Origin of gases and chemical equilibrium among them in steams from Matsukawa geothermal area, Northeast Japan

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Gas components contained in geothermal steams discharged from wells at the Matsukawa geothermal areas were examined geochemically. The original deep seated gases of Northeast Japan are suggested to be uniform with respect to He, Ar and N₂ and are emitted through geothermal wells and/or fumaroles after mixing in various proportions with atmospheric air dissolved in ground water.

Geothermal wells of the Matsukawa area are divided into two groups by the geological structure, of the area which controls the variation in concentrations of tritium and major gas components occurs. The influence of the geological barrier can be considered to be limited in a shallow horizon.

The correlation between gas components indicates that the reaction, $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$, is in equilibrium, but the reaction, $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$, is not in equilibrium under the condition of the Matsukawa geothermal reservoir.

INTRODUCTION

The Matsukawa geothermal area is a vapor dominated type geothermal system which is unique among geothermal systems so far explored in Japan. The first geothermal power station in Japan was completed in this area by Japan Metals and Chemicals Co., Ltd. in 1966. At present, 22MW of electricity is generated by geothermal steam discharged from eight production wells. As the geothermal steam is produced directly from zones deeper than 1,000m through a casing pipe, the contamination of organic material, shallow meteoric water and atmospheric air does not occur significantly during the passage of steam through the well.

The components of high-temperature volcanic gases have been studied from the point of view of chemical equilibrium (ELLIS, 1957; MATSUO, 1960; HEALD *et al.*, 1963; STOIBER *et al.*, 1974; GERLACH, 1979). In recent years, geothermal development has become active all over the world, and geochemical studies of geothermal systems have made a great progress (D'AMORE *et al.*, 1980; GIGGENBACH, 1980).

Moreover, rare gases in volcanic gases are studied recently in relation to the origin of gases (MATSUO *et al.*, 1978; NAGAO *et al.*, 1980; TORGERSEN *et al.*, 1982; KIYOSU, 1983a).

In the present study, an attempt is made to examine the origin of gases on the basis of the analytical results of steam discharged from geothermal wells in the Matsukawa area. In this paper, steam means the mixture of water vapor and other gas components such as CO₂, H₂S, H₂, He and so forth.

GEOLOGICAL SETTING

The Matsukawa geothermal power station is located in the Hachimantai volcanic region which is one of the most active geothermal areas in Northeast Japan (Fig. 1). Geological investigations in this area have been carried out by NAKAMURA *et al.* (1961) and SUMI (1966, 1968), and abundant geological data have been accumulated by Japan Metals and Chemicals Co., Ltd.

The basement of this region consists of the Miocene Kunimitoge, Takinoue-onsen and Yamatsuda formations, which are composed of

shale, sandstone, tuff and conglomerate, and is overlain by the Pliocene andesitic-dacitic Tamagawa welded tuff. The Tamagawa welded tuff is covered by the Pleistocene Matsukawa andesite which is regarded as the cap rock of the geothermal system in this area. Several Pleistocene formations composed of andesitic volcanic rocks overlie the Matsukawa andesite. Most of the geothermal steams are derived from the lower part of the Tamagawa welded tuff formation and the Yamatsuda formation.

The depth of eight production wells and one exploration well ranges from 1,000 to 1,600m, and at present, the steam is perfectly dry and superheated by 20 to 70°C as compared with the liquid-vapor equilibrium temperature at the well-head pressure.

The altered rock zone extends along the Matsukawa river in the direction from ENE to WSW, comprising an area 7km long and 0.5 - 1.0km wide. The altered rock zone is classified into some subzones as shown in Fig. 1, on the basis of the mode of occurrence of mineral

assemblage. These zones are not only distributed horizontally but also vertically as shown in Fig. 2, and kaolinite, anhydrite, pyrite and other alteration minerals are found in boring-core and cutting samples.

SAMPLING AND ANALYSES

Sample collection and chemical analyses of the geothermal steam from wells of the Matsukawa geothermal power station were carried out in September and December 1982, and steam condensates were analyzed in April 1982. Samples of steam condensates for the measurement of tritium concentration were collected in 1975 and 1980. Localities of wells are shown in Fig. 1.

The methods of sampling and analyses were similar to that of OZAWA (1967), but partly modified for the sake of convenience. Samples of steam condensates were collected through a glass coil condenser. Non-absorbable gases in alkaline solution were analyzed by the

Fig. 1. Map of the Matsukawa geothermal area showing the localities of wells and distribution of altered rock zones. ●: well-head locality, →: well-bottom locality.

gas chromatographic method (SUGISAKI *et al.*, 1980; KAWABE *et al.*, 1981). The Hitachi model 164 gas chromatograph combined with a pre-amplifier, Ohkura model AM1001B micro-voltmeter was used for He, Ar and N₂ measurements. Tank oxygen was used as carrier gas at the flow rate of 5ml/min. The separation column consisted of teflon tubing (3mm inner diameter) 5m in length packed by 60/80 mesh Molecular Sieve 5A. The oven temperature was set at 40°C. Since this gas chromatograph was modified to remove hydrogen gas by heated stainless steel column packed with CuO grains, the Hitachi model 163 gas chromatograph was also used for H₂, N₂ and CH₄ measurements. Tank argon was used as carrier gas at the flow rate of 30ml/min. The separation column with 3mm (I.D.) stainless steel tubing 2m in

length was packed with 60/80 mesh Molecular Sieve 5A. The oven temperature was set at 40°C. The analytical error for He was about 10% and for the others less than 5%.

The NH₃ concentration in steam condensate was analyzed colorimetrically. The measurement of tritium concentrations in steam condensates was performed at Gakushuin University by gas counting method described by YONEDA *et al.* (1967), after electrolytic enrichment of tritium.

RESULTS AND DISCUSSION

He, Ar and N₂ concentrations in geothermal steam Results of chemical analyses of geothermal steam are listed in Table 1. In this table, all the gas concentrations are expressed by volume concentration in the steam. The He/Ar and N₂/Ar ratios are further normalized to the corresponding atmospheric ratios (Fig. 3). As seen in Fig. 2, sample points are distributed mostly along the curve which connects point A with B. Point A shows the dissolved air in water which is in equilibrium with the atmospheric air at 10°C and B indicates the gas (M-3, December 13, 1982) with the highest ratios of He/Ar and N₂/Ar. Point B can be considered to represent the gas derived from a deeper horizon of this area. The curve is a calculated mixing line of gases with the composition of points A and B.

In such a small geothermal area as Matsukawa, it can be postulated that the deep seated gas with a homogeneous composition exists in a deeper horizon of the area. In other words, variation of He/Ar and H₂/Ar ratios of geothermal steam is not due to the variation in He/Ar and N₂/Ar ratios of the original deep seated gases but to the change in mixing ratio of deep seated gases and dissolved air. The mixing may occur in the reservoir formation processes. Corresponding ratios of fumarolic gases from volcanoes of Northeast Japan (KIYOSU, 1983a) are also distributed along the extended curve in Fig. 2. The positive correlation between He/Ar and N₂/Ar ratios common for the original

Fig. 2. Schematic cross section of alteration zones in the Matsukawa geothermal field. 1: Zone of montmorillonite and iron-rich saponite, 2: Zone of chlorite, 3: Zone of kaolinite, 4: Zone of alunite, 5: Zone of pyrophyrite (after KIMBARA, 1983).

Table 1. Composition of geothermal steam from geothermal wells at Matsukawa

Well	Depth m	Date	Gas concentration in steam (by volume)								
			Total gas	H ₂ S	CO ₂	H ₂	N ₂	CH ₄	Ar	He	NH ₃
			%	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppm
M-1	1006	9/28, 1982	0.87	487	8010	22.4	115	61.9	1220	24.0	10.0
		12/13, 1982	0.83	540	7550	33.0	111	64.2	1120	21.7	—
M-2	1080	9/28, 1982	0.30	441	2480	42.6	25.9	12.2	324	3.90	15.3
		12/13, 1982	0.33	492	2730	44.9	20.9	9.77	268	5.02	—
M-3	1170	9/28, 1982	0.71	525	6350	88.0	88.0	50.7	930	16.8	54.4
		12/13, 1982	0.74	555	6660	94.0	58.1	32.5	528	14.2	—
M-5	1190	9/28, 1982	0.35	410	2960	32.0	61.3	32.3	693	9.21	4.7
		12/13, 1982	0.33	360	2810	35.0	65.0	34.7	726	15.4	—
M-6	1203	9/28, 1982	0.32	368	2630	33.0	51.2	20.7	643	8.77	5.9
		12/13, 1982	0.31	474	2510	55.5	44.0	17.6	543	9.05	—
M-7	1280	9/28, 1982	0.26	403	2110	34.6	36.4	14.3	523	5.15	6.2
		12/13, 1982	0.24	384	1910	45.1	43.2	16.7	562	7.49	—
M-8	1406	9/28, 1982	0.42	760	3360	30.5	35.4	17.7	496	7.48	8.3
		12/13, 1982	0.36	673	2830	37.1	38.5	17.6	479	5.90	—
M-9	1599	9/28, 1982	1.14	616	10600	128	40.2	36.7	456	6.73	51.0
		12/13, 1982	1.08	572	10100	108	35.6	29.2	455	8.42	—
T-24	1050	12/13, 1982	0.43	443	3820	12.8	19.6	6.02	288	2.84	—

Total gas: Gases other than water vapor.

NH₃: Samples were collected on April 20, 1982.

deep seated gas of the Matsukawa area and fumarolic gases from volcanoes of Northeast Japan may be related to the fact that the original deep seated gas of Northeast Japan is uniform with respect to nitrogen and noble gases and is emitted through geothermal wells and/or fumaroles after mixing with dissolved air in various proportions.

As seen in Fig. 3, He/Ar and N₂/Ar ratios of the original deep seated gas of Northeast Japan are more than hundred times and three times as large as those of atmospheric air, respectively. According to SUGISAKI *et al.* (1978), four expected sources of nitrogen are as follows: 1. penetrating atmospheric air, 2. bacterial decomposition of organic matter contained in sediments, 3. pyrolysis of organic matter, 4. release of inorganic nitrogen from igneous and/or metamorphic rocks. The most probable origins of nitrogen which raises the N₂/Ar ratio are (3) and (4) among four possibilities described above.

On the other hand, MATSUO *et al.* (1978) suggested that one of the reasons for high N₂/Ar ratios in volcanic gases from island arc

volcanoes is the contribution of factor (3) due to sedimentary materials transferred into the lower crust or upper mantle through subduction.

It can be suggested that N₂/Ar ratio of the original deep seated gas to which there is no contribution of dissolved air has a fixed value controlled by sedimentary materials. It can also be concluded that He, Ar and N₂ gases contained in both of geothermal steams and fumarolic gases of Northeast Japan are derived from a common source.

Geothermal reservoir Eight production wells and one exploration well produce steam at the Matsukawa geothermal power station. Wells except M-2 and M-5 were drilled by directional drilling as indicated in Fig. 1. Table 1 shows that CO₂ concentrations of steam from M-1, 3 and 9 range from 6,350 to 10,600ppm and those of the others from 1,910 to 3,820ppm. The H₂S concentration of steam has a range from 360 to 760ppm, and the variation in the concentration of H₂S is smaller than that of CO₂.

The relationship among CO_2 , H_2S and R-gas (residual gases after the gas is washed with 5N KOH solution) is shown in Fig. 4. As shown in Fig. 3, eight production wells are divided into two groups, i.e., wells M-1, 3 and 9 and wells M-2, 5, 6, 7, and 8. The exploration well T-24 does not belong to both of the two groups. Two production well groups can be distinguished from each other also by their localities. Wells M-1, 3 and 9 are located in the zone of weak alteration, and other wells are located in the zones with the occurrence of montmorillonite, kaolinite and alunite as shown in Fig. 1. The zonal distribution on the exposed surface is observed in the vertical section; the alunite zone occurs in center, successively surrounded

Fig. 3. Relationship between He/Ar and N_2/Ar ratios of geothermal gases. ●: M-1, 3 and 9, ○: M-2, 5, 6, 7 and 8, □: Fumarolic gas of Northeast Japan (after Kiyosu, 1983a). Point A shows dissolved air in water which is in equilibrium with atmospheric air at 10°C , and point B the gas from M-3 with the highest ratios of He/Ar and N_2/Ar . The curve is calculated mixing line of gases of points A and B. Three fumarolic gases with $(\text{N}_2/\text{Ar})_{\text{sample}}/(\text{N}_2/\text{Ar})_{\text{air}} > 2$ are excluded from this Figure.

Fig. 4. Gas composition of geothermal steam of Matsukawa shown by triangle diagram for CO_2 , H_2S and R-gas (residual gases). ●: M-1, 3 and 9, ○: M-2, 5, 6, 7 and 8, △: T-24.

by the kaolinite zone and montmorillonite zone (Fig. 2). Calcite exists in the zones of weak alteration (SUMI, 1968), and the coincidence of the localities of wells which discharge CO_2 rich steam and the zone of weak alteration suggests that calcite is one of the sources of CO_2 in steam from wells M-1, 3 and 9.

The tritium concentrations of condensates of wells M-3 and M-9 are 1.09–1.19 T.U., and those of wells M-5 and M-8 are 0.28–0.40 T.U. (Table 2).

The variety of the concentrations of major gas components and tritium as well as He/Ar and N_2/Ar ratios suggests a possibility that the reservoir or steam channel for wells M-1, 3 and 9 is separated by some barrier (faults, which are assumed from the upheaval structure of the Yamatsuda formation) from the other reservoir

Table 2. Tritium concentration in condensate of steam from Matsukawa

Well	Date	T (T.U.)
M-3	8/13, 1980	1.09
M-5	12/ 8, 1975	0.28
M-8	8/13, 1980	0.40
M-9	8/13, 1980	1.19

$$T.U. = (T/{}^1\text{H}) \times 10^{18}.$$

Table 3. Correlation coefficients(*r*) between gas components in geothermal steam at Matsukawa

H ₂ S	CO ₂	H ₂	N ₂	CH ₄	Ar	He	NH ₃	
0.443	0.999	0.682	0.402	0.653	0.335	0.448	0.737	Total gas
	0.416	0.336	-0.051	0.107	-0.083	-0.009	0.372	H ₂ S
		0.681	0.400	0.650	0.333	0.445	0.735	CO ₂
			-0.070	0.195	-0.147	-0.005	0.942	H ₂
				0.944	0.985	0.967	0.014	N ₂
					0.907	0.928	0.275	CH ₄
						0.935	-0.097	Ar
							0.094	He

or steam channel for wells M-2, 5, 6, 7, 8 and T-24. Since He/Ar and N₂/Ar ratios of the original deep seated gas of the Matsukawa area are uniform, the influence which causes the variation of concentrations of tritium and chemical components can be considered to be limited in a shallower horizon than that in which the original geothermal gas of the Matsukawa area exists.

Correlation between individual gas components

Gas composition of geothermal steam gives us two interesting problems. One is the origin of each component and the other is the chemical reactions taking place in the geothermal systems. The origin of He, Ar and N₂ has been discussed in the previous section. In order to elucidate the origin of gas components such as CO₂, CH₄, H₂S, H₂ etc., correlation coefficients(*r*) between the gas components are calculated first, and are given in Table 3. The *|r|* values higher than 0.693 indicate significant correlation at the confidence level of 99.9%. Very strong positive correlation (*r*=0.999) between CO₂ and total gas* implies that contribution of CO₂ concentration and its variation to those of total gas is great. Strong positive correlations are also indicated for the pairs of N₂-CH₄, N₂-Ar, N₂-He, CH₄-Ar, CH₄-He and Ar-He.

On the other hand, H₂S and H₂ have no correlation with other gas components, while H₂ shows an appreciable correlation with NH₃. Kiyosu (1980) showed that the sulfur isotopic exchange equilibrium is established at the well-bottom temperature between H₂S, pyrite and anhydrite in the Matsukawa geothermal area.

In this connection, an independent behavior of H₂S seems to be due to the buffer reaction, e.g., sulfide + H₂O = oxide + H₂S. Kiyosu (1983b) showed also the possibility that the hydrogen isotopic exchange equilibrium is also established between H₂O and H₂ through the following reaction,

It can be said that weak correlations indicated for the pairs of gas components including H₂ and H₂S come from high reactivity of H₂ and H₂S through chemical reactions. Some of possible reactions are described above. Beside reaction (1), following two reactions including H₂ can be considered among major components to investigate the reactivity of H₂.

When reaction (2) is in equilibrium, its equilibrium expression in terms of fugacities *f_i* becomes

$$K_N = \frac{f_{\text{N}_2} \cdot f_{\text{H}_2}^3}{f_{\text{NH}_3}^2} \quad (4)$$

where *K_N* denotes the equilibrium constant.

Since fugacity coefficients can be assumed to be close to unity under the condition of common geothermal reservoir, reaction (4) can be converted using partial pressure, *p_i*, to be

$$K_N = \frac{p_{\text{N}_2} \cdot p_{\text{H}_2}^3}{p_{\text{NH}_3}^2} \quad (5)$$

* Total gas is defined in this study as all gases except water vapor (refer to Table 1).

As the partial pressure can not be measured directly at present, we have to use the measured concentrations for discussion. The fact that neighboring Kakkonda and Ohnuma geothermal fields (Fig. 1) are water dominated-type systems suggests that water exists originally in liquid phase even in the Matsukawa reservoir. Since the steam is dry, we can assume that a part of liquid phase in the reservoir evaporates completely, so that all the chemical components found at the well-head are originally dissolved in the liquid. Then, the concentration C_i of component i measured at the well-head can be used to check the establishment of chemical equilibrium in the liquid reservoir.

Equation (5) can be converted using concentration of species i in the discharging steam to equation (6),

$$C_{\text{NH}_3}^2 = A \cdot C_{\text{N}_2} \cdot C_{\text{H}_2}^3 \quad (6)$$

where A is a constant at a fixed temperature. If reaction (2) is in equilibrium, $C_{\text{NH}_3}^2$ should be proportional to $C_{\text{N}_2} \cdot C_{\text{H}_2}^3$. In order to examine reaction (2), correlation coefficient was calculated. A strong positive correlation ($r=0.986$) between $C_{\text{NH}_3}^2$ and $C_{\text{N}_2} \cdot C_{\text{H}_2}^3$ suggests that reaction (2) is in equilibrium.

As the measured well-bottom temperature at Matsukawa shows a rather narrow range from 223 to 260°C, reservoir temperature is assumed probably to be constant near 300°C. Rates of chemical reaction and carbon isotopic exchange in reaction (3) are considered to be very slow at temperatures around 300°C (HULSTON, 1977; SACKETT *et al.*, 1979; NUTI *et al.*, 1980; GIGGENBACH, 1982). If reaction (3) is in equilibrium at a constant temperature, following two equations should hold,

$$p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}^2 = \frac{1}{K_c} \cdot p_{\text{CO}_2} \cdot p_{\text{H}_2}^4 \quad (7)$$

$$\text{and } C_{\text{CH}_4} = B \cdot C_{\text{CO}_2} \cdot C_{\text{H}_2}^4 \quad (8)$$

where K_c and B are an equilibrium constant and a constant, respectively. In the case of constant temperature, $p_{\text{H}_2\text{O}}$ (saturated water vapor pres-

sure) can be regarded as constant. Again, the correlation between C_{CH_4} and $C_{\text{CO}_2} \cdot C_{\text{H}_2}^4$ is examined. The correlation coefficient is obtained to be 0.149, which suggests that reaction (3) is not in equilibrium. It suggests that carbon isotope exchange reaction between CO_2 and CH_4 is also not in equilibrium. This disequilibrium state can be regarded as the result of contamination of CO_2 and/or CH_4 from outside the geothermal system. The contributions of organic matter to CO_2 and CH_4 production can not be neglected in some cases (D'AMORE *et al.*, 1977; WELHAN *et al.*, 1979). It is necessary to reconsider the applicability of carbon isotopic geothermometer method.

On the basis of the facts mentioned above, NH_3 is considered to be controlled by chemical reaction with H_2 and N_2 . It is considered also that H_2 is controlled by chemical reactions between Fe(II) in minerals, H_2O and H_2S in the Matsukawa geothermal reservoir.

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