Method Development and Evaluation of the infiTOF Time-of-Flight Mass Spectrometer for On-site Helium Isotopes Analysis

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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, which has two stable isotopes, ^3He and ^4He. The ratio of these two isotopes in geochemical reservoirs such as the atmosphere, ocean, crust, and mantle are different depending on the balance of primordial (relatively enriched in ^3He compared to the atmosphere) and radiogenic (predominantly ^4He) helium. The $^3He/^4He$ ratios of hot springs and groundwater around a volcano have values between magmatic (up to 1.1 x 10^{-5} or more) and crustal (less than 1 x $10^{\hat{}-7}$) helium isotope ratios, the latter resulting from dissolution of radiogenic helium into groundwater from crustal rocks. When magma becomes active, the $^3He/^4He$ ratios of nearby hot springs/groundwater may increase as the relative contribution of magmatic helium is expected to be higher. Such $^3He/^4He$ increases preceding volcanic eruptions have been reported for El Hierro Island, Canary (Padrón *et al.*, Geology, 41, 2013) and Ontake, Japan (Sano *et al.*, Scientific Reports, 5, 2014). The $^3He/^4He$ ratio of hot springs/groundwater around a volcano has great potential for monitoring magmatic activity. Currently, magnetic-sector mass spectrometry (MS) is used to measure $^3He/^4He$, however, adequate mass resolution to discriminate ^3He from HD and a high-vacuum line to purify and separate helium from other gaseous species are required to measure $^3He/^4He$ ratios because helium concentration is generally quite low (1-100 ppmv in gas samples or 1-100 ppt in water samples). 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 $^3He/^4He$ around a volcano is almost impossible.

The "infiTOF" is a small, portable, time-of-flight (TOF) mass spectrometer capable of high mass resolution and high mass accuracy. The applicability of infiTOF for helium isotope monitoring was investigated by using software-based ion counting and a high-speed digitizer (commonly used in modern TOF instruments instead of a traditional time-digital-converter (TDC)), to measure extremely low-level signals. This configuration is advantageous compared to a TDC-based system because the averaged profile waveform can be used to monitor the overall spectrum, including high concentration ions. The concentration ratio of ^3He compared to ^4He in the expected sample is in the range of 10^{-6} to 10^{-8}, and because of this large difference, they can not be monitored together without saturating the detector. Therefore, $^4He^{2+}$ was measured as a quantitative reference for $^4He^+$. The $^3He^+/^4He^{2+}$ ratio of a sample was measured using the infiTOF MS by counting ion peaks from each TOF trigger waveform. A ^3He standard was measured to verify the ^3He peak and measure mass accuracy, which was observed with an error of 4.30 x 10^{-5} Da. The $^3He^+/^4He^{2+}$ ratio was measured for three different helium gas cylinders by infiTOF. Mass accuracy for $^4He^{2+}$ and $^3He^+$ was also determined for sample cylinders with errors of 3.00 x 10^{-8} Da and 2.25 x 10^{-4} Da respectively. All cylinders were also measured by magnetic sector MS at University of Tokyo using standard helium gas HESJ (Helium standard of Japan, Matsuda *et al.*, Geochem. J., 36, 2002). Using one cylinder as a secondary standard, the $^3He^+/^4He^{2+}$ ratios for the other cylinders were determined using infiTOF measurements, which were then compared to the magnetic sector MS measurements and found to be in agreement with less than 5% error. Mass drift was also investigated and found to be less than 50 x 10^{-6} Da over ten hours. Results indicate that this method is accurate, stable, and has enough

resolving power to differentiate helium isotopes, and may be a viable tool in future on-site analysis and prediction of volcanic activity.

Keywords: Helium Isotope, On-site Analysis, Volcanic Activity, Mass Spectrometry, Ion Counting, Time-of-Flight