios of H₂ obtained through this method in the final
210 results.

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

218

219 3.2 Analysis

220 Concentrations and D/H ratios of H₂ were determined using the CF-IRMS system at
221 Hokkaido University (*e.g.* Tsunogai *et al.*, 2002; Ishimura *et al.*, 2004; Kawagucci *et al.*,
222 2005; Komatsu *et al.*, 2005; Komatsu *et al.*, 2008; Hirota *et al.*, 2010). This system consists of
223 an original helium-purged pre-concentration system for H₂ and a Delta V Advantage (Thermo
224 Fisher Scientific, Waltham, MA, USA) with a modified GC-C/TC III interface and Thermo
225 Trace GC ULTRA gas chromatograph. The analytical procedures are outlined below, details
226 will be presented elsewhere.

227 For each measurement, a gas sample of appropriate volume (250 mL at STP for a 0.5
228 ppm plume sample, and 0.25 mL at STP for a 5,000 ppm fumarolic gas sample, where ppm
229 means parts per million by volume), was introduced into our original stainless steel line
230 (pre-flushed with carrier gas stream of ultra pure helium). In this line, H₂ in each sample was
231 purified from the other coexisting components, such as O₂, Ar, N₂, CH₄, CO₂, SO₂, H₂S, and
232 H₂O, by passing the sample through a cold condensation trap (4 mm ID) held at -197°C and a

233 column (4 mm ID) packed with Molecular sieve 5A held at -110°C . The H_2 was gathered
234 onto the head of a column (2 mm ID) packed with Molecular sieve 5A held at -197°C and
235 where the carrier pressure was greater than 3,000 Torr. The temperature of the column was
236 then ramped up to room temperature, and the eluted H_2 portion was concentrated again at the
237 head of an HP-PLOT Molsieve capillary column (30 m, 0.32 mm ID) held at -197°C
238 (Tsunogai *et al.*, 2002). The column head was then quickly heated to room temperature under
239 a continuous helium flow rate of 0.4 mL/min and the column-separated H_2 was passed into a
240 mass spectrometer to determine both content and D/H ratios by simultaneous monitoring of
241 the masses of H_2^+ ($m/z=2$) and HD^+ ($m/z=3$). We introduced pure H_2 before and after the
242 sample H_2 peak, as a calibration standard for the D/H ratios (Tsunogai *et al.*, 2002).

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

$$245 \quad \delta\text{D} = \frac{R_X}{R_{\text{STD}}} - 1 \quad (3.1)$$

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

251 Whilst quantifying samples, as a quality control measure we also analyzed a
252 working-standard gas mixture containing H_2 of known concentration (221 ppm) and known
253 $\delta\text{D}(\text{H}_2)$ values at least once a day in the same manner as the samples themselves. The δD
254 values of H_2 in the working-standard gas mixture were precisely calibrated by using
255 commercial standards of pure H_2 . By using the peak area ratios of m/z 2 vs. 3, we calculated
256 the δ value between the sample and the running standard during sample analysis. For
257 normalization to the international standard, the following relation was applied:

$$258 \quad \delta_{\text{sa-std}} = \delta_{\text{sa-rs}} + \delta_{\text{rs-std}} + (\delta_{\text{sa-rs}} \times \delta_{\text{rs-std}}) \quad (3.2)$$

259 where $\delta_{\text{rs-std}}$ is the δD value for the running standard against the international standard, which
 260 was determined from the measurement of the working-standard gas mixture that contains H_2
 261 of known δD compositions ($\delta_{\text{ws-std}}$) via the following calculation:

$$262 \quad \delta_{\text{rs-std}} = \frac{\delta_{\text{ws-std}} - \delta_{\text{ws-rs}}}{\delta_{\text{ws-rs}} + 1} \quad (3.3)$$

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

270 The stable hydrogen isotopic compositions of H_2O ($\delta\text{D}(\text{H}_2\text{O})$) were determined using
 271 the same CF-IRMS system in Hokkaido University, after converting 0.5 μl of sample H_2O to
 272 H_2 using chromium at 880°C under vacuum condition (Itai and Kusakabe, 2004). A portion
 273 (about 2%) of H_2 was sub-sampled and introduced into the stainless steel line while flushing
 274 with the carrier gas stream of ultra pure helium. It was pre-concentrated on the head of a
 275 column (2 mm ID) packed with Molecular sieve 5A held at -197°C . Subsequent procedures
 276 were the same with the $\delta\text{D}(\text{H}_2)$ analysis. In addition to analyzing the samples, we also
 277 analyzed our internal working-standards (filtered deep-sea water, filtered tap water, and
 278 filtered Antarctic ice water, each having known $\delta\text{D}(\text{H}_2\text{O})$ values). We did these measurements
 279 at least twice every day in the same manner as the samples themselves to calibrate the
 280 $\delta\text{D}(\text{H}_2\text{O})$ values of sample to the international scale. The δD values of the working-standards
 281 had been precisely calibrated by using international standards of VSMOW and VSLAP

282 (Coplen and Hopple, 1995). An analytical precision of 0.8‰ for δD can be achieved for a
 283 single sample analysis within the 20 minutes required for analysis.

284

285 3.3 Calculation of apparent equilibrium temperature

286 By using the temperature-dependent variation in the equilibrium fractionation factor of
 287 hydrogen isotopes between H_2O and H_2 ($\alpha_{H_2O-H_2}$), we can estimate the apparent equilibrium
 288 temperature (isotope temperature) for δD (AET_D) from the values of $\delta D(H_2O)$ and $\delta D(H_2)$,
 289 assuming hydrogen isotope exchange equilibrium between H_2O and H_2 (*i.e.* $\alpha_{H_2O-H_2} =$
 290 $(\delta D_{H_2O}+1)/(\delta D_{H_2}+1)$). In this study, AET_D less than 1,000 °C is estimated from $\alpha_{H_2O-H_2}$ using
 291 the following equation (3.4), which we obtained through least squares fitting to the
 292 relationship between AET_D (°C) and $10^3 \times \ln(\alpha_{H_2O-H_2})$ as presented in Richet et al. (1977):

$$293 \quad AET_D = \left\{ 4.474 \times 10^{-12} \times \Delta^2 + 3.482 \times 10^{-9} \times \Delta + 9.007 \times 10^{-8} \right\}^{\frac{1}{2}} - 273.15 \quad (3.4)$$

294 where Δ represents $10^3 \times \ln(\alpha_{H_2O-H_2})$. The relationship between AET_D and $10^3 \times \ln(\alpha_{H_2O-H_2})$ is
 295 schematically shown in Fig. 3.

296

297 4. RESULTS & DISCUSSION

298 4.1 H_2 in Fumaroles

299 The chemical and isotopic compositions of the fumarolic gases are presented in Table 1.
 300 The concentrations of H_2 were expressed relative to H_2O concentration in $\mu\text{mol/mol}$. Both
 301 H_2/H_2O ratios and $\delta D(H_2O)$ values agreed well with those reported for each volcano in past
 302 studies. For example, Mambo and Yoshida (1993) reported H_2/H_2O ratios of 430 ± 340
 303 $\mu\text{mol/mol}$ for a 232°C fumarole at Vent B (Tarumae) (recalculated from their data assuming
 304 the mixing ratio of H_2 within the total non-acidic gases, such as H_2 , N_2 , He, CH_4 , CO and Ar,
 305 to be $50 \pm 40\%$, in which most of high-temperature fumarolic gas data are included; Symonds
 306 et al., 1994). For Kuju, Amita and Ohsawa (2003) reported H_2/H_2O ratio of 41.8 $\mu\text{mol/mol}$

307 and $\delta D(H_2O)$ value of -49.9‰ for a 157°C fumarole in Field A, Saito *et al.* (2002) reported
308 H_2/H_2O ratios of ca. $70 \mu\text{mol/mol}$ and $\delta D(H_2O)$ values of ca. -50‰ for a 351°C fumarole in
309 Field C, and Mizutani *et al.* (1986) reported H_2/H_2O ratio of $5 (\mu\text{mol/mol})$ and $\delta D(H_2O)$ value
310 of -37‰ for a 165°C fumarole in Field A. At E-san, Mambo and Yoshida (1993) reported
311 H_2/H_2O ratios of $360\pm 290 \mu\text{mol/mol}$ for a 225°C fumarole (recalculated from their data
312 assuming H_2 occupies $50\pm 40\%$ of the non-acidic gases) and Matsubaya *et al.* (1978) reported
313 $\delta D(H_2O)$ values of -32‰ and -36‰ for fumaroles showing temperatures of 157 and 185°C ,
314 respectively, and Hedenquist and Aoki (1991) reported $\delta D(H_2O)$ values from -50 to -30‰
315 for fumaroles at 100 to 225°C . Taking into account that both H_2/H_2O ratios and $\delta D(H_2O)$
316 values tend to increase with both outlet temperatures (e.g. Matsuo, 1961; Symonds *et al.*,
317 1994; Goff and McMurtry, 2000; Botcharnikov *et al.*, 2003) and mixing ratios of magmatic
318 water relative to meteoric water (e.g. Mizutani *et al.*, 1986; Goff and McMurtry, 2000;
319 Botcharnikov *et al.*, 2003), our data on the H_2/H_2O ratios and the $\delta D(H_2O)$ values (see Table
320 2) are not unreasonable for those of fumarolic discharges from these volcanoes. The $\delta D(H_2O)$
321 values imply that local meteoric water also contributed to fumarolic H_2O , especially at Kuju.
322 The mixing ratios, however, were always less than 50% . That is to say, the major portion of
323 fumarolic H_2O was magmatic in these fumaroles.

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

331 At Tarumae, where the highest outlet temperature of 609°C was recorded in this study,
332 the calculated AET_D was 626°C . These values agree well with each other (Table 1). We

333 conclude that the re-equilibration via reaction (1.1), almost reached the isotope exchange
334 equilibrium under the outlet temperature of 609°C at this fumarole.

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

345 In case of Kuju, where an outlet temperature of 203°C was recorded in this study, the
346 calculated AET_D (185°C) was similar to the observed outlet temperature (Table 1). We
347 conclude that the reaction (1.1) almost reached the isotope exchange equilibrium at 203°C,
348 even though this temperature is lower than 400°C. With the exception of results from the
349 Showashinzan volcano, previous work shows that for fumarole outlet temperatures of 200 -
350 400°C there is usually reasonably close agreement of temperature and $\delta D(H_2)$ values close to
351 the isotope exchange equilibrium with coexisting fumarolic H_2O at the temperatures of outlet
352 (Fig. 4). While the reaction rate of equation (1.1) would be slow below 400°C, the key is
353 probably whether there is sufficient time for re-equilibration before emission, and these
354 results seem to indicate that for this fumarole, there was indeed sufficient time.

355 In conclusion, we can apply the AET_D as a tracer of temperature to fumaroles with
356 outlet temperatures greater than 200°C. We are able to estimate accurate outlet temperatures
357 for fumaroles having outlet temperatures of more than 400°C from their AET_D . On the other
358 hand, for fumaroles having outlet temperatures of between 200 and 400°C, the quality of the

359 estimates are dependent on the residence time of the fumarolic fluids/gases within volcano,
360 since the final reduction of temperature at depths until emission from fumaroles. For the
361 fumaroles for which the outlet temperatures is as low as 200°C, for instance, the potential
362 errors of up to 150°C on the calculated AET_D are possible (Fig. 4). For fumaroles having
363 outlet temperatures of less than 200°C, significant deviations from the outlet can be expected.

364 Even for the fumaroles for which the outlet temperatures are less than 200°C, the
365 absolute δD values of fumarolic H_2 and their temporal variation can provide important
366 information about the magmatic/hydrothermal system under the volcano. For instance, we can
367 estimate the temperature of fumarolic gases at depths just prior to cooling, from the $\delta D(H_2)$
368 value (e.g. Mizutani, 1983; Taran et al., 2010). Furthermore, we can detect variations in the
369 temperature of fumarolic gases prior to the cooling by continuous monitoring the δD values of
370 fumarolic H_2 .

371 The difference of AET_D from the actual temperatures of the outlets (200–400°C) of
372 fumaroles of Showashinzan volcano reported in the literature may have a different
373 explanation. It is possible that contamination of the δD value by $\delta D(CH_4)$ could be an
374 alternative possible cause. Under this scenario, while H_2 attained isotope exchange
375 equilibrium with fumarolic H_2O at temperatures as low as 200°C, the contribution of
376 fumarolic CH_4 to H_2 during δD analysis could have increased the observed $\delta D(H_2)$ values of
377 the 200–400°C fumaroles and thus AET_D (see Appendix for the detail). If so, we could extend
378 our application of AET_D as a tracer of temperature to the fumaroles to reliably predict
379 temperatures at outlet temperatures as low as 200°C, e.g. the Kuju volcano, see above. To
380 verify this possibility, further studies on fumarolic H_2 are needed, especially for those in
381 fumaroles showing the outlet temperatures between 200 and 400°C.

382

383 **4.2 H_2 in the Volcanic Plumes**

384 Both concentrations and δD values of H_2 in the plume samples were presented in Table
385 2, together with the approximate distance to the fumarole from which each plume cloud
386 apparently derived. All the plume samples can be characterized by significant enrichment in
387 H_2 . The average H_2 concentration of the plume samples taken apparently within the volcanic
388 plume in each volcano were for Tarumae, 17 ppm (from 0.65 ppm to 47.6 ppm, $n = 7$), for
389 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
390 ppm, $n = 7$), and 1.2 ppm (from 0.54 ppm to 2.3 ppm, $n = 12$) for Aso. Those samples taken
391 apparently outside the volcanic plume were 0.51 ppm, 0.53 ppm, 0.53 ppm, and 0.53 ppm
392 respectively. The highest H_2 concentration in each area was always obtained at the sampling
393 points closest to the targeted fumarole, usually at distances less than 1 m. While most of the
394 samples showed significant H_2 enrichment, the air samples taken outside the volcanic plume
395 exhibited H_2 concentrations close to the minimum in each area, indeed close to those in
396 background tropospheric air (*ca.* 0.5 ppm; Novelli *et al.*, 1999). We concluded that fumarolic
397 H_2 was the source of the excess H_2 in the plume samples. That is to say, variations in the
398 mixing ratios of fumarolic gases within ambient air resulted in the variable H_2 concentrations
399 in the plume samples. The average (maximum) mixing ratios of fumarolic H_2 within the total
400 H_2 of the plume were roughly estimated to be 97 (99)% at Tarumae, 89 (96)% at Kuju, 97
401 (99)% at E-san, and 59 (78)% at Aso, assuming that the excess H_2 corresponds to fumarolic
402 H_2 in each plume sample.

403 This conclusion was also supported by the δD values of the H_2 in the plume samples. As
404 shown in Figure 5, the reciprocal of the H_2 concentration in the plume samples showed a good
405 linear relationship with the δD values. Similar linear relationships between the reciprocal of
406 concentrations and their isotopic compositions were recognized in H_2 from urban atmospheres
407 (Gerst and Quay, 2001). The linear relationships suggested that both the concentrations and
408 the δD values of H_2 in the samples from each site can be explained by simple mixing between
409 two end-members, both of which can be classified to a single category at least for the δD

410 values of H₂ (e.g. Keeling, 1958; Tsunogai et al., 1998; Tsunogai et al., 2003; Tsunogai et al.,
411 2005; Tsunogai et al., 2010). Furthermore, the H₂-depleted end-member seems to be almost
412 common irrespective of the volcano under study, showing an H₂ concentration of ca. 0.5 ppm
413 and D-enriched δD values of around +100 ‰. The H₂-depleted end-member must be H₂ in
414 background tropospheric air, certainly both compare well with literature values (Gerst and
415 Quay, 2001; Rice *et al.*, 2010). On the other hand, the H₂-enriched end-member containing
416 highly D-depleted H₂ (compared to background tropospheric H₂) must be the fumarolic H₂,
417 because fumarolic H₂ are always characterized by lower δD values than those in the
418 tropospheric H₂ (Table 1).

419 By extrapolating the linear relationship between $1/H_2$ and δD to $1/H_2 = 0$ to exclude the
420 contribution of the tropospheric H₂ (the H₂-depleted end-member) from the δD value of each
421 sample (e.g. Keeling, 1958; Tsunogai et al., 2003), we estimated the δD values of fumarolic
422 H₂ (the H₂-enriched end-member) to be $-260 \pm 30\text{‰}$ at Tarumae, $-509 \pm 23\text{‰}$ at Kuju, and
423 $-437 \pm 14\text{‰}$ at E-san (Fig. 5) through the least squares fitting of straight lines. Because the data
424 errors were variable especially in $1/[H_2]$, we fitted each line taking into account the
425 differences in the errors (York, 1966).

426 The $1/H_2$ values of the fumarolic H₂ were larger than 0, which means that the δD values
427 of the H₂-enriched end-members must be larger than the δD values estimated. The $1/H_2$ values
428 of the fumarolic H₂ were around 10^{-4} (ppm⁻¹) and the slopes of the linear fitted relationships
429 (Fig. 5) were always less than +500‰ per ppm⁻¹ so that the differences were less than 0.05‰.
430 As a result, we disregarded this difference and used 0 for the $1/H_2$ value of the H₂-enriched
431 end-members.

432 The estimated δD values of Tarumae, Kuju, and E-san corresponded to those in each
433 fumarolic H₂ within the error of the fitting (Fig. 5). We concluded that each fumarolic H₂ was
434 the only source of the excess H₂ in each volcanic plume. Furthermore, δD values of fumarolic
435 H₂ were always quenched in volcanic plume without interactions with the other components,

436 including H₂O in volcanic plume, during mixing with ambient air, hence holding the same δD
437 values as those at the fumarole. As a result, we can deduce the δD value of fumarolic H₂
438 without sampling of fumarolic gases directly, by determining both the concentrations and the
439 δD values of H₂ in its volcanic plume and correcting the contribution of the tropospheric H₂
440 from the δD values as we did in Tarumae, Kuju, and E-san.

441 It is possible that each volcanic plume cloud derived from not one (targeted) fumarole,
442 but from many fumaroles located in each fumarolic area. That is to say, the excess H₂ in the
443 plume samples could comprise most of the fumarolic H₂ from nearby fumaroles. This could
444 lead to heterogeneities in the outlet temperatures in a fumarolic area, which could change the
445 δD values of fumarolic H₂ estimated from the plume.

446 However, as shown above, each end-member δD value estimated from the plume H₂
447 corresponded to those of the targeted fumarole (Fig. 5). Furthermore, all the plume samples
448 showed good linear correlation on the mixing line (Fig. 5). As a result, contribution of
449 fumarolic H₂ from the nearby low temperature fumaroles seems to be minimal. This is
450 especially true at Kuju and E-san, probably because of the depletion of H₂ in the low
451 temperature fumaroles (*e.g.* Giggenbach, 1987; Symonds *et al.*, 1994; Taran *et al.*, 1995). It is
452 also possible that the emission fluxes might be smaller from the low temperature fumaroles
453 than the targeted ones. In conclusion, we have shown that the end-member δD value deduced
454 from the plume H₂ is close to the δD value of H₂ in the fumarole showing highest outlet
455 temperature in each fumarolic area.

456

457 **4.3 Application to Remote Temperature Sensing on the Aso Volcano**

458 By extrapolating the linear relationship between $1/H_2$ and δD in the plume samples
459 taken at Aso to $1/H_2 = 0$, we estimated the average δD value of fumarolic H₂ to be $-172 \pm$
460 16‰ (Fig. 5). The δD value of fumarolic H₂ was much higher than that of the 609°C fumarole
461 at Tarumae (-247‰), but much lower than that of the tropospheric H₂. We concluded that the

462 major source of the excess H₂ in the volcanic plume were the fumaroles at the bottom of the
463 crater. By applying the average δD value of magmatic H₂O obtained from the active
464 volcanoes in convergent margins ($-24.5 \pm 7.3\%$) (the average and the 1 σ dispersion range of
465 the fumarolic H₂O in high temperature fumaroles on convergent-plate volcanoes; Giggenbach,
466 1992), we estimated the AET_D of the Aso fumaroles to be $868 \pm 97^\circ\text{C}$. While the range of δD
467 value applied to the fumarolic H₂O in Aso was assumed from the high-temperature fumaroles
468 in the volcanoes on convergent margins worldwide, the value is reasonable for H₂O in such
469 locally occurring high-temperature fumaroles as well. This includes those in high-temperature
470 fumaroles of nearby volcanoes within the possible variation range, such as those at the
471 Satsuma-Iwojima volcano showing an outlet temperature more than 800°C (from -31 to
472 -23% ; Shinohara *et al.*, 2002), and at the Kuju volcano, showing the outlet temperatures of
473 more than 480°C (-18.9% and -17.0% ; Mizutani *et al.*, 1986).

474 Neither direct sampling of fumarolic gases nor direct measurement of fumarolic
475 temperatures have been practical in the deep crater of Aso. Instead, remote sensing has been
476 employed at the crater edge in past studies, at distances of about 200 m from the fumarolic
477 area (Mori and Notsu, 1997; Saito *et al.*, 2005; Furukawa, 2010; Shinohara *et al.*, 2010). The
478 highest temperature of the fumarolic area at Aso (Fig. 2), has been monitored periodically (at
479 least monthly) by the Japan Meteorological Agency (JMA) since 1993 using a dedicated IR
480 thermometer (operating at wavelengths of 8–13 μm). That work reported that the outlet
481 temperature was ca. 300°C in Nov., 2010 when we took our plume samples (Japan
482 Meteorological Agency, 2010). Although the highest temperature of the fumarolic area at the
483 Aso volcano as determined by JMA has varied widely in past, showing the maximum of ca.
484 500°C in 2003 and 2009, and a minimum of less than 100°C in 1999 and 2006. It is true
485 though, that the highest temperature determined by JMA was much lower than the AET_D we
486 estimated from the fumarolic area.

487 On the other hand, some glowing spots (red glow) have been observed with the unaided
488 human eye at night in the fumarolic area at times since November 2000. Given this, the
489 temperature of the red glow must be more than 500°C (Saito *et al.*, 2005). The latest
490 observation of red glow prior to our sampling was in May, 2010. Therefore, that the
491 temperatures determined by JMA (*e.g. ca.* 350°C in May, 2010) must be lower than the actual
492 outlet, by at least 150°C. Furthermore, Mori and Notsu (2008) determined CO/CO₂ ratios of
493 the fumarolic gases at the Aso volcano remotely using FT-IR on six occasions from 1996 to
494 2003, and estimated the equilibrium temperature of fumarolic gases was almost stable at
495 670°C to 870°C, using the empirical relation between the equilibrium temperatures and
496 CO/CO₂ ratios in the fumarolic gases. Shinohara *et al.* (2010) also obtained similar
497 equilibrium temperatures from 750°C to 950°C for the fumarolic gases during the
498 observations from 2006 and 2009 using both H₂/H₂O ratios and SO₂/H₂S ratios in the
499 volcanic plume determined by using a portable multi-sensor system (Shinohara, 2005).
500 Although the equilibrium temperatures could be higher than the outlet to some extent (*e.g.*
501 Symonds *et al.*, 1994), both the presence of the red glow only 5 months before and the
502 equilibrium temperatures close to the AET_D suggest that the calculated AET_D was a
503 reasonable estimate of the fumarole outlet temperatures.

504 The azimuthal resolution of the IR thermometer of JMA is 1°, and this corresponds to a
505 spatial resolution of more than 1 m at their measurements at the distance of *ca.* 200 m from
506 the fumarolic area. The dimension of each fumarole at the surface must be much less than 1 m
507 (Furukawa, 2010), so that the lower spatial resolution as compared to the dimension of each
508 fumarole is likely to be responsible for the lower temperatures in the IR thermometer
509 measurements of JMA. This hypothesis is also supported by the observation on the fumarolic
510 area using a high resolution IR thermometer having *ca.* two order of magnitude better
511 resolution than that of JMA instrument (Saito *et al.*, 2005). The highest temperature of up to
512 800°C was detected on November 2003 (Saito *et al.*, 2005), when the highest temperature

513 determined by JMA was only 350°C. Although the estimated temperatures using the high
514 resolution IR thermometer decreased to less than 500°C in September 2003, and less than
515 300°C in March 2005 (Furukawa, 2010), we concluded that the AET_D (868 ± 97°C in Nov.
516 2010) represented the highest outlet temperature of the fumaroles at Aso and that further
517 reduction in the dimensions of the fumaroles at the surface has been responsible for the
518 declines in the temperatures determined by using the high-resolution IR thermometer since
519 September 2003. That is to say, temporal variation in the dimensions of fumaroles at surface,
520 probably because of variation in the emission flux of fumarolic gases, was responsible for the
521 temporal variation in the temperature determined by the IR thermometers, as well as the
522 appearance/disappearance of the red glow. Hence we conclude that the actual outlet
523 temperature of the Aso fumaroles keeps the temperature close to the chemical equilibrium
524 temperature between H₂-H₂O, SO₂-H₂S, and CO-CO₂. These features of the fumarolic area at
525 the Aso volcano resemble those at the Satsuma-Iwojima volcano, which is characterized by
526 the continuous, long-term emission of volcanic gases from the fumaroles. The highest outlet
527 temperatures vary very little being around 850°C (*e.g.* Shinohara *et al.*, 1993), and also have
528 the accompanying “red glows” on the fumarolic area.

529

530 **4.4 Application to Remote Temperature Sensing on Volcanic Fumaroles in general**

531 Our observations on the Aso plume suggest that the average δD value of fumarolic H₂
532 for a fumarolic area should be amenable to estimation with a similar precision as that at Aso
533 (less than ±20‰) from those in the plume, provided the plume is enriched in H₂ to a similar
534 degree as is the Aso plume (from 0.54 ppm to 2.3 ppm). This means that the excess H₂ (*i.e.*
535 the fumarolic H₂) occupies 59 % (on average) and 78 % (maximum) of total H₂ in the plume.
536 The observed H₂ enrichment in the Aso plume was not a special characteristic limited to Aso,
537 but is fairly general. For example, the average excess H₂ in comparison with the ambient
538 atmospheric H₂ in the July 29, 1980 plume (non-eruptive) of Mount St. Helens, for instance,

539 was +0.59 ppm at 16 km downwind from the fumarolic area (McGee, 1992), so that the
540 average mixing ratio of fumarolic H₂ within total H₂ in the plume was greater than 50 %
541 (calculated assuming the H₂ concentration of ambient air to be 0.5 ppm H₂; Novelli *et al.*,
542 1999). Because the average mixing ratio is very similar to that in the Aso plume samples we
543 obtained in this study, we could estimate the δD values of fumarolic H₂ of Mount St. Helens
544 precisely, with a similar precision to that at Aso ($\pm 16\%$), if we had sampled the plume of
545 Mount St. Helens at the distances of 16 km downwind from the fumarolic area and
546 determined both concentrations and δD values of H₂ in the plume in 1980.

547 Sufficient H₂ enrichment in volcanic plumes derived from high-temperature volcanic
548 fumaroles is a promising way ahead. The H₂/H₂O ratio in the fumarolic gases at Aso,
549 estimated from those in the plume to be 10³ to 10⁴ $\mu\text{mol/mol}$ (Shinohara *et al.*, 2010), can be
550 classified as having a lower H₂/H₂O ratio than most of the high-temperature fumarolic gases
551 in world volcanoes, such as St. Augustine (5,800 $\mu\text{mol/mol}$), Etna (11,000 $\mu\text{mol/mol}$), Merapi
552 (12,000 $\mu\text{mol/mol}$), Momotombo (4,700 $\mu\text{mol/mol}$), St. Helens (5,300 $\mu\text{mol/mol}$), Poas
553 (5,800 $\mu\text{mol/mol}$), Showashinzan (1,900 $\mu\text{mol/mol}$), Usu (3,200 $\mu\text{mol/mol}$), Ardoukoba
554 (22,000 $\mu\text{mol/mol}$), Erta' Ale (22,000 $\mu\text{mol/mol}$), Nyiragongo (34,000 $\mu\text{mol/mol}$), Surtsey
555 (27,000 $\mu\text{mol/mol}$), Kilauea summit lava lake (15,000 $\mu\text{mol/mol}$), and Kilauea East Rift Zone
556 (12,000 $\mu\text{mol/mol}$), [mean values of those compiled in Symonds *et al.* (1994)]. Thus, as far as
557 the extent of dilution by ambient air is the similar, we can anticipate similar H₂ enrichment
558 (more than a 50% contribution of fumarolic H₂ in the plume H₂ on average) in a typical
559 volcanic plume.

560 In the case of low temperature fumaroles, the concentrations of fumarolic H₂ are small
561 in general (*e.g.* Giggenbach, 1987; Symonds *et al.*, 1994; Taran *et al.*, 1995). As a result, the
562 estimation on fumarolic $\delta D(\text{H}_2)$ from H₂ in the volcanic plume might be difficult for them
563 because of the small H₂ enrichment in the plume. However, even if the plume is too depleted
564 in H₂ at the point where it is safe enough to sample by hand, recent advances in remote

565 sampling tools such as manned aerial vehicles (*e.g.* Fiske and Sigurdsson, 1982; Shinohara *et*
566 *al.*, 2003; Wardell *et al.*, 2004), unmanned aerial vehicles (*e.g.* Saiki and Ohba, 2010),
567 balloons (*e.g.* Belousov and Belousova, 2004), and robots (*e.g.* Muscato *et al.*, 2003) could be
568 utilized to take more concentrated samples in places where people cannot safely go.

569 In the case of high temperature fumaroles, care must be taken when the variation in δD
570 values under the isotope exchange equilibrium becomes relatively insensitive to temperature
571 variation, especially for those having temperatures exceed 1,000 °C (Fig. 3). That is to say,
572 variations in $\delta D(H_2)$ values in response to the same degree of temperature variation becomes
573 relatively smaller at higher temperatures. In the case of Aso, for instance, we estimated the
574 outlet temperature (868 °C) within an error of 97°C, by using both the fumarolic $\delta D(H_2)$ with
575 an error of 16‰ and the fumarolic $\delta D(H_2O)$ with an error of 7.3‰ (see section 4.3 for the
576 detail). Even if we determined both $\delta D(H_2)$ and $\delta D(H_2O)$ in a fumarole with the same degree
577 of errors as those in the case of Aso ($\pm 16\%$ and $\pm 7.3\%$, respectively), the error accompanied
578 in its estimated temperature would be ca. ± 120 °C when the outlet temperature was 1,000 °C,
579 and ca. ± 170 °C when the outlet temperature was 1,200 °C. As a result, for the fumaroles
580 having elevated outlet temperatures, we have to estimate fumarolic $\delta D(H_2)$ more precisely
581 from H_2 in the volcanic plume, to attain a similar precision to that of with Aso (smaller than
582 ± 100 °C). For instance, precisions smaller than 11‰ and 6‰ are needed for 1,000 °C and
583 1,200 °C fumaroles, respectively, to attain a similar precisions to those of Aso. The
584 concentrations of fumarolic H_2 are large in general in the high temperature fumaroles (*e.g.*
585 Giggenbach, 1987; Symonds *et al.*, 1994; Taran *et al.*, 1995). As a result, precise estimation
586 of fumarolic $\delta D(H_2)$ from H_2 in the volcanic plume might be possible.

587 In addition to the problem of insensitivity to temperature variation in the high
588 temperature region, care must be taken because no reliable fractionation factors are available
589 at temperatures greater than 1,300 °C (Richet *et al.*, 1977). To apply HIRETS to fumaroles
590 having temperatures greater than 1,300 °C, we must calculate/estimate equilibrium

591 fractionation factors for the temperatures greater than 1,300 °C. However, 1,300 °C is
592 sufficient as the upper limit to determine the temperature for most of the volcanic fumaroles
593 throughout the world.

594 The δD value of fumarolic H_2 estimated from plume samples will enable us to estimate
595 the highest outlet temperature of the fumaroles of interest if the temperature exceed 400 °C,
596 assuming the isotope exchange equilibrium between the fumarolic H_2 and fumarolic H_2O . For
597 the estimation of temperature, however, data on the δD value of fumarolic H_2O is also
598 essential. In contrast to H_2 , it is rather difficult to estimate δD value of fumarolic H_2O from
599 the plume because the concentration of H_2O in background air is much higher than that of H_2 ,
600 about 10^3 to 10^4 ppm is usual. Furthermore, both concentrations and δD values of H_2O in air
601 can be quite varied. Based on the knowledge obtained on the fumarolic H_2O from past studies,
602 however, we can estimate the value precisely in several ways outlined below.

603 In case of fumarolic H_2O in high-temperature magmatic discharges on convergent-plate
604 volcanoes, we can assume an approximate δD value from the literature to be $-24.5 \pm 7.3\%$ (the
605 average and the 1σ variation range of the fumarolic H_2O in high-temperature fumaroles on
606 convergent-plate volcanoes; Giggenbach, 1992). This is the same data previously applied to
607 Aso in section 4.3. It may be that such a general δD value for H_2O cannot be applied to the
608 fumarolic H_2O studied. However, because H_2O is the major component in most fumarolic
609 fluids and the alternative end-member is local meteoric water, we can restrict the most
610 extreme δD value from the magmatic fluids to that of local meteoric water (Giggenbach,
611 1992; Goff and McMurtry, 2000). Furthermore, because H_2O is the major component in
612 fumarolic gases that have fumarolic H_2/H_2O ratios less than 0.04 (e.g. Symonds *et al.*, 1994),
613 typical variation range of δD values in fumarolic H_2O are much narrower than that of
614 fumarolic H_2 (e.g. Bottinga, 1969; Mizutani, 1983; Giggenbach, 1992; Taran *et al.*, 1995;
615 Kiyosu and Okamoto, 1998; Goff and McMurtry, 2000; Taran *et al.*, 2010). As a result, we
616 can approximate the δD values of fumarolic H_2O to be uniform irrespective of variations in

617 the temperature of fumaroles. In the case of the decline in temperature over time shown at
618 Showashinzan and Nasudake, which was discussed in section 1, for example, while $\delta D(H_2)$
619 declined at the rates of $-1.9 \pm 1.0\%$ /yr at Showashinzan and $-12.9 \pm 2.5\%$ /yr at Nasudake,
620 $\delta D(H_2O)$ showed little variation, with values of $-0.4 \pm 0.8\%$ /yr and $-1.8 \pm 1.0\%$ /yr,
621 respectively (Mizutani, 1983). Hence, it may be that if some past data on the $\delta D(H_2O)$ were
622 available for a particular fumarolic area, the values could be applicable to the present as well.
623 It may also be that we could use the δD value of magmatic H_2O estimated for the volcano
624 using alternative methods: such as measuring that found in fresh volcanic rocks (*e.g.* Newman
625 *et al.*, 1983; Taylor *et al.*, 1983; Kusakabe *et al.*, 1999). Furthermore, H_2 data alone is
626 sufficient to estimate relative temperature variation. In conclusion, we can remotely estimate
627 the temperature of the fumaroles (or at least for their temporal variations) at a distance based
628 only on H_2 in the plume.

629

630 **4.5 Comparison with the Traditional Methods**

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

640 Most of the advantages of HIRETS described above are applicable to the other remote
641 temperature sensing methods that determine the chemical compositions of fumarolic gases
642 remotely and estimate the equilibrium temperature (*e.g.* Mori and Notsu, 1997; Shinohara,

643 2005). In practice, however, it is difficult to deduce accurate and precise fumarolic
644 concentrations for all of the components of the chemical equilibrium from those in the plume.
645 This is especially true when the measurements on the plume are being done at a distance from
646 the fumarolic area (Symonds *et al.*, 1994). As a result, the estimate of equilibrium
647 temperature comes with significant errors (*e.g.* ± 150 to $\pm 200^\circ\text{C}$; Mori and Notsu (2008)).
648 Furthermore, the equilibrium temperature is the temperature at depth - potentially somewhat
649 higher than that at the outlet (*e.g.* Symonds *et al.*, 1994). While the information on the
650 equilibrium temperature is useful in many respects, HIReTS is preferable to determine the
651 outlet temperature of fumaroles remotely.

652 On the other hand, the disadvantage of using HIReTS compared to the traditional
653 methods is the time needed to determine temperature. While most of the IR thermometers can
654 determine the temperature on site, the HIReTS methodology needs more than a few days to
655 estimate temperature for a fumarolic area subsequent to the field and laboratory work. Also,
656 to avoid potentially large errors (see section 4.1), prior to applying HIReTS, we would have
657 to verify the fumarolic temperature to be more than 400°C (or at least more than 200°C),
658 using some alternative method, such as a traditional IR thermometer. Furthermore, ambiguity
659 in the δD values of fumarolic H_2O could reduce the accuracy of the absolute temperature
660 obtained from HIReTS in some volcanoes.

661 In conclusion, HIReTS can be a better or only choice for remote temperature sensing of
662 fumaroles in many volcanoes, but care must be exercised because each applications is likely
663 to be different. It would be better to combine HIReTS with the other traditional methods
664 during the actual temperature sensing in field. Moreover, to be certain of collecting plume
665 samples enriched in H_2 , it might be preferable to measure H_2 concentration real-time during
666 the field work at volcanoes, applying some portable sensors (Shinohara et al., 2010).

667

668

5. CONCLUSIONS

669 For a fumarolic area in a volcano having outlet temperatures of more than 400°C, we
670 can remotely estimate an accurate temperature of the fumaroles by using HIReTS developed
671 in this study. This method estimates the δD value of fumarolic H₂ from those in the plume. It
672 is possible that HIReTS can be expanded to temperatures as low as 200°C in the future,
673 although it will depend on the results of further studies on fumarolic H₂. HIReTS can be a
674 better or indeed the only choice for accurate remote temperature sensing of fumaroles at many
675 volcanoes. Furthermore, even for fumaroles showing temperatures lower than the HIReTS
676 lower limit, we can obtain novel information concerning the magmatic/hydrothermal systems
677 under the volcano. However, as we have to presume the δD value of fumarolic H₂O without
678 actual measurement to obtain absolute temperature of these fumaroles using HIReTS, the
679 accuracy of temperatures estimated by HIReTS could be worse for fumaroles for which we
680 cannot presume accurate δD values for fumarolic H₂O.

681

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695 **APPENDIX**

696 The data set on AET_D in high-temperature volcanic fumaroles used in this study (Fig. 4)
697 was compiled from past work and did not include the AET_D data from the Kuju volcano
698 reported by Mizutani (1983), in which the AET_D estimated at the Kuju volcano were very
699 different from that at the outlet. The observed outlet temperature was 151°C, but AET_D was
700 790°C, in 1964. While Mizutani (1983) proposed that the AET_D represented the elevated
701 temperature in the gas reservoir at depth below the Kuju volcano, we concluded that the
702 values were affected by artifacts and hence removed them from the figures and discussions of
703 this paper. Our reasons for this were:

704 (1) The δD values of fumarolic H₂ reported for the same Field A in Mizutani (1983)
705 showed significant deviation from those that we determined in this study (2010).

706 (2) Because of the little apparent variation in Field A of the Kuju volcano since 1964,
707 (highest outlet temperatures were 183°C in 1964, 214°C in 1984, 200°C in 2000, and
708 203°C in this study; Mizutani *et al.*, 1986; Amita and Ohsawa, 2003), it is difficult to
709 attribute such significant variation in the δD values of fumarolic H₂ between Mizutani
710 (1983) and this study to temporal variation in the fumarolic H₂.

711 The most important difference between Mizutani (1983) and this study is the analytical
712 method employed to determine the $\delta D(H_2)$ values. While our method did not include gases
713 other than H₂ in the determined $\delta D(H_2)$ values, the $\delta D(H_2)$ values used by Mizutani (1983)
714 was the total δD value of the gases that had not dissolved in NaOH solution during sampling.
715 These gases included H₂, N₂, CO, Ar, He, and CH₄. As a result, the differences of the $\delta D(H_2)$
716 value produced by the method would be significant if the fumarolic gases contained elevated
717 CH₄ relative to H₂. While Mizutani (1983) disregarded this possibility based on analytical
718 results from only one fumarolic gas sample taken at a fumarole in Field C of the Kuju volcano
719 in 1961 that showed an outlet temperature of 400°C and a CH₄/H₂ ratio of 0.0014. We

720 concluded that the actual CH₄/H₂ ratios of the samples, for which Mizutani (1983) determined
721 δD(H₂) values, were much higher than 0.0014 and that the δD(H₂) value was contaminated by
722 CH₄, and this was responsible for the elevated δD(H₂) values reported in that work. Our
723 reasons for thinking this are:

724 (1) While the sample showing the CH₄/H₂ ratio of 0.0014 was taken at 1961, the
725 samples for which Mizutani (1983) determined δD(H₂) values were taken during 1964
726 to 1967. Because the CH₄/H₂ ratios at the fumaroles on the Kuju volcano increased to
727 0.04–2.0 in their subsequent observation on August 1984 (Mizutani *et al.*, 1986), the
728 CH₄/H₂ ratios during 1964 to 1967 would have been much larger than 0.0014.

729 (2) While the sample showing the low CH₄/H₂ ratio of 0.0014 was taken at a fumarole
730 with an outlet temperature of 400°C, the samples for which Mizutani (1983) determined
731 the δD values of H₂ were taken at fumaroles with outlet temperatures from 121 to
732 360°C. Because the CH₄/H₂ ratios at Kuju tended to increase in proportionally with the
733 decrease in the outlet temperatures (the CH₄/H₂ ratio of a fumarole showing an outlet
734 temperature of 170°C in 1984, for example, was 2.0; Mizutani *et al.*, 1986), the samples
735 for which he determined δD(H₂) values could have more elevated CH₄/H₂ ratios.

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

739 To test our hypothesis, we recalculated the δD(H₂) value and AET_D for the 151°C
740 fumarole; using 2 for the actual CH₄/H₂ ratio (that of a 170°C fumarole at Kuju determined in
741 1984) and –100 ‰ for the δD(CH₄) value (the δD value of CH₄ in deep-sea hydrothermal
742 fluids; Welhan and Craig, 1983). The δD(CH₄) value also corresponds to the δD(CH₄) value
743 that is at isotope exchange equilibrium with coexisting fumarolic H₂O at 600°C. While
744 Mizutani (1983) determined the δD(H₂) value of this fumarole to be –185‰ and the AET_D

745 790°C, the recalculated $\delta D(H_2)$ value became -525‰ , and the recalculated AET_D became
746 175°C; almost corresponding to the outlet (151°C). Thus, we concluded that all the $\delta D(H_2)$
747 values of Kuju in Mizutani (1983) were affected by artifacts, such as contamination of CH_4 to
748 the $\delta D(H_2)$ values.

749 The problems on the CH_4 contamination could also have impacted some past $\delta D(H_2)$
750 data of low temperature fumaroles ($< 400^\circ C$), such as those in the Showashinzan volcano.
751 The AET_D in the 200–400°C fumaroles correspond to the outlet in most of the volcanoes,
752 except the Showashinzan volcano (see Fig. 4). While the $\delta D(H_2)$ data included fumaroles
753 showing outlet temperatures less than 400°C (Mizutani, 1983), data on the CH_4/H_2 ratio were
754 from those of more than 500°C in the volcano (Mizutani and Sugiura, 1982). Because
755 $\delta D(CH_4)$ is much higher than the $\delta D(H_2)$ under the isotope exchange equilibrium as stated
756 above, CH_4 contamination is likely to be responsible for the overestimated AET_D as well.
757 Differ from the Kuju volcano, however, it is difficult to verify $\delta D(H_2)$ again in the
758 Showashinzan volcano at present. As a result, further studies on the other volcanoes are
759 needed to compare the AET_D with the outlet temperatures of the fumaroles showing
760 200–400°C, as presented in section 4.2.

761

Table 1

Chemical and isotopic compositions of fumarolic gas samples, together with apparent equilibrium temperature calculated for $\delta D(H_2O)$ and $\delta D(H_2)$ (AET_D).

		temp. (°C)	H ₂ /H ₂ O (μ mol/mol)	$\delta D(H_2O)$ (‰)	$\delta D(H_2)$ (‰)	AET_D (°C)
Tarumae	Vent A	609	811	-33.4	-247.0 \pm 0.6	626
Kuju	Field A	203	47	-44.3 \pm 1.0	-527.7 \pm 10.1	185
E-san	X field	107	18	-35.3	-432.1 \pm 2.5	287

Table 2
Chemical and isotopic compositions of H₂ in volcanic plume samples.

No.	distance* (m)	H ₂ (ppm)	δD(H ₂) (‰)	Remark
<i>Tarumae volcano</i>				
TA-01	50	0.51	+86.2	Background air
TA-02	50	2.1	-187.3	
H-16	15	12.5	-244.7	
K-13	8	34.3	-243.3	
H-91	3	19.0	-246.4	
H-89	3	2.1	-219.1	
K-07	1	47.6	-226.3	
H-87	100	0.65	-40.8	
<i>Kuju volcano</i>				
ASO-04	>10	0.53	+61.9	Background air
K-10	5	0.62	-47.1	
H-28	1	4.4	-438.0	
K-91	1	13.0	-477.4	
K-07	3	2.9	-410.5	
K-13	3	2.0	-364.5	
<i>E-san volcano</i>				
H-16	1	7.8	-394.4	
H-28	1	17.7	-424.0	
K-13	3	0.68	-66.1	
H-87	10	0.53	+69.5	
K-07	20	0.53	+70.1	Background air
H-89	50	0.89	-134.8	
H-91	>100	0.49	+96.2	
H-53	0.3	82.9	-435.1	
<i>Aso volcano</i>				
ASO-C07	150	0.61	+44.1	A [#]
ASO-C08	150	2.1	-104.5	A [#]
ASO-C05	150	1.0	-27.2	A [#]
ASO-C09	150	1.1	-31.9	A [#]
ASO-C02	150	1.2	-46.9	A [#]
ASO-C10	300	0.54	+98.7	E [#]
ASO-C04	150	0.54	+94.8	F [#] , Background air
ASO-C01	150	0.52	+107.7	F [#] , Background air
ASO-01	300	2.3	-99.5	D [#]
ASO-02	200	2.1	-99.6	C [#]
ASO-03	200	0.67	+44.2	C [#]
H-04	300	1.6	-83.1	D [#]
TGA08	200	0.77	-6.5	B [#]
H-87	150	0.94	-45.7	A [#]

* approximate distance from the targeted fumarole.

the sampling point shown in Fig. 2.

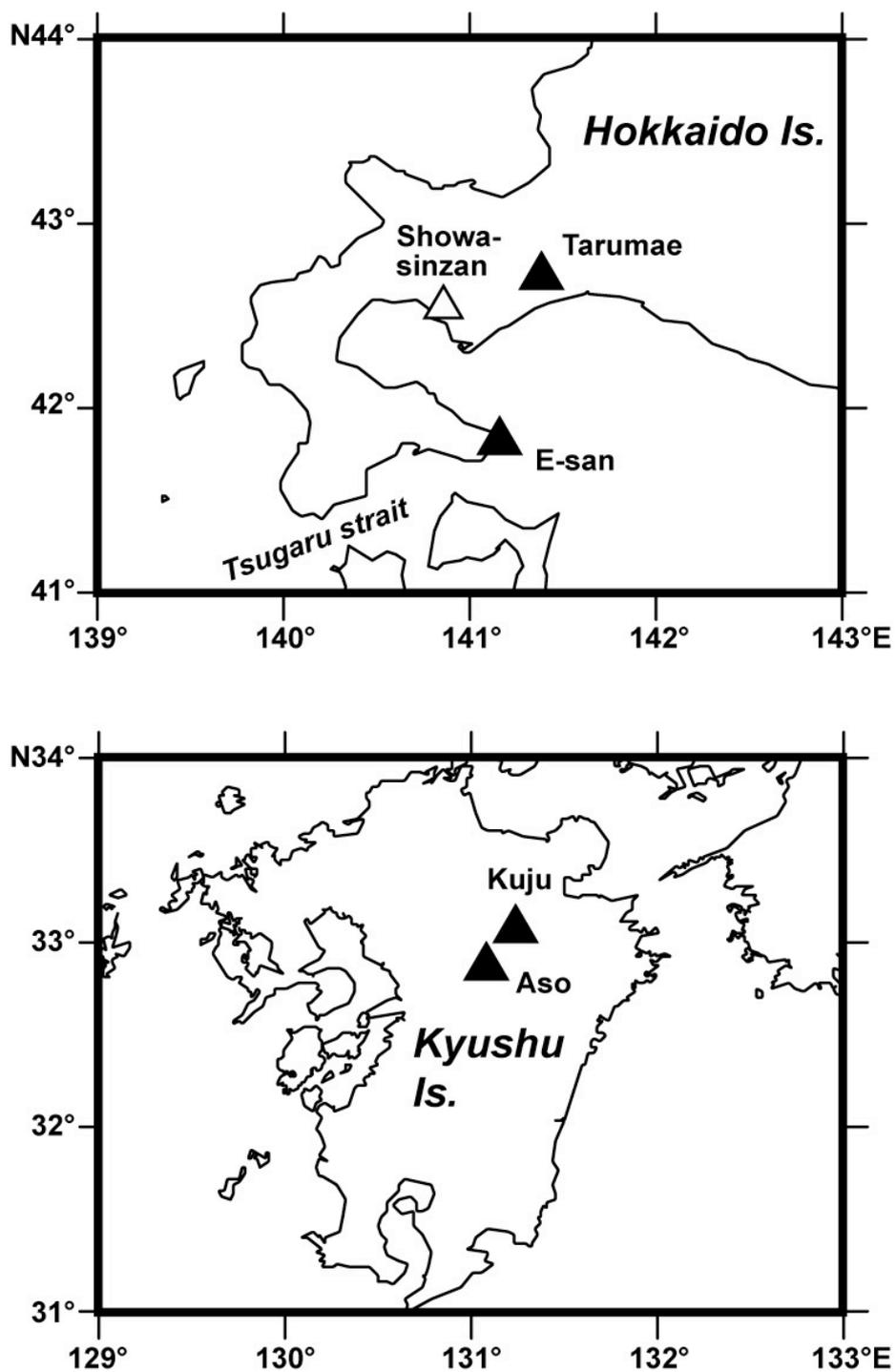


Fig. 1
A map showing the location of the study volcanoes.

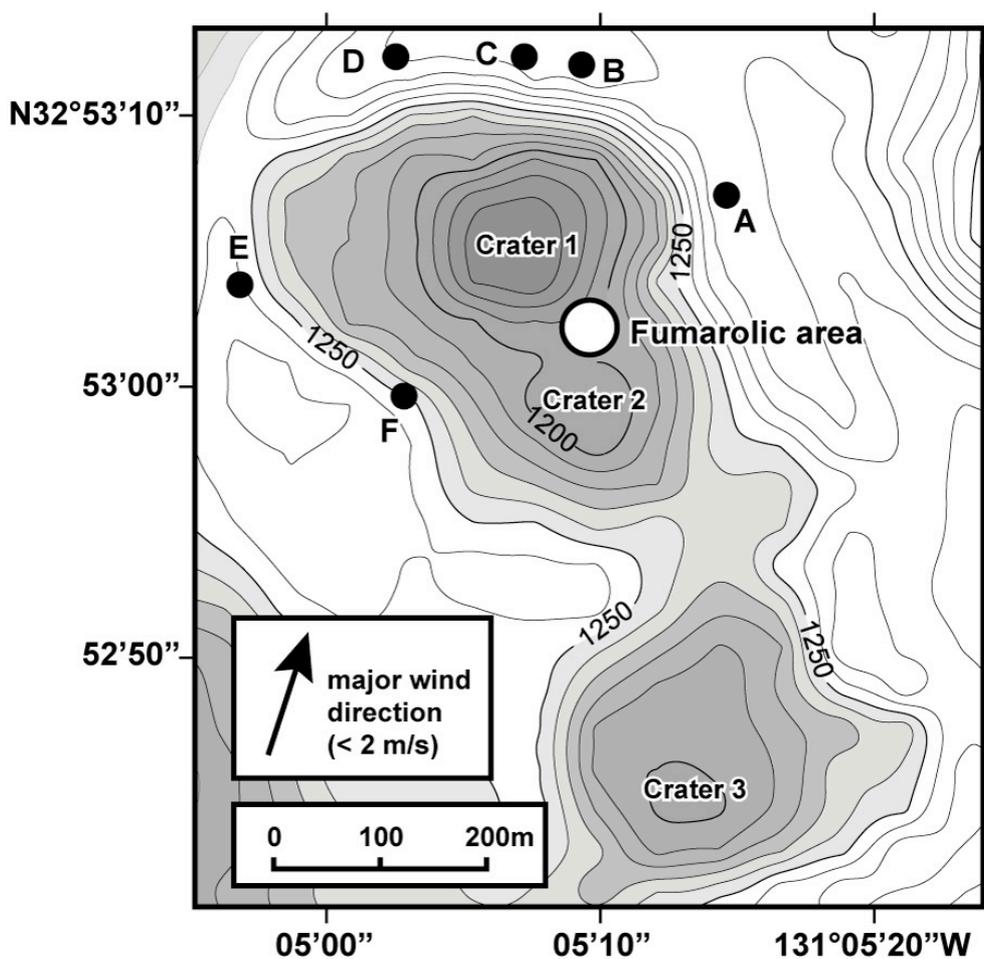


Fig. 2

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.

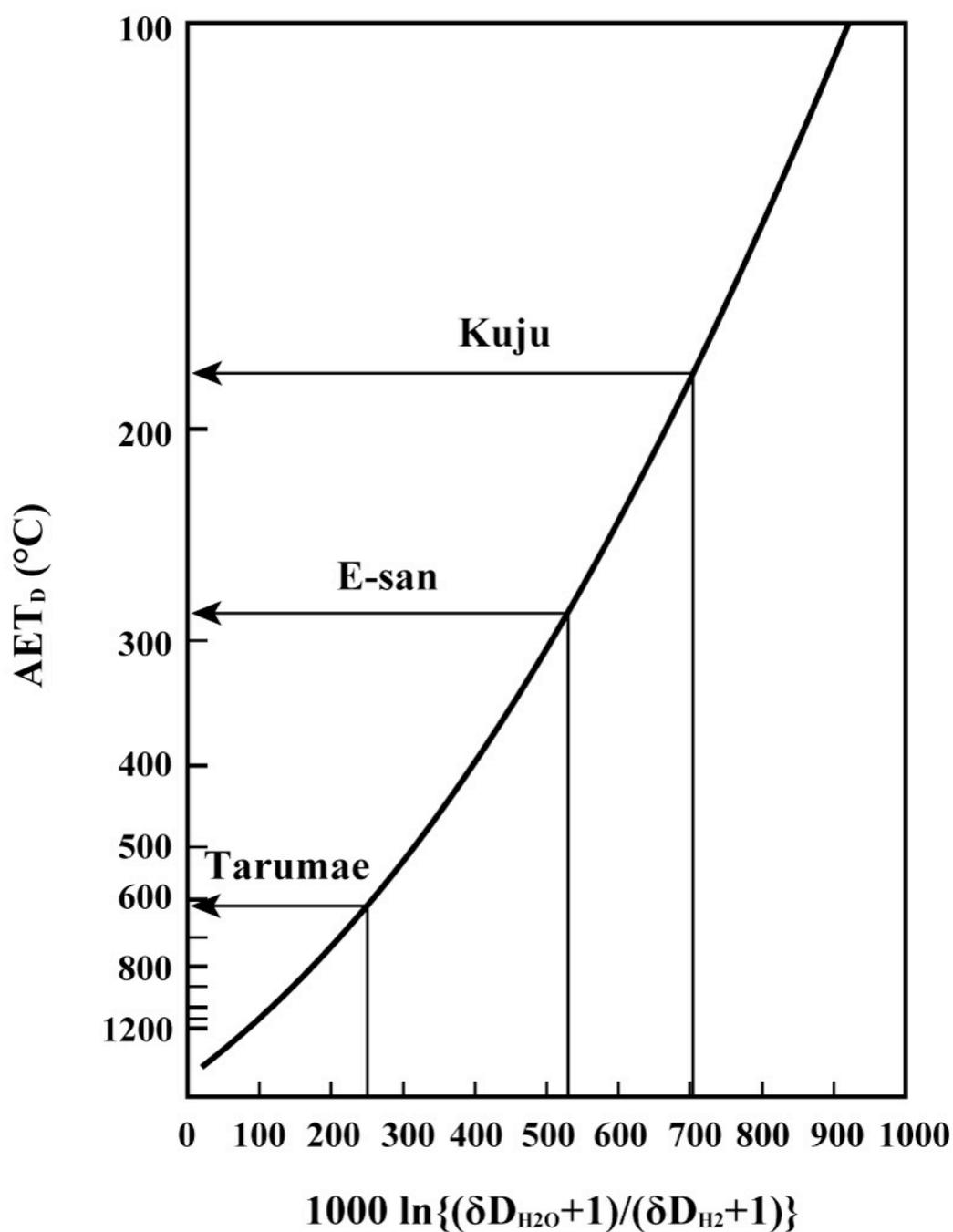


Fig. 3

Relationships between the apparent equilibrium temperature assuming hydrogen isotope exchange equilibrium between H_2O and H_2 (AET_D) and the value of $1000 \ln\{(\delta D_{H_2}+1)/(\delta D_{H_2O}+1)\}$, estimated from the fractionation factors in Richet *et al.* (1977).

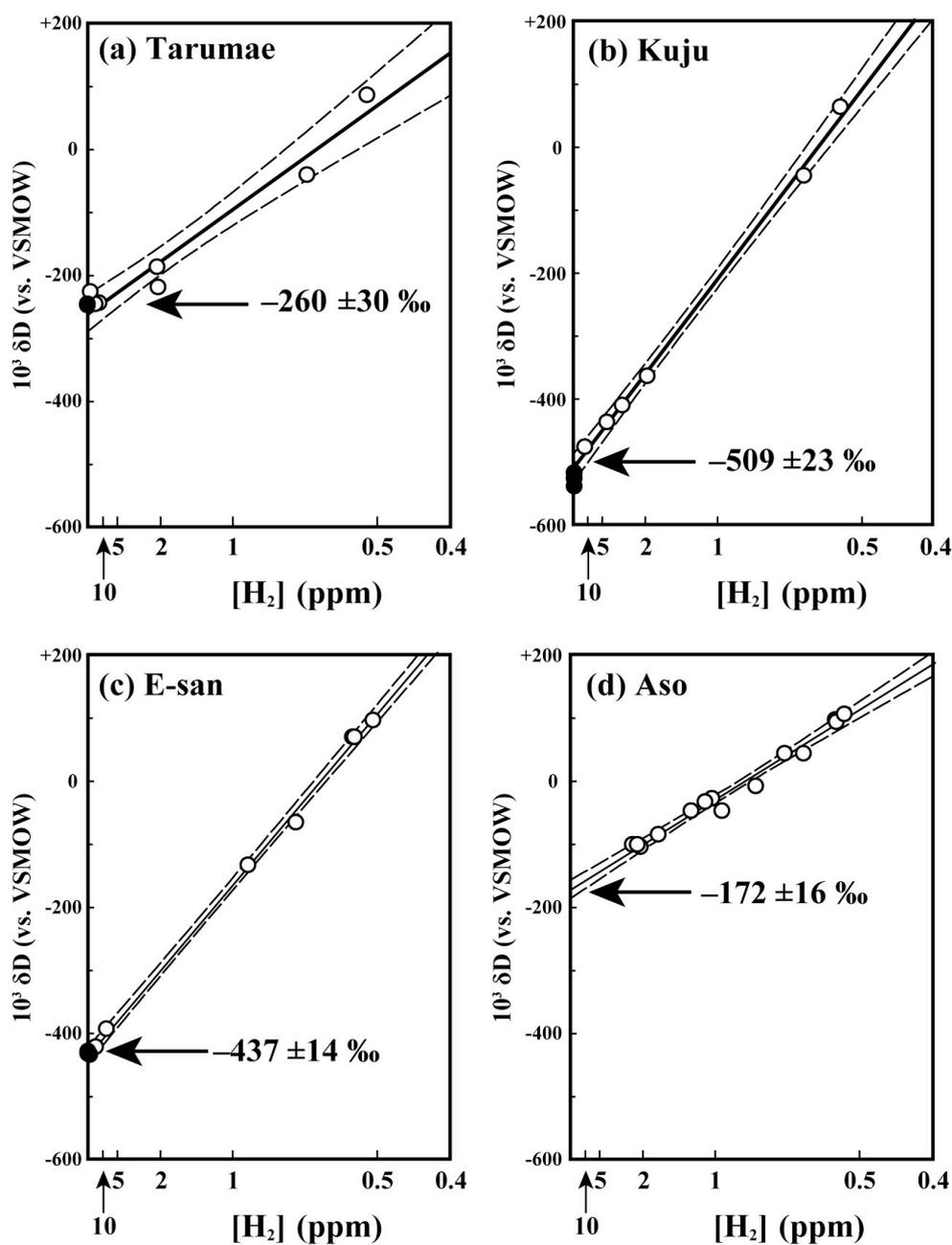


Fig. 5

Relationship between δD of H_2 and the reciprocal of H_2 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.

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