Spatial and temporal variations of gas geochemistry at Mt. Ontake, Japan

Takanori Kagoshima [a], Yuji Sano [a,b,*], Naoto Takahata [a], Akizumi Ishida [a,1], Yama Tomonaga [a,c], Emilie Roulleau [d], Daniele L. Pinti [e], Tobias P. Fischer [f], Tefang Lan [g], Yoshiro Nishio [h], Urumu Tsunogai [i], Zhengfu Guo [j]

[a] Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Chiba, Japan
[b] Department of Geosciences, National Taiwan University, Taipei 10617, Taiwan
[c] Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse, Dübendorf, Switzerland
[d] Centro de Excelencia de Geotermia de los Andes, Department of Geology, Universidad de Chile, Santiago, Chile
[e] GEOTOP & Department des sciences de la Terre et de l'atmosphere, Universite du Quebec a Montreal, Montreal, Canada
[f] Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, USA
[g] Institute of Earth Sciences, Academia Sinica, Taipei 11529, Taiwan
[h] Reseach and Education Faculty, Kochi University, Kochi, Japan
[i] Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan
[j] Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT

This report describes spatial and temporal variations of helium, carbon, and nitrogen isotopes measured in CO_2-rich bubbling gases from natural springs associated with Mt. Ontake (central Honshu, Japan) from November 1981 through September 2015. During the entire period, the $^3He/^4He$ ratio decreased concomitantly with increasing distance of the sampling site from the central cone. In contrast, the $CO_2/^3He$ ratios and the $\delta^{13}C$ values of CO_2 increased with distance. These spatial trends became more pronounced after the September 27, 2014 Ontake eruption, suggesting reactivation of the volcano plumbing system with enhanced emission of magmatic volatiles, although the spatial trend of nitrogen isotopes disappeared. The $^3He/^4He$ ratios of the most proximal site to the central cone remained constant until 2000, apparently increasing from June 2003 through October 2014. They became constant soon after the eruption until September 2015. The ten-year ^3He enhancement might have been a precursor of the 2014 Ontake eruption. In contrast, $\delta^{13}C$ values of CO_2 at the same site remained constant through this period. The lack of $\delta^{13}C$ anomaly might be attributable to 1) negligibly small amounts of magmatic CO_2 introduced into the source of hot springs compared to ambient CO_2 in the air-saturated aquifer, or 2) close resemblance of the carbon signature of magmatic CO_2 to that of ambient CO_2. Therefore its addition cannot change the overall $\delta^{13}C$ value of the sampled hot springs. At distal sampling sites, no measurable change of helium, carbon, or nitrogen isotopes was observed in relation to the 2014 Ontake eruption, suggesting that the effect of this eruption on the Ontake hydrothermal system was geographically localized.

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1. Introduction

Among volatile elements, ^3He is the isotope that is most sensitive to the addition of magmatic components to volcanic hydrothermal systems (Hilton et al., 2002; Sano and Fischer, 2013). Spatial distribution of helium isotopic ratios was first recognized in springs associated with Mt. Ontake, where the $^3He/^4He$ ratio decreased concomitantly with increasing distance from the central cone (Sano et al., 1984). This spatial trend was confirmed for the Nevado del Ruiz volcano in Colombia (Williams et al., 1987). It has been further verified since in many other hydrothermal systems (Sano and Fischer, 2013) such as Mt. Hakone, Mt. Kusatsu-Shirane, and Mt. Unzen in Japan, the Lesser Antilles islands in the Caribbean Sea, and Mt. Purace in Colombia. Such a tendency is explainable as mantle helium moving from a volcanic conduit through fissures and permeable channels to the surrounding hot springs, followed by dilution by radiogenic helium produced in aquifer rocks. Since helium is a trace element of magmatic volatile addition to hydrothermal fluids, it is expected to be associated with a flux of other magmatic volatiles such as water, CO_2, H_2S, and N_2. If so, it might be expected that some of these volatiles would show similar spatial variations. For example, a coupled spatial distribution of carbon isotopes ($^{13}C/^{12}C$) in CO_2 with helium isotopes was first observed in natural springs associated with Kusatsu-Shirane volcano (Sano et al., 1994).

The $^{13}C/^{12}C$ ratios increased concomitantly with increasing distance from the central cone to the sampling sites, suggesting a negative correlation between helium and carbon isotopes. This spatial variation was verified at Mt. Ontake (Sano et al., 1998). In contrast, carbon isotopes decreasing with distance from the central cone were observed for Sakurajima Island (Roulleau et al., 2013) and in volcanic centers of Hokkaido (Roulleau et al., 2015), resulting in positive relations between helium and carbon isotopes. Spatial distribution of nitrogen isotopes ($^{15}N/^{14}N$) in N_2 was also observed at Mt. Ontake, with a positive correlation between $^{15}N/^{14}N$ ratios and distance from the central cone to the sampling site (Takahata et al., 2003), whereas no apparent correlation was found for Sankurajima Island (Roulleau et al., 2013) or the Hokkaido region (Roulleau et al., 2015). The primary purpose of this paper is to present discussion of spatial variations in the isotopic composition of magmatic volatiles based on helium, carbon, and nitrogen data for Mt. Ontake.

Temporal variations of helium isotopes in a volcano over time can be expected if the state of the magma chamber changes because of degassing by depressurization or new magma injection (Sano and Fischer, 2013). Clear correlations between $^3He/^4He$ ratios and eruption cycles have been observed in a steam well on the flanks of Izu-Oshima volcano in Japan (Sano et al., 1995). The $^3He/^4He$ ratios of volcanic gases at Galeras volcano in Colombia showed systematic variation correlated with magmatic activity (Sano et al., 1997). In contrast, Tedesco and Scarsi (1999) reported that the cyclic variations in $^3He/^4He$ ratios of crater fumaroles at Vulcano in Italy do not correlate with parameters such as temperature and seismicity. Temporal variations of $^3He/^4He$ ratios recorded at five sites on the periphery of Mt. Etna in Italy indicate coincident increases and decreases, suggesting their connections with a single magmatic system (Rizzo et al., 2006). Precursory changes of $^3He/^4He$ ratios were reported in fumarolic gases during the 2002–2003 eruption of Stromboli volcano in Italy (Capasso et al., 2005). If all the helium changes described above have been related to magmatic eruptions (i.e. involving emission of liquid magma), then only one example has been reported for hydro-volcanic eruptions. Recently, we reported a ten-year $^3He/^4He$ anomaly related to 2014 Mt. Ontake eruption (Sano et al., 2015), which was a sudden hydro-volcanic eruption with no precursor signal such as increased seismicity or edifice inflation. However, data related to temporal variations of light element stable isotopes are sparse in the literature. Allard (1983)) reported temporal variations of $^{13}C/^{12}C$ ratios of CO_2 in gases released from La Soufriere in Guadeloupe before, during, and after the eruption activity of 1976–1977. Initially rapid and then slow enhancement of $^{13}C/^{12}C$ ratios was observed on the flanks of Izu-Oshima volcano from October 1986 through July 1992, which positively correlated with the helium isotope variations at the same site (Sano et al., 1995). Temporal changes of carbon isotopes were found at Galeras crater fumaroles from April 1988 through July 1995. The variation appeared to be attributable to activity of the volcano (Sano et al., 1997). Negative correlation was found between carbon and helium isotopes, which is contrary to the case of Izu-Oshima. In contrast, the secular change of $^{13}C/^{12}C$ ratios of crater fumarole at Stromboli volcano was harmonic with that of $^3He/^4He$ ratios (Capasso et al., 2005). In addition, Hilton et al. (2010) showed that $^{13}C/^{12}C$ ratios of fumaroles increased before an episode of phreatic eruptions at Poas volcano, Costa Rica, although helium isotopes remained constant. Recently, Rizzo et al. (2015) reported real-time high frequency plume $^{13}C/^{12}C$ ratios at Mt. Etna, whose short-term variations may be indicative of new batches of magma entering the volcanic system and degassing CO_2 with heavy $^{13}C/^{12}C$ ratios. Therefore, temporal variation of carbon isotopes is more complicated than that of helium when both data are available; it has never been compared with that of helium isotopes before and after hydro-volcanic eruptions. The second purpose of this paper is therefore to present discussion of the temporal variation of carbon isotopes together with helium related to the 2014 Mt. Ontake eruption to elucidate relations between them. Furthermore, nitrogen isotope changes related to the eruption are also discussed herein.

2. Sampling site and analytical methods

Mt. Ontake (3067 m elevation) is located in central Honshu, Japan (35°54′N, 137°29′E). Mt. Ontake is an "independent" stratovolcano, which means that no other active volcano exists within a radius of 40 km, suggesting that the magma plumbing system is isolated. The first historic eruption of the volcano took place on October 28, 1979, forming several new craters and ejecting large amounts of volcanic ash and steam (Sawada, 1981). After several years of quiescence, the 1984 Western Nagano Earthquake (M6.8) occurred at shallow depth about 10 km southeast of the volcano on September 14, 1984 (Japan Meteorological Agency, 1985). After the earthquake, a small magma chamber was detected in the lower crust beneath the earthquake fault region (Mizoue et al., 1985). On May 20, 1991, a new crater with large fumaroles was found about 400 m south of the summit (Japan Meteorological Agency, 1991). On November 12, 1992, seismic activity occurred beneath the summit, followed by a white plume rising to 100 m above the crater (Japan Meteorological Agency, 1993). On April 23, 1993, a M5.1 earthquake occurred at the west end of the fault formed by the M6.8 earthquake (Nagoya University, 1993). Earthquake swarm activity had been observed since then in the region close to both earthquakes. Also, 3–6 mm ground uplift was detected during 2002–2004 (Kimata et al., 2004). Intense seismic activity was observed beneath the volcano summit at the end of December 2006 (Nakamichi et al., 2007). Newly formed ashfall deposits in the fumarole region suggested a small hydro-volcanic eruption in late March 2007 (Japan Meteorological Agency, 2007). All these lines of evidence suggested reactivation of the volcano, but Mt. Ontake remained quiescent from 2008 to 2014. On September 10, 2014, some seismic activity was observed at the summit region. The number of events decreased slightly during the following two weeks, but remained at a considerably higher than background level (Japan Meteorological Agency, 2014). The Mt. Ontake eruption occurred at 11:53 am, September 27, 2014, forming several new craters. Large amounts of volcanic ash, rock, and steam were ejected, creating a 7–10 km high ash plume. Juvenile magmatic material was not detected in the ash, suggesting that it was a hydro-volcanic eruption (Earthquake Research Institute, 2014). Approximately two hundred hikers were in the region surrounding the crater and on the volcano's slope at that time. Volcanic gas, ash, and rocks killed 58 people. Five others are still missing. It was the worst fatal eruption in the postwar history of Japan. Since then, the volcano has become quiescent gradually. In June 2015, the Japan Meteorological Agency reduced volcanic alert levels from 3 to 2. Today, only the crater region is closed to visitors.

Several hot and mineral springs are associated with the volcanic hydrothermal system of Mt. Ontake, located northwest to southeast of the central cone (Fig. S1). The distribution might be attributable to tectonically weakened areas. Fig. S1 shows seven natural springs with bubbling gases around Mt. Ontake. We did not take samples from any artificial water lifting pump system. In the field, gas samples were recovered by water displacement into lead-glass containers (Sano and Fischer, 2013). We did not measure the temperature precisely. Nigorigo and Kanose sites show temperatures higher than 25 °C, although others show temperatures lower than 25 °C.

Chemical compositions of gas samples collected during 1984–1991, and those after the 2014 eruption were measured in almost identical analytical systems equipped with a quadrupole mass spectrometer (QMS) at Hiroshima University and The University of Tokyo. The system was calibrated using a CO_2-He-air standard mixture with different proportions (Sano et al., 1992). To avoid CO interference on N_2 by cracking of the CO_2 molecule, we separated the N_2-CH_4 fraction from CO_2 by a trap held at liquid-nitrogen temperature. A small portion of the gas sample was introduced into a QMS through a variable leak valve. Chemical compositions were determined by comparing peak heights of the sample with those of standard gases and summarized in Sano et al. (1998). Those of the samples collected between 1993 and 2000 were analyzed using gas chromatography (GC) equipped with a TCD detector using Ar carrier gas,

following the method of Urabe et al. (1985) and listed in Takahata et al. (2003). Argon contents were measured using the same system as that used for N_2 carrier gas. Overall error of analysis was approximately 10% at 2σ, which is the reproducibility of standard measurements. We did not check the bias between QMS and GC systems. Chemical compositions of the samples between 2003 and 2009 were not analyzed.

A portion of the gas samples was introduced into an all metal high-vacuum line where helium and neon were purified using hot Ti getters and charcoal traps at liquid nitrogen temperature. Then $^4He/^{20}Ne$ ratios were measured using a QMS on-line. The $^3He/^4He$ ratios of samples before 1990 and 2003 were measured using a noble gas mass spectrometer at Hiroshima University without separating helium from neon (6-60-SGA; Nuclide Co.; Sano and Wakita, 1985). Those after 1990, except for 2003 were analyzed by a modified noble gas mass spectrometer (VG5400; Waters Corp.) at The University of Tokyo (Sano and Wakita, 1988). Because of neon interference on helium isotope measurements, an experimental bias of about 9% exists between the two systems (Sano et al., 1998). However the difference was corrected through careful treatment using the same sample (Takahata et al., 2003). The $^3He/^4He$ and $^4He/^{20}Ne$ ratios of 24 samples collected after the 2014 eruption were measured using the same system as that for the 1993–2009 samples, except for 2003. Consequently, no bias of helium isotopes is expected among all samples studied here. The overall error of helium isotopes was approximately 2% at 2σ measured using the mass spectrometer system. Data of November 1981 through November 2014 were presented by Sano et al. (2015).

Carbon isotopes ($^{13}C/^{12}C$ ratios) of CO_2 gas in the samples taken during 1982–2000 were measured using a conventional stable isotope mass spectrometer with a switching valve system (Finnigan MAT 250) at The University of Tokyo. Analysis followed separation of CO_2 from the other chemical components using a liquid nitrogen trap, a trap at dry-ice ethanol temperature, and a trap with an evacuated 1 N $CuCl_2$ solution to remove H_2S from CO_2 (Nishio et al., 1995). The overall error of analysis was approximately 0.3‰ at 2σ, estimated by repeated analysis of a laboratory standard, which had been calibrated against an international standard of PDB carbonate. The carbon isotopes of samples collected during 2003–2009 were measured using a continuous-flow GC-IRMS system at Hokkaido University. The CO_2 was separated from the other chemical components using a capillary gas chromatograph (HP6890; Agilent) with helium carrier gas. The $^{13}C/^{12}C$ ratios were ascertained using a conventional mass spectrometer (Finnigan MAT 252). Those of recent samples were measured using a similar continuous flow GC-IRMS system (IsoPrim100 with vario-EA system; Isoprime Ltd.) at The University of Tokyo. The overall error of analysis was approximately 0.3‰ at 2σ. We did not check the bias between the switching valve and continuous flow systems.

Nitrogen isotopes ($^{15}N/^{14}N$ ratios) of N_2 gas in the samples collected between 1996 and 2000 were measured using a modified noble gas mass spectrometer (VG3600; Waters Corp.) under static vacuum conditions at The University of Tokyo. Analysis followed separation and purification of N_2 from other chemical components using a hot CuO getter, hot platinum foil, and a trap held at liquid nitrogen temperature. The $^{15}N/^{14}N$ ratio was determined from the observed 29/28 ratio and was calibrated against atmospheric standard gas (Takahata et al., 1998). The overall error of analysis was approximately 1‰ at 2σ. The nitrogen isotopes of samples after the 2014 eruption were measured using a continuous flow GC-IRMS system (IsoPrim100 with vario-EA system) at The University of Tokyo at the same time as carbon analysis. The overall error of analysis was approximately 0.3‰ at 2σ. We did not check the bias between two systems. Nitrogen isotopes of the samples obtained during 2003–2009 were not analyzed.

3. Results

Chemical compositions of hot and mineral spring gases obtained after the 2014 Mt. Ontake eruption are presented in Table 1 together

Table 1
Chemical compositions of hot and mineral spring gases obtained after the 2014 eruption around Mt. Ontake together with those in 2000.

No. site	Distance from cone (km)	He (ppm)	CH_4 (%)	N_2 (%)	O_2 (%)	Ar (%)	CO_2 (%)
October 2014							
1 Kanose	8.0	42.9	0.08	18.3	1.16	0.28	80.2
2 Nigorigo	4.2	135	0.48	43.9	0.08	0.59	55.0
3 Shirakawa	11.2	1.7	0.02	5.2	1.27	0.06	93.5
4 Shojima	22.2	0.8	0.11	0.5	0.12	0.01	99.2
5 Yuya	15.0	11.0	0.58	1.8	0.50	0.03	97.1
November 2014							
6 A ki garni	14.0	8.3	2.00	78.7	17.1	0.93	1.2
7 Kakehashi	21.0	7.7	1.08	4.9	1.30	0.10	92.6
8 Kanose	8.0	35.3	0.06	24.5	2.66	0.35	72.4
9 Nigorigo	4.2	139	0.44	36.6	<0.01	0.38	62.6
10 Shirakawa	11.2	2.2	0.02	1.0	0.23	0.02	98.7
11 Shojima	22.2	1.6	0.11	0.7	0.08	0.01	99.1
12 Yuya	15.0	27.5	1.32	6.0	2.08	0.11	90.5
March 2015							
13 Kakehashi	21.0	4.8	0.58	2.4	0.81	0.05	96.1
14 Kanose	8.0	49.6	0.06	16.7	<0.01	0.29	83.0
15 Shirakawa	11.2	1.3	0.01	0.7	0.21	0.02	99.1
16 Shojima	22.2	1.3	0.13	1.3	0.38	0.03	98.1
17 Yuya	15.0	7.5	0.39	1.5	0.47	0.03	97.6
September 2015							
18 Akigami	14.0	3.6	28.8	4.4	0.86	0.10	65.6
19 Kakehashi	21.0	4.7	0.47	2.5	0.83	0.05	96.1
20 Kanose	8.0	38.4	0.07	15.0	0.13	0.26	84.5
21 Nigorigo	4.2	123	0.43	49.4	0.21	0.65	49.3
22 Shirakawa	11.2	1.5	0.02	1.5	0.50	0.03	97.9
23 Shojima	22.2	1.1	0.10	0.8	0.20	0.02	98.9
24 Yuya	15.0	13.5	0.77	4.5	1.51	0.09	93.1
1996–2000[a]							
25 Akigami	14.0	1.5	0.08	44.7	2.78	0.79	46.5
26 Kakehashi	21.0	4.4	1.98	28.8	2.25	0.34	64.5
27 Kanose	8.0	7.4	0.01	4.2	0.03	0.07	94.4
28 Nigorigo	4.2	6.0	0.14	29.3	1.30	0.35	65.8
29 Shirakawa	11.2	1.8	0.05	20.9	1.43	0.33	75.4
30 Shojima	22.2	3.4	1.03	5.4	0.57	0.11	90.7
31 Yuya	15.0	130	5.98	47.6	0.98	0.80	39.0

[a] Data from Takahata et al. (2003).

with those of average concentrations found during 1996–2000 referred from Takahata et al. (2003). Major chemical constituents of samples are CO_2 together with N_2 in some gases after the 2014 eruption, except for the Akigami spring with 13.5 °C in September 2015, which contains large amounts of CH_4. This chemical signature is consistent with those measured about a decade prior, during 1996–2000 (see Table 1). Generally, O_2 contents are lower than 3%, except at Akigami spring in November 2014 with 17.1%, suggesting that low direct contamination of air. It is noteworthy that no gas seep was found at the original Akigami site after the eruption. Therefore, we collected bubbling gas in a place a few hundred meters up-stream of the Akigami River. Generally, hot spring gases in the volcanic arc region of Japan are CO_2-rich (Urabe et al., 1985). The present status of Mt. Ontake agrees well with that report. Helium contents vary considerably from 0.8 ppm to 139 ppm, where some samples show higher abundance than air, 5.24 ppm (v/v), but others are lower than air. Helium concentrations are high in N_2-rich gases and low in CO_2-rich gases, which is again consistent with the general feature of natural gases in Japan (Urabe et al., 1985). After the 2014 eruption, positive correlation was found between N_2 and He contents with a correlation coefficient (R^2) of 0.922 (Fig. S2a). They are higher at sites close to the central cone such as Kanose (t = 28.6 °C) and Nigorigo (t = 54.0 °C), but lower at distal sites such as Shojima (t = 16.3 °C) and Kakehashi (t = 12.8 °C). Correlation coefficients (R^2) between the distance and N_2, and that with He are, respectively, 0.588 (Fig. S2b) and 0.542 (Fig. S2c).

Table 2
Helium, carbon and nitrogen isotopic compositions of hot and mineral spring gases obtained after the 2014 eruption of Mt. Ontake together with those in 2000.

No. site	^{3}He/^{4}He (Ra)	^{4}He/^{20}Ne	^{3}He/^{4}He$_{cor}$ (Ra)	Error (2σ)	δ^{13}C (‰)	Error (2σ)	δ^{15}N (‰)	Error (2σ)
October 2014								
1 Kanose	6.99	17	7.10	0.34	−8.8	0.2	1.6	0.3
2 Nigorigo	7.17	28	7.24	0.30	−9.0	0.3	0.9	0.3
3 Shirakawa	4.65	1.8	5.45	0.42	−6.6	0.2	0.8	0.3
4 Shojima	2.63	6.9	2.71	0.13	−7.5	0.2	0.5	0.3
5 Yuya	2.24	47	2.25	0.09	−7.6	0.2	0.0	0.3
November 2014								
6 Akigami	3.67	1.6	4.33	0.15				
7 Kakehashi	3.46	10	3.54	0.09	−4.3	0.2	2.0	0.2
8 Kanose	7.33	16	7.46	0.24	−8.7	0.2	1.3	0.3
9 Nigorigo	7.38	42	7.43	0.31	−8.6	0.2	1.7	0.3
10 Shirakawa	6.08	12	6.22	0.23	−6.1	0.2	−0.1	0.3
11 Shojima	2.56	11	2.61	0.11	−7.2	0.2	1.4	0.3
12 Yuya	2.24	43	2.25	0.09	−6.1	0.2	1.4	0.3
March 2015								
13 Kakehashi	3.43	9.8	3.51	0.10	−4.3	0.3	1.0	0.3
14 Kanose	7.37	30	7.44	0.39	−8.2	0.2	1.3	0.3
15 Shirakawa	5.66	6.6	5.89	0.34	−5.5	0.2	−0.3	0.3
16 Shojima	2.50	3.7	2.65	0.17	−6.4	0.2	0.7	0.2
17 Yuya	2.35	28	2.37	0.13	−6.7	0.2	0.4	0.3
September 2015								
18 Akigami	3.85	2.6	4.24	0.18	−6.0	0.3	−1.2	0.2
19 Kakehashi	3.10	7.2	3.19	0.12	−3.9	0.4	0.4	0.2
20 Kanose	7.36	51	7.40	0.44	−8.1	0.3	1.8	0.2
21 Nigorigo	7.30	21	7.40	0.44	−8.3	0.3	0.6	0.2
22 Shirakawa	5.64	4.5	6.00	0.20	−5.6	0.3	−0.5	0.3
23 Shojima	2.42	8.1	2.47	0.14	−6.8	0.3	0.4	0.3
24 Yuya	2.25	23	2.26	0.11	−6.1	0.4	−0.4	0.2
1996–2000[a]								
25 Akigami			4.15		−6.0		0.2	
26 Kakehashi			4.31		−4.9		2.0	
27 Kanose			6.97		−8.8		0.2	
28 Nigorigo			6.49		−8.4		−0.9	
29 Shirakawa			6.72		−5.0		0.5	
30 Shojima			2.74		−6.7		1.7	
31 Yuya			2.35		−6.6		1.5	

[a] Data referred from Takahata et al. (2003).

Helium, carbon, and nitrogen isotopic compositions of hot and mineral spring gases obtained after the 2014 Mt. Ontake eruption are presented in Table 2 together with average values for those collected during 1996–2000, as reported by Takahata et al. (2003). The ^{3}He/^{4}He and ^{4}He/^{20}Ne ratios of October 2014 and November 2014 were reported by Sano et al. (2015). The ^{3}He/^{4}He ratios are expressed in R_a notation, where R_a is the atmospheric ratio of 1.382×10^{-6} (Sano et al., 2013). Observed ^{3}He/^{4}He ratios are corrected for atmospheric contamination using ^{4}He/^{20}Ne ratios (Sano et al., 1997). Corrected ^{3}He/^{4}He ratios vary from 2.25 R_a to 7.46 R_a. The lower limit is the value of Yuya samples collected in 2014, whereas the upper limit is that of the Kanose sample collected in November 2014 (Table 2). All values are higher than the air ratio, suggesting the influence of subduction-type mantle helium with 7.4 ± 1.3 R_a (Sano and Fischer, 2013). The ^{13}C/^{12}C ratios of CO_2 in gas samples are expressed in δ^{13}C notation in parts per thousand (per mil, ‰) deviation from an international standard of VPDB. The δ^{13}C values vary from −9.0‰ to −3.9‰, which agree well with those of samples obtained during 1996–2000, and which are consistent with data of volcanic hydrothermal gases in subduction zones (Kagoshima et al., 2015). The ^{15}N/^{14}N ratios of N_2 in gas samples are expressed in δ^{15}N as parts per thousand (per mil, ‰) deviation from the air standard value. The δ^{15}N values vary from −1.2‰ to +2.0‰, which are again similar to those of 1996–2000 samples. They are principally close to the air value and lighter than data of high-temperature volcanic gases at island arcs of 0.1–4.6‰ (Sano et al., 2001). A slight negative correlation was found between ^{3}He/^{4}He ratios and δ^{13}C values, with a correlation coefficient (R^2) of 0.297 (Fig. S2d), if one considers all data after the 2014 eruption. However, no significant correlation was found between ^{3}He/^{4}He ratios and δ^{15}N values, and between δ^{13}C and δ^{15}N values. Table 3 presents carbon and helium isotopic compositions of samples obtained before the 2014 eruption with the typical temperatures of spring waters. Helium data were referred from Sano et al. (2015).

4. Discussion

4.1. Spatial variation of helium isotopes

As summarized in the introduction, spatial variations of helium isotopes are common features of modern hydrothermal systems in subduction zones (Sano and Fischer, 2013). The ^{3}He/^{4}He ratio decreases in the sampling site with increasing distance from the central cone of a volcanic edifice, as observed also at nine distinct volcanic systems worldwide: Hakone, Kusatsu-Shirane, Ontake and Unzen in Japan, Lesser Antilles in the Caribbean Sea, and Purace and Nevado del Ruiz in Colombia. Fig. 1a presents geographical variations of ^{3}He/^{4}He ratios in 1996–2000 and after the 2014 eruption in the Mt. Ontake region. The ^{3}He/^{4}He ratios of Nigorigo and Kanose springs, which are close to the central cone (see Fig. S1), increased from values of <7 R_a of 1996–2000 to those higher than 7 R_a after the 2014 eruption. In contrast the ^{3}He/^{4}He ratio decreased at the mid-range Shirakawa site. No significant R_a change was found at distal sites, except for Kakehashi spring, where the ^{3}He/^{4}He ratio decreased from 4.3 R_a to 3.4 R_a. Negative correlations with distance appear to be greater after the 2014 Mt. Ontake

Table 3
Carbon and helium isotopic compositions of hot and mineral spring gases obtained before 2014 eruption around Mt. Ontake.

Name	Date	$\delta^{13}C$ (‰)	Error (2σ)	^{3}He/^{4}He$_{cor}$ (Ra)	Error (2σ)
Akigami t = 13.5 °C	3-Nov-81			4.14	0.34
	22-Sep-84	−5.8	0.3	4.09	0.41
	1-Apr-85	−5.7	0.3	4.25	0.32
	3-Jun-91	−5.5	0.3	4.37	0.29
	9-Jun-93	−6.0	0.3	4.28	0.30
	7-Jun-96	−6.1	0.3	4.02	1.23
	5-Jun-00			4.28	4.11
	3-Jun-03	−5.1	0.3	4.38	0.27
	21-Jun-05			4.39	0.13
	25-Jun-07	−27.1	0.3	4.40	4.85
	29-Jul-09			4.13	0.62
Kakehashi t = 12.8 °C	3-Nov-81			3.28	0.20
	23-Sep-84	−4.8	0.3	3.33	0.20
	2-Apr-85	−4.4	0.3	3.75	0.23
	4-Jun-91	−4.4	0.3	3.90	0.24
	10-Jun-93	−4.7	0.3	4.11	0.25
	8-Jun-96			4.09	0.59
	1-Jun-98	−4.8	0.3	4.35	0.26
	4-Jun-00	−4.9	0.3	4.48	0.27
	3-Jun-03	−5.3	0.3	4.58	0.31
	20-Jun-05			3.63	0.08
	26-Jun-07	−4.9	0.3	3.67	0.08
	30-Jul-09			3.73	0.08
Kanose t = 28.6 °C	2-Nov-81	−8.0	0.3	6.35	0.38
	22-Sep-84	−8.6	0.3	6.59	0.40
	2-Apr-85	−8.7	0.3	6.50	0.39
	3-Jun-91	−8.3	0.3	7.12	0.43
	10-Jun-93	−8.3	0.3	6.99	0.47
	7-Jun-96	−8.8	0.3	7.01	0.43
	2-Jun-98	−8.8	0.3	7.13	0.44
	4-Jun-00			6.78	3.29
	3-Jun-03	−8.4	0.3	6.95	0.23
	20-Jun-05			7.19	0.22
	26-Jun-07	−8.0	0.3	7.02	0.22
	30-Jul-09	−8.0	0.3	7.27	0.22
Nigorigo t = 54.0 °C	2-Nov-81	−8.4	0.3	6.76	0.42
	23-Sep-84	−8.6	0.3	6.56	0.40
	1-Apr-85	−8.3	0.3	6.66	0.41
	3-Jun-91	−8.5	0.3	6.43	0.40
	9-Jun-93	−8.6	0.3	6.56	0.42
	7-Jun-96	−8.5	0.3	6.50	0.92
	1-Jun-98	−8.3	0.3	6.44	0.57
	5-Jun-00	−8.4	0.3	6.53	0.46
	4-Jun-03	−8.6	0.3	6.88	0.42
	21-Jun-05			7.00	0.24
	26-Jun-07	−8.4	0.3	7.29	0.23
	29-Jul-09			7.35	0.24
Shirakawa t = 18.6 °C	1-Apr-85			5.71	0.36
	4-Jun-91	−6.2	0.3	6.44	0.79
	10-Jun-93	−6.5	0.3	6.75	6.22
	7-Jun-96	−6.7	0.3	6.40	1.74
	2-Jun-98	−5.4	0.3	6.68	0.69
	4-Jun-00	−4.9	0.3	7.09	0.79
	3-Jun-03	−4.6	0.3	6.84	0.99
	20-Jun-05	−5.8	0.3	6.06	0.90
	26-Jun-07			5.48	0.26
Shojima t = 16.3 °C	3-Nov-81	−6.7	0.3	2.22	0.14
	22-Sep-84	−6.9	0.3	2.30	0.15
	2-Apr-85	−6.8	0.3	2.36	0.17
	3-Jun-91	−6.9	0.3	2.53	0.15
	9-Jun-93	−6.6	0.3	2.84	0.19
	8-Jun-96	−7.0	0.3	2.77	0.17
	2-Jun-98	−6.6	0.3	2.71	0.18
	5-Jun-00	−6.4	0.3	2.74	0.17
	3-Jun-03	−6.4	0.3	2.82	0.18
	20-Jun-05			2.50	0.09
	26-Jun-07	−6.4	0.3	2.36	0.08
	30-Jul-09	−7.0	0.3	2.50	0.08
Yuya t = 12.7 °C	21-Nov-81			2.34	0.14
	23-Sep-84	−6.2	0.3	2.23	0.13
	1-Apr-85	−6.3	0.3	2.32	0.14
	4-Jun-91	−6.1	0.3	2.29	0.14
	10-Jun-93	−6.6	0.3	2.27	0.14
	7-Jun-96	−6.8	0.3	2.36	0.14

Table 3 (continued)

Name	Date	$\delta^{13}C$ (‰)	Error (2σ)	^{3}He/^{4}He$_{cor}$ (Ra)	Error (2σ)
Yuya t = 12.7 °C	1-Jun-98	−7.2	0.3	2.33	0.14
	4-Jun-00	−5.7	0.3	2.37	0.14
	4-Jun-03	−6.4	0.3	2.32	0.14
	21-Jun-05			2.40	0.07
	25-Jun-07			2.41	0.07
	29-Jul-09	−6.1	0.3	2.32	0.07

Data before 2000 referred from Takahata et al. (2003) Geochemical Journal 37, 299–310 and Sano et al. (1998) Journal of Geophysical Research 103, 23,863–23,873.

eruption (Fig. 1a), suggesting reactivation of the volcanic plumbing system with enhanced emission of magmatic volatiles into the hydrothermal circuit closer to the central cone.

One might estimate the variation of ^{3}He/^{4}He ratio at Mt. Ontake based on the fluid dispersion model using the following equation (Sano et al., 1990; Sano et al., 2015).

$$^3He/^4He(r) = \left(^3Pr + \alpha^3C_m/r\right)/\left(^4Pr + \alpha^4C_m/r\right) \quad (1)$$

In that equation, r, ^3P, ^4P, ^3C_m, and ^4C_m respectively denote the distance, nucleogenic and radiogenic production rates of ^{3}He and ^{4}He, and the concentrations of ^{3}He and ^{4}He at the conduit. The constant α equals $(2A$-$4D)/(1$-$Re)$ where A, D and Re respectively denote a constant, the molecular diffusion coefficient of He in water, and retention of radiogenic He in the porous material of the aquifer. It is possible to calculate α^3C_m and α^4C_m values by fitting the observed He isotope distribution to the equation above by the least-squares method under the assumption that ^3P and ^4P are 1.5×10^6 atom/m^3 s and 3×10^{-2} atom/m^{3}s, respectively, in typical sedimentary materials composing the aquifer. Despite the model simplicity, the method is applied to the spatial dataset of 1996–2000 and those after the 2014 eruption. The least-squares fitted curves are also presented in Fig. 1a. Best estimates of α^3C_m and α^4C_m values are, respectively, $(3.3 \pm 0.2) \times 10^7$ and $(3.8 \pm 0.4) \times 10^{12}$ in 1996–2000, and $(3.1 \pm 0.1) \times 10^7$ and $(2.8 \pm 0.1) \times 10^{12}$ after the 2014 eruption. These numbers can be converted into more practical features such as ^{3}He flux using a α^3C_m/r value. Assuming that the fringe of the conduit is 1 km distant from the hypothetical center of the volcano by the dike model using seismological data (Japan Meteorological Agency, 2007), it is possible to calculate ^{3}He and ^{4}He fluxes. They are, respectively, $(3.3 \pm 0.2) \times 10^6$ atoms/m^2 s and $(3.8 \pm 0.4) \times 10^{11}$ atoms/m^2 s in 1996–2000, and $(3.1 \pm 0.1) \times 10^6$ atoms/m^2 s and $(2.8 \pm 0.1) \times 10^{11}$ atoms/m^2 s after the 2014 eruption. It is noteworthy that ^{3}He flux of 1996–2000 is consistent with that after the 2014 eruption, although ^{4}He flux decreased significantly, being 26% from the initial value.

### 4.2. Spatial variation of carbon isotopes

Spatial variations of carbon isotopes are well documented in modern hydrothermal systems (Allard, 1983; Capasso et al., 2005; Hilton et al., 2010; Roulleau et al., 2013; Roulleau et al., 2015). The variation is more complicated than that of helium. The $\delta^{13}C$ values of CO_2 increase concomitantly with increased distance from the central cone in springs around Mt. Kusatsu-Shirane and Mt. Ontake, although the trend was reversed at the Sakurajima Island and in Hokkaido volcanoes. A plausible explanation does exist for these discrepancies and complexity. Calcite precipitation might not change $\delta^{13}C$ values of CO_2 (Sano and Marty, 1995; Tardani et al., 2016). Thereby these observations are explainable by a two-component mixing hypothesis. At Sakurajima Island and Hokkaido volcanoes, the magmatic fluids might have $\delta^{13}C$ signatures between −5‰ and −7‰, whereas crustal CO_2 might be affected by organic carbon with $\delta^{13}C = -30‰$ (Roulleau et al., 2013; Roulleau et al., 2015). Then $\delta^{13}C$ value would decrease concomitantly with increased distance because of a stronger contribution of organic

carbon. For the Ontake volcano, Fig. 1b presents geographical variations of $\delta^{13}C$ values of CO_2 in 1996–2000 and after the 2014 eruption. The $\delta^{13}C$ values were constant at the most proximal sites to the central cone (Nigorigo and Kanose, which are located respectively at 4.2 km and 8.0 km distance) from 1996 to 2000 to after the 2014 eruption. They decreased from −5.0‰ to −6.0‰ at mid-range Shirakawa site, although they are similar at more distal sites except for Kakehashi site where the $\delta^{13}C$ value increased from −4.9‰ to −4.2‰. Then the spatial trends with positive correlation with distance have greater significance after the 2014 Mt. Ontake eruption, even though overall $\delta^{13}C$ variations are contrary to those of helium. Based on negative correlation between helium and carbon isotopes between 1981 and 1993 at Mt. Ontake, the two-component mixing hypothesis was presented (Sano et al., 1998). Estimated end-members were magmatic fluids at Mt. Ontake with ^{3}He/^{4}He = 8 ± 1.5 R_a (Sano et al., 2013) and $\delta^{13}C = -8.7 \pm 0.8‰$ (2σ; Sano et al., 1998), and crustal fluids with ^{3}He/^{4}He = 0.02 R_a (Mamyrin and Tolstikhin, 1984) and $\delta^{13}C = -5.2 \pm 0.6‰$ (2σ; Sano et al., 1998). This suggests that the decrease in $\delta^{13}C$ value resulted from either enhanced contribution of magmatic CO_2 or depleted contribution of crustal CO_2 at Shirakawa site after the 2014 eruption. At Nigorigo and Kanose sites, their $\delta^{13}C$ values of −8.4‰ and −8.8‰ in 1996–2000 were previously overlapped with the magmatic end-member of −8.7‰. For that reason, it is difficult to alter them either by the addition of magmatic CO_2 or by the decreased contribution of crustal CO_2.

Fig. 1c depicts spatial variations of $CO_2/^3$He ratios (v/v) during 1996–2000 and after the 2014 eruption, for which the ratios were calculated from CO_2 and He contents reported in Table 1 and ^{3}He/^{4}He ratios from Table 2. An increasing trend of $CO_2/^3$He ratio was found with increasing distance from the cone in 1981–1993 (Sano et al., 1998) and in 1996–2000 (Takahata et al., 2003) except for Yuya spring samples, which are characterized by a N$_2$-rich signature with 47.6%. Marty et al. (1989) reported that the $CO_2/^3$He ratios of natural gas samples might be altered by the difference of solubility between He and CO_2 in spring water and that enrichment of He in N$_2$-rich gases (Urabe et al., 1985) was attributed to the fractional removing of CO_2 from aquifers. This is probably the case for Yuya samples in 1996–2000 (Fig. 1c). After the 2014 eruption, the $CO_2/^3$He ratios of Nigorigo and Kanose sites decreased significantly by more than a factor of ten, whereas that of Yuya site increased by a factor of ten. Consequently, positive correlation existing between the distance and $CO_2/^3$He ratios appears to have greater significance after the 2014 Mt. Ontake eruption, again suggesting reactivation of the volcano with either enhanced emission of magmatic volatiles, or decreased contribution of crustal CO_2. The latter might be the case because ^{4}He flux decreased considerably after the eruption.

4.3. Spatial variation of nitrogen isotopes and origin of nitrogen

The N$_2$ contents of Nigorigo and Kanose sites increased from 1996 to 2000 to after the 2014 eruption, whereas that of Yuya site decreased significantly (see Table 1). These variations are concordant with those of $CO_2/^3$He ratios, as described above. Fig. 1d shows spatial variations of $\delta^{15}N$ values of N$_2$ gases in 1996–2000 and after the 2014 eruption. From the dataset of 1996–2000, an apparent positive correlation was
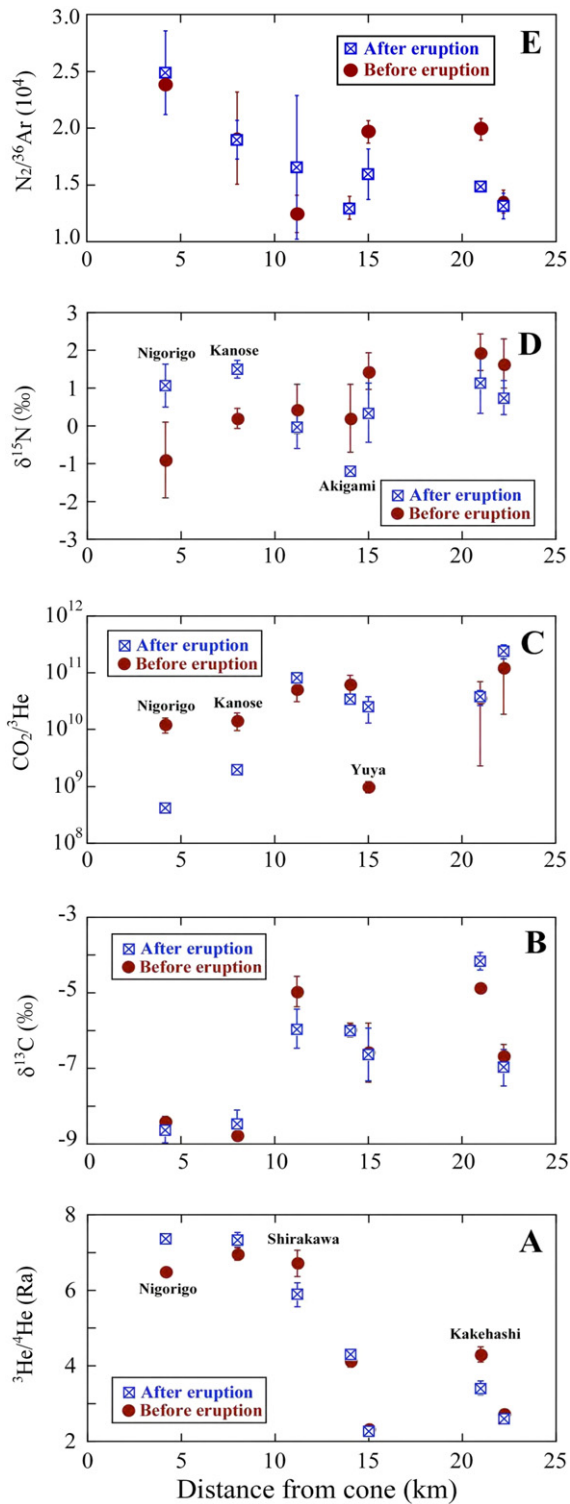
Fig. 1. (A) Correlation diagram of the distance from the central cone of Mt. Ontake to the sampling site and corrected ^{3}He/^{4}He ratios of hot and mineral spring gases in R_a units. Open squares and solid circles respectively portray the average of samples collected after the 2014 eruption and those of 1996–2000. Bars represent 2σ variation. (B) Relation between distance and δ^{13}C values of CO_2 gases. (C) Relation between distance and CO_2/^{3}He ratios. (D) Relation between distance and δ^{15}N values of N_2 gases. (E) Relation between distance and N_2/^{36}Ar ratios.

found between the distance and the δ^{15}N value. Based on this relation, Takahata et al. (2003) reported that the spatial variation was attributable to the binary mixing of nitrogen of two types: a magmatic end-member with δ^{15}N = −3‰ and crustal one with +3‰. This hypothesis is

consistent with the progressive decrease in the ^{15}N-depleted mantle contribution from springs closer to the cone to the distal ones, corresponding to a decrease in the ^{3}He/^{4}He ratio (Fig. 1). After the 2014 eruption, however, the trend changed considerably. The δ^{15}N values of Nigorigo and Kanose sites increased appreciably, whereas those of Akigami and Yuya decreased. From results, no positive correlation was found between the distance and δ^{15}N value after the 2014 eruption. It is difficult to explain the trend using the binary mixing hypothesis (Takahata et al., 2003). It is therefore important to discuss the origin of N_2 in these natural spring gases.

Based on a δ^{15}N — N_2/^{36}Ar diagram, the origin of nitrogen in subduction zones can be discussed as resulting from three-component mixing (Sano et al., 2001). Hypothetical end-members are mantle-derived, sedimentary, and atmospheric nitrogen. Fig. 2 portrays the relation between δ^{15}N values and N_2/^{36}Ar ratios of Ontake gas samples during 1996–2000 and after the 2014 eruption. The N_2/^{36}Ar ratios of 1996–2000 samples were calculated using N_2 and Ar contents, and observed ^{40}Ar/^{36}Ar ratios (Takahata et al., 2003), whereas those after the 2014 eruptions were derived from N_2 and Ar contents in Table 1 and under the assumption of ^{40}Ar/^{36}Ar = 302, which is an average of 1996–2000 samples. Although we did not measure the ^{40}Ar/^{36}Ar ratios of samples after the 2014 eruptions, the assumption of air-like argon is plausible because most gas samples from arc hydrothermal and volcanic systems have ^{40}Ar/^{36}Ar ratios that were close to the air value of 295.5 (Sano and Fischer, 2013). Except for one outlier (Akigami sample in September 2015), all nitrogen in bubbling gases from Mt. Ontake region is located in the mixing area and is explained by the three end members of mantle-derived, sedimentary, and atmospheric nitrogen, when incorporating consideration of the error of analysis. The Akigami sample was collected at a different place from the original point. It is a CH_4-rich gas, chemically discrepant from all other samples. For that reason, it is reasonable to exclude its nitrogen data. When considering data obtained after the 2014 eruption, a positive correlation can be found between δ^{15}N values and N_2/^{36}Ar ratios. If one assumes atmospheric nitrogen as an end-member, then it is possible to estimate non-air nitrogen as another end-member (see the arrow in Fig. 2). The non-air nitrogen is calculated as a mixture of 36% upper mantle and 64% nitrogen derived from marine sediment with the δ^{15}N value of +2.7‰, which is comparable to those of high-temperature volcanic gases ranging from +0.1‰ to +4.6‰ (Sano et al., 2001). The non-air nitrogen component, which is calculated using the N_2/^{36}Ar ratio, decreases with increased distance from the central cone after the 2014 eruption. In addition, δ^{15}N values of distal sites such as Yuya, Kakehashi, and Shojima decreased after the eruption, even though they are consistent within two sigma error. There is no plausible reason for the variations: it should be clarified in future studies.

4.4. Temporal variation of helium and carbon isotopes

Secular variations of ^{3}He/^{4}He ratios in Mt. Ontake hydrothermal system from November 1981 through November 2014 were reported by Sano et al. (2015). Their results can be summarized as follows: The ^{3}He/^{4}He ratios of natural spring at the most proximal site to the central cone (Nigorigo) remained constant during November 1981 through June 2000. Then they increased considerably from June 2003 through November 2014, although those of distal sites such as Yuya and Shojima exhibited no marked change. These data suggest recent reactivation of Mt. Ontake and suggest that ^{3}He anomaly might have been a precursor of the 2014 eruption. We measured ^{3}He/^{4}He ratios of samples around Mt. Ontake in March and September 2015. They are mainly consistent with those of October and November 2014 immediately after the 2014 eruption. September 2015 observations include seven data of helium isotopes (Table 2). From them, one can calculate ^{3}He flux at the central conduit of volcano using the hydrodynamic dispersion model based on Eq. (1). The value of September 2015 becomes $(2.9 \pm 0.1) \times 10^6$ atoms/m^2 s, which is consistent with that of October 2014, $(2.8 \pm$
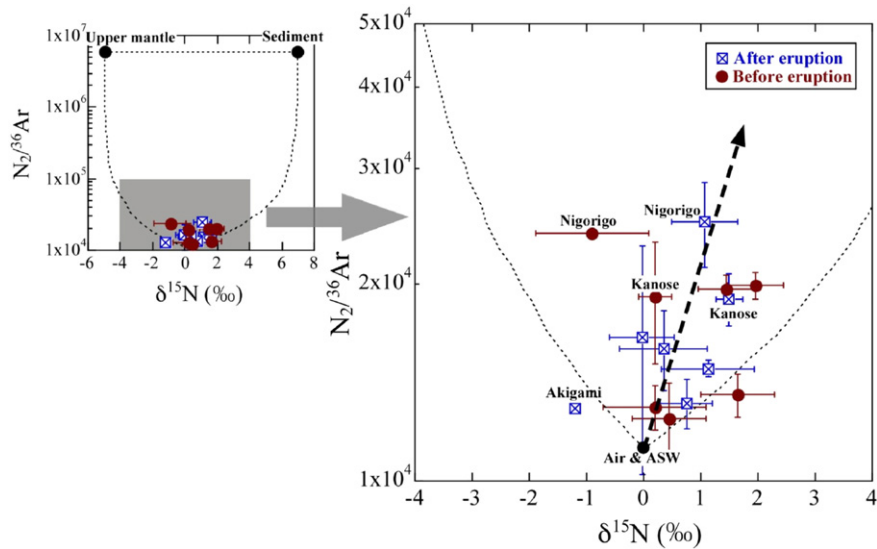
Fig. 2. Correlation diagram of $\delta^{15}N$ values of N_2 and $N_2/^{36}Ar$ ratios of hot and mineral spring gases on Mt. Ontake. Open squares and solid circles respectively show the average of samples collected after the 2014 eruption and those of 1996–2000. Bars represent 2σ variation. Lines show mixing lines among the model end-members: air and air saturated water, organic nitrogen in sediment, and upper mantle component in mid-ocean ridge basalt (Sano et al., 2001). The dotted arrow suggests non-air nitrogen as an end-member.

$0.1) \times 10^6$ atoms/m^2 s, but which is significantly smaller than $(3.6 \pm 0.1) \times 10^6$ atoms/m^2 s in July 2009. Therefore, the activity of Mt. Ontake is quiescent in terms of ^3He flux and the reduction of the volcano alert level from 3 to 2 by the Japan Meteorological Agency is probably adequate.

Even though temporal variations of 3He/4He ratios were observed in hot springs close to the cone before the 2014 eruption, helium is a trace element in hydrothermal systems. There might be associated temporal variations of other volatiles such as water, N_2, and CO_2 because they are major components. We have measured $\delta^{13}C$ values of CO_2 in some

hot and mineral spring gases collected between June 2003 and July 2009 and reserved in the laboratory after their helium measurements. Unfortunately some of them had been evacuated. Moreover, it was difficult to obtain $\delta^{13}C$ values for November 1981 through July 2009. Nevertheless, we can estimate the general trend of the carbon secular variations. Carbon and helium isotopic compositions of hot and mineral spring gases obtained before the 2014 eruption are presented in Table 3.

Fig. 3 presents temporal variations of $\delta^{13}C$ values at seven sampling sites together with those of $^3He/^4He$ ratios. At the Nigorigo site, 4.2 km from the central cone, the $^3He/^4He$ ratios increased significantly from
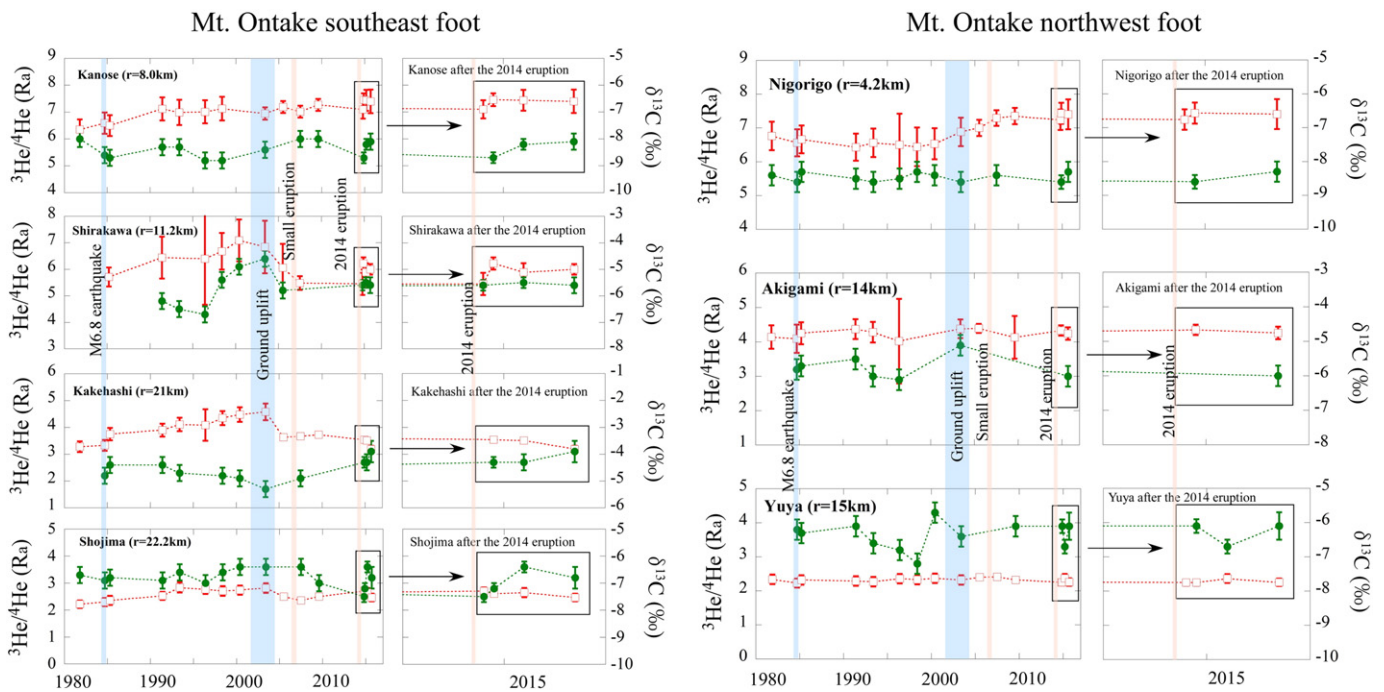
Fig. 3. Temporal variations of corrected $^3He/^4He$ ratios (open squares) and $\delta^{13}C$ values (solid circles) of CO_2 of hot and mineral spring gases on Mt. Ontake from November 1981 to September 2015. Errors are given as 2σ. Left and right respectively portray data of sites during 1980–2015 and only after the 2014 eruption at the southeast foot and northwest foot of the volcano. Blue and red bars represent recent geotectonic events in the region explained in the text. After the 2014 eruption, no apparent change of $^3He/^4He$ ratios has been observed. The $^3He/^4He$ ratios during 1980–2014 are also reported in Sano et al. (2015).

June 2003 through November 2014, although no temporal change was found in $\delta^{13}C$ values of CO_2. At the Kanose site, 8.0 km distant from the cone, the helium isotopic ratios increased gradually with a constant rate from November 1981 through November 2014, although $\delta^{13}C$ values showed no marked change. No correlation was found between $^3He/^4He$ ratios and $\delta^{13}C$ values at the Kanose site. This is also the case at Nigorigo site. The question is why is there a helium isotope anomaly before the 2014 eruption, but not one for carbon isotopes. The first hypothesis was suggested in Section 4.2. Estimated magmatic CO_2, based on the binary mixing hypothesis has a $\delta^{13}C$ value of $-8.7 \pm 0.8‰$ (Sano et al., 1998). The observed $\delta^{13}C$ values of Nigorigo and Kanose sites were $-8.0‰$ to $-9.0‰$, resembling the magmatic value. Therefore, the addition of magmatic CO_2 cannot alter the $\delta^{13}C$ values of Nigorigo and Kanose sites, even though increases of $CO_2/^3He$ ratios at these sites suggest a substantial magmatic CO_2 input. A second hypothesis is more quantitative than the first, and based on the hydrodynamic dispersion model (Sano et al., 1990). Assuming that the aquifer depth was 30 m and using a volcanic conduit diameter of 2 km, then the total ^3He flux from the central cone of Mt. Ontake before June 2003 was 78 nmol/day (Sano et al., 2015). The magmatic $CO_2/^3He$ ratio of high-temperature arc volcanic gases, summarized as 1×10^{10}, is well documented (Sano and Marty, 1995). This value is consistent with the $CO_2/^3He$ ratios of Nigorigo and Kanose sites before the 2014 eruption (see Fig. 1c). Using these values, one can calculate the magmatic CO_2 flux as 7.3 kg/day based on the ^3He flux and $CO_2/^3He$ ratio. The magmatic CO_2 flux increased to 9.1 kg/day in June 2005 as the ^3He flux increased. This excess CO_2 supply of 1.8 kg/day likely continued during the past ten years, leading to an accumulated CO_2 amount of 27 tons. However, assuming 30 m aquifer depth, 4 km diameter from the cone to the Nigorigo site in vertical section, and average porosity of 0.2, the amount of total water becomes 3×10^8 tons. Again assuming the solubility of CO_2 in spring water as 1 cm^3/g, the total ambient CO_2 existing in the hydrothermal system becomes 6×10^5 tons, which is >20.000 times larger than the excess CO_2 supply because of volcanic activity. Even given total uncertainty of a factor of 30 in the parameters used for the calculation above, the excess CO_2 is still <1% of the ambient CO_2 in the aquifer system. Therefore, the addition of magmatic CO_2 related to the 2014 eruption cannot alter the $\delta^{13}C$ values of Nigorigo site, even though the $^3He/^4He$ ratios increased significantly, which also caused the decrease in $CO_2/^3He$ ratios after the eruption. Temporal variations of other volatile isotopes cannot be discussed precisely like helium and carbon in CO_2 because data are too sparse or not available. Including nitrogen, isotope variations of other volatile elements should be investigated more in the future.

5. Conclusion

Variations of helium, carbon, and nitrogen isotopes of natural springs associated with Mt. Ontake from November 1981 to September 2015 were found in this study. The $^3He/^4He$ ratios corrected for air contamination of spring gases decreased with distance from the central cone to the sampling sites, whereas $CO_2/^3He$ ratios and $\delta^{13}C$ values of CO_2 increased with distance in general. The observed trend is explained by the transport of magmatic helium and carbon with fluid flowing through the volcanic conduit. As helium and carbon move from the conduit through fissures and permeable channels to surrounding natural springs, they are diluted by crustal helium and carbon in the aquifer system. The $^3He/^4He$ ratios of the most proximal site to the central cone stayed constant until 2000 and increased significantly from June 2003 through October 2014. The ten-year helium anomaly was attributed to be a precursor of the 2014 Mt. Ontake eruption. In contrast, no valuable change of $\delta^{13}C$ values was found at the same site. Lack of $\delta^{13}C$ anomaly is explained by either a similar $\delta^{13}C$ value of the magmatic CO_2 and the ambient CO_2, so any mantle C contribution cannot substantially modify the $\delta^{13}C$ value of the natural spring, or that the amount of magmatic CO_2 introduced into the source of natural spring is negligibly small

compared with ambient CO_2 in the aquifer. At the distal sites from the cone, no change of helium and carbon isotopes was found in association with the 2014 eruption. These lines of evidence confirm that ^3He is the most sensitive tracer that can be measured in distal springs on the volcano's flanks for magmatic activity in subduction zones. For nitrogen, $\delta^{15}N$ values of N_2 in the most proximal site to the central cone increased after the 2014 eruption, which indicates that the source of nitrogen changed from the mantle-like component to the high-temperature volcanic gas-like component. Temporal variations of nitrogen isotopes possibly reflect volcanic activity. They should be investigated in the future. Herein, we presented the first data supporting comparison of spatial and temporal variations of He, C, and N isotopes before and after the eruption of an individual volcano.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jvolgeores.2016.06.013.

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