**In situ analyses of hydrogen and sulfur isotope ratios in basaltic glass using SIMS**

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(Received October 22, 2018; Accepted March 22, 2019)

We developed in situ analyses of hydrogen and sulfur isotope ratios of basaltic glass using high-resolution, multi-collection secondary ion mass spectrometry (CAMECA IMS-1280HR). Hydrogen and sulfur isotopes of standard basaltic glasses were determined by a high-temperature conversion elemental analyzer/isotope ratio mass spectrometer (IRMS) and IRMS, respectively. For the in situ analysis of sulfur isotopes, a defocused Cs beam (~0.5 nA; ~10 μm diameter) was used, but for hydrogen isotopes, we used a larger defocused beam (~5 nA; ~15 μm diameter) to decrease the hydrogen background. For analyses of D/H (34S/32S) ratios, 16OH (32S) and 16OD (34S) were measured in multi-detection mode with a Faraday cup and an axial electron multiplier, respectively. Each measurement time was 6–7 minutes. Precisions (2 standard errors) for D/H and 34S/32S ratios were ~6‰ (H2O > 1 wt%) and ~0.6‰ (S > 1000 ppm), respectively. Our developed method for rapid and high spatial resolution analysis can determine multiple elements and isotopes of volatiles in a single small melt inclusion of ~30 μm diameter. Using this method, we analyzed hydrogen and sulfur isotope ratios of submarine basaltic glasses from mid-oceanic ridges and oceanic islands of Hawaii and confirmed that their D/H and S isotope ratios were consistent with reported values.

Keywords: hydrogen isotope, sulfur isotope, basaltic glass, secondary ion mass spectrometry, in situ analysis

**INTRODUCTION**

Hydrogen isotope ratios of volcanic glasses and melt inclusions are an important tool to constrain the behavior of water in the Earth’s interior and to understand magma degassing processes (Aubaud et al., 2006; Clog et al., 2013; Dixon et al., 2017; Hallis et al., 2015; Martin et al., 2017; Shaw et al., 2008; Walowski et al., 2015). There are several methods for determining hydrogen isotope ratios of volcanic glasses. The conventional method is based on the off-line extraction of water from a relatively large sample aliquot (~300–1000 mg) using a furnace, followed by manometric measurements of extracted yields. Extracted water is reduced to H2 by a U-, Zr-, or Cr-furnace prior to mass-spectrometric analysis (e.g., Clog et al., 2012). Another method is based on the instantaneous extraction of water from the sample by a high-temperature furnace (~1450°C). Extracted water is reduced to H2 and transported into the mass spectrometer by helium carrier gas. This method requires much smaller sample aliquots (1–10 mg) than the conventional method does.

Finally, there is in situ analysis of hydrogen isotope ratios of glass using secondary ion mass spectrometry (SIMS) (Gaetani et al., 2012; Hauri et al., 2002; Hauri et al., 2006). High spatial resolution allows the measurement of smaller volumes of volcanic glass, such as melt inclusions. However, the SIMS method is thought to be severely affected by matrix effects with unstable reproducibility (up to 50‰ drift during an analytical session) (Hauri et al., 2006). It also relies on the calibration of standard materials that have been measured by the above methods of bulk-rock analysis. To determine the D/H ratio by SIMS, the intensities of H+ and D+ or 16OH+ and 16OD+ anions are usually measured by a single electron multiplier (EM) using the magnetic peak switching method, which takes ~10–30 minutes per analysis, depending on the water content of the sample (e.g., Hauri et al., 2006; Gaetani et al., 2012). Therefore, the precise determination of in situ hydrogen isotope ratios of volcanic glass is difficult.

Sulfur isotope ratios of volcanic glass and melt inclusions are important for detecting subduction-related recycled materials, because the sulfur content and 34S/32S isotope ratio of seawater differ significantly from those...
of the mantle (Alt et al., 1993). Sulfur loss by degassing and crystallization/separation of sulfide mineral/melt from magma can drastically change the $^{34}$S/$^{32}$S isotope ratio of magma under various redox states (Marini et al., 2011; Sakai et al., 1982, 1984). Despite sulfur isotope ratios of volcanic rocks being an important tool, as mentioned above, most published studies have relied on analysis of bulk rock using isotope ratio mass spectrometry (IRMS), and $\textit{in situ}$ analyses of sulfur isotope ratios of glass and melt inclusions using SIMS are rarely published. Previous materials for $\textit{in situ}$ analyses of sulfur isotope ratios have mostly been sulfide minerals (e.g., Cabral et al., 2013; Delavault et al., 2016; Kozdon et al., 2010; Ushikubo et al., 2014).

In this paper, we report on an analytical method for rapid and accurate $\textit{in situ}$ measurements of hydrogen and sulfur isotope ratios in basaltic glass using high-resolution, multi-collection SIMS, which we applied to the least degassed basaltic glasses sampled from the deep seafloor.

**SAMPLES**

The glass standards prepared for this study were all from Shimizu et al. (2017). Vol-3A, Vol-1B, and Vol-05A were used for hydrogen isotope ratios (Table 1). They are synthetic basaltic glasses whose water contents are 3.6, 0.94, and 0.5 wt\%, respectively. EPR-G3 and FJ-G2 are natural seafloor basaltic glasses that are used for determining sulfur isotope ratios (Table 2). EPR-G3 is a mid-oceanic ridge basalt (MORB) sampled from the East Pacific Rise whose sulfur content is 1269 ppm. FJ-G2 is a back arc basin basalt (BABB) sampled from the North Fiji Basin whose sulfur content is 1372 ppm. Details of these glasses are described by Shimizu et al. (2017). In addition, we analyzed hydrogen isotope ratios by bulk analyses of a rhyolitic glass from the Southern Mariana Trough (MRN-G1) and a boninitic glass from the Bonin forearc recovered by the International Ocean Discovery Program (IODP) Expedition 352 (U1439C201-W106/111). Using SIMS, we also analyzed hydrogen and sulfur isotope ratios of volcanic glasses of MORBs from the East Pacific Rise (EPR-G3, -G4), Indian Ocean (IND-G1, -G2), and Atlantic Ocean (MAR-G1), BABB from the North Fiji Basin (FJ-G2, -G3), and oceanic island basalt (OIB) from Hawaii (HW-G1, -G2). Details of the samples are described by Shimizu et al. (Submitted).

**METHODS**

**Hydrogen isotope ratios in glasses determined by TCEA-IRMS**

We conducted hydrogen isotope ratio and water content analyses of the basaltic glass standards using a Thermo Fischer MAT 253 mass spectrometer connected
with a thermal conversion elemental analyzer (TCEA), following the methods of Nomura et al. (2014) and Sharp et al. (2001). Powdered glass samples were accurately weighed (1000–3000 μg) and wrapped in a pure silver foil capsule. The sample was dried in a vacuum oven at 40°C for 4 hours prior to analysis and was then placed in a graphite crucible filled with glassy carbon in the reactor at 1450°C. Water was released from the glass and reduced to molecular hydrogen. The hydrogen gas was purified in a Molecular Sieve 5A gas chromatographic column and was then introduced into the ion source of the isotope ratio mass spectrometer equipped with Faraday cup (FCs) to allow simultaneous determination of mass 2 and 3 (HH⁺ and HD⁺, respectively). D/H ratios of the samples were compared with that of Vienna Standard Mean Ocean Water (VSMOW, D/H = 0.00015576) (Coplen, 1988), expressed as δDVMOW = [(D/H)unknown/(D/H)VSMOW] – 1) × 1000, in units of per mil (%). A polyethylene standard from the International Atomic Energy Agency (IAEA-CH-7, δDVMOW = –100.3 ± 2.0‰, 1 standard deviation; 1 SD) was measured between every unknown sample to determine the instrumental mass fractionation (IMF) and to decrease the memory effect unknown sample to determine the instrumental mass standard deviation; 1 SD) was measured between every analytical session to check stability of the two standards during the analytical session was 0.22‰ (1 SD; n = 6).

The sulfur concentrations of the EPR-G3 and FJ-G2 glasses extracted by the Kiba reagent method were 1174 and 1298 ppm, respectively, which was identical, within error, to those measured by ion chromatography following pyro-hydrolysis (1269 and 1372 ppm, respectively) (Table 2). This indicates that the sulfur isotope ratios determined by IRMS were representative of their volcanic glasses.

**Table 2. Sulfur isotope ratio (δSVCdT) of silicate glasses by IRMS. Major and volatile contents are also shown.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lithology</th>
<th>$S$ [ppm],_collected</th>
<th>$δ^{34}S_{VCDT}$</th>
<th>2 s.d.</th>
<th>$S$ [ppm],IC</th>
<th>$S_yield$ [%]</th>
<th>$SO_2$</th>
<th>$TiO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPR-G3</td>
<td>natural basaltic</td>
<td>1174</td>
<td>–0.09</td>
<td>0.55</td>
<td>1269</td>
<td>92</td>
<td>50.2</td>
<td>1.7</td>
</tr>
<tr>
<td>FJ-G2</td>
<td>natural basaltic</td>
<td>1298</td>
<td>+0.72</td>
<td>0.55</td>
<td>1372</td>
<td>95</td>
<td>49.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$Al_2O_3$</th>
<th>$FeO$</th>
<th>$MnO$</th>
<th>$MgO$</th>
<th>$CaO$</th>
<th>$Na_2O$</th>
<th>$K_2O$</th>
<th>$P_2O_5$</th>
<th>$H_2O$</th>
<th>$CO_2$</th>
<th>$F$</th>
<th>$Cl$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPR-G3</td>
<td>14.6</td>
<td>10.8</td>
<td>0.19</td>
<td>7.5</td>
<td>11.9</td>
<td>2.9</td>
<td>0.10</td>
<td>0.16</td>
<td>0.22</td>
<td>269</td>
<td>147</td>
<td>158</td>
<td>1269</td>
</tr>
<tr>
<td>FJ-G2</td>
<td>14.4</td>
<td>12.2</td>
<td>0.21</td>
<td>7.2</td>
<td>11.8</td>
<td>2.7</td>
<td>0.08</td>
<td>0.14</td>
<td>0.23</td>
<td>307</td>
<td>151</td>
<td>118</td>
<td>1372</td>
</tr>
</tbody>
</table>

Major element by LA-ICP-MS, $H_2O$ and $CO_2$ by FTIR, $F$, $Cl$ and $S$ by IC following pyrohydrolysis (see Shimizu et al. (2017) for the detail).

**Hydrogen and sulfur isotope ratios determined by SIMS**

We developed a method for analyzing hydrogen and sulfur isotope ratios using a CAMECA IMS-1280HR SIMS at the Kochi Institute of Core Sample Research, Japan Agency for Marine-Earth Science Technology. We prepared sample mounts for SIMS analysis following the method of Shimizu et al. (2017). Polished glass samples were prepared for SIMS analysis by the methods of Nomura et al. (2014) and Sharp et al. (2001). Powdered glass samples were accurately weighed (1000–3000 μg) and wrapped in a pure silver foil capsule. The sample was dried in a vacuum oven at 40°C for 4 hours prior to analysis and was then placed in a graphite crucible filled with glassy carbon in the reactor at 1450°C. Water was released from the glass and reduced to molecular hydrogen. The hydrogen gas was purified in a Molecular Sieve 5A gas chromatographic column and was then introduced into the ion source of the isotope ratio mass spectrometer equipped with Faraday cup (FCs) to allow simultaneous determination of mass 2 and 3 (HH⁺ and HD⁺, respectively). D/H ratios of the samples were compared with that of Vienna Standard Mean Ocean Water (VSMOW, D/H = 0.00015576) (Coplen, 1988), expressed as δDVMOW = [(D/H)unknown/(D/H)VSMOW] – 1) × 1000, in units of per mil (%). A polyethylene standard from the International Atomic Energy Agency (IAEA-CH-7, δDVMOW = –100.3 ± 2.0‰, 1 standard deviation; 1 SD) was measured between every unknown sample to determine the instrumental mass fractionation (IMF) and to decrease the memory effect unknown sample to determine the instrumental mass standard deviation; 1 SD) was measured between every analytical session to check stability of the two standards during the analytical session was 0.22‰ (1 SD; n = 6).

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**Sulfur isotope ratios of glasses determined by IRMS**

We conducted sulfur isotope analyses of the basaltic glass standard using a Thermo Fischer MAT 253 mass spectrometer at the Tokyo Institute of Technology, following the methods of Matsu’ura et al. (2016), Shimizu et al. (2015), and Ueno et al. (2008). Approximately 0.1 g of sample reacted with hot tin(II) phosphate solution (Kiba reagent method of Sasaki et al., 1979) at 350°C for 1 hour to convert all the sulfur in the sample to $H_2S$. The $H_2S$ was subsequently converted to $Ag_2S$ through a reaction with silver(I) nitrate solution. The dried $Ag_2S$ was weighed to gravimetrically determine the sulfur concentration of the glass.

The $^{34}S/{^{32}S}$ ratios of the samples were compared with that of the Vienna Canyon Diablo Troilite (VCDT, $^{34}S/{^{32}S} = 1/22.6436$) (Ding et al., 2001), expressed as $δ^{34}SVCDT = [(^{34}S/^{32}S)_{unknown}/(^{34}S/^{32}S)_{VCDT}] – 1) × 1000$, in units of per mil (%). The silver sulfide standard from the IAEA (IAEA-S1, $δ^{34}SVCDT = –0.3‰$) was measured to calibrate the $δ^{34}SVCDT$ value. The reproducibility of the standards during the analytical session was 0.22‰ (1 SD; n = 6).

The sulfur concentrations of the EPR-G3 and FJ-G2 glasses extracted by the Kiba reagent method were 1174 and 1298 ppm, respectively, which was identical, within error, to those measured by ion chromatography following pyro-hydrolysis (1269 and 1372 ppm, respectively) (Table 2). This indicates that the sulfur isotope ratios determined by IRMS were representative of their volcanic glasses.
were embedded in indium metal mounts to decrease the hydrogen background. The sample mounts were ultrasonically washed with deionized water and dried in a high vacuum oven at 80°C for >48 hours before gold coating. The gold-coated sample mounts were kept in the sample chamber of the SIMS for >12 hours before being placed in the analysis chamber. The pressure in the analysis chamber was 1.2 × 10⁻⁵ mbar during measurements.

For the analysis of hydrogen isotope ratios, a 20 keV defocused cesium ion beam of ~70 nA (~15 μm diameter) was used. A 10 keV electron beam of ~100 μm diameter was flooded on the sample surface for electrostatic charge compensation. Negative secondary ions were accelerated to 10 kV. The secondary ion image optics was set to 200 × magnification, and the field aperture size was set to 1.4 × 1.4 mm², which corresponds to the field of view of 7 × 7 μm². The energy slit width was set to 50 eV. By setting the field aperture size smaller than the primary beam size, we were able to collect secondary ion signals from the center of the beam spot and minimize hydrogen contamination on the sample surface, particularly from the edge of the primary beam.

Negative secondary ions of ¹⁶OH⁻ and ¹⁶OD⁻ were measured in multi-detection mode with an FC of 10¹¹ Ω resistance and axial EM, respectively. The mass resolving power (M/ΔM) of the axial detector was set to ~10000 to sufficiently separate the ¹⁶OD⁻ from ¹⁶O⁻, ¹⁷OH⁻, and ¹⁷OHH⁻ (Fig. 1). The mass resolving power of the FC detector was set to ~5000 with a slit of 250 μm in width, which was sufficient to separate the ¹⁷OH⁻ signal from the ¹⁷O⁻ signal. Under these conditions, the signal sensitivity of ¹⁶OH was ~2 Mcps/wt% H₂O. Each measurement consisted of 20 seconds pre-sputtering with a rastered beam of 20 × 20 μm, ~120 seconds for autocentering of ¹⁶OH⁻ to the field and contrast apertures, and 4 seconds × 50 cycles for measurements. The total measurement time for each analysis was ~6 minutes. Field background stability was ~700 cps (2 SD), which did not affect the D/H ratios as long as OH was >0.4 Mcps or H₂O was >0.2 wt%. We were not able to measure basaltic glass with a low water content (<0.2 wt%) or OH intensity (<0.4 Mcps), which affected the D/H ratio by FC background stability (700 cps/0.4 Mcps: ~2‰).

We also checked the OH background by measuring anhydrous synthetic quartz glass (H₂O < 1 ppm, SUPRASIL-300, Shinetsu Quartz, Japan) using the axial EM detector. The detection of OH was always lower than 100 cps, which is negligible for the target sample of basaltic glass (H₂O > 0.2 wt%, or OH > 0.4 Mcps).

The IMF for δD measurement was defined using standard basaltic glasses:

\[
\text{IMF(OD/OH)} = \frac{[\text{OD/OH}_{\text{STD-RAW}}/\text{OD/OH}_{\text{STD-VSMOW}} - 1] \times 1000}{(\%e)}
\]

For the analysis of sulfur isotope ratios, we used a 20 keV defocused cesium ion beam of ~0.5 nA (~10 μm diameter). The conditions of the electron gun and field of view were the same as those for the hydrogen isotope analyses. The field aperture size was set to 15 × 15 μm of the field of view of the secondary ion image to collect all secondary ions, eliminate aberration of secondary ion optics, and minimize unexpected sulfur signals from sample surfaces outside of the targeted area. Negative secondary ions of ³²S⁻ and ³⁴S⁻ were measured in multi-detection mode with an FC and axial EM, respectively. The M/ΔM of the FC and EM detectors were set to ~2200 and ~5000 to separate the ³⁴S⁻ signal from ³¹PH⁻ and ³³S⁻ from ³³SH⁻, respectively.

Under these conditions, the signal of ³²S was ~1.3 Mcps/1000 ppm S. Each measurement consisted of 20 seconds pre-sputtering, 120 seconds auto-centering of ³²S⁻ to the field and contrast apertures, and 5 seconds × 50 cycles for measurements. The total measurement time for each analysis of sulfur isotope was ~7 minutes. Since FC background stability was ~700 cps (2 SD), sulfur isotope measurement of glass with low sulfur content (S < 500 ppm or ³²S < 0.7 Mcps) was influenced by FC instability (700 cps/0.7 Mcps: ~1‰). Thus, in this study, we measured glass with high sulfur content (S < 1000 ppm).

The IMF for δ³⁴S was defined using standard basaltic glasses:

\[
\text{IMF(}^{34}\text{S)} = \frac{[\text{³⁴S/³²S}_{\text{STD-RAW}}/\text{³⁴S/³²S}_{\text{STD-VCDT}} - 1] \times 1000}{(\%e)}
\]

and ³⁴S values of the unknown samples were determined as follows:

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Fig. 2. (A) Instrumental mass fractionation factor (IMF) of D/H ratios determined by secondary ion mass spectrometry. (B) Relative IMF difference to Vol-3A as a function of measured δD$_{\text{VSMOW}}$ by thermal conversion elemental analysis/isotope ratio mass spectrometry of volcanic glasses. The slopes of the lines between basaltic glasses of Vol-3A and Vol-1B (and Vol-05A) are the isotope scaling parameters used for determining the IMF of unknown samples during each analytical session (Paul et al., 2007). Note the boninitic glass plot on the IMF trend of basaltic glass (blue triangles with blue dashed line), but that of the rhyolitic glass is much lower (green triangle with green dashed line). Error bars show reproducibility by 2 standard deviations (2SD). Also note that an electron multiplier detector efficiency recalibration was conducted between the sessions of June 2017 and January 2018, and IMF consequently decreased by ~80‰.
RESULTS AND DISCUSSION

Hydrogen isotope measurements by SIMS

We conducted multiple sessions of hydrogen isotope analyses of glass standards to evaluate the reproducibility of individual measurements, matrix effects of IMF, and reproducibility of results among multiple sessions. We also performed a prolonged test analysis (~40 minutes) to investigate the benefits and limitations of longer measurement times.

The IMF values of the hydrogen isotopes that derived from basaltic glasses with different water contents (0.54–3.6 wt%) were identical within errors (Figs. 2A and 2B). However, the OD/OH IMF of glass with a low δD\textsubscript{VSMOW} of approximately −110‰ (Vol-1B: 0.94 wt% H\textsubscript{2}O; Vol-05A: 0.54 wt% H\textsubscript{2}O) was always lower than that of glass with a high δD\textsubscript{VSMOW} of +37‰ (Vol-3A: 3.6 wt% H\textsubscript{2}O) in each session by 5–15‰ (Figs. 2A and 2B). This suggests that there may be an effect on (or systematic error in) the OD/OH IMF values due to the distinct δD\textsubscript{VSMOW} values of the standard glasses. We are not certain of this subtle contradiction of SIMS data with IRMS data whether it is due to different ionization mechanism between IRMS and SIMS, or combination of detectors we used for SIMS analyses. Although the IMF difference between Vol-1B (and/or Vol-05A) and Vol-3A is within analytical error (5–15‰ versus −10‰) over their δD\textsubscript{VSMOW} difference of ~150‰ (Fig. 5B), we applied the two-point linear normalization of Paul et al. (2007) to correct the accuracy of the data. This normalization is commonly used by IRMS measurements using two certified reference materials and assumes that the systematic error introduced during analyses is linear in a dynamic range (Paul et al., 2007). In addition, the D/H IMF of the boninitic glass fits well with the IMF trend of basaltic glass (blue triangles with blue dashed lines in Figs. 2A and 2B), but the IMF of rhyolite was lower than that of the basaltic glass by ~25‰ (green triangles with green dashed lines in Figs. 2A and 2B). These results indicate that the matrix effect of IMF for basaltic and boninitic glass using OH− and OD− signals is small in contrast with the results of Hauri et al. (2006), which measured H− and D− signals. A possible reason is that the IMF of OD/OH measurements is less sensitive to the composition of glass than the IMF of D/H measurements is. Although we are not certain of this contradiction, the two lightest anions of H− and D− may exert much more influence on the D/H IMF by “kinetic energy transfer during sputtering” (see Hauri et al., 2006), than the OH/OH IMF.

We used the IMF with a two-point linear normalization (IMF\textsubscript{T}) to determine the δD of unknown samples:

\[
\text{IMF}_T = a \times [(\text{OD/OH})_{\text{unknown}} - (\text{OD/OH})_{\text{WS}}] + \text{IMF}_{\text{WS}}
\]

where WS denotes the averaged value of the working standard glass (Vol-3A or HW-G1), and a is the slope of the IMF between Vol-3A and Vol-1B as a function of their OD/OH ratios as follows:

\[
a = \frac{(\text{IMF}_{\text{Vol-3A}} - \text{IMF}_{\text{Vol-1B}})}{[(\text{OD/OH})_{\text{Vol-3A}} - (\text{OD/OH})_{\text{Vol-1B}}]}
\]

Finally, δD\textsubscript{VSMOW} values of the unknown samples were determined as follows:

\[
\delta D_{\text{VSMOW}} = \left(\frac{(\text{OD/OH})_{\text{RAW}}}{\text{IMF}_T/1000}\right)\left(\frac{1}{(\text{IMF}_T/1000)} - 1\right) \times 1000 \text{ (‰)}.
\]

We performed a longer OD/OH measurement to see whether the measured OD/OH value changed and recognized that the IMF (or D/H ratios) decreased by nearly 100‰ over the 40 minutes of the analysis (Fig. 3A). As a result, the in-run precision became larger after 15 minutes, even though the accumulated counts of ion signals...
Table 3. $\delta D_{\text{VSMOW}}$ and $\delta^4$S$_{\text{VCDT}}$ of submarine basaltic glass by SIMS. Their major and volatile concentrations are from Shimizu et al. (submitted).

| Handling name | Sample name | Cruise | Locality | Lithology | Latitude [°] | Longitude [°] | Depth [mbsf] | $\delta D_{\text{VSMOW}}$ | S
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>EPR-G3</td>
<td>RY380-R04</td>
<td>YK97-05</td>
<td>East Pacific Rise</td>
<td>Tholeite</td>
<td>-17.44</td>
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<td>-65</td>
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<tr>
<td>EPR-G4</td>
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<td>YK97-05</td>
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<td>Tholeite</td>
<td>-18.41</td>
<td>-113.36</td>
<td>2627</td>
<td>-69</td>
<td>11</td>
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<tr>
<td>IND-G1</td>
<td>6K1164-R01</td>
<td>YK09-13</td>
<td>Central Indian Ridge</td>
<td>Tholeite</td>
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<td>2748</td>
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<td>7</td>
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<tr>
<td>IND-G2</td>
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<td>YK08-07</td>
<td>Southwest Indian Ridge</td>
<td>Tholeite</td>
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<td>-67</td>
<td>8</td>
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<tr>
<td>MAR-G1</td>
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<td>YK98-05</td>
<td>Mid Atlantic Ridge/Cape Verde Fracture Zone</td>
<td>Tholeite</td>
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<td>Hawaii Kilauea East Rift</td>
<td>Alkalic basalt</td>
<td>19.49</td>
<td>-54.36</td>
<td>5564</td>
<td>-95</td>
<td>6</td>
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<td>HW-G2</td>
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| Handling name | $\delta^4$S | S
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increased in proportion to the measurement time. An apparent and constant decrease in the IMF value was probably due to the deepening of the measurement pit (e.g., Ushikubo et al., 2014). This result indicates that a change in total measurement time can introduce additional uncertainty in the IMF, even if in-run precision apparently improves due to counting statistics (Fig. 3B). As the slope of the D/H ratio decay during each measurement was generally not the same, we applied shorter durations or cycles to minimize D/H ratio decay (<10 minutes or 50 cycles, up to the red diamond in Fig. 3A). With this shorter duration, we had a larger in-run standard error (2 SE) of 3‰ for the Vol-3A glass than the 2‰ with ~15 minutes or 150 cycles (Fig. 3B). The errors may become considerably larger, particularly for glass with low water contents (2 SE: ~12% for 0.2 wt% H2O, Table 3), but more plausible D/H ratios may be obtained by minimizing the decay of the D/H ratios.

To determine the D/H ratios of unknown samples, we measured the standard glasses of Vol-3A and Vol-1B, and the working standard of the Hawaiian glass HW-G1 (H2O content of 1.44 wt% and δDSMOW of −95 ± 6‰, Table 3) at the beginning of an analytical session to (1) monitor the reproducibility of the OD/OH IMF, (2) determine the two-point normalization parameter of Paul et al. (2007) (effect or systematic error on OD/OH IMF by the δDSMOW value of glasses, Fig. 2), and (3) confirm the δDSMOW of HW-G1. Determination of the δDSMOW of HW-G1 is discussed in a later section.

We applied the standard bracketing method to determine D/H ratios of unknown basaltic glass samples (e.g., Ushikubo et al., 2014, and Kita et al., 2009). The working standard of HW-G1 or Vol-3A was embedded in the same mount as the unknown samples were, and the working standard was measured 4–5 times for every 10–15 unknown samples. By averaging 8–10 data points of the working standard glass, the OD/OH IMF and analytical error of 2 SD were calculated. If the 2 SE of the unknown sample was greater than the 2 SD, we adopted the former as the analytical error; otherwise, we adopted the latter as the analytical error (Fig. 4).

**Sulfur isotope measurements by SIMS**

The 34S/32S IMF by SIMS gradually decreased over time (Fig. 5), because the sensitivity of the axial EM was lowered by detecting a large amount of 34S ions (nearly 0.1 Mcps) on the EM. The reproducibility of 20 measurements of the standard glass (EPR-G3) was 1.0‰ (2 SD) without drift correction but was 0.7‰ with drift correction.
Fig. 6. Example of the analytical sequence of sulfur isotope ratios of basaltic glasses by the standard bracketing method. Gray arrows indicate the timing of the electron multiplier high voltage adjustment.

The working standard of EPR-G3 or FJ-G2 was embedded in the same mount as the unknown samples, and the working standard was measured 4–5 times for every 10–15 unknown samples. The definition of the analytical error in the $^{34}\text{S}/^{32}\text{S}$ ratio was the same as that of the D/H ratio mentioned above. The analytical error for basaltic glass with $>1000$ ppm S was $-0.6 \pm 0.1\%$ (2 SD), depending on the analytical reproducibility of the bracketing standard. Beyond that, the error increased with decreasing sulfur content of the glass due to the counting statistics of the $^{34}\text{S}$ and $^{32}\text{S}$ intensities. The quantification limit for sulfur isotopes in basaltic glass depends on the sulfur isotope variation of the samples from the intended study, but it may be $-300$ ppm S under the present analytical conditions, whose error would be $-2\%$ (2 SE).

Hydrogen and sulfur isotope ratios of unknown basaltic glasses

In this subsection, we present hydrogen and sulfur isotope ratios of basaltic glass erupted in deep submarine settings at various localities (East Pacific Rise, Indian...

Fig. 7. Beam pits of secondary ion mass spectrometry analyses of volatiles ($\text{H}_2\text{O}$, $\text{CO}_2$, S, F, Cl) and $\text{P}_2\text{O}_5$ concentrations (V), hydrogen (H), and sulfur (S) isotope ratios on (A) volcanic glass and (B) $50$ $\mu$m melt inclusion in olivine.
Fig. 8. Hydrogen isotope ratios of EPR-G3 (blue diamonds) and HW-G1 (orange circles) between different analytical sessions, showing reproducibility of hydrogen isotope ratios. Solid and open symbols indicate actual and session-averaged data, respectively.

Fig. 9. Hydrogen and sulfur isotope ratios of volcanic glasses of Pacific, Atlantic, and Indian mid-oceanic ridge basalts (MORBs), Fiji back arc basin basalts (BABBs), and Hawaiian oceanic island basalts (OIBs) used in this study. (A) $\delta^{34}$S_VCDT versus $\delta^{18}$O_VSMOW. (B) H$_2$O wt% versus $\delta$D_VSMOW. The correlation line in (B) was drawn using all data, except for IND-MORB, for containing a component of recycled material.

We demonstrated the reproducibility of hydrogen isotopes in the two glass samples of EPR-G3 and HW-G1 during individual sessions over a period of two years (Fig. 8). In-run precision of the $\delta$D_VSMOW of EPR-G3 was $\sim$12‰ (2 SE) because of its low water content (0.22 wt%), but the reproducibility of $\delta$D_VSMOW became 3‰ (2 SE) inclusion as small as ~30 μm across (Fig. 7B).
by repeated measurements (n = 28) and 4‰ (2 SE) for the session averaged data (n = 5) (Fig. 8); $\delta^{34}$S_VSMOW of EPR-G3 was ~64‰ for averaged data. For HW-G1 glass, in-run precision of the $\delta^{34}$S_VSMOW was ~6‰, and reproducibility became 2‰ by repeated measurements (n = 36) and 6‰ for the session averaged data (n = 4). However, $\delta^{34}$S_VSMOW of HW-G1 was ~95‰ for the averaged data, the maximum and minimum session averaged $\delta^{34}$S_VSMOW of HW-G1 were ~88 and ~102‰, respectively (Fig. 8), the ranges of which did not overlap, even if the 2 SE of ~6‰ in-run precision was applied. This may be attributed to the small number of analytical data that did not conform with the statistics. Although we applied the HW-G1 $\delta^{34}$S_VSMOW of ~95 ± 6‰, smaller errors and a more appropriate $\delta^{34}$S_VSMOW may be obtained by data accumulation in the future. Because of the limited supply of Vol-3A, we used HW-G1 as the working standard for the standard bracketing method from 2018 onwards.

Figure 9 shows the results for all the measured samples. The $\delta^{34}$S_VCDT of the measured volcanic glasses ranged from ~1.1 to +0.7‰. Although there were no clear statistical differences in $\delta^{34}$S_VCDT among the samples, as their analytical precisions were ~0.6‰ (2 SE), the average $\delta^{34}$S_VCDT of Hawaiian OIB glass (~0.8 ± 0.6‰) was slightly lower than that of MORB glass (~0.3 ± 0.6‰) (Fig. 9A). Hawaiian OIB may represent a deep mantle source (e.g., Jackson et al., 2007), whereas MORBs represent an upper mantle source, and the $^{34}$S/$^{32}$S ratio of the deep mantle may therefore be lower than that of the upper mantle. The MORB and Hawaiian OIB data in this study were within the ranges of previously reported data with high precision using IRMS, e.g., Labidi et al. (2013) (~0.8 ± 1.16‰ (2 SD)) or Sakai et al. (1984) (~0.51 ± 1.28‰ (2 SD)). Our method was not sufficiently accurate to reveal small isotopic differences but can be a powerful tool for small melt inclusions with larger variation in sulfur isotope ratios, such as arc tholeiites.

On the other hand, the $\delta^{34}$S_VSMOW of MORB glasses and Hawaiian OIB were clearly distinguishable (Figs. 9A and 9B). The average $\delta^{34}$S_VSMOW of MORB glass was ~68 ± 10‰ (2 SD), which was within the range of previously suggested MORB values (~60 ± 10‰, Clog et al., 2013). We observed a negative correlation between H$_2$O content and $\delta^{34}$S_VSMOW among submarine basaltic glasses ($R^2$ = 0.94), with the exception of the Indian MORBs (Fig. 9B). Because these Indian MORBs can be highly influenced by recycled materials (Shimizu et al., submitted), the data should be considered separately. Shimizu et al. (submitted) reported on the strong linear correlation between H$_2$O and F contents among MORBs and Hawaiian OIBs, which are the same volcanic glasses analyzed in this study. It was implied that this trend is attributable to the mixing of the depleted MORB mantle (DMM) and the focal zone distributed ubiquitously in the deep mantle (FOZO) (e.g., Strac.ke et al., 2005). The negative trend of H$_2$O content and $\delta^{34}$S_VSMOW among submarine basaltic glasses may indicate a DMM-FOZO array, and the $\delta^{34}$S_VSMOW of Hawaiian source mantle (FOZO) should be lower than that of DMM. However, further study is required to become more certain of the determination of the FOZO $\delta^{34}$S_VSMOW.

**CONCLUDING REMARKS**

In this study, we developed in situ analyses of hydrogen and sulfur isotope ratios using high-resolution SIMS. Multi-collection of $^{16}$OH and $^{18}$OD for hydrogen isotopes and $^{32}$S and $^{34}$S for sulfur isotopes enabled us to measure these isotopes in ~6 minutes, with relatively good precision, namely ~6 and ~0.6‰ (2 SE) for hydrogen and sulfur isotopes, respectively. We were able to measure volatile element concentrations, and hydrogen and sulfur isotope ratios of basaltic melt inclusions of as small as ~30 μm by using a beam size of <15 μm for these applications. Matrix effects on D/H IMF for volcanic glass may not be significant as long as its composition is basaltic or boninitic, but the D/H IMF of rhyolitic glass differs from that of basaltic glass by ~40‰. We are not certain about the matrix effect of chemical composition on $^{34}$S/$^{32}$S IMF other than for basaltic glass. Further research on the matrix effects on IMFs of both hydrogen and sulfur isotope ratios is required to expand quantitative analysis to include volcanic glass with other compositions.

**Acknowledgments**—We thank M. Ito and T. Ishikawa for fruitful discussions, and F. Tomiyasu, J. Foriel, and M. Takeda for analytical support. This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Nos. JP15H03751, JP17H2994, JP18H01320, and JP25610160 for K.S.; JP25600526 and JP17H184580 for T.U., and 26287145 for Y.U.

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