NOTE

D/H ratio of hydrogen and gas chemistry in three active geothermal systems, Northeast Japan

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D/H ratios of molecular hydrogen and chemical composition were analyzed for well and fumarole steam from the Matsukawa, Takinoue and Onikōbe active geothermal fields in Northeast Japan. The δD values ranged from -364 to -594‰. The temperatures estimated from the hydrogen-water deuterium isotope equilibrium fractionation are 200 to 300°C for most samples. The relationship between H2/H2S ratios and the hydrogen isotope geothermometer suggests that hydrogen and hydrogen sulfide concentrations in geothermal waters are controlled by equilibria with iron mineral buffers.

INTRODUCTION

Hydrogen in many geothermal systems is a particularly important volatile that in favorable cases offers information on physicochemical conditions (e.g., fO2) in deep reservoirs.

A few studies on the hydrogen isotopic composition of H2 in some geothermal systems (Arnason, 1977; Kiyosu, 1983; Lyon and Hulston, 1984) suggest that the hydrogen-water isotope geothermometer is useful in evaluating temperatures of geothermal reservoirs.

Hydrogen content of geothermal fluids may be controlled by temperature dependent equilibria with mineral buffers (e.g., Giggenbach, 1980; D’Amore and Gianelli, 1984; Arnórsson and Gunnlaugsson, 1985). Hydrogen gas is possibly produced in geothermal wells by the reaction of steam and/or hydrogen sulfide with steel of well casing. Thus, the origin of hydrogen in geothermal areas is not fully understood.

In the present study, we measured the gas concentrations and D/H ratios of hydrogen in steam from three active geothermal areas in Northeast Japan (Fig. 1) and examined the reactions controlling molecular H2 in geothermal fluids.

Fig. 1. Location of the geothermal fields studied.
EXPERIMENTAL

Sampling

Detailed geology and geochemistry are available for Matsukawa (Nakamura and Sumi, 1961; Sumi, 1966, 1968), Takinoue (Nakamura and Sumi, 1981; Sato, 1982) and Onikôbe (Yamada, 1972; Ozawa and Nagashima, 1975; Ozawa et al., 1980; Liou et al., 1985). Fumarole activity is minor in the Matsukawa geothermal area.

Fumarolic and well gases were introduced in water-cooled KOH solution. Residual gases which include hydrogen for the present study were collected in a 100 ml Pyrex gas collectors. After sampling, both ends of the collector were sealed off with a torch.

Analysis

The CO₂ and H₂S concentrations in steam condensate were analyzed according to method described by Ozawa (1966). Other gases (N₂, H₂, CH₄, Ar, and He) were analyzed by gas chromatography (Kiyosu, 1985).

Hydrogen was separated from other alkali-unabsorbed gases (e.g., CH₄, N₂, Ar) by gas chromatographic method (Kiyosu, 1983). After separation, the hydrogen was passed over a copper oxide furnace at 400°C, and the combustion product, H₂O was trapped from the helium carrier gas. Water samples were reduced to hydrogen over hot uranium at 700°C and adsorbed on active charcoal at liquid nitrogen temperature.

D/H ratios of hydrogen were measured with a dual collector mass spectrometer and the results are expressed by δD values relative to the SMOW standard. The overall reproducibility of δD values determined by multiple analyses of a working standard is ±5.0‰.

RESULTS AND DISCUSSION

The analytical results of geothermal steam are presented in Table 1. The predominant gases exclusive of the major component H₂O are carbon dioxide and hydrogen sulfide. Hydrogen gas concentrations in a wide range 1~300 ppm are lower than those in other geothermal areas such as Larderello, Italy; Geyser, U.S.A.; Cerro Prieto, Mexico (Ellis and Mahon, 1977; Nehring and D’Amore, 1984), but higher than in New Zealand (Giggenbach, 1980). In contrast, the geothermal steam contains dominantly hydrogen sulfide. The concentrations of H₂ and H₂S in the Onikôbe geothermal field are slightly higher than those in Matsukawa and Takinoue.

The gas compositions of well steam from Takinoue (Akeno, 1978) and Onikôbe are similar to those of several different fumarole steam. At Onikôbe and Takinoue, the isotopic compositions of waters from deep wells and fumaroles suggest that water-vapor separation has occurred as hot water traveled to the surface through natural channels and that the vapor phase corresponds to fumarole steam (Kiyosu, 1986; Kiyosu and Yoshida, 1986).

Isotopic composition of hydrogen

Variation in δD values of hydrogen is considerable: -364 to -594‰. The δD values of H₂ from Northeast Japan are similar to those from Iceland (-359 ~ -632‰ according to Arnason, 1977) and New Zealand (-310 ~ -600‰ according to Lyon and Hulston, 1984). The Matsukawa hydrogen shows more variable and higher deuterium content than do those from the other two areas. At Takinoue, isotope compositions (av. -551‰) for the fumarole samples lie in a small range, but are slightly lighter than at Onikôbe (av. -525‰). Variation in δD of geothermal hydrogen is predominantly due to temperature changes, as described below.

In geothermal systems, water, hydrogen, methane and hydrogen sulfide possibly constitute hydrogen isotope fractionation pairs. The hydrogen isotope exchanges between H₂S and H₂ proceeds probably much faster than other reactions. The hydrogen-methane deuterium exchange reaction suggests that no equilibrium is established between them in some volcanic areas, Northeast Japan (Kiyosu, 1983). On the other hand, the δD value of hydrogen would be
controlled by the equilibrium with the dominant species, water, because the rate of deuterium exchange should be rapid at elevated temperatures. The hydrogen-water deuterium fractionation factors used are the experimental scale by Rolston et al. (1976). This scale is nearly consistent with the theoretical hydrogen-water vapor scale by Bottinga (1969). Water vapor-liquid water deuterium equilibrium fractionation is obtained by using the equation of Bottinga and Craig (1968). Geothermal waters at Matsukawa, Takinoue and Onikobe are of meteoric origin and have δD values of -72.8, -72.5 and -58.0‰, respectively (Kiyosu, 1985). Hydrogen isotope temperatures obtained are given in Table 1.

In the Matsukawa area, the hydrogen isotopic temperatures (about 300°C) are higher than the temperature actually measured at the well bottom, but they are close to the sulfur isotope temperatures estimated from δ34S values of H2S, pyrite and anhydrite (Kiyosu, 1980). These temperatures estimated by isotopes may be related to a temperature at a depth below the reservoir of thermal fluids exploited in the field.

At Takinoue fumaroles (Table 1), the hydrogen isotope temperatures are somewhat lower than the reservoir temperatures of 200~270°C.
measured by Akeno (1978). At Onikobe, the hydrogen isotope temperatures at fumaroles are slightly lower than those isotopically estimated at wells (Table 1). The latter values are consistent with the well-bottom temperature reported by Ozawa and Nagashima (1975). The result shows that, in both geothermal areas of Takinoue and Onikobe, isotopic temperatures at fumaroles are a little lower than those at wells implies re-equilibration between hydrogen and water at a shallow depth.

Arnason (1977) obtained a reasonable agreement between actual temperatures and isotopic temperatures at wells in Iceland geothermal systems. In New Zealand, isotopic temperatures at wells are lower than those estimated for hot springs, but are generally consistent with temperatures actually measured in thermal fluid reservoir (Lyon and Hulston, 1984).

$H_2/H_2S$ ratios of geothermal gases are plotted against isotope temperatures in Fig. 2. The $H_2/H_2S$ ratios decrease with increasing temperature. The data points can be fitted to eqn. (1)

$$\log \frac{X_{H_2}}{X_{H_2S}} = -3.25 + 1173/(t + 273.15)$$

where $X$ indicates the mole fraction of gas species; $t$ represents temperature ($°C$). This suggests that these gas contents have been controlled by chemical reactions. In other geothermal systems, $H_2/H_2S$ ratios display a distinct relation with the temperature of aquifer (e.g., Giggenbach, 1980; Arnórsson and Gunnlaugsson, 1985).

Chemical reactions controlling hydrogen content

Yoshida (1984) examined the correlation between gas components in the Matsukawa geothermal area and concluded that the chemical reaction involving $CO_2$, $CH_4$ and $H_2$ is not in equilibrium. Arnórsson and Gunnlaugsson (1985) also concluded that this reaction does not closely approach an equilibrium in most geothermal systems. Geothermal hydrogen is, therefore, produced by the following reactions:

$$H_20 = H_2 + \frac{1}{2}O_2\quad (2)$$
$$H_2S = H_2 + \frac{1}{2}S_2\quad (3)$$

The equilibrium constants for the reactions (2) and (3) can be written as

$$K_w = (X_{H_2}/X_{H_2O})fO_2^{1/2}$$
$$K_s = (X_{H_2}/X_{H_2S})fS_2^{1/2}$$

where $f$ is fugacity; $K_w$ and $K_s$ are pressure independent. Using thermodynamic data of Holland (1965), we obtain $K_w$ and $K_s$ of reactions (2) and (3).

On the other hand, Giggenbach (1980) concluded that the equilibrium between $H_2$ and $H_2S$ is closely approached in New Zealand geothermal systems and that hydrogen and hydrogen sulfide contents are controlled by the temperature and the proportions of vapor and liquid in the equilibrated reservoir fluid. The boiling in the aquifer plays, therefore, an important role.
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for controlling the gas compositions. According to Giggenbach (1980), the effect of vapor gain or loss on the discharge gas (i) concentration \( X_{ci} \) can be estimated from the following equation:

\[
X_{ci} = X_{li} (1 - y + B_i y)^{\pm 1} = X_{li} D_i^{\pm 1}
\]

where \( B_i \) indicates the distribution coefficient of gases between vapor (vi) and liquid (li) phase defined by \( X_{vi} = X_{li} / B_i \), \( y \) represents the reservoir steam fraction, and plus and minus indicate vapor gain and loss, respectively. Using this relationship, new equilibrium constant estimated by eqn. (5) may be defined for which theoretical values can be calculated as function of temperature and \( y \).

\[
K'_s = K_s B_{H_2S}/B_{H_2}(D_{H_2}/D_{H_2S})^{\pm 1} = (X_{H_2}/X_{H_2S})_{fs}^{1/2}
\]

The distribution coefficients of hydrogen and hydrogen sulfide are obtained from Giggenbach’s regression equations (1980). Sulfur fugacity should be determined by the mineral buffers with which it equilibrates (Giggenbach, 1980; D’Amore and Gianelli, 1984; Arnórsson and Gunnlaugsson, 1985).

The relationship between \( CO_2/N_2 \) and \( N_2/Ar \) ratios of gases from Northeast Japanese geothermal fields suggests that these geothermal systems constitute essentially a single phase and that equilibration takes place for all gas species dissolved in the liquid phase (Kiyosu, 1986; Kiyosu and Yoshida, 1986). By accepting equilibration liquid phase for the geothermal systems (\( y = 0 \)), we can estimate sulfur fugacity from eqn. (7) on the basis of the observed \( H_2/H_2S \) ratios and isotope temperatures (Fig. 3). The sulfur fugacities for Northeast Japanese geothermal fluids in the range 100~300°C are nearly in agreement with these values for other geothermal fields which are defined by a mineral assemblage consisting of epidote, chlorite, K-feldspar, quartz and pyrite (D’Amore and Gianelli, 1984). This suggests that this assemblage controls \( fS_2 \) in many geothermal systems. In fact, these minerals have frequently been found in Northeast Japanese geothermal systems (e.g., Liou et al., 1985).

Fig. 4 shows the relationship of \( H_2/H_2S \) ratios with temperature and \( y \) calculated from eqn. (7) by using the sulfur fugacities estimated above. These ratios are affected by vapor gain or loss from the equilibrium liquid phase, especially, at low temperature. This diagram shows that all reservoir fluids in three geothermal areas are nearly pure liquid and that gain or loss of equilibrium vapor from the liquid phase is less than 1%. Data points for three areas follow a trend suggesting an increase in the \( H_2/H_2S \) ratio.
Fig. 4. Values of $H_2/H_2S$ ratios for well samples as a function of temperature and $y$. •: Matsukawa (Yoshida, 1984); ○: Takinoue (Akeno, 1978); ◊: Onikobe (Ozawa and Nagashima, 1975).

Matsukawa well temperature is the averaged value of isotope and measured temperatures.

with decreasing temperature. The observed trend suggests that $H_2$ and $H_2S$ concentrations of waters in geothermal reservoirs are controlled by mineral buffers involving iron minerals.

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