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<https://doi.org/10.15017/17112>

出版情報：比較社会文化. 16, pp.65-72, 2010-03-20. 九州大学大学院比較社会文化学府
バージョン：
権利関係：

Geochemical characteristics of carbonate hot-springs in Japan

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Received 30 October 2009, Accepted 16 December 2009

Abstract

Chemical and isotopic compositions of water were measured at 46 carbonate hot-springs in Japan, by applying the methods avoiding the post-sampling alternation. Measured stable isotopic values indicate that CO₂ of an endogenic origin was dissolved in water of a meteoric origin, in many cases. The carbonate springs are generally in intermediate temperature for sustaining a high solubility of CO₂, and near-neutral pH as a result from the reactions between weak carbonate acid and rock-forming minerals. Although carbonate acid effectively dissolved carbonate minerals, this reaction is often unimportant among the water-rock reactions because the many water samples appear alkalinity-excess, relatively low Ca concentration, and high dissolved silica. However, a significant dissolution of ¹³C-enriched carbonate minerals was recognized in some samples showing a high carbon isotopic value and high equilibrate CO₂ partial pressure. Dissolved oxygen content implies a contact with the atmosphere or mixing with oxidative underground water, both of which decrease the initial CO₂ partial pressure and the concentration of dissolved chemical components.

Keywords : carbonate hot-spring, water chemistry, stable isotope

Introduction

Deep-sourced CO₂ from decarbonation of carbonate rock and degradation of organic matter is largely dissolved in underground water before it effuses as gaseous CO₂ near the Earth's surface. In the pre-industrial Earth, this endogenic CO₂ contributed a substantial fraction of CO₂ flux to the Earth's surface and therefore played a major role in the long-term change of the global climate (Berner, 1991, 2003). Because the CO₂ is normally

generated in heated settings by volcanism, it is often emitted with hot spring water, as commonly seen in Japanese Islands. However, reactions with rock-forming minerals and CO₂ in geothermal fluid largely reduces emitted fraction of CO₂.

Carbon dioxide can exist in a supercritical phase in a deeper geothermal setting below the depth of ~800 m (Xue, 2005), but it transfers to a gaseous phase in a shallower setting by decreasing temperature and pressure. Solubility of CO₂ increases with decreasing tem-

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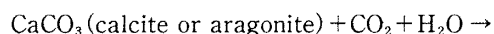
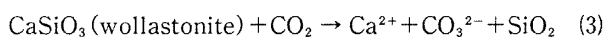
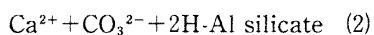
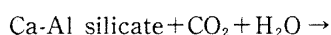
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perature [$\log f\text{CO}_2 = 0.016T (^{\circ}\text{C}) - 3.78$; Giggenbach, 1980, 1984]. In a depth where the water is still too hot to hold an amount of liquid CO_2 , the degassed CO_2 moves upwards or laterally along a permeable layer, and is dissolved in an aquifer of lower temperature. This is the second step. Because the moved CO_2 occurs as gaseous phase, and will be later dissolved in underground water that has normally a meteoric origin and avoids receiving a significant amount of acidic components, such as H_2SO_4 and HCl . Therefore, the carbonate water normally exhibits neutral or weakly acidic pH (Giggenbach, 1988).

The CO_2 dissolution produces protons (reaction 1) in underground and activates water-rock interactions (reaction 2-4), in another word, hydrothermal alteration (Henley and Ellis, 1983).



These are important reactions that contribute to increase Ca^{2+} concentration in water (Giggenbach, 1984) and decrease CaO in rocks. Despite of consumption along with these reactions, the water can fold dissolved carbon dioxide, until the equilibrate partial pressure ($p\text{CO}_2$) reaches interstitial pressure. The following equation 5 expresses that concentration of aqueous carbon dioxide ($m\text{CO}_2$) is in a function of $p\text{CO}_2$. K_H is Henry's law constant for CO_2 .

$$m\text{CO}_2 = K_H p\text{CO}_2 \quad (5)$$

It is known that the constant K_H decreases with temperature (Plummer and Busenberg, 1982). Going up to several hundred-ten meters deep in a hydrothermal aquifer, lowered temperature increases $m\text{CO}_2$, but lowered interstitial pressure decreases $m\text{CO}_2$. The two effects operate in the opposite way, and compensate each other. Then, the water of this depth range can keep a substantial amount of CO_2 . However in shallower depth, effect from the lowered pressure becomes predominant and generates CO_2 degassing. The degassed

CO_2 bubbles decrease the fluid density, and give the force for self-emission to the carbonate hot-spring water.

This is the theoretical consequence of the carbonate hydrothermal water. The CO_2 is further degassed when the water discharges and becomes non-equilibrium with the very low atmospheric $p\text{CO}_2$ (0.37 matm). The degassing on the ground is much quicker than in underground, and induces precipitation of calcium carbonate approximately following to the reaction 6.



The carbonate deposits are called travertines, "calcareous deposits by *in-situ* mineral precipitation in hot spring water", as defined by Ford and Pedley (1996). There are a number of travertine sites in Japanese Islands (Kitano et al., 1963), which has been recently subjected to biogeochemical studies by our research group (e.g., Kano et al., 2006; Takashima et al., 2008; Takashima and Kano, 2008).

For a part of the PhD study of the first author (Takashima, 2008), we have investigated a number of localities of carbonate hot-springs and travertines. The first author has applied a wide range of analyses including chemical and isotopic compositions of the hot-spring water. Purposes of this paper are to represent analytical methods of hot-spring water and to examine how the water chemistry follows the geochemical processes in the theoretical consequence. Carbonate hot-springs have been focused by geological and geobiological studies recently (e.g., Renaut and Jones, 2003; Jones et al., 2005; Pentecost, 2005), because they could be the modern analogs for the ancient warmer and CO_2 -rich oceans.

Material and methods

Water was collected from the site, as close as possible from the vent at 46 carbonate hot springs that are distributed in 12 prefectures in Japan (Table 1). Because the chemical and isotopic compositions of water samples are sensitive to the post-sampling alteration, we have experienced many failures and reached the recommended methods, as summarized in Fig. 1.

Dissolved oxygen (DO), alkalinity, and dissolved silica (SiO_2) were measured in the field within 3h. DO

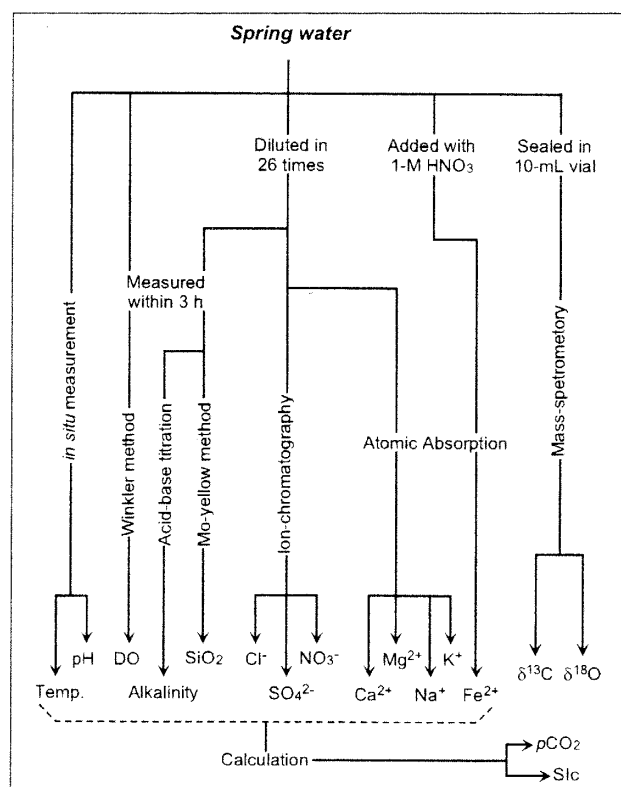


Figure 1. Methods of chemical and isotopic measurements for carbonate hot-spring water.

measurement was in the following procedures (Winkler-method). Water samples were collected a glass bottle, after adding a few drops of MnSO_4 solution and potassium iodated-sodium oxide solutions to fix DO. The bottle was sealed with a rubbers stopper and an aluminum cap. After DO was completely fixed to brown-colored precipitates, the bottle was opened, and H_2SO_4 was added in the water to dissolve the precipitates. Afterward, the sample were titrated by $\text{Na}_2\text{S}_2\text{O}_3$ solution, until the water becomes colorless. DO in mg/L was calculated from the consumed volume of the $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Two different water-sampling methods were applied to prevent changes in concentration of dissolved chemical components before the measurement. One uses adding 1M HNO_3 (containing 1%-La and 0.5%-Ce) of 10% volume of the water sample, for Fe^{2+} concentration measured by atomic absorption (Shimadzu AA-646). The added La and Ce compensate the interfering effect by SiO_2 , which reduces activity of Ca and Mg (Nyagah and Wangdiga, 1979). Another was dilution of 26 times with pure water, and used for other cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) with atomic absorption, anions (Cl^- , NO_3^- , SO_4^{2-}) with ion-chromatography (JASCO Gul-

liver), alkalinity titration with 0.05N H_2SO_4 (Bromocresol Green-Methyl Red method), and measuring SiO_2 (molybdenum yellow method) with a spectrophotometer. Based on the ion concentration (cation; mCi, anion; mAi) and electric charge (Z_i) of the relevant ion, the ionic balance (IB) was calculated with the following equation 7.

$$\text{IB (\%)} = (\Sigma \text{mCi}Z_i - \Sigma \text{mAi}Z_i) / (\Sigma \text{mCi}Z_i + \Sigma \text{mAi}Z_i) \times 100 \quad (7)$$

Our methods minimize the effect of precipitation in the bottles from collecting to measuring. We abandoned the results that were likely affected by the post-sampling precipitation. In the results from the successful analyses, a deviation was less than 3% for alkalinity, Ca^{2+} , Mg^{2+} , Cl^- , and SiO_2 , and was less than 10% for other components.

Equilibrate partial pressure of carbon dioxide (pCO_2) and Saturation Index for calcite (SIc) were calculated using the equations of Plummer and Bosenberg (1982).

$$\text{pCO}_2 = a\text{HCO}_3^- \times a\text{H}^+ / K_H K_1 \quad (8)$$

$$\text{SIc} = \log (a\text{Ca}^{2+} + a\text{CO}_3^{2-} / K_{\text{spc}}) \quad (9)$$

In equations 8 and 9, the letter a refers to ionic activity; K_H and K_1 are the equilibrium constants between gaseous and aqueous CO_2 , and between bicarbonate and aqueous CO_2 , respectively (see reaction 1); and K_{spc} is a solubility product of calcite. When $\text{SIc} = 0$, the water is exactly saturated with respect to calcite. Negative and positive values indicate undersaturation and supersaturation, respectively.

The water samples for isotopic analysis were carefully collected into a 10-mL glass vial without filtering to avoid degassing of CO_2 that significantly alters the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC). The bottle was then sealed with a rubber stopper and an aluminum cap for preventing a gas exchange. For analyzing both $\delta^{18}\text{O}$ of water and $\delta^{13}\text{C}$ of DIC, ca. 0.5-mL of sample water was added in a 12-mL glass bottle filled with 1-atm He and one drop (~ 0.02 mL) of H_3PO_4 . Here, DIC mostly degasses as gaseous CO_2 , and the rest of a tiny portion remains as aqueous CO_2 . Then the sample was kept at 25.0°C for three days to gain the

isotopic equilibrium. The prepared samples were analyzed with a Finnigan Delta Plus accompanied by the Gas Bench. This method advances the previous methods, because a single analysis provide both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. For calibration of $\delta^{18}\text{O}$, SMOW (standard mean ocean water) samples were also analyzed. The measured $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_\text{M}$) were recalculated by equation 10 considering a minor amount of dissolved inorganic carbon in the water sample, which depends on the volume of water (V in mL).

$$\delta^{13}\text{C}_\text{DIC} = [(12-V)\delta^{13}\text{C}_\text{M} + KV(\alpha(1000 + \delta^{13}\text{C}_\text{M}) - 1000)]/12 \quad (10)$$

Fractionation factor (α) between gaseous and aqueous CO_2 of Zhang et al. (1995) was used in the calculation. K is the factor between $\text{CO}_{2(\text{aq})}$ contents in a unit volume of the water vs. in a unit volume of the gas. Reproducibility (2SD) of the isotopic analysis is $\pm 0.18\text{‰}$ for $\delta^{18}\text{O}$, and $\pm 0.04\text{‰}$ for $\delta^{13}\text{C}$ (Hori et al., 2009).

Results and discussions

Physico-chemical properties of spring water of the 46 localities are listed in Table 1. Though a wide range in temperature from 10.3 (11 Uchinamigawa) to 91.6°C (3 Kaminoyu), waters in many localities are intermediate temperature (25–55 °C). The measured pH values are from 5.57 (26 Sambe) to 8.42 (3 Kaminoyu) and the near neutral pH is a characteristic of the calcareous hot spring water.

Alkalinity ranges from 3.38 (17 Oda) to 62.53 mM (25 Kada), and Ca concentration ranges from 56.7 (23 Ushio) to 1105 mg/L (5 Furofushi; Table 1). Cross-plots of alkalinity and Ca shows that just a few data are on the ionic balance between bicarbonate and Ca^{2+} ions (Fig. 2A). This implies that dissolution of carbonate minerals (reaction 4) was not the dominant underground reaction. The alkalinity-excess observed in many data (especially prominent for 23 Ushio and 25 Koda) means that the endogenic CO_2 reacts with non-carbonate minerals, as shown in reactions 2 and 3.

The extremely high concentrations of the other cations and anions at Tsubakihara (and also at 5 Furofushi) result from mixing with seawater. Even after eliminating these two samples, the concentrations are

highly variable; Mg^{2+} from 5.3 (10 Chugu) to 356 mg/L (38 Satonoyu), Na^+ from 2 (11 Uchinamigawa) to 4540 mg/L (31 Nakayamaga), K^+ from undetected (43 Myoken Tajima) to 510 mg/L (31 Nakayamaga), Fe^{2+} from undetected to 18.6 mg/L (20 Shioido), Cl^- from 4 (11 Uchinamigawa) to 6870 mg/L (20 Shioido), SO_4^{2-} from undetected to 1740 mg/L (9 Yunokura out). For many samples, Na^+ is the most abundant cation, and Ca^{2+} is the second (Table 1) implying that Na-silicates were substantially subjected to hydrothermal alternation. Concentration of dissolved silica (SiO_2) ranges from 5.2 (11 Uchinamigawa) to 270 mg/L (33 Daimaru vent), and is also high at other localities in Ohita Prefecture (Table 1). Because SiO_2 of ordinary freshwater hardly attains 10 mg/L, and its high concentration (generally >20 mg/L) indicates that the reaction with silicates is important. The ionic balance ranges from -8.6 to 6.9% , but generally ranges within $\pm 4\%$ (Table 1), which supports the overall accuracy of the chemical measurements.

Calculated pCO_2 values also appear a wide range from 8 (3 Kaminoyu) to 1830 matm (24 Chihara). For seven samples, pCO_2 exceeds 1 atm meaning that the water discharges quickly before the degassing reduces the interstitial pressure to the atmospheric level. SIc is from an extremely low value (-1.52) at Sambe vent (26; Table 1) to the highest value ($+1.68$) at Kibeya (22; Table 1). Among the 46 water samples, 30 are supersaturated ($\text{SIc} > 0$) with calcium carbonate, and eight samples are more than 10 times supersaturated ($\text{SIc} > 1$). There is a tendency that the high- pCO_2 water is closed to the saturation ($\text{SIc} = 0$).

Dissolved oxygen (DO) is diverse from undetected (0.0 mg/L at nine localities) to the saturated value (8.29 mg/L at 43 Myoken Tajima; Table 1). Assuming that the hydrothermal aquifer is basically oxygen free, the DO content implies a contact with the atmosphere or mixing with oxic underground water. A contact with the atmosphere induces CO_2 degassing, and mixing with underground water depletes the concentration of dissolved chemical components. Therefore, both processes reduce pCO_2 and increase DO, resulting in the negative correlation between pCO_2 and DO (Fig. 2B).

Carbon isotopic values of dissolved inorganic carbon are mostly within a range from $+1.01\text{‰}$ (2 Tenyu) to -8.17‰ (32 Ramune). The sample from Oda (17;

Table 1. Chemical and isotopic compositions of water samples collected from 46 carbonate hot springs; No.1–9 from Hokkaido and Tohoku, 10–27 from central-western Honshu, and 28–46 from Kyushu district. Dissolved oxygen (DO) and concentrations of ions (including SiO₂) are shown in mg/l. Alkalinity and ionic balance (IB) are in mM. pCO₂ is in atm.

No	Samples	Prefecture	Date	Temp	pH	Alkalinity	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ²⁺	Cl ⁻	SO ₄ ²⁻	SiO ₂	IB	pCO ₂	Sic	DO	δ ¹³ C	δ ¹⁸ O
1	Futamata	Hokkaido	02-06-14	35.0	6.24	26.65	514.4	78.7	1676	499.4	1.3	3336	89	20.2	-2.0	909	0.44	0.31	-4.57	-8.15
2	Tenyu	Hokkaido	02-06-15	52.8	7.25	22.75	85.3	12.9	496	26.0	0.0	174	16	43.3	-0.8	111	0.97	2.34	1.01	-
3	Kaminoyu	Hokkaido	02-06-16	91.6	8.42	12.79	82.7	9.3	1974	119.2	0.0	1947	992	49.9	3.0	8	-	2.23	-2.82	-
4	Furutobe	Aomori	04-09-03	43.1	6.87	23.71	507.9	93.6	809	62.0	10.3	1243	805	59.2	-3.9	200	1.13	0.23	-0.12	-9.00
5	Furofushi	Aomori	04-09-05	44.1	6.69	33.87	1105.2	664.4	5698	306.2	19.4	12414	1393	-	-6.1	366	1.18	0.24	-2.34	4.56
6	Tsubakiyama	Aomori	04-09-05	51.5	6.69	20.84	898.6	1297.0	11491	589.6	25.7	22909	2383	-	-3.6	248	0.91	0.07	-1.42	-2.09
7	Okuoku-hachikuro	Akita	04-09-03	43.3	6.63	27.62	789.4	149.6	509	25.1	6.8	1269	766	54.0	-3.2	386	1.10	0.00	0.98	-9.50
8	Hirokawachi	Yamagata	04-09-06	35.2	6.90	29.96	294.7	64.9	541	59.7	8.7	734	23	-	-6.3	224	0.99	0.12	0.96	-11.71
9	Yunokura out	Fukushima	04-09-06	59.9	7.12	16.41	392.9	76.4	1548	110.0	2.7	1724	1735	-	-2.6	102	1.28	3.37	-0.27	-10.86
10	Chugu	Ishikawa	02-09-17	52.8	6.67	11.10	62.4	5.3	46	67.0	-	1080	98	68.6	-	203	-0.02	1.67	-	-10.63
11	Uchinamigawa	Fukui	02-09-18	10.3	7.31	8.45	149.0	20.7	2	0.6	0.0	4	31	5.2	0.3	19	0.38	6.97	-1.18	-9.78
12	Uchinami	Fukui	02-09-18	14.6	6.53	34.20	177.5	36.2	1442	281.0	-	1343	173	12.2	-	476	0.22	3.59	-	-
13	Shionoha	Nara	05-03-14	39.2	6.46	35.30	348.0	46.2	671	52.1	6.2	757	0	37.4	-	760	0.71	0.00	-4.30	-9.25
14	Kibeya geyser	Shimane	02-08-17	19.5	6.09	35.43	292.4	-	-	-	-	1753	0	34.3	-	1432	0.05	0.00	-	-
15	Tsuwano	Shimane	02-08-17	18.8	6.22	24.13	72.4	26.7	-	-	5.6	666	19	20.2	-	731	-0.53	0.00	-4.81	-
16	Yunotsu	Shimane	02-08-18	48.8	5.95	15.38	381.2	23.3	809	36.4	0.6	2707	1061	39.5	-8.6	1282	-0.01	0.33	-7.25	-
17	Oda	Shimane	02-08-18	16.7	7.23	3.38	62.1	60.3	1780	76.0	1.8	201	164	28.2	-1.2	10	-0.36	1.98	-18.02	-
18	Ikeda radium	Shimane	02-08-18	20.9	6.01	24.25	293.3	9.6	215	10.6	0.3	3629	419	51.1	-5.4	1141	-0.23	0.00	-	-7.48
19	Sambe	Shimane	02-08-18	35.0	6.50	4.83	92.4	119.6	-	238.9	0.4	956	11	68.0	-	98	-0.55	4.55	-4.48	-
20	Shioido	Shimane	06-06-09	19.3	6.61	40.02	352.4	186.4	4461	152.3	18.6	6870	60	-	-1.3	412	0.49	0.60	-4.40	-6.34
21	Hatonoyu	Shimane	06-06-09	30.5	6.15	20.01	390.7	50.5	1078	22.6	8.6	1646	5	-	3.3	756	0.12	0.00	-6.11	-9.04
22	Kibeya	Shimane	06-06-09	22.9	7.71	30.02	364.6	33.0	1161	42.4	4.8	1557	0	-	-1.0	28	1.68	-	-1.15	-8.63
23	Ushio	Shimane	06-06-10	19.8	6.21	53.53	56.7	14.3	2056	76.5	15.5	1400	48	-	0.7	1561	-0.46	0.34	-4.54	-7.46
24	Chihara	Shimane	06-06-10	31.7	5.94	30.02	239.2	47.8	2580	127.4	2.7	3363	299	-	0.1	1827	-0.21	0.26	-4.75	-8.29
25	Kada	Shimane	06-06-10	16.0	6.42	62.53	369.8	166.1	1025	34.7	15.1	465	29	-	1.9	1039	0.55	0.00	-5.37	-8.21
26	Sambe Vent	Shimane	06-06-10	35.1	5.57	3.75	102.8	41.1	405	47.5	8.8	867	10	-	-1.9	644	-1.52	3.87	-7.36	-8.31
27	Koyabaru	Shimane	06-06-11	31.9	6.61	12.51	230.5	69.6	1043	125.8	2.7	1918	185	-	-3.4	171	0.19	4.54	-3.82	-7.58
28	Kyusukei	Ohita	05-02-09	27.1	6.58	16.15	71.7	63.5	309	40.1	0.0	110	172	48.8	0.9	243	-0.17	-	-6.35	-9.13
29	Ukenokuchi	Ohita	05-02-09	43.8	6.24	16.83	121.3	72.6	338	156.2	0.0	211	335	88.8	1.7	699	-0.10	0.09	-5.84	-9.41
30	Ganiyu	Ohita	05-08-29	40.2	6.63	47.45	198.1	306.0	466	103.5	2.0	176	325	84.0	-1.0	711	0.71	0.97	-6.13	-9.79
31	Nakayamaga	Ohita	05-07-28	39.9	7.40	44.29	146.9	107.8	4543	512.3	0.0	6034	300	98.8	-1.4	102	1.18	-	-1.72	-7.15
32	Ramune	Ohita	05-08-29	33.2	6.19	20.84	76.0	136.5	215	59.0	2.9	89	218	176.8	-3.7	831	-0.39	0.00	8.17	-10.20
33	Daimaru vent	Ohita	05-08-29	45.8	6.55	42.90	160.0	232.1	471	94.1	1.7	186	388	270.4	-5.9	860	0.59	0.90	-6.63	-10.30
34	Dajmaru parking	Ohita	05-08-29	45.1	6.37	35.75	148.4	229.8	432	82.7	1.5	156	325	244.8	0.3	1083	0.33	0.29	-6.58	-10.53
35	Shichirida	Ohita	05-08-29	29.8	6.85	34.06	156.6	248.7	449	70.2	1.0	142	562	236.6	-0.2	266	0.63	0.81	-7.74	-9.51
36	Mifune	Ohita	05-08-29	46.2	6.96	35.10	157.6	231.0	477	82.7	0.6	175	566	221.1	-2.0	275	0.94	4.32	-6.69	-9.49
37	Naganoyu	Ohita	05-08-29	43.3	6.48	39.52	148.4	266.8	516	85.3	2.0	174	524	187.2	-1.2	891	0.43	5.47	-7.40	-8.71
38	Satonoyu	Ohita	06-11-19	30.9	6.72	36.27	114.5	355.5	560	87.7	0.6	218	600	73.3	5.7	386	0.38	5.51	-4.77	-8.39
39	Shiroyama	Miyazaki	06-11-20	36.6	6.62	33.77	335.4	196.1	943	67.0	4.4	530	1057	-	3.3	470	0.75	5.05	-0.47	-6.41
40	Yunoo	Miyazaki	06-11-20	53.0	6.35	15.01	75.2	18.8	561	25.2	0.2	309	172	-	5.2	578	-0.10	4.34	-2.92	-6.81
41	Amaturikawa	Kagoshima	05-02-09	51.1	6.20	15.11	99.9	72.2	206	54.9	1.7	119	87	81.3	2.4	802	-0.13	0.68	-7.23	-8.09
42	TM vent	Kagoshima	05-02-10	38.4	6.53	35.17	242.5	73.5	424	54.4	2.5	135	13	74.8	-1.7	602	1.02	0.00	-0.67	-7.30
43	Myoken Tajima	Kagoshima	06-11-21	35.7	6.68	10.01	104.3	55.7	146	0.0	1.2	89	74	-	6.9	138	0.05	8.29	-6.29	-6.78
44	Anraku Rakuen	Kagoshima	06-11-21	43.3	7.64	16.26	141.1	77.6	201	27.3	0.6	135	76	-	2.7	27	1.35	5.77	-4.35	-6.84
45	Shiohitari	Kagoshima	06-11-21	50.1	6.23	16.26	131.5	92.7	210	37.8	2.8	153	69	-	4.9	780	0.02	1.37	-7.39	-6.76
46	Wake	Kagoshima	06-11-21	32.8	6.55	12.51	104.3	69.0	137	46.5	2.6	107	86	-	2.1	221	-0.04	5.26	-6.12	-6.65

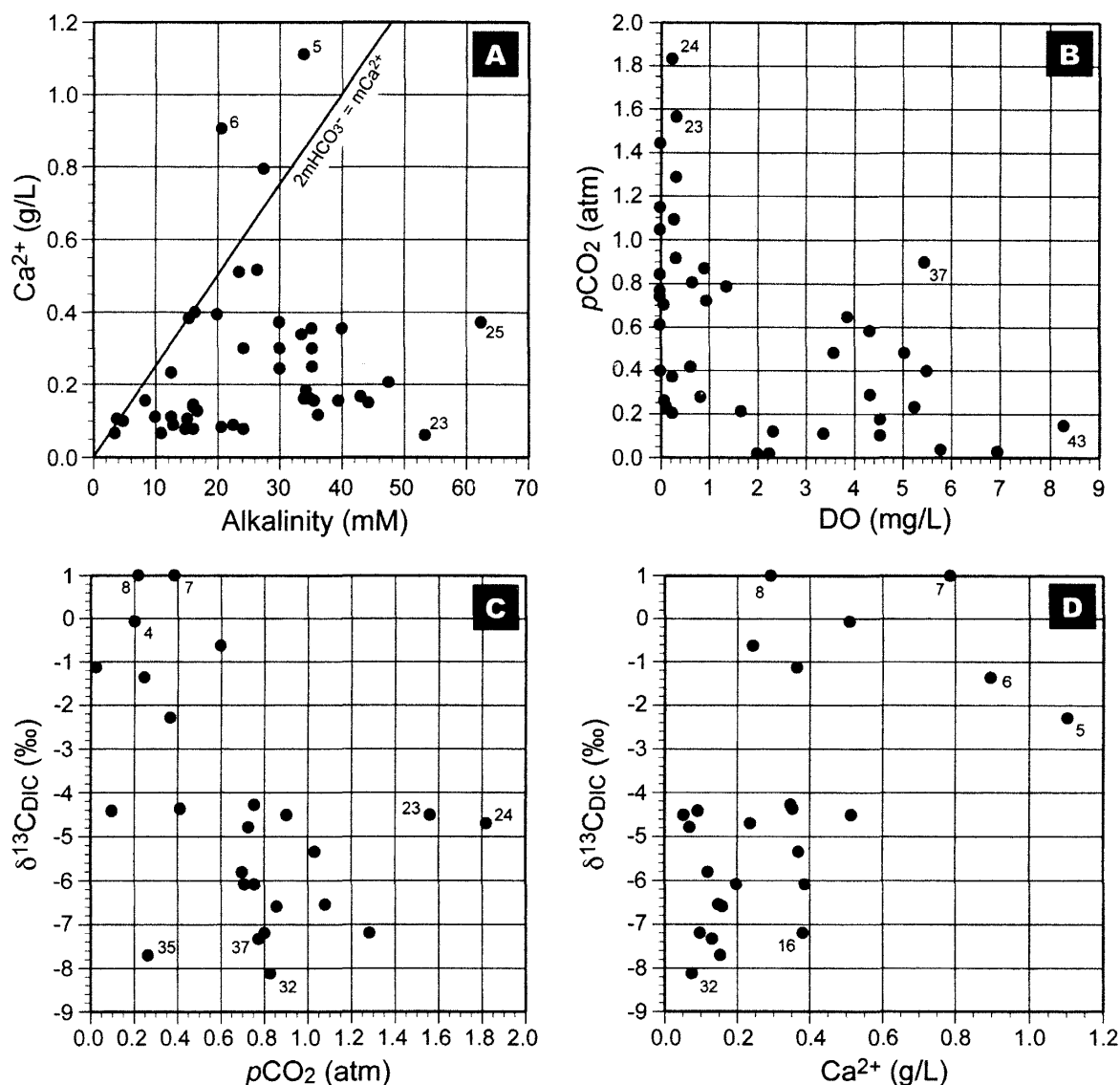


Figure 2. Cross-plots of geochemical and isotopic compositions of carbonate hot-springs, in Japan. A) Alkalinity vs Ca concentration (the line assumes the charge balance between bicarbonate and calcium ion), B) DO vs $p\text{CO}_2$, C) $p\text{CO}_2$ vs $\delta^{13}\text{C}$ for water with DO less than 1 mg/L, D) Ca concentration vs $\delta^{13}\text{C}$ for water with DO less than 1 mg/L. Numbers beside a plot correspond to locality numbers in Table 1.

Table 1) records an exceptionally low value (-18.02 ‰) that cannot be attained by an endogenic source (around -6 ‰; Berner, 1991), and requires a flux from soil CO_2 (around -25 ‰), or oxidized methane (generally below -65 ‰; e.g., Matsumoto, 1995), and alternatively the endogenic source mainly from degraded organic carbon. For relatively low $\delta^{13}\text{C}$ values in hot-springs in central Ohita Prefecture (32 Ramune, 35 Shichirida, 37 Naganoyu; Table 1), contribution of soil CO_2 was suspected by Iwakura et al. (2000). The additional influence to $\delta^{13}\text{C}$ value is CO_2 degassing that increases the value due to preferential extraction of ^{13}C -depleted DIC. Therefore, a negative correlation

between $\delta^{13}\text{C}$ value and $p\text{CO}_2$ (Fig. 2C) is an expected trend for calcareous hot springs. Another interesting trend is a possible positive correlation between $\delta^{13}\text{C}$ value and Ca concentration (Fig. 2D), which likely associated with the high $\delta^{13}\text{C}$ values of carbonate minerals (around 0 ‰). For samples having low $\delta^{13}\text{C}$ value and low Ca concentration, dissolution of carbonate minerals (reaction 2) is unimportant.

Oxygen isotopic values of water range from -2.09 (6 Tsubakiyama) to -11.71 ‰ (8 Hirokawachi). The values are consistent with the data set of meteoric water in Japanese Island (Mizota and Kusakabe, 1994), which generally appear the latitude gradient (low in high

latitudes, and high in low latitudes). Two high values from two localities of western Aomori Prefecture (5 Furofushi and 6 Tsubakiyama) are ascribed to the seawater mixing.

Conclusions

Chemical characteristics of carbonate hot-springs indicate the principal processes for generating this type of hot spring water, as summarized below.

(1) Carbonate springs are generally intermediate temperature and near-neutral pH, likely because of the neutralization reaction with rock-forming minerals under the temperature for a high solubility of CO₂.

(2) Among the Ca-dissolving reactions (e.g., reaction 2-4), dissolution of carbonate minerals are not always important, as indicated by alkalinity-excess (Fig. 2A), low Ca²⁺ relative to Na⁺, and generally high dissolved silica (Table 1).

(3) The $\delta^{13}\text{C}$ value of DOC can be an indication of the CO₂ source unless the CO₂ degassing is sufficient. Degree of the degassing is evaluated by DO content, and the $\delta^{13}\text{C}$ values of the low-DO water can be explained by the reaction between endogenic CO₂ and carbonate minerals (Fig. 2D), except for a few cases (e.g., 17 Oda).

(4) The $\delta^{18}\text{O}$ values indicate that the water is basically originated from regional meteoric water circulated in a shallow part of the hydrothermal system. However, two samples from Aomori Prefecture clearly indicate mixing with seawater, which is supported by an extremely high content of Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻ (Table 1).

Acknowledgements

The manuscript was carefully reviewed by Dr. Nobuhiko Nakano. This study was supported by grants from the Ministry of Education, Culture, Sports, Science and Technology, Japan (18654085 and 20654047 to A.K.).

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日本における炭酸温泉の地球化学的特徴

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要 旨

日本国内の46ヶ所の炭酸泉について、採水後の成分変質に留意した方法で、化学組成・同位体組成の測定を行った。安定同位体の測定値は、深部起源の二酸化炭素が天水起源の水に溶解したことを示す。炭酸泉は一般に、高い二酸化炭素の溶解度を保持するために中温であり、弱酸である炭酸と造岩鉱物の中和反応により中性のpHを示す。炭酸は効果的に炭酸塩鉱物を溶解する性質を持つが、多くの水試料が過剰なアルカリ度、比較的低いカルシウム濃度、高い溶存シリカ濃度を示すことから考えると、炭酸塩鉱物の溶解反応は重要でないことが多い。ただし、高い溶存炭酸の炭素同位体比と高い平衡二酸化炭素分圧を示す試料では、 ^{13}C に富む炭酸塩鉱物の溶解が重大に起こっていた。溶存酸素濃度は大気との接触もしくは酸化的な地下水との混合を示し、このような場合、初生的な二酸化炭素分圧と溶存化学成分の濃度は低下する。

キーワード：炭酸温泉，化学組成，安定同位体