32. ^{3}He/^{4}He RATIOS OF PORE GASES IN PORE WATERS, SITES 583 AND 584[1]

Yuji Sano and Hiroshi Wakita, Laboratory for Earthquake Chemistry, The University of Tokyo[2]

ABSTRACT

We have measured the ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios of gases dissolved in the pore water in sediments at two sites in the Nankai Trough (Site 583) and the Japan Trench (Site 584). The ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios vary from 0.215 × 10^{-6} to 1.23 × 10^{-6} and from 50 × 10^{-3} to 2700 × 10^{-3}, respectively. These values can be explained by mixing two components, one from the atmosphere and one with a ^{3}He/^{4}He ratio of (0.2 to 0.3) × 10^{-6}. The latter component may be derived from the ocean crust near the subduction zone.

INTRODUCTION

Since the first finding of excess ^{3}He in deep Pacific water (Clarke et al., 1969), intensive investigations have been carried out all over the world to search for the Earth's primordial ^{3}He. Primordial He emissions are commonly found in Cenozoic volcanic areas, such as mid-ocean ridges, hot spots, and subduction zones.

The ^{3}He/^{4}He ratios of fresh basalt glasses obtained from mid-ocean ridges, including the Mid-Atlantic Ridge and the East Pacific Rise, are high, with an almost constant value of 1.2 ± 0.2 × 10^{-5} (e.g., Lupton and Craig, 1975; Craig and Lupton, 1976; Rison, 1980; Kyser and Rison, 1982; Allègre et al., 1983; Ozima and Zashu, 1983). The constancy of the ratio is considered to be evidence that the upper mantle is well mixed with respect to He on a global scale.

The first indication of mantle-derived He in subduction zones (island arcs and continental margins) was reported for volcanic gases from Kamchatka and the Kurile Islands by Baskov and others (1973). Subsequent studies carried out on gaseous samples in the circum-Pacific areas indicate that those ^{3}He/^{4}He ratios are almost uniform, with values ranging from 7 × 10^{-6} to 11 × 10^{-6} (Craig et al., 1978; Nagao et al., 1981; Torgersen et al., 1982; Sano et al., 1982). For reasons not fully understood, the highest ^{3}He/^{4}He ratio found in subduction zones is slightly lower than that observed in mid-ocean ridges.

Pore water in deep-sea sediments is an ideal material in which to preserve gases emitted from the interior of the Earth, except for fresh basalt glasses. Gases from various other sources may also be dissolved and trapped in the pore water in sediments. Because the distance from the ocean surface to the seafloor is great, the chance of atmospheric contamination in the sediment is small. The ^{3}He/^{4}He ratios of gases dissolved in pore water at subduction zones provide useful information on the He budget of forearc regions. We measured the ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios of gases dissolved in pore water in sediments from the Nankai Trough (Site 583) and the Japan Trench (Site 584).

METHODS

Sample Collection

The samples were collected using a Barnes-type *in situ* pore-water sampler. A precise description of this downhole instrument designed to collect pore waters from sediments has been provided by Sibuet, Ryan, and others (1979). Using the sampler, we filtered pore water in sediments from the *in situ* solid particles and sealed it against gas loss and atmospheric contamination. Pore water containing dissolved gases was collected in a 50-cm^3 coiled copper tube (0.476 cm outer diameter × 6.1 m long). An adjustable spring-loaded check value sealed the sample tube, maintaining positive pressure of up to 40 atm. Before sample collection, a water inlet tubing and sample tube were filled with distilled water to eliminate possible air contamination. The sampler, in conjunction with the Uyeda-Kinoshita downhole temperature probe (Yokota et al., 1980), was installed in the core-barrel assembly and dropped down the drilled pipe. The probe projects through the bit and penetrates about 1 m into the sediments at the depth drilled. Water samples containing gases flow into the copper tube under hydrostatic pressure, displacing distilled water from the inlet line into an overflow cylinder (Mottl et al., 1983). After recovery of the downhole probe, the copper tube was crimped-sealed at each end and refrigerated on board.

When we received these Nankai Trough samples in the laboratory, we noted that gas leakage had occurred at the crimp-seals because of deformation of the tube; evidently the method used for sealing the copper tubes did not maintain the original high pressure. The gases in these sample tubes were immediately transferred by water displacement to high-vacuum containers made of Pb-glass. At the same time, we asked for tighter sealing for the Leg 87B (Japan Trench) samples (welding on tube ends in addition to crimp-seals). Because most samples were at a pressure slightly higher than 1 atm, we could only recover a few ml of gas samples. Samples from 583A-11,CC, 583F-18,CC, and 584-30-5 were not recovered. The gas pressures of Samples from 583F-18,CC and 584-30-5 were extremely low, and these water samples were directly transferred to vacuum containers using an O-ring vacuum connector. Gases dissolved in the water were further extracted using a new vacuum container (Sano, 1983). Because significant water leakage was observed for Sample 583A-11,CC, analysis of this sample was not attempted.

He Isotopic and He to Ne Ratio Measurements

Approximately 1 cm^3 of gas at standard temperature and pressure was introduced into a metallic high-vacuum purification line. He and Ne were purified in a CuO furnace at 500°C, and all other gases were removed by a charcoal trap at −196°C. A static mass spectrometer (6-60-SGA Nuclide Company, State College, Pennsylvania) was used for ^{3}He/^{4}He and ^{20}Ne/^{4}He ratio measurements. A resolving power of about 600 was attained for the complete separation of the ^{3}He beam from those of H_3 and HD. Atmospheric He was used as a standard. Precise

description of the ^{3}He/^{4}He measurement procedure is reported elsewhere (Sano et al., 1982). Qualitative analyses of major compositions were made by gas chromatography.

Chemical Analyses of Sediments

About 0.1 g of powdered sediment was dissolved with 10 ml HF (40%), 5 ml HClO$_4$ and 5 ml HNO$_3$ in a teflon beaker, and the solution was evaporated to incipient dryness. The residue was dissolved with 2.5 ml 6 N HCl. The solution was diluted to 25 ml in a volumetric flask and used for analyses of Li. One ml of the solution was further diluted to 10 ml for analyses of major elements. Standard rock samples (GSP-1, GA, NIM-G, and JB-1) were also processed in a similar manner.

The concentrations of major and minor elements in each solution were determined using an inductively coupled plasma (ICP) source spectrometer. Calibration was made by comparison of the emission intensities with each element in rock standards.

RESULTS AND DISCUSSION

We obtained nine samples representing the Nankai Trough (Sites 583A, 583D, and 583F) and three from the Japan Trench (Site 584) (Fig. 1). Several samples are from varying depths at one site. The ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios vary significantly (Table 1): (0.215 to 1.23) $\times$ 10^{-6} and (50 to 2700) $\times$ 10^{-3}, respectively. No apparent correlation was observed between the measured ^{3}He/^{4}He ratios and locations, depths, and major chemistry. The major composition of gas samples from the Nankai Trough was CH$_4$, and from the Japan Trench, N$_2$. The gas pressure of samples from the Japan Trench was low, regardless of the tighter sealing of these samples. Higher methane gas contents in samples from the Nankai Trough are in accordance with the observation of a higher precipitation rate of organic matter in the area (Ingle, Karig, et al., 1975), compared with that of the Japan Trench (Lang, this volume).

The ^{3}He/^{4}He ratios and ^{20}Ne/^{4}He ratios are positively correlated (Fig. 2). All data lie on a mixing line between

Table 1. ^{3}He/^{4}He and ^{20}Ne/^{4}He ratios in pore water from the Nankai Trough and the Japan Trench.

Our sample number	Core-Section	Sub-bottom depth (m)	Type	^{3}He/^{4}He (x 10^{-6})	^{20}Ne/^{4}He (x 10^{-3})
Nankai Trough					
1	583A-11,CC	54			
2	583D-8-2	123.5	CH$_4$	0.989 ± 0.036	2700
3	583D-14,CC	172	CH$_4$	0.989 ± 0.034	2400
4	583D-18,CC	220.2	CH$_4$	0.595 ± 0.028	950
5	583D-24,CC	278.4	CH$_4$	0.645 ± 0.018	1200
6	583D-29,CC	326.6	CH$_4$	0.690 ± 0.030	1200
7	583F-2,CC	169.6	CH$_4$	0.386 ± 0.020	260
8	583F-7,CC	217.7	CH$_4$	0.779 ± 0.053	2300
9	583F-18,CC	323.9	CH$_4$	1.23 ± 0.02	2400
Japan Trench					
10	584-8,CC	77	N$_2$	0.330 ± 0.010	400
11	584-16,CC	153.7	N$_2$	1.08 ± 0.03	2300
12	584-30-5	287	N$_2$-CH$_4$	0.215 ± 0.008	50
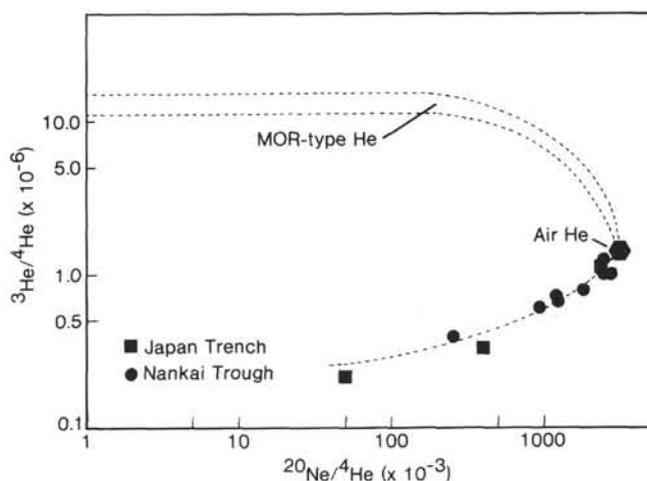
Figure 2. ^{3}He/^{4}He ratios plotted against ^{20}Ne/^{4}He ratios. Dashed lines show the mixing lines between mid ocean ridge–type He (MOR-type He) and atmospheric He, and between gases with a ^{3}He/^{4}He ratio of (0.2 to 0.3) $\times$ 10^{-6} and atmospheric He.

the atmospheric He and gas with the ^{3}He/^{4}He ratio of (0.2 to 0.3) $\times$ 10^{-6}. This pattern suggests that He in the pore water is explained by the mixing of two end members: atmospheric He and radiogenic He. Two water samples, 583F-18,CC and 584-16,CC, show a ratio close to that of air.

The atmospheric He has two possible sources. One is atmospheric He dissolved in the seawater, and the other is direct contamination during sample storage and/or at the time of sample transfer. Because the atmospheric ^{20}Ne/^{4}He ratio of 3.15 is almost the same as the 3.76 of air-saturated water, it is difficult to estimate the degree of atmospheric contamination. Either a more appropriate preservation method for sample gas or immediate transfer of the gas sample to a reliable container on board is absolutely necessary in future sample collection and study.

The identity of the other end member, radiogenic He with the ^{3}He/^{4}He ratio of (0.2 to 0.3) $\times$ 10^{-6}, is not easy to determine. The value is about 1/10 lower than that of the atmosphere. This radiogenic He is thought
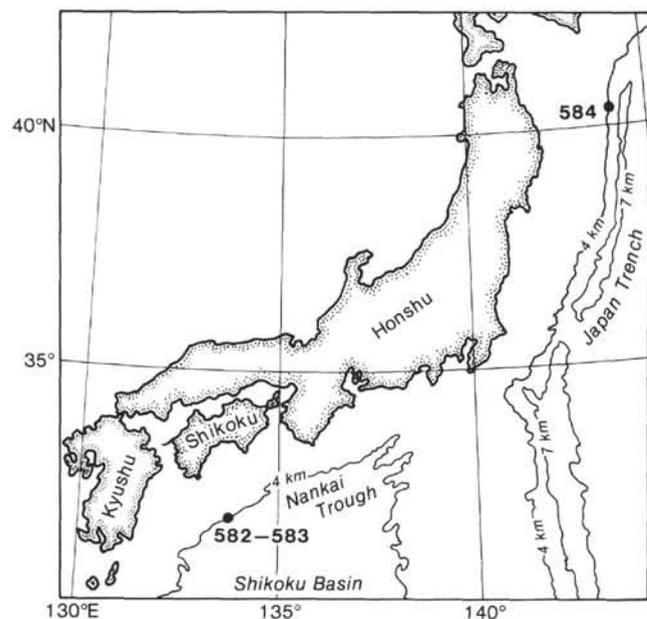
Figure 1. Sampling sites of pore water in sediment. Nine samples were collected in the Nankai Trough (Site 583) and three samples in the Japan Trench (Site 584).

to be produced by radioactive decay of U and Th in the sediments and trapped He from the ocean crust.

Besides the primordial component, ^{3}He is also produced by nuclear reactions in the sediments, as is also ^{4}He in the following: ^{6}Li(n,α)^{3}H $\xrightarrow{\beta^-}$ ^{3}He. The *in situ* radiogenic ^{3}He/^{4}He ratio depends on the contents of U, Th, Li, and other light elements such as O, Si, Al, K, and B. We measured concentrations of 11 major and minor elements in four samples from Site 582 in the Nankai Trough (Table 2). SiO$_2$ contents are scaled to make the total amount 100%. The concentrations of Be, B, F, and Gd are taken from data by Wedepohl (1969). The theoretical ^{3}He/^{4}He ratio is calculated as follows:

$$^3\text{He}/^4\text{He} = (n_f + n_a) \times P_t \times \frac{\sigma_{Li}N_{Li}}{\sum_i \sigma_i N_i},$$

where n_f is the ratio of neutrons produced by spontaneous fission of ^{238}U and other heavy nuclides to alpha particles produced by α-decay of U and Th series nuclides. The value (n/α) of 0.8×10^{-7} was calculated by Morrison and Pine (1955); n_a is the ratio of neutrons to alpha particles, both produced by (α,n) reactions with light elements in the sediments. P_t is the probability that a neutron will reach thermal energy, which is about 0.8 for a rock with average elemental abundances (Morrison and Pine, 1955). N_i is the number of atoms of the element (i) in 1 g sediment, and σ_i is the thermal-neutron-capture cross section of the element (i). According to Gerling and others (1971), n_a is expressed as follows:

$$n_a = \frac{\sum_k g_k S_k N_k}{\sum_i S_i N_i},$$

where q_k is the neutron yield produced by an α particle in a thick target composed of the element (k), and S_k is the relative stopping power of the element (k).

Adopting the above variables and observed concentrations of elements, we can calculate the ^{3}He/^{4}He ratios produced in the sediments (Table 2). The observed ^{3}He/^{4}He ratios in the pore water are one order of magnitude higher than the calculated values.

This investigation reveals that the ^{3}He/^{4}He ratio in the forearc region of the subducting zone is radiogenic, but the ratio is higher by a factor of 10 than the calculated ratio based on *in situ* production of radiogenic He. Lower ^{3}He/^{4}He ratios observed in the area around subduction zones compared to higher ratios in mid-ocean ridges may be interpreted as the result of input of the radiogenic He.

REFERENCES

Allègre, C. J., Staudacher, T., Sarda, P., and Kurz, M., 1983. Constraints on evolution of Earth's mantle from rare gas systematics. *Nature*, 303:762–766.

Baskov, Y. A., Vetshteyu, U. Y., Surikov, S. N., Tolstkhin, I. N., Malyuk, G. A., and Mishna, T. A., 1973. Isotope composition of H, O, C, Ar and He in hot springs and gases in the Kurile-Kamchatka volcanic region as indicators of formation condition. *Geokhimiya*, 1973:180–189.

Clarke, W. B., Beg, M. A., and Craig, H., 1969. Excess ^{3}He in the sea: evidence for terrestrial primordial helium. *Earth Planet. Sci. Lett.*, 6:213–220.

Craig, H., and Lupton, J. E., 1976. Primordial neon, helium and hydrogen in oceanic basalts. *Earth Planet. Sci. Lett.*, 62:24–40.

Craig, H., Lupton, J. E., and Horibe, Y., 1978. A mantle helium component in circum-Pacific volcanic gases: Hakone, the Marianas and Mt. Lassen. *In* Alexander, E. C., and Ozima, M. (Eds.), *Terrestrial Rare Gases:* Tokyo (Jpn. Sci. Soc. Press), Adv. Earth Planet. Sci., 3:3–16.

Gerling, E. K., Mamyrin, B. A., Tolstkhin, I. N., and Yokovleva, S. S., 1971. Helium isotope composition in some rocks. *Geochem. Int.*, 8:755–761.

Ingle, J. C., Jr., Karig, D. E., and Shipboard Scientific Party, 1975. Site 298. *In* Karig, D. E., Ingle, J. C., Jr., et al., *Init. Repts. DSDP*, 31: Washington (U.S. Govt. Printing Office), 317–350.

Kyser, M. D., and Rison, W., 1982. Systematics of rare gas isotopes in basic lavas and ultramafic xenoliths. *J. Geophys. Res.*, 87:5611–5630.

Lupton, J. E., and Craig, H., 1975. Excess ^{3}He in oceanic basalts: evidence for terrestrial primordial helium. *Earth Planet. Sci. Lett.*, 26:133–139.

Morrison, P., and Pine, J., 1955. Radiogenic origin of the helium isotopes in rock. *Ann. N.Y. Acad. Sci.*, 62:71–92.

Mottl, M. J., Lawrence, J. R., and Keigwin, L. R., 1983. Elemental and stable-isotope composition of pore waters and carbonate sediments from Deep Sea Drilling Project Sites 501/504 and 505. *In* Cann, J. R., Langseth, M. G., Honnorez, J., Von Herzen, R. P., White, S. M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 461–473.

Nagao, K., Takaoka, N., and Matsubayashi, O., 1981. Rare gas isotopic compositions in natural gases of Japan. *Earth Planet. Sci. Lett.*, 53:175–188.

Ozima, M., and Zashu, S., 1983. Noble gases in submarine pillow volcanic glasses. *Earth Planet. Sci. Lett.*, 62:24–40.

Rison, W., 1980. Isotopic studies of the rare gases in igeous rocks: implications for the mantle and atmosphere [Ph. D. dissert.]. University of California, Berkeley, California.

Table 2. Chemical composition in percent of sediments and calculated ^{3}He/^{4}He ratios.

Elements	Hole-Core-Section			
	583D-7-10	583D-8-1	583F-2-1	583F-18-3
O	52.3	52.9	52.7	53.1
Si	25.7	27.5	26.6	27.1
Al	8.42	7.46	7.84	8.05
Fe	4.83	3.92	4.13	3.85
Mg	1.87	1.51	1.63	1.45
K	1.99	2.16	1.83	2.08
Na	2.15	2.15	2.45	2.23
Ca	2.36	2.00	2.43	1.71
Ti	0.43	0.40	0.44	0.41
Li	0.0050	0.0048	0.0048	0.0042
Be[a]	0.0003	0.0003	0.0003	0.0003
B[a]	0.0050	0.0050	0.0050	0.0050
F[a]	0.0730	0.0730	0.0730	0.0730
Gd[a]	0.00055	0.00055	0.00055	0.00055
Calculated ^{3}He/^{4}He ($\times 10^{-6}$)	0.021	0.020	0.018	0.020

[a] Wedepohl (1969).

Sano, Y., 1983. Distribution of ^{3}He/^{4}He ratios and geotectonic structure of the Japanese Islands. [Ph. D. dissert.]. University of Tokyo, Tokyo, Japan.

Sano, Y., Tominaga, T., Nakamura, Y., and Wakita, H., 1982. ^{3}He/^{4}He ratios of methane-rich natural gases in Japan. *Geochem. J.*, 16:337–345.

Sibuet, J.-C., Ryan, W. B. F., and Shipboard Scientific Party, 1979. Introduction and Explanatory Notes. *In* Sibuet, J.-C., Ryan W. B. F., et al., *Init. Repts. DSDP*, 47, Pt. 2: Washington (U.S. Govt. Printing Office), 5–22.

Torgersen, T., Lupton, J. E., Sheppard, D., and Giggenback, W., 1982. He isotope variations in the thermal areas of New Zealand. *J. Volcanol. Geotherm. Res.*, 12:283–298.

Yokota, T., Kinoshita, H., and Uyeda, S., 1980. New DSDP (Deep Sea Drilling Project) downhole temperature probe utilizing IC RAM (memory) elements. *Bull Earthquake Res. Inst. Univ. Tokyo*, 55:75–78.

Wedepohl, K. H. (Exec. Ed.), 1969. *Handbook of Geochemistry*: Heidelberg (Springer-Verlag Berlin).