Spatial and secular variations of helium and carbon isotopes at Ontake volcano, Japan Y. Sano[1], T. Kagoshima[1], N. Takahata[1], A. Ishida[1], Y. Tomonaga[2], E. Roulleau[3], D.L. Pinti[4]. T.P. Fischer[5], T. Lan[6], Y. Nishio[7], U. Tsunogai[8]. [1]Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Japan (*correspondence: ysano@aori.u-tokyo.ac.jp), [2]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland. [3]Department of Geology, Universidad de Chile, Santiago, Chile. [4]GEOTOP & Département des sciences de la Terre et de l'atmosphère, Université du Québec à Montréal, Montréal, Canada. [5]Department of Earth and Planetary Sciences, University of New Mexico, Albuquergue, USA.[6]Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan. [7]Research and Education Faculty, Kochi University, Kochi, Japan. [7]Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan.

Introduction: Helium-3 is the most important tracer among volatile species in volcanic-hydrothermal studies because of its mantle signature [1,2]. Temporal variations of helium isotopes and volcanic activity are very well correlated, as shown in a steam well on the flanks of Izu-Oshima volcano, Japan [3], in crater fumaroles at Galeras volcano, Colombia [4], and in springs around Mt. Etna, Italy [5]. Precursory changes of helium isotopes were reported also in fumarolic gases during the 2002-2003 eruption of Stromboli volcano, Italy [6]. All helium isotopic anomalies mentioned above were related to magmatic eruptions. In the case of hydro-volcanic eruptions empirical evidence is scarce and therefore it is difficult to relate changes in the helium isotopes to volcanic activity. Recently we reported a ten-year helium anomaly prior to the 2014 Mt. Ontake phreatic eruption [7].
In addition to helium, carbon isotopes of CO_2 could provide constraints on the origin of volcanic fluids [8] and may show variations related to volcanic activity [9]. We present here secular variations of the carbon isotope signature at Ontake volcano, Japan based on measurements conducted in the same samples showing the recently reported helium anomaly.

Sampling site and analytical methods: Mt. Ontake is a strato-volcano (elevation 3067 m a.s.l.) located in central Honshu, Japan (35˚54'N, 137˚29'E). There is no other active volcano within a radius of 40 km of Mt. Ontake.

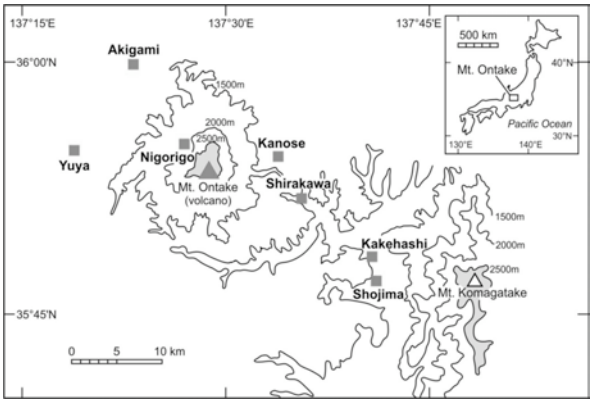

Figure 1: Location of the sampling sites around Mt. Ontake, Japan.

The volcano suddenly erupted on September 27th 2014, resulting in 58 casualties (5 people are still missing). It was a phreatic eruption and ejection of new magmatic material was not detected. We collected 104 gas samples in seven bubbling hot and mineral springs around the volcano (Fig.1) once every few years since November 1981 [10]. Twenty-four samples were collected after the 2014 eruption. A portion of gas sample was introduced into a metallic high vacuum line in the laboratory, where helium and neon were purified by hot Ti getters and charcoal traps at liquid nitrogen temperature. Then the $^4He/^{20}Ne$ ratios were measured by a quadrupole mass spectrometer and helium was separated from neon by a cryogenic charcoal trap. Samples collected before 1990 and those acquired in 2003 were measured by a Nuclide noble gas mass spectrometer without separating helium from neon, while all other samples were analyzed by a VG5400 mass spectrometer. An experimental bias of about 9% between the two analytical systems was successfully corrected by a careful data treatement [11]. Carbon isotopes of samples before June 1993 were measured by a conventional mass spectrometer after separation of CO_2 from the other chemical components using a trap held at liquid nitrogen temperature, a trap at dry-ice/ethanol temperature and a trap with degassed 1 N $CuCl_2$ solution in order to remove H_2S from CO_2 [12]. Samples collected after June 1993 were analyzed by a continuous flow GC-IRMS system either at Hokkaido University or The University of Tokyo. The δ-notation of the isotopic values is conventionally represented with respect to the Vienna PeeDee Belemnite (VPDB). Analytical errors of the $\delta^{13}C$ measurements are lower than ± 0.3‰.

Results and discussion: The $^3He/^4He$ and $^4He/^{20}Ne$ ratios vary significantly from 1.25 Ra to 7.38 Ra (where Ra is the atmospheric air $^3He/^4He$ ratio [13] of $1.382x10^{-6}$) and from 0.34 to 285 respectively. All helium isotope ratios are higher than the air value, suggesting the influence of fluids with a mantle signature typical for arc volcanoes [1,2]. The observed $^3He/^4He$ ratios are corrected for atmospheric contamination using the measured $^4He/^{20}Ne$ ratios. During the whole observation period, the $^3He/^4He$ ratio generally

decreases with increasing distance from the central cone to the sampling sites suggesting that the most primitive magmatic ^{3}He is carried with fluids flowing preferentially through the volcanic conduit. As helium moves from the volcanic conduit through fissures and permeable channels to surrounding hot and mineral springs, the magmatic helium is diluted by radiogenic helium (0.02 Ra) produced in aquifer rocks [14]. The δ^{13}C values range from -8.8‰ to -3.9‰ with an average of -6.7‰. All carbon isotope signatures are similar to those observed at subduction zones [8,9]. Consistent with the spatial variations of the helium isotope ratios, the δ^{13}C values increase with increasing distance from the central cone to the sampling sites, which may be explained by similar processes affecting the helium isotopes. There may be a simple two-component mixing between magmatic (δ^{13}C=-8.7±0.4‰, ^{3}He/^{4}He=8Ra) and crustal (δ^{13}C=-5.2±0.3‰, ^{3}He/^{4}He=0.02Ra) end-members [12], even though the carbon variation may also result from isotope fractionation during migration.

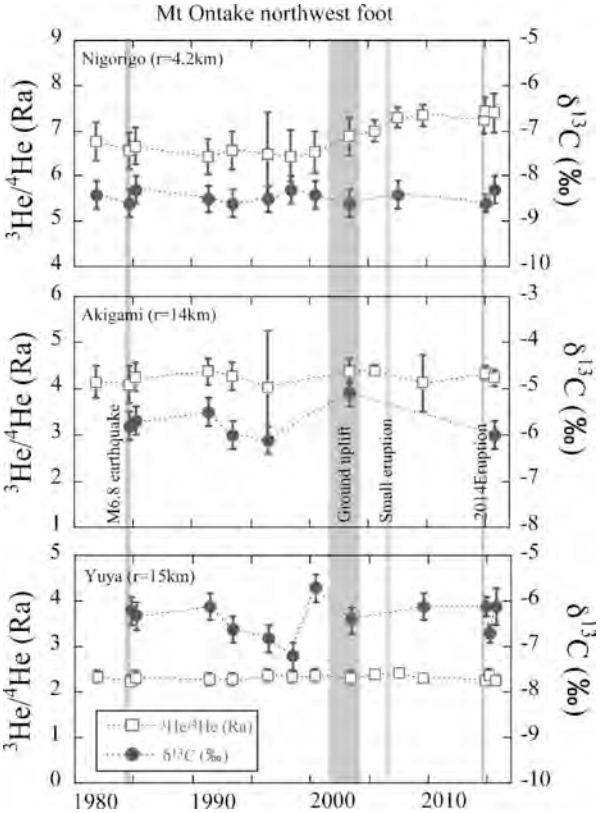

Figure 2: Secular variations of helium and carbon isotope ratios in the northwest section of Mt. Ontake. The uncertainties assigned to the ratios are at the two sigma level. Gray bars indicate recent geotectonic events in the region.

Figure 2 shows the secular variations of helium and carbon isotopes in the northwest section of Mt. Ontake (Nigorigo, Akigami and Yuya sites in Fig. 1). This data set comprehends ^{3}He/^{4}He and δ^{13}C values measured in bubbling gas samples collected over a time span of 35 years since November 1981 which is the longest known record of hydrothermal data.
In the northwest section the ^{3}He/^{4}He ratios were generally constant within the two sigma error range from November 1981 to June 2000. Then the ratio increased significantly from June 2003 to October 2014 at Nigorigo hot spring, the closest site to the central cone. After the 2014 eruption the ratios remained smilar until September 2015 (i.e., the last sampling campaign). In contrast, at locations distant from the cone (Akigami and Yuya mineral springs) the ratios stayed constant during the same period . On the other hand, the variations in the δ^{13}C values do not follow a patterns as simple as the one observed for the helium isotopes. At Nigorigo site, the δ^{13}C values are virtually constant from November 1981 to September 2015.

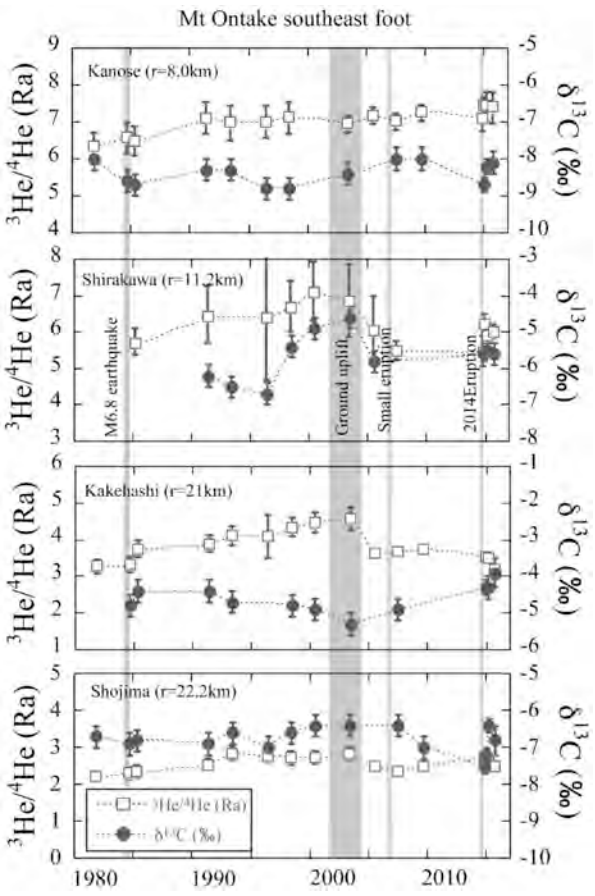

Figure 3: Secular variations of helium and carbon isotope ratios in the southeast section of Mt. Ontake. The uncertainties assigned to the ratios are at the two sigma level. Gray bars indicate recent geotectonic events in the region.

In the southeast section (Kanose, Shirakawa, Kakehashi and Shojima sites; see Fig. 3), the $^3He/^4He$ ratios show rather variable patterns in time. At the Kanose site close to the cone, the ratio increased gradually and with a constant rate from November 1981 to October 2014. After the 2014 eruption the helium isotope ratio remained constant. On the other hand, two steplike changes in the helium isotope ratios were observed at Shirakawa, Kakehashi and Shojima, sites located relatively distant from the cone. The $^3He/^4He$ ratios increased significantly from November 1981 to June 2003 and then suddenly decreased and remained at a constant value even after the 2014 eruption. This variation was attributed to the after effect of the 1984 Western Nagano Eartrhquake [7]. In contrast to the helium isotope ratios, the $\delta^{13}C$ values show more site-specific patterns. There is no significant change in the $\delta^{13}C$ values at Kanose site where the $^3He/^4He$ ratios increased with time. The $\delta^{13}C$ values appear to be correlated with the $^3He/^4He$ ratios at Shirakawa site while they are anti-correlated at Kakehashi site. In summary, spatial and secular variations of helium and carbon isotopes are complex and there is no simple relationship except for recent ten-year increases of the $^3He/^4He$ ratio at Nigorigo and Kanose sites closest to the central cone. These increases in the helium isotope ratios were attributed to a recent re-activation of Mt. Ontake and suggested as a precursor of the 2014 eruption [7].

To evaluate the risk of a possible hydro-volcanic eruption, it is important to study the rate of volatile input into the volcanic edifice. Using observed data it is possible to estimate helium-3 flux at the conduit by a hydrodynamic dispersion model [15] applied to the spatial variation of helium isotopes in a given year. The calculated helium-3 flux is generally constant at approximately 78 nmol/day from November 1981 to June 2003. Afterwards the flux increased in June 2005 and stayed constant until June 2009 at about 97 nmol/day. After the 2014 eruption, the flux returned to the value prevailing before 2005 [7]. These calculations suggest that the magmatic activity may have decreased after the 2014 eruption.

The magmatic water flux is estimated to be 1.4 tons/day before June 2003 based on the helium-3 flux and on the $H_2O/^3He$ ratio of $1x10^{12}$ in high temperature volcanic gases in island arc systems [16]. The magmatic water flux increased to 1.7 tons/day in June 2005 as the helium-3 flux was enhanced. This excess water supply of 0.3 tons/day, which most likely continued over the last 10 years, led to the accumulation of 1000 tons of water. This amount of water was introduced into the surrounding hydrothermal system and excess water vapor may have been trapped in the conduit just beneath the central cone. This excess water vapor could have provided the driving force for the 2014 eruption [7]. Assuming the $CO_2/^3He$ ratio of $1x10^{10}$ in high temperature volcanic gases [8], the excess CO_2 supply may be 7.3 kg/day in the last ten years. If this is the case, an accumulated excess magmatic CO_2 may amount to 24 ton in total. A part of the carbon may be transferred into the surrounding hot and mineral springs. However, there is no temporal change of carbon isotopes at Nigorigo and Kanose sites closest to the central cone in recent ten-year. This suggests that either the amounts of magmatic CO_2 introduced at these sites are negligibly small compared with ambient CO_2 in the aquifer system or the $\delta^{13}C$ values of magmatic CO_2 are already very similar to those in ambient and normal CO_2 of the Nigorigo and Kanose sites, so that addition of excess CO_2 cannot change the $\delta^{13}C$ values. Therefore, helium isotopes are more sensitive than carbon to magmatic input in the studied hydrovolcanic thermal system. The generalization of this hypothesis should be verified by future work.

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