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Hydrogen and oxygen isotope ratios of thermal waters of Okayama Prefecture, Japan

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Hydrogen and oxygen isotope ratios of thermal waters from 46 spas in Okayama Prefecture range from -62.6 to -29.2‰ in δD and from -10.0 to -4.4‰ in $\delta^{18}O$, respectively. The isotope ratios indicate that all but one of the thermal waters in Okayama Prefecture are meteoric in origin. The Ofuku thermal water is the only exception, which is probably a mixture of seawater and meteoric water with the ratio of about 1.

Sulfur isotope ratios of dissolved sulfate in the thermal waters range from -6.2 to 59.3‰ in $\delta^{34}S$. The high $\delta^{34}S$ values observed in some thermal waters may be due to bacterial reduction of sulfate.

keywords: Hydrogen isotope ratio, Oxygen isotope ratio, Sulfur isotope ratio, Thermal water, Spa, Okayama

I. Introduction

In the comprehensive isotope study of Japanese thermal water systems by Matsubaya *et al.* (1973) it was shown that the hydrogen and oxygen isotope ratios of thermal waters of Okutsu, Komori, and Yubara Spas of Okayama Prefecture were all on the meteoric water line of Japan. Hydrogen and oxygen isotope ratios of meteoric waters in Okayama Prefecture were determined by Yamamoto *et al.* (1993). In that study it was reported that the thermal waters from Yubara Spa had δD and $\delta^{18}O$ values similar to the nearby Asahigawa river waters.

There are now more than 80 spas in Okayama Prefecture. The present paper reports hydrogen and oxygen isotope ratios of thermal waters newly collected from the spas in Okayama Prefecture. Sulfur isotope ratios of dissolved sulfate in the thermal waters are also presented. At almost all the spas, thermal waters are pumped out to the surface from bored wells. Many of the waters are actually not hot at outlets, although they may be warm or hot underground. In this paper, all the waters from the spas are called as thermal waters as a matter of convenience.

II. Samples and analytical procedures

Thermal water samples were collected from 46 spas in Okayama Prefecture. Location of the spas is given in Fig. 1. They are numbered approximately from north to south.

Major elements were determined as follows: Na and K by flame photometry, Ca, Mg and SiO_2 by ICP-AES, Cl and SO_4 by ion chromatography, and HCO_3 by acidimetry.

Isotope ratios of hydrogen and oxygen of water were determined at the Institute for Study of the Earth's Interior, Okayama University. For D/H measurements, water was reduced using uranium metal. For $^{18}O/^{16}O$ analyses, water was equilibrated with tank CO_2.

Sulfur isotope ratios of dissolved sulfate were measured at the Central Research Institute of Mitsubishi Materials Co. Ltd. The results are given in conventional δ values as permil deviations from standards. The standards are SMOW for hydrogen and oxygen, and CDT for sulfur.

III. Results and discussion

Hydrogen and oxygen isotope ratios of water and sulfur isotope ratios of dissolved sulfate of thermal waters of Okayama Prefecture are listed in Appendix 1, together with their temperatures, pH and contents of major elements.

Most Okayama thermal waters are low in concentrations of dissolved materials. Of 51 thermal waters analyzed, only 7 thermal waters have TDS (total dissolved solids) more than 1,000mg/l. The most saline water is that of Ofuku, which has the TDS of 17,500mg/l, about half the average seawater. The next is Tamano, whose TDS is 8,520mg/l, about a quarter of the average seawater. Twenty-four thermal waters have TDS of less than 200mg/l, not so much higher than the average TDS of river waters of Japan (85mg/l) (Kitano, 1995).

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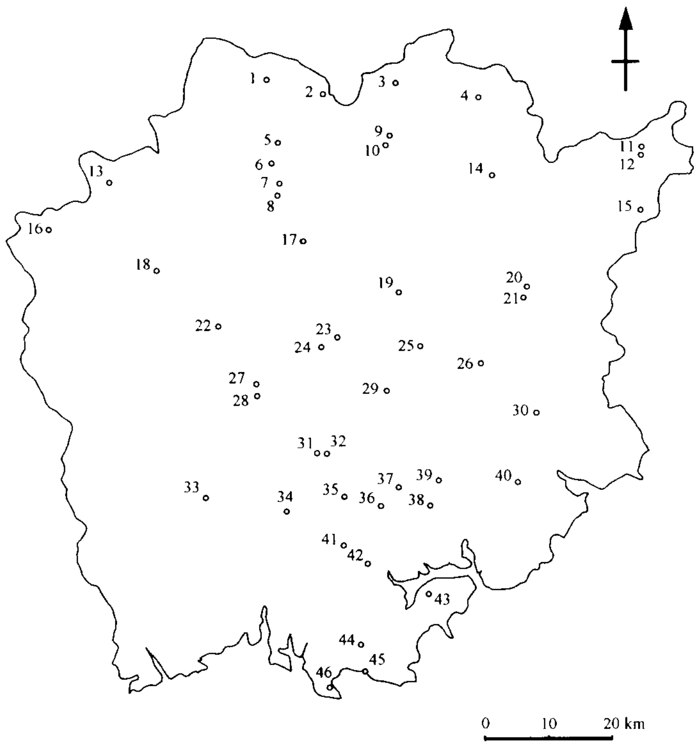

Fig. 1. Distribution of spas in Okayama Prefecture. Numbering is approximately from north to south. 1: Hiruzen, 2: Tsuguro-Kogen, 3: Kamisaibara, 4: Kurami, 5: Yubara, 6: Goroku, 7: Taru, 8: Maga, 9: Okutsu, 10: Otsuriso, 11: Awakura-Motoyu, 12: Awakura, 13: Niimi-Chiya, 14: Dodo, 15: Miyamoto-Musashi, 16: Shingo, 17: Kuse, 18: Kumatani, 19: Futagami, 20: Yunogo-Sagi, 21: Mimasaka, 22: Hokubo, 23: Komori, 24: Yunose, 25: Yugenohara, 26: Yume, 27: Tsukinohara, 28: Saginosu, 29: Yahata, 30: Wake-Ugaidani, 31: Uita, 32: Awai, 33: Onigadake, 34: Soja, 35: Inariyama, 36:Matsuo, 37: Tomada, 38: Yuba, 39: Okayama-Momotaro, 40: Yumeji, 41: Seto-Ohashi, 42: Ofuku, 43: Ikatsukayama, 44: Seto-Yuka, 45: Tamano, 46: Washuzan-Fukiage.

Hydrogen and oxygen isotope ratios of thermal waters range from -62.6 to -29.2‰ in δD and -10.0 to -4.4‰ in $\delta^{18}O$, respectively. They are plotted on the δD-$\delta^{18}O$ diagram in Fig. 2, together with the isotope ratios of river waters in Okayama Prefecture (Yamamoto *et al.*, 1993). It is shown that most thermal waters are plotted in the area similar to, but somewhat lower and wider than, the river waters. The plot indicates that most thermal waters in Okayama Prefecture are actually meteoric in origin.

Only exceptions are Ofuku and Yugenohara. Ofuku is plotted on the middle of the typical seawater (both δD and $\delta^{18}O$ are 0‰) and the river waters. This suggests that Ofuku is a mixture of seawater and meteoric water with the ratio of about 1. The chemical composition of the Ofuku thermal water supports the above suggestion: the content of Cl, the most conservative element, (10,100mg/l) is nearly half the average seawater (18,900mg/l) (Mason and Moore, 1982). As Ofuku Spa, Tamano Spa is located close to the coast of the Inland Sea and the thermal water is also saline, but the isotope ratios show no sign of mixing with seawater. The Tamano thermal water may have been formed by dissolution of salts initially precipitated from seawater with meteoric water.

Yugenohara is, although not so much as Ofuku, also high both in δD and $\delta^{18}O$. However, the possibility that Yugenohara is a mixture of meteoric water and seawater will be eliminated, because the Cl content of Yugenohara is too low for assuming mixing with seawater. In addition, the high concentrations of NO_3 (up to 19mg/l) (not included in Appendix 1) and Mg (3.7mg/l) compared to other low-TDS thermal waters suggest that Yugenohara is a very inmature groundwater. The higher δD and $\delta^{18}O$ values of Yugenohara may be due to kinetic isotope effect during evaporation, although it is not known in which stage of the thermal water-forming process evaporation occurred.

The d parameters of the thermal waters except Ofuku and Yugenohara are in the range from 9.5 to 21.2‰. The d parameters are plotted against the location Nos. of thermal waters in Fig. 3. It is seen that the d parameter decreases with increasing location No. The spas are numbered roughly from north to south. Therefore, the trend indicates that the d parameter of thermal waters decreases from the northern mountainous area to the southern coastal area of the Prefecture. Combined with the narrow isotope distribution range

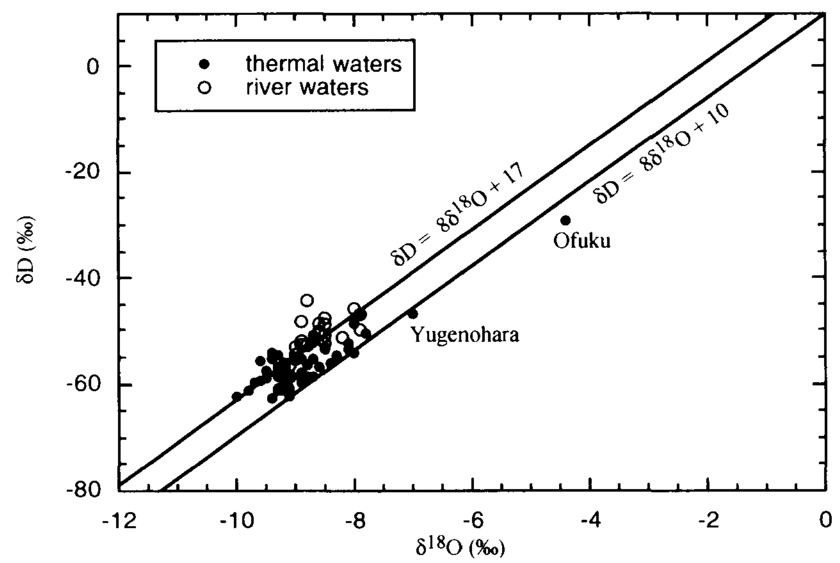

Fig. 2. Relationship between hydrogen and oxygen isotope ratios of thermal and river waters of Okayama Prefecture.

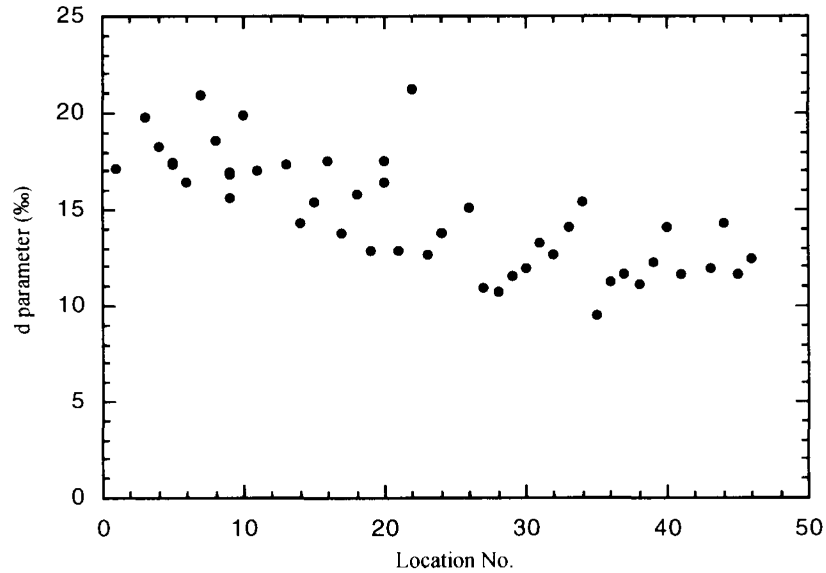

Fig. 3. Plot of d parameter vs location No.

for river waters (Fig. 2), this may indicate that each spa accumulates meteoric water from more restricted catchment area than each river does.

$\delta^{34}S$ values range from -6.2 for Yumeji to 59.3‰ for Seto-Ohashi. No apparent relationship is found between the $\delta^{34}S$ values and contents of sulfate in the thermal waters.

As discussed above, the Ofuku water is suggested to be a mixture of seawater and meteoric water with the proportion of 1 to 1. However, the $\delta^{34}S$ value of sulfate for Ofuku is 34.7‰, which is remarkably higher than the present seawater sulfate (20.4‰). On the other hand, the sulfate concentration (412mg/l) is significantly low compared to the expected value 1,300mg/l for simple mixing. This implies that bacterial reduction of seawater sulfate to sulfide made the remaining sulfate heavier (Sakai and Matsubaya, 1977). The $\delta^{34}S$ values greater than 20‰ found in Tamano, Yunogo-Sagi, Seto-Ohashi and others may also be due to bacterial reduction of original sulfate, because there seem to be few sulfur sources which have heavier $\delta^{34}S$ values than the present seawater sulfate. In about half of the thermal waters, the $\delta^{34}S$ values of sulfate are less than 10‰, which may reflect the $\delta^{34}S$ values of sulfide sulfur in host rocks, mostly granitic rocks. However, it is possible that the $\delta^{34}S$ values of sulfate in the low-temperature thermal waters in the present case do not always reflect the $\delta^{34}S$ values of source sulfur, because of modification to higher values by bacterial reduction of sulfate.

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Appendix 1. Isotope compositions of water and sulfate and chemical compositions of thermal waters in Okayama Prefecture, Japan

No.*	Well**	Date	Temp.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	TDS***	$\delta^{18}O_{SMOW}$	δD_{SMOW}	$\delta^{34}S_{CDT}$
			°C		mg/l								permil		
42	Ofuku	95.11.30	17.5	6.52	4230	30.0	912	771	10100	412	580	17500	-4.4	-29.2	34.7
45	Tamano	95.12.13	23.1	6.37	1040	10.0	1930	41.4	4730	384	176	8520	-8.6	-56.8	24.0
20	Yunogo-Sagi No.3	95.01.11	40.1	8.29	375	11.0	222	0.2	1010	15.7	15.0	1700	-9.2	-56.0	31.0
20	Yunogo-Sagi No.1	95.01.09	39.7	8.59	340	9.2	224	0.1	860	14.8	8.8	1500	-9.2	-57.2	31.0
1	Hiruzen-Yatsuka	96.11.12	22.9	8.00	350	4.2	12.0	14.3	6.6	8.8	975	1440	-9.8	-61.2	12.0
15	Miyamato-Musashi	95.08.06	18.6	8.79	386	2.3	98.6	1.9	745	7.0	37.2	1300	-8.9	-55.5	28.3
41	Seto-Ohashi	95.12.20	29.6	6.16	290	3.8	46.3	0.2	553	4.8	21.0	1230	-9.1	-61.2	59.3
16	Shingo	96.07.18	29.1	8.17	167	3.4	9.9	2.4	57.2	8.2	361	655	-9.7	-59.6	17.8
17	Kuse	96.11.12	24.4	7.86	173	1.7	28.8	1.0	228	1.8	108	578	-9.3	-60.7	27.8
43	Ikatsukayama	96.11.05	17.3	7.17	57.2	2.4	55.5	20.2	55.6	48.3	221	533	-7.8	-50.5	-0.7
21	Mimasaka	97.06.13	22.9	9.18	154	1.4	25.4	0.2	179	30.3	34.6	496	-8.9	-58.1	25.1
11	Awakura-Motoyu	97.03.18	13.5	8.45	108	1.5	19.5	2.9	48.4	9.4	190	413	-8.7	-52.3	16.1
39	Okayama-Momotaro	95.11.29	40.0	9.35	114	1.0	15.0	0.0	179	4.8	24.7	382	-9.1	-60.7	8.1
46	Washuzan-Fukiage	96.07.16	43.2	7.50	27.3	1.9	43.6	11.9	21.4	18.1	168	359	-8.1	-52.6	7.4
30	Wake-Ugaidani	97.03.24	31.7	9.64	97.2	0.5	3.0	0.2	112	6.8	37.2	318	-8.9	-59.6	-1.4
13	Niimi-Chiya	97.03.25	24.0	9.24	78.9	0.7	1.8	0.4	3.7	1.3	178	309	-10.0	-62.5	15.8
35	Inariyama	96.07.12	19.1	6.50	21.2	1.9	28.3	3.4	19.9	9.8	97.2	296	-8.0	-54.4	7.3
36	Matsuo	98.10.29	24.4	7.45	26.2	2.3	29.9	1.9	14.6	1.7	138.0	255	-8.4	-56.2	
29	Yahata	95.07.28	27.0	8.02	55.6	0.9	10.4	0.4	60.9	6.8	76.6	250	-8.3	-54.8	11.4
44	Seto-Yuka	96.07.16	21.1	6.69	27.2	1.5	15.3	1.2	10.8	4.2	103	246	-8.7	-55.5	16.8
31	Uita	96.07.13	20.9	9.89	71.6	0.5	0.8	0.1	15.0	4.3	60.6	232	-9.3	-61.1	11.8
32	Awai	96.07.13	22.8	9.40	70.2	0.7	2.3	1.2	40.9	4.3	55.2	231	-9.2	-61.1	21.8
37	Tomada	96.11.27	15.6	7.87	50.8	0.4	12.9	1.7	14.9	6.7	103	229	-8.8	-58.8	17.0
23	Komori	95.07.28	28.5	9.18	61.1	0.9	1.7	0.1	31.1	7.4	63.7	225	-8.9	-58.5	18.5
24	Yunose	96.07.17	29.4	9.59	58.5	0.4	1.7	0.1	26.7	5.0	66.6	222	-9.2	-59.4	12.7
5	Shimoyubara	95.01.11	37.6	9.21	65.3	1.8	1.6	0.0	35.1	15.3	39.3	213	-9.3	-56.9	6.1
26	Yume	95.07.28	18.3	8.09	38.3	1.0	11.1	1.6	15.5	7.7	93.0	209	-8.5	-53.0	0.8

(continued)

No.*	Well**	Date	Temp.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	TDS***	$\delta^{18}O_{SMOW}$	δD_{SMOW}	$\delta^{34}S_{CDT}$
			°C					mg/l						permil	
18	Kumatani	96.11.12	22.4	9.29	54.2	0.5	2.7	0.0	41.7	22.4	30.7	190	-9.3	-58.8	12.5
28	Saginosu	96.07.17	19.2	9.60	52.6	0.5	1.1	0.1	11.4	3.4	71.7	189	-9.1	-62.2	18.8
40	Yumeji	96.11.05	21.3	10.11	59.1	0.3	2.4	0.0	39.9	12.8	15.3	186	-9.1	-58.8	-6.2
27	Tsukinohara	96.07.17	38.5	9.10	44.2	0.6	3.2	0.4	14.4	4.3	75.7	185	-8.7	-58.8	13.8
12	Awakura	97.03.18	12.1	7.21	33.9	1.0	13.8	1.8	28.0	7.7	67.0	182			8.7
19	Futagami	96.07.11	21.7	8.29	43.1	1.0	2.4	0.2	14.9	13.2	75.6	173	-9.4	-62.6	16.1
38	Yuba	95.07.28	17.8	5.82	12.2	1.3	5.5	2.5	9.8	11.7	20.4	168	-8.1	-53.5	5.5
33	Onigatake	96.11.27	15.1	9.29	43.0	0.3	5.0	0.6	11.7	1.5	61.0	164	-8.8	-56.5	8.4
8	Maga	95.01.11	39.4	9.06	44.8	1.2	2.2	0.1	14.6	13.9	35.4	156	-9.5	-57.4	7.4
34	Soja	96.11.26	15.5	6.64	6.4	1.0	19.6	3.1	10.1	11.1	58.6	154	-8.0	-48.8	1.3
3	Kamisaibara	96.07.29	28.9	9.10	24.3	0.9	2.2	0.3	5.8	8.2	57.2	142	-9.4	-55.2	4.5
5	Onsenkanshita	95.01.11	47.7	9.14	40.0	1.4	2.0	0.1	16.9	7.4	32.3	142	-9.6	-59.4	6.9
14	Dodo	96.07.29	26.2	8.63	19.6	0.6	9.4	1.2	13.8	6.4	60.3	140	-8.5	-53.6	5.1
5	Sunayu	95.01.11	41.1	9.09	37.5	1.3	3.2	0.1	14.8	6.6	39.0	139	-9.2	-56.2	6.6
9	Okutsuso-Kagi	95.01.09	43.6	9.04	31.4	1.1	2.7	0.0	6.2	10.7	27.9	125	-9.3	-57.5	6.3
9	Bijin'noyu	95.01.09	34.2	9.07	30.5	1.1	3.1	0.1	6.1	10.7	27.1	124	-9.5	-59.2	5.8
6	Goroku	95.01.11	34.6	9.18	29.0	0.5	3.6	0.2	6.7	10.7	30.4	122	-7.9	-46.8	8.1
25	Yugenohara	98.11.25	17.2	6.55	10.7	2.8	14.1	3.7	15.6	12.3	46.5	121	-7.0	-46.9	
10	Otsuriso	95.01.09	37.6	9.30	30.5	1.0	2.1	0.0	6.7	10.3	22.8	120	-9.3	-54.5	6.2
2	Tsuguro-Kogen	96.07.29	28.9	9.10	20.4	1.0	3.1	0.1	4.7	9.3	38.4	113	-9.5		4.6
7	Taru	95.01.11	37.0	9.44	30.0	0.5	2.5	0.0	7.4	13.5	19.8	111	-9.6	-55.9	6.8
22	Hokubo	96.07.18	27.4	6.00	4.3	1.7	6.8	0.7	3.8	6.7	21.8	109	-9.4	-54.1	2.3
9	Yunokuchi	95.01.09	25.3	9.07	17.8	0.5	4.9	0.2	4.4	6.5	29.0	92	-9.3	-58.8	5.8
4	Kurami	96.07.29	17.3	6.29	4.1	0.5	3.1	0.6	5.3	2.3	14.3	60	-8.7	-50.9	8.3

*No. is the location of the spa shown in Fig. 1.

**The well name is identical with the spa name in most spas, but Yubara Spa (No.5) and Okutsu Spa (No.9) each have 3 wells with different names.

***TDS = Total dissolved solids. Thermal waters are listed in order of decreasing TDS downward.