Geochemical Journal Vol. 17, pp. 161 to 164, 1983.

NOTE

Deuterium fractionation between water vapor and hydrogen gas in fumarolic gases

YOSHIHIKO MIZUTANI

Department of Earth Sciences, Faculty of Science, Toyama University, Toyama 930, Japan

(Received December 7, 1981: Accepted October 3, 1982)

The fumarolic condensate and hydrogen gas samples collected from the Showashinzan, Nasudake, Yakedake and Kuju-Ioyama volcanoes, Japan, have been analyzed for the D/H ratio. A comparison between temperatures for isotopic equilibrium and measured outlet temperatures indicates that in high temperature fumarolic gases the deuterium exchange reaction between water vapor and hydrogen gas is rapid enough to readjust the equilibrium to the outlet temperature of fumaroles. For low temperature fumarolic gases, however, the isotopic temperature refers to equilibrium conditions deep in the fumarole.

INTRODUCTION

ARNASON and SIGURGEIRSSON (1968) measured D/H ratios of water vapor and hydrogen gas in volcanic gases collected from the Surtsey volcano, Iceland. According to BOTTINGA (1969), their measurement indicates 1,133°C as the temperature at which the isotopic equilibrium between water vapor and hydrogen gas was quenched. The temperature estimated is in good agreement with the measured crater temperature of 1,150 - 1,160°C. The deuterium fractionation between water vapor and hydrogen gas was also tested for geothermal well discharges as a geothermometer, in conjunction with water vapor - liquid fractionation. A reasonable agreement between temperatures for isotopic equilibrium and measured bottom temperatures was obtained for some geothermal well discharges of New Zealand, Iceland and U.S.A. (e.g.; HULSTON, 1977 and ARNASON, 1977).

The purpose of this study is to examine the attainment of isotopic equilibrium between water vapor and hydrogen gas in fumarolic gases with temperatures ranging from 121 to 830°C, and to discuss the implication of isotopic temperatures obtained, in comparison with measured outlet temperatures of fumaroles.

SAMPLING AND ISOTOPIC ANALYSES

Fumarolic condensate and non-condensible gas samples were collected by the method described by MIZUTANI (1962). For the D/H ratio measurement by mass spectrometry, the hydrogen gas in the non-condensible gas was purified by a modification of the method of ARNASON and SIGURGEIRSSON (1968). Any isotopic contribution of the methane coexisted in the non-condensible gas sample to the purified hydrogen gas could be ignored, because of low methane content of fumarolic gases (Table 1). The fumarolic condensate sample was converted into hydrogen gas over hot uranium as described by BIGELEISEN *et al.* (1952). The D/H ratios obtained are expressed in the δ value relative to SMOW. The analytical errors of the measurements are ±5‰ for the hydrogen gas in the non-condensible gas and ±2‰ for the fumarolic condensate.

RESULTS AND DISCUSSION

Table 2 shows the δD values obtained for water vapor and hydrogen gas in the fumarolic gases collected from the Showashinzan, Nasudake, Yakedake and Kuju-Ioyama volcanoes,

Table 1. Chemical composition of fumarolic gases typical of each volcano (Vol. %)

	Showashinzan* A-1 fumarole 1954	Nasudake M-1 fumarole 1960	Yakedake** F-1 fumarole 1977	Kuju-Ioyama KH-1d fumarole 1961
Outlet temp., °C	800	489	127	400
H_2O	98.0	99.1	97.9	96.9
H_2	0.63	0.051	0.062	0.010
CO_2	1.2	0.15	1.7	0.45
SO_2	0.043	0.34	0.003	0.69
H_2S	0.0004	0.32	0.25	1.4
HCl	0.053	0.022	0.0087	0.48
HF	0.024	0.0038	0.0000	0.097
N_2	0.057	0.0031	0.052	0.0015
Ar	0.000025	0.000021	0.000058	0.000011
CH_4	0.0017	0.00027	0.0000	0.000014

*: *MIZUTANI and SUGIURA (1982).*
**: *SUGIURA and MIZUTANI (1978).*

Japan (Fig. 1). In Table 2 are also given the results reported by EBA *et al.* (1971) and comparisons between temperatures for isotopic equilibrium and measured outlet temperatures of fumaroles. Figure 2 shows the plot of the isotopic temperatures against the measured outlet temperatures.

At the Showashinzan volcano (dacite lava dome formed in 1944 - 1945), the isotopic temperatures are in good agreement with the measured outlet temperatures at temperatures above 500°C, indicating that the deuterium exchange reaction between water vapor and hydrogen gas is rapid enough to readjust the equilibrium to the outlet temperature of fumaroles. Discrepancies are, however, found at temperatures below 500°C and tend to be wider with lowering temperature. This is considered to be due mainly to quenching of high temperature equilibrium by rapid cooling of fumarolic

Fig. 1. Map showing the volcanoes from which fumarolic gases were collected. 1: Showashinzan, 2: Nasudake, 3: Yakedake, 4: Kuju-Ioyama.

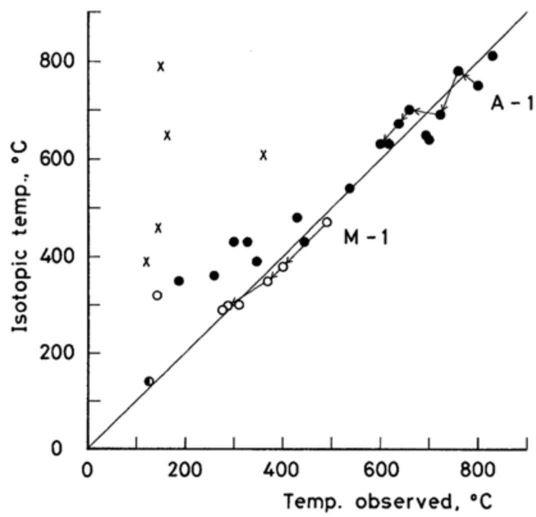

Fig. 2. Comparison of isotopic temperatures with observed outlet temperatures of fumaroles.
●: Showashinzan, ○: Nasudake, ◐: Yakedake, ×: Kuju-Ioyama. The arrows show variations of temperature with time.

Table 2. Deuterium fractionation between H_2 and H_2O in fumarolic gases

Sample		Temp. observed °C	δD_{H_2} ‰	δD_{H_2O} ‰	Isotopic# temp. °C
Showashinzan					
A - 1,*	1954	800	−217	−46.0	750
〃	1958	759	−205	−41.4	780
〃	1960	722	−244	−58.4	690
〃	1962	662	−246	−63.9	700
〃	1964	637	−244	−50.7	670
〃	1973	600	−255	−47.5	630
〃	1977	617	−254	−45.6	630
A - 4c,	1955	830	−197	−39.1	810
A - 6a,	1959	700	−250	−45.3	640
A - 6,	1960	695	−237	−54.4	700
B - 1a,	1959	328	−345	−49.4	430
B - 1b,	1960	260	−398	−63.5	360
B - 4b,	1959	300	−344	−48.3	430
B - 5,	1960	446	−352	−59.7	430
B - 6,	1960	347	−368	−52.1	390
C - 2,	1962	538	−286	−43.1	540
C - 3,	1960	187	−400	−56.4	350
C - 4,	1959	430	−314	−43.4	480
Nasudake					
M - 1,	1960	489	−326	−50.6	470
〃	1963	400	−378	−57.0	380
〃	1965	370	−393	−50.5	350
〃 **	1969	277	−447	−65.6	290
M - 4,**	1969	310	−438	−63.2	300
O - 1,**	1969	143	−425	−65.1	320
OE - 1,**	1969	288	−441	−64.4	300
Kuju-Ioyama					
KH - 1d,	1964	360	−242	−20.3	610
KX - 3,	1964	151	−185	−19.8	790
KX - 9,**	1967	163	−238	−35.3	650
KO - 1b,**	1967	144	−320	−39.0	460
KO - 4,**	1967	121	−362	−37.7	390
Yakedake					
F - 1,	1977	127	−575	−43.6	140

#: Estimated from the calculations of RICHET *et al. (1977) for the H_2 - H_2O system.*
**: MIZUTANI and SUGIURA (1982).*
***: EBA et al. (1971).*

gases caused by mixing of the low temperature steam and/or subsurface waters near the fumarole. The contamination with subsurface waters also hinders the fumarolic gases, to a small extent, from readjusting the high temperature equilibrium to the outlet temperature of fumaroles, because the waters have somewhat lower δD values than the high temperature fumarolic steam (MIZUTANI, 1978).

The M - 1 fumarole of the Nasudake volcano (strato volcano with an andesite lava dome on the summit), however, shows a good agreement between the isotopic and measured temperatures even at temperatures below 500°C, down to 300°C, along decreasing outlet temperature during the period from 1960 to 1969. It appears that, at an old volcano like Nasudake, a long passage from the gas reservoir to the surface may allow the fumarolic gases to readjust the equilibrium to the outlet temperature as low as 300°C.

In the case of the Kuju-Ioyama volcano (andesite lava dome), the isotopic temperatures estimated are much higher than the measured outlet temperatures. A temperature of 500°C was, however, recorded at the KH - 1 fumarole in 1960, though there is no historic record of eruption at this volcano. It is, therefore, possible that the fumarolic gases had temperatures as high as 500°C near the surface for some years after 1960. This seems to be supported by the evidence that the gases are characterized by very high sulfur and halogen contents (Table 1).

For the gases from the Yakedake volcano (andesite lave dome), a close agreement between the isotopic and measured temperatures has been obtained. In 1962 - 1963, this volcano had several explosions on its flank and discharged a large amount of mud (products of hydrothermal alteration; OSSAKA and OZAWA, 1966) and water from the fissures formed on the flank soon after the explosive activity. According to OSSAKA and OZAWA (1966), there is a possibility for this volcano to have a reservoir of mud and water at a relatively shallow place. The 1962 - 1963 explosions may have taken place by discharge of high temperature gases from the deep-seated magma into the reservoir (SUGIURA and MIZUTANI, 1978). The isotopic temperature estimated seems to be the temperature of reequilibration between the gases in the reservoir.

In summary, it can be said that in high temperature fumarolic gases the deuterium exchange reaction between water vapor and hydrogen gas is rapid enough to readjust the equilibrium to the outlet temperature of fumaroles. The degree of reequilibration apparently depends on the mode of fumarolic activity at each volcano. For low temperature fumarolic gases, the isotopic temperature refers to equilibrium conditions deep in the fumarole. In such a case, there is a possibility that the deuterium fractionation between water vapor and hydrogen gas may be of use estimating the change in volcanic activity at depth.

Acknowledgements—The author wishes to thank the staff and students of Nagoya University who helped him throughout this work. Most of this work was performed at Naogya University while the author was a student and then a member of the staff there.

REFERENCES

ARNASON, B. (1977) The hydrogen and water isotope thermometer applied to geothermal areas in Iceland. *Geothermics* **5**, 75–80.

ARNASON, B. and SIGURGEIRSSON, T. (1968) Deuterium content of water vapour and hydrogen in volcanic gas at Surtsey, Iceland. *Geochim. Cosmochim. Acta* **32**, 807–813.

BIGELEISEN, L., PERLMAN, M. L. and PROSSER, H. C. (1952) Conversion of hydrogenic materials to hydrogen for isotopic analysis. *Anal. Chem.* **24**, 1356–1357.

BOTTINGA, Y. (1969) Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geochim. Cosmochim. Acta* **33**, 49–64.

EBA, H., NAKAI, N. and HORIE, Y. (1971) $^{13}C/^{12}C$ and D/H ratios of volcanic gases. Abs. Symp. Geochem. Tokyo, Oct. 15–17 (in Japanese).

HULSTON, J. R. (1977) Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand. *Geothermics* **5**, 89–96.

MIZUTANI, Y. (1962) Chemical analysis of volcanic gases. *J. Earth Sci. Nagoya Univ.* **10**, 125–134.

MIZUTANI, Y. (1978) Isotopic compositions of volcanic steam from Showashinzan volcano, Hokkaido, Japan. *Geochem. J.* **12**, 57–63.

MIZUTANI, Y. and SUGIURA, T. (1982) Variations in chemical and isotopic compositions of fumarolic gases from Showashinzan volcano, Hokkaido, Japan. *Geochem. J.* **16**, 63–71.

OSSAKA, J. and OZAWA, T. (1966) The 1962 ejecta from Mt. Yake Nagano-Gifu prefectures, and its mechanism of eruption. *Kazan* 2nd Ser. **11**, 17–29 (in Japanese).

RICHET, P., BOTTINGA, Y. and JAVOY, M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Annu. Rev. Earth. Planet. Sci.* **5**, 65–110.

SUGIURA, T. and MIZUTANI, Y. (1978) Variations in isotopic and chemical compositions of fumarolic gases from Yakedake volcano, Honshu, Japan. *Kazan* 2nd Ser. **23**, 241–248 (in Japanese).