Origin of thermal waters from the Hakone geothermal system, Japan

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In the Hakone geothermal system a variety of waters including precipitation, surface water, ground water, thermal water and steam condensate were analyzed for δD and $\delta^{18}O$, dissolved sulfate and carbonate for $\delta^{34}S$, $\delta^{18}O$ and $\delta^{13}C$, and some sulfur-bearing gases for $\delta^{34}S$. Fifteen samples were collected monthly to see if there is any monthly change in the isotopic composition of water. Except in precipitation and steam condensates, no significant monthly changes were observed.

$\delta^{18}OSO_4$ and $\delta^{34}SSO_4$ analyses indicate that surface oxidation of volcanic sulfur produces isotopically light sulfate in water occurring at relatively high elevations. Sulfate minerals in the basement rocks formed by the Miocene submarine volcanism are another source of dissolved sulfate in waters at lower elevations. CO_2 originally derived from decomposition of marine carbonate is suggested as a carbon source for dissolved bicarbonate at higher elevations, although contribution of organic carbon becomes significant in waters at lower elevations.

In a δD versus $\delta^{18}O$ plot, surface waters including precipitation and ground water lie on the line, $\delta D = 8\delta^{18}O + 17$. On the other hand, thermal waters lie on a regression line, $\delta D = 2.1\delta^{18}O - 33.5$. Around the intersect of the two lines, $\delta D = -51\text{‰}$ and $\delta^{18}O = -8.5\text{‰}$, there is a swarm of point for groundwaters. We call the ground water with $\delta D = -51\text{‰}$ and $\delta^{18}O = -8.5\text{‰}$ "representative" ground water (RGW). From both chemical and isotopic view points, thermal waters are interpreted to be a mixture of RGW and high temperature dense steam (HTDS), the latter being ultimately evolved from hydrothermal interaction of RGW with rocks containing appreciable amounts of hydrous silicates.

Values of δD and $\delta^{18}O$ for HTDS have been interpreted to be a result of rock-RGW interaction with the rock/water weight ratio of about 10, on the basis of isotopic material balance in a closed system with the use of δD of hydrous silicates in rocks as well as δD and $\delta^{18}O$ values of RGW. When the ratio of about 10 is compared with those of other geothermal areas, the Hakone geothermal system is rock-dominated. Interaction between meteoric water and rocks including hydrous silicates under a rock-dominated condition can account for both hydrogen and oxygen isotopic shifts found in thermal waters.

INTRODUCTION

Isotopic study, especially that of hydrogen and oxygen isotopes of water is now an essential approach to the origin and behavior of geothermal waters, because geothermal waters are characterized by their isotopic and chemical compositions. Hydrogen and oxygen isotopic ratios of geothermal waters are controlled by a) mixing of meteoric water with various types of water such as sea water, connate water, metamorphic water, and magmatic water, b) altera-

tion through water-rock interactions, and c) subsurface boiling. In most cases the above factors contribute to different extents.

The Hakone geothermal system may be one of the best fields to study the hydrological feature of various types of thermal waters, since the caldera can be regarded as an independent hydrological unit. The Hakone volcano, situated 80km south-west of Tokyo, is a strato-volcano with double caldera and is composed of three geological units, i.e., old somma, young somma and central cones (Kuno, 1950). The volcanic

activity started in the late Pleistocene and still continues in the form of fumarolic activity in the Kamiyama and Komagatake (the central cones) with occasional volcanic earthquake swarms. Many hot springs are found along the deep valleys dissected by the rivers Hayakawa and Sukumogawa. The Hakone caldera with dimensions of 11km (north-south) and 7km (east-west) is morphologically separated from the surrounding area by a distinct old somma (Fig. 1).

A thorough study of the geology of the Hakone volcano and adjacent areas has been made by Kuno (1950, 1951). Yuhara *et al.* (1966) and Yuhara (1968) measured the amount of steam and heat discharge from the active fumaroles, which enabled estimation of the energy output in the Hakone geothermal system. There are a number of chemical studies on thermal waters of this system. Among these, Sato (1962) emphasized a zonal distribution of the thermal waters. Oki and Hirano (1970,

1974) extended the scope and discussed the genetic relationship of thermal waters on the basis of extensive chemical analyses.

Since thermal waters are mostly of meteoric origin (Craig *et al.*, 1956), a better understanding of the isotopic features of the local meteoric water helps interpret the isotopic characteristics of local thermal waters. In this respect, Matsuo *et al.* (1979) estimated in the Hakone caldera quantitatively the hydrological water budget, using hydrogen and oxygen isotopic composition and chloride content of rain-, river-, lake- and ground-waters of the area.

In this paper we discuss the ultimate origin of thermal waters in the caldera on the basis of isotopic information referring to the previous chemical and hydrological studies.

SAMPLES AND ANALYTICAL METHODS

About seventy samples were collected from the Hakone caldera for isotopic analyses as

Fig. 1. Sample localities in the Hakone caldera. Heavy lines indicate the zonal distribution of thermal waters with various chemical compositions (after Oki and Hirano, 1970).

described in Table 1. They are precipitation, river and lake water, ground water, thermal water from the four zones in the caldera which were proposed by Oki and Hirano (1970) and steam condensates from steam wells and fumaroles. Fifteen samples with asterisks in Table 1 were collected once a month from May 1971 to May 1972 in order to see if there were any seasonal variations. These samples were chosen so that they cover the various types of waters occurring in the caldera.

Figure 1 shows sampling localities in the Hakone caldera with the zonal distribution of thermal waters. In Table 1 are included isotopic analyses, water temperature, pH values, chloride contents, sampling localities with altitude above sea level, and the registered numbers for thermal waters (numbered by Kanagawa Prefecture). It should be noted that the *in situ* pH value is certainly not retained, since most of the thermal waters are discharged by an air-lift pump. Condensates from steam wells and fumaroles were collected by sucking steam through a cold trap with the help of a manually operated pump. Some rock samples from the Yugashima group, the basement rocks consisting of thick piles of submarine pyroclastic sediments of the Miocene age, were analyzed for D/H ratio in order to estimate the extent of interaction between the thermal water and rocks.

D/H ratio analyses of water samples were carried out by passing 5 to 10 mg of water over uranium metal heated to 700°C (Bigeleisen *et al.*, 1952) and comparing D/H ratio of the resulting hydrogen with that of the standard hydrogen on a mass spectrometer with a dual-inlet and dual-collector system. Hydrogen extraction from hydrous silicates in rock samples was made in the following way. Each sample was powdered, dried and then loaded in a platinum crucible, and hydrogen in the form of water was extracted by means of induction heating in vacuum at 1,200°C after absorbed and interlayer water had been removed at 200°C (Savin and Epstein, 1970). A small amount of H₂ gas formed during heating was converted to H₂O through a CuO furnace and the H₂O recovered

was combined with the water evolved as water vapor. The water thus collected was analyzed for D/H ratio in the manner described for water samples. ¹⁸O/¹⁶O ratio of water samples was measured by the established CO₂-H₂O exchange technique, followed by the mass spectrometric measurement. Both isotopic ratios are presented in the δ -notation with SMOW as the standard. The overall error was $\pm 1.3\text{‰}$ (one sigma) for δD and $\pm 0.2\text{‰}$ (one sigma) for $\delta^{18}O$.

For carbon and sulfur isotopic analyses of the dissolved materials, 1 to 2 liters of water samples were taken into plastic bottles to which a small amount of mercuric chloride had been added to suppress any biological activity after collection. Dissolved sulfate was precipitated as BaSO₄ for which $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ analyses were made on CO₂ and SO₂ gases respectively, obtained by using the preparation techniques described by Rafter (1957), Mizutani (1971) and Robinson and Kusakabe (1975). Sulfur-bearing gases from steam wells were recovered in the following manner; steam was introduced into a water-cooled alkaline solution containing cadmium acetate, and the cadmium sulfide thus formed and other sulfur species in higher oxidation state remaining in the solution were recovered for sulfur isotopic analyses.

The total dissolved carbonate was extracted from the samples by acidifying a solution in vacuum with concentrated phosphoric acid (Deuser and Hunt, 1969), and $\delta^{13}C$ values of the resulting CO₂ were determined mass spectrometrically.

GENERAL FEATURES AND MONTHLY VARIATION OF ISOTOPIC RATIOS

The results of hydrogen and oxygen isotopic analyses of the water samples are presented in Fig. 2. In Fig. 2 we draw a straight line representing the relationship between δD and $\delta^{18}O$ of meteoric water in Japan proposed by Sakai and Matsubaya (1974), i.e., $\delta D = 8\delta^{18}O + 17$. It is seen in Fig. 2 that the average rain and most of ground water samples in the Hakone caldera fit quite well the straight line. Likewise, a

Table 1. List of samples and analytical results

Sample	Isotopic δD	Ratio $\delta^{18}O$	Elevation a.s.l. (m)	Well depth (m)	Water temp. (°C)	pH	Sampling date	Locality, description or registered number†	Reference for chemistry††
Meteoric precipitation									
P-1*	-61.7	-9.9	1050	-	-	-	*	Ōwaku-dani	-
River water									
RW-1*	-49.0	-8.0	220	-	14.9	7.7	*	Sukumo-gawa	E
RW-2	-52.5	-8.2	450	-	17.6	8.0	710510	Jyakotsu-gawa	-
RW-3	-56	-8.3	700	-	7.3	6.8	761207	River head of the Sukumogawa	-
Surface water									
SW-1*	-42.6	-6.9	723	-	14.7	7.8	*	Ashinoko, lake water	D
SW-2	-51.4	-8.4	750	-	-	-	720414	Otamaga-ike, pond water	-
SW-3	-35.1	-6.3	850	-	-	-	720414	Syōjiga-ike, pond water	-
SW-4	-36.0	-5.9	850	-	-	-	720508	Syōjiga-ike, pond water	-
Ground water									
GW-1	-49.8	-8.1	700	30	13.8	7.7	710511	Sengoku-bara, On-ken No. 1 well	D
GW-2	-51.8	-9.0	725	0	13.4	-	710500	Kohan Golf field	D
GW-3	-44.1	-6.4	750	50	16.1	-	711214	Ooshiba-suigen No. 1 well	-
GW-4	-49.8	-8.2	750	100	15.6	-	711214	Ooshiba-suigen No. 2 well	-
GW-5	-50.9	-8.4	730	-	11.7	-	711214	Hakone-suigen well	-
GW-6	-50.1	-8.5	735	196	-	-	7112	Motohakone, On-ken observation well	-
GW-7	-51.9	-8.3	685	980	24.1	8.0	710731	Sengoku-bara, Mochiji well	-
GW-8	-49.1	-8.1	850	-	26.7	7.7	710511	Kamiyu, Ōwakudani	-
GW-9	-48.7	-8.3	230	-	12.2	-	710511	Koke-daki	E
GW-10	-52.4	-8.2	700	100	24.4	7.1	691004	Onsen-Kyokyu-Sen No. 1	D
Hot spring water from zone I									
I-1*	-50.0	-7.9	895	0	49.3	3.1	*	Syumei-Kan, MO-4	D, A
I-2**	-48.0	-8.1	948	91	59.1	2.5	**	Sengoku-kōgen Kaihatsu No. 4, MO-18	D, A
Hot spring water from zone II									
II-1*	-48.5	-7.6	935	280	74.2	7.8	*	Hakone-machi No. 1, AS-10	A
II-2**	-52.2	-8.7	840	525	57.1	7.9	**	Sugiyama Hideo, MO-19	A
II-3	-48.9	-8.1	855	-	59.6	7.9	710511	Matsuzaka-ya No. 5, AS-9	-
II-4	-47.9	-7.7	780	-	62.1	7.1	710511	Sō-un-kaku No. 1, MY-56	F
II-5	-50.5	-7.9	850	0	35.0	6.7	710106	Kinokuni-ya	-
Hot spring water from zone III									
III-1*	-46.3	-6.0	550	217	95.0	7.8	*	Taki-gensen, OS-104	B
III-2**	-46.1	-5.3	590	409	92.7	7.7	**	Suikou-kan, MY-50	B
III-3***	-43.4	-5.7	535	223	97.4	8.3	***	Yamatani-gensen, OS-105	B
III-4	-45.9	-5.3	620	516	-	-	711214	Kowaki-ken No. 20, MY-99	C, A

To be cont'd.

III-5	-41.0	-4.3	-	-	-	711214	Syōzan kaihatsu No. 278	A
III-6	-47.2	-5.4	730	460	92	711214	Yoshimoto-gensen, MY-83	C, A
III-7	-44.8	-4.9	-	-	-	711214	On-ken No. 306, MY-90	C
III-8	-43.0	-5.9	-	499	-	711214	On-ken No. 307, MY-98	C
III-9	-44.9	-5.5	710	516	93	711214	Kobayashi Heizou No. 1, MY-95	A, C
Hot spring water from zone IVa								
IVa-1*	-46.5	-6.7	450	0	86.4	*	Jyakotsu-yusen, OS-30, 31, 33	B
IVa-2**	-46.9	-7.1	578	351	66.5	**	Hakone-tozan No. 2, MY-86	B
IVa-3	-50.2	-7.4	875	438	51.3	710511	Kanpou-rou, SG-9	C, A
IVa-4	-49.7	-7.5	580	-	54.4	710511	Syōzan Kaihatsu, MY-88	C
IVa-5	-47.1	-6.6	690	500	87.5	710511	Kowaki-en No. 15, MY-111	-
IVa-6	-48.2	-6.9	500	-	95.3	710511	Ohira-dai gensen, OS-91	-
IVa-7	-48.2	-6.9	500	0	96.5	710511	Moto-onsen, OS-29	-
IVa-8	-50.1	-8.0	420	0	44.0	720904	Asahi Seimei, MY-4	C (Cl: 381 ppm)
IVa-9	-48.6	-7.1	450	0	56.0	-	Mampei Hotel	H (Cl: 577 ppm)
Hot spring water from zone IVb								
IVb-1*	-48.3	-7.5	230	493	55.9	*	Hatsuhana No. 90, YM-90	E
IVb-2**	-48.5	-7.3	170	548	54.9	**	Amano Masutarō, YM-105	E
IVb-3	-49.4	-7.5	270	700	71.3	710511	Okada-ya ue, YM-97	E
IVb-4	-53.1	-8.3	150	0	44.2	8.3	Yumoto shinyu, YM-7	E
IVb-5	-51.0	-7.6	230	-	61.8	8.0	Shiritsu gakkō Kyōsai, OS-123	F
IVb-6	-46.8	-7.0	200	545	55.9	7.8	Mitsui Shinako, YM-95	E
IVb-7	-50.0	-7.1	140	550	61.6	7.1	Chyūō shōji, YM-94	E
Steam condensate from steam wells and fumaroles								
CW-1*	-39.8	-4.7	950	256	103	*	Kokudo-keikaku No. 2, YH-25	bottom 172°C
CW-2*	-24.5	+1.4	940	100	143	*	Oowaku-dani doboku 1970 No. 1	G
CW-3	-29.4	-0.1	-	-	96	711214	Oowaku-dani Kōkyō No. 1, steam well	-
CW-4	-43.1	-6.2	-	-	-	711214	Oowaku-dani Kurumaishi	-
CW-5	-45.5	-5.6	-	-	96.2	711214	Sōun-zan, steam well	-
CW-6	-44.2	-4.8	-	-	97.0	711214	Sōun-zan, fumarole	-
CW-7	-42.2	-5.7	-	-	-	711214	Hakone-machi iyōki No. 1, steam well, YH-27	-

* averaged values of monthly collected samples from May 1971 to April 1972.

** averaged values for the samples collected from May to August 1971.

*** averaged values for the samples collected in May, June and December 1971.

† sample number registered by the Health Office at Odawara, Kanagawa Prefecture, with the following abbreviations: MO; Moto-Hakone,

AS; Ashi-no-yu, MY; Miyaginomura, OS; Onsenmura, SG; Sengokubara, YM; Yumoto and YH; Yunohana-zawa.

†† A; Oki et al. (1968), B; Hirano et al. (1968), C; Hirano and Tajima (1970), D; Hirano and Oki (1971), E; Hirano et al. (1972), F; Tajima and Hirano (1966), G; Watanuki (1966), and H; Hirano (pers. com.).

straight line, $\delta D = 2.1\delta^{18}O - 33.5$, can be drawn by the least squares best fit method for all the thermal waters except steam condensates. The two lines intersect at $\delta D = -51\text{‰}$ and $\delta^{18}O = -8.5\text{‰}$. There is a swarm of points of ground water centered at this point which we call "representative ground water" (RGW) hereafter. It is seen in Fig. 2 and Table 1 that δD and $\delta^{18}O$ values of the surface water having open surface such as lake water (SW-1) and pond waters (SW-3, -4) are higher than those of most of the ground and thermal waters, and the isotopic enrichment relative to RGW is most likely to be due to kinetic evaporation.

If the line for thermal waters, $\delta D = 2.1\delta^{18}O - 33.5$, represents a mixing line of RGW with another component, the latter, presumably a high temperature water, should lie somewhere along the thermal water line in Fig. 2. This idea will be pursued in the later section.

One of the purposes of this study is to see whether or not any systematic change in isotopic ratios of monthly collected water of

various types exists. The results of hydrogen and oxygen isotopic analyses of monthly collected samples are given in Tables 2 and 3, respectively. The isotopic variation is the greatest for precipitation. The variation with month in δD and $\delta^{18}O$ of the other waters is almost equal to or slightly greater than the accuracy of measurement except for the two steam condensates. This means that the monthly fluctuation in precipitation has been smoothed out under the ground (Matsuo *et al.*, 1979). The same conclusion has been obtained in the Nasu volcanic area, Japan (Kusakabe *et al.*, 1970).

The discharge rate of I-1 hot spring, spouting from the slope of a central cone, is known to be positively correlated with precipitation intensity, and the water temperature and salt concentration are inversely correlated (Hirano and Tajima, 1969; Hirota and Odaka, 1975). The isotopic ratios, however, show practically no monthly fluctuation, and the annual averages of δD and $\delta^{18}O$ values are only slightly higher than those of the precipitation by about 10‰ and

Fig. 2. δD versus $\delta^{18}O$ plot of the Hakone water samples. The isotopic compositions of thermal waters excluding steam condensates are best approximated by a least square regression equation, $\delta D = 2.1\delta^{18}O - 33.5$. The isotopic compositions of the representative ground water (RGW) are defined by the intersection of the thermal water line and the meteoric water line, $\delta D = 8\delta^{18}O + 17$. A point at the far-right end of the thermal water line indicates the isotopic composition of the hot water reservoir occurring below the active fumarolic areas of the Hakone volcano.

Table 2. Variation with time in hydrogen isotope ratio of monthly collected samples and precipitation depth

Sampling date	P-1	Amount (mm)	RW-1	SW-1	I-1	II-1	III-1	IVa-1	IVb-1	CW-1	CW-2
1971											
May	—	—	-48.9	-42.7	-50.7	-44.6	-44.2	-45.3	-48.9	-47.2	-24.1
June	-68.0	220	-49.3	-42.4	-51.7	-46.5	-47.9	-45.7	-49.1	-45.8	-24.6
July	-71.1	184	-49.1	-41.7	-51.1	-52.3	-47.1	-44.6	-49.1	-42.1	-22.6
August	-38.2	141	-49.4	-42.4	-49.0	-49.7	-46.9	-46.2	-47.7	-41.7	-25.0
Sept.	-60.4	645	-50.2	-42.8	-50.8	-49.4	-46.5	-46.6	-48.8	-39.0	-26.7
Oct.	-52.9	309	-47.2	-42.3	-50.0	-46.7	-46.2	-47.7	-48.6	-32.5	-22.5
Nov.	-79.6	289	-50.4	-43.9	-50.0	-48.3	-46.5	-46.6	-47.6	—	-30.5
Dec.	-49.0	29	-47.9	-41.3	-50.0	-47.1	-45.3	-47.3	-48.4	-23.6	-19.3
1972											
Jan.	-82.0	238	-51.5	-42.5	-51.1	-50.3	-46.4	-46.8	-46.9	-45.3	-26.3
Feb.	-62.0	152	-48.5	-42.4	-48.6	-47.8	-47.7	-47.9	-49.3	-43.7	-24.0
March	-67.9	74	-48.2	-44.4	-47.9	-51.6	-44.0	-46.4	-47.5	-37.1	-23.2
April	-46.1	262	-47.4	-42.4	-49.4	-47.6	-46.8	-47.1	-47.6	-40.0	-25.0
May	-46.5	>115									
average	-61.7*	—	-49.0	-42.6	-50.0	-48.5	-46.3	-46.5	-48.3	-39.8	-24.5
standard deviation	—	—	1.1	0.8	1.1	2.1	1.2	0.9	0.8	6.5	2.6

* weighted for precipitation amount.

Table 3. Variation with time in oxygen isotope ratio of monthly collected samples and chloride content of meteoric precipitation

Sampling date	P-1	Cl (ppm)	RW-1	SW-1	I-1	II-1	III-1	IVa-1	IVb-1	CW-1	CW-2
1971											
May	—	—	-7.9	-7.4	-8.3	-7.7	-5.5	-7.0	-7.6	-6.0	+1.2
June	-10.5	—	-8.4	-7.3	-8.0	-8.1	-6.0	-6.8	-8.0	-5.0	+1.4
July	-9.9	—	-7.7	-7.4	-8.4	-7.8	-6.2	-6.8	-7.6	-4.1	+1.6
August	-5.4	3.0	-7.5	-6.4	-8.2	-7.9	-6.2	-6.7	-7.8	-4.2	+0.8
Sept.	-9.4	—	-8.2	-7.4	-7.9	-6.9	-6.0	-6.4	-6.3	-4.0	+1.9
Oct.	-8.7	2.3	-8.2	-7.1	-7.5	-7.6	-6.2	-7.1	-7.5	-3.9	+1.1
Nov.	-12.2	1.6	-8.0	-6.6	-7.8	-7.2	-5.7	-6.6	-7.6	—	+1.1
Dec.	-9.6	5.8	-8.3	-6.7	-7.9	-7.1	-6.2	-6.4	-7.6	-2.4	+1.9
1972											
Jan.	-13.4	1.4	-7.5	-6.2	-7.8	-7.5	-6.1	-6.5	-6.8	-5.1	+1.5
Feb.	-11.5	1.3	-8.7	-6.9	-7.8	-7.7	-6.1	-6.7	-7.8	-5.5	+1.4
March	-11.5	2.4	-7.7	-6.4	-7.1	-7.8	-5.8	-6.3	-7.7	—	+2.3
April	-8.2	2.5	-8.0	-7.0	-8.4	-7.7	-6.5	-6.8	-8.1	-5.4	+1.0
May	-7.0	—									
average	-9.9*	2.1*	-8.0	-6.9	-7.9	-7.6	-6.0	-6.7	-7.5	-4.6	+1.4
standard deviation	—	—	0.4	0.4	0.4	0.3	0.3	0.2	0.5	1.0	0.4

* weighted for precipitation amount.

1‰, respectively. Considering a relatively large annual isotopic variation in precipitation (P-1 in Tables 2 and 3), we can conclude that I-1 is an essentially well-mixed ground water of shallow depth discharged by the water-head built up by precipitation.

A large monthly variation has been found for a steam condensate, CW-1. The steam tem-

perature ranged from 93 to 123°C. The sample consisted of steam and mist. Steam discharge was made each time only for sampling with different extent of valve opening, which may determine the outlet steam temperature. In addition, there is no relationship between isotopic values of steam and outlet temperature of steam. This implies that the mist to steam

ratio in each sample is not related to the measured outlet temperature. The observed monthly isotopic variation may be a reflection of secondary factors during sampling and not be related to the real variation in the original thermal water.

We see in this section that monthly change in isotopic ratios of water in the caldera is negligible except for precipitation and steam condensates. It can be safely said that thermal and ground waters collected at an arbitrary time of year have isotopic compositions close to the annual averages. In the following discussion, we will use one-shot samples together with the averages of monthly collected samples with an equal weight.

BEHAVIOR OF SURFACE AND GROUND WATER IN THE CALDERA

In order to reveal more detailed isotopic features of surface and ground water in the caldera, we collected rain water samples from September 9 to October 20, 1971 at five different altitudes on the south-western slope of Komagatake (one of the central cones) from 730 to 1,350m elevation at about 200m intervals. The result of D/H measurement is given in Table 4. It is seen in Table 4 that δD decreases about 1‰ per 100m at this particular site. This rate is about one fourth to one half of the rates in the Alps (Moser and Stichler, 1970) and the Sierra Nevada (Friedman and Smith, 1970, 1972), probably reflecting the smaller size of the field investigated. So we do not take into consideration the change in isotopic ratios of precipitation with altitude and we will use the annual average values of $\delta D = -61.7‰$ and $\delta^{18}O = -9.9‰$ (Table 1) for isotopic ratios of the precipitation supplied to the caldera.

The values of δD and $\delta^{18}O$ of ground water (almost the same as those of RGW) are distributed in a narrow range and are practically independent of their altitudinal and lateral position in the caldera. In other words, ground water in this caldera is isotopically homogeneous. However, δD and $\delta^{18}O$ values of ground

Table 4. Altitude effect on δD of precipitation observed at south-western slope of the Komagatake

Altitude (m)	δD (‰)	Precipitation amount (mm)
730	-65.9	405
920	-68.5	397
1050	-72.3	438
1190	-72.2	496
1350	-70.8	492
780*	-66.3	478

* collected at Shimoyu Earthquake Observatory, Gōra, Hakone.

water are definitely higher than those of the average precipitation. This indicates that the annual average of isotopic composition of precipitation fluctuates with year and/or the average precipitation has undergone enrichment of heavy isotopes through evaporation and evapotranspiration during the formation of the homogenized ground water (Matsuo *et al.*, 1979).

The annual averages of isotopic ratios of the lake water are $\delta D = -43‰$ and $\delta^{18}O = -7‰$, which are even much higher than those of RGW. The possibility that RGW is a mixture of the lake water and average precipitation is unlikely because ground waters with δD values almost equal to that of RGW can be found even at topographically higher levels than the lake. The permeable pumice formation extending towards the lake bottom is found at the uppermost region of the Sukumogawa River. The water sample (RW-3) collected in this area has isotopic values not close to those of the lake water, but to RGW. This indicates that no appreciable subsurface leakage of lake water occurs. There is a possibility, however, that the bottom water of the lake is isotopically different from the surface water which was actually sampled, and the bottom water is the major source of the ground water in the caldera. In order to check this possibility, a δD profile at the deepest point of the lake was measured in June 1971 when the thermal stratification started. The water samples from 0, 10, 20, 30 and 38m (almost the bottom) showed no appreciable vertical change in δD values which were -41.5 , -41.5 , -42.0

−44.1 and −42.8‰ respectively. It should be concluded that no sizable contribution of the lake water to ground water is expected, though the lake water is the largest surface water reservoir in the caldera.

RELATIONSHIP BETWEEN CHEMICAL ZONING AND ISOTOPIC COMPOSITION OF HOT SPRING WATERS

As mentioned already, Oki and Hirano (1970) divided the occurrence of thermal waters into the four zones according to anion composition of the waters (see Figs. 1 and 3).

Zone I waters have low pH values (2~3) and high sulfate ion concentrations. They are located near the top level of the Kamiyama, one of the central cones (see Fig. 1) and have δD and $\delta^{18}O$ values as low as those of ground waters (Table 1).

Zone II waters are characterized by high pH values (~8), and high bicarbonate and sulfate ion concentrations. Zone II waters are pumped from depths of several hundred meters around the central cones. According to Oki and Hirano (1970), the waters may come from a major aquifer beneath the central cones. As seen in

Fig. 3. Anion composition of the thermal waters studied with respect to the zonal distribution (Oki and Hirano, 1970). The symbols are the same as those in Figs. 1 and 2.

Fig. 2, Zone I and II waters can be regarded as ground water in origin. Zone I water extracted SO_4^{2-} and Zone II water extracted HCO_3^- from central cone materials without significant isotopic exchange. The origin and behavior of SO_4^{2-} and HCO_3^- will be discussed in the next section

Zone III waters are represented by high temperatures (near boiling point) and intermediate pH values, major constituent being sodium chloride. Three tongue-like branches of the zone III waters are recognized in the eastern flank of the Kamiyama (Fig. 1). It is seen in Fig. 2 that δD values of the Zone III waters are slightly higher than those of waters from the other zones, and $\delta^{18}O$ values are definitely higher than those of the others.

Oki and Hirano (1970) postulated the existence of "high temperature dense steam (HTDS)" (White, 1957; White *et al.*, 1971) at depths of the Hakone geothermal system and estimated its contribution to the zone III waters to be 25~30%, assuming that HTDS contains only sodium chloride, and that sulfate ions of the zone III waters are supplied exclusively by the zone II waters. They also estimated the contribution of HTDS to the zone III waters on the basis of the enthalpy budget to be 17~23%. Oki and Hirano (1974) later revised their value to 30~50% on the basis of chemistry. The validity of these figures will be discussed in a later section in view of isotopic data.

Zone IV waters are sodium chloride-bicarbonate-sulfate type or mixed type (Fig. 3). Oki and Hirano (1970) further divided zone IV waters occurring on the eastern side of the caldera into two subgroups, IVa and IVb; the former occurs at higher levels in the Quaternary volcanic rocks around the central cones and the latter in the Yugashima group, the Miocene basement rocks at lower levels.

The chloride content is plotted against $\delta^{18}O$ for thermal water as shown in Fig. 4. It is clear that zone III waters with a few exceptions have the highest $\delta^{18}O$ and chloride content, and that zone IV waters result from mixing of zone II and III waters. The results of isotopic

analyses agree quite well with the chemical zoning of thermal waters in the Hakone geothermal system.

ISOTOPIC EVIDENCE FOR THE DISSOLVED MATERIALS

The results of sulfur and oxygen isotopic analyses of sulfate ions dissolved in the various types of thermal waters are given in Table 5, together with some additional sulfur isotopic results for sulfur-bearing gases from the steam wells. Figure 5 shows the isotopic relationship between oxygen and sulfur of dissolved sulfate.

There is a positive correlation between $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values, with a trend that the sulfate in zone I and II waters is isotopically lighter

Fig. 4. Relationship between chloride content and $\delta^{18}\text{O}$ value of the thermal waters. Symbols are the same as those in Figs. 1 and 2.

Table 5. Sulfur, oxygen and carbon isotopic composition of dissolved sulfate and bicarbonate of thermal waters, and sulfur-bearing gases from steam wells in the Hakone geothermal system

Sample	SO_4^{2-}			HCO_3^-	
	conc. (ppm)	$\delta^{34}\text{S}$ (CDT)	$\delta^{18}\text{O}$ (SMOW)	conc. (ppm)	$\delta^{13}\text{C}$ (PDB)
Hot spring water from zone I					
I-1	405	-3.2	+0.3	—	—
I-2	502	-3.4	+0.1	—	—
Hot spring water from zone II					
II-1	551	-2.2	+3.2	121	+0.4
II-2	370	+14.1	+8.5	443	+2.0
II-5	202	-2.5	+3.0	113	+2.1
Hot spring water from zone III					
III-2	93	+5.8	+2.0	196	+1.0
III-3	107	+4.9	+1.8	61	-2.3
Hot spring water from zone IVa					
IVa-1	81	+4.2	+2.5	73	+0.6
IVa-2	174	+6.7	+4.1	254	-0.2
IVa-8	140	+5.9	+4.3	178	-1.5
IVa-9	54	+4.1	+1.7	77	-6.7
Hot spring water from zone IVb					
IVb-1	34	+12.1	+5.9	51	-12.1
IVb-2	409	+17.5	+8.7	15	-11.2
IVb-4	127	+10.0	+6.6	25	-14.1
Groundwater					
GW-10	193	+7.2	+5.4	43	-6.4
Gases from steam well					
CW-1	H_2S	-5.3			
	SO_2^*	-3.2			
	total sulfur	-3.7			
	CO_2				-0.7**
CW-2	H_2S	-4.0			
	SO_2^*	+2.9			
	total sulfur	0.0			

* sulfur compounds other than H_2S .

** taken from Craig *et al.* (1978).

(with an exception for the sample II-2), the sulfate in zone IV_b waters heavier and the sulfate in zone III and IV_a waters intermediate. Similar results have been given by Matsubaya *et al.* (1973) and Sakai and Matsubaya (1977). The range of $\delta^{34}\text{S}$ values of sulfur-bearing species from steam wells is indicated on a $\delta^{34}\text{S}$ axis of Fig. 5. Zone I waters are typical acid sulfate water. Such sulfate is considered to have resulted from the surface oxidation of volcanic sulfur at shallow depths where atmospheric oxygen is available. Bacterial oxidation of reduced sulfur to form sulfate in geothermal environments may also be possible (Mosser *et al.*, 1973). Agreement of $\delta^{34}\text{S}$ values between the zone I sulfate and sulfur gases in volcanic steam from the Owakudani fumarolic area supports the view of supergene origin of the sulfate, since it has been known that the isotopic ratio of sulfur of reduced form is inherited by oxidized sulfur through oxidation processes (Sakai, 1957; Ivanov *et al.*, 1968; Schoen and Rye, 1970).

When atmospheric oxygen is utilized in oxidative sulfate formation in an aqueous medium, the oxygen isotopic ratio of the resulting sulfate is determined by the isotopic ratios of both atmospheric and water oxygen with relative contribution of about 1/3 and 2/3, respectively (Lloyd, 1967). If the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values are taken to be -8.5‰ for zone I waters (Table 1) and 23.5‰ for atmospheric oxygen (Kroopnick and Craig, 1972) with the kinetic fractionation factor of -8.7‰ for the incorporation of atmospheric oxygen in the sulfate (Lloyd, 1967), then the resulting sulfate should have the $\delta^{18}\text{O}$ value of about -0.7‰ , which is in good agreement with the observed values of 0‰ for sulfate in zone I waters.

Similarity in sulfur isotopic ratios in zone I and II waters (excluding II-2) suggests that sulfate in zone II waters may also have a similar origin. In other words, acid zone I waters are neutralized during permeation through the central cone materials to form zone II waters which occur about several hundred meters below the zone I level, forming a major aquifer

(Oki and Hirano, 1970). The fact that the $\delta^{18}\text{O}_{\text{SO}_4}$ values of zone II waters are slightly higher than those of zone I waters is due probably to partial oxygen isotopic exchange with water in which the sulfate is dissolved. The dissolved sulfate should have $\delta^{18}\text{O}$ value of about $+9\text{‰}$, if complete equilibrium was attained in water with $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -8\text{‰}$ at 100°C (Mizutani and Rafter, 1969). Recent studies on reaction kinetics show that only partial equilibration is possible under low temperature (100°C) and neutral to weakly acid (pH down to 2) conditions encountered in the Hakone geothermal system (Chiba, pers. com.).

As mentioned previously zone III waters are considered to be formed by mixing of sulfate-rich zone II waters with deeply generated dense steam carrying predominantly sodium chloride. Zone III and IV_a waters are isotopically similar to each other as far as dissolved sulfate is concerned, suggesting a common origin. Both $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of sulfate in these waters, however, are higher than those of zone I waters, and are close to those of a groundwater sample GW-10. According to a hydrogeochemical study of ground-waters in the Hakone caldera (Hirano and Oki, 1971), a shallow groundwater flow from which GW-10 was sampled is estimated to come down from zone I through the central cone debris. GW-10 contains sulfate as well as a measurable amount of ferrous ion with a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio as high as 25. Eh-pH calculations indicate that sulfate ion, rather than hydrogen sulfide, is the stable form of aqueous sulfur species under the redox and pH conditions estimated for GW-10 assuming attainment of equilibrium between Fe^{2+} and ferric hydroxide (Hirano and Oki, 1971). However, the solution can become more reducing during down-permeation through rocks containing ferrous minerals. Under such reducing conditions, dissolved sulfate can be reduced probably by anaerobic bacteria. Bacterial reduction of sulfate is mostly accompanied by the enrichment of heavier isotopes in the remaining sulfate (Mizutani and Rafter, 1973), to which isotopic enrichment observed for

sulfate in zone III and IV_a waters relative to that in zone II water may be ascribed.

If HCO_3^- in the Hakone hot spring waters is derived from decomposition of fossil organic materials intercalated in the volcanic rocks as was proposed by Oki and Hirano (1970), its $\delta^{13}\text{C}$ values are expected to be close to those of terrestrial plants which are typically in the range of -20 to -25‰ (PDB). Carbon isotopic analyses given in Table 5, however, show existence of isotopically much heavier HCO_3^- . The average $\delta^{13}\text{C}$ value of $-0.5 \pm 2.7\text{‰}$ for HCO_3^- dissolved in zone II, III and IV_a waters indicates only small contribution of CO_2 of organic origin. This average value is consistent with a $\delta^{13}\text{C}$ value of -0.7‰ for CO_2 in the zone II steam well (CW-1) reported by Craig *et al.* (1978). The above isotopic evidence suggests that the ultimate source of carbon in the zone II, III and IV_a waters is sought in marine carbonates which occur as secondary minerals in the Yugashima formation, the Miocene basement of submarine basalts and andesites underlying the Hakone caldera. The CO_2 may have been carried up from the depths upon decomposition of carbonate and dissolved in groundwater at the uppermost part of the Hakone geothermal system. Such carbonate-rich water may be mixed with descending sulfate-bearing ground waters to give isotopically heavy HCO_3^- -rich waters in zones II and III.

Zone IV_b waters form a group characterized by sulfate with high oxygen and sulfur isotopic ratios as shown in Fig. 5. Concentration of HCO_3^- in these waters is low and its $\delta^{13}\text{C}$ value is more negative than the others (Table 5), indicating higher contribution of organically derived carbon. These waters occur at the lowest elevation of the Hakone geothermal system, where the Yugashima formation is exposed. It is most likely that the zone IV_b sulfate was leached out of the Yugashima formation which contains sulfate as anhydrite (or gypsum) with $\delta^{34}\text{S}$ values of $+15 \sim +16\text{‰}$ (Mizutani *et al.*, 1975, Matsubaya *et al.*, 1973). The points for zone IV_b waters extend towards lower $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values in Fig. 5,

implying mixing of down-permeating sulfate with lower isotopic ratios as discussed previously.

ORIGIN OF THE THERMAL WATER

Estimation of isotopic composition of HTDS

The highest fumarolic activity in the caldera is seen in the Owakudani area, about 1,000m above sea level at the northern slope of the Kamiyama, one of the central cones. There are several steam wells of which highest temperature is 180°C (CW-2) and natural fumaroles with boiling temperature of water. The thermal output due to steam and hot water discharge of this area, $1.1 \times 10^7 \text{ cal} \cdot \text{s}^{-1}$ (Yuhara, 1968) is about one third to one half of the entire thermal output from the Hakone geothermal system (Oki and Hirano, 1970). There is also a fumarolic area in the So-unzan area at the north-eastern flank of the Kamiyama, where several shallow steam wells are installed. The temperature of steam from this area is slightly less than 100°C . There are two steam wells in the Yunohanazawa area at about 1,000m level of the eastern slope of the Komagatake, one of the central cones.

Fig. 5. $\delta^{18}\text{O}$ versus $\delta^{34}\text{S}$ plot of dissolved sulfate in the Hakone thermal waters. The range of $\delta^{34}\text{S}$ values for sulfur from the steam wells is given on a horizontal axis for comparison. Symbols are the same as those in Figs. 1 and 2.

Since the steam discharge from the Owakudani area is the greatest in the caldera as far as thermal output is concerned, the following discussion will mainly be based on the isotopic data of steam condensate from the Owakudani area (CW-2), which exhibits the highest δD and $\delta^{18}O$ values among all the Hakone samples studied.

The high δD and $\delta^{18}O$ values of the Owakudani steam (CW-2) suggest a close relationship between CW-2 steam and HTDS. The average values of CW-2 (a triangle at the far right end of Fig. 2), however, do not lie on the extension of the thermal water line, $\delta D = 2.1\delta^{18}O - 33.5$, but slightly above the line. Yuhara (1968) estimated the temperature of subsurface reservoir of hot water beneath the central cones to be as high as $240^{\circ}C$ on the basis of the enthalpy measurement of the steam. We estimated the isotopic composition of the liquid in the reservoir to be $\delta D = -26\text{‰}$ and $\delta^{18}O = +3\text{‰}$, assuming the isotopic exchange equilibrium between the liquid and steam with the average observed isotopic composition of $\delta D = -25\text{‰}$ and $\delta^{18}O = +1\text{‰}$, with the help of the liquid-vapor fractionation factors at $240^{\circ}C$ given by Bottinga and Craig (1968). This set of values for the liquid lies just on the extension of the thermal water (liquid) line in Fig. 2. Let us assume here that the liquid water with $\delta D = -26\text{‰}$ and $\delta^{18}O = +3\text{‰}$ is a subsurface condensate of HTDS derived from a depth.

We can now set the isotopic ratios of the two extremes, i.e., HTDS and RGW to be $\delta D = -26\text{‰}$, $\delta^{18}O = +3\text{‰}$ and $\delta D = -51\text{‰}$, $\delta^{18}O = -8.5\text{‰}$, respectively. As mentioned already zone III waters are the mixture of HTDS and RGW. The contribution of HTDS to zone III waters is then calculated to be 25%, ranging from 20 to 36%, reflecting a slight change in isotopic ratios of zone III water. This estimate agrees well with the HTDS contribution of 30% estimated by Oki and Hirano (1970) on the basis of the chemistry of zone III waters. When the chloride content of zone III waters and mixing ratio of HTDS to zone III waters are taken to be respectively 2,500ppm and 25%,

the chloride content of HTDS is estimated to be 10,000ppm.

According to our latest experimental results (Shinohara *et al.*, 1984) chlorine bearing species in the steam phase coexisting with acidic silicate melt saturated with water are mostly NaCl with much less HCl, in the range from the total pressure of 1 to 6kb at the temperature of $800 \sim 900^{\circ}C$. So that the steam derived from a deep-seated magma can contain a significant amount of NaCl. According to Sourirajan and Kennedy (1962), the vapor with the temperature higher than $390^{\circ}C$ with the pressure higher than 150b can contain 10,000ppm of chloride ions in the form of NaCl. A large proportion of HTDS with the minimum temperature of $390^{\circ}C$ encounters the major aquifer of RGW to form zone III waters. A small portion of HTDS, however, ascends through conduits without mixing with RGW aquifer and condenses at a shallower and cooler place to form a liquid reservoir at the temperature around $240^{\circ}C$ beneath the Owakudani area. The isotopic composition of HTDS may be taken to be the same as that of the $240^{\circ}C$ reservoir which has been estimated above. Most of the dissolved NaCl in HTDS should be left behind during the ascent owing to the temperature drop from 390 to $240^{\circ}C$ to form the final liquid reservoir. So that chlorine-bearing compounds in the final reservoir should be mostly HCl. On the other hand, the concentration of volatile components such as HCl and H_2S in HTDS is almost kept unchanged before the condensation occurs. The steam from the subsurface liquid reservoir reaches the surface to reveal fumarolic activity. The acid gases explain low pH of 1 to 2 of the steam condensate, CW-2.

Origin of HTDS The estimated values of $\delta D = -26\text{‰}$ and $\delta^{18}O = +3\text{‰}$ of HTDS can be compared with $\delta D = -25$ to -30‰ and $\delta^{18}O = +8\text{‰}$ of the deep-lying hot brine of the Arima hot spring area, Hyogo Pref., Japan, estimated by Matsubaya *et al.* (1974), a narrow range centered at $\delta D = -25\text{‰}$ and $\delta^{18}O = +7\text{‰}$ of high temperature fumarolic gas condensates of

Satsuma-Iwojima, off south end of Kyushu, Japan, measured by Matsuo *et al.* (1974) and Matsubaya *et al.* (1975), and $\delta D = -28$ to $+6\text{‰}$ and $\delta^{18}\text{O} = +7\text{‰}$ of steam condensates from White Island fumaroles, New Zealand (Stewart and Hulston, 1975).

When we assume that the difference in $\delta^{18}\text{O}$ values of the above cited thermal waters is due to the difference in the extent of rock-water interaction at different temperatures, $\delta^{18}\text{O}$ of the deep thermal waters gives us no definite information on the ultimate origin of the deep thermal waters. On the other hand, the similarity in δD values for the above cited systems may be an interesting problem to be solved. The similarity in δD values, however, does not imply the direct contribution of "juvenile water", since there is no positive reason to imagine that the upper mantle beneath active zones such as Japanese and New Zealand island arcs has retained the juvenile water throughout its histories and the mantle water is estimated to have δD values between -90 and -75‰ (Matsuo *et al.*, 1978). The facts that high $^3\text{He}/^4\text{He}$ ratio of the gas from CW-1 of 8.6×10^{-6} is about six times as high as the atmospheric value of 1.4×10^{-6} and that He/Ne ratio is 140 times higher than that of the atmosphere (Craig *et al.*, 1978), however, indicate that most of the helium must have derived from the juvenile helium retained in the mantle. This fact is a clear indication of the least contamination for the mantle helium during the degassing of mantle volatiles, in contrast to the overwhelmingly large contribution of local surface water that erases the isotopic signature of (juvenile?)

water.

Why is the δD value of HTDS of the Hakone geothermal system -26‰ ? We will present a model which may account for the origin of HTDS. The Hakone volcano (Pleistocene) is underlain by thick piles composed mostly of submarine pyroclastic sediments of the lower to middle Miocene (the Yugashima group). Common alteration products of this group are calcite, zeolites and chlorite (Kuno, 1950). When a fluid reaches the Yugashima group at depths, the fluid interacts with pre-existing hydrous silicates and changes its original D/H ratio. The final δD value of the fluid should be -26‰ .

In order to check this possibility, rock samples of the Yugashima group were analyzed for D/H ratio. Description of the samples and analytical results are given in Table 6. The δD values of samples 1 and 2 in Table 6 can be considered to represent those of typical pre-existing hydrous silicates in the Yugashima group, and in this sense these samples are regarded as "fresh". Samples 3 and 4 with lower δD values, on the other hand, can be considered to have been subjected to later interaction with recent thermal waters pertinent to the system. Thus samples 3 and 4 can be regarded as "altered" ones. Since chlorite is the predominant hydrous silicate mineral in the rock samples, chlorite can be considered to represent the hydrous silicates in the samples on the first approximation.

A close look at Table 6 reveals that the water content of the altered samples to be almost doubled as compared with that of the fresh

Table 6. Total water content and D/H ratio of hydrous silicates from the Yugashima group

Sample number	Sample description	Water content (bulk, %)	δD (‰)
1	Typical Yugashima group at Atsugi (80m thick)	1.63	-55.0
2	Core sample from the basement rock of the Hakone area. Taken by Kuno which is located in the zone IVa 209m deep	1.27	-53.1
3	Core sample from the Yugashima group interacted with the Hakone thermal water. Taken from Suzawa which is located in the middle of zone III, 293m deep	3.22	-62.4
4	Yugashima group interacted with the Yugawara thermal water. Taken from Fudo-taki, Yugawara geothermal area	3.28	-71.5

samples. This indicates that during water-rock interaction a part of water was incorporated into the hydrous mineral phases to give a net increase in chlorite content of the altered samples. In a closed system we get the following isotopic material balance equation for the water-rock interaction,

$$W\delta_w^i + C\delta_c^i = (W - \Delta W)\delta_w^f + (C + \Delta W)\delta_c^f \quad (1),$$

where W and C are the number of hydrogen atoms of water and chlorite, respectively, ΔW the increase of chlorite hydrogen at the expense of the equivalent amount of water, and i, f, c and w denote initial, final, chlorite and water, respectively. If we assume attainment of hydrogen isotopic exchange equilibrium, the following relation holds,

$$\delta_c^f - \delta_w^f = 10^3 \ln \alpha \quad (2),$$

where α is the fractionation factor between chlorite and water. Since the water content of the altered samples is twice as much as that of the fresh samples,

$$\frac{C + \Delta W}{C} \simeq 2 \quad (3).$$

Combining equations (1), (2) and (3), we get

$$\frac{C}{W} = \frac{\delta_w^f - \delta_w^i}{\delta_c^i - \delta_w^f - 2 \times 10^3 \ln \alpha} \quad (4).$$

We can now put the following values into equation (4); $\delta_c^i = -54\text{‰}$ for the fresh chlorite (average of samples 1 and 2) and $\delta_w^f = -26\text{‰}$ for δD of HTDS. $10^3 \ln \alpha$ for the chlorite-water system can be found in Taylor (1974) and Marumo *et al.* (1980), and the value of -40 for the temperature around 400°C is tentatively taken for the purpose of calculation.

Since the C/W ratio is positive, $\delta_w^f - \delta_w^i$ should also be positive, i.e., δ_w^i should be more negative than -26‰ . From this, the water with relatively high δD values such as seawater (fossil

or present-day) cannot be considered to be the candidate for the initial water. For the same reason, the 1:1 mixture of sea water and RGW, which gives chloride content of $\sim 10,000\text{ppm}$ (the estimated chloride content of HTDS), can also be excluded. If we assume RGW as the initial water whose δD value is -51‰ , however, C/W ratio is calculated to be 0.5, which roughly corresponds to a weight ratio of rock to water of 14 for the rock containing 30% chlorite by weight. The rock/water weight ratio $(R/W)_w$ estimated above is higher than those for the Salton Sea $((R/W)_w = 2, \text{Clayton } et al., 1968)$ and Wairakei $((R/W)_w = 0.2, \text{Clayton and Steiner, 1975})$ geothermal systems, indicating the Hakone geothermal system to be more rock-dominated.

The above results show that RGW can be a source water of HTDS. If this is the case, δD value of the altered chlorite should be -66‰ , since $\delta_c^f - \delta_w^f = 10^3 \ln \alpha = -40$. The hydrous silicates in the Yugashima group which have interacted with the thermal waters give δD values of -62‰ (sample 3 in Table 6) and -72‰ (sample 4 in Table 6), which are in good agreement with the estimated value.

Oxygen isotopic material balance can be expressed in a form simpler than the case of hydrogen isotopes as follows,

$$W\delta_w^i + R\delta_r^i = W\delta_w^f + R\delta_r^f \quad (5),$$

where W and R denote respectively the number of oxygen atoms of water and rock including not only hydrous silicates but also other rock-forming minerals, δ_r^i stands for initial $\delta^{18}\text{O}$ value of the rock, and other notations are the same as those in equation (1) but hydrogen is replaced by oxygen. Equation (5) can be rewritten as follows using oxygen isotope fractionation factor, $10^3 \ln \alpha$, between rock and water,

$$\frac{R}{W} = \frac{\delta_w^f - \delta_w^i}{\delta_r^i - \delta_w^f - 10^3 \ln \alpha} \quad (6).$$

The numerator of equation (6), $\delta_w^f - \delta_w^i$, is so-called oxygen isotopic shift of water, and the

value of 11.5‰ corresponding to the isotopic difference between HTDS and RGW can be allotted. If we further assume $\delta_r^i = +7\text{‰}$ for the initial rock, $\delta_w^f = +3\text{‰}$ for the final water (HTDS) and $10^3 \ln \alpha = 2$ which is the fractionation factor for the system plagioclase ($\text{Ab}_{50}\text{An}_{50}$)-water at 400°C (O'Neil and Taylor, 1967) in equation (6), then R/W is calculated to be 5.8. This value corresponds roughly to rock/water weight ratio of 11.5, which is close to the value estimated from the hydrogen isotopic evidence and shows that the Hakone geothermal system is rock-dominated, probably owing to the limited supply of RGW in the caldera which is an independent hydrological unit (Matsuo *et al.*, 1979).

On these bases, we conclude that the ultimate source of HTDS is meteoric in origin of which isotopic composition is similar to that of RGW. A schematic presentation of our con-

clusion is shown in Fig. 6. The present results suggest that thermal and volcanic waters with δD values as high as -30 to -20‰ often observed for thermal water system (see the beginning part of section "Origin of HTDS") may have been evolved from hydrothermal interaction of meteoric water with rocks containing hydrous silicates.

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Fig. 6. A schematic presentation of a genetic model for the thermal waters in the Hakone geothermal system. See text for details.

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