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Chemical properties of surface waters in the limestone regions of western Japan: Evaluation of chemical conditions for the deposition of tufas

By

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with 1 table and 4 figures

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Abstract: In order to understand the chemical conditions for the deposition of tufas, chemical properties of were investigated for the 201 surface waters collected from the limestone regions including newly discovered localities of tufas. The collected waters were categorized, according to the association with tufas, mainly into; category N (waters without tufa deposition), category T (waters depositing tufas), and category S (spring waters of tufa-depositing streams). These three categories clearly differ in Ca contents, equilibrium CO_2 partial pressure (P_{CO_2}), and saturation index for calcite (SIC); all of which are the most important chemical properties for the deposition of tufas. The waters of the category N are characterized by small Ca contents (mainly 15~35 ppm) and low P_{CO_2} (350~1,000 μatm) which indicate that they are basically flowing on a limestone substrate without an efficient CO_2 uptake from soils. Their SIC never exceeds +0.5. The waters depositing tufas (category T) normally exhibit Ca contents more than 45 ppm and P_{CO_2} ranging 500~2,000 μatm. The waters of category S show comparable or slightly larger Ca contents than category T, however their P_{CO_2} is considerably higher (than 2,000 μatm). Their raised values of Ca contents and P_{CO_2} are ascribed to efficient CO_2 uptake in a soil layer and subsequent dissolution of $CaCO_3$. Furthermore, their SIC around 0.0 indicates that the waters dissolve $CaCO_3$ until they reach the saturation in underground water systems. The large difference in P_{CO_2} between categories T and S results from degassing of CO_2 during flowing on the streams. The degassing increases pH and SIC of the waters. The SIC of category T mostly exceeds +0.5, that is probably the most important chemical condition for an efficient deposition of tufas. This study indicates that tufas are not very rare, but also that their distribution tends to be concentrated in a certain area, such as northwestern Okayama Prefecture. Local geological and hydrological conditions can be also important controls for deposition of tufas.

I. Introduction

Since recent recognition of the presence of tufas in Japan (Yoshimura et al., 1996b), the tufas become well-known among the Japanese geoscientists. Although we realize that the tufas involve important records of terrestrial climate, we still need to understand the geological, biological, and chemical backgrounds of tufas in order to decipher the climatic records.

A tufa was defined as a carbonate deposit formed in an open-air freshwater environment of ambient temperature (Ford and Pedley, 1996). Biologically, the most important associate is cyanobacteria; its colonization and metabolism act as a catalyst of carbonate precipitation on the surfaces of tufas (Pentecost and Riding, 1986).

The source of tufa-bearing water is normally an aquifer of carbonate rock. A stream originated from a limestone cave is one of the typical environments of tufas. The water in an underground water system is generally close to the saturation with respect to carbonate minerals (in the most cases, calcite). It contains raised concentrations of the dissolved CO_2-species (dissolved CO_2, HCO_3^-, and CO_3^{2-}) and calcium ion. The raised concentrations are largely ascribed to CO_2 uptake in a soil layer covering limestone. Meteoric water becomes aggressive (acidic by containing carbonate acid) in a soil layer, and dissolve a large amount of $CaCO_3$ during its residence time. When such the water once issues from an exit of a cave and is exposed to the air, the dissolved CO_2 of the water suddenly becomes disequilibrate to the P_{co_2} of the atmosphere. Thus, a part of the dissolved

CO_2 (up to 400 mg/l; Ford, 1988) is consequently degassed from the water. The precipitation of calcite is caused by and processed together with the CO_2 degassing which increases the saturation index of the water (Emeis et al., 1987).

This paper firstly presents chemical data of the waters collected from limestone regions of Japan; the waters are categorized according to the presence/absence of tufas. Geology and geography of the several tufa localities are also briefly described. Chemical condition of the tufa development are discussed with comparison in the chemical compositions between the different categories of the waters.

II. Method

We have visited more than 200 localities of limestone regions mostly located in the western part of Japan (Okinawa, Kochi, Ehime, Hiroshima, Okayama, Mie, Shiga, Aichi, Gifu, and Fukushima Prefectures) from January to December (until Christmas Eve) 1997. For each locality, temperature and pH of water were measured, and the water was collected with a 100 ml bottle with using a 0.45 μm membrane filter. The pH was determined by a pH-meter (Horiba D-21) calibrated with standard solutions at pH 6.86 and 9.18 (pH of all the waters settle within the range) in field.

The water samples were stored in a refrigerator and analyzed as soon as possible. Fifty milliliter of each water sample was used for acid-base titration with 0.05 M H_2SO_4 standard solution in order to determine alkalinity. Cations (Ca^{2+}, Mg^{2+}, Na^+, and in many cases K^+) were analyzed by an atomic absorption spectro-photometry; ionizing interference was excluded by analyzing mixing solution of 5 ml of sample water and 0.5 ml of 1% La and 0.5% Cs solution. For Ca^{2+}, measurement was done more than twice. Anions were analyzed by an ion-chromatography; SO_4^{2-}, NO_3^-, and Cl^- are important, however several waters contain a small amount of F^- and PO_4^{3-}. We have succeeded to reduce the measuring error; less than 1×10^{-5} mol/l for alkalinity; less than 2 % for Ca^{2+}, Mg^{2+} and anions; less than 5~10 % for Na^+ and K^+.

Saturation index for calcite (SIC) and equilibrium CO_2 partial pressure (P_{CO_2}) were calculated using an algorithm based on the techniques of Truesdell and Jones (1978). We used the most recently available equilibrium constants for the CO_2 system by Plummer and Busenberg (1982) and Morse and MacKenzie (1990). The former is defined as,

$$SIC = \log (a_{Ca^{2+}}, a_{CO_3^{2-}} / Ksp_{(calcite)})$$

Ionic balance (IB) is calculated by molar value of concentration of the analyzed cations minus anions.

III. Result

Table 1 shows the result of chemical analysis of the 201 water samples. The reference numbers (in the most left-hand column; Table 1) are used in the following description. Only firstly-collected data were shown for 4 localities (Shirokawa, Takatsuma, Sugano North, and Yasuhaya), because too many data were collected in several times in 1997. Tufa-bearing streams longer than 200 m in distance are surveyed with settling station-numbers descending from the spring to downstream; they are Shirokawa, Shimoida, Takatsuma, Kaminoro, and Yasuhaya.

Measured ionic balance (IB; Table 1) is normally low (in the order of 10^{-5} mol/l) with some exceptions, such as Fujiwara 2 (163) where a metal oxidite is deposited from the water. Large values of IB results from contents of unmeasured ions (probably cations) and partly from the accumulation of measuring errors, that may influence the calculation of SIC and P_{CO_2}. Therefore, the data of such waters (with $|IB| > 3.0 \times 10^{-4}$ mol/l) are not presented in Figs. 1 and 2.

The waters are categorized into 5 due to the presence and absence of calcite deposits. They are; waters without any deposition (N), the waters depositing tufas (T), the spring of tufa-depositing water (S), the water depositing pisoids (P), and the water with mat-like deposits (M) (Table 1).

For different categories of the waters, Ca contents and $\log P_{CO_2}$ are plotted on Fig. 1. Ca contents of the categories S, T, and P normally exceed 45 ppm (the lowest value is 44.1 ppm) and are high than those of the category N. The waters of S exhibit high $\log P_{CO_2}$ (mostly more than −2.8; Fig. 1).

Values of SIC is also dependent on the categories of the waters; normally less than 0.0 and never exceeds +0.5 for the waters of N; narrowly ranges from 0.0 to +0.5 for S; normally exceeds +0.5 for T and P.

IV. Description of the tufa localities

This section briefly describes important localities; some of them were already described in Yoshimura et al. (1996b), Kano (1997), and Kaneko et al. (1997).

A. Gizabanta

Gizabanta is the name of a cliff located on the southern coast of the Okinawa Island. Water is issuing from the middle of the cliff located near the boundary between the upper Naha (limestone) and the lower Chinen (calcareous sandstone) Formations. The water which initially represents high P_{CO_2} and relatively low SIC, escapes CO_2 during flowing a steep slope and deposits a tufa of a cascade shape, about 3 m in height, and several meters in width (Fig. 3a). Large difference in the Ca contents between the spring (1) and downstream waters (2) indicates a sufficient deposition of $CaCO_3$ during flowing only 20 m in distance. The water from the downstream records the highest value of SIC (=1.25). Chemistry of the waters contains a high amount

Table 1. Chemical properties of the 201 waters collected from limestone areas of Japan during the yaar of 1997. U, D, and T in the locality names indicate upperstream (often spring), lowerstream, and tributary. Prefectures are abbreviated; On = Okinawa, Kc = Kochi, Eh = Ehime, Hs = Hiroshima, Oy = Okayama, Me = Mie, Sg = Shiga, Ac = Aichi, Gf = Gifu, and Fs = Fukushima. Concentration of cations and anions are shown in ppm, alkalinity (Alk) is in 10^{-3} mol/l, and ionic balance is in 10^{-4} mol/l. Categories (Cat; refer the text) and remarks of the waters are also shown.

No.	Locality Name	Area	Latitude	Longitude	Date & time	T (°C)	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Alk	Cl^-	NO_3^-	SO_4^{2-}	SIC	$logPco_2$	IB	Cat	Remarks
1	Gizabanta-U	Gushikami, On	26°05'50"	127°44'12"	Nov.3-11:35	23.0	7.31	111.3	10.0	31.5	1.8	4.261	57.9	47.2	56.1	0.25	−1.93	0.69	S	
2	Gizabanta-D	Gushikami, On	26°05'49"	127°44'12"	Nov.3-11:45	23.8	8.46	98.7	10.0	33.3	1.5	3.487	–	–	–	1.25	−3.17	–	T	
*3	Ukijyu-hainjyu	Tamagusuku, On	26°07'50"	127°47'28"	Nov.3-13:00	23.5	7.85	137.2	17.8	37.9	2.2	5.045	68.1	40.4	94.7	0.92	−2.41	4.27	P	
4	Kakinohana-higya-U	Tamagusuku, On	26°08'38"	127°47'50"	Nov.3-10:45	23.4	8.01	97.2	5.4	17.6	2.2	4.668	38.7	9.0	20.1	0.94	−2.59	−2.07	T	
5	Kakinohana-higya-D	Tamagusuku, On	26°08'38"	127°47'50"	Nov.3-10:50	24.2	8.23	87.3	5.4	19.3	2.3	4.136	–	–	–	1.08	−2.86	–	T	
6	Irazuyama 3	Higashitsuno, Kc	33°26'07"	133°01'50"	Apr.20-12:40	11.3	7.58	2.7	0.6	3.6	0.4	0.250	1.8	1.1	2.0	−2.30	−3.45	−0.20	N	F^- = 0.2
7	Irazuyama 2	Higashitsuno, Kc	33°26'19"	133°03'12"	Apr.20-10:40	10.0	7.23	3.0	0.7	3.6	0.3	0.240	1.8	0.9	3.4	−2.65	−3.12	−0.05	N	
8	Shimanto-genryu	Higashitsuno, Kc	33°26'20"	133°04'30"	Apr.20-14:20	9.6	7.23	2.7	0.6	2.8	0.3	0.220	1.7	1.0	2.8	−2.74	−3.17	−0.29	N	
9	Irazuyama 1	Higashitsuno, Kc	33°26'23"	133°03'12"	Apr.20-10:10	8.9	7.52	2.8	0.7	5.0	0.3	2.350	2.0	0.0	3.1	−2.42	−3.43	0.71	N	
10	Nagano	Yusuhara, Kc	33°27'38"	132°56'48"	Apr.21-11:00	12.4	8.34	35.7	1.4	1.3	0.2	1.860	2.5	2.0	2.5	0.38	−3.36	−0.62	N	
11	Shikoku Karst	Higashitsuno, Kc	33°27'59"	132°59'47"	Apr.20-16:40	9.3	7.51	3.6	1.1	3.6	0.2	0.336	1.6	0.9	1.6	−2.16	−3.27	0.00	N	
12	Torigata-yama 2	Niyodo, Kc	33°29'02"	133°03'32"	Apr.19-13:35	10.6	8.01	19.3	0.5	1.8	0.3	0.994	2.0	1.5	4.4	−0.48	−3.30	−0.76	N	
13	Torigata-yama 1	Niyodo, Kc	33°29'03"	133°03'33"	Apr.19-13:30	10.3	8.33	28.4	0.5	2.3	0.3	1.325	2.4	2.1	6.9	0.11	−3.50	−0.15	N	F^- = 0.2
14	Kaminano	Agawa, Kc	33°33'44"	133°03'59"	Apr.19-15:55	9.5	8.20	30.6	0.5	1.0	0.3	1.510	3.0	2.4	3.5	0.05	−3.32	−0.90	N	
15	Nagasaka	Agawa, Kc	33°33'54"	133°04'57"	Apr.19-15:03	10.2	7.95	18.8	1.6	2.3	0.2	0.950	2.4	1.2	8.5	-0.58	−3.26	−0.39	N	
16	Kaneishi	Kagami, Kc	33°35'28"	133°45'15"	Aug.30-10:15	21.1	8.04	55.8	3.3	6.1	0.7	2.940	8.3	1.9	10.0	0.56	−2.81	−0.73	T	
17	Enjitsuji-U	Tosayamada, Kc	33°35'40"	133°44'28"	Aug.24-16:45	16.1	7.85	48.4	2.1	3.5	0.4	2.623	4.5	2.1	3.7	0.21	−2.70	−1.11	S	
18	Enjitsuji-D	Tosayamada, Kc	33°35'39"	133°44'28"	Aug.24-16:30	17.6	8.30	47.5	1.9	3.1	0.4	2.575	–	–	–	0.65	−3.15	–	T	
19	Nishi-gonyu	Tosayamada, Kc	33°38;41"	133°43'08"	Aug.28-16:20	17.0	7.49	33.9	4.6	3.8	0.4	2.025	3.8	5.5	4.6	−0.39	−2.44	−0.71	N	
20	Kinma Chyaya	Kahoku, Kc	33°41'16"	133°47'58"	Sep.13-12:30	18.7	8.12	10.8	1.5	3.2	0.3	0.676	2.9	1.1	3.5	-0.65	−3.53	−0.40	N	
21	Yasumori-do-U	Hiromi, Eh	33°17'42"	132°44'48"	Nov.9-15:00	14.8	7.89	32.8	2.6	3.1	0.5	1.809	3.8	3.0	4.4	−0.08	−2.90	−0.58	N	
22	Yasumori-do-D	Hiromi, Eh	33°17'42"	132°44'48"	Nov.9-14:50	14.9	8.29	32.9	2.6	2.9	0.5	1.814	–	–	–	0.32	−3.30	–	N	
23	Kan-nonsui-U	Uwa, Eh	33°20'34"	132°34'41"	Oct.13-10:55	14.7	7.88	25.9	1.3	1.9	0.5	1.432	3.8	1.3	2.5	−0.28	−2.99	−1.17	N	
24	Kan-nonsui-D	Uwa, Eh	33°20'33"	132°34'40"	Oct.13-10:40	14.4	8.10	24.9	1.4	1.7	0.5	1.377	3.7	1.3	2.5	−0.10	−3.32	−1.10	N	
25	Ikenono	Shirokawa, Eh	33°21'45"	132°47'38"	Nov.9-07:45	9.2	7.89	8.1	2.1	5.2	0.9	0.457	4.1	2.7	13.2	−1.32	−3.52	−0.65	N	
26	Shirokawa 29	Shirokawa, Eh	33°22'31"	133°48'54"	Mar.9-15:04	13.8	7.85	56.6	1.9	3.5	–	2.821	4.1	0.9	6.4	0.26	−2.68	0.48	S	
27	Shirokawa 28	Shirokawa, Eh	33°22'31"	133°48'54"	Mar.9-15:00	13.7	7.93	56.4	1.9	3.5	–	2.811	4.1	0.9	6.4	0.34	−2.77	0.48	S	
28	Shirokawa 26	Shirokawa, Eh	33°22'32"	133°48'55"	Mar.9-15:10	13.3	8.09	54.7	1.9	3.5	–	2.761	4.1	1.0	6.5	0.47	−2.94	0.10	T	
29	Shirokawa 25	Shirokawa, Eh	33°22'32"	133°48'55"	Mar.9-15:15	13.7	8.12	55.3	1.9	3.5	–	2.801	4.0	1.0	6.5	0.51	−2.96	0.03	T	
30	Shirokawa 22	Shirokawa, Eh	33°22'33"	133°48'56"	Mar.9-15:31	12.3	8.14	52.7	2.0	3.5	–	2.631	4.0	0.9	6.4	0.47	−3.01	0.55	T	
31	Shirokawa 18	Shirokawa, Eh	33°22'33"	133°48'56"	Mar.9-15:43	11.5	8.17	52.6	2.0	3.5	–	2.671	3.9	0.9	6.4	0.49	−3.04	0.14	T	
32	Shirokawa 15	Shirokawa, Eh	33°22'34"	133°48'57"	Mar.9-15:49	11.2	8.27	48.6	2.0	3.5	–	2.440	3.9	0.9	6.8	0.52	−3.18	0.36	T	
33	Shirokawa 13	Shirokawa, Eh	33°22'35"	133°48'58"	Mar.9-15:57	10.6	8.26	51.2	1.9	3.5	–	2.591	4.2	1.0	6.8	0.54	−3.15	0.05	T	
34	Shirokawa 10	Shirokawa, Eh	33°22'36"	133°48'59"	Mar.9-16:07	10.2	8.26	50.7	1.9	3.5	–	2.560	4.4	1.1	7.0	0.53	−3.15	−0.09	T	
35	Shirokawa 7	Shirokawa, Eh	33°22'37"	133°49'00"	Mar.9-16:17	9.8	8.29	48.9	2.0	3.5	–	2.470	4.2	1.1	7.0	0.52	−3.20	0.05	T	
36	Shirokawa 3	Shirokawa, Eh	33°22'37"	133°49'04"	Mar.9-16:41	9.5	8.30	51.3	2.0	3.5	–	2.580	4.6	1.2	7.0	0.56	−3.20	0.02	T	
37	Shirokawa 1	Shirokawa, Eh	33°22'37"	133°49'05"	Mar.9-16:45	9.4	8.31	48.0	1.9	3.5	–	2.400	4.6	1.2	7.1	0.51	−3.24	0.07	T	
38	Shirokawa-T	Shirokawa, Eh	33°22'37"	133°49'01"	Mar.9-16:25	10.1	8.09	68.2	1.6	3.6	–	3.300	9.2	7.5	7.2	0.58	−2.88	−1.39	T	

Table 1. (continued)

No.	Locality Name	Area	Latitude	Longitude	Date & time	T (°C)	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Alk	Cl^{-}	NO_3^{-}	SO_4^{2-}	SIC	$logPco_2$	IB	Cat	Remarks
39	Nakatsugawa	Shirokawa, Eh	33°22'37"	133°49'06"	Mar.9-16:55	9.2	8.05	27.1	1.9	3.5	–	1.426	4.3	1.5	10.8	−0.18	−3.19	−1.35	N	
40	Jiyoshi 1	Yanadani, Eh	33°28'06"	132°55'56"	Apr.21-11:55	9.3	8.07	23.7	0.4	2.0	0.2	1.210	2.1	1.5	1.6	−0.28	−3.28	−0.25	N	PO_4^{3-} = 0.2
41	Jiyoshi 3	Yanadani, Eh	33°28'15"	132°55'18"	Apr.21-12:30	8.6	7.84	14.3	0.7	3.4	0.3	0.760	2.9	1.3	2.5	−0.92	−2.35	0.12	N	
42	Jiyoshi 2	Yanadani, Eh	33°28'18"	132°55'40"	Apr.21-12:10	9.2	7.94	16.6	0.4	1.7	0.2	0.920	2.4	1.2	1.9	−0.66	−3.27	−1.06	N	
43	Oonogahara	Nomura, Eh	33°28'24"	032°53'17"	Apr.21-15:30	8.9	7.66	7.9	0.8	3.1	0.6	0.430	3.4	2.1	3.1	−1.58	−3.31	−0.14	N	
44	Inuse	Jinseki, Hs	34°50'27"	133°13'34"	Dec.18-15:10	10.2	8.17	53.4	1.2	4.2	1.6	2.703	4.5	7.6	4.9	0.48	−3.04	−0.68	N	
45	Gotani	Tojo, Hs	34°50'48"	133°16'07"	Dec.18-13:20	13.1	7.57	69.6	1.2	3.4	0.7	3.588	3.4	3.9	2.0	0.15	−2.31	−0.51	N	
46	Kamidani	Tojo, Hs	34°50'56"	133°15'38"	Dec.18-13:00	12.5	7.48	82.1	1.6	3.2	0.3	4.070	3.9	4.5	4.2	0.17	−2.17	0.35	N	
47	Kushiro	Tojo, Hs	34°51'27"	133°17'15"	Dec.18-11:55	10.3	7.86	13.9	1.7	6.2	1.4	0.764	4.5	4.1	5.3	−0.87	−3.25	0.42	N	
48	Miyahara	Tojo, Hs	34°51'55"	133°17'35"	Dec.18-11:25	10.5	8.69	44.1	1.7	4.4	0.7	2.312	3.6	4.8	2.8	0.85	−3.63	0.01	T	
49	Haba	Tojo, Hs	34°52'55"	133°17'10"	Dec.18-09:25	12.6	7.76	59.3	1.1	2.7	1.3	2.980	–	–	–	0.20	−2.58	–	N	
50	Norakuji	Tojo, Hs	34°51'57"	133°15'31"	Dec.18-13:40	11.7	8.00	50.0	1.0	2.4	0.7	2.523	2.8	8.6	1.7	0.29	−2.89	−0.76	N	
51	Shimotaki	Tojo, Hs	34°52'20"	133°17'46"	Dec.18-10:40	9.3	8.33	54.3	1.9	3.7	1.1	2.794	3.5	6.6	4.1	0.65	−3.19	−0.30	T	
52	Tobita-noro	Tojo, Hs	34°52'32"	133°17'44"	Dec.18-10:10	8.8	8.17	27.7	1.7	5.1	0.7	1.472	3.8	2.8	7.7	−0.05	−3.30	−0.23	N	
53	Taisyaku Gorge	Tojo, Hs	34°52'59"	133°20'22"	Nov.24-14:00	11.7	7.86	48.7	0.5	2.5	0.1	2.528	3.1	1.2	0.8	0.14	−2.75	−0.68	N	
54	Ueno-U	Takahashi, Oy	34°54'48"	133°34'05"	Nov.24-15:00	13.4	7.48	89.7	0.6	3.0	0.3	4.442	3.2	1.4	3.0	0.25	−2.13	0.46	S	
55	Ueno-D	Takahashi, Oy	34°54'49"	133°34'05"	Nov.24-14:55	9.3	8.22	61.3	0.6	2.3	0.5	3.166	3.2	1.4	3.1	0.64	−3.03	−1.22	T	
56	Ikurado frank	Niimi, Oy	34°55'10"	133°31'47"	May18-16:30	15.3	7.86	94.1	1.1	2.7	0.2	4.490	11.1	1.5	18.0	0.67	−2.50	−0.30	M	
57	Ikurado Cave	Niimi, Oy	34°55'27"	133°31'38"	Sep.27-15:00	14.7	7.86	72.0	1.8	1.7	0.2	3.387	4.5	13.8	11.1	0.45	−2.62	−1.22	N	in the cave
58	Ikurado enterance	Niimi, Oy	34°55'27"	133°31'38"	Sep.27-14:30	15.9	8.10	73.3	1.0	1.7	0.2	3.296	–	–	–	0.70	−2.86	–	P	
59	Shimoida cave	Niimi, Oy	34°56'55"	133°30'33"	Dec.23-14:10	13.5	7.56	84.6	1.8	5.0	1.3	3.834	6.1	21.0	10.0	0.24	−2.27	0.67	N	in the cave
60	Shimoida 23	Niimi, Oy	34°56'55"	133°30'33"	Dec.23-14:02	13.5	7.64	83.9	1.8	4.4	1.3	3.859	6.1	21.0	10.0	0.32	−2.35	−0.19	S	
61	Shimoida 22	Niimi, Oy	34°56'55"	133°30'33"	Dec.23-13:47	13.1	8.05	84.1	1.8	4.6	1.2	3.860	–	–	–	0.72	−2.76	–	T	
62	Shimoida 21	Niimi, Oy	34°56'55"	133°30'33"	Dec.23-13:40	12.8	8.14	83.8	1.8	4.2	1.2	3.854	–	–	–	0.80	−2.85	–	T	
63	Shimoida 20	Niimi, Oy	34°56'56"	133°30'32"	Dec.23-13:31	12.3	8.35	82.9	1.8	4.2	1.1	3.814	6.1	20.9	10.0	0.99	−3.07	−0.36	T	
64	Shimoida 19	Niimi, Oy	34°56'56"	133°30'32"	Dec.23-13:23	11.9	8.41	80.5	1.8	4.0	1.3	3.734	6.1	21.0	10.0	1.02	−3.15	−0.81	T	
65	Shimoida 18	Niimi, Oy	34°56'57"	133°30'32"	Dec.23-13:14	11.4	8.46	76.7	1.8	3.0	1.1	3.477	6.1	21.0	10.0	1.02	−3.23	−0.16	T	
66	Shimoida 17	Niimi, Oy	34°56'57"	133°30'32"	Dec.23-13:04	10.2	8.37	75.4	1.8	3.0	1.1	3.422	–	–	–	0.90	−3.15	–	T	
67	Shimoida 16	Niimi, Oy	34°56'58"	133°30'32"	Dec.23-12:57	9.3	8.46	73.7	1.8	3.0	1.2	3.176	–	–	–	0.94	−3.28	–	T	
68	Shimoida 15	Niimi, Oy	34°56'59"	133°30'32"	Dec.23-12:27	8.5	8.38	71.0	1.8	3.7	1.1	3.196	–	–	–	0.84	−3.20	–	T	
69	Shimoida 14	Niimi, Oy	34°56'59"	133°30'32"	Dec.23-12:17	8.5	8.45	70.7	1.7	3.8	1.2	3.146	–	–	–	0.90	−3.27	–	T	
70	Shimoida 13	Niimi, Oy	34°57'00"	133°30'32"	Dec.23-12:10	8.2	8.46	70.0	1.8	3.6	1.2	3.131	6.1	20.3	10.0	0.89	−3.29	−0.10	T	
71	Shimoida 12	Niimi, Oy	34°57'01"	133°30'31"	Dec.23-12:04	8.0	8.48	67.8	1.8	4.9	1.3	3.105	–	–	–	0.90	−3.31	–	T	
72	Shimoida 11	Niimi, Oy	34°57'01"	133°30'31"	Dec.23-11:59	7.8	8.49	67.8	1.8	4.4	1.3	3.045	–	–	–	0.89	−3.33	–	T	
73	Shimoida 10	Niimi, Oy	34°57'02"	133°30'31"	Dec.23-11:43	7.6	8.49	67.7	1.8	3.5	1.1	3.025	–	–	–	0.89	−3.33	–	T	
74	Shimoida 9	Niimi, Oy	34°57'03"	133°30'31"	Dec.23-11:45	8.3	8.39	68.2	1.8	3.5	1.1	3.045	–	–	–	0.80	−3.23	–	T	
75	Shimoida 8	Niimi, Oy	34°57'04"	133°30'31"	Dec.23-11:38	8.2	8.39	67.7	1.7	3.8	1.2	3.045	–	–	–	0.80	−3.23	–	T	
76	Shimoida 7	Niimi, Oy	34°57'05"	133°30'31"	Dec.23-11:32	8.3	8.37	67.5	1.7	3.3	1.0	3.005	5.9	19.5	9.9	0.78	−3.21	−0.15	T	
77	Shimoida 6.5	Niimi, Oy	34°57'06"	133°30'31"	Dec.23-11:25	8.2	8.40	67.3	1.7	3.8	1.2	3.005	–	–	–	0.81	−3.24	–	T	
78	Shimoida 5	Niimi, Oy	34°57'07"	133°30'31"	Dec.23-11:14	7.9	8.34	67.0	1.7	3.1	1.2	2.985	–	–	–	0.74	−3.18	–	T	
79	Shimoida 4	Niimi, Oy	34°57'08"	133°30'31"	Dec.23-11:10	7.6	8.37	66.4	1.7	3.3	1.1	2.975	–	–	–	0.76	−3.22	–	T	

Table 1. (continued)

No.	Locality Name	Area	Latitude	Longitude	Date & time	T (°C)	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Alk	Cl^-	NO_3^-	SO_4^{2-}	SIC	$logPco_2$	IB	Cat	Remarks
80	Shimoida 3	Niimi, Oy	34°57'09"	133°30'31"	Dec.23-11:06	7.5	8.40	66.1	1.8	3.7	1.1	2.940	–	–	–	0.79	–3.25	–	T	
81	Shimoida 2	Niimi, Oy	34°57'10"	133°30'31"	Dec.23-10:50	7.1	8.46	64.9	1.8	3.8	1.2	2.915	5.9	19.5	9.9	0.82	–3.32	–0.19	T	
82	Ishiga 1	Niimi, Oy	34°56'55"	133°28'43"	Dec.24-12:30	13.1	7.74	52.1	1.1	3.0	0.4	2.573	3.3	2.7	8.1	0.07	–2.62	–0.47	N	
83	Ishiga 2	Niimi, Oy	34°57'09"	133°28'48"	Dec.24-13:10	13.8	7.74	58.1	1.8	4.5	1.0	2.925	3.7	4.7	8.6	0.18	–2.56	–0.16	N	
84	Takatsuma 14	Hokubo, Oy	34°56'57"	133°39'15"	Aug.16-13:35	14.5	7.42	80.3	0.9	3.0	0.2	4.040	3.2	2.5	4.2	0.13	–2.10	–0.41	S	
85	Takatsuma 13	Hokubo, Oy	34°56'58"	133°39'15"	Aug.16-13:40	15.6	7.38	79.6	0.8	2.3	–	3.985	–	–	–	0.09	–2.06	–	S	
86	Takatsuma 12	Hokubo, Oy	34°56'59"	133°39'14"	Aug.16-13:50	16.5	8.08	70.5	0.9	2.4	–	3.789	–	–	–	0.73	–2.78	–	T	
87	Takatsuma 11	Hokubo, Oy	34°56'57"	133°39'14"	Aug.16-13:55	17.2	8.19	68.1	0.9	2.1	–	3.598	–	–	–	0.82	–2.91	–	T	
88	Takatsuma 10	Hokubo, Oy	34°57'00"	133°39'14"	Aug.16-14:00	18.1	8.20	63.7	0.9	2.5	–	3.286	–	–	–	0.78	–2.95	–	T	
89	Takatsuma 9	Hokubo, Oy	34°57'00"	133°39'13"	Aug.16-14:10	18.7	8.16	59.5	0.8	2.1	–	3.211	–	–	–	0.71	–2.91	–	T	
90	Takatsuma 7	Hokubo, Oy	34°57'01"	133°39'13"	Aug.16-14:15	17.1	7.96	76.9	0.8	2.2	0.1	3.894	3.4	1.9	4.4	0.67	–2.64	–1.11	T	
91	Takatsuma 4.5	Hokubo, Oy	34°57'04"	133°39'12"	Aug.16-14:35	15.6	7.97	66.8	1.1	2.1	0.2	3.533	3.3	2.2	4.3	0.56	–2.70	–2.30	T	
92	Takatsuma 4	Hokubo, Oy	34°57'04"	133°39'12"	Aug.16-14:40	16.5	8.05	70.4	1.1	1.8	–	3.709	–	–	–	0.69	–2.76	–	T	
93	Takatsuma 3	Hokubo, Oy	34°57'05"	133°39'12"	Aug.16-14:50	19.5	8.11	63.5	1.1	2.3	–	3.327	–	–	–	0.71	–2.85	–	T	
94	Takatsuma 0	Hokubo, Oy	34°57'06"	133°39'13"	Aug.16-15:00	14.7	7.39	80.4	1.4	2.2	0.6	3.955	4.6	8.3	5.8	0.09	–2.08	–1.01	S	
95	Takatsuma well	Hokubo, Oy	34°57'11"	133°39'15"	Aug.16-10:00	15.8	7.38	86.8	1.7	2.6	0.3	4.312	3.5	3.5	7.8	0.16	–2.03	–0.37	N	water from a well
96	Komatsu-U	Hokubo, Oy	34°57'05"	133°38'57"	May18-12:40	13.3	7.54	70.3	0.6	2.5	0.2	3.440	2.3	1.9	1.5	0.11	–2.30	1.27	S	
97	Komatsu-D	Hokubo, Oy	34°57'06"	133°38'57"	May18-13:00	13.3	8.03	70.3	0.6	2.5	–	3.440	–	–	–	0.59	–2.79	–	T	
98	Kanno North-U	Hokubo, Oy	34°57'28"	133°40'05"	Jan.26-14:00	11.1	7.86	96.9	2.1	3.5	–	4.380	9.2	13.4	13.3	0.61	–2.53	0.28	S	
99	Kanno North-D	Hokubo, Oy	34°57'28"	133°40'05"	Jan.26-14:10	8.9	8.41	93.8	2.1	3.7	–	4.340	9.2	13.4	13.3	1.10	–3.10	–0.78	T	
*100	Kanno North-T	Hokubo, Oy	34°57'28"	133°40'05"	Jan.26-14:20	5.9	8.11	76.7	2.2	4.9	–	3.560	19.3	11.7	13.2	0.60	–2.89	–3.46	N	F^- = 0.1
101	Azae West-b	Hokubo, Oy	34°57'33"	133°37'43"	Dec.4-13:05	11.6	7.89	27.5	1.7	2.9	0.2	1.347	3.4	7.6	5.0	–0.32	–3.05	–0.26	N	
102	Azae Weat-a	Hokubo, Oy	34°57'40"	133°37'46"	Dec.2-16:15	14.0	7.34	81.5	1.6	4.4	1.0	3.935	5.8	11.3	6.4	0.03	–2.04	0.02	N	
103	Shiroyama South-a2	Hokubo, Oy	34°57'47"	133°38'19"	Dec.2-15:00	11.8	7.22	10.3	1.2	4.6	0.2	0.663	3.5	1.9	2.7	–1.68	–2.67	–0.31	N	
104	Shiroyama South-ab	Hokubo, Oy	34°57'47"	133°38'18"	Dec.2-14:45	9.6	8.06	46.0	1.5	4.2	0.3	2.407	3.8	2.1	4.7	0.26	–2.98	–0.37	N	
105	Shiroyama South-a1	Hokubo, Oy	34°57'49"	133°38'24"	Dec.2-13:05	8.2	8.11	24.0	2.7	5.6	0.4	1.548	4.4	1.8	4.2	–0.15	–3.22	–1.15	N	
*106	Shiroyama South-b-U	Hokubo, Oy	34°57'52"	133°38'20"	Dec.2-13:50	13.1	7.97	88.0	1.3	2.8	0.3	4.809	3.5	2.4	4.7	0.75	–2.59	–4.17	S	
107	Shiroyama South-b-D	Hokubo, Oy	34°57'48"	133°38'19"	Dec.2-14:30	9.6	8.37	65.3	1.5	3.5	0.4	3.337	3.8	2.4	5.5	0.83	–3.16	–0.53	T	
108	Sugano North-U	Hokubo, Oy	34°57'55"	133°37'30"	Dec.22-14:57	13.3	7.88	68.4	1.8	2.3	0.4	3.342	3.3	4.4	3.4	0.43	–2.65	0.93	S	
109	Sugano North-D	Hokubo, Oy	34°57'54"	133°37'31"	Dec.22-14:40	11.9	8.13	65.2	1.8	2.1	0.5	3.261	–	–	–	0.62	–2.92	–	T	
110	Sugano North-T	Hokubo, Oy	34°57'53"	133°37'31"	Dec.22-14:25	11.8	7.87	66.9	1.8	1.7	0.5	3.327	3.3	4.2	3.3	0.38	–2.65	0.04	S	
111	Kaminoro 12	Hokubo, Oy	34°57'52"	133°37'32"	Dec.22-14:05	10.3	8.17	65.1	1.8	2.1	0.5	3.266	3.3	4.1	3.4	0.64	–2.96	0.05	S	
112	Kaminoro 11	Hokubo, Oy	34°57'52"	133°37'32"	Dec.22-13:50	9.9	8.30	65.0	1.8	1.2	0.5	3.261	–	–	–	0.76	–3.10	–	T	
113	Kaminoro 10	Hokubo, Oy	34°57'51"	133°37'33"	Dec.22-13:42	9.4	8.39	64.3	1.8	1.6	0.4	3.226	–	–	–	0.83	–3.19	–	T	
114	Kaminoro 9	Hokubo, Oy	34°57'51"	133°37'33"	Dec.22-13:31	9.1	8.35	63.8	1.8	2.2	0.4	3.226	–	–	–	0.78	–3.16	–	T	
115	Kaminoro 8	Hokubo, Oy	34°57'51"	133°37'34"	Dec.22-13:19	8.3	8.32	61.3	1.8	1.8	0.5	3.085	3.3	4.0	3.3	0.71	–3.15	–0.09	T	
116	Kaminoro 7	Hokubo, Oy	34°57'50"	133°37'35"	Dec.22-13:05	7.8	8.35	60.4	1.8	1.8	0.4	3.045	–	–	–	0.72	–3.19	–	T	
117	Kaminoro 6	Hokubo, Oy	34°57'50"	133°37'35"	Dec.22-12:55	7.3	8.37	59.0	1.8	2.2	0.5	2.980	3.3	4.0	3.3	0.71	–3.22	–0.06	T	
118	Kaminoro 5	Hokubo, Oy	34°57'49"	133°37'36"	Dec.22-12:44	7.0	8.32	58.4	1.8	2.3	0.5	2.935	–	–	–	0.65	–3.17	–	T	
119	Kaminoro 4	Hokubo, Oy	34°57'48"	133°37'36"	Dec.22-12:32	6.7	8.32	57.3	1.9	3.0	0.4	2.925	–	–	–	0.64	–3.18	–	T	
120	Kaminoro 3	Hokubo, Oy	34°57'48"	133°37'36"	Dec.22-12:23	6.4	8.33	57.9	1.8	3.3	0.3	2.915	–	–	–	0.64	–3.19	–	T	

Table 1. (continued)

No.	Locality Name	Area	Latitude	Longitude	Date & time	T (°C)	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Alk	Cl^{-}	NO_3^{-}	SO_4^{2-}	SIC	$logPco_2$	IB	Cat	Remarks
121	Kaminoro 2.5	Hokubo, Oy	34°57'47"	133°37'36"	Dec.22-12:09	6.4	8.28	57.9	1.8	3.1	0.4	2.899	3.3	4.0	3.4	0.59	−3.14	0.55	T	
122	Shiroyama East-d	Hokubo, Oy	34°57'59"	133°38'39"	Dec.2-12:00	11.2	8.08	20.7	1.9	7.1	0.2	1.146	4.7	4.1	7.7	−0.32	−3.31	−0.02	N	
123	Shiroyama East-c	Hokubo, Oy	34°58'05"	133°38'39"	Dec.1-16:20	10.4	8.09	32.6	2.8	6.9	0.2	1.809	4.7	4.1	7.7	0.05	−3.13	−0.06	N	
124	Shiroyama East-b	Hokubo, Oy	34°58'10"	133°38'39"	Dec.1-15:15	9.3	8.17	31.4	2.7	6.1	0.5	1.638	4.7	7.6	6.9	0.05	−3.26	0.30	N	
125	Shiroyama East-a	Hokubo, Oy	34°58'13"	133°38'36"	Dec.1-14:40	12.0	8.00	14.4	2.8	7.0	0.6	1.065	3.0	3.2	2.2	−0.58	−3.25	0.06	N	
126	Shiroyama-U	Hokubo, Oy	34°58'01"	133°38'14"	Jul.18-15:00	13.5	7.50	86.0	0.8	3.5	0.2	4.432	2.8	1.9	4.5	0.25	−2.15	−1.12	S	
127	Shiroyama-D	Hokubo, Oy	34°58'00"	133°38'14"	Jul.18-14:35	17.6	8.21	67.9	1.1	3.3	0.2	3.593	2.9	2.8	4.8	0.84	−2.93	−1.93	T	
128	Suwou-ana	Hokubo, Oy	34°58'02"	133°37'36"	Oct.18-15:45	14.0	7.93	67.0	1.8	2.5	0.6	3.131	4.0	12.1	6.6	0.45	−2.72	0.39	N	
129	Shiroyama West-a1	Hokubo, Oy	34°58'20"	133°38'04"	Dec.3-13:20	7.5	8.34	46.5	2.9	5.3	0.3	2.598	4.1	1.2	5.2	0.54	−3.24	−0.44	T	
130	Shiroyama West-a2	Hokubo, Oy	34°58'20"	133°38'05"	Dec.3-13:40	5.6	8.44	61.1	4.4	5.9	0.7	3.427	3.5	2.0	7.6	0.82	−3.24	−0.31	T	
131	Shiroyama West-b	Hokubo, Oy	34°58'24"	133°38'12"	Dec.4-14:45	12.4	7.67	3.4	0.9	5.5	0.4	0.221	3.6	5.3	2.1	−2.16	−3.59	0.39	N	
*132	Maruyama	Hokubo, Oy	34°58'24"	133°38'09"	Jul.18-16:25	13.5	7.63	61.0	0.7	3.3	0.2	3.834	3.7	3.1	2.0	0.19	−2.33	−7.80	S	
133	Yasuhaya 19	Hokubo, Oy	34°58'32"	133°37'01"	Sep.26-15:00	13.1	7.26	72.8	0.7	1.5	0.5	3.538	5.3	6.1	3.1	−0.15	−2.00	−0.79	S	
134	Yasuhaya 18	Hokubo, Oy	34°58'32"	133°37'01"	Sep.26-14:45	13.3	7.58	72.8	0.7	1.5	0.5	2.528	–	–	–	0.18	−2.32	–	S	
135	Yasuhaya 16	Hokubo, Oy	34°58'32"	133°37'02"	Sep.26-14:30	13.5	8.03	71.6	0.7	1.6	0.5	3.528	–	–	–	0.62	−2.77	–	T	
136	Yasuhaya 14	Hokubo, Oy	34°58'32"	133°37'03"	Sep.26-14:05	13.6	8.21	73.3	0.7	1.8	0.4	3.527	–	–	–	0.80	−2.96	–	T	
137	Yasuhaya 12	Hokubo, Oy	34°58'31"	133°37'04"	Sep.26-13:45	13.7	8.30	72.9	0.7	1.5	0.4	3.482	5.6	5.9	3.1	0.88	−3.05	−0.24	T	
138	Yasuhaya 10	Hokubo, Oy	34°58'31"	133°37'04"	Sep.26-13:25	13.9	8.30	79.4	0.7	1.4	0.4	3.824	6.7	5.1	4.1	0.96	−3.01	−0.97	T	
139	Yasuhaya 8	Hokubo, Oy	34°58'31"	133°37'05"	Sep.26-12:30	13.9	8.20	74.5	0.7	1.4	0.4	3.653	–	–	–	0.82	−2.93	–	T	
140	Yasuhaya 6	Hokubo, Oy	34°58'32"	133°37'06"	Sep.26-12:20	14.0	8.28	73.0	0.7	1.7	0.4	3.502	6.2	5.4	3.7	0.87	−3.03	−0.54	T	
141	Yasuhaya 4	Hokubo, Oy	34°58'32"	133°37'07"	Sep.26-12:10	14.3	8.16	73.5	0.8	1.6	0.4	3.583	–	–	–	0.77	−2.90	–	T	
142	Yasuhaya 2	Hokubo, Oy	34°58'32"	133°37'08"	Sep.26-12:00	14.4	8.21	72.4	0.8	1.5	0.4	3.482	–	–	–	0.80	−2.96	–	T	
143	Yasuhaya 1	Hokubo, Oy	34°58'32"	133°37'09"	Sep.26-11:30	14.5	8.21	70.7	0.8	1.5	0.5	3.447	5.9	5.1	4.0	0.79	−2.96	−1.07	T	
144	Yasuhaya 2-T	Hokubo, Oy	34°58'32"	133°37'08"	Sep.26-11:45	15.6	7.82	89.4	0.8	1.5	0.2	4.382	–	–	–	0.61	−2.46	–	T	
145	Sora	Hokubo, Oy	34°58'32"	133°37'14"	Oct.19-11:25	13.6	7.59	65.2	1.6	2.0	0.3	3.155	8.2	5.4	1.7	0.10	−2.38	−0.29	S	
146	Yasuhaya North-U	Hokubo, Oy	34°58'36"	133°37'04"	Oct.18-11:00	13.0	7.68	80.6	0.7	1.8	0.4	4.005	4.2	1.4	3.6	0.36	−2.37	−0.53	S	
147	Yasuhaya North-D	Hokubo, Oy	34°58'35"	133°37'11"	Jul.18-18:35	14.9	8.19	65.7	0.8	4.3	0.3	3.377	7.9	1.5	4.3	0.74	−2.95	−1.75	T	
148	Yasuda	Hokubo, Oy	34°58'47"	133°37'01"	Jul.18-18:00	16.4	7.84	13.0	1.4	5.7	0.4	0.704	3.8	3.4	5.5	−0.84	−3.25	0.42	N	
149	Hokubo Dum 1	Hokubo, Oy	34°59'40"	133°35'49"	Oct.20-13:50	13.0	8.17	65.7	1.4	3.0	0.7	2.015	3.6	3.9	2.7	0.28	−3.15	−0.41	N	
150	Hokubo Dum 2	Hokubo, Oy	34°59'41"	133°35'45"	Oct.20-14:26	13.1	8.14	7.3	1.5	3.2	0.8	0.387	3.5	2.0	3.5	−1.12	−3.82	0.56	N	
151	Tamadare Fall	Katsuyama, Oy	35°06'41"	133°41'00"	Nov.28-15:45	12.5	8.37	47.9	2.1	4.8	0.2	2.533	3.9	2.4	5.1	0.64	−3.26	−0.11	T	
152	Kasugadani 1	Miyakawa, Me	34°17'58"	136°16'27"	May3-14:05	13.1	8.20	27.2	0.8	3.0	0.3	1.410	2.3	2.4	2.7	-0.03	−3.33	−0.09	N	
153	Kasugadani 2	Miyakawa, Me	34°17'58"	136°16'30"	May3-14:20	13.8	8.10	27.7	1.1	1.9	–	1.410	2.1	1.3	2.7	-0.05	−3.23	0.09	N	
154	Aso Yataniyama	Oomiya, Me	34°19'43"	136°26'57"	May3-16:50	13.8	8.01	27.8	1.3	1.8	–	1.410	4.4	1.6	3.7	−0.14	−3.13	−0.64	N	
155	Aso-fuketsu Cave	Oomiya, Me	34°19'55"	136°26'49"	May3-16:30	13.2	7.96	21.6	1.6	2.2	–	1.170	4.1	0.7	3.2	−0.38	−3.17	−0.58	N	
156	Aso-fuketsu	Oomiya, Me	34°19'58"	136°26'29"	May3-16:00	12.5	8.03	22.6	1.6	1.7	–	0.930	5.1	0.5	4.3	−0.40	−3.34	1.62	N	
157	Hachisu	Iidaka, Me	34°20'39"	136°07'00"	May3-09:20	12.1	7.93	20.7	1.2	3.0	0.6	0.780	2.1	1.9	13.4	−0.61	−3.32	1.29	N	
158	Amano-iwado	Isobe, Me	34°24'15"	136°45'59"	May2-17:30	14.5	7.95	28.9	1.5	3.7	0.5	1.540	6.4	3.0	3.5	−0.14	−3.03	−1.03	N	
159	Fujiwara 5	Hokusei, Me	35°08'33"	136°45'59"	Jun.30-12:05	20.2	8.44	48.9	1.7	2.5	0.1	2.417	4.7	5.0	6.2	0.81	−3.31	−0.68	P	
160	Fudomyo-ou	Hokusei, Me	35°08'40"	136°28'44"	Jun.30-10:05	14.9	8.30	34.3	2.1	1.3	0.3	1.749	3.2	5.2	7.6	0.33	−3.33	−1.33	N	
161	Fujiwara 4	Hokusei, Me	35°08'45"	136°28'11"	Jun.30-11:30	15.2	8.31	22.0	2.7	3.2	0.4	1.226	2.7	2.7	8.0	0.02	−3.49	−0.43	N	

Table 1. (continued)

No.	Locality Name	Area	Latitude	Longitude	Date & time	T (°C)	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Alk	Cl^-	NO_3^-	SO_4^{2-}	SIC	$\log Pco_2$	IB	Cat	Remarks
162	Fujiwara 1	Fujiwara, Me	35°09'04"	136°28'59"	Jun.30-08:45	15.4	8.23	28.5	3.8	2.8	–	1.563	3.4	5.1	9.5	0.15	–3.30	–0.82	N	
*163	Fujiwara 2	Fujiwara, Me	35°09'04"	136°28'59"	Jun.30-08:50	16.3	7.33	70.4	21.9	4.2	1.7	1.347	3.3	11.8	226.7	–0.51	–2.49	–7.78	M	Fe^{2+} = 1.5
164	Fujiwara 3	Fujiwara, Me	35°09'08"	136°28'52"	Jun.30-09:08	15.0	8.10	25.0	3.2	3.0	0.4	1.312	8.3	6.1	10.7	–0.11	–3.25	–2.16	N	
165	Taga Jyuman	Taga, Sg	35°11'41"	136°22'09"	Apr.30-12:10	10.5	8.26	14.2	2.1	3.0	–	0.670	5.1	0.6	5.8	–0.53	–3.72	0.47	N	F^- = 0.4
166	Suzukita-dake	Taga, Sg	35°11'41"	136°24'20"	Jun.30-13:40	15.6	8.01	12.5	1.8	2.0	0.3	0.754	3.3	2.0	2.8	–0.70	–3.39	–0.71	N	
167	Momohara	Taga, Sg	35°14'35"	136°19'28"	Jun.30-14:30	16.1	8.29	48.6	3.1	3.4	0.3	2.628	4.5	3.7	6.4	0.64	–3.14	–1.12	T	
168	Kochi Fudomyo-ou	Taga, Sg	35°15'14"	136°21'57"	Apr.30-08:40	11.6	8.03	31.4	2.1	2.6	–	1.670	3.8	2.6	3.5	–0.04	–3.09	–0.39	N	
169	Otokooni 2	Hikone, Sg	35°15'56"	136°20'01"	Apr.29-18:20	9.8	8.07	22.9	1.7	1.3	0.3	1.270	4.3	1.7	2.7	–0.26	–3.26	–1.28	N	
170	Otokooni 1	Hikone, Sg	35°15'56"	136°20'02"	Apr.29-18:10	12.2	7.72	16.6	2.1	2.4	0.4	0.870	4.9	2.2	5.2	–0.87	–3.06	–0.36	N	
171	Shiratani	Taga, Sg	35°16'37"	136°23'37"	Apr.30-09:35	10.6	7.92	11.5	1.6	2.0	–	0.610	3.8	3.6	1.9	–0.99	–3.42	–0.22	N	
172	Natanegawa	Maibara, Sg	35°17'20"	136°19;27"	Apr.29-17:00	11.2	7.76	34.7	1.9	1.8	0.5	1.750	5.4	4.7	3.6	–0.25	–2.81	–0.74	N	
173	Reisenzan	Maibara, Sg	35°17'23"	136°21'43"	Apr.29-14:40	12.1	7.93	38.8	2.2	2.7	–	2.050	5.5	2.6	2.6	0.04	–2.91	–0.67	N	
174	Urushidaki 1	Maibara, Sg	35°17'24"	136°23'21"	May1-13:15	9.8	8.06	32.9	0.9	1.7	0.2	1.600	3.7	2.7	2.8	–0.03	–3.15	–0.11	N	
175	Samegai Trout	Maibara, Sg	35°17'26"	136°20'28"	May1-10:00	12.3	8.05	33.2	2.8	3.1	–	1.830	5.8	2.8	3.1	0.05	–3.07	–0.81	N	
*176	Soyagawa	Maibara, Sg	35°17'28"	136°21'10"	Apr.29-11:55	12.0	8.06	30.5	2.3	1.8	0.5	1.780	5.6	2.5	7.0	0.02	–3.10	–3.22	N	
177	Urushidaki 2	Maibara, Sg	35°17'28"	136°23'22"	May1-13:40	11.0	8.09	24.4	1.1	2.1	–	1.230	4.4	4.2	2.0	–0.21	–3.29	–0.64	N	
178	Nino-tani	Maibara, Sg	35°17'33"	136°22'39"	May1-12:00	12.1	8.33	36.5	1.1	2.2	–	1.680	5.2	3.8	3.7	0.33	–3.39	0.43	N	
179	Maibara	Maibara, Sg	35°17'45"	136°19'12"	Apr.29-16:00	12.7	7.95	28.5	3.7	2.1	0.3	1.580	5.5	4.6	6.6	–0.16	–3.03	–1.21	N	
180	Onowari-sui	Maibara, Sg	35°18'11"	136°20'14"	Apr.29-13:30	12.8	8.17	34.7	1.6	2.8	0.9	1.780	7.4	2.7	4.1	0.18	–3.20	–1.16	N	PO_4^{3-} = 0.2
181	Azusagawa 1	Santo, Sg	35°18'11"	136°23'53"	May1-15:50	11.3	8.00	18.5	1.7	3.2	–	1.080	4.6	5.0	4.2	–0.47	–3.25	–1.75	N	
182	Azusagawa 2	Santo, Sg	35°18'32"	136°24'01"	May1-16:10	11.4	7.70	7.0	1.2	3.2	–	0.350	4.3	4.1	5.4	–1.64	–3.43	–0.63	N	
183	Samegai	Maibara, Sg	35°19'19"	136°21'16"	Apr.30-17:50	12.4	7.94	28.2	2.7	4.5	–	1.440	12.0	4.6	5.1	–0.22	–3.06	–1.34	N	
184	Tenjinsui	Maibara, Sg	35°19'34"	136°21'15"	Apr.30-18:00	12.0	7.53	35.6	2.4	3.4	–	1.910	7.5	5.1	5.4	–0.43	–2.54	–1.94	N	
185	Ibukiyama	Ibuki, Sg	35°23'28"	136°23'11"	Apr.27-20:30	12.8	7.48	38.7	6.6	3.1	0.2	2.360	2.5	3.2	3.4	–0.35	–2.39	0.61	N	
186	Ibuki 1	Ibuki, Sg	35°24'06"	136°22'54"	Jun.28-11:40	15.6	8.41	27.2	7.4	2.4	0.2	1.904	2.5	2.6	4.9	0.38	–3.40	–0.43	N	
187	Ibuki 2	Ibuki, Sg	35°24'11"	136°22'47"	Jun.28-11:55	16.9	8.25	44.6	6.6	2.1	2.1	2.809	4.2	1.2	4.9	0.60	–3.07	–1.45	M	PO_4^{3-} = 0.3
188	Ibuki 3	Ibuki, Sg	35°24'11"	136°22'47"	Jun.28-12:00	14.1	8.38	25.5	6.7	2.3	0.2	1.910	–	–	–	0.31	–3.38	0.19	N	
189	Okusen-sui	Ibuki, Sg	35°24'20"	136°22'42"	Jun.28-12:11	12.3	8.25	29.2	7.2	2.2	0.2	2.010	3.5	2.7	4.9	0.23	–3.23	–1.04	N	
190	Ishimaki	Toyohashi, Ac	34°46'49"	137°27'52"	Jun.29-15:30	18.4	7.99	22.5	3.2	4.9	0.5	1.266	6.8	6.2	3.5	–0.23	–3.14	–0.19	N	
*191	Sekigahara Cave	Sekigahara, Gf	35°22'04"	136°25'48"	Apr.27-15:30	14.2	7.33	38.4	3.6	4.6	–	1.830	23.1	12.9	9.5	–0.59	–2.34	–5.01	N	F^- = 0.5
192	Sasamata 1	Kasuga, Gf	35°24'54"	136°25'54"	Apr.28-09:20	10.3	8.07	29.7	4.6	2.3	0.2	1.770	2.4	2.1	2.7	–0.02	–3.12	0.38	N	
193	Sasamata 2	Kasuga, Gf	35°24'55"	136°25'56"	Apr.28-09:30	10.0	8.10	30.0	5.3	1.3	–	1.900	2.3	2.8	3.4	0.04	–3.11	–0.91	N	
194	Nakayama 1	Kasuga, Gf	35°27'24"	136°26'42"	Jun.28-08:40	12.5	8.01	28.5	2.3	2.4	0.2	1.578	2.2	2.8	3.2	–0.11	–3.09	–0.31	N	
195	Nakayama 2	Kasuga, Gf	35°27'34"	136°27'00"	Jun.28-08:50	15.6	8.27	26.0	3.9	3.0	1.1	-	4.4	3.6	6.1	–	–	–	N	
196	Kawai	Kazuga, Gf	35°28'08"	136°27'28"	Jun.28-09:05	14.6	8.18	17.5	4.3	2.7	1.3	1.236	3.0	3.1	4.8	–0.21	–3.36	–0.93	N	
197	Irimizu	Takine, Fs	37°21'09"	140°40'08"	Aug.3-	-	-	37.7	1.1	3.2	1.2	1.975	3.4	3.0	2.8	–	–	–0.36	N	
198	Kotakane	Haranomachi, Fs	37°39'30"	140°52'29"	Jul.24-	16.5	7.22	5.8	0.7	4.3	0.3	0.392	3.6	1.2	2.5	–2.07	–3.87	–0.23	N	
199	Koyamada	Kashima, Fs	37°42'23"	140°55'09"	Jul.24-	16.5	7.22	72.5	1.4	5.3	0.5	3.794	4.7	1.1	6.1	–0.11	–1.92	–0.95	N	
200	Mano	Kashima, Fs	37°42'48"	140°50'43"	Jul.24-	20.3	7.10	7.7	1.5	4.3	0.4	0.518	3.6	3.2	3.7	–1.90	–2.61	–0.43	N	
201	Tochikubo	Kashima, Fs	37°43'50"	140°53'15"	Jul.24-	16.8	7.46	20.7	4.7	9.4	0.4	1.683	4.8	1.1	7.9	–0.70	–2.49	–1.62	N	

* water samples excluded from using in Figs. 1 and 2 because of their seriously large values of ionic balance (IB).

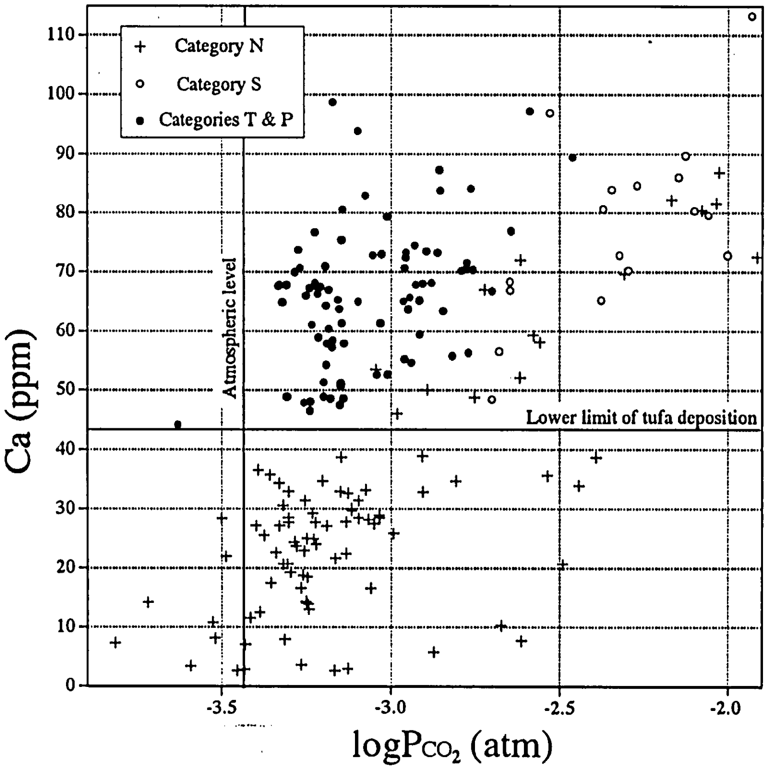

Fig. 1. Ca contents (PPM) and logPCO_2 (atm) of the different categories of the waters: N = waters without tufas (+), S = spring waters of tufa-depositing streams (O), T = waters depositing tufas (●). Category N shows its dense distribution in the domain of small Ca contents and low PCO_2. Whereas, category S exhibits large Ca contents and high PCO_2. The distinct difference in PCO_2 between categories S and T (including P) results from degassing of CO_2. The lower limit of Ca contents for deposition of tufas can be drawn at 40 ppm.

of ions originated from sea water (Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}). The tufas of an unknown age are cropped out along the coast.

B. Kakinohana-higya

The two spring waters issuing from the talus deposits covering the boundary between the Naha and Chinen Formations (Kaneko et al., 1997), are pooled for use of local people at Kakinohana-higya. Sufficient deposition of tufa starts at the overflowing point from the two pools. From the western pool, the tufa forms a cascade, about 3.6 m in height and 6 m in width. There is no shade from the sunlight, and the cascade is mainly vegetated by lichens. During flowing on the cascade (only 5 m in distance) Ca contents of the water decreases from 97.2 (4) to 87.3 ppm (5). Calcite with a dense texture was found in a polyethylene tube transporting the water for agricultural use. Much more details were described in Kaneko et al. (1997).

C. Enjitsugi

The Triassic limestone largely occupies the ridge along the Ryuga-do Skyline. Enjitsuji is a temple located beside this road. On the northern frank, the water is issuing from mudstone beds, tens meters lower than the base of the limestone. The amount of the spring water (17) is small, and a thin tufa covers the mudstone bedrock for 20 m in distance (18). Cyanobacteria and algae are dominant biota on the tufa surface. Ca contents of the water is almost lowest (47~49 ppm) among the tufa-barring localities.

D. Shirokawa

This is, so far, one of the largest localities of tufas in Japan, and is named after the Town of Shirokawa. The tufa is developed along a stream, a tributary of the Nakatsugawa River, located 1.5 km ESE of Doi. Geology of the locality belongs to the Jurassic–Cretaceous Torinosu Group (Kano and Jiju, 1995). The strata around the locality strike ENE–WSW and dip 10–20 degrees to the north. The mudstone is exposed along the stream of the tufa, and it changes to the upper limestone occupying the hill located on the south.

The tufa depositing stream is about 450 m long. The altitude difference between the spring (26) and the end of the stream (37) is about 120 m. The tufas are almost continuously developed in the upstream, (27~30) whereas in the downstream (31~37) the tufas mainly form cascades in a small scale (less than 1 m in height). Parallel-banded growth lines can be seen on the vertical sections of the cascade tufas (Fig. 3b). The Ca contents of the waters collected on 9th of March range from 48.0~56.6 ppm; appearing a general decreasing trend to the downstream.

E. Shimoida

Tufas were recently discovered from a stream flowing from a small limestone cave (59) in Niimi City, Okayama Prefecture. Although details have not been researched yet, the stream is about 450 m long and its difference in altitude is 145 m, that is comparable at least in size with Shirokawa.

Tufas are continuously developed except for the issuing point of the spring (60). Thick deposition of the tufas forms a wide (10 m in width) stream bed in the middle of the stream (66~69). In this portion of the stream, the gradient of decreasing Ca-contents is largest, that probably indicates an active deposition of the tufas. The tufas form the "rim-pool" structures (Fig. 3c) in several locations of the stream. Tufas in a cascade form are common in the lower part of the stream; their height can be more than 1 m (Fig. 3d). Paleotufas are exposed along the stream, especially in the upstream localities.

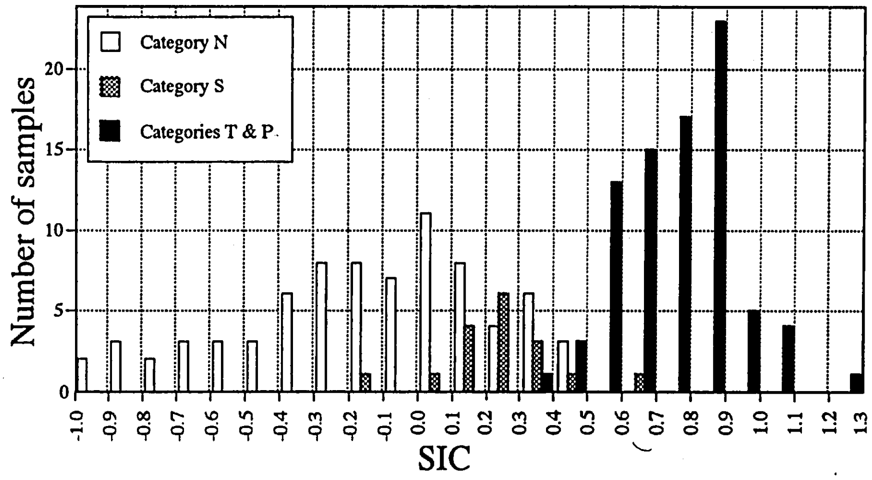

Fig. 2. Frequencies in SIC (saturation index for calcite) of the different categories of the water samples collected from limestone regions of Japan. SIC of the category T (tufa-depositing water) mostly exceeds 0.5. Water sapmles with SIC less than −1.0 are excluded from the figure.

F. Takatsuma

We found several localities of tufas in Hokubo Town, Okayama Prefecture. Takatsuma is one of them. The water system of Takatsuma is complicated because a newly-constructed road truncates the stream, and because the stream represent a system of several springs (84 and 85). These circumstances abruptly changes the discharge and chemical properties of the water. However, several waterfalls of the tufas can be seen along the stream. The tufas form a stair-like structure in the downstream locality (Fig. 3f). Ca contents of the waters collected on 16th of August range 85~70 ppm.

Geology of the Hokubo area was described by Naka (1995).

G. Kaminoro

Kaminoro is the largest among the tufa streams found in Hokubo Town. This stream flows southwards from a small pond and minor springs (108 and 110) located upstream of the pond. The stream is about 300m long, from the pond, it flows on a steep slope down, 100 m in altitude.

Tufas are almost continuously developed along the stream. They forms several water falls probably due to growth of the tufas to the downstream direction. Biota settling on the tufa surfaces seems to be dependent on the luminosity and flowing conditions of the water (flow amount and velocity). The stream is relatively deep, and therefore sufficient sunlight on the stream surface is limited only during mid-day. Places poor in light and covered with water are normally colonized by cyanobacteria. Whereas in places directly faced to sunlight, lichens are dominant. The tufas exhibiting a shape of fish scales are occasionally developed (Fig. 3e); its unique appearance is probably due to quick growing of lichens.

Ca-contents (ranging 68.4~57.3 ppm; on 22nd of Dec.) generally decrease to the downstream.

H. Yasuhaya

It is spring generally flowing eastwards from a spring located at the base of a Carboniferous-Permian limestone cliff. The stream is about 270 m long and there is 70 m difference in altitude. Tufas are not developed in the uppermost 15 m in the stream (133 and 134), but then almost continuously developed along the stream (135~143). Lichens and cyanobacteria are dominant biota on the tufas. Ca contents of the water ranges 79.4~70.7 ppm, on 26th of September. The maximum value is recorded in the middle of stream (138) where the water with high Ca contents is discharged into the stream.

I. Fujiwara 5

This is the locality on a path along the river near Fujiwara-dake. Water issues from limestone beds along the path and made a small pool (159). In the pool, pisoids (gravel coated by calcite precipitates) are found together with algae and lichens. Relatively high pH value (8.44) probably result in consumption of CO_2 species by photosynthesis of these plats. Ca contents of the water is 48.9 ppm.

Pisoids were found in several other localities: their Ca-contents are relatively high. No significant differences were found in chemical properties between the waters of categories P and T. The difference is in physical; the localities of pisoids generally represent environments of small water velocity, such as minor springs and shallow ponds.

I. Ibuki 2

Several water springs issuing from talus deposit are found along the road near Ibuki. Some of the springs (187) exhibit calcite deposits with a stalactitic shape. No vegetation (such as, cyanobacteria and algae) is found on the surface of deposits. Ca contents of the water ranges 44.6 ppm which is the second lowest among waters exhibiting calcite precipitation. Mat-like deposits containing algae and

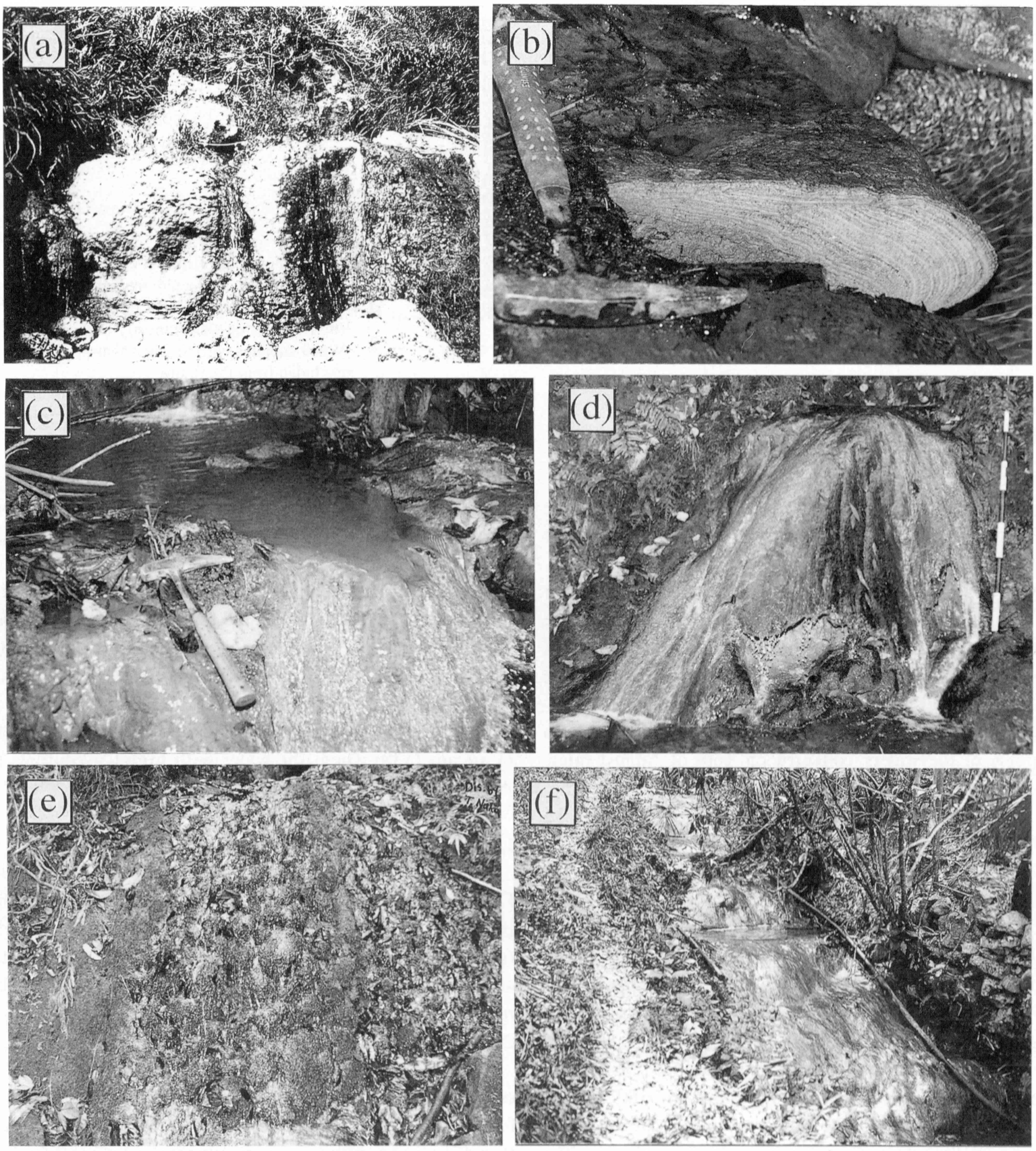

Fig. 3. Tufas in western Japan. (a) The tufa forms a small water fall of 3 m high on a limestone bed rock at Gizabanta-D (2), Okinawa Prefecture. The surface of the tufa is directly faced to sunlight and vegetated by lichens. (b) A small cascade tufa of a tongue-like shape at Shirokawa 9, Ehime Prefecture. The vertical section of tufa cut by an ordinary saw shows a parallel-banded structure lucks like the rings of a tree. The banding is due to the seasonal change in depositional processes of the tufa. The surface of the tufa is relatively smooth and colonized by cyanobacteria. This photograph was taken on 24th of Nov., 1996. (c) A 'rim-pool' formed by a tufa at Shimoida 19 (94), Okayama Prefecture. Dominated biota on the rim is cyanobacteria. Such rim-pools are commonly developed other localities of tufas. (d) A cascade tufa exhibiting a mushroom-like form 160 cm high, at Shimoida 8 (75). The surface of the tufa is entirely covered with cyanobacteria and the flowing water. There is a hollow space behind the superficial part of the tufa. This is one of the largest cascade tufas found in Japan, so far. (e) A small water fall, 5 m in height, covered by a tufa, at Kaminoro 9 (114), Okayama Prefecture. The tufa exhibits a fish scale-like surface probably because the growing of lichens is quick due to the surface directly facing to sunlight. The photograph was taken on 28th Dec., 1997. (f) A tufa developed into a stairs-like shape at Takatsuma 2, Okayama Prefecture. The photograph was taken on 18th May, 1997.

calcite crystals are also found in this locality. Comparable deposits are also found in Ikurado frank (56) and Momohara (167); no shade from sunlight is common to these localities.

V. Discussion

A. Ca contents and Pco_2

Morse and MacKenzie (1990, p. 57) show calculations of Ca contents of the waters flowing limestone area. According to the result, rain water (without any acid content other than CO_2 species) falling on limestone contains 20.7 ppm of Ca^{2+} by equilibrating with atmosphere (Pco_2 = 330 μatm) and calcite (at 25 ℃). Considering acid (SO_4^{2-} and NO_3^-) contents and a lower temperature, the rain can dissolve Ca more than this value. However, the Ca content cannot exceeds 30~40 ppm as long as it flows only on the surface.

Ca contents of the waters without tufa deposition (N) commonly ranges 15~35 ppm with the highest frequency of 20~30 ppm (Fig. 1). This range of Ca contents indicates that the waters of category N are basically or largely originated from waters flowing on limestone ground. Otherwise, CO_2 uptake from a soil layer must be limited. This is supported by relatively low equilibrium Pco_2 values (normally $\log Pco_2$ = –3.5 ~ –3.0) which is comparable or slightly higher than the atmospheric Pco_2 level (350 μatm; $\log Pco_2$ = –3.46; Fig. 1).

The waters barring tufas and pisoids (categories T and P) are characterized by raised equilibrium Pco_2 ($\log Pco_2$ mostly –3.3~–2.7) and Ca contents (> 44 ppm; Fig. 1). Spring waters of the tufa-depositing streams (category S) show comparable value of Ca contents, but very high equilibrium Pco_2 (more than –2.7 = 2,000 μatm; Fig. 1). The higher Pco_2 values of category S simply indicate the values before the degassing of CO_2 during flowing of the waters.

More importantly, high Pco_2 and Ca contents of these waters indicate that the waters have took up CO_2 probably when they permeate through a soil layer covering the limestone before dissolving $CaCO_3$ (Fig. 4). Because of respiration of roots and decomposition of organic matter, Pco_2 of soil air raised to 1,000~35,000 (rarely up to 100,000) μatm under temperate climates (Ford and Williams, 1988). The dissolution of soil-originated CO_2 decreases pH of the water and increases aggressiveness in dissolving $CaCO_3$. Therefore, more uptake of CO_2 causes more dissolution of $CaCO_3$. Urushibara (1991), who studied dissolution of limestone of several localities in Japan, reported that dissolved amount of limestone is generally larger in the southern localities, probably because of higher soil-Pco_2.

This latitude-dissolution relation is consistent with the high Ca contents of the waters collected from the Okinawa Island. However, the waters of category T collected from the northwestern Okayama Prefecture (Takahashi, Niimi, and

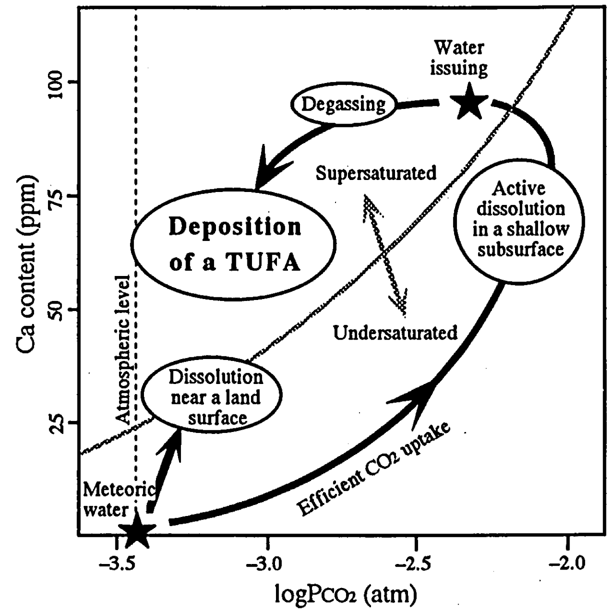

Fig. 4. Important processes in a subsurface and a stream for the deposition of tufas on the basis of the plotts of Fig. 1. Scales of the horizontal and vertical axes are approximate.

Hokubo) shows a relatively broad range of Ca^{2+} (94.1~46.5 ppm; Table 1). Ca contents are also dependent on the local conditions.

B. Saturation index of calcite (SIC)

Different categories of the waters shows different distribution of saturation index of calcite (SIC; Fig. 2). Although there are a few exceptions, the critical values of SIC for deposition of tufas is +0.5. This result is consistent with other studies on SIC of the tufa-depositing waters. In the result of the Plitevice National Park, Croatia (Emeis et al., 1987), the spring water records its SIC at –0.03, whereas SIC of the tufa-depositing waters ranges +0.53 ~ +0.74. Pentecost (1992) who extensively investigate water chemistry of a karst region of the Yorkshire Dale (UK), reported that SIC of the tufa-depositing waters ranges from +0.24 to +1.05 (in average, +0.72). Deposition of calcite theoretically possible if SIC exceeds 0.0. However, a raised value of SIC is kinetically necessary for efficient precipitation of calcite, and it can be easily gained by degassing of CO_2.

SIC of category S shows that the spring waters are close to saturation for calcite (peak frequency of SIC = +0.15; Fig. 2). This may indicate that the dissolving reaction is processed in the underground water systems, until the waters become saturated and that exchange of the air between underground and atmosphere is limited. In case of underground water system which is open to the atmosphere, degassing of CO_2 is largely processed inside of the cave. An example of Akiyoshi-do Cave (Yoshimura et al., 1996a) shows that the spring water exhibits relatively low equilibrium Pco_2 (660 μatm) and high SIC (+0.50), and that deposition of calcite is already efficient inside of the cave.

VI. Conclusions

Considering with chemical properties of the waters and description of localities of the tufas, some of the conditions for development of tufas are concluded as followings.

(1) The most important condition is SIC exceeding 0.5 of the tufa-depositing waters (category T) that is necessary for an efficient deposition of tufas. SIC is always less than 0.5 for the waters without deposition of tufas (N).

(2) When the equilibrium PCO_2 is close to the level of atmosphere ($logPCO_2 = -3.46$), SIC over +0.5 is achieved by Ca-content more than 45 ppm. This level of the Ca contents are hardly gained in the waters only flowing on the ground.

(3) Raised Pco_2 (normally $logPco_2 > -2.5$) of the spring waters of T (category S) indicates that the waters take up CO_2 in soils and keep the high Pco_2 during flowing the underground water systems. Development of tufas requires presence of a thick soil layer on a limestone.

(4) The underground water systems should be sealed in order to limit gas exchange with the atmosphere may be also important. Otherwise, calcite is deposited more efficiently in a cave rather than outside of the cave.

(5) Tufas are not very rare, but their distribution probably tends to be concentrated in a certain area, such as the northwestern Okayama Prefecture (Atetsu Limestone Plateau). Local geological and hydrological conditions may controls the deposition of tufas.

(6) Most of the tufas presented here are associated with cyanobacteria and algae. Therefore, some biological condi- tions (such as photosynthesis; e.g., Yoshimura et al., 1996a) are also critical. Too much sunlight activates the growth of algae and development of mat-like deposits rather than tufas.

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