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Paper:

Measurement of H_2O Molecule and Hydroxyl Concentrations in Hydrous Rhyolitic Glass by UV–Vis–NIR Dispersive Microspectroscopy

Takahiro Miwa

National Research Institute for Earth Science and Disaster Resilience (NIED)
3-1 Tennodai, Tsukuba, Ibaraki 305-0006, Japan
E-mail: miwao@bosai.go.jp

The speciation of water in volcanic glass, as indicated by the relative proportions of H_2O and OH^-, provides information on the processes of volcanic eruptions. Earlier studies of water species used ultraviolet–visible–near-infrared (UV–Vis–NIR) dispersive spectroscopy to examine the NIR spectra of volcanic glass but were unable to confirm whether areas as small as 100 μm across could be studied. Here, UV–Vis–NIR dispersive microspectroscopy was applied in a study of hydrous rhyolitic glass synthesized by decompression in a cold-seal pressure vessel at 880°C. The concentrations of water species were determined by transmittance spectroscopy, with results consistent with those of Fourier-transform infrared microspectroscopy. The measured total water contents were consistent with the known solubility of water in rhyolitic magma, and, therefore, it is concluded that UV–Vis–NIR microspectroscopy can be applied in determining the concentrations of H_2O and OH^- in hydrous rhyolitic glass.

Keywords: UV–Vis–NIR dispersive microspectroscopy, rhyolite glass, speciation, H_2O molecule, OH^- group

1. Introduction

The speciation of water in volcanic glass provides information on the physical processes occurring during volcanic eruptions. Water is present in silicate melts as H_2O molecules or hydroxyl groups (OH^-). These species exchange readily with each other via equilibrium reactions involving the silicate oxygen framework [1, 2]. The relative concentrations of the two species are controlled mainly by temperature and by the total water content of silicate melt [2]. H_2O dominates at low temperatures and high total water contents, while OH^- becomes dominant at high temperatures and low total water contents. On the basis of the water speciation, previous studies have revealed the effects of hydration of natural eruptive products under low-temperature conditions [3–5] and pyroclast quenching after fragmentation [6, 7].

The concentrations of water species in silicate glass were determined by the near-infrared absorbances of H_2O and OH^- at 1920 nm and 2220 nm, respectively [1]. These absorbances were measured by using two spectroscopic methods: dispersive spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy. Dispersive spectroscopy directly measures the intensity of light passing thorough a sample. The spectrum of the light is obtained by using a monochromator to successively change the wavelength of the incident light reaching the sample. On the other hand, FT-IR spectroscopy detects the light of all wavelengths simultaneously by using an interferometer. The spectrum is then calculated from an interferogram by Fourier transformation. Because FT-IR spectroscopy does not use a slit, the amount of energy reaching the detector is much higher in this method, resulting in higher signal-to-noise ratio than that of dispersive spectroscopy.

Early studies used ultraviolet–visible–near-infrared (UV–Vis–NIR) dispersive spectroscopy to obtain the concentrations of water species; however, the smallest area analyzed was only 140 μm across [1, 8]. To measure the concentration in natural volcanic glass, researchers prefer that the analytical area be less than 100 μm [6]. For this purpose, most recent studies have used FT-IR microspectroscopy, which combines an FT-IR spectrometer with a micro-optical system, because of its higher signal-to-noise ratio [7]. In contrast, an instrument has been recently developed that optically optimizes a dispersive spectrometer and a micro-optical system to evaluate the optical properties of micro-devices relevant to industry [9]. Although this instrument can collect UV-Vis-NIR spectrum in analytical areas < 100 μm, it has not been quantitatively examined whether the concentrations of water species can be measured by dispersive microspectroscopy with the same accuracy as that of FT-IR microspectroscopy.

This study has confirmed that dispersive microspectroscopy can be applied to rhyolitic glass with analytical areas of < 100 μm. Four hydrous glass samples were prepared in a cold-seal pressure vessel, and the H_2O and OH^- contents were determined by UV–Vis–NIR dispersive microspectroscopy. The results were compared with those obtained using well-established FT-IR techniques and a solubility model of water in rhyolitic magma.

Table 1. Synthesizing condition of the hydrous glasses.

Sample name	Temperature [°C]	Initial pressure [MPa]	Final pressure [MPa]
JR1-07	880	170	100
JR1-11	880	170	30
JR1-12	880	170	170
JR1-13	880	170	60
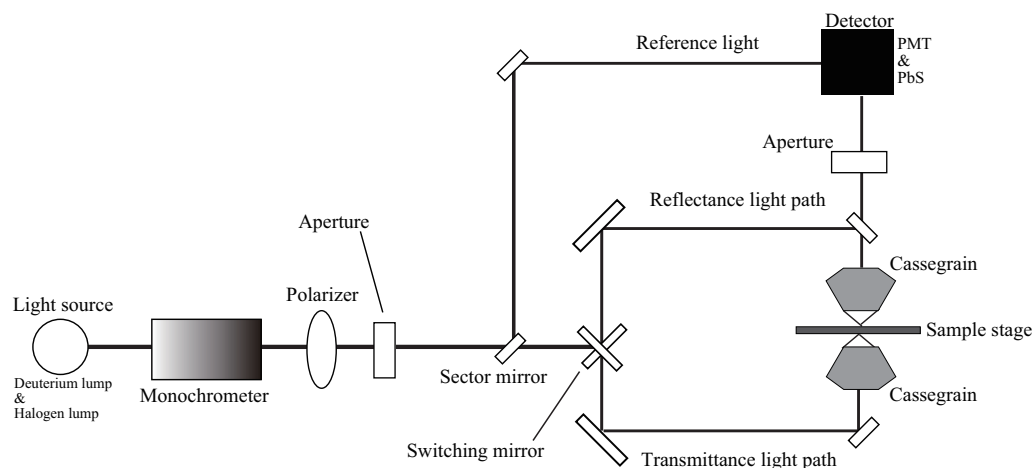
Fig. 1. Configuration of the JASCO MSV-5200 UV–Vis–NIR dispersive spectrometer. PMT, photomultiplier tube; PbS, Peltier-cooled lead sulfide photoconductive cell.

2. Methods

2.1. Sample Preparation

Four hydrous glasses were synthesized (**Table 1**) from JR-1 powder (a standard rhyolite provided by the Geological Survey of Japan [10]) with an SiO_2 content of 75.45 wt.%. The rhyolite powder and water were sealed in a gold tube (outer diameter of 3 mm and length of ∼15 mm) using a tungsten inert gas (TIG) welder. The water content was adjusted to achieve a melt water content of ∼6 wt.%. The hydrous glasses were synthesized in a cold-seal pressure vessel at the National Research Institute for Earth Science and Disaster Resilience (NIED), Tsukuba, Japan, using an Inconel bomb with water as the pressure medium. The gold tubes were inserted into the bomb with a nickel filler rod and heated at 880°C and 170 MPa for 24 h. One tube was quenched at 170 MPa, and three were decompressed to 30, 60, and 100 MPa at 1.5 MPa min^{-1} to maintain an equilibrium water content [11], left for 1 or 2 h, and then quenched. The decompression rate was controlled by a syringe pump controlling the flux of the water pressure medium into the bomb. Rapid final quenching was achieved using compressed air. All four experimental products were hydrous glasses that had tiny bubbles with a size of a few to a few tens of microns and sparsely distributed crystals.

Doubly polished thin sections of the hydrous glasses were prepared for analysis, as follows. Glass samples were carefully removed from the gold tubes and mounted on a glass slide using cyanoacrylate glue. A quartz glass ring (inner diameter of 3 mm and outer diameter of 5 mm) was attached to ensure uniform polishing. Polishing involved abrasive films of grades 400, 600, and 2000 under running water on a grooved glass surface [12], with a final polish with a 1-μm diamond paste. The glass sample and the quartz ring were then removed from the slide by immersion in acetone for several hours and reattached inverted to allow polishing of the reverse side. The polished disk was finally removed by dissolving the glue in acetone.

2.2. Spectroscopy

A JASCO MSV-5200 UV–Vis–NIR dispersive microspectrometer at NIED (**Fig. 1**) was used to obtain the transmittance spectra of the doubly polished thin sections of the hydrous glass. The instrument operates at wavelengths of 220–2700 nm, with adjustment by a single monochromator. Deuterium and halogen lamps were used at wavelengths of 220–340 nm and 340–2700 nm, respectively. A photomultiplier tube and a Peltier-cooled lead sulfide photoconductive cell were used as detectors at 220–900 nm and 750–900 nm, respectively. The monochromator was a Czerny-Turner mount type with groove densities of 1200 and 300 lines mm^{-1} for the UV-Vis and NIR regions, respectively. A double-beam system allowed the simultaneous observation of the sample and the reference to ensure stability. The scanning rate was 400 nm min^{-1}, with resolutions of 2 nm for UV–Vis and 4 nm for NIR, giving approximately 6 min per scan.

Air transmittance was used as a background. The aperture size was set to 30, 50, and 100 μm. The number of scans was set to one or two times. Bubbles and sparsely distributed crystals in the glass were avoided during the analysis. A CMOS camera provided digital imaging of the microscopic field of the Cassegrain objective. The Cassegrain objective has a magnification of $16\times$ and a numerical aperture of 0.57.

We collected the transmittance spectra of the same four hydrous glasses using FT-IR microspectroscopy for comparison with those collected using dispersive microspectroscopy. The FT-IR microspectroscopy was performed using JASCO FT/IR-660 Plus and JASCO IRT-30 systems at the Geological Survey of Japan, Tsukuba. The transmittance spectra were collected for 400 scans at a spectral resolution of 4 cm^{-1} using a ceramic IR source, a KBr beam splitter, and a mercury-cadmium-telluride detector. The aperture size was set to 100×100 μm. The Cassegrain objective has a magnification of $16\times$ and a numerical aperture of 0.57.

This study focused on the NIR spectra (1200–2500 nm) to evaluate the concentrations of H_2O molecules and OH^- in the hydrous glasses. The concentration of water species, c (wt. fraction), can be expressed by the Lambert–Beer law as

$$c = \frac{MA}{d\rho\varepsilon},$$

where M is the molecular weight (g mol^{-1}), A is the absorbance, d is the sample thickness (cm), ρ is the sample density (g L^{-1}), and ε is the molar absorptivity (L mol^{-1} cm^{-1}). Absorbance was measured by peak heights from a linear baseline flanking the 1920 nm and 2220 nm peaks for the combinations of the stretching + bending mode of the H_2O molecules and X-OH^- groups, respectively [1]. Typical uncertainties in absorbance around the peaks were estimated to be 0.0035 and 0.0061 for the dispersive and FT-IR methods, respectively, on the basis of the jaggedness in the spectra. The molar absorptivity values were 1.61 ± 0.05 and 1.73 ± 0.05 L mol^{-1} cm^{-1} at 1920 and 2220 nm, respectively [8]. Glass density (2340 ± 10 g L^{-1} was based on that of rhyolitic obsidian at the Wadatouge district [13]. The thicknesses of the thin sections were measured using a digital micrometer (Mitutoyo Co., Ltd.), with an error of ± 1 μm.

3. Results and Discussion

The transmittance spectra of the hydrous rhyolitic glass samples are shown in **Fig. 2** for the entire UV–NIR wavelength range, with strong UV absorption being indicated for all samples, regardless of the synthesis technique. The spectra were similar to those obtained earlier for fused silica glass and alkali silica glass [14]. Although there were some variations in the visible-light spectra, there were no clear relationships with the synthesis technique or sample thickness (a detailed study of the UV–Vis absorbance will
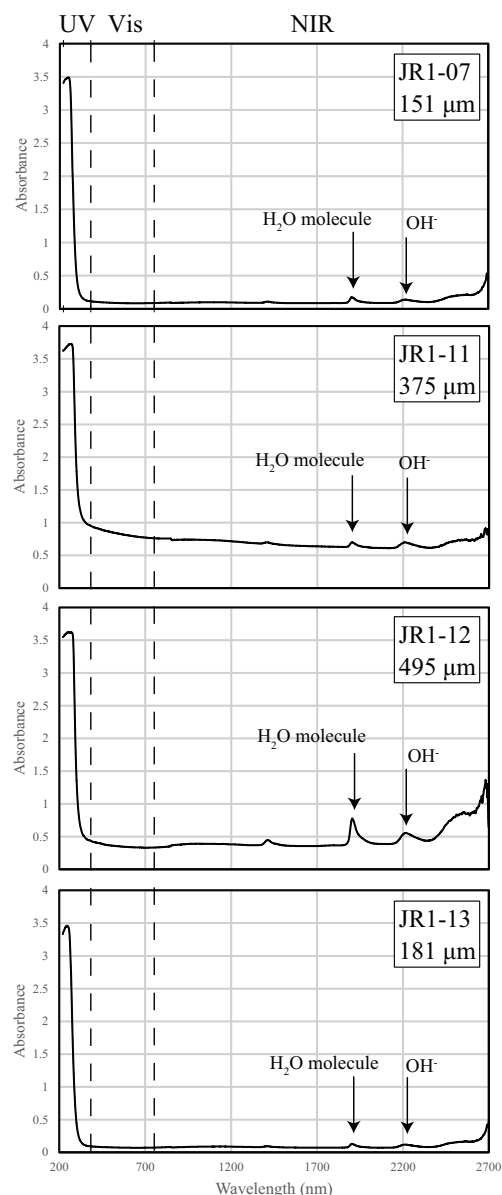
Fig. 2. UV–Vis–NIR spectra of the hydrous glasses. Sample numbers and thickness are indicated at the upper right. NIR spectra span: 1200–2500 nm. Aperture size: 100 μm.

be the subject of a future work).

The NIR spectra (**Fig. 2**) clearly display absorption bands around 2220 nm (OH^-) and 1920 nm (H_2O). **Table 2** summarizes the results of the spectroscopic measurements. The concentrations of OH^- and H_2O were homogeneous in each sample within the analytical errors. There was a one-to-one proportional relationship between the results obtained here and those obtained by FT-IR spectroscopy within the analytical errors (**Fig. 3**), confirming the applicability of UV–Vis–NIR microspectroscopy. **Fig. 4** illustrates the relationship between total water content (the sum of the H_2O and OH^- contents) and synthesizing pressure, which was consistent with the calculated solubility of water in rhyolite at 880°C, as determined by the VolatileCalc program [15]. The deviation from the calculated solubility found in JR1-07 (final pres-

Table 2. Results of the microspectroscopy.

			Dispersive				
Sample name	Thickness [μm]	ABS2220[1]	ABS1920[1]	n[2]	H_2O molecule[3] [wt.%]	OH^-[3] [wt.%]	Total water[4] [wt.%]
JR1-07	151	0.0451	0.0921	3	2.92 (0.15)	1.33 (0.10)	4.25 (0.18)
JR1-11	375	0.0859	0.0710	3	0.91 (0.05)	1.02 (0.04)	1.92 (0.07)
JR1-12	495	0.1545	0.4090	3	3.95 (0.13)	1.39 (0.04)	5.34 (0.13)
JR1-13	181	0.0414	0.0622	3	1.64 (0.11)	1.02 (0.09)	2.66 (0.14)
			FT-IR				
Sample name	Thickness [μm]	ABS2220[1]	ABS1920[1]	n[2]	H_2O molecule[3] [wt.%]	OH^-[3] [wt.%]	Total water[4] [wt.%]
JR1-07	151	0.0461	0.0903	4	2.86 (0.21)	1.36 (0.18)	4.22 (0.28)
JR1-11	375	0.0877	0.0772	5	0.98 (0.08)	1.04 (0.07)	2.03 (0.11)
JR1-12	495	0.1545	0.4095	4	3.96 (0.14)	1.39 (0.06)	5.35 (0.15)
JR1-13	181	0.0401	0.0571	5	1.51 (0.17)	0.99 (0.15)	2.50 (0.23)

[1] Average absorbance heights at wavelengths of 2220 and 1920 nm in multiple measurements.
[2] Number of multiple measurements at different positions in the same sample.
[3] Numbers in parentheses indicate the analytical errors of the same samples determined including the error propagation of the uncertainties in the absorbance, molar absorptivity, density, and thickness of the samples.
[4] Calculated from the sum of the H_2O and OH^- concentrations. Numbers in parentheses indicate the analytical errors of the same samples.
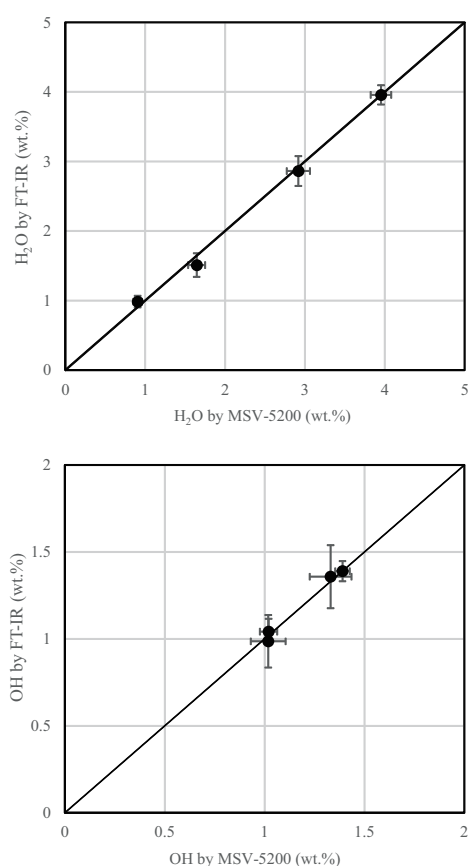

Fig. 3. Comparison of water-species concentrations between UV–Vis–NIR dispersive and FT-IR microspectroscopy. Both methods used an aperture size of 100 μm. The analytical errors of measurements, which are represented by error bars, include the effect of the error propagation of the uncertainties in the absorbance, molar absorptivity, density, and thickness of the samples.
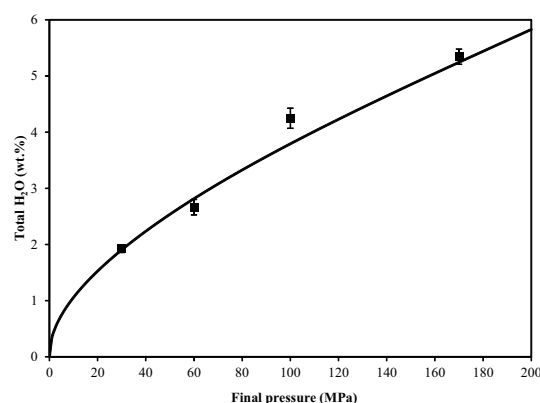
Fig. 4. Comparison of the total water content calculated from the UV–Vis–NIR results with the solubility curve of the water in rhyolite [15]. The aperture size of this analysis was 100 μm. The analytical errors of measurements, which are represented by vertical bars, include the effect of the error propagation of the uncertainties in the absorbance, molar absorptivity, density, and thickness of the samples.

sure of 100 MPa) might have been caused by the short duration of the experiment relative to the required time for complete dehydration.

The uncertainties in water-species concentrations were caused mainly by errors in reading the absorbance peak heights, owing to spectral noise [16]. The noise level varied with the aperture and the numbers of scans, as these factors control the light energy reaching the detector. The spectra over wavelengths of 1200–2500 nm of the JR1-13 sample were collected using various numbers of scans and aperture sizes to evaluate the noise levels at almost the same analytical position (**Fig. 5**). The noise level was defined as the 2σ value for the difference between
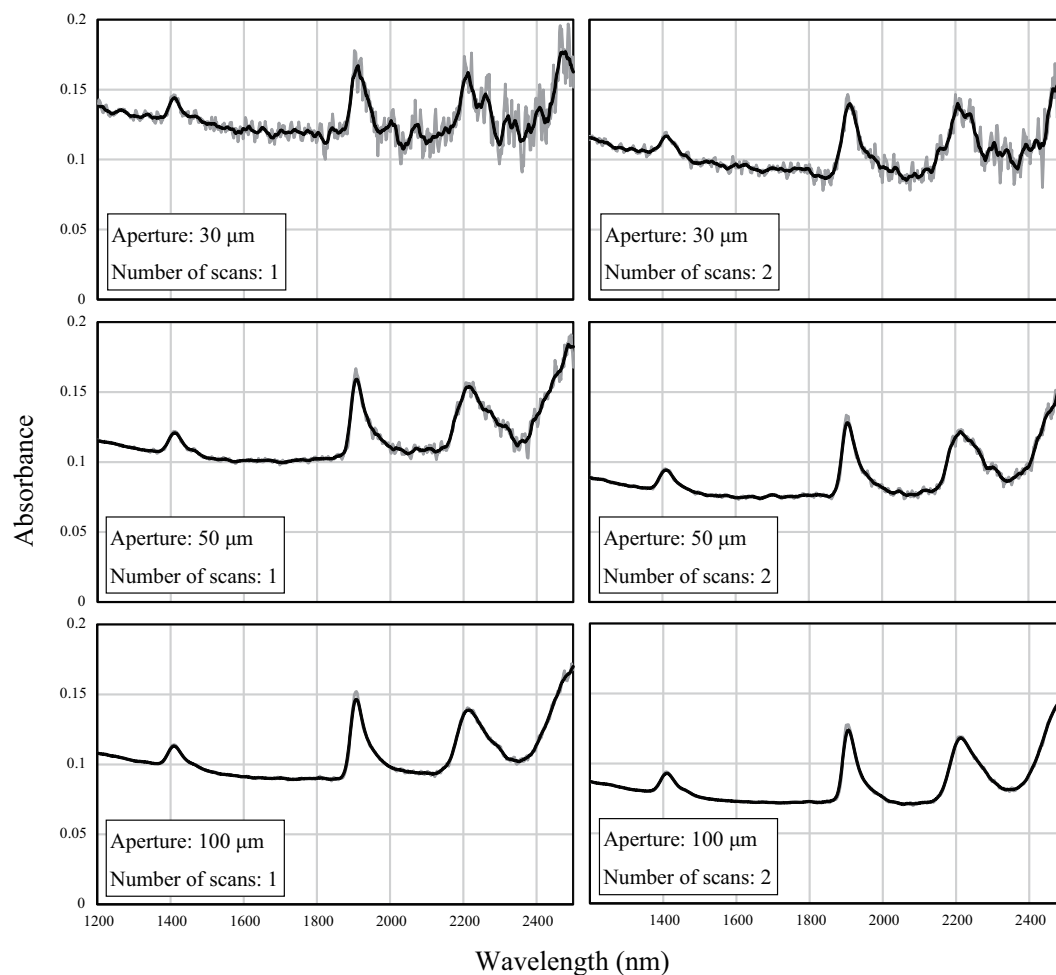
Fig. 5. Effect of the number of scans and aperture size on spectral noise. The black and gray lines indicate the moving average and the raw data, respectively.

Table 3. Uncertainty in the concentrations of the water species.

Aperture size [μm]	Number of scans	2σ of Abs	ΔH_2O molecule* [wt.%]	ΔOH* [wt.%]
30	1	0.0101	0.27	0.25
50	1	0.0040	0.11	0.10
100	1	0.0017	0.04	0.04
30	2	0.0078	0.21	0.19
50	2	0.0029	0.08	0.07
100	2	0.0014	0.04	0.03

* ΔH_2O and ΔOH represent the uncertainties of the H_2O and OH^- species, respectively.

the raw spectra and the moving average obtained with a wavelength spectral width of 20 nm. The uncertainties in H_2O and OH^- concentrations increased with decreasing number of scans and aperture size (**Table 3**). For the aperture size of 30 μm with two scans, the uncertainties were 0.21 wt.% and 0.19 wt.% for H_2O and OH^-, respectively. Therefore, we suggest that the UV–Vis–NIR dispersive microspectroscopy technique can be applied to the analysis of the water species in natural volcanic glass with an aperture size down to 30 μm, although it may be

prudent to increase the number of scans to more than three for situations where a higher accuracy is needed.

UV–Vis–NIR dispersive microspectroscopy allows us to assess water speciation (NIR) and transition-metal speciation (Vis) at the same location. This method has been used to obtain the transition-metal speciation of glasses from visible light spectra [17, 18]. The transition-metal speciation such as Fe reflects a redox condition of magma [19]. Thus, the simultaneous determination of water and transition-metal speciations is expected to provide

an insight into the redox evolution of magma during the process of eruption.

4. Conclusion

UV–Vis–NIR dispersive microspectroscopy can be successfully applied in measuring the H_2O and OH^- concentrations in hydrous rhyolitic glasses with an aperture size down to < 100 μm. The analytical results were consistent with those obtained by FT-IR analysis. The estimated total water contents were consistent with the calculated solubility of water in rhyolitic magma. The uncertainties in water-species concentrations increased with decreasing aperture size and were estimated to be 0.21 wt.% and 0.19 wt.% for H_2O and OH^-, respectively, for an aperture size of 30 μm with two scans.

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Name:
Takahiro Miwa

Affiliation:
Researcher, National Research Institute for Earth Science and Disaster Resilience (NIED)

Address:
3-1 Tennodai, Tsukuba, Ibaraki 305-0006, Japan
Brief Career:
2011- COE fellow, Tohoku University
2013- Postdoctral, Kyushu University
2014- NIED
Selected Publications:
● T. Miwa, M. Nagai, and R. Kawaguchi, "Resuspension of ash after the 2014 phreatic eruption at Ontake volcano, Japan," J. of Volcanology and Geothermal Research, Vol.351, pp. 105-114, 2018.
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