Isotopic compositions of rare gases in the Matsushiro earthquake fault region

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Elemental and isotopic compositions of rare gases in gas samples from “Helium spots” and CO2-spring in the fault zone formed by the Matsushiro earthquake swarms, reported by WAKITA et al. (1978), have been analyzed mass spectrometrically.

Isotopic compositions of rare gases were atmospheric except for 3He/4He and 40Ar/36Ar ratios. 3He/4He ratios were (9.12 ± 0.58) X 10~ and (9.10 ± 0.69) X 10~ for “Helium spots” and CO2-spring, respectively.

Rare gas elemental abundance patterns for both samples were similar to a pattern produced by the dissolution equilibrium of atmospheric rare gases in water. The origin of rare gases is discussed.

The 3He/4He ratio found in the fault zone suggests that the systematic observation of 3He/4He ratio may be useful for the detection of precursory phenomena of an earthquake.

INTRODUCTION

WAKITA et al. (1978) reported “Helium spots” along the fault zone formed by the Matsushiro earthquake swarms, where a significant amount of He up to 350ppm with six times higher 3He/4He ratio than that in the atmosphere has been out-gassing. The earthquake swarms occurred during the period between 1965 and 1967 in the Matsushiro area, central Japan (36°33'N, 138°13'E), and more than 60,000 felt earthquakes were counted. The maximum magnitude of the earthquakes was 5.3 on the Richter scale and the total energy released was equivalent to an M6.3 earthquake. Most extensive field studies have been continued since the initial stage (Research on the Matsushiro Earthquakes (1)-(6)). Various physical and geochemical phenomena have been observed. These include changes in seismic activities, in geomagnetic field and in gravity; crustal deformation, such as tilt and uplift; formation of fault; heavy outflow of groundwater and others. A more comprehensive overview of the swarms is obtained from a report by OHTAKE (1976).

Above all, the most peculiar phenomenon was the gushing of a significant amount of groundwater during the earthquake activity. Chemical composition of the water was quite different from the local surface water, including hot springs. The gushing water contained chlorine and calcium ions of several thousands ppm and was supersaturated with carbon dioxide (NOGUCHI et al., 1969; YOSHIOKA et al., 1970). The area of the groundwater gushing was con-
fined to a narrow zone along the fault and several CO₂-springs were formed in it at this stage. A total volume of the released water was estimated to be approximately 10⁶ m³ (Iijima, 1969). There seems to exist a correlation between the migration of groundwater and the progression of seismic activities. In other words, the depth of the foci moved upward from the initial position of about 4 ~ 5 km to near the ground surface (Ohtake and Hamada, 1975). After the termination of the gushing of groundwater on a large scale, the seismic activities declined significantly. Apparently the gushing of groundwater played an important role in the occurrence of the earthquake swarms. Though various explanations have been already presented (Nakamura, 1971; Nur, 1974; Kisslinger, 1975; Stuart and Johnston, 1975), the complete understanding of the cause for the swarms remains unsolved.

Recently, Wakita et al. (1978) proposed a diapiric model based on the geochemical field studies and the detection of He with high ³He/⁴He ratio in the out-flowing gases. According to their model, the formation of “Helium spots” and the occurrence of earthquakes are interpreted as a result of a diapiric uprise of an andesitic magma originated from the upper mantle.

Recent isotopic analyses of He in volcanic gases (Mamyrin et al., 1969; Kamenskiy et al., 1976; Craig et al., 1978a; Craig et al., 1978b), in oceanic water (Clarke et al., 1969; Clarke et al., 1970; Lupton, 1976; Lupton et al., 1977a; Lupton et al., 1977b), in oceanic basalts (Krylov et al., 1974; Lupton and Craig, 1975; Craig and Lupton, 1976), and in mantle derived minerals (Tolstikhin et al., 1974; Takaoka and Ozima, 1978; Takaoka and Ozima, 1978; Kaneoka et al., 1978; Saito et al., 1978) have shown high ³He/⁴He ratios relative to the ratio of atmospheric He. The high ³He/⁴He ratio has been interpreted as the evidence that the primordial He is still emanating from the deep interior of the earth (Mamyrin et al., 1969).

The Japanese Island Arc is located on a subducting zone of the oceanic plate. Craig et al. (1978a) first detected a high ³He/⁴He ratio, about six times the atmospheric ratio, in a fumarolic gas from the Hakone volcano in Japan. Wakita et al. (1978) and Nagao et al. (1979) also detected high ³He/⁴He ratios in gas samples collected in the region of an earthquake fault formed by the Matsushiro earthquake swarms and in the Nigorikawa geothermal area, Hokkaido, respectively.

Here, we report the analysis of elemental and isotopic compositions of rare gases in the gas samples collected at “Helium spots” and near-by CO₂-spring ten years after the Matsushiro earthquake swarms. The detection of mantle He in these samples suggests that ³He/⁴He ratio in the fault zone may be changed according to the release of mantle and crustal He and that the systematic observation of ³He/⁴He ratio may be useful for the detection of earthquake precursors.

**EXPERIMENTAL**

Gas samples 770613-1 and 770613-3 were collected at “Helium spots” and a CO₂-spring on June 13, 1977, respectively. Figure 1 shows a sketch map of sampling location. Collecting method and bulk compositions of gas samples have been reported by Wakita et al. (1978) and more in detail will be published elsewhere by Fujii et al. (in preparation).

For rare gas analyses, the gas samples were divided into borosilicate glass ampoules with breakable seals and attached to a sample holder of the gas handling system. The technical details in mass spectrometry were essentially the same as described by Takaoka (1976) and Nagao et al. (1979). A change in ³He/⁴He ratio caused by permeation of atmospheric He through the glass wall of sampling vessel was estimated to be negligible compared with experimental errors. The relative elemental abundances and mass discrimination coefficients for the rare gas isotopes were determined by measuring the known amount of atmospheric rare gases prepared with the same procedure as applied for samples. The mass discrimination for ³He/⁴He ratio was deter-
RESULTS AND DISCUSSION

Isotopic compositions of Ne, Kr and Xe in the samples were atmospheric within the experimental error. The $^{3}$He/$^{4}$He ratios were $(9.12 \pm 0.58) \times 10^{-6}$ and $(9.10 \pm 0.69) \times 10^{-6}$ for “Helium spots” and CO$_2$-spring, respectively, about 6.5 times the ratio of atmospheric He. These ratios averaged the values of additional several analyses and are in agreement with the ratios previously reported by WAKITA et al. (1978) within the experimental error.

The $^{40}$Ar/$^{36}$Ar ratios were $308 \pm 9$ and $304 \pm 8$ for “Helium spots” and CO$_2$-spring, respectively. The ratios show small excesses of radiogenic $^{40}$Ar compared with the atmospheric value of 295.5. The $^{38}$Ar/$^{36}$Ar ratios for both samples were atmospheric.

Concentrations of rare gases in the sample gases are given in Table 1. Figure 2 shows the rare gas elemental abundance patterns for the sample gases, where \( F(m) \) is defined by

\[
F(m) = \frac{(mX/36Ar)_{\text{samp}}}{(mX/36Ar)_{\text{atmosphere}}},
\]

and $mX$ represents a rare gas isotope of mass “m”. An abundance pattern which represents the atmospheric rare gases dissolved in low temperature water is also shown in Fig. 2 for comparison. Both samples are highly enriched in He relative to atmospheric air. The abundance patterns of $^{16}$Ne, $^{36}$Ar, $^{84}$Kr and $^{132}$Xe for both samples are similar to type 1 defined by OZIMA

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**Table 1. Chemical and rare gas compositions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>770613-1 (“Helium spots”)</th>
<th>770613-3 (CO$_2$-spring)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ (%)</td>
<td>80#</td>
<td>83#</td>
<td>78</td>
</tr>
<tr>
<td>CO$_2$ (%)</td>
<td>20#</td>
<td>93#</td>
<td>0.03</td>
</tr>
<tr>
<td>He (ppm)</td>
<td>350#</td>
<td>5.3#</td>
<td>5.2</td>
</tr>
<tr>
<td>$^{4}$He/$^{36}$Ar</td>
<td>0.27</td>
<td>0.24</td>
<td>0.166</td>
</tr>
<tr>
<td>$^{23}$Ne/$^{36}$Ar</td>
<td>0.031</td>
<td>0.053</td>
<td>0.524</td>
</tr>
<tr>
<td>$^{36}$Ar/$^{36}$Ar</td>
<td>0.0017</td>
<td>0.0049</td>
<td>0.00073</td>
</tr>
<tr>
<td>$^{3}$He/$^4$He</td>
<td>$(9.12 \pm 0.58) \times 10^{-6}$</td>
<td>$(9.10 \pm 0.69) \times 10^{-6}$</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>$^{40}$Ar/$^{36}$Ar</td>
<td>308 ± 9</td>
<td>304 ± 8</td>
<td>295.5</td>
</tr>
<tr>
<td>He/Ar</td>
<td>0.16</td>
<td>0.016</td>
<td>5.6 $\times 10^{-4}$</td>
</tr>
<tr>
<td>H$_2$/Ar</td>
<td>360</td>
<td>210</td>
<td>84</td>
</tr>
</tbody>
</table>

# WAKITA et al. (1978).
and Alexander (1976), a pattern produced by the dissolution equilibrium of atmospheric rare gases in water. A comparison between the abundance patterns for two samples shows that the CO₂-spring gas is depleted in He and Ne and enriched in Kr and Xe relative to the "Helium spots" gas.

The high He/He ratios found in the gas samples collected in the fault zone formed by the 1966 Matsushiro earthquake swarms imply that the He was not crustal He enriched in radiogenic ⁴He but mantle-derived He enriched in ³He. This result led to the model of "a diapiric magma" from the upper mantle as a cause of the earthquake swarms (Wakita et al., 1978). The model suggested that the released CO₂ gas might have been produced by a chemical reaction of hydrochloric acid from the magma with calcareous sediments in the crust. With this model, the low He concentration in the CO₂-spring gas could be attributed to dilution of He-rich magmatic gas with the CO₂ gas produced by the chemical reaction in the crust. Hence, the gas sample from "Helium spots" should be more representative of the magmatic gas composition than CO₂-spring gas.

The rare gas abundance patterns for two samples shown in Fig. 2 indicate that the CO₂-spring gas is more enriched in Kr and Xe relative to the patterns given by the "Helium spots" gas and by the solubility of atmospheric rare gases in water. The heavy rare gas enrichment in CO₂-spring gas can be understood in terms of the addition of heavy rare gases released from calcareous sediment. The heavy rare gas enrichment found in shale has been attributed to that heavy rare gases such as Kr and Xe are more adsorptive than light rare gases (Fanale and Cannon, 1971). Since shale and calcareous rock are sedimentary materials, it is expected that the heavy rare gases are also enriched in calcareous sediments. Oana (1965) noted that δ¹³C values in volcanic gases from the Japanese Islands were different from those of carbon in organic materials and in igneous rocks, and were similar to those in calcareous rocks. δ¹³C values of -1 to -3 per mil for CO₂ gas collected in the Matsushiro earthquake fault zone (Wakita et al., 1978) are also similar to those for calcareous rocks and support the origin of CO₂ and the mechanism for the heavy rare gas enrichment in the CO₂ gas sample. The abundance pattern of rare gases in calcareous rocks should be determined to examine the model for the production of CO₂ and heavy rare gas enrichment.

The abundance pattern for the "Helium spots" sample is between those for atmospheric air and the CO₂-spring gas. The N₂/Ar ratios for "Helium spots" and CO₂-spring are 360 and 210, respectively. These ratios are higher than the atmospheric value of 84. Matsuo et al. (1978) pointed out that the N₂/Ar ratio in volcanic gases from the Japanese Island Arc is higher than the atmospheric ratio, and attributed the high N₂/Ar ratio to the addition of N₂ from sedimentary materials supplied by subduc-
Isotopic composition of rare gases

The similarity of N$_2$/Ar ratios between the volcanic gases and the gas samples from Matsushiro suggests the same origin for both the volcanic gases and the gases from Matsushiro. The abundance patterns of rare gases for the Showa-shinzan and the Usu volcanoes (NAGAO et al., in preparation) are similar to those for “Helium spots” and CO$_2$-spring gases.

In spite of the difference in the chemical composition between the two samples, the $^3$He/$^4$He ratios were identical. This means the same origin of He in both samples and the negligible atmospheric and crustal He contamination despite an admixing of CO$_2$ gas produced by the chemical reaction mentioned already.

The presence of mantle He in the gas emanation first discovered at the earthquake fault in Matsushiro strongly suggests that the He isotopic composition may be a useful measure for the detection of earthquake precursors. The detection of earthquake precursors is not only interesting in a scientific aspect, but also important for the earthquake prediction. The earthquake prediction is one of the present-day social requisitions to science. Various geophysical and geochemical methods are applied to the detection of earthquake precursors. Methods for the detection of earthquake precursors, however, have not been established to date because of the lack of sufficient knowledge about the occurrence of an earthquake, and because of the lack of sufficient observations of phenomena accompanied by the earthquakes. Geochemical methods as well as geophysical ones are considered to be useful for the detection of precursory phenomena of an earthquake. For example, the precursory changes of Rn and He concentrations in groundwater have been reported (GORBUSHINA et al., 1971; SULTAN-KHODJAEV, 1979). SUGISAKI (1978) claimed the change of He/Ar and N$_2$/Ar ratios in gas samples collected on a fault prior to some earthquakes, and showed that the continual observation of these ratios is useful for the detection of earthquake precursors.

A theoretical production ratio of radiogenic $^4$He to radiogenic $^4$Ar is about 10 in common crustal rocks, which is $10^4$ times higher than the atmospheric He/Ar ratio (SUGISAKI, 1978). Based on the production ratio, SUGISAKI (1978) interpreted the observed increase of He/Ar and N$_2$/Ar ratios prior to the earthquakes as an admixing of lithospheric gases expelled by deformation of crustal rocks to the out-flowing gases. However, the He/Ar ratios more than 30 times the atmospheric ratio of $5.6 \times 10^{-4}$ were also observed in the gas samples “Helium spots” and CO$_2$-spring, and the $^3$He/$^4$He ratios in these samples are 6.5 times the atmospheric ratio. He with the high $^3$He/$^4$He ratio is not the crustal but the mantle He enriched in the primordial He. Therefore, only the high He/Ar ratio is not a sufficient condition to identify the origin of He and Ar.

The depth of the foci of the Matsushiro earthquake swarms was about 4~5 km as noted earlier. In spite of the shallow foci, He with high $^3$He/$^4$He ratio was emitted through the out-flowing gases in the fault zone. Helium observed in these gases should have been derived from deep interior of the earth such as the upper mantle. The mantle He is also continuously emitted through naturally out-flowing gases obtained from various parts of Japan (CRAIG et al., 1978a; NAGAO et al., 1979; NAGAO et al., in preparation). In contrast to the mantle He, the $^3$He/$^4$He ratio of radiogenic He accumulated in crustal rocks is much lower than the atmospheric value. Because of the great mobility of He in the crust, release of He from crustal rocks is sensitive to stress field causing crustal deformation. Hence He in naturally out-flowing gas may not be stable with respect to the mixing ratio between mantle He and radiogenic He. Since the difference in $^3$He/$^4$He ratio between mantle He and radiogenic He is large, a large change in $^3$He/$^4$He ratio corresponding to stress change in the deeper part of the earth is expected from out-flowing gases before an earthquake. Hence the $^3$He/$^4$He ratio may be a sensitive measure to detect precursory phenomena of an earthquake. It is, however, difficult to estimate the contribution of radiogenic He released by
deformation of crustal rocks prior to an earthquake to the mantle He emanation.

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