

Noble gas isotope analysis using a multi-turn time-of-flight mass spectrometer

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Active volcanoes can cause devastating destruction, and as such, it would be desirable to be able to predict these disasters before their occurrence. One possibility involves measuring helium isotope ratio ($^3\text{He}/^4\text{He}$), which shows different values in geochemical reservoirs such as the atmosphere, ocean, crust, and mantle depending on the balance of primordial (relatively enriched in ^3He compared to the atmosphere) and radiogenic (predominantly ^4He) helium. The $^3\text{He}/^4\text{He}$ ratios of hot springs and groundwater around a volcano have values between magmatic (up to 1.1×10^{-5} or more) and crustal (less than 1×10^{-7}) helium isotope ratios, the latter resulting from dissolution of radiogenic helium into groundwater from crustal rocks. When magma becomes active, the $^3\text{He}/^4\text{He}$ ratios of nearby hot springs/groundwater may increase as the relative contribution of magmatic helium is expected to be higher. Such $^3\text{He}/^4\text{He}$ increases preceding volcanic eruptions have been reported for El Hierro, Canary Islands [1], Mt. Etna, Italy [2], and Ontake, Japan [3]. The $^3\text{He}/^4\text{He}$ ratio of hot springs/groundwater around a volcano has great potential for monitoring magmatic activity. Currently, magnetic-sector mass spectrometry is used to measure $^3\text{He}/^4\text{He}$, however, adequate mass resolution to discriminate $^3\text{He}^+$ from HD^+ and a high-vacuum line to purify and separate helium from other gaseous species are required to measure $^3\text{He}/^4\text{He}$ ratios because helium concentration is generally quite low (1-100 ppmv in gas samples or 1-100 ppt in water samples) [4, 5]. Moreover, ^3He accounts for only 0.1-10 ppm of total helium. For these reasons, helium isotope analysis is limited to a suitable laboratory, and on-site, real-time monitoring of $^3\text{He}/^4\text{He}$ around a volcano is almost impossible.

We have been developing a new technique of noble gas analysis using “infiTOF” (infiTOF-UHV, MSI-Tokyo, Inc., Tokyo, Japan), which is a small, portable, time-of-flight (TOF) mass spectrometer derived from the MULTUM-S II multi-turn TOF mass spectrometer and is capable of high mass resolution [6, 7], in order to monitor $^3\text{He}/^4\text{He}$ ratio in volcanic gas on site. The high mass resolution achieved by infiTOF ($>30,000$) is more than enough to distinguish $^3\text{He}^+$ and $^{20}\text{Ne}^+$ from their interferences, HD^+ and $^{40}\text{Ar}^{++}$, respectively. However, sensitivity of normal infiTOF was not high enough to analyze noble gases in volcanic gas because most of the noble gas molecules admitted to the infiTOF were pumped out by a vacuum pump before ionized by an electron ionization source. To increase ionization efficiency by suppressing the number of exhausted gas molecules, we installed a gate valve between the ion source and pump. A getter pump, which absorbs active gases but not noble gases, was also installed to keep the pressure in the ion source low during the operation. Furthermore, we made an attempt to improve sensitivity by making a smaller aperture between the ion source and mass analyzer to reduce the number of noble gas molecules leaking out to the mass analyzer before ionized. Currently the 140 times sensitivity compared to that of normal infiTOF has been achieved. Although ^3He in natural samples has not yet been observed with our infiTOF, of which ion current signals collected by a secondary electron multiplier are averaged for each flight cycle, it is expected to be detected in the future by processing the signals with pulse counting method [8, 9].

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