Title	Precise Measurement of Helium Isotopes in Groundwater
Author(s)	SANO, Yuji; TAKAHATA, Naoto; MAHARA, Yasunori; YASUIKE, Sinji
Citation	Journal of science of the Hiroshima University. Series C, Geology and mineralogy , 9 (4) : 603 - 610
Issue Date	1993-07-30
DOI	
Self DOI	10.15027/53124
URL	https://ir.lib.hiroshima-u.ac.jp/00053124
Right	
Relation	

Precise Measurement of Helium Isotopes in Groundwater

by

Yuji SANO, Naoto TAKAHATA, Yasunori MAHARA and Sinji YASUIKE

---

with 3 Tables and 5 Figures

(received, March 31, 1993)

Abstract: In order to estimate the origin and resident time of groundwater, the helium isotope ratio ($^3He/^4He$) should be analyzed precisely. We present here experimental details of an analytical system including a helium purification vacuum line, the purification procedure, and the adjustment of a noble gas mass spectrometer. A resolving power of about 550 at the 5% level of the peak height was attained for the complete separation of ^3He ions from those of HD and H_3. The reproducibility of the helium isotope ratio was about 1%, examined by repeated measurements of an air standard. The accuracy of the ratio was checked by comparing observed data with reports in the literature. The results show that it is possible to apply the present system to geohydrology.

Contents

I. Introduction

Water is one of the most abundance substances on the surface of the Earth and it is circulating as clouds, rain, rivers and oceans. Rain water which permeates through the surface soil forms groundwater in geological stratum.

For irrigation and industrial use, groundwater is an important resource second to river water in Japan. It is important to study the origin of groundwater, not only for developing water resources and environmental assessments but also for basic research on hydrology and geochemistry.

In order to investigate the circulation of groundwater in a sedimentary basin, several natural tracers have been used. Studies on the geohydrological system have been based on anions and cations in water, resolved gas components, and isotopes of hydrogen and oxygen (Kaufman and Orlob, 1956; Fritz et al., 1974; Rauert and Stichler, 1974; Rodhe, 1983). Radioactive tracers such as tritium and carbon-14 provide valuable information on the age of groundwater (Zimmermann et al., 1966; Sukhija and Shah, 1976; Kayane et al., 1980; Martin, 1985; Paul et al., 1986).

Although many tracer studies have been published noble gas research is relatively sparse (Sugisaki, 1961; Marine, 1979; Mizutani and Oda, 1983). This is partly due to the difficulty of determining the small amount of noble gases in groundwater. Since noble gases are chemically inert, they retain information on their source (Ozima and Podosek, 1983). Gaseous components such as carbon dioxide and methane may provide significant information on the circulation of groundwater if combined effectively with noble gas data.

Helium-3 is the most important nuclide in geochemistry which clearly shows the mantle signature (Lupton, 1983; Mamyrin and Tolstikhin, 1984). A contour map of excess $^3He/^4He$ ratios relative to the air in Pacific water indicates the mantle helium flux from the East Pacific Rise and the circulation of deep sea water

(Lupton and Craig, 1981). Helium-3 provides further information on the age of groundwater since it is a decay product of tritium (Takaoka and Mizutani, 1987; Schlosser et al., 1988; Mahara et al., 1991). Determining the distribution of $^3He/^4He$ ratios in groundwater of typical sedimentary basins is valuable for research on the origin and circulation of groundwater.

In order to measure helium isotopes in groundwater precisely, several developments of the analytical system are necessary. Basic experiments are also required to obtain reliable data. We present here experimental details including the helium purification and separation technique, resolving power and sensitivity of the noble gas mass spectrometer, and the precision and accuracy of the isotope ratio. Helium isotope data for distilled water is also given in this work.

Acknowledgments

II. Purification and separation of helium

We have improved the high vacuum line for extraction, purification and separation of helium from
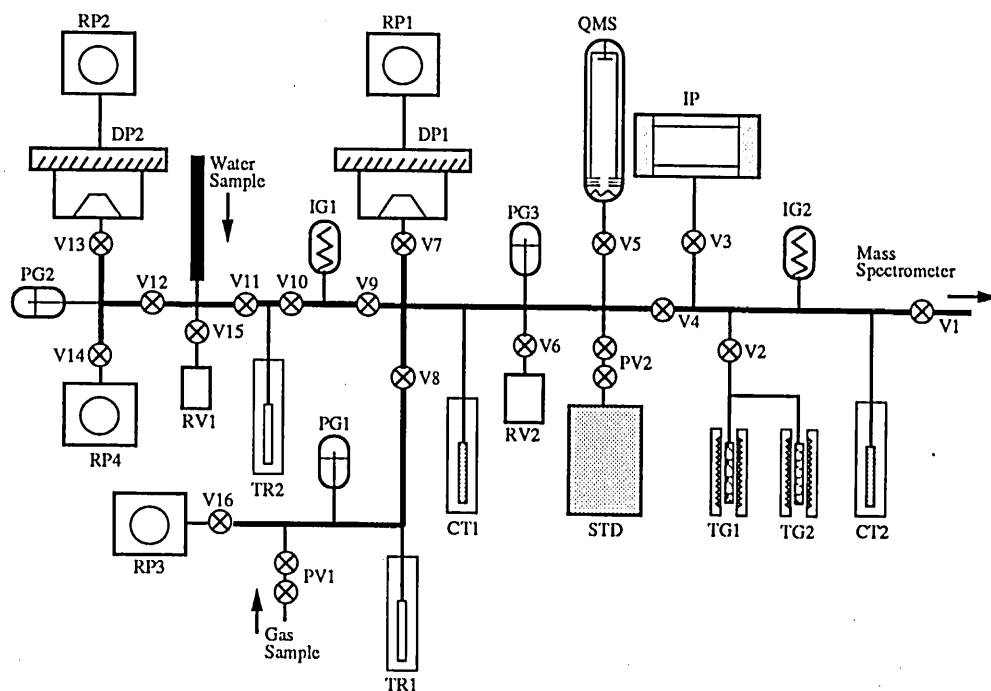

Figure 1. Helium purification vacuum line. QMS: quadrupole mass spectrometer, IG: ionization gauge, PG: Pirani gauge, TG: titanium getter, CT: charcoal trap, RP: rotary pump, DP: oil diffusion pump, IP: sputter ion pump, V: valves, STD: standard gas reservoir.

groundwater samples installed at the Abiko Laboratory, Central Research Institute of Electric Power Industry. The extraction vacuum line was connected to the purification line and noble gas mass spectrometer by stainless steel tubing.

A. Outline of high vacuum line

Figure 1 shows an outline of the high vacuum line used for helium extraction, purification and separation from groundwater samples. All parts of the vacuum line including gauges were made of stainless steel in order to prevent the permeation of helium, since air helium penetrates normal Pyrex glass rapidly. The line was separated into four parts by all metal bellows valves (V1, V4, V8 and V10). Helium and gas components were extracted between V10 and V12. First, purification and separation of helium and neon were conducted between V4, V8 and V9. Second, purification was performed between V1 and V4. The extracted part was evacuated by an oil diffusion pump (DP2) down to 10^{-5} Torr. The inlet part of gaseous samples (between V16 and V18) was sucked by a rotary pump (RP3). The first and second parts of purification were evacuated by an oil diffusion pump (DP1) and ion spatter pump (IP) down to 10^{-5} and 10^{-8} Torr, respectively. This vacuum line is principally the same as that already reported except for the cryogenic charcoal trap (Sano and Wakita, 1988).

B. Helium purification and separation procedure

Generally, gas samples such as volcanic and geothermal gases or natural gases are collected and held in lead glass containers with vacuum stop cocks (Sano and Wakita, 1985). A lead glass container was connected with the inlet part of gas samples using a high vacuum O-ring connector. About 1 ccSTP of gas sample was introduced into the vacuum line by a pipette valve (PV1).

At first, carbon dioxide, water vapor and the other condensable gases were separated by a U-trap (TR1) kept at liquid nitrogen boiling temperature. Then, the non-condensable gases were admitted into the first part of purification by opening V8. Nitrogen, oxygen, argon and methane were adsorbed in the activated charcoal trap (CT1) held at liquid nitrogen boiling temperature. Purified gases were introduced into the second part by opening V4. Chemically active gases such as hydrogen were absorbed by a hot titanium getter (TG1). Gases except helium and neon were further adsorbed in the activated charcoal trap (CT2) held at liquid nitrogen boiling temperature.

The quantities of purified and separated helium and neon were measured by a quadrupole mass spectrometer (QMS). When the amount of helium was larger than 2×10^{-6} ccSTP, the pressure of the sample gas was reduced by expanding to a reservoir (RV2) and the part between V1 and V4 was admitted into the noble gas mass spectrometer. When the amount of helium was still larger than 2×10^{-6} ccSTP, the reservoir was evacuated by the oil diffusion pump (DP1), then sample gas was expanded

again. By the above procedures, the size of sample helium was balanced with that of standard helium.

The atmospheric helium standard was reserved in a large volume metal container (STD). Standard gas was introduced into the vacuum line by using a pipette valve (PV2). Purification and separation of helium and neon were similar to those of sample gases.

Groundwater samples are usually held in a copper tube of 3/8 inch diameter pinched off by stainless steel cramps at both ends (Mahara et al., 1988). A copper tube containing the groundwater sample was connected with the water inlet part by a metal connector.

After being evacuated well by an oil diffusion pump (DP2), valves (V10 and V11) were closed while V15 was opened. The cramp was released, then the sample water in the copper tube was introduced into a metal reservoir (RV1). During this the part between V10, V11, and V15 was kept at 150°C by tape heaters. Most of the helium and neon were remained in the gas phase. Resolved helium and neon in water were completely degassed by vibrating the metal reservoir (RV1) using an ultrasonic cleaner.

The gases extracted from the groundwater were introduced into the U-trap (TR2) held at liquid nitrogen boiling temperature. Carbon dioxide, water vapor and the other condensable gases were separated here. Further purification was similar to those for the gas samples described above.

It takes about one hour to process a single groundwater sample including extraction, purification, separation of helium and neon, and measurements by quadrupole mass spectrometer. Before admitting a new sample, another hour is necessary to clean the vacuum line.

III. Measurement of helium isotopes

There are two difficulties in determining helium isotopes in terrestrial samples. The first difficulty is interference from hydrogen. At a pressure of about 10^{-9} Torr when the noble gas mass spectrometer is operated, hydrogen is the most abundant component in the residual gases. The molecules of HD and H_3 derived from the hydrogen with mass number 3 interfere with ^3He. The mass spectrometer needs a high resolving power. The second difficulty is the very small amount of ^3He in terrestrial samples. The concentration of ^3He in atmosphere is about 7 ppt by volume and the mass spectrometer must be very sensitive. Generally, a high resolving power is obtained by narrowing the source and collector slits. However, this makes the sensitivity of the machine low, it is difficult to attain a high resolving power and sensitivity at the same time. This is the reason why there are only four laboratories in the world which could provide terrestrial helium isotope data until 1980.

A. Adjustment of noble gas mass spectrometer

The noble gas mass spectrometer used in this study was VG5400 (VG Isotope) installed at the Abiko Laboratory, Central Research Institute of Electric Power Industry in 1987. No overall adjustment had been made since then and the main ion sputter pump was dull and the ion source conditions were not optimized. Also control of the electromagnet was problematic. We improved these problems by baking out the analytical tube, repairing the electric components and adjusting the geometry of the main electromagnet.

B. Resolving power and sensitivity of mass spectrometer

We optimized the ion source conditions of the noble gas mass spectrometer by using atmospheric standard helium. Table 1 summarizes the analytical conditions.

Table 1. Optimized analytical conditions of noble gas mass spectrometer

Vacuum	<1×10^{-9} Torr
Acceralating voltage	4.5 kV
Dispersion length	54 cm
Main collector	Daly multiplier
Sub-collector	Faraday cup
Ion source condition	
Trap current	800 μA
Electron energy	100 V
Emission current	3.0 mA
Repeller voltage	-13 V
Filament current	2.7 A

Figure 2 shows a typical mass spectrum at mass number 3. Ion beams of ^{3}He and HD + H_3 were detected by the main Daly multiplier. It is noted that separation of ^{3}He (mass number 3.0160) from HD + H_3 (mass number 3.0219, 3.0235) is attained when there is a good sensitivity to detect ^{3}He of 3 x 10^7 atoms. The resolving power of this condition is calculated to be about 550 at 5% of peak height. The noise level of the Daly multiplier is estimated to be 1.7 x 10^{-18} A by 5 second integration. The ion beam of ^{4}He was detected by a Faraday cup and the resolving power of the Faraday cup was about 200.

The amount of helium admitted from the pipette valve (PV2) was estimated to be 8.4 x 10^{-7} ccSTP, taking into account the volume between the pipette of 0.16 cm^3 and content of helium in the air of 5.24 ppm by volume. The output of the Faraday cup detector for the ^{4}He ion beam was measured to be about 0.79V. Since the Faraday cup is equipped with a high register of 1.0 x 10^{10} Ω, the sensitivity for ^{4}He is calculated to be 1.1 x 10^4 ccSTP/A. Assuming that the mass discrimination effect on ^{3}He and ^{4}He is not significant, the detection limit can be obtained based on the sensitivity and noise level of the Daly multiplier detector. Finally, we can measure at least 1.9 x 10^{-14} ccSTP of ^{3}He, which is equivalent to 5 x 10^5 atoms.

C. Precision of helium isotope ratio

In order to check the analytical precision of the present system, helium isotopes and helium/neon ratios in standard air were measured repeatedly. Helium/neon ratios of samples provide information on the extent of
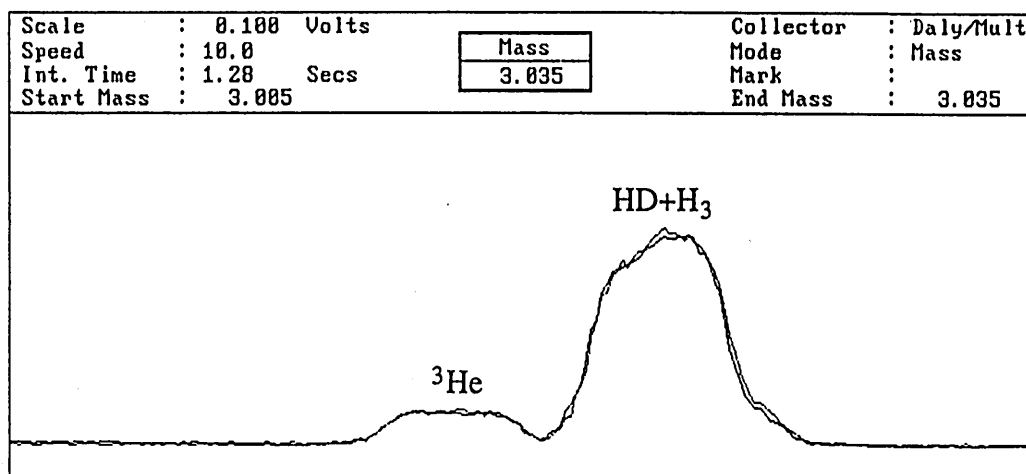
Scale	: 0.100 Volts	Mass	Collector	: Daly/Mult
Speed	: 10.0	3.035	Mode	: Mass
Int. Time	: 1.20 Secs		Mark	:
Start Mass	: 3.005		End Mass	: 3.035

Figure 2. A typical mass spectrum of purified helium from the atmosphere of 0.16 cm^{3}STP.

atmospheric contamination and measurements should be made for the same sample for the groundwater study. After being admitted into the noble gas mass spectrometer, beam intensities of ^{20}Ne, ^{22}Ne and ^{4}He ions were measured by the Faraday cup detector. Usually, helium/neon ratios are expressed as ^{4}He/^{20}Ne. ^{22}Ne was measured to check interference of doubly charged ^{40}Ar with ^{20}Ne. When the effect of doubly charged ^{40}Ar is negligibly small, the neon isotopes (^{20}Ne/^{22}Ne) should indicate the atmospheric value of 9.80. This was the case for all samples analyzed in this work, thus the purity of helium and neon are acceptable. Since the reproducibility of ^{4}He/^{20}Ne ratios is within 5%, we include an analytical error of about 5% for the helium/neon ratio in actual groundwater samples.

After analysis of the ^{4}He/^{20}Ne ratio, the helium isotope ratio (^{3}He/^{4}He) was determined by measuring ^{3}He in the Daly multiplier detector and ^{4}He in the Faraday cup detector, respectively. The integrating time of the ^{4}He beam was three seconds while that of ^{3}He was ten seconds. Fifty sets of ^{3}He/^{4}He measurements were conducted and the ratio was extrapolated at the time of sample admission into the mass spectrometer. The statistical error of the ^{3}He/^{4}He measurements is about 0.5% for typical samples.

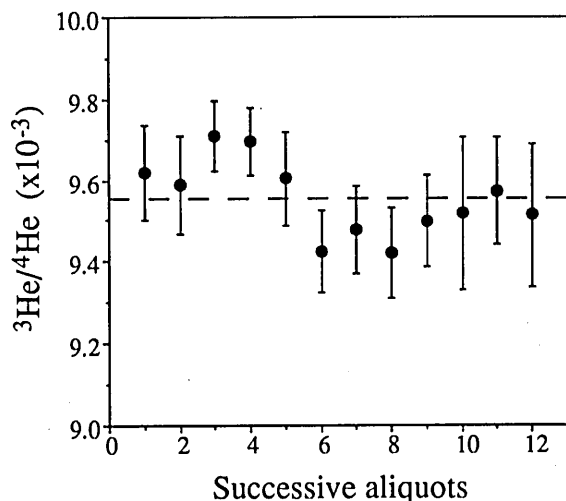Figure 3. Repeated measurement of atmospheric ^{3}He/^{4}He ratio.

Figure 3 indicates the reproducibility of ^{3}He/^{4}He ratio measurements in air standard. Overall reproducibility is estimated to be about 1 %, which is larger than the statistical error of a single sample analysis, therefore, we should include an error of about 1 % for actual samples. The real ^{3}He/^{4}He ratio can be obtained by dividing the

observed ratio by the gain of the Daly multiplier over the Faraday cup.

We tried to adjust the sample helium size to balance with the air standard as described before. However, it is difficult to make the size of the sample helium exactly equal to that of the standard. Generally a noble gas mass spectrometer in static operation shows the pressure effect on the results of the isotope ratio. That is, the isotope ratios may vary with the size of the samples. We measured ^{3}He/^{4}He ratios of standard helium for varying amounts. Figure 4 shows the pressure effect of ^{3}He/^{4}He ratio measurement, the helium isotopes vary slightly with the amount of helium. However, the ratio is constant within 1 % when the sample size is adjusted between 1 ~ 2 x 10^{-6} ccSTP and the analytical error of the helium isotope measurement is estimated to be about 1 %.
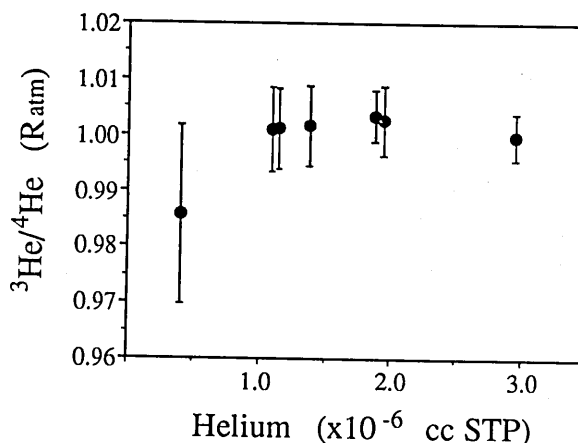

Figure 4. Pressure dependence of the atmospheric ^{3}He/^{4}He ratios in the mass spectrometer.

We checked the accuracy of the helium isotope ratio obtained in this work using the sample ^{3}He/^{4}He ratios published in the literature. Figure 5 compares the observed helium isotopes and the reported values. Open circles (O) shows reported values whose helium was not separated from neon before admission into the mass spectrometer. Solid circles (●) are samples whose helium was separated from neon using the cryogenic charcoal trap held at 40 K. It was experimentally established that helium isotope ratios are significantly compromised by coexisting neon (Rison and Craig, 1982; Sano and Wakita, 1988). This effect may be sensitive to the condition of the ion source. Rison and Craig (1982) suggested that the helium isotope ratio increases with neon, while Sano and Wakita (1988) reported contrary results, that is, a decrease of the ratio. Even though the same type of mass spectrometer

(VG5400) was used, the helium isotope ratio increased with neon in some cases (Sano et al., 1992).
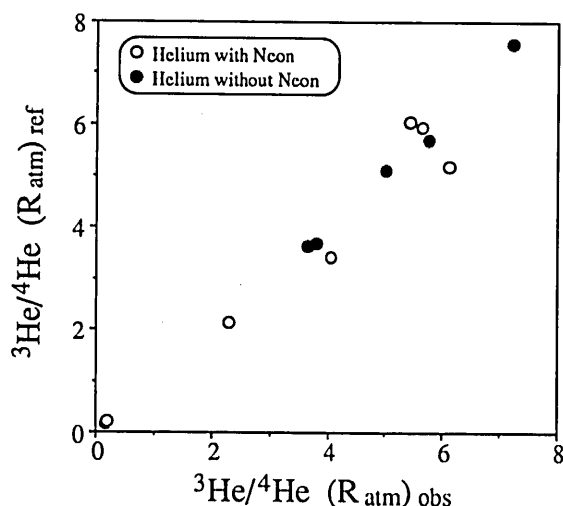

Figure 5. Comparison of helium isotopes between observed and reported values.

According to our results in Fig. 5, the helium isotopes observed in this work agree well with data whose helium was separated from neon, as listed in Table 2. The accuracy is calculated to be 2.4% if the reported data are correct, but in contrast helium isotopes with neon are scattered significantly. It should be noted that the accuracy of the present analytical system is within 3%.

Table 2. Comparison of observed helium isotopes with those in literature

Sample	$^3He/^4He_{obs}$ (R_{atm})	$^3He/^4He_{lit}$ (R_{atm})	obs./lit. (%)
Izu-Oshima Volcano, Japan			
Geothermal well gas	3.66	3.65[a]	100.7
Kusatsu-Shirane Volcano, Japan			
Sesshogawara	7.31	7.55[b]	96.8
Shiriyaki hot spring	3.80	3.69[b]	103.0
Yubatake hot spring	5.02	5.12[b]	98.1
Galeras Volcano, Colombia			
Crater fumarole	5.75	5.71[c]	100.7

a: Sano et al. (1991)
b: Sano and Marty (1993)
c: Williams et al. (1992)

D. Blank level and analysis of distilled water

In order to simulate actual measurement of groundwater samples, we measured the helium contents, isotopes, and helium/neon ratios of distilled water samples equilibrated with atmospheric noble gas at 20°C.

Before the analysis, the blank level of the system was assessed by performing the experiment without a groundwater sample. The system blank of ^4He and ^{20}Ne thus measured were 3.9 x 10^{-8} ccSTP and 2.2 x 10^{-7} ccSTP, respectively.

Table 3 lists the results of distilled water collected in a copper tube similar to groundwater samples. The concentration of helium was calculated by the beam intensity of ^4He by the Faraday cup and the sensitivity. Listed values are blank corrected. Observed values of helium content are about 5 % larger than reported values. However, the concentration attained by the sensitivity method used here has about a 10 % error, thus the observed helium content agrees with reported values within experimental error.

Since the solubility of ^3He is slightly lower than that of ^4He, helium isotopes of distilled water indicate a value 1.63% lower than that of coexisting air (Benson and Krause, 1980). Taking an average of the observed helium isotopes, the value of -1.56% agrees well with the reported value. In addition the helium/neon ratio shows elemental fractionation when the gases are dissolved in water (Ozima and Podosek, 1988). The observed

Table 3. Helium contents, isotopes and helium/neon ratios of distilled water samples.

Sample	^4He (ccSTP/g)	$^3He/^4He$ (R_{atm})	$^4He/^{20}Ne$
No. 1	4.72x10^{-8}	0.9743	0.285
No. 2	4.85x10^{-8}	0.9924	0.274
No. 3	4.94x10^{-8}	0.9865	0.284
Average	4.84x10^{-8}	0.9844	0.281
Reference	4.6x10^{-8}	0.9837	0.2665

discrimination of 5 % is similar to the experimental error of the helium/neon measurement.

IV. Summary

This study established a technique for analyzing helium isotopes in groundwater samples. The results obtained are summarized as follows:

(1) We connected a gas extraction vacuum line from groundwater with the helium and neon purification line, which makes sample handing easy and reliable.

(2) The noble gas mass spectrometer was baked out to reduce the blank level and the ion source conditions were adjusted to optimize helium isotope measurement.

(3) Using standard air helium, the reproducibility of helium isotope measurement and the pressure effect on the ratio were assessed. The reproducibility and pressure effect suggests that analytical error is within 1%.

(4) Accuracy of the system was checked by comparing observed data with reported data in the literature. Reported helium isotope data whose helium was separated from neon agree well with the data observed in this study.

(5) Groundwater sample analysis was simulated using distilled water sample collected in a copper tube. The observed values of helium content, helium isotopes, and helium/neon ratios are compatible with data in the literature.

References

Benson, B.B. and Krause, D.Jr., 1980: Isotope fractionation of helium during solution: a probe for the liquid state. J. Solution Chem., 9, 895-909.

Fritz, P., Drimmie, R.J. and Render, F.W., 1974: Stable isotope contents of a major prairie aquifer in Central Manitoba, Canada. Isotope Techniques in Groundwater Hydrology, 1, 379-396, IAEA-SM-182/22.

Kaufman, W.J. and Orlob, G.T., 1956: An evaluation of groundwater tracers. Transaction, American Geophysical Union, 37, 297-306.

Kayane, I., Tanaka, T. and Shimada, J., 1980: Sol water movement in Kanto loam as traced by environmental tritium. Geograph. Rev. Japan, 53, 225-237*.

Lupton, J.E. and Craig, H., 1981: A major helium-3 source at 15°S on the East Pacific Rise. Science, 214, 13-18.

Lupton, J.E., 1983: Terrestrial inert gases: Isotope tracer studies and clues to primordial components in the mantle. Ann. Rev. Earth Planet. Sci., 11, 371-414.

Mahara, Y., Osumi, T., Nakagawa, K. and Igarashi, T., 1988: Development of dating methods of groundwater (Part I): The sampling technique of the deep groundwater. Abiko Research Laboratory Rep. U88020, pp 18*.

Mahara, Y., Igarashi, T. and Tanaka, Y., 1991: Survey of groundwater using H-3 + He-3 dating method. Proceedings of 3rd Intern. Symp. Adv. Nuc. Energy Res., Ibaraki, 85-89.

Mamyrin, B.A. and Tolstikhin, I.N., 1984: Helium isotopes in nature. Elsevier, Amsterdam, 273p.

Marine, I.W., 1979: The use of naturally occurring helium to estimate groundwater velocities for studies of geologic storage of radioactive waste. Water Resource Res., 15, 1130-1136.

Martin, J.F., 1985: Natural iodine-129 as an environmental tracer. Geochim. Cosmochim. Acta, 49, 337-347.

Mizutani, Y. and Oda, M., 1983: Stable isotope study of groundwater recharge and movement in the Shogawa Fan, Toyama. Chikyukagaku, 17, 1-9*.

Ozima, M. and Podosek, F.A., 1983: Noble gas geochemistry. Cambridge University Press, Cambridge, 367p.

Paul, H., Kaufman, A., Magaritz, M., Fink, D., Henning, W., Kaim, R., Kutschera, W. and Meirav, O., 1986: A new ^{36}Cl hydrological model and ^{36}Cl systematics in the Jordan River/Dea Sea system. Nature, 321, 511-515.

Rauert, W. and Stichler, W., 1974: Groundwater investigations with environmental isotopes. Isotope Techniques in Groundwater Hydrology, 1, 431-441, IAEA-SM-182/24.

Rison, W. and Craig, H., 1983: Helium isotopes and mantle volatiles in volcanic rocks from Loihi seamount and the island of Hawaii. Earth Planet. Sci. Lett., 66, 407-426.

Rodhe, A., 1983: Groundwater contribution to stream flow in Swedish forested till soil as estimated by oxygen-18. Isotope Hydrology, 55-66, IAES-SM-270/65.

Sano, Y. and Wakita, H., 1985: Geographical distribution of ^{3}He/^{4}He ratios in Japan: implications for arc tectonics and incipient magmatism. J. Geophys. Res., 90, 8728-8741.

Sano, Y. and Wakita, H., 1988: Precise measurement of helium isotopes in terrestrial gases. Bull. Chem. Soc. Japan, 61, 1153-1157.

Sano, Y., Notsu, K., Ishibashi, J., Igarashi, G. and Wakita, H., 1991: Secular variations of helium isotopes at active volcano: eruption and plug hypothesis. Earth Planet. Sci. Lett., 107, 95-100.

Sano, Y., Sasaki, S. and Nagao, K., 1992: Noble gas isotopes and chemical compositions in gas seeps from Northwestern Cameroon. Bull. Volcan. Soc. Japan, 37, 85-93*.

Sano, Y. and Marty, B., 1993: Origin of carbon in volcanic gas from subduction zones. submitted to Bull. Volcan. Soc. Japan.

Schlosser, P., Stute, M., Dörr, H., Sonntag, C. and Münnich, K.O., 1988: Tritium/^{3}He dating of shallow

groundwater. Earth Planet. Sci. Lett., 89, 353-362.

Sugisaki, R., 1961:   Measurement of effective flow velocity of ground water by means of dissolved gases. Am. J. Science, 259, 144-153.

Sukhija, B.S. and Shah, C.R., 1976:   Conformity of groundwater recharge rate by tritium method and mathematical modelling.   J. Hydrology, 30, 167-178.

Takaoka, N. and Mizutani, Y., 1987: Tritiogenic ^{3}He in groundwater in Takaoka. Earth Planet. Sci. Lett., 85, 74-78.

Williams, S.N., Sano, Y. and Wakita, H., 1992: ^{3}He/^{4}He variations at erupting volcanoes. Abstract 29th Iintern. Geol. Cong., Kyoto, p. 608.

Zimmermann, U., Münnic, K.O., Roethe, W., Kreutz, W., Schubac, K., Siege, O., 1966: Tracers detemine movement of soil moisture and evapotranspiration. Science, 152, 346-347.

*: in Japanese with English abstract

Yuji SANO, Naoto TAKAHATA
    Department of Earth and Planetary Systems Science, Faculty of Science, Hiroshima University, Higashi Hiroshima, 724, Japan.

Yasunori MAHARA and Sinji YASUIKE
    Abiko Research Laboratory, Central Research Institute of Electric Power Industry, Abiko, Chiba, 270-11, Japan.