NOTE

Variations in N_2/Ar and He/Ar ratios of gases from some volcanic areas in Northeastern Japan

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Fumarolic and geothermal well gases from several volcanic areas in Northeastern Japan have been examined for the N_2/Ar and He/Ar ratios. The N_2/Ar and He/Ar ratios of the gas samples are 40 to 2,000 and 10^{-3} to 1, respectively, higher than those of the atmospheric air dissolved in groundwaters. The N_2/Ar ratio becomes larger with increasing ratio of He to Ar. The data also show that nitrogen and helium in gases increase with increasing contribution of magmatic gas to the discharges and with decreasing contribution of groundwater. This suggests that the observed volcanic and geothermal gases may be mixtures of magmatic gas of uniform N_2/Ar ($\approx 4,000$) and He/Ar ratios (≈ 2) and local meteoric waters.

INTRODUCTION

Nitrogen, argon and helium are generally found in volcanic gases. Fumarolic gases from island arc volcanoes have higher N_2/Ar ratios than do atmospheric air and gases from Hawaiian hot spot volcanoes and Nyiragong and Erta' Ale volcanoes in Africa (Matsuo *et al.*, 1978). This suggests that the nitrogen released from organic matter in sediments may mix with volcanic gases from the depths of island arc volcanoes. Most of helium and argon are radiogenic 4He and ^{40}Ar derived from U, Th and ^{40}K . The ratio of He/Ar from deep-seated gases in lithosphere ranges from 1 to 6, and is higher than that of atmospheric value of 5.6×10^{-4} (Mazor, 1977).

The N_2/Ar ratio of high-temperature gases from the A-1 fumarole of the Showashinzan volcano, Hokkaido, Japan was 2,200, 10 years after its formation, and has been decreasing yearly, approaching the value of air dissolved in groundwater (40) (Matsuo *et al.*, 1978; Mizutani and Sugiura, 1982). This fact shows the increase in the contribution of groundwater to the primary volcanic gases with time. Nagao *et al.*, (1980) also obtained the same conclusion from their study on the rare gas composition ($^3He/^4He$, $^4He/^{20}Ne$) of the fumarolic gases at Showashinzan. The number of data on the N_2/Ar and

He/Ar ratios of gases from island arc andesitic volcanoes, however, are still insufficient to discuss the origin of volcanic and geothermal gases. In this study gases from several active volcanic areas in Northeastern Japan have been examined for the N_2/Ar and He/Ar ratios.

EXPERIMENTAL

Sampling

Volcanic gas samples were collected from fumaroles of the Zaō, Azuma-Issaikyō, Nasu, and Kusatsu-Shirane volcanoes from 1980 to 1983. Steam samples were also collected from wells and fumaroles in the Matsukawa, Tainoue and Onikōbe geothermal areas from 1980 to 1983. The sample localities are shown in Fig. 1. The sampling method used was a modification of that of Ozawa (1966). The temperature of fumaroles was measured with a mercury thermometer.

Analytical method

Carbon dioxide was determined by the micro-diffusion method (Ozawa, 1966). Nitrogen, argon and helium were analyzed by the Hitachi model 263 gas chromatograph combined with a preamplifier, Ohkura model AM 1001 B, on a 5m molecular sieve 5 A column with

Fig. 1. Locations of volcanoes and geothermal systems studied. Dashed line indicates the volcanic front in East Japan.

oxygen carrier gas. In this way He separated from Ne was determined. On the basis of the O_2 content determined by the gas chromatograph, using argon carrier gas, corrections were made for the air contaminated into gas samples. Error of the determination was about 5% for He and less than 2% for the others. The analytical method of other chemical components was already reported in Kiyosu (1983).

RESULTS AND DISCUSSION

The analytical results of gas samples from volcanic and geothermal areas are listed in Table 1. These samples are rich in CO_2 and H_2S , and HCl is not found except for Nasu (Kiyosu, 1983). Volcanic gases from the Japanese island arc are divided into two types; high-temperature type ($\geq 400^\circ C$) consisting mainly of H_2O , CO_2 , SO_2 , HCl and H_2S , and low-temperature type ($< 400^\circ C$) which is poor in hydrogen chloride, although rich in CO_2 and H_2S (Iwasaki *et al.*, 1966). The gases studied belong to the low-temperature type according to their chemical composition.

N_2/Ar and He/Ar ratios of gases

Figure 2 shows N_2/Ar ratios for each sample,

Fig. 2

Table 1. Chemical analyses of gases from fumaroles and geothermal wells in Northeastern Japan

Location	Date	Outlet temp. (°C)	CO ₂ (vol.%)	N ₂ (ppm)	Ar (ppm)	He	N ₂ /Ar	He/Ar
<i>Volcanic areas</i>								
F-1, Tamagawa ^a	8/1979	101	1.15	131	0.55	0.14	238	0.25
F-2	8/1979	102	2.75	275	0.90	0.28	306	0.31
F-3	8/1979	98	0.821	63.1	0.30	0.068	210	0.23
F-4	8/1979	99	0.403	62.7	1.2	0.011	52.3	0.0092
F-1, Zaō	6/1980	94	2.51	3976	25	6.1	159	0.244
F-1	10/1980	96	1.98	883	4.0	2.0	221	0.50
F-1	10/1982	96	1.66	238	0.92	—	259	—
F-3 ^b , Issaikyō	10/1980	87	86.6	5.7	0.02	—	285	—
F-1	5/1981	94	2.30	538	1.73	0.30	311	0.173
F-2	10/1982	93	2.59	599	1.50	0.71	399	0.473
F-1	7/1983	95	1.76	328	1.42	0.23	231	0.162
F-2	7/1983	91	3.02	519	2.54	0.38	204	0.150
F-1, Ōana, Nasu	5/1981	110	0.244	564	4.6	0.1	123	0.022
F-1	10/1981	112	0.210	81.5	0.65	0.039	125	0.06
F-1	10/1981	113	0.213	55.3	0.26	0.013	213	0.05
F-1	5/1982	113	0.199	195	1.59	0.048	123	0.030
F-1	5/1983	113	0.214	41.9	0.313	0.010	134	0.032
F-1	6/1983	114	0.288	43.9	0.387	0.011	113	0.029
F-2	5/1983	98	0.455	109	0.973	0.023	112	0.024
F-1, Mugen, Nasu	5/1981	149	0.298	169	3.15	0.007	53.3	0.0022
F-2	10/1981	169	0.156	47.3	0.6	0.018	78.8	0.03
F-1	10/1981	154	0.243	38.8	0.28	0.014	139	0.050
F-2	5/1983	143	0.316	86.3	0.759	0.0253	114	0.033
Kusatsu-Shirane	8/1980	98	1.35	4391	28	1.1	157	0.0393
Sesshōgawara, Kusatsu	8/1980	95	3.55	2250	16	0.82	141	0.051
Yubatake, Kusatsu ^c	8/1980	64	49.6	47.3	0.87	14	54.4	0.0016
Karabuki, Manza	8/1980	96	0.052	391	5.2	0.069	75.2	0.013
	11/1981	94	0.146	39	0.36	0.012	108	0.033
<i>Geothermal areas</i>								
Well 2, Matsukawa	7/1983	—	0.177	29.0	0.49	0.009	59.2	0.0184
Well 5, Matsukawa	7/1983	—	0.174	57.1	0.63	0.017	90.6	0.0217
F-1, Takinoue	7/1983	99	0.044	32.4	0.72	0.0058	45.0	0.0081
F-2, Takinoue	7/1983	98	0.0326	39.0	0.91	0.0063	42.9	0.0069
F-3, Takinoue	7/1983	98	0.0143	3.9	0.078	0.0003	50	0.0038
Well 127, Onikōbe	10/1983	—	0.0504	154	1.2	0.0033	128	0.0028
Well 128, Onikōbe	10/1983	—	0.0644	110	2.0	0.0031	55	0.0016
Well 129, Onikōbe	10/1983	—	0.374	61.6	0.26	0.019	237	0.073
Katayama, Onikōbe	10/1983	98	0.308	143	1.9	0.021	72.3	0.011
Okunoin, Onikōbe	10/1983	98	0.141	49.7	0.55	0.0086	90.4	0.016
Arayu, Onikōbe	8/1983	96	73.2	4.5	0.11	0.85	40.9	0.00077

a : Kurahashi (1982). b, c and d : excluding H₂O, N₂ and Ar contents are vol.%. F : Fumarole.

together with those for high-temperature volcanic gases from Showashinzan (Mizutani and Sugiura, 1982) and Usu (Matsuo *et al.*, 1982). Except for a few data, most of volcanic gases have N₂/Ar ratios in the range from 50 to 1,000. These values are higher than that of air dissolved

in groundwater (≈ 40) and similar to those for Showashinzan and Usu. This suggests that the N₂/Ar ratio is independent of outlet temperatures. The values of N₂/Ar ratio for geothermal systems ranging from 40 to 250 agree with those for low-temperature fumaroles at Nasu and

Fig. 2. N₂/Ar ratios of gases in volcanic and geothermal areas. Volcanic area: Showashinzan, 1954–1978 (Mizutani and Sugiura, 1982); Usu, 1979 (Matsuo *et al.*, 1982); Tamagawa; Zaō; Issaikyō, 1979 (Ozawa *et al.*, 1981); Nasu; Kusatsu-Shirane. Geothermal area: Matsukawa; Takinoue; Onikōbe. Large and small circles indicate fumarolic and well gases, respectively.

Fig. 3. He/Ar ratios of volcanic and well gases. Volcanic area : Showashinzan, 1958 (Nagao *et al.*, 1980); Usu, 1979 (Matsuo *et al.*, 1982); Tamagawa; Zaō; Issaikyō, 1979 (Ozawa *et al.*, 1981); Nasu; Kusatsu-Shirane. Geothermal area : Matsukawa; Takinoue; Onikōbe. Large and small circles represent fumarolic and well gases, respectively.

Kusatsu-Shirane.

As shown in Fig. 3, He/Ar ratios of volcanic and geothermal gases range from 10^{-3} to 1 and are much higher than that of air dissolved in groundwater ($\approx 2 \times 10^{-4}$). This indicates that lithospheric helium is concentrated in volcanic and geothermal gases.

Variations in the N_2/Ar and He/Ar ratios from each area may be ascribed to the mixing of rising primary volcanic gases with groundwater in the depths (Matsuo *et al.*, 1978; Mizutani and Sugiura, 1982; Yoshida, 1984) or the liquid-vapor separation near the ground surface (Mazor, 1977, 1979; Mazor and Truesdell, 1984).

Relationships among N_2/Ar , He/Ar and CO_2/N_2 ratios

N_2/Ar ratios of the gas samples normalized to that of air are plotted against the He/Ar ratios likewise normalized, as shown in Fig. 4. The N_2/Ar ratio tends to become higher with increasing ratio of He/Ar. This implies that nitrogen and helium in the volcanic and geothermal gases

may have been derived from the same source. In Fig. 4, the mixing line represents the composition of mixtures of magmatic gases from Showashinzan with high N_2/Ar and He/Ar ratios and air dissolved in groundwater. All the data fall nearly on the mixing line, except for some samples whose He/Ar ratios are slightly higher than the others. This suggests that gases in Northeastern Japan may have resulted from mixing of magmatic gases, such as those of Showashinzan, with groundwater.

In most of them, carbon dioxide constitutes a large proportion of the gases exclusive of H_2O . Figure 5 is a correlation diagram of N_2/Ar and CO_2/N_2 ratios normalized to those of air. It can be noted that the higher the N_2/Ar ratio in volcanic and geothermal gases, the higher the CO_2/N_2 ratio. This suggests that carbon dioxide and nitrogen of the gases are of the same origin, and that the gases may be mixture of magmatic gases and groundwater. The observed values of CO_2/N_2 ratios in some volcanic and geothermal areas, however, are distributed below the mixing

Fig. 4. Relationship between N_2/Ar and He/Ar ratios normalized to those of air.

$(ratio)_x$ represents the ratio of the sample. Solid line : See text. $\oplus$: Showashinzan (Mizutani and Sugiura, 1982; Nagao et al., 1980). $\ominus$: Usu (Matsuo et al., 1982). $\oplus$: Tamagawa. $\bullet$: Zaō. $\odot$: Issaikyō. $\circ$: Nasu. $\circ$: Kusatsu-Shirane. $\ominus$: Matsukawa. $\ominus$: Takinoue. $\bullet$: Onikōbe. $\blacklozenge$: Magmatic gas. $\otimes$: Air dissolved in water $10^\circ C$.

line (Fig. 5). These gases may contain carbon dioxide derived from an extraneous carbon source such as calcareous rocks or organic sediments. The origin of carbon dioxide in volcanic and geothermal gases may be clarified when a systematic carbon isotope study is done.

Origin of gases

Several researchers have pointed out the importance of meteoric water contamination into volcanic gases (e.g., White and Waring, 1963; Mizutani, 1962, 1978; Mizutani and Sugiura, 1982). Permeation of groundwater is evident for some particular volcanoes, showing temperature variations related to rain fall (Stoiber and Rose, 1970).

Fig. 5. Plot of N_2/Ar ratios for gases versus CO_2/N_2 ratios normalized to air values.

Solid line : See text. $\oplus$: Showashinzan (Mizutani and Sugiura, 1982). $\ominus$: Usu (Matsuo et al., 1982). $\oplus$: Tamagawa. $\bullet$: Zaō. $\odot$: Issaikyō. $\circ$: Nasu. $\circ$: Kusatsu-Shirane. $\ominus$: Matsukawa. $\ominus$: Takinoue. $\bullet$: Onikōbe. $\blacklozenge$: Magmatic gas. $\otimes$: Air dissolved in water at $10^\circ C$.

In order to estimate the magmatic fraction in the gases, the following assumption has been made:

(1) D/H , $^{18}O/^{16}O$, N_2/Ar and He/Ar ratios of magmatic gases are uniform in Northeastern Japan.

(2) Groundwater is equilibrated with atmospheric air at $10^\circ C$.

On the basis of δD and $\delta^{18}O$ values of fumarolic condensates, Mizutani (1978) suggested that the fumarolic condensates from the Showashinzan volcano are mixtures of magmatic water, having the isotopic composition of -32‰ (SMOW) in δD and $+7.4\text{‰}$ (SMOW) in $\delta^{18}O$, and the local surface water as follows;

$$\delta_o = X\delta_M + (1 - X)\delta_m \quad (1)$$

where δ_o , δ_M and δ_m represent the δD and $\delta^{18}O$ values of the observed volcanic gases, magmatic gases and meteoric water, respectively. X indicates the fraction of magmatic gases.

Similarly,

$$(N_2/Ar)_o = X (N_2/Ar)_M + (1 - X) (N_2/Ar)_m \quad (1)$$

$$(He/Ar)_o = X (He/Ar)_M + (1 - X) (He/Ar)_m \quad (2)$$

where o , M , m and X are the same as eq. (1).

By using eqs. (1), (2) and (3), the N_2/Ar and He/Ar ratios of magmatic gases in Showashinzan can be estimated as follows. The value of X in 1954 was obtained from eq. (1), based on the data of Mizutani (1978). With the value of X thus obtained and the observed N_2/Ar ratio of volcanic gases in 1954 (Mizutani and Sugiura, 1982), eq. (2) gives us the N_2/Ar ratio of magmatic gases of 4250. This value is consistent with the observed values (2,000 to 4,000) of N_2/Ar ratio in sediments reported by Matsuo *et al.* (1978). Similarly, the He/Ar ratio of primary magmatic gases of 2.1 was estimated from eq. (3) with the value of X obtained from eq. (2) and the data for the 1958 sample from the Showashinzan volcano (Nagao *et al.*, 1980). This value is also in agreement with the ratio of He/Ar ranging from 1 to 6 in the thermal waters of aquifer rocks (Mazor, 1977). When these magmatic gases, with such a high N_2/Ar and Hg/Ar ratios, are cooled and/or condensed by groundwater near the ground surface, low-temperature fumarolic gases, geothermal systems and hot springs in Northeastern Japan may be formed. In Fig. 4, the fraction of magmatic gases is plotted on the mixing line, and high-temperature volcanic gases, low-temperature volcanic gases, and geothermal and hot spring gases are found to be in the range of 0.5 ~ 0.1, 0.1 ~ 0.01 and 0.01 ~ 0.001, respectively. Similar results are obtained from the relationship between the N_2/Ar and CO_2/N_2 ratios (Fig. 5).

On the basis of the isotopic composition of water, Kiyosu (1985) also concluded that some

Table 2. Comparison of N_2/Ar ratio and δD values for fumarolic condensates from volcanic and geothermal areas in Northeastern Japan.

Location	N_2/Ar	$\delta D^*_{obs.}$ (‰)	$\delta D_{calc.}$ (‰)
Tamagawa	306	-53.3	-63.0
Zaō	259	-62.2	-65.2
Issaikyo	399	-69.7	-77.0
Nasu	213	-60.3	-66.5
Kusatsu-Shirane	157	-75.9	-77.1
Matsukawa	90.6	-72.8	-72.5
Takinoue	50	-72.5	-69.0
Onikōbe	237	-58.0	-57.1

* Kiyosu (1983, 1985). obs.: Observed
calc.: Calculated.

low-temperature volcanic condensates and acid sulfate-chloride waters in Northeastern Japan may be a mixture of magmatic water, such as the Showashinzan magmatic water, and local surface water. Based on the fraction of magmatic gas in the condensates and waters estimated from their N_2/Ar ratios, the δD values of volcanic condensates and geothermal waters in Northeastern Japan are obtained with the hydrogen isotopic compositions of the magmatic water ($\approx -32\text{‰}$) and local surface water as listed in Table 2. The δD values estimated agree well with the observed values in each volcanic area.

The value of $N_2/He \div 2,200$ for primary magmatic gases, estimated from these N_2/Ar and He/Ar ratios, is nearly consistent with the value of hot and mineral spring gases derived from pre-Tertiary rocks such as the Sanin and Abukuma granites, and Sanbagawa metamorphic rocks (e.g., Motojima *et al.*, 1966; Maki *et al.*, 1966; Inai *et al.*, 1967; Hirukawa, 1968). This suggests that most of N_2 , Ar and He in the magmatic gases may be gases released from pre-Tertiary basement rocks. The high $^3He/^4He$ ratio of magmatic gases in Showashinzan, however, indicates that much of this He is of mantle origin (Nagao *et al.*, 1980). It is therefore possible that a part of the helium measured in this study is being discharged from the mantle through these basement rocks.

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