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Sulfur isotopic systematics during the October 2017 eruption of the Shinmoe-dake volcano, Japan



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Keywords: Shinmoe-dake volcano Sulfur isotopic composition Pyrite Sulfates Volcanic hydrothermal system	pyroclastic materials ejected during October 11–14, 2017, contain sulfur-bearing minerals. Time-series sulfur isotopic compositions of sulfur species in the samples ejected during the 2017 eruption were measured in order to reveal the geochemical characteristics of the volcanic hydrothermal system that developed after the 2011 eruption and its evolution during the 2017 eruption. δ^{34} S values for water-leached sulfate (+16.09% to +17.51%), acetone-leached native sulfur (-1.23% to +0.42%), fine-grained pyrite (-1.81% to -0.90%) and coarse-grained pyrite (-3.48% to -2.57%) remained relatively constant with time. The hydrochloric acid-leached sulfates of the pyroclastic materials ejected from October 11 to October 12 exhibit a relatively limited range of δ^{34} S (+9.87% to +13.17%). Then, on October 14, the δ^{34} S value suddenly increased to +16.85%, which is similar to that of the water-leached sulfate from the same day (+16.09%). δ^{34} S values for all the sulfur species were probably controlled by the disproportionation of magmatic SO ₂ in the presence o water in the hot (about 400 °C) deep and cooler (about 300 °C) shallow acidic hydrothermal alteration zones below the summit crater. These zones existed separately before and during the first few days of eruption, bu were ruptured in succession as the eruption progressed. The sulfur isotopic similarity between the hydrochloric acid-leached sulfate and the water-leached sulfate of the pyroclastic material on October 14 implies that the mixing, dissolution, and re-equilibration of the recycled sulfate from both alteration zones occurred at abou 300 °C after the second day of the eruption.		

1. Introduction

Sulfur isotope studies can provide useful information on source reservoirs of sulfur and the temperature of formation of sulfur-bearing minerals (e.g., Rye, 2005; Seal, 2006). Therefore, sulfur isotopes of these minerals are widely used to understand magmatic-hydrothermal ore-forming processes (e.g., Arribas, 1995; Rye, 2005; Seal, 2006). Temperature of volcanic hydrothermal systems is related to volcanic activity, as well as deposition of ore minerals. Sulfur-bearing minerals derived from deep-seated volcanic hydrothermal systems can be sampled after edifice collapse or deep erosion (e.g., Reid et al., 2001; John et al., 2008). Pyroclastic materials of phreatomagmatic and phreatic eruption also contain these minerals. Rye et al. (1984) analyzed sulfur isotopic compositions of anhydrite and pyrrhotite in the ejecta from the 1982 eruption of El Chichón in Mexico. In that study, average sulfur isotopic temperature determined from hydrothermal anhydrite-pyrrhotite pairs in the accidental lithic fragments (510 °C) was lower than that of magmatic anhydrite-pyrrhotite pairs in fresh pumices (810 ± 40 °C) (Rye et al., 1984; Rye, 2005). Ikehata and Maruoka (2016) investigated mineralogical and sulfur isotopic characteristics of pyroclastic materials from the 2014 phreatic eruption of Mt. Ontake in Japan, and compared the results with those from the 1979 phreatic eruption of Mt. Ontake (Kusakabe et al., 1982). Because no significant differences in the mineral assemblages or sulfur isotopic compositions of the pyroclastic materials were observed between the 2014 and 1979 eruptions, the authors concluded that the hydrothermal systems below the crater before each eruption had similar geochemical features. However, sulfur isotopic characteristics of magmatic-hydrothermal environments within an unexposed volcano's interior just before or during eruption are not yet well-understood, and they may provide information to help elucidate ongoing hydrothermal activities and incipient hydrothermal mineralization.

Shinmoe-dake (elevation: 1421 m a.s.l.) is one of the active volcanoes in the Kirishima mountain range on the southern part of Kyushu Island, Japan (Fig. 1). It is an andesitic stratovolcano that consists of lava flows and pyroclastic materials (Imura and Kobayashi, 2001).

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Fig. 1. Map of the sampling points for pyroclastic materials, KS-1, KS-2, and KS-3. KS-1 is located approximately 7.5 km east of the Shinmoe-dake crater. KS-2 is located approximately 7.9 km northeast of the crater, and KS-3 is located approximately 10.4 km south-southwest of the crater. The map is based on the GSI Maps by the Geospatial Information Authority of Japan.

Historically, several phreatic eruptions have been observed at the volcano (Imura and Kobayashi, 2001; JMA, 2013). A magnetotelluric (MT) survey revealed the existence of deep and shallow conductive layers beneath the Shinmoe-dake crater (Utada et al., 1994; Kagiyama et al., 1996). The deep conductive layer (resistivity of approximately 10 Ω ·m) at a depth of approximately 2 or 3 km beneath the crater is considered as magma supplied from a deeper region. Outside of the crater, this conductive layer is located even deeper, approximately 10 km below the surface. The shallow conductive layer (resistivity of a few Ω ·m) at a depth of approximately 100 m to a few hundred meters beneath the crater is interpreted as a water saturated porous layer (aquifer) associated with hydrothermal systems (Utada et al., 1994; Kagiyama et al., 1996). They suggested that hydrothermal activities and phreatic eruptions tend to occur at Shinmoe-dake as a result of interactions between the water and hot volcanic gases supplied from the ascending magma.

Magmatic eruption occurred at Shinmoe-dake in 2011 for the first time since 1716-1717 (Nakada et al., 2013). A series of phreatomagmatic eruptions commenced on January 19, 2011, which were followed by a series of magmatic eruptions that began on January 26, 2011 (Nakada et al., 2013). The 2011 event ended with phreatomagmatic eruptions occurring during June-September 2011. Shinmoe-dake again began to erupt at ca. 05:34 JST (Japan Standard Time; UTC + 9 h) on October 11, 2017, after a six-year period of quiescence (MRI and JMA, 2018). The 2017 eruption continued intermittently until at ca. 00:30 JST on October 17 (MRI and JMA, 2018). Soon after the eruptions, we collected several pyroclastic materials that contained an abundance of hydrothermal minerals such as pyrite and anhydrite. In this paper, we present time-series variation in sulfur isotopic composition of sulfurbearing minerals in the pyroclastic materials from the 2017 Shinmoedake eruption to describe the geochemical characteristics of the redeveloping hydrothermal system within the volcano following the 2011

eruption and changes in the hydrothermal system during the 2017 eruption.

2. Sampling locations

Pyroclastic materials from the 2017 Shinmoe-dake eruption were collected at three locations: KS-1, located approximately 7.5 km east of the Shinmoe-dake crater; KS-2, located approximately 7.9 km northeast of the crater; and KS-3, located approximately 10.4 km south-southwest of the crater (Fig. 1). Volcanic ash samples erupted on the morning (Day1M) and afternoon (Day1AE: after 1 p.m. JST; Day1AL: after 4 p.m. JST) of October 11 were collected from the surface of bales of silage wrapped in white plastic in the grassland at KS-1 (Fig. 2). Ash samples erupted on October 12 (Day2) were collected from gravestones at the graveyard at KS-2, and ash erupted on October 14 (Day4) were collected from an outside corridor at Kirishima junior high school (KS-3). Pyroclastic materials appropriate for our chemical analyses were not obtained during October 15–17 due to rain.

3. Analytical methods

The mineral compositions were determined separately for settled large grains and suspended fine grains after several rounds of ultrasonication. Minerals were identified using a stereo-microscope and a polarizing-microscope, as well as an X-ray diffractometer.

About 5 g of bulk ash samples were soaked for 12 h in about 120 ml of 18 M Ω de-ionized water. The supernatant liquid was separated from the H₂O-leached ash sample by filtration using mixed cellulose ester membrane filters with a pore size of 0.2 µm (Advantec Tokyo, Japan). About 10 ml of water solution was preserved in glass vials for chemical analyses. About 5 ml of 30% hydrogen peroxide (H₂O₂) was added to



Fig. 2. Photograph of pyroclastic materials erupted on October 11, 2017 from Shinmoe-dake. Samples were collected from the surface of bales of silage wrapped in white plastic in the grassland at KS-1.

the remaining solutions to ensure oxidation of elemental sulfur and sulfite. The solutions were acidified to pH of about 3 by addition of 2 M HCl. About 20 ml of 10% BaCl₂ solution was added to the solutions to precipitate barium sulfate. The barium sulfate samples precipitated from H₂O solution (H₂O-S in Table 1) were collected by filtration and rinsed with de-ionized water. The water-leached ash samples were treated with 100 ml of 2 M HCl for 2 h at 80 °C. After filtration using a membrane filter, pH of the solutions was adjusted to about 2-3 by addition of 6 N KOH and 20 ml 10% BaCl₂ solution was added to the solutions to precipitate barium sulfate. The barium sulfate samples precipitated from the HCl solutions (HCl-S in Table 1) were collected by filtration and rinsed with de-ionized water. About 100 ml of acetone was added to the HCl-treated ash samples. The acetone solutions were filtered by glass fiber filter (GC-50, Advantec, Tokyo, Japan) and were dried in a vacuum chamber of 0.02 MPa at room temperature in order to obtain elemental sulfur from acetone solutions (Native-S in Table 1). Pyritic sulfide grains were collected from acetone-treated ash samples by density separation using 1,1,2,2-Tetrabromoethane (2.967 g/cm^3) . The grains were rinsed with ethanol and dried in the oven setting at 60 °C. The pyrite grains were separated into two fractions (fine-grained pyritic sulfur, F-Py-S and coarse-grained pyritic sulfur, C-Py-S in Table 1) using size separation, with the size boundary set to about 10 μ m, as determined by the sedimentation velocity and the length of centrifuge tube. The fractions of large grains were ground into less than 10 μ m powder using agate mortar and pestle.

Sulfur isotopic compositions were determined for barium sulfate precipitates, and pyritic and elemental sulfur using a helium gas continuous flow isotope ratio mass spectrometer (CF-IR-MS; ISOPRIME-EA; Isoprime Ltd., UK) at the University of Tsukuba (Ikehata and Maruoka, 2016).

The sulfur isotopic compositions are expressed in terms of δ^{34} S (‰) relative to the V-CDT (Vienna-Canyon-Diablo-Troilite) standard. The results of three IAEA (International Atomic Energy Agency) silver sulfide standards (IAEA-S-1, -0.3‰; IAEA-S-2, +21.80‰; IAEA-S-3, -31.95‰; Mayer and Krouse, 2004) were compared to constrain the δ^{34} S values. The isotopic compositions of sulfur were determined to a precision of ± 0.1‰ (1\sigma) for 30 µg of sulfur. The precision was determined using the standard deviations of repeated analyses of samples and standards (Maruoka et al., 2003).

4. Results and discussion

4.1. Sample description

All collected pyroclastic materials contain hydrothermally-altered rock fragments, pyrite, anhydrite, gypsum, alunite, clay minerals (e.g., kaolin minerals and pyrophyllite), quartz, plagioclase, clinopyroxene, orthopyroxene, olivine, magnetite, and Fe-Ti oxides. Pyrite, anhydrite, gypsum, alunite, kaolin minerals, and pyrophyllite are commonly observed in acidic and neutral-pH alteration zones of geothermal areas and fumaroles (e.g., Utada, 1980; Reyes, 1990; Hedenquist et al., 1996). Sulfur-bearing minerals such as pyrite, anhydrite, and gypsum are present in washed pyroclastic materials and in the suspended grains after ultrasonic washing. The grain sizes of most pyrite (fine-grained pyrite) in the suspended grains are less than 10 µm in diameter (Fig. 3).

Table 1

Sulfur isotopic values of sulfur species for the pyroclastic materials of the 2017 Sinmoe-dake eruption, Japan.

Sample	Eruption day	Sulfur species	$\delta^{34}S$	± 1σ	
			(‰)	(‰)	
Day1M	10/11/2017 (morning)	Water-leached sulfate (H ₂ O-S)	+17.51	0.09	
Day1M	10/11/2017 (morning)	Hydrochloric-acid-leached sulfate (HCl-S)	+10.66	0.09	
Day1M	10/11/2017 (morning)	Acetone-leached native sulfur (Native-S)	-1.00	0.07	
Day1M	10/11/2017 (morning)	Coarse-grained pyritic sulfur (C-Py-S)	-2.57	0.09	
Day1M	10/11/2017 (morning)	Fine-grained pyritic sulfur (F-Py-S)	-1.81	0.09	
Day1AE	10/11/2017 (after 1 p.m. JST)	Water-leached sulfate (H ₂ O-S)	+17.25	0.07	
Day1AE	10/11/2017 (after 1 p.m. JST)	Hydrochloric-acid-leached sulfate (HCl-S)	+12.63	0.07	
Day1AE	10/11/2017 (after 1 p.m. JST)	Acetone-leached native sulfur (Native-S)	-1.11	0.08	
Day1AE	10/11/2017 (after 1 p.m. JST)	Coarse-grained pyritic sulfur (C-Py-S)	-3.32	0.07	
Day1AE	10/11/2017 (after 1 p.m. JST)	Fine-grained pyritic sulfur (F-Py-S)	-1.38	0.07	
Day1AL	10/11/2017 (after 4 p.m. JST)	Water-leached sulfate (H ₂ O-S)	+17.32	0.08	
Day1AL	10/11/2017 (after 4 p.m. JST)	Hydrochloric-acid-leached sulfate (HCl-S)	+9.87	0.05	
Day1AL	10/11/2017 (after 4 p.m. JST)	Acetone-leached native sulfur (Native-S)	-1.23	0.07	
Day1AL	10/11/2017 (after 4 p.m. JST)	Coarse-grained pyritic sulfur (C-Py-S)	-2.87	0.10	
Day1AL	10/11/2017 (after 4 p.m. JST)	Fine-grained pyritic sulfur (F-Py-S)	-1.53	0.13	
Day2	10/12/2017	Water-leached sulfate (H ₂ O-S)	+17.29	0.12	
Day2	10/12/2017	Hydrochloric-acid-leached sulfate (HCl-S)	+13.17	0.05	
Day2	10/12/2017	Acetone-leached native sulfur (Native-S)	-0.63	0.07	
Day2	10/12/2017	Coarse-grained pyritic sulfur (C-Py-S)	-3.48	0.15	
Day2	10/12/2017	Fine-grained pyritic sulfur (F-Py-S)	-0.90	0.06	
Day4	10/14/2017	Water-leached sulfate (H ₂ O-S)	+16.09	0.08	
Day4	10/14/2017	Hydrochloric-acid-leached sulfate (HCl-S)	+16.85	0.08	
Day4	10/14/2017	Acetone-leached native sulfur (Native-S)	+0.42	0.14	
Day4	10/14/2017	Coarse-grained pyritic sulfur (C-Py-S)	-2.79	0.14	
Day4	10/14/2017	Fine-grained pyritic sulfur (F-Py-S)	-1.15	0.09	



Fig. 3. Representative photomicrograph of the suspended grains after ultrasonic washing of pyroclastic material (Day1M sample) from the 2017 Shinmoedake eruption under a stereo-microscope. Note that the fine gypsum crystals in this photograph are precipitates from calcium and sulfate dissolved in the water during ultrasonication, rather than suspended fine grains, because such fine gypsum crystals cannot be observed before the ultrasonication. Such precipitation might occur because the water was not fully removed from the suspension. Py: Pyrite; Gp: Gypsum.



Fig. 4. Representative photomicrograph of the washed pyroclastic material (Day1M sample) of the 2017 Shinmoe-dake eruption under a stereomicroscope. Py: Pyrite; Qz: Quartz; Pl: Plagioclase; Cpx: Clinopyroxene; Opx: Orthopyroxene; Ol: Olivine; Mt: Magnetite.

In contrast, the grain sizes of the coarse-grained pyrite in the washed pyroclastic materials are up to $450 \,\mu\text{m}$ in diameter (Fig. 4). The existence of kaolin minerals implies a relatively low temperature (less than 200 °C), acidic environmental origin. In contrast, the existence of pyrophyllite implies a relatively high temperature (200–300 °C), acidic environment (Reyes, 1990; Hedenquist et al., 1996). Thus, these hydrothermal minerals were likely derived from at least two acidic alteration zones of Shinmoe-dake. Previous authors have shown that a volcano's interior contains several such alteration zones defined by the presence of temperature-sensitive minerals (e.g., Utada, 1980; Reyes, 1990; Hedenquist et al., 1996; Rye, 2005).

4.2. Sulfur isotope data

Sulfur isotope compositions of the water-leached sulfate (H₂O-S), hydrochloric-acid-leached sulfate (HCl-S), acetone-leached native sulfur (Native-S), fine-grained pyritic sulfur (F-Py-S), and coarsegrained pyritic sulfur (C-Py-S) of the pyroclastic materials (Day1M, Day1AE, Day1AL, Day2, and Day4 samples) from the 2017 Shinmoe-

dake eruption are presented in Table 1 and Fig. 5. Although the sulfur isotope compositions of the HCl-S from Day1M through Day2 fall within a relatively limited range ($\delta^{34}S = +9.87\%$ to +13.17%), the δ^{34} S value on Day4 showed a significant increase (+16.85‰). On the other hand, the δ^{34} S values for H₂O-S, Native-S, F-Py-S, and C-Py-S are relatively constant from Day1M through Day4 ranging from +16.09‰ to +17.51‰, -1.23‰ to +0.42‰, -1.81‰ to -0.90‰, and -3.48% to -2.57%, respectively. These narrow isotopic ranges of the respective sulfur species indicate that a single sulfur source or process was involved in their formation. Sulfur isotope values of HCl-S and H₂O-S in this study lie within the typical range for sulfates from a magmatic-hydrothermal environment ($\delta^{34}S = +10\%$ to +25%), and these values are outside of the typical range for sulfates in supergene or steam-heated environments ($\delta^{34}S = -3\%$ to +4%) derived from lowtemperature atmospheric oxidation of pyrite or H₂S (Rye et al., 1992; Rye, 2005; Seal, 2006)(Fig. 5). From this we suggest the sulfate components (HCl-S and H2O-S) did not form from the oxidation of pyrite or H₂S near the Shinmoe-dake crater. This interpretation is supported by the fact that Fe-oxide minerals such as hematite, goethite, and jarosite that frequently form during surficial oxidation of pyrite (Zimbelman et al., 2005) are not observed in our Shinmoe-dake samples. Sulfur isotopic values of F-Py-S, C-Py-S, and Native-S are also within the characteristic range (δ^{34} S = -10% to +10%) of sulfides (e.g., pyrite) and native sulfur that have been observed in magmatic-hydrothermal environments as recognized from the study of alteration minerals in debris-flow deposits of active stratovolcanoes and epithermal deposits (Arribas, 1995; Rye, 2005; Seal, 2006).

In a magmatic-hydrothermal environment, sulfur isotope fractionation between reduced sulfur and oxidized sulfur species occurs during disproportionation of magmatic SO_2 in the presence of water according to the reaction (Holland, 1965):

$$4SO_2 + 4H_2O = 3H_2SO_4 + H_2S,$$

which generally produces isotopically light sulfides and heavy sulfates (Ohmoto and Rye, 1979; Williams et al., 1990; Kusakabe et al., 2000; Rye, 2005). Also, as proposed for the study of sulfur species in the tephra of the 1979 and 2014 Mount Ontake eruption, Japan (Kusakabe et al., 1982; Ikehata and Maruoka, 2016), some volcanic native sulfur was probably formed in the presence of water through a different disproportionation reaction (Holland, 1965):

$3SO_2 + 2H_2O = 2H_2SO_4 + S.$

The sulfur isotope data on pyroclastic materials from the 2017 Shinmoe-dake eruption can be explained by the above two reactions. These reactions occur below the crater in hydrothermal systems that were inferred from the results of a previous MT survey (Utada et al., 1994; Kagiyama et al., 1996). Because the sulfur isotope range of F-Py-S is higher than that of C-Py-S, fine-grained pyrite and coarse-grained pyrite in the samples may not be contemporaneous. The $\delta^{34}S$ values of HCl-S do not overlap with those of H2O-S in the same sample except for in the Day4 sample. Thus, HCl-S and H2O-S in the samples also may not be contemporaneous. Two types of pyrite-alunite pairs with different sulfur isotopic composition were found in hydrothermally altered dacitic volcanics at Red Mountain, Lake City, Colorado, USA (Bove et al., 1990). Bove et al. (1990) indicated that these pyrite and alunite pairs were derived from the disproportionation of magmatic SO₂ at a temperature of about 400 °C and about 200 °C, respectively. As discussed above, the hydrothermal minerals in our Shinmoe-dake samples were likely derived from at least two acidic alteration zones in the volcano. A water saturated porous layer (aquifer) associated with hydrothermal systems extended from a depth of approximately 100 m to a few hundred meters just beneath the Shinmoe-dake crater (Utada et al., 1994; Kagiyama et al., 1996). Small puddles observed within the crater during the 2017 Shinmoe-dake eruption (Nakano et al., 2017) also imply a shallow hydrothermal system was present.



Fig. 5. (a) Variations in δ^{34} S values of water-leached sulfate (H₂O-S), hydrochloric-acid-leached sulfate (HCl-S), coarse-grained pyritic sulfur (C-Py-S), fine-grained pyritic sulfur (F-Py-S), and acetone-leached native sulfur (Native-S) for the pyroclastic materials from Day1M through Day4 of the 2017 Shinmoe-dake eruption. The typical sulfur isotopic range of sulfates from magmatic-hydrothermal environments and from supergene or steam-heated environments are from Rye et al. (1992), Rye (2005), and Seal (2006), (b) Variations in the sulfur-isotope temperatures calculated from H₂O-S–F-Py-S pairs and HCl-S–C-Py-S pairs from Day1M through Day4 samples of the 2017 Shinmoe-dake eruption.

Table 2

Sulfur isotope-temperatures of sulfate-sulfide pairs in the pyroclastic materials of the 2017 Shinmoe-dake eruption, Japan.

Sample	Eruption day	⊿HCl-S–C-Py-S	T, °C	$ ightarrow H_2O$ -S-F-Py-S	T, °C
Day1M	10/11/2017 (morning)	13.2	420	19.3	298
Day1AE	10/11/2017 (after 1 p.m. JST)	16.0	356	18.6	308
Day1AL	10/11/2017 (after 4 p.m. JST)	12.7	434	18.9	305
Day2	10/12/2017	16.7	342	18.2	316
Day4	10/14/2017	19.6	293	17.2	332

Temperatures calculated from delta values using empirical equations of Ohmoto and Rye (1979) and Ohmoto and Lasaga (1982).

In our Shinmoe-dake data, if the sulfur isotopic differences between sulfate (HCl-S) and pyrite (C-Py-S) and between sulfate (H₂O-S) and pyrite (F-Py-S) represent the effects of primary equilibrium isotopic exchange reactions at the time of their formation, then sulfur isotopic equilibration temperatures were calculated based on empirical equations of Ohmoto and Rye (1979) and Ohmoto and Lasaga (1982). The sulfur-isotope temperatures calculated from H₂O-S–F-Py-S pairs from Day1M through Day4 samples are remarkably constant (332 °C to 298 °C, with an average of 310 °C) (Fig. 5; Table 2). In contrast, the sulfur-isotope temperatures obtained from HCl-S–C-Py-S pairs are variable (434 °C to 293 °C, with an average of 390 °C excluding the Day4 sample) throughout the period and are mostly higher than those obtained from the H₂O-S–F-Py-S pairs (Fig. 5; Table 2). Both temperature ranges are similar to those typical of magmatic-hydrothermal environments within a volcano's interior (Kusakabe et al., 1982; Rye, 2005; Seal, 2006; Ikehata and Maruoka, 2016) and are much lower than the sulfur isotopic temperature (810 ± 40 °C) obtained from magmatic anhydrite-pyrrhotite pairs in the fresh pumices of the 1982 eruption of El Chichón in Mexico (Rye et al., 1984). Therefore, sulfide and sulfate species from magmatic temperatures did not contribute significantly to those in the pyroclastic materials of the 2017 Shinmoe-dake eruption.

The H₂O-S-F-Py-S pairs probably originated from a shallow acidic

hydrothermal alteration zone beneath the Shinmoe-dake crater. In contrast, the HCl-S-C-Py-S pairs were probably derived from a deep acidic hydrothermal alteration zone below the shallow hydrothermal alteration zone. Despite the ongoing eruptions, temperatures in the shallow and deep hydrothermal alteration zones remained constant from Day1M through Day2 (Fig. 5; Table 2). The results suggest that the hydrothermal alteration zones were widely distributed beneath the summit crater. The zones probably ruptured in succession as the eruption progressed. The time required to attain sulfur isotopic equilibrium between aqueous sulfate and sulfide in low pH solutions ranges from hours at 300 °C to minutes at 400 °C (Ohmoto and Lasaga, 1982; Rye, 2005). Therefore, the isotopic equilibration temperatures for these hydrothermal alteration zones beneath the Shinmoe-dake crater reflected those just prior to or during the 2017 eruption. Only the Day4 sample had similar sulfur isotopic compositions for HCl-S and H2O-S (Fig. 5; Table 1). A plausible explanation for this similarity is a mixing of sulfate (e.g., HCl-S of Day2) from the deep hydrothermal alteration zone with sulfate (e.g., H₂O-S of Day2) from the shallow hydrothermal alteration zone after the Day2 eruption. The mixing, dissolution, and reequilibration of the recycled sulfate from both sources could lead to an increase in the sulfur isotopic value for the HCl-S in the Day4 sample. The eruption temporarily ceased on October 13 (one day before Day4). However, the crater continuously discharged white steam clouds during that time. This pause in eruption provided enough time to attain sulfur isotopic equilibrium between aqueous sulfate and sulfide in a hydrothermal environment beneath the Shinmoe-dake crater at about 300 °C.

The carbon isotope exchange equilibrium temperature between CO_2 and CH_4 in a fumarolic gas from Shinmoe-dake was calculated to be about 400 °C (Sato et al., 1999). The authors concluded that carbon isotopic equilibrium between CO_2 and CH_4 occurred in an aquifer at about 400 °C beneath the Shinmoe-dake crater. Thus, a hydrothermal system (probably deep acidic hydrothermal alteration zone) with a similar temperature may have been repeatedly developed beneath the crater after eruptions. Our study demonstrates that time-series sulfur isotopic measurements of pyroclastic materials from the eruption provide information pertaining to the geochemical characteristics and evolution of hydrothermal systems within an unexposed volcano's interior.

Competing interests

The authors declare that they have no competing interests.

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