EXPRESS LETTERS

A new method for quantitative analysis of total water contents and estimating molecular water and hydroxyl contents in rhyolitic glasses by SIMS

Akimasa Suzumura^{1,2*}, Satoshi Okumura³, Chikashi Yoshimoto¹, and Shoichi Itoh^{1*}

¹ Department of Earth and Planetary Sciences, Kyoto University, Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

³ Division of Earth and Planetary Materials Science, Department of Earth Science, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki-aza, Aoba, Sendai 980-8578 Miyagi, Japan

* Corresponding author E-mail: suzumura.akimasa.5k@kyoto-u.ac.jp (A. S.); sitoh@kueps.kyoto-u.ac.jp (S. I.)

Abstract

We have succeeded in developing a new analytical method to estimate the concentration of hydrous chemical species (molecular water; H₂O_m and hydroxyl groups; OH) and total water (H₂O_{total}) in rhyolitic glass using secondary ion mass spectrometry (SIMS). This method makes it possible to estimate the H_2O_m contents, OH contents, and H_2O_{total} contents at the micrometer scale (<10 μ m) in silicate glasses such as melt inclusions by SIMS. With a ${}^{16}O^{-}$ primary ion beam, a linear correlation between ${}^{1}H^{+/30}Si^{+}$ ratios and $H_{2}O_{total}$ contents is observed. On the other hand, there is a linear correlation between ${}^{1}H^{-/30}Si^{-}$ ratios and OH contents when using a ${}^{133}Cs^{+}$ primary ion beam. These results suggest that the ${}^{1}H^{+/30}Si^{+}$ ratios reflect the $H_{2}O_{total}$ contents, while the ${}^{1}H^{-/30}Si^{-}$ ratios mainly reflect the OH contents. Therefore, the selective estimation of the H₂O_{total} or OH contents can be achieved through the selection of the primary ion beam (16O- and 133Cs+). This new method will aid in the estimation of the pressure and temperature of the magma reservoir in the Earth's interior depending on the solubilities of H_2O_m , OH, and H_2O_{total} in silicate melts, and in the understanding of water transport in the silicate glasses and melts.

Keywords SIMS, rhyolitic glass, water content, chemical species Dates Received: December 21, 2023 Accepted: March 18, 2024 Advance publication: April 9, 2024

Introduction

Considering the influence of water on volcanism and mantle processes and properties, including melting temperature, rheology, seismic wave propagation, electrical conductivity, and degassing behavior (e.g., Peslier et al., 2017), it is important to understand the water contents in volcanic glasses. Hydrogen is mainly dissolved in volcanic glasses as molecular water (H2Om) and hydroxyl groups (OH), and the speciation of dissolved water depends on the total water content (H₂O_{total}), temperature, and pressure (e.g., Ihinger et al., 1999; Zhang, 1999; Hui et al., 2008). Therefore, if the concentrations of hydrous chemical species and total water in volcanic glasses can be determined, this could help to estimate several physico-chemical conditions and processes such as the temperature, pressure, cooling rate, and co-existence of other volatile elements. Fourier transform infrared spectroscopy (FT-IR) may be the most powerful method for identifying the hydrous chemical species, including H_2O_m and OH, and determining the water concentrations in volcanic glasses (e.g., Stolper, 1982). However, FT-IR has several disadvantages, particularly in analyzing small samples such as melt inclusions.

1 of 7

Geochemical Journal Vol. 58 No. 3 (2024) pp. e1-e7 DOI: 10.2343/geochemi.GJ24008

Suzumura, A., Okumura, S., Yoshimoto, C. and Itoh, S. (2024) A new method for quantitative analysis of total water contents and estimating molecular water and Citation hydroxyl contents in rhyolitic glasses by SIMS. Geochem. J., 58, e1-e7.



Copyright © 2024 The Geochemical Society of Japan. This is an open access article distributed under the terms of the Creative Commons BY-ND (Attribution-NoDerivs) License (https://creativecommons.org/licenses/by-nd/4.0/legalcode), which permits use, distribution, and reproduction in any medium, provided that the article is properly cited, and no modifications or adaptations are made.

² Present affilliation: Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan

| | H_2O_{total} (wt%) | σ | OH (wt%) | σ | H_2O_m (wt%) | σ |
|--------|----------------------|-------|----------|-------|----------------|-------|
| SAI5 | 0.520 | 0.006 | 0.419 | 0.003 | 0.089 | 0.005 |
| SAI3 | 1.600 | 0.042 | 1.092 | 0.023 | 0.557 | 0.035 |
| SAI2 | 1.872 | 0.065 | 1.165 | 0.028 | 0.707 | 0.059 |
| SAI6 | 2.560 | 0.107 | 1.404 | 0.057 | 1.212 | 0.091 |
| SAIKU1 | 4.562 | 0.274 | 1.972 | 0.245 | 2.590 | 0.124 |
| SAIKU3 | 3.536 | 0.020 | 1.872 | 0.007 | 1.664 | 0.018 |

Table 1. Total water cotents, H₂O_m contents, and OH contents of rhyolitic glass standards

Secondary ion mass spectrometry (SIMS) is one of the most powerful tools for measuring the water content insitu analysis at high spatial resolution (~10 µm scale). Two different primary ion beams ($^{16}O^{-}$ and $^{133}Cs^{+}$) are usually used in SIMS and are selected depending on the secondary ion yields of the target elements. Several previous studies have been conducted to estimate the water content dissolved in volcanic glasses (e.g., Hauri et al., 2002; Shimizu et al., 2017). However, it has been reported that the calibration curve for water in rhyolitic glasses (H2Ototal vs. 1H-/30Si- or 16O1H-/30Si-) becomes non-linear at higher water contents (>2 wt%) using the ¹³³Cs⁺ primary ion beam (e.g., Hauri *et al.*, 2002; Hervig et al., 2003; Shimizu et al., 2022), with an approximate power-law relationship between water contents and secondary ion ratios (1H-/30Si- or 16O1H-/30Si-) in rhyolitic glasses. In this case, the accuracy of the water content estimated from SIMS data with the error obtained for unknown samples at higher water contents (>2 wt%) is inferred to become lower than that estimated from the linear calibration curve. This non-linear relationship between water contents and secondary ions ratio (1H-/ ${}^{30}\text{Si}^-$ or ${}^{16}\text{O}^1\text{H}^{-/30}\text{Si}^-$) obtained by SIMS may be due to the matrix effect on the SIMS-estimated water contents and/or chemical compositions. Several studies have examined the matrix effect of chemical composition for the calibration curve of water contents (e.g., Miyagi and Yurimoto, 1995; Rhede and Wiedenbeck, 2006; Aubaud et al., 2007; Shimizu et al., 2022).

On the other hand, it is known that the ratios of the hydrous chemical species in rhyolitic glasses change depending on the H_2O_{total} content (e.g., Ihinger *et al.*, 1999; Zhang, 1999). It is possible that differences in the ionization efficiency of different chemical species of water can be a cause of the non-linear calibration curve. Nevertheless, in SIMS measurements, it has been assumed that secondary hydrogen ions reflect the total water content regardless of the chemical species (H_2O_m and OH), since the abundance of hydrogen in different chemical species cannot be measured separately. Therefore, it is likely to be important to establish the calibration method considering the different hydrous chemical species. However, there are no studies of calibration methods that focus on each chemical species of hydrogen

in silicate glass, let alone oxides, silicates, and other minerals. In this study, we clarify the relationship between the ${}^{1}\text{H}^{+/30}\text{Si}^{+}$ ratios or the ${}^{1}\text{H}^{-/30}\text{Si}^{-}$ ratios estimated by SIMS using both primary ion beams (${}^{16}\text{O}^{-}$ and ${}^{133}\text{Cs}^{+}$) and the concentrations of hydrous chemical species (H_{2}O_{m} and OH) and total water ($\text{H}_{2}\text{O}_{total}$) in the synthetic rhyolitic glass standards. Here we report a new analytical method for selective estimation of the molecular water and hydroxyl content in rhyolitic glasses.

Sample and Methods

Rhyolitic glass standards

Six synthetic rhyolitic glasses were used as standards for SIMS analysis. The anhydrous chemical compositions of all rhyolitic glass standards are the same (SiO₂ = 77.3, TiO₂ = 0.1, Al₂O₃ = 12.6, FeO = 0.6, MnO = 0.1, MgO = 0.1, CaO = 0.5, Na₂O = 3.7, K₂O = 5.1 in wt%). The starting material is the rhyolitic obsidian from Wadatouge, Japan. Four samples (SAI2, 3, 5, and 6) with varying water contents (**Table 1**) were prepared using an internally heated pressure vessel at 1000°C and 100 MPa for 240 h by Okumura and Nakashima (2005). In this study, we synthesized two additional samples (SAIKU1 and 3) with relatively high water contents (**Table 1**) using a cold seal pressure vessel at 900°C and 90 and 120 MPa for ~96 h, using the method of Okumura *et al.* (2021).

The H₂O_m and OH contents of the rhyolitic glass standards were determined using a FT-IR microscope (MFT-2000, Jasco Co and Nicolet iN-10, Thermo Fisher Scientific Inc: MCT detector, ceramic IR source, and KBr beam splitter). The H₂O_m and OH contents of the rhyolitic glass standards were determined from the density, the sample thickness, the peak intensity of the ~5230 cm⁻¹ band for H_2O_m absorption and the ~4500 cm-1 band for OH absorption, and the molar absorptivities of the ~5230 cm⁻¹ band (1.75 L/mol·cm) and the ~4500 cm⁻¹ band (1.42 L/mol·cm), respectively (Okumura and Nakashima, 2005). All the spectra were corrected using two straight baselines in the range of 4240 to 4670 cm⁻¹ and 4900 to 5400 cm⁻¹ (Okumura and Nakashima, 2005). The internally calibrated molar absorptivities were applied in this study because they

depend on chemical composition (e.g., Withers and Behrens, 1999; von Aulock et al., 2014) and the calibration methods such as peak position and baselines. Okumura and Nakashima (2005) determined the densities of the samples based on their weight of the volume measured by weighing samples in air and deionized water. The densities of samples synthesized in this study were calculated based on the relationship between water contents and the density of rhyolitic glass reported by Okumura and Nakashima (2005). As reported in Okumura and Nakashima (2005), the thicknesses of the samples were measured by a laser scanning confocal microscope (LSCM) (KEYENCE, Color Laser 3D Profile Microscope VK-8500, and VK-8510) and a micrometer. The precision of the thickness measurement is less than 1 µm. The H₂O_{total} contents are assumed to be equal to the sum of the H₂O_m and OH contents. This can be described by the following equation:

$$C[H_2O_{total}] = C[H_2O_m] + C[OH]$$
⁽¹⁾

where $C[H_2O_{total}]$, $C[H_2O_m]$, and C[OH] are the H_2O_{total} contents, H_2O_m contents, and OH contents, respectively. The analytical conditions are described in previous work (Okumura *et al.*, 2003; Okumura and Nakashima, 2005). **Table 1** shows the H_2O_{total} contents, the OH contents, and the H_2O_m contents of the rhyolitic glass standards used in this study. The OH contents are saturated with increasing the H_2O_{total} contents. On the other hand, the H_2O_m contents increase exponentially with the increase of the H_2O_{total} contents.

SIMS analysis

Hydrogen contents were measured with stigmatic ion optics using a SIMS (Cameca, ims-4fE7) at Kyoto University. All samples were also stored in the SIMS airlock chamber at $<2 \times 10^{-7}$ Pa for >48 h prior to the analyses to reduce the effect of adsorbed H₂O. All rhyolitic glass standards were mounted in indium metal contained in an aluminum disk sample holder with diameter of 1 inch and thickness of 10 mm to reduce degassing from the sample mount. The detailed method of sample mounting for volatile analysis in small samples using SIMS is described in Shimizu et al. (2017). To reduce the residual hydrogen species in the sample chamber, we used a liquid nitrogen cold trap manufactured by Techno-IS Corporation. During the analyses, the vacuum of the sample chamber was maintained at $1.0-4.0 \times 10^{-10}$ Torr. To remove the contamination signal from the crater edge of the primary beam, secondary ions were generated from the center of the primary beam irradiation area (7 µm in diameter) using a mechanical field aperture. Before and after the analyses, we carefully checked the presence/ absence of cracks in the analytical spots by hydrogen ion images using the microchannel plate/fluorescent screen/ charge coupled device camera (MCP/FS/CCD) system developed at Kyoto University.

Our ¹⁶O⁻ primary ion beam analytical set-up employed a 17.5 keV with a beam spot diameter of 20-30 µm and a beam current of approximately 6-11 nA. A voltage offset removes background H⁺ counts by eliminating H⁺ ions desorbed from the sample surface via abundant secondary electrons produced during the impact of the primary ion beam (e.g., Yurimoto et al., 1989). Kinetic energy filtering to eliminate such interference was achieved by offsetting the sample accelerating voltage (-100 eV) while keeping the setting of the electrostatic analyzer voltage and the width and position of the energy slit constant. The energy slit was set to accept a 50 eV window. Compared to the measurements with the offset of the sample accelerating voltage, the measurements without the offset of the sample accelerating voltage were also performed for all samples. Positive secondary ions (¹H⁺ and ³⁰Si⁺) were collected using an electron multiplier (EM). The ${}^{30}Si^+$ secondary intensity was 1.0–7.7 × 10³ cps. The measurement sequence was conducted with ¹H⁺ for 1 s and ³⁰Si⁺ for 1 s for each cycle, and the cycle was 10 cycles. The analytical procedures were reported by Okumura et al. (2021).

The ¹³³Cs⁺ primary ion beam was 14.5 keV with a beam spot diameter set to 20–30 μ m and with a beam current of 3–4 nA. A normal incidence electron gun was applied to compensate for the electrical charge build-up of the analysis area. Negative secondary ions (¹H⁻ and ³⁰Si⁻) were measured using an EM. The secondary ion intensity of ³⁰Si⁻ was 1.3–2.0 × 10⁴ cps. Each measurement was conducted for 5 cycles, with a counting sequence of ¹H⁻ for 1 s and ³⁰Si⁻ for 1 s. The analytical procedures were reported by Kuwahara *et al.* (2021).

The ${}^{30}\text{Si}^+$ and ${}^{30}\text{Si}^-$ intensities are almost constant in all rhyolitic glass standards under each analytical condition (Table S1). For example, the ${}^{30}\text{Si}^-$ ion intensities for counts per second at 26th July 2022 session are ~2.0 × 10⁴ for SAI5, ~1.8 × 10⁴ for SAI3, ~1.7 × 10⁴ for SAI2, ~1.9 × 10⁴ for SAI6, ~1.6 × 10⁴ for SAIKU1, and ~1.6 × 10⁴ for SAIKU3, respectively. These data suggest that the ${}^{30}\text{Si}^+$ and ${}^{30}\text{Si}^-$ intensities are not dependent on the water contents and the ${}^{1}\text{H}^{+/30}\text{Si}^+$ ratios and the ${}^{1}\text{H}^{-/30}\text{Si}^$ ratios reflect the differences in the ${}^{1}\text{H}^+$ or ${}^{1}\text{H}^-$ secondary ions. In all figures in this study, the measured ${}^{1}\text{H}^{+/30}\text{Si}^+$ ratios by the ${}^{16}\text{O}^-$ primary ion beam and the measured ${}^{1}\text{H}^{-/30}\text{Si}^-$ ratios by the ${}^{133}\text{Cs}^+$ primary ion beam are plotted as the vertical axes against the H₂O_{total} contents or the OH contents as the horizontal axes.

Results

Figure 1 shows the relationship between the H_2O_{total} or the OH contents estimated by FT-IR and the ${}^{1}H^{+/30}Si^{+}$ ratios of rhyolitic glass standards obtained by SIMS

| | ¹ H ^{-/30} Si ⁻ | 2σ | ¹ H ⁺ / ³⁰ Si ⁺ | 2σ |
|--------|--|------|---|------|
| SAI5 | 1.20 | 0.09 | 0.23 | 0.04 |
| SAI3 | 3.19 | 0.15 | 0.67 | 0.05 |
| SAI2 | 4.07 | 0.23 | 0.84 | 0.08 |
| SAI6 | 4.20 | 0.21 | 1.07 | 0.11 |
| SAIKU1 | 5.92 | 0.15 | 1.98 | 0.24 |
| SAIKU3 | 5.15 | 0.20 | 1.60 | 0.07 |





Fig. 1. The relationship between H_2O_{total} or OH contents vs. ${}^{1}H^{+/30}Si^{+}$ in rhyolitic glasses by the ${}^{16}O^{-}$ primary ion beam. Solid line represents the calibration curve of H_2O_{total} vs. ${}^{1}H^{+/30}Si^{+}$.

using the ¹⁶O⁻ primary ion beam. The average ¹H⁺/³⁰Si⁺ ratios are shown in **Table 2**. Note that these data are obtained with the offset of the sample accelerating voltage. The SIMS data are linearly correlated with the H₂O_{total} contents. The calibration curve of ¹H⁺/³⁰Si⁺ ratio is fitted to the H₂O_{total} contents using York's regression method for uncorrelated errors (York, 1969). It is expressed as:

$$R[{}^{1}H^{+}/{}^{30}Si^{+}] = 0.45 (\pm 0.02) \cdot C[H_{2}O_{total}] - 0.01 (\pm 0.04)$$
(2)

where the R[¹H^{+/30}Si⁺] is ¹H^{+/30}Si⁺ ratios obtained by SIMS, and the errors on the slope and the intercept are 2σ . The SIMS data without the offset of the sample accelerating voltage also show a good linear correlation with the H₂O_{total} contents (Fig. S1), similar to that with the measurement with the offset of the sample accelerating voltage. It implies that the linear correlation between ¹H^{+/30}Si⁺ ratios and H₂O_{total} contents is not significantly affected by the sample accelerating voltage. On the other hand, there is no linear correlation between OH contents and ¹H^{+/30}Si⁺ ratios (**Fig. 1**). With increasing the OH contents, the deviation of ¹H^{+/30}Si⁺ ratios from linearity are enhanced.

Figure 2 is a plot of the H_2O_{total} or the OH contents



Fig. 2. The relationship between H_2O_{total} or OH contents vs. ${}^{1}H^{-}/{}^{30}Si^{-}$ in rhyolitic glasses by the ${}^{133}Cs^{+}$ primary ion beam. Solid line represents the calibration curve of OH vs. ${}^{1}H^{-}/{}^{30}Si^{-}$.

determined by FT-IR vs. the ${}^{1}H^{-/30}Si^{-}$ ratio obtained by SIMS using the ${}^{133}Cs^{+}$ primary ion beam for rhyolitic glass standards. SIMS data of average ${}^{1}H^{-/30}Si^{-}$ ratios for rhyolitic glass standards are summarized in **Table 2**. A good linear correlation between ${}^{1}H^{-/30}Si^{-}$ ratios and OH contents in all rhyolitic glass standards is found. The calibration curve of ${}^{1}H^{-/30}Si^{-}$ vs. OH is estimated in the same way as those for ${}^{1}H^{+/30}Si^{+}$ vs. H_2O_{total} and is defined as:

$$R[^{1}H^{-/^{30}}Si^{-}] = 2.89 (\pm 0.40) \cdot C[OH] + 0.04 (\pm 0.40) (3)$$

where the R[¹H^{-/30}Si⁻] is ¹H^{-/30}Si⁻ ratios obtained by SIMS, and the errors on the slope and the intercept are 2σ . Whereas the ¹H^{-/30}Si⁻ ratio has no linear correlation with the H₂O_{total} contents except over a range of low H₂O_{total} contents. At the low H₂O_{total} contents (≤ 2 wt%) of samples such as SAI5, SAI3, and SIA2, the ¹H^{-/30}Si⁻ ratio is a nearly linear function of H₂O_{total} contents. However, the ¹H^{-/30}Si⁻ ratios of rhyolitic glass standards with higher H₂O_{total} contents. Similar behavior has been reported in several papers (e.g., Hauri *et al.*, 2002; Hervig *et al.*, 2003; Shimizu *et al.*, 2022).

In order to estimate the OH and H₂O_m contents for an

Table 3. Total water cotents, H₂O_m contents, OH contents, and the ¹H/³⁰Si ratio of synthetic rhyolitic glass

| determined by FT-IR | | | | | obtained by SIMS | | | | |
|---|-------|----------|-------|----------------|------------------|--|------|---|------|
| H ₂ O _{total} (wt%) | σ | OH (wt%) | σ | H_2O_m (wt%) | σ | ¹ H ^{-/30} Si ⁻ | 2σ | ¹ H ⁺ / ³⁰ Si ⁺ | 2σ |
| 4.191 | 0.017 | 2.022 | 0.007 | 2.170 | 0.015 | 5.68 | 0.26 | 1.78 | 0.05 |

unknown sample, we also measured the synthetic rhyolitic glass (SAIKU4) with both primary ion beams (**Table 3**). SAIKU4 was prepared using a cold seal pressure vessel at 900°C and 120 MPa for ~96 h. The chemical composition of the anhydrous starting material was identical to those of the six rhyolitic glass standards. The H_2O_{total} , H_2O_m , and OH contents were determined by the FT-IR (**Table 3**), in a similar way as for the six rhyolitic glass standards.

Discussion

Estimation of the concentrations of hydrous chemical species with ¹³³Cs⁺ and ¹⁶O[−] primary ion beams

For the ${}^{16}O^{-}$ primary ion beam, a linear correlation between ${}^{1}H^{+/30}Si^{+}$ ratios and H_2O_{total} contents is observed. This result suggests that, independent of the ratios of H_2O_m and OH (**Table 1**), the ionization efficiencies of both hydrous chemical species are identical to each other and that the ${}^{1}H^{+/30}Si^{+}$ ratios are derived from the integrated values of the H⁺ secondary ions from both hydrous chemical species. Therefore, when we obtain the H⁺ secondary ions of rhyolitic glass using the ${}^{16}O^{-}$ primary ion beam, it is expected that the linear calibration curve of H_2O_{total} vs. ${}^{1}H^{+/30}Si^{+}$ can accurately estimate the H_2O_{total} contents of unknown samples.

For the ¹³³Cs⁺ primary ion beam, there is a linear correlation between ¹H^{-/30}Si⁻ ratios and OH contents rather than H_2O_{total} contents. This would seem to indicate that the measured H⁻ secondary ions are dominated by the ionization of OH rather than those from both OH and H_2O_m . Therefore, when the ¹³³Cs⁺ primary ion beam is used for the measurement, it suggests that the linear calibration curve of OH vs. ¹H^{-/30}Si⁻ can be used as the estimation of the OH contents of unknown samples.

The difference in the polarity of hydrogen secondary ions (${}^{1}\text{H}^{+}$ or ${}^{1}\text{H}^{-}$) is likely to reflect the difference in the measured hydrous chemical species ($\mathrm{H}_{2}\mathrm{O}_{m}$ and OH) in rhyolitic glass. The calibration curve of eq. (2) using the ${}^{16}\mathrm{O}^{-}$ primary ion beam allows us to estimate the $\mathrm{H}_{2}\mathrm{O}_{\text{total}}$ contents (**Fig. 1**). In addition, it is possible to determine the OH contents with the calibration curve in eq. (3) from the measurement of the H⁻ secondary ions using the ${}^{133}\mathrm{Cs}^{+}$ primary ion beam (**Fig. 2**). In the literature, it is assumed that the efficiency of secondary ionization for chemical species of $\mathrm{H}_{2}\mathrm{O}_{m}$ and OH are equal (e.g., Hervig *et al.*, 2003). For rhyolitic glasses, it has previously been reported that the calibration curve for water in rhyolitic glasses becomes non-linear at high water contents (e.g., Hauri et al., 2002; 2006, Shimizu et al., 2022). On the other hand, there is a linear correlation between ¹H^{-/30}Si⁻ ratios and OH contents within analytical error in our experiments. Although it cannot be excluded that this linear correlation results from several factors including matrix effects, perhaps the simplest interpretation is that we can selectively estimate the OH contents using the ¹³³Cs⁺ primary ion beam. It is generally accepted that the dominant hydrous chemical species in rhyolitic glasses changes from OH to H2Om with increasing the total water contents (e.g., Ihinger et al., 1999). In our SIMS measurements, the ${}^{1}\text{H}^{+/30}\text{Si}^{+}$ ratios show a sharp increase as a function of OH content above 1 wt% OH (Fig. 1), while the ¹H^{-/30}Si⁻ ratios exhibit a significant decrease as a function of H₂O_{total} content above a H₂O_{total} content of 1 wt% (Fig. 2). If our interpretation is correct, these trends likely reflect the change in the dominant hydrous chemical species dissolved in the rhyolitic glasses.

Examination of selectively estimating molecular water and hydroxyl contents applied to the rhyolitic glass for SAIKU4

Our results suggest that SIMS measurement can estimate the OH contents and the H2Ototal contents, and using eq. (1) leads the H_2O_m contents. We have made a preliminary test of this by estimating the concentration of hydrous chemical species in the synthetic rhyolitic glass SAIKU4. The average ¹H⁺/³⁰Si⁺ ratios and ¹H⁻/³⁰Si⁻ ratios of SAIKU4 are 1.78 \pm 0.05 (2s) and 5.68 \pm 0.26 (2s), respectively. The H2Ototal content in SAIKU4 is estimated to be 3.997 ± 0.252 wt% (2 σ) using eq. (2), consistent with the determined H_2O_{total} content by FT-IR of 4.191 ± 0.034 wt% (2σ) (Fig. 3a). Thus, the ability to estimate the H₂O_{total} contents in unknown samples is established. In addition, the estimated OH content of 1.953 ± 0.317 wt% (2σ) using the eq. (3), and the determined OH content of 2.022 ± 0.015 wt% (2 σ) by FT-IR are identical to each other within the measurement errors (Fig. 3b). Moreover, based on eq. (1), the H_2O_m content of SAIKU4 is calculated to be 2.045 ± 0.405 wt% (2 σ). The uncertainty is expressed by the error propagation of the error for slope, intercept, and SIMS measurement. It is consistent with the H_2O_m content (2.170 ± 0.030 wt%) determined by FT-IR. Although it cannot be completely ruled out that the non-linearity correlation between ¹H^{-/} ³⁰Si⁻ and total water may be the result of several factors



Fig. 3. (a) Estimating the H_2O_{total} contents by SIMS calibration of the H_2O_{total} vs. ${}^{1}H^{+/30}Si^{+}$. The red circle is the H_2O_{total} contents estimated by ${}^{1}H^{+/30}Si^{+}$ ratio obtained using SIMS. The bule line is the H_2O_{total} contents estimated by FT-IR and the black dotted lines are expressed as the error range of 2σ . (b) Estimating the OH contents by SIMS calibration of the OH vs. ${}^{1}H^{-/30}Si^{-}$. The red circle is the OH contents estimated by ${}^{1}H^{-/30}Si^{-}$. The red circle is the OH contents by SIMS calibration of the OH vs. ${}^{1}H^{-/30}Si^{-}$. The red circle is the OH contents estimated by ${}^{1}H^{-/30}Si^{-}$. The red circle is the OH contents estimated by ${}^{1}H^{-/30}Si^{-}$ ratio obtained using SIMS. The bule line is the OH contents estimated by FT-IR and the black dotted lines are expressed as the error range of 2σ .

such as matrix effects, these results strongly suggest that the H_2O_{total} content, the OH content, and the H_2O_m content of the unknown sample can be estimated by SIMS with ¹³³Cs⁺ and ¹⁶O⁻ primary ion beam. Although the previous power-law calibration using the ¹³³Cs⁺ primary ion beam can also estimate the total water contents (e.g., Shimizu *et al.*, 2022), our method will be useful for researchers wanting to also estimate the concentration of hydrous chemical species. Applying our method to natural volcanic glasses (such as melt inclusions) may make it possible to constrain the temperature and pressure conditions of the magma reservoir in the Earth's interior according to the solubilities of the hydrous chemical species and the H₂O_{total}, and contribute to the understanding of water transport in the silicate glasses and melts.

Conclusions

The relationship between the ${}^{1}\text{H}{}^{/30}\text{Si}^{+}$ ratios or ${}^{1}\text{H}{}^{-/30}\text{Si}^{-}$ ratios and the H₂O_{total} contents and OH contents in synthetic rhyolitic glasses were revealed by SIMS using the ${}^{133}\text{Cs}^{+}$ and ${}^{16}\text{O}^{-}$ primary ion beams. In a ${}^{16}\text{O}^{-}$ primary ion beam, the ${}^{1}\text{H}{}^{+/30}\text{Si}^{+}$ ratios linearly correlate with the H₂O_{total} contents, indicating that the H⁺ ions are ionized from both hydrous chemical species (OH and H₂O_m) with similar efficiencies. By contrast, a linear correlation between ${}^{1}\text{H}{}^{-/30}\text{Si}{}^{-}$ ratios and OH contents rather than H₂O_{total} contents is observed when using a ${}^{133}\text{Cs}{}^{+}$ primary ion beam. It suggests that the H⁻ ions are mainly generated from OH. Therefore, the ${}^{1}\text{H}{}^{+/30}\text{Si}{}^{+}$ ratios reflect the H₂O_{total} contents, and the ${}^{1}\text{H}{}^{-/30}\text{Si}{}^{-}$ ratios reflect the OH contents. Using calibration curves for both primary ion beams, the H₂O_{total} contents, OH contents, and H₂O_m contents in rhyolitic glasses can be estimated and it are consistent with those determined by FT-IR. These results suggest that the selective estimation of the concentration of hydrous chemical species can be achieved through the selection of the primary ion beam. This new SIMS method would contribute to the quantitative analysis of molecular water and hydroxyl groups at the micrometer scale (<10 μ m) in silicate glass.

Acknowledgments The authors appreciate the associate editor of Conel M, O'D. Alexander and two anonymous reviewers for constructive reviews of this manuscript. We thank Kenji Shimizu and Takuo Okuchi for the helpful discussions. This work was partly supported by JST SPRING, (JPMJSP2110), the Sasakawa Scientific Research Grant from The Japan Science Society (2022-6044) to A. S., Monka-sho Grants to S. I. (22K18280, 21H04519, 21H04511, 21H01177, 20H01994, 19H00716, 18H04367, 18H01296, 16H01118), and the Grants-in-aid for Scientific Research in Japan (No. 18H01296) to S.O.

References

- Aubaud, C., Withers, A. C., Hirschmann, M. M., Guan, Y., Leshin, L. A., Mackwell, S. J. and Bell, D. R. (2007) Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals. *Am. Mineral.* **92**, 811–828. https://doi.org/10.2138/am.2007.2248
- Hauri, E. H., Shaw, A. M., Wang, J., Dixon, J. E., King, P. L. and Mandeville, C. (2006) Matrix effects in hydrogen isotope analysis of silicate glasses by SIMS. *Chem. Geol.* 235, 352–365. https:// doi.org/10.1016/j.chemgeo.2006.08.010
- Hauri, E., Wang, J., Dixon, J. E., King, P. L., Mandeville, C. and Newman, S. (2002) SIMS analysis of volatiles in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chem. Geol.* 183, 99–114. https://doi.org/10.1016/S0009-2541(01)00375-8

- Hervig, R. L., Mazdab, F. K., Moore, G. and McMillan, P. F. (2003) Analyzing hydrogen (H₂O) in silicate glass by secondary ion mass spectrometry and reflectance Fourier transform infrared spectroscopy. *Developments in Volcanology* 5, 83–103. https://doi.org/ 10.1016/S1871-644X(03)80025-6
- Hui, H., Zhang, Y., Xu, Z. and Behrens, H. (2008) Pressure dependence of the speciation of dissolved water in rhyolitic melts. *Geochim. Cosmochim. Acta* 72, 3229–3240. https://doi.org/10.1016/j.gca. 2008.03.025
- Ihinger, P. D., Zhang, Y. and Stolper, E. M. (1999) The speciation of dissolved water in rhyolitic melt. *Geochim. Cosmochim. Acta* 63, 3567–3578. https://doi.org/10.1016/S0016-7037(99)00277-X
- Kuwahara, H., Itoh, S., Suzumura, A., Nakada, R. and Irifune, T. (2021) Nearly carbon-saturated magma oceans in planetary embryos during core formation. *Geophys. Res. Lett.* 48, e2021GL 092389. https://doi.org/10.1029/2021GL092389.
- Miyagi, I. and Yurimoto, H. (1995) Water content of melt inclusions in phenocrysts using secondary ion mass spectrometer. *Bull. Volcanol. Soc. Jpn.* **40**, 349–355. https://doi.org/10.18940/kazan.40.5_349
- Okumura, S. and Nakashima, S. (2005) Molar absorptivities of OH and H₂O in rhyolitic glass at room temperature and at 400–600 °C. Am. Mineral. 90, 441–447. https://doi.org/10.2138/am.2005.1740
- Okumura, S., Nakamura, M. and Nakashima, S. (2003) Determination of molar absorptivity of IR fundamental OH-stretching vibration in rhyolitic glasses. *Am. Mineral.* 88, 1657–1662. https://doi.org/ 10.2138/am-2003-11-1204
- Okumura, S., Ishibashi, H., Itoh, S., Suzumura, A., Furukawa, Y., Miwa, T. and Kagi, H. (2021) Decompression experiments for sulfur-bearing hydrous rhyolite magma: Redox evolution during magma decompression. *Am. Mineral.* **106**, 216–225. https:// doi.org/10.2138/am-2020-7535
- Peslier, A.H., Schönbächler, M., Busemann, H. and Karato, S. (2017) Water in the earth's interior: Distribution and origin. *Space Sci. Rev.* 212, 743–810. https://doi.org/10.1007/s11214-017-0387-z
- Rhede, D. and Wiedenbeck, M. (2006) SIMS quantification of very low hydrogen contents. *Appl. Surf. Sci.* 252, 7152–7154. https://doi.org/ 10.1016/j.apsusc.2006.02.245

Shimizu, K., Ushikubo, T., Hamada, M., Itoh, S., Higashi, Y.,

Takahashi, E. and Ito, M. (2017) H_2O , CO_2 , F, S, Cl, and P_2O_5 analyses of silicate glasses using SIMS: Report of volatile standard glasses. *Geochem. J.* **51**, 299–313. https://doi.org/10.2343/ geochemj.2.0470

- Shimizu, K., Ushikubo, T., Kuritani, T., Hirano, N. and Yamashita, S. (2022) Modification for the matrix effect in SIMS-derived water contents of silicate glasses. *Geochem. J.* 56, 223–230. https:// doi.org/10.2343/geochemj.GJ22019
- Stolper, E. M. (1982) Water in silicate-glasses: An infrared spectroscopic study. *Contrib. Mineral. Petrol.* 81, 1–17. https://doi.org/ 10.1007/BF00371154
- von Aulock, F. W., Kennedy, B. M., Schipper, C. I., Castro, J. M., Martin, D. E., Oze, C., Watkins, J. M., Wallace, P. J., Puskar, L., Bégué, F., Nichols, A. R. L. and Tuffen, H. (2014) Advances in Fourier transform infrared spectroscopy of natural glasses: From sample preparation to data analysis. *Lithos* 206–207, 52–64. https:// doi.org/10.1016/j.lithos.2014.07.017
- Withers, A. C. and Behrens, H. (1999) Temperature-induced changes in the NIR spectra of hydrous albitic and rhyolitic glasses between 300 and 100 K. *Phys. Chem. Miner.* 27, 119–132. https://doi.org/ 10.1007/s002690050248
- York, D. (1969) Least squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.* 5, 320–324. https://doi.org/10.1016/ S0012-821X(68)80059-7
- Yurimoto, H., Kurosawa, M. and Sueno, S. (1989) Hydrogen analysis in quartz crystals and quartz glasses by secondary ion mass spectrometry. *Geochim. Cosmochim. Acta* 53, 751–755. https://doi.org/ 10.1016/0016-7037(89)90018-5
- Zhang, Y. (1999) H₂O in rhyolitic glasses and melts: Measurement, speciation, solubility, and diffusion. *Rev. Geophys.* 37, 493–516. https://doi.org/10.1029/1999RG900012

Supplementary Materials

https://www.jstage.jst.go.jp/article/geochemj/58/3/ 58_GJ24008/_article