Measurement of helium isotope ratio using multi-turn time-of-flight mass spectrometer

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The helium isotope ratio ($^{3}He/^{4}He$ ratio) of volcanic gas has a great potential as a monitoring tool of volcanic activity. $^{3}He/^{4}He$ ratio shows different values in geochemical reservoirs such as the atmosphere, crust, and mantle, depending on the balance of primordial (relatively enriched in ^{3}He compared to the atmosphere) and radiogenic (predominantly ^{4}He) helium. The $^{3}He/^{4}He$ ratios of volcanic gases have values between magmatic (up to 1.1×10^{-5} or lower) and crustal (less than 1×10^{-7}) values. When magma becomes active, the $^{3}He/^{4}He$ ratio of volcanic gas may increase as the contribution of magmatic helium is expected to be higher. Such $^{3}He/^{4}He$ ratio increases preceding volcanic eruptions have been reported for El Hierro, Canary Islands[1], Mt. Etna, Italy[2], and Ontake, Japan[3].

Continuous analysis of volcanic gas is necessary to monitor volcanic activity; however, it is difficult for $^{3}He/^{4}He$ ratio because magnetic-sector mass spectrometer equipped with a massive electromagnet is currently used to analyze helium isotopes. Adequate mass resolution to distinguish $^{3}He^{+}$ from HD^{+} and high sensitivity to detect trace amounts of ^{3}He are required to measure $^{3}He/^{4}He$ ratio. Furthermore, high-vacuum line is also needed to purify and separate helium from other gaseous species because helium concentration in volcanic gas is generally quite low. For these reasons, helium isotope analysis is limited to suitable laboratory, and on-site, real-time measurement of the $^{3}He/^{4}He$ ratio around volcano is almost impossible.

We have been developing a new technique of noble gas analysis using "infiTOF" (MSI TOKYO, Inc., Japan), which is a small and portable time-of-flight (TOF) mass spectrometer derived from the MULTUM-S II multi-turn TOF mass spectrometer[4, 5], in order to measure the $^{3}He/^{4}He$ ratio of volcanic gas on site and in real time. The high mass resolution achieved by infiTOF is more than enough to distinguish $^{3}He^{+}$ and $^{20}Ne^{+}$ from their interferences, HD^{+} and $^{40}Ar^{++}$, respectively. However, sensitivity of a normal infiTOF was not high enough to analyze noble gases in volcanic gas because most of noble gas molecules admitted to the infiTOF were pumped out by vacuum pumps directly connected to the spectrometer before ionized by an electron ionization source. In order to realize static operation (*i.e.* the spectrometer is isolated from the vacuum pumps so that sample gas molecules are closed off within the spectrometer envelope and analyzed for a long time enough to accumulate signals), we installed valves between the spectrometer volume and the vacuum pumps. Getter pumps, which absorb active gases but not noble gases, were also installed to keep the pressure in the spectrometer low during the operation. In addition, we introduced the ion counting method for signal processing to detect weak signals of ^{3}He. As a result, significant number of ^{3}He in the helium standard gas (HESJ[6]) has been detected. Although as high sensitivity as that of the magnetic-sector mass spectrometer has not yet been achieved, accumulating number of ^{3}He signals with a longer time will increase statistical precision of $^{3}He/^{4}He$ ratio enough to distinguish the origin of helium in volcanic gas sample based on its isotope ratio.

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