Measurements of $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^4\text{He}$ ratios in 12 CH$_4$-rich natural gas samples were made with a magnetic deflection mass spectrometer equipped with a metallic high-vacuum purification line. In order to check the resolving power, sensitivity and stability of the mass spectrometer, atmospheric air in Tokyo was measured repeatedly. The mean $^3\text{He}/^4\text{He}$ ratio in Tokyo air was $(1.43 \pm 0.03) \times 10^{-6}$.

CH$_4$-rich gases with significantly high $^3\text{He}/^4\text{He}$ ratios were first observed in this study. The $^3\text{He}/^4\text{He}$ ratios for 5 natural gas samples collected from hot springs and mineral springs in inland basins were as high as $(1.7 - 7.3) \times 10^{-6}$, probably due to the large contribution of the upper mantle-derived He. In comparison, the $^3\text{He}/^4\text{He}$ ratios for 2 samples from water wells distributed in coastal areas facing the Pacific Ocean and 5 samples from gas fields in the southern Kanto district were as low as $\sim 10^{-7}$. Most of the He in these gases is inferred to be radiogenic and of crustal origin.

INTRODUCTION

After the first finding of isotope $^3\text{He}$ with a cyclotron by ALVAREZ and CORHOG (1939), few measurements of $^3\text{He}/^4\text{He}$ ratios in terrestrial samples were made. In 1948, ALDRICH and NIER reported a wide variation in the $^3\text{He}/^4\text{He}$ ratios for various minerals using a newly developed mass spectrometer. CLARKE et al. (1969) found a great enrichment of $^3\text{He}$ in deep Pacific water, relative to the atmospheric $^3\text{He}/^4\text{He}$ ratio. They concluded that the excess $^3\text{He}$ is due to leakage into ocean water of remnants of the earth's primordial $^3\text{He}$, a trapped component of solar nebula at the time of the accretion of the earth. Simultaneously MAMYRIN et al. (1969) found that $^3\text{He}/^4\text{He}$ ratios of volcanic gases in the southern Kurile Islands are clearly higher than the ratio in the atmosphere. They also considered that the increment was derived from deep-seated materials.

Since then more intensive investigations have been carried out all over the world. It has been noticed that natural gases and rock samples collected in the same tectonic regions show quite similar $^3\text{He}/^4\text{He}$ ratios. These ratios seem to be correlated with such geological features as the age and evolution of tectonic activities in the area. Emission of the primordial He is commonly found in Cenozoic volcanic areas. The $^3\text{He}/^4\text{He}$ ratios of rock samples obtained from the Mid-Oceanic Ridge, including the Mid-Atlantic Ridge and the East Pacific Rise, are extremely high at an almost constant value of $(1.3 \pm 0.2) \times 10^{-5}$. This value is defined as the MOR-type He (LUPFON and CRAIG, 1975). The $^3\text{He}/^4\text{He}$ ratios in hot spot regions such as the Hawaiian islands and Iceland are $(2.0 - 5.0) \times 10^{-5}$ (KANEOKA and TAKAOKA, 1980) and are apparently higher than that of the MOR-type He. In areas along subduction zones like Japan (NAGAO et al., 1981) and Kamchatka (KAMSKY et al., 1971), the upper limit of the $^3\text{He}/^4\text{He}$ ratios is $1.1 \times 10^{-5}$, which is interpreted to be produced by a mixing of the MOR-type He and radiogenic He in the crustal sediment by motion of the subducting slab. On the other hand, $^3\text{He}/^4\text{He}$ ratios in continental samples are...
generally low. They vary with the geological age of the area where the sample is collected. The mean \(^3\)He/\(^4\)He ratio of some gas deposits in the Precambrian basement is \(2.4 \times 10^{-8}\) and in the Hercynian basement \(6.2 \times 10^{-8}\) (KAMENSKY et al., 1971).

Recently, WELHAN and CRAIG (1979) reported that hydrothermal vents at 21°N on the East Pacific Rise are discharging turbid waters; mixtures of the plumes with ambient seawater contain significant amounts of dissolved \(\text{H}_2\) and \(\text{CH}_4\) as well as mantle-derived He. This \(\text{H}_2\) and/or \(\text{CH}_4\) is thought to be produced within the basalt-water system by chemical reactions or extracted from the basalts as an intrinsic mantle component. Emanation of non-biological \(\text{CH}_4\) from the mantle is likely to be observed in the crust. More systematic investigations on the occurrence of \(\text{CH}_4\)-rich natural gas are highly desired.

In this paper, we report \(^3\)He/\(^4\)He and \(^{20}\)Ne/\(^4\)He ratios in various \(\text{CH}_4\)-rich natural gases in Japan. Based on the observed \(^3\)He/\(^4\)He and \(^{20}\)Ne/\(^4\)He ratios, the origin of He in natural gases is discussed. Technical problems of the measurements such as purifying He and Ne and making a calibration standard for \(^3\)He/\(^4\)He ratio measurements are also mentioned.

**EXPERIMENTAL**

Mass spectrometer and purification line

\(^3\)He/\(^4\)He and \(^{20}\)Ne/\(^4\)He ratios were measured with a 6-inch mass spectrometer (6-60-SGA, Nuclide Co.). Ion beams were detected by a double collector system: those of \(^4\)He and \(^3\)He were collected by a Farady cup detector and a secondary electron multiplier (S.E.M.) detector, respectively. In order to obtain precise \(^3\)He/\(^4\)He ratios in samples, high sensitivity and low background are required of the measuring system. The sensitivity of the mass spectrometer must be sufficiently high to measure \(2 \times 10^8\) \(^3\)He atoms, which are equivalent to \(^3\)He in 1 cc STP atmospheric air. The system must have a high resolving power of about 600 in order to separate the \(^3\)He ion beam from those of \(\text{H}_2\) and HD molecules.

**Fig. 1. Rare gas purification line and mass spectrometer system.** MASS: mass spectrometer, V: valves, I.P.: sputter ion pump, I.G.: ionization guage, CT: charcoal trap, P.G.: Pirani guage, TiZr: titanium-zirconium getter furnace, CuO: copper oxide furnace, O.D.P.: oil diffusion pump and R.P.: rotary pump.
In order to purify He and Ne from original gas samples, an ultra-high-vacuum line was constructed (Fig. 1). Considering the permeation of He, stainless steel 304 was used for most parts of the line except for an ionization gauge made of glass. The line consists of three-step purification parts separated by ultra-high-vacuum-valves (V1, V2 and V3). The first part is composed of inlet valves V10 and V11 (the volume between those valves is about 1 cc) and a charcoal trap (CT-0). The second part has a copper oxide furnace (CuO), a charcoal trap (CT-1) and a Pirani gauge (P.G.). The third part includes a titanium-zirconium getter furnace (Ti-Zr), a charcoal trap (CT-2) and an ionization gauge (I.G.). The first part was evacuated to below $10^{-5}$ Torr by an oil diffusion pump (O.D.P.). Vacua below $2 \times 10^{-8}$ Torr in an almost oil-free condition were obtained for the second and third parts by a sputter ion pump (I.P.). Metal valves V8, V9 and V12 attached to the respective charcoal traps are used to keep adsorbed species. The total volume of the purification line is about 300 cc. The background level of H$_2$ in the line was as low as that in the mass spectrometer.

**Purification procedure** A sample reservoir or atmospheric air tank was directly connected to the inlet part using a Cajon Ultra Torr Fitting. A sample of about 1 cc STP was introduced into the space between inlet valves (V10 and V11) and was transferred to the purification line. At the first step, major adsorbable components, such as N$_2$, O$_2$, CH$_4$ and CO$_2$, in the sample gas were roughly removed by the charcoal trap (CT-0) kept at $-196^\circ$C. Unadsorbed components containing He and Ne were transferred to the second part. In the copper oxide furnace maintained at 550°C, H$_2$ and CH$_4$ were oxidized to CO$_2$ and H$_2$O (for 30 min.) and removed by the CT-1 kept at $-196^\circ$C. Then the purified fraction was expanded to the third part. The CT-2 kept at $-196^\circ$C was used to completely adsorb residual active gases and heavy rare gases (for 30 min.). Finally purified fraction containing He and Ne was introduced into the mass spectrometer. Analysis was made by a static mode. In the above process the Ti-Zr was only used to obtain an oil-free ultra-high-vacuum condition, since the Ti-Zr releases significant amounts of H$_2$. Total purification time required for an individual sample was about 2 hours.

**Background levels of $^3$He, $^4$He and $^{20}$Ne** The static backgrounds of the mass spectrometer, i.e. cold blank and hot blank, were examined for $^3$He, $^4$He and $^{20}$Ne, respectively. Cold blank indicates the static background of the measuring system including the purification line. Hot blank indicates the static background after the actual purification procedure done without sample gas.

$^3$He beam was measured by the S.E.M. detector, and $^4$He and $^{20}$Ne beams were measured by the Farady cup detector. Peak heights of $^3$He and $^4$He ion beams were obtained by a digital integrator and a calculator (Tectronix 31).

Static backgrounds (cold blank) of $^3$He, $^4$He and $^{20}$Ne ion beams were below $7 \times 10^{-14}$, $3 \times 10^{-10}$ and $9 \times 10^{-9}$ cc STP, respectively. In the hot blank, $^3$He and $^{20}$Ne ion beams were below $1 \times 10^{-13}$ and $9 \times 10^{-9}$ cc STP, respectively, and $^4$He ion beam of 0.001 V, which was equivalent to $3 \times 10^{-9}$ cc STP, was detected by the Farady cup detector. This amount, however, is negligibly small in the measurement of actual samples.

**Pressure dependence of $^3$He/$^4$He ratio** The relation between the $^3$He/$^4$He ratio of atmospheric He and total pressure in the mass spectrometer was examined in the range from $3.2 \times 10^{-6}$ to $4.2 \times 10^{-4}$ Torr. In the pressure range lower than $1 \times 10^{-6}$ Torr, the $^3$He/$^4$He ratio was almost constant. The higher the total pressure in the mass spectrometer, the higher becomes the $^3$He/$^4$He ratio. A remarkable increase in the $^3$He/$^4$He ratio was observed in the pressure range higher than $1 \times 10^{-6}$ Torr. This is attributed to sensitivity depression of $^4$He ion beam in the mutual electrostatic repulsion of $^4$He ions due to space charge effect. In actual measurements of natural gas samples, total pressure of He and Ne fractions in the mass spectrometer was con-
trolled to lower than $1 \times 10^{-6}$ Torr.

**Calibration standard for $^3$He/$^4$He ratio**

A standard sample for He isotope measurements was made by mixing known amounts of pure $^3$He and $^4$He gases. Mass discrimination factor of the measuring system was calculated by the standard sample. The theoretical mixing ratio of $^3$He/$^4$He of the standard sample was $(1.25 \pm 0.01) \times 10^{-6}$. One pipet of the standard sample contains $5.0 \times 10^{-10}$ cc STP $^3$He and $4.0 \times 10^{-6}$ cc STP $^4$He. The high voltage of the S.E.M. was 1.8kV. The Farady cup detector and S.E.M. detector were equipped with high registor of $10^{11}$ and $10^{9}$ ohm, respectively. The net gain of the S.E.M. detector over the Farady cup detector which was calculated by using $^4$He ion beam, was $6.0 \times 10^3$. The mean value of the observed $^3$He/$^4$He ratio was $(9.77 \pm 0.15) \times 10^{-5}$. A mass discrimination factor (d) of $-21.8\%$ was obtained from the following formula:

$$d = \frac{[(^3\text{He}/^4\text{He})_{\text{obs.}} - (^3\text{He}/^4\text{He})_{\text{theoretical}}]}{100}.$$ 

$^{20}$Ne/$^4$He ratios of gaseous samples were calculated by the following formula:

$$(^{20}\text{Ne}/^4\text{He})_{\text{sample}} = (^{20}\text{Ne}/^4\text{He})_{\text{air}} \times \frac{(^{20}\text{Ne}/^4\text{He})_{\text{sample}}}{(^{20}\text{Ne}/^4\text{He})_{\text{air}}}$$

where $(^{20}\text{Ne}/^4\text{He})_{\text{sample}}$ and $(^{20}\text{Ne}/^4\text{He})_{\text{air}}$ denote ion beam intensity ratios of $^{20}$Ne to $^4$He observed in the sample and atmospheric air, respectively, and $(^{20}\text{Ne}/^4\text{He})_{\text{air}}$ denotes an elemental abundance ratio of $^{20}$Ne to $^4$He in the air, that is, 3.15.

In general, interference from doubly-charged ions of $^{40}$Ar with $^{20}$Ne was unavoidable. In this work, however, intensities of $^{40}$Ar ion currents were less than $1\%$ of $^{20}$Ne. Furthermore, the low production rates of $^{40}$Ar$^{2+}$/$^{40}$Ar$^+$ indicate that such interference is negligibly small.

**RESULTS AND DISCUSSION**

**$^3$He/$^4$He ratio in Tokyo air**

It is known that the atmospheric air shows a constant $^3$He/$^4$He ratio of $(1.40 \pm 0.03) \times 10^{-6}$ irrespective of latitude, longitude and elevation (MAMyrin et al., 1970). Therefore, atmospheric air is regarded as an ideal standard for samples with lower $^3$He/$^4$He ratios. One pipet of Tokyo air corresponding to about 1 cc STP was introduced into the purification line. Purified He and Ne fractions were measured by the mass spectrometer. A typical mass spectrum of $^3$He and $^4$He in Tokyo air is shown in Fig. 2. An excellent separation between $^3$He and HD plus $^3$H was observed. Stability of the $^4$He ion beam was sufficient. The sensitivity of $^3$He was high enough to measure one-tenth of $^3$He in the air, which corresponds to $2 \times 10^7$ atoms $^3$He. Reproducibility of $3\%$ was obtained for beam intensities of both $^3$He and $^4$He from 7 individual runs. In the case of $^{20}$Ne, the reproducibility was $8\%$. Correction for mass discrimination in the $^3$He/$^4$He ratio was made by the following formula:

$$(^3\text{He}/^4\text{He})_{\text{corr.}} = \frac{(^3\text{He}/^4\text{He})_{\text{obs.}}}{1 + d/100}.$$ 

Beam intensities of $^3$He, $^4$He and $^{20}$Ne are summarized in Table 1 together with the observed and corrected $^3$He/$^4$He ratios. The mean value of the corrected $^3$He/$^4$He ratio in Tokyo air is $(1.43 \pm 0.03) \times 10^{-6}$. This value is in good agreement with the critical value of $(1.399 \pm 0.013) \times 10^{-6}$ reported by MAMyrin et al. (1970).

**$^3$He/$^4$He and $^{20}$Ne/$^4$He ratios of natural gas samples**

Natural gas samples were collected
$^{3}$He/$^{4}$He ratios of methane-rich natural gases

Table 1. $^{3}$He/$^{4}$He ratio in Tokyo air

<table>
<thead>
<tr>
<th>No.</th>
<th>$^{3}$He(multi)</th>
<th>$^{4}$He(direct)</th>
<th>($^{3}$He/$^{4}$He)$_{obs}$</th>
<th>($^{3}$He/$^{4}$He)$_{corr}$</th>
<th>$^{20}$Ne/$^{4}$He(direct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.354±0.03V</td>
<td>0.547±0.03V</td>
<td>1.08±10$^{-6}$</td>
<td>1.38±10$^{-6}$</td>
<td>0.46</td>
</tr>
<tr>
<td>2</td>
<td>0.337</td>
<td>0.501</td>
<td>1.12</td>
<td>1.43</td>
<td>0.52</td>
</tr>
<tr>
<td>3</td>
<td>0.358</td>
<td>0.525</td>
<td>1.14</td>
<td>1.46</td>
<td>0.55</td>
</tr>
<tr>
<td>4</td>
<td>0.375</td>
<td>0.549</td>
<td>1.14</td>
<td>1.46</td>
<td>0.53</td>
</tr>
<tr>
<td>5</td>
<td>0.360</td>
<td>0.549</td>
<td>1.10</td>
<td>1.41</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>0.367</td>
<td>0.551</td>
<td>1.11</td>
<td>1.42</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>0.376</td>
<td>0.560</td>
<td>1.12</td>
<td>1.43</td>
<td>0.53</td>
</tr>
<tr>
<td>av.</td>
<td>0.361±0.013</td>
<td>0.540±0.020</td>
<td>1.12±0.02</td>
<td>1.43±0.03</td>
<td>0.53±0.04</td>
</tr>
</tbody>
</table>

...in a 50-ml Pb-glass reservoir with a vacuum cock in the field. Collection was made in water either via simple transfer or displacement method.

Observed $^{3}$He/$^{4}$He and $^{20}$Ne/$^{4}$He ratios of 12 natural gas samples are shown in Table 2. The sampling sites (Fig. 3), major chemical components and He concentrations from a paper by Urabe (1982) are also listed. The $^{3}$He/$^{4}$He ratios vary significantly over a range from 7.26 × 10$^{-6}$ to 1.02 × 10$^{-7}$. The highest ratio is nearly five fold, and the lowest is less than one-tenth of the atmospheric ratio. The $^{20}$Ne/$^{4}$He ratios range from 0.010 to 0.53. There is no correlation between $^{3}$He/$^{4}$He ratios and $^{20}$Ne/$^{4}$He ratios. The range of observed $^{3}$He/$^{4}$He and $^{20}$Ne/$^{4}$He ratios for gases obtained from hot springs and mineral springs (Nos. 1-5) is in good agreement with previous values reported by NAGAO et al. (1981). The extremely low $^{3}$He/$^{4}$He ratios for two gases from water wells and five fuel gases from gas fields in the southern Kanto district are reported first in this study.

Based on the observed $^{3}$He/$^{4}$He ratios, the CH$_4$-rich gas samples in this study can tentatively be grouped into two types as follows:

1. Type 1 ($^{3}$He/$^{4}$He $\geq$ 1.43 × 10$^{-6}$): The $^{3}$He/$^{4}$He ratios of the Type 1 gases are significantly higher than the atmospheric ratio. Sample Nos. 1 - 5 are bubble gases from hot springs and mineral springs in various basins located in inland areas. The CH$_4$ content varies from a maximum value of 76% (No. 3) to a minimum of 24% (No. 1). Helium concentrations are markedly higher than that of the atmosphere, except for No. 2.

2. Type 2 ($^{3}$He/$^{4}$He < 1.43 × 10$^{-6}$): The $^{3}$He/$^{4}$He ratios of the Type 2 gases are apparently lower than that of the atmosphere. Sample Nos. 6 - 10 are fuel gases from gas fields in the southern Kanto district, where large-scale artificial pumping of groundwater has been carried out to obtain fuel gas in the area. The discharging rates of gases are greater than 5,000 m$^3$/d. These samples are characterized by high concentrations of CH$_4$ up to more than 90% and low He content, less than one-tenth of the atmospheric content.

Sample Nos. 11 and 12 are bubble gases from the Sea of Japan.
### Table 2. $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^4\text{He}$ ratios of 12 CH$_4$-rich natural gases in Japan

<table>
<thead>
<tr>
<th>No.</th>
<th>Code</th>
<th>Name, Location</th>
<th>Depth (m)</th>
<th>Temperature (°C)</th>
<th>CH$_4$ (%)</th>
<th>N$_2$ (%)</th>
<th>CO$_2$ (%)</th>
<th>He (ppm)</th>
<th>$^3\text{He}/^4\text{He}$ (x 10$^{-2}$)</th>
<th>$^{20}\text{Ne}/^4\text{He}$ (x 10$^{-2}$)</th>
<th>Calculated ratios</th>
<th>Heat flow#$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SGE</td>
<td>Sagae, Yamagata</td>
<td>–</td>
<td>46</td>
<td>24</td>
<td>63</td>
<td>2.0</td>
<td>100</td>
<td>72.6 ±0.4</td>
<td>50</td>
<td>54.9</td>
<td>42.8</td>
</tr>
<tr>
<td>2</td>
<td>KZW</td>
<td>Kazawa, Gunma</td>
<td>$^$</td>
<td>36</td>
<td>52</td>
<td>13</td>
<td>37</td>
<td>0.9</td>
<td>43.6 ±0.7</td>
<td>530</td>
<td>31.1</td>
<td>51.5</td>
</tr>
<tr>
<td>3</td>
<td>NNB</td>
<td>Nunobiki, Nagano</td>
<td>580</td>
<td>36</td>
<td>76</td>
<td>19</td>
<td>&lt;0.1</td>
<td>25</td>
<td>49.7 ±2.2</td>
<td>82</td>
<td>37.2</td>
<td>59.6</td>
</tr>
<tr>
<td>4</td>
<td>BWK</td>
<td>Biwako, Shiga</td>
<td>934</td>
<td>35</td>
<td>72</td>
<td>22</td>
<td>3.0</td>
<td>150</td>
<td>18.2 ±1.0</td>
<td>22</td>
<td>13.2</td>
<td>85.4</td>
</tr>
<tr>
<td>5</td>
<td>SKN</td>
<td>Shikano, Hyogo</td>
<td>$^$</td>
<td>11</td>
<td>31</td>
<td>63</td>
<td>&lt;0.1</td>
<td>1200</td>
<td>16.6 ±0.3</td>
<td>9.4</td>
<td>11.7</td>
<td>86.9</td>
</tr>
<tr>
<td><strong>Type 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NRS</td>
<td>Narashino, Chiba</td>
<td>1700</td>
<td>–</td>
<td>99</td>
<td>0.14</td>
<td>1.5</td>
<td>&lt;0.5</td>
<td>2.13±0.06</td>
<td>20</td>
<td>0.8</td>
<td>98.4</td>
</tr>
<tr>
<td>7</td>
<td>YKS</td>
<td>Yokoshiha, Chiba</td>
<td>1224</td>
<td>–</td>
<td>90</td>
<td>0.66</td>
<td>3.2</td>
<td>1.1</td>
<td>3.49±0.11</td>
<td>71</td>
<td>1.6</td>
<td>95.4</td>
</tr>
<tr>
<td>8</td>
<td>SRK</td>
<td>Shirako, Chiba</td>
<td>493</td>
<td>–</td>
<td>99</td>
<td>0.32</td>
<td>0.72</td>
<td>0.68</td>
<td>3.10±0.05</td>
<td>210</td>
<td>0.9</td>
<td>91.7</td>
</tr>
<tr>
<td>9</td>
<td>CNN</td>
<td>Chonan, Chiba</td>
<td>$^$</td>
<td>&lt;20</td>
<td>98</td>
<td>2.2</td>
<td>0.26</td>
<td>&lt;0.5</td>
<td>2.21±0.10</td>
<td>240</td>
<td>0.2</td>
<td>91.5</td>
</tr>
<tr>
<td>10</td>
<td>HIW</td>
<td>Heiwajima, Tokyo</td>
<td>900</td>
<td>36</td>
<td>96</td>
<td>1.1</td>
<td>1.2</td>
<td>&lt;0.5</td>
<td>1.37±0.10</td>
<td>10</td>
<td>2.5</td>
<td>98.7</td>
</tr>
<tr>
<td>11</td>
<td>NRH</td>
<td>Naraha, Fukushima</td>
<td>200</td>
<td>17</td>
<td>61</td>
<td>34</td>
<td>0.14</td>
<td>140</td>
<td>3.80±0.10</td>
<td>30</td>
<td>2.1</td>
<td>96.2</td>
</tr>
<tr>
<td>12</td>
<td>OMZ</td>
<td>Omaezaki, Shizuoka</td>
<td>100</td>
<td>19</td>
<td>94</td>
<td>11</td>
<td>0.82</td>
<td>6.9</td>
<td>1.02±0.04</td>
<td>150</td>
<td>0.0</td>
<td>95.0</td>
</tr>
</tbody>
</table>

$^*$: Data from URABE (1982).

$^\pm$: 1σ of statistical error.

$^\$: Gushing out.

#: Heat flow data from

(1) YOSHII (1979).

(2) NAKAMURA and WAKITA (1982).

(3) MATSUBARA and FUJI (1979).
from water wells with depths of 200 and 100 m drilled for the purpose of earthquake prediction study. The wells are separately located on the coast of the Pacific Ocean, one in the eastern part of Fukushima Prefecture and the other at the Omaezaki Point, Tokai district. The surficial geology of both areas is of sandstone and mudstone of Tertiary and Quaternary sediments. Discharging rates of gases are extremely small, less than 1 cc/min. The He contents of these gases, particularly No. 11, are significantly high as compared with the atmosphere. Both sites are in a sense related to CH4-rich gas fields. In the area about 60 km southwest of the site Naraha (No. 11), Joban coal field is widely developed and the fuel gas was being used. In the area next to the Omaezaki Point (No. 12), the presence of a small scale gas field (Yaizu gas field) is known.

Origin of He in natural gases In general, He in natural gases is composed of three components: atmospheric He, crustal or radiogenic He and primordial He derived from the upper mantle. We try to estimate the mixing ratio of these components on the basis of the observed $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^4\text{He}$ ratios.

The atmospheric ($^3\text{He}/^4\text{He})_a$ and ($^{20}\text{Ne}/^4\text{He})_a$ ratios are $1.4 \times 10^{-6}$ and 3.15, respectively. If the following assumptions are valid, the mixing ratios of the respective three components can be calculated: 1) changes in the $^{20}\text{Ne}/^4\text{He}$ ratio due to fractionation effects such as solubility difference between He and Ne in water and partitioning of He and Ne in various minerals are negligibly small; 2) isotopic ratios of the upper mantle-derived He and Ne, ($^3\text{He}/^4\text{He})_m$ and ($^{20}\text{Ne}/^4\text{He})_m$, are $1.3 \times 10^{-5}$ and $2 \times 10^{-4}$, respectively; 3) the crustal or radiogenic ($^3\text{He}/^4\text{He})_c$ and ($^{20}\text{Ne}/^4\text{He})_c$ are $1.0 \times 10^{-7}$ and lower than $1 \times 10^{-8}$, respectively. In the above assumptions, values for the upper mantle and for the crust are derived from data for MOR-type samples (Lupton and Craig, 1975; Craig and Lupton, 1976, and Rison, 1980) and the calculation of Morrison and Pine (1955), respectively.

When He and Ne in natural gas samples are composed of atmospheric (A), crustal (C) and upper mantle (M) components, the following equations are derived:

$$\frac{^3\text{He}}{^4\text{He}}_s = \left(\frac{^3\text{He}}{^4\text{He}}_m \times M + \frac{^3\text{He}}{^4\text{He}}_c \times C + \frac{^3\text{He}}{^4\text{He}}_a \times A\right) \times C + \left(\frac{^3\text{He}}{^4\text{He}}_m \times M + \frac{^3\text{He}}{^4\text{He}}_c \times C + \frac{^3\text{He}}{^4\text{He}}_a \times A\right) \times A$$

$$M + C + A = 1$$

where subscript s represents sample. The calculated mixing ratios for each component air, the upper mantle and the crust are listed in Table 2. A similar approach of estimating the mixing ratios of three components in natural gases was made by Kamenskiy et al. (1976).

Type 1: For CH4-rich natural gases from hot springs and mineral springs, the apparent contributions of the upper mantle-derived He are as large as up to 55%. Sample No. 1 (Sagae hot springs in the Yamagata basin, Tohoku district) has the maximum value of 54.9%. A significant increment of the upper mantle-derived He may be closely related to the geothermal activity of the area. The volcanic front of NE Japan is passing near the basin, and many hot springs at high temperature, such as Higashine, Kaminoyama, Tendo and others, are distributed in the basin nearby. Samples Nos. 2 and 3 show 31.1 and 37.2% additions of the upper mantle component, respectively. The samples were collected at hot springs near and in the Ueda basin, Chubu district. The basin is located on the volcanic front and is surrounded by several active volcanos such as Mts. Asama and Kusatsu-Shirane. The large contribution of the upper mantle He component in these samples may be attributed to the magmatic activity. Sample No. 4 was bubble gas from a 1,000 m well on the east coast of Lake Biwa, Omi basin. Sample No. 5 was obtained from a mineral spring at Yashiro in the Sanda basin. The rather small contribution of the upper mantle He component (that is, about 10%) in these samples may reflect the tectonic structure of the area, such as subsiding movements.

Type 2: The contribution of the upper mantle He in type 2 gases is extremely low ranging from 0 to 2.5%. Most of the He is radio-
genic or of crustal origin. The radiogenic origin of He in samples from the southern Kanto gas field has also been suggested by Sugisaki et al., (1963). Significant contamination of the air component may be due to gas sampling by pumping.

Polyak et al. (1979) reported that the regional variations in $^{3}\text{He}/^{4}\text{He}$ ratios in terrestrial gases in USSR coincide with those in heat flow. An overall similarity is also observed for CH$_4$-rich gas in Japan (Table 2), although a complete comparison between $^{3}\text{He}/^{4}\text{He}$ ratios and HF data is not attained because of scarceness of the HF data on land. According to a compilation by Yoshii (1979), heat flow values in areas facing the Pacific Ocean are generally as low as 1 HFU (42 mW/m$^2$), while heat flow values in the area along the inner zone of Honshu are higher than 2 HFU (84 mW/m$^2$). In volcanic areas their values are enormously high. Precise comparison has to be made after accumulation of both kinds of data in Japan.

In conclusion, the observed $^{3}\text{He}/^{4}\text{He}$ ratios of CH$_4$-rich natural gases in Japan vary from $7.26 \times 10^{-6}$ to $1.02 \times 10^{-7}$. Natural gas samples are classified into two types: Types 1 and 2, based on their $^{3}\text{He}/^{4}\text{He}$ ratios. Contribution of the upper mantle-derived He is estimated using $^{3}\text{He}/^{4}\text{He}$ and $^{20}\text{Ne}/^{4}\text{He}$ ratios in samples. Type 1 gases are highly enriched in the upper mantle He, whereas type 2 gases are depleted. In order to discuss the genetic relation of natural gases and their production mechanism, isotopic data on $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ and data for heavier hydrocarbon would be useful.

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