April, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 1153—1157 (1988)* 1153

Precise Measurement of Helium Isotopes in Terrestrial Gases

Yuji Sano* and Hiroshi Wakita
Laboratory for Earthquake Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received August 7, 1987)

Helium isotope ratios of terrestrial natural gas samples were measured using a high-precision mass spectrometer and an ultrahigh-vacuum purification line. The line is equipped with a charcoal trap held at 40 K using a helium expansion refrigerating machine. To avoid interference, Ne was completely separated from He by the trap before the gas was admitted to the mass spectrometer. Ion beams of ^{3}He and ^{4}He were measured at the same time by a double collector system. A resolving power of about 550 at the 5% level of the peak height was attained for the complete separation of ^{3}He ions from those of HD and H_3. Precision and reproducibility of the helium isotope ratio were less than 1%, examined by repeated measurements of an air standard. Accuracy of the ratio was checked by comparing observed data with reports in the literature.

Helium has two stable isotopes, of mass number 3 and 4. Most ^{3}He in terrestrial samples is considered to be a trapped component of solar nebulae at the time of the Earth's accretion (primordial He). In contrast ^{4}He is produced by radioactive decay of U and Th in crustal rocks (radiogenic He). The ^{3}He/^{4}He ratio provides useful information on the origin of He[1,2] (primordial or radiogenic). It is well-established that heliums with ^{3}He/^{4}He ratios higher than that of the air (1.40×10^{-6}) are found in gas and rock samples from volcanic and geothermal areas.[3] The helium is thought to be an emanation of the primordial He which still remains deep in the earth. On the other hand, heliums with lower ^{3}He/^{4}He ratios than the air He ratio are reported for non-volcanic regions.[4] This suggests that degassing of the primordial helium has a close relation to geotectonic activity in the region, and particularly to magmatic activity. Thus, the ^{3}He/^{4}He ratio is an important key to the study of magmatic volatiles.[5]

Precise measurements of the ^{3}He/^{4}He ratio can also provide a powerful and convenient method for analysis of environmental tritium. Using a mass spectrometer with extremely high sensitivity, it is possible to detect excess ^{3}He which has accumulated for a sufficient amount of time by in situ decay of tritium in groundwater. The method has been developed by Clarke et al.[6] and is applied to environmental and limnological studies.[7,8] In addition helium isotope ratios can be used in research on the origin of natural gases,[9] on marine ferromanganese nodules,[10] and on the problem of the atmospheric helium budget.[11,12]

In this paper we report precise measurements of ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios in terrestrial natural gas samples. Since ^{20}Ne/^{4}He ratios of mantle-derived and crustal gases are significantly lower than that of air, the ^{20}Ne/^{4}He ratio of the sample can be used as an indicator of air contamination. The analytical system used included a high-precision mass spectrometer, a quadrupole mass spectrometer, a purification and separation vacuum line, and a charcoal trap equipped with a He expansion refrigerator. Performance data are also given. With its high precision and accuracy, the present ^{3}He/^{4}He measurement system is applicable to various fields of geochemistry and environmental sciences.

Experimental

Helium Purification Vacuum Line and Purification Procedure. In order to purify He and Ne from original gas samples and to separate He from Ne, an ultrahigh-vacuum line was constructed (Fig. 1). Since He permeates normal glass quickly, stainless steel was used for all parts of the line. The line consists of three purification and separation parts divided by all-metal bakable valves (V1, V3, and V4). The system in principle resembles that reported by Sano et al.,[13] but several improvements were made. A turbo molecular pump (TMP) is used for creating a rough vacuum instead of an oil diffusion pump. A quadrupole mass spectrometer (QMG112, Balzers) is used in the third part of the line to measure the ^{20}Ne/^{4}He ratio in a gas sample and to ensure adsorption of Ne in a cryogenic charcoal trap (CT3) held at 40 K. A Pirani gauge (PG) is attached to the first part to examine the vacuum when an original gas sample is being introduced.

Hot spring and natural gas samples were collected via the water displacement method in the field using a 50-cm^3 lead glass container with vacuum valves at both ends. After the container was brought back to the laboratory, it was connected directly to the inlet part of the line using an O-ring high-vacuum connector or Tygon tube. A sample of about 1 cm^3 STP was admitted to the first part, and major components such as N_2, O_2, Ar, CH_4, H_2O, and CO_2 were removed by a charcoal trap (CT1) kept at liquid nitrogen temperature (77 K). Unadsorbed components including He and Ne were expanded to the second part. Using a titanium-zirconium getter furnace (TZ1) held at 550 °C and a charcoal trap (CT2) kept at 77 K, He and Ne were purified. When the TZ1 reached room temperature, the purified fraction was introduced into the third part.

The ^{20}Ne/^{4}He ratio of the purified sample was measured by a quadrupole mass spectrometer (QMS) in the third part. No other chemical species except He and Ne were detected by QMS. Interference from doubly charged ions of ^{40}Ar with ^{20}Ne was reduced by a charcoal trap (CT2) held at 77 K and was checked by measurements of the ^{20}Ne/^{22}Ne ratio. Even in the case of a small Ne content, the ^{20}Ne/^{22}Ne ratio showed an atmospheric value of about 10, suggesting negligible contribution of the doubly-charged ^{40}Ar ions. Since the ^{20}Ne/^{4}He ratio was determined by a peak height method, uncer-

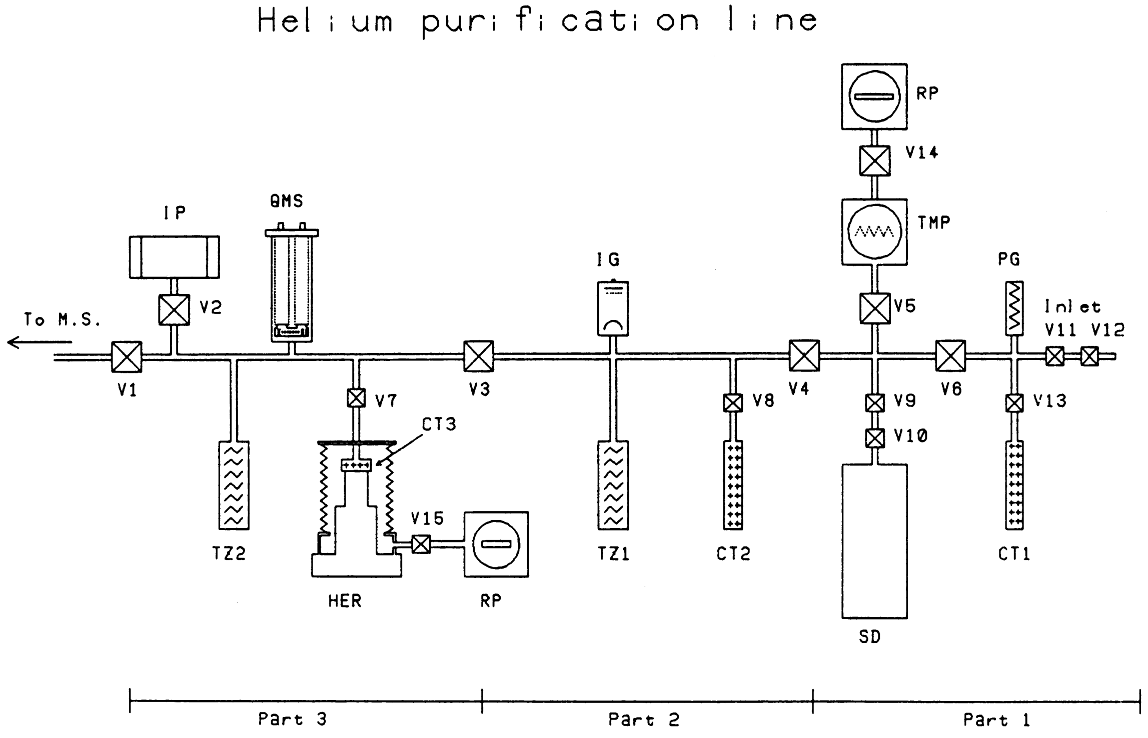

Fig. 1. Helium purification vacuum line. M.S.: mass spectrometer. V: valves, IP: sputter ion pump, QMS: quadrupole mass spectrometer, IG: ionization gauge, PG: Pirani gauge, TZ: titanium-zirconium getter, CT: charcoal trap, HER: helium expansion refrigerator, RP: rotary pump, TMP: turbo molecular pump, SD: standard gas reservoir.

tainty was about 10% at maximum.

Separation of Helium from Neon. According to Rison and Craig,[14] varying He/Ne ratios in a mass spectrometer affected the measured $^3He/^4He$ ratio by up to 10%. If atmospheric He is used as a working standard without separating the Ne, measured values on samples whose He/Ne ratios are quite different from that of air would be significantly erroneous and require major correction. Similar results were suggested by several groups[15] using special $^3He/^4He$ mass spectrometers originally designed by Clarke et al.[6] Thus, it is necessary to separate He from Ne when a precise $^3He/^4He$ ratio is required.

A cryogenic charcoal trap (CT3) was attached to the third part of the purification line (Fig. 1) in order to adsorb Ne completely. The mechanism is in principle similar to that of the improved charcoal trap reported by Reynolds et al.[16] Cooling was done by a commercial He expansion refrigerating machine (Cryomini-S, Osaka-sanso Co.), which was constantly operated at full cooling level. Temperature can be readily controlled by a feedback system (PID) composed of a variable heater and a thermometer. Since the working He in the compressor and the expansion head is sealed by a metal wall, no He leak to the laboratory air is possible.

About 2000 cm^3 STP air was introduced into the vacuum line and was purified by charcoal traps (CT1 and CT2) and a titanium zirconium getter (TZ1). The purified He and Ne were stored in a 2000 cm^3 stainless steel vessel (SD in Fig. 1) and used as a running standard gas. About 0.5 cm^3 STP of standard gas, the volume in the space between the valves (V9 and V10), was expanded into the line and the separation of He from Ne was examined. Figure 2 shows equilibrium ion currents by QMS (normalized to 100% release) versus trap temperature at CT3. The sorption curves agree well with those reported by Reynolds et al.[16] An excellent separation of He from Ne is attained at approximately 40 K in our system.

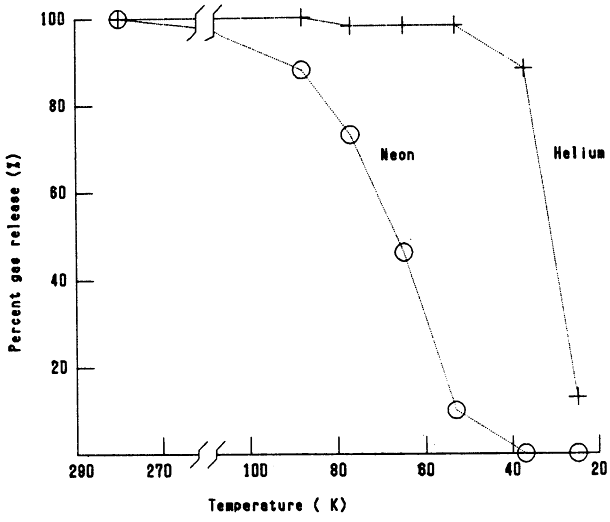

Fig. 2. Equilibrium ion currents for ^4He and ^{20}Ne versus charcoal temperature.

Mass Spectrometer and Helium Isotope Ratio Measurement. The $^3He/^4He$ ratio was measured with a 27 cm radius extended geometry static gas mass spectrometer. Our instrument was a catalogue model, VG5400 (VG Isotopes, Winsford), modified somewhat in order to detect ^3He and ^4He ion beams simultaneously. The ^3He beam was measured by a Daly multiplier collector and the ^{4}He beam by a conventional Faraday cup. The resolving power of the Daly collector was higher than 510; that of the Faraday cup, about 200. In order to obtain coincidence of ^{3}He and ^{4}He beams—that is, simultaneous collection of the two beams—the position of the Faraday cup is adjustable by a manipulator. If the coincidence of ^{3}He and ^{4}He beams is sufficient, it is not necessary to perform the peak jumping procedure. These modifications lead to a highly precise ^{3}He/^{4}He ratio measurement. Peak heights of ^{3}He and ^{4}He ion currents were obtained simultaneously by dual-digital electrometers, and the ratio was calculated by a computer. Twenty-five measurements of the ratio were conducted in an individual run, and the ratios were extrapolated to the initial time when the sample was introduced into the mass spectrometer.

Results and Discussion

Neon Interference and Pressure Dependence of the Helium Isotope Ratio. As stated above, varying He/Ne ratios in samples may affect the measured ^{3}He/^{4}He ratio. The relation between the ^{3}He/^{4}He ratio of an air standard and co-existing Ne content, here expressed as ^{20}Ne/^{4}He ratio, is examined (Fig. 3). There is a negative correlation between the ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios: the higher the ^{20}Ne/^{4}He ratio, the lower the observed ^{3}He/^{4}He ratio. The measured ^{3}He/^{4}He ratio of air He containing Ne with the ^{20}Ne/^{4}He ratio of 3.14 (which is air composition) shows a value about 11% lower than the ^{3}He/^{4}He ratio of air He without Ne. If we compare the peak heights of the ^{3}He and ^{4}He, ion currents of ^{4}He are almost constant against varying ^{20}Ne/^{4}He ratios, whereas those of ^{3}He decrease with the ^{20}Ne/^{4}He ratios. This may be attributed either to suppression of the ion beam of ^{3}He in the presence of Ne or to depression of the efficiency of the Daly multiplier by Ne.

The relation between the ^{3}He/^{4}He ratio of air He and total pressure in a mass spectrometer (6-60-SGA, Nuclide Co.) was reported by Sano et al.[13] The higher the total pressure in the mass spectrometer, the higher was the ^{3}He/^{4}He ratio. A similar relation is examined in this work in the range from about 2.0×10^{-5} to 2.5×10^{-4} Pa (Fig. 4). There is a negative correlation between the ^{3}He/^{4}He ratio and the pressure, in contrast to the previous results.[13] In the pressure range below 9×10^{-5} Pa, the ^{3}He/^{4}He ratio is almost constant within an experimental error margin. In contrast, a remarkable decrease in the ^{3}He/^{4}He ratio is observed in the pressure range of about 2×10^{-4} Pa. The discrimination is up to about 6% of the ratio. Taking into account this effect, the total pressure of He was kept lower than 9×10^{-5} Pa in the actual measurements of natural gas samples.

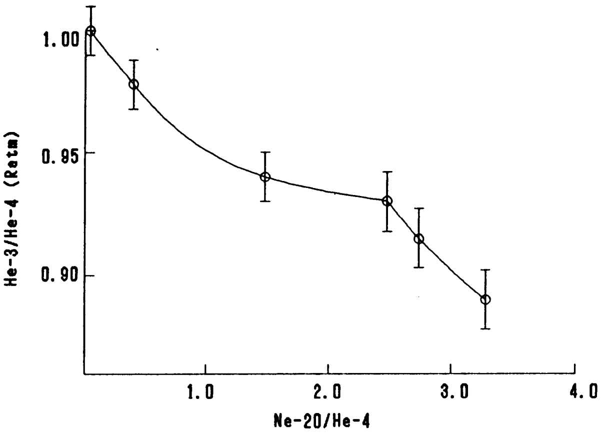

Fig. 3. Correlation between the ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios.

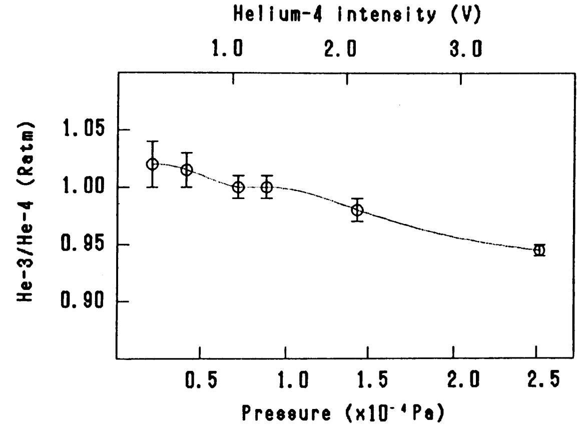

Fig. 4. Pressure dependence of the atmospheric ^{3}He/^{4}He ratios in the mass spectrometer.

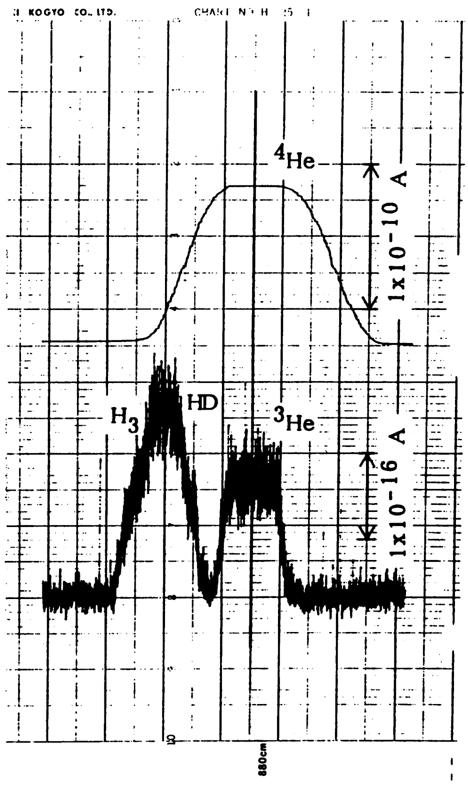

Fig. 5. A typical mass spectrum of purified He from the atmosphere of about 0.3 cm^3 STP.

Reproducibility of the Helium Isotope Ratio Measurements. Since the atmospheric ^{3}He/^{4}He ratio shows a constant value of $(1.40\pm0.03)\times10^{-6}$, irrespective of latitude, longitude and elevation,17) air He is regarded as an ideal standard gas. Generally the observed ^{3}He/^{4}He ratio was represented as a form of the ratio to the air He.3) The unit of R/R_{atm} is defined here to indicate the ^{3}He/^{4}He ratio relative to the air value of 1.40×10^{-6}. In this work accuracy and reproducibility of the ^{3}He/^{4}He ratio were examined by repeated measurements of air He in a standard vessel. In the process He of about 1.8×10^{-6} cm^{3} STP was admitted to the mass spectrometer and the ^{3}He/^{4}He ratio was measured. A typical mass spectrum of ^{3}He and ^{4}He in the air standard is shown in Fig. 5. An excellent separation of ^{3}He from HD plus H_3 beams was observed on the Daly collector with a flat peak shape. A resolving power of about 550 at the 5% level of the peak height was attained. The sensitivity of the Faraday cup was estimated to be about 5×10^{-5} A cm^{-3} STP ^{4}He and that of the Daly collector to be 3×10^{-3} A cm^{-3} STP ^{3}He. Taking into account the noise level of the Daly collector of 2×10^{-18} A, the detection limit of ^{3}He is calculated to be 3×10^{-14} cm^{3} STP, which is equivalent to 8×10^{5} atoms and about 25 times lower than the previous system.13)

Table 1. Repeated Measurements of Atmospheric ^{3}He/^{4}He Ratio

No.	Date	^{3}He/^{4}He ($\times10^{-6}$)	^{4}He ($\times10^{-10}$A)	^{20}Ne/^{4}He
1	Oct. 23, 1986	1.518±0.007	1.09	0.680
2	Oct. 24, 1986	1.498±0.006	1.14	0.699
3	Oct. 24, 1986	1.524±0.006	1.10	0.685
4	Oct. 25, 1986	1.502±0.007	1.14	0.676
5	Oct. 27, 1986	1.489±0.006	1.14	0.676
6	Oct. 28, 1986	1.518±0.007	1.11	0.662
7	Oct. 29, 1986	1.511±0.006	1.12	0.658
8	Oct. 30, 1986	1.520±0.005	1.09	
9	Oct. 31, 1986	1.507±0.006	1.12	0.667
10	Nov. 1, 1986	1.507±0.005	1.12	0.649
11	Nov. 8, 1986	1.505±0.006	1.02	0.662
12	Nov. 13, 1986	1.520±0.007	1.09	0.662
	av.	1.510±0.011	1.11±0.03	0.671±0.014

Results of repeated measurements of the ^{3}He/^{4}He ratio in air are summarized in Table 1 together with the ^{20}Ne/^{4}He data obtained by QMS. The ^{3}He/^{4}He ratios were calculated by the observed ratio of the Daly collector's output to the Faraday's output and by the gain of the Daly over the Faraday. The gain was independently determined using different amounts of ^{4}He. The mass discrimination factor of the measuring system was examined by comparing the mean value of $(1.510\pm0.010)\times10^{-6}$ with the critical ratio of $(1.399\pm0.013)\times10^{-6}$. The discrimination factor of about 7.9% is smaller than that of the previous system.13) The reproducibility of the ^{3}He/^{4}He ratio is 0.69% within three weeks, and the value is comparable to the precision of each individual run. The value of 0.69% is the lowest one so far reported.13,18,19) The ^{20}Ne/^{4}He ratios were calculated using ion current ratios of ^{4}He to ^{20}Ne in QMS, which show almost constant values of (0.671±0.014) during this period.

Accuracy of the Helium Isotope Ratio Measurements. The ^{3}He/^{4}He ratios of eight volcanic and hot spring gases collected at representative sites were measured. At the time of measurement, the pressure dependency of the ^{3}He/^{4}He ratio was taken into account. The observed ^{3}He/^{4}He ratios were calibrated against that of the air standard obtained on the same day. The results are listed in Table 2 together with reference data including the institutions where the ratios were measured. The error assigned to the observed ^{3}He/^{4}He ratios is one standard deviation, including a statistical error of an individual run and an error of the air standard to which the ^{3}He/^{4}He ratio is calibrated. Thus calculated, the net uncertainty of the measurement in this study is less than 1% of the ^{3}He/^{4}He ratio.

The observed ^{3}He/^{4}He ratios range from 0.331 R/R_{atm} to 16.23 R/R_{atm}. These agree well with the reference data except for the Kakehashi sample (No. 6).

Table 2. ^{3}He/^{4}He Ratios of Terrestrial Gases

No.	Name	$(^{3}\mathrm{He}/^{4}\mathrm{He})_{obs}$ (R/R_{atm})	$(^{3}\mathrm{He}/^{4}\mathrm{He})_{ref}$ (R/R_{atm})	Ref.	Lab.
1	Mud volcano Yellowstone, USA	16.23±0.10	16.45	14	SIO
			15.8	22	UCB
2	Hakone Kanagawa, Japan	6.13±0.03	6.2	20	SIO
			6.08	25	OU
			5.92	23	UT
3	Nigorigo Gifu, Japan	6.02±0.05	6.06±0.17	21	UT
4	Shirakawa Nagano, Japan	5.21±0.04	5.18±0.07	21	UT
5	Uminokuchi Nagano, Japan	5.15±0.03	5.16±0.11	23	UT
6	Kakehashi Nagano, Japan	3.70±0.02	3.43±0.05	21	UT
7	Yuya Gifu, Japan	2.04±0.01	2.13±0.06	21	UT
8	Kashima Fukushima, Japan	0.331±0.07	0.335±0.011	24	UT

SIO: Scripps Institution of Oceanography, University of California. UCB: Berkeley, University of California. OU: Osaka University. UT: University of Tokyo.

The discrepancy observed in No. 6 is about 7% of the ratio. Excluding this sample, differences are about 4% at maximum and equivalent to the experimental errors of the reference data. This suggests that the present system gives sufficiently accurate $^3He/^4He$ ratio measurements, assuming the reliability of the reference data.

The $^3He/^4He$ ratio of the Yellowstone sample (No. 1), 16.23 R/R_{atm}, is significantly higher than the $^3He/^4He$ ratios of 8—9 R/R_{atm} in mid-ocean ridge basalt (MORB).3) Since the composition of the MORB is considered to be representative of the Earth's upper mantle, the source region of the Yellowstone sample is more primitive than that of the upper mantle. Gas samples from the Hakone volcano (No. 2) and the Nigorigo hot spring near the Ontake volcano (No. 3) show $^3He/^4He$ ratios of about 6 R/R_{atm}, identical to those in the circum Pacific volcanic region and slightly lower than the MORB. The $^3He/^4He$ ratio of bubbling gas in a Kashima well (No. 9), situated on the forearc region of Northeast Japan, is lower than the air ratio. Radiogenic He produced in crustal rock and sediment may be dominant in the sample.

Conclusion

The present analytical system has a high sensitivity of 5×10^{-5} A cm^{-3} STP of ^4He measured with a Faraday cup, an extreme precision of less than 1%, and sufficient accuracy of $^3He/^4He$ ratio measurement. The system can be applied to various fields of geoscience research, such as mantle geology, volcanology, marine chemistry, and environmental and limnological studies.

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