Chemical Characteristics of Solfataric-Acidic Pond Waters in the Kirishima Geothermal Area, Kagoshima Prefecture

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鹿児島県霧島地域における酸性硫黄泉水の化学的特徴

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要　　旨

　高温・強酸性の温泉生態系に生息する唯一の生物は，化学合成を行う原核生物であり，それらに最も影響を与える主要環境要因は温度および化学成分である．本研究では，火山性強酸性高温泉が分布する対象地域として鹿児島県霧島地熱地域を選択し，21ヵ所の温泉水の温度，pH および化学成分（Li, Na, Mg, Al, Si, P, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Cd, Cs, Pb）を測定した．その結果，21ヵ所の温泉水の温度，pH，総化学成分量の範囲は，それぞれ63〜94℃，1.8 〜 4.0，3.1〜82 mmol L^{-1} であり，全温泉水に共通する主要元素は S および Si であった．さらに，環境要因間の関係性を明らかにするため，ピアソンの積率相関係数を算出したところ，いくつかの元素間では強い正の相関が認められた．また，総化学成分量は 7 元素（Fe, S, Al, Mg, P, Rb, Cs）と強い相関を示した．一方，pH は Ca, Na, As と強い正の相関を示すとともに，温度は Mg および Cs と相関を示した．温度および検出された各元素の 13 環境変数を用いて主成分分析を行った結果，第一主成分（PC1）および第二主成分（PC2）に強く影響を与えていたのは，8 元素（Fe, S, Al, Mg, P, As, Rb, Cs）および温度であった．従って，霧島地熱地域に分布する 21ヵ所の強酸性高温泉は次に示した通りの 4 種類の化学的特徴を有する温泉群に分類された：PC1 および PC2 が共に相対的に高い温泉群（Type A）；PC1 が相対的に高く，PC2 が相対的に低い温泉群（Type B）；P PC1 が相対的に低く，PC2 が相対的に高い温泉群（Type C）；PC1 および PC2 が共に相対的に低い温泉群（Type D）．本研究により明らかにされた火山性強酸性高温泉における化学的特徴は，高温・強酸性の温泉生態系に生息する多様な原核生物群集との関係性を理解する上での一助となるであろう．

キーワード：霧島温泉群，化学成分，温度，環境要因

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Abstract

The biosphere in terrestrial, highly acidic hot springs is composed solely of chemotrophic prokaryotic communities. The major environmental factors affecting these organisms are expected to be temperature and chemical composition. The Kirishima geothermal area surrounding the Kirishima volcano in Japan, in which highly acidic hot springs occur, was selected as the study area. Water samples were collected from 21 ponds and the temperature and pH of these samples were measured. The amount of 21 elements (Li, Na, Mg, Al, Si, P, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Cd, Cs, and Pb) was quantified using inductively coupled plasma atomic emission spectroscopy. The temperature, pH, and total concentrations of measured chemical components were 63–94℃, 1.8–4.0, and 3.1–82 mmol L^{-1}, respectively. Major elements common to all pond waters were S and Si. Calculation of Pearson's correlation coefficients to clarify the relationships between the environmental factors demonstrated that several chemical components showed significant linear relationships with each other. For example, Fe was strongly correlated with S, Al, P, and Rb, and S was strongly correlated with Al, Mg, P, Rb, and Cs. The total concentration of the measured chemical components was also strongly correlated with six elements (Fe, S, Al, Mg, P, Rb, and Cs). Conversely, pH was strongly correlated with Ca, Na, and As, and temperature was statistically correlated with Mg and Cs. Based on the high factor loadings observed between these elements and temperature, the 21 water samples in the highly acidic hot ponds within the Kirishima geothermal area were chemically classified using principal component analysis. The hot springs could be separated on the basis of differing values of principal component 1 (PC1), which was most strongly influenced by the concentrations of eight elements (Fe, S, Al, Mg, P, As, Rb, and Cs) and principal component 2 (PC2), which was mainly controlled by temperature. The springs were classified into four types : hot springs with relatively high values of both PC1 and PC2 (Type A) ; hot springs with relatively high PC1 and relatively low PC2 (Type B) ; hot springs with relatively low PC1 and relatively high PC2 (Type C) ; and hot springs with relatively low values of both PC1 and PC2 (Type D). The new information obtained in this study on the chemical characteristics of these volcanic, highly acidic hot springs will be helpful for understanding the relationships of the diverse prokaryotic communities that inhabit the solfataric-acidic hot-spring ecosystem.

Key words : Kirishima geothermal area, chemical component, temperature, environmental factor

1. Introduction

Terrestrial geothermal areas are located in various parts of the world, particularly around the edges of tectonic plates and in areas where the crust is relatively thin (Johnson *et al.*, 2003). Hot springs generally fall into two types : vapor-dominated (acid-sulfate) systems and water-dominated (alkaline-chloride and carbonate) systems (Fournier, 1989 ; Meyer-Dombard *et al.*, 2005). Springs at higher elevation are small and acidic and those at lower levels are large and alkaline (Allen and Day, 1935 ; Barth 1950 ; Sahm *et al.*, 2013). Vapor-dominated systems are fed by reduced gases (e.g., H$_2$ and H$_2$S) via fractures from magma bodies 3 to 10 km below the surface (Fournier and Pitt, 1985 ; Kennedy *et al.*, 1985 ; Fournier *et al.*, 1994). As the gases approach the surface, the sulfides are oxidized in accordance with, for example,

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+, \tag{1}$$

resulting in acidic fluids with elevated sulfate concentrations capable of causing considerable chemical weathering, which releases cations into solution (White *et al.*, 1971). The elevated

temperatures and extreme acidity in solfataric fields accelerate the dissolution of minerals, so these environments may contain high concentrations of soluble metals and silica (Johnson *et al.*, 2003). The biosphere in terrestrial, highly acidic hot springs is only composed of chemotrophic prokaryotic communities (Brock, 1967 ; Brock, 1978 ; Madigan *et al.*, 2008 ; Cox *et al.*, 2011). Therefore, the major environmental variables affecting prokaryotic communities in these environments are expected to be the temperature and the chemical composition.

The Japanese Islands lie at the junction of four major tectonic plates : the Pacific and Philippine Sea oceanic plates and the North American and Eurasian continental plates. The Pacific plate is subducting beneath the Kuril Arc and the Izu-Ogasawara Arc, forming the Kuril Trench, Japan Trench, and Izu-Ogasawara Trench. The Philippine Sea plate is subducting beneath the Southwest Japan Arc and the Ryukyu Arc, forming the Nankai trough and Ryukyu Trench. Quaternary volcanoes lie parallel to these trenches and form a "volcanic front" (Nuclear Waste Management Organization of Japan, 2004). Volcanic geothermal areas containing hot springs are present around the Quaternary volcanoes. The general spatial distribution of acidic groundwater around Quaternary volcanoes in Japan was examined using a database of approximately 9,300 data points of groundwater geochemistry (Asamori *et al.*, 2002). The results showed that acidic groundwater with pH $<$ 4.8 is mostly found in volcanic regions and occurs from between several and approximately ten kilometers from Quaternary volcanoes. The pH value of groundwater tends to increase with increasing distance from a volcano. We selected a geothermal area containing highly acidic hot springs as the sampling area for this study.

The Kirishima volcano, which is one of the largest Quaternary volcanoes in Japan, is part of the northern section of the Kagoshima graben, a volcano-tectonic depression caused by subduction of the Philippine Sea plate (Tsuyuki, 1969). The volcano occupies a 20×30 km area that is elongated northwest-southeast and contains more than 20 small volcanoes (Imura *et al.*, 2001). The Kirishima geothermal region surrounding the Kirishima volcano experienced extensive volcanic activity during the Pleistocene Epoch ; these activities have continued and resulted in the formation of a thick sequence of volcanic rocks (Goko, 2000). The basement rocks of the Kirishima volcano are the Mesozoic to Paleogene Shimanto Supergroup and the Pleistocene Kakuto Volcanic Rocks (Imura *et al.*, 2001).

In this study, a number of ponds located in a relatively wide geothermal field, the Kirishima geothermal area, Kagoshima Prefecture, Japan, were randomly selected. The temperature, pH, and chemical components of pond waters were measured as these are representative of major environmental factors. We chemically characterized the highly acidic hot ponds distributed in this solfataric field by statistical analysis, and established a classification of the pond waters based on environmental variability.

2. Experiments

2. 1 Study area and sample collection

The ponds investigated in this study are all located in a 1 km^2 field in or near the region of the Tearai hot spring (Tsuyuki, 1980). This district is situated 3 km southwest of the Ohnami-Ike volcanic crater lake in the Kirishima geothermal area, Kagoshima Prefecture, Japan (Fig. 1).
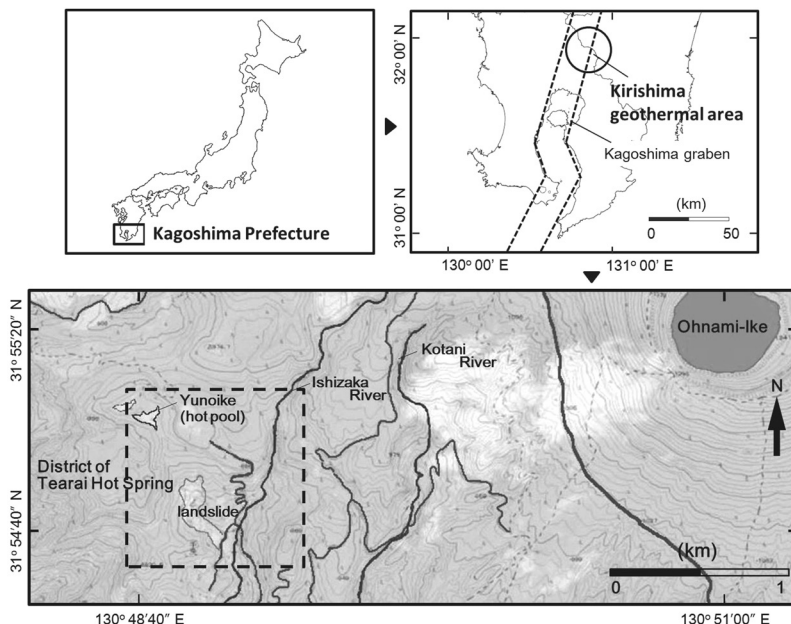
Fig. 1　Map of the sampling site in and near the region of the Tearai hot spring in the Kirishima geothermal area, Kagoshima Prefecture, Japan.
The dotted box shows the area sampled in this study.

The rocks around this region belong to the Younger Kirishima volcano and are composed of andesitic lava and pyroclastic rocks (Imura *et al.*, 2001). The altitude in this area is generally 800−1,000 m (Goko, 2000). The sampling field within the Kirishima geothermal area is located on private land ; thus, the area is not usually exposed to human activity. We obtained permission from the landowner to obtain samples of hot-spring and pond water as well as soil and various other samples of organisms native to the area. There are many hot springs and muddy ponds present in this district, which have a variety of temperatures and sediment colors.

　　The sampling was conducted in July 2005 and February and June 2006. Elemental sulfur is deposited around many fumaroles in this area. We randomly selected a number of hot ponds and collected samples of surface muddy water from each pond in sterile 100-mL glass bottles. The temperature and pH of samples were measured at each sampling site. Part of each sample was filtered using a 0.22-μm membrane filter (Asahi Glass) and 1% (v/v) nitric acid (HNO_3) was added as appropriate preservation and pretreatment. Water samples were stored at 4℃ until analysis of the chemical composition was carried out.

2.2　Analysis of chemical composition

　　Elemental composition analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP-7000 Ver. 2, Shimadzu). Twenty-one elements (Li, Na, Mg, Al, Si, P, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Cd, Cs, and Pb) were chosen for quantitative analysis from the 72 elements that were preliminarily surveyed by ICP-AES analysis.

2.3 Statistical analysis

To clarify the relationships between temperature, each chemical component, and total concentrations of the measured chemical components of 21 ponds in the Kirishima geothermal area, Pearson's correlation coefficients (r) were calculated. Principal component analysis was performed to reveal the environmental variables (temperature and each chemical component) affecting the differences between ponds using XLSTAT software (Addinsoft, New York).

3. Results

3.1 Water chemistry

Sampling was conducted at 21 stations in the Kirishima geothermal area (Table 1, Fig. 2). The 21 ponds are located in a $1\,km^2$ field between 759 and 896 m in altitude. The sediment colors of the ponds were determined by visual observation. The colors were gray or brown and were different for each pond. Temperature, pH, and chemical components of 21 pond waters are listed in Table 2. Temperature ranged from 63–94℃ with a mean of 83℃. The pH values of the ponds were 1.8–2.9 with a mean of 2.4 except for one station, St. 5, where the pH value was 4.0. Thus, the ponds in this area are highly acidic and hot. The concentrations of nine elements (Li, Cr, Mn, Ni, Cu, Zn, Sr, Cd, and Pb) were below the limit of detection in the waters of all sampled ponds. The concentrations of Na and K were also below the limit of detection in many pond-water samples. Major elements constituting more than 1% of total concentrations of measured chemical components in all pond waters were S and Si. The concentration of Si in all pond-water samples also had low values of coefficient of variation. The total concentrations of the measured chemical components were 3.1–82 mmol L^{-1}, with a mean of 26 mmol L^{-1}. The total concentrations of measured chemical components are plotted against the temperatures of the 21 ponds in Fig. 3. Two-thirds of all pond waters had relatively lower total concentrations of measured chemical components (less than 20 mmol L^{-1}) despite showing a wide range of temperatures. These pond waters were mostly obtained from the north side of Yunoike (hot pool). Conversely, the pond waters of seven sites showed relatively higher concentrations of measured chemical components (more than 30 mmol L^{-1}). In these ponds, the concentrations and percentages of Fe, S, and Al, in particular, tended to be higher than those in the other ponds (Table 3). The waters of these six ponds were at relatively high temperature, approximately 90℃. However, only one pond, St. 2, had a lower temperature and a higher total concentration of chemical components.

3.2 Correlation of environmental variables

To clarify the relationships between temperature, pH, each chemical component, and total concentrations of measured chemical components (which were standardized with respect to silicon, /Si) of the 21 pond waters in the Kirishima geothermal area, Pearson's correlation coefficients (r) were calculated (Table 4). Several chemical components were found to be statistically correlated with each other. For example, Fe/Si was strongly and positively correlated with S/Si, Al/Si, P/Si, and Rb/Si with a significance level of $\alpha = 0.05$. The total concentration of the measured chemical components was also strongly and positively correlated

Table 1　Locations of sampling stations and sediment colors of pond waters in the Kirishima geothermal area.

Station	Position		Altitude (m)	Color of sediments
	Latitude	Longitude		
1	31°54'52.60"N	130°48'50.20"E	844	light gray
2	31°54'52.40"N	130°48'50.30"E	842	light brown
3	31°54'52.10"N	130°48'49.90"E	839	gray
4	31°54'52.90"N	130°48'50.30"E	847	light gray
5	31°54'37.90"N	130°49'15.70"E	859	brown gray
6	31°54'33.70"N	130°48'57.00"E	761	brown
7	31°54'37.70"N	130°49'00.60"E	759	brown
8	31°54'37.70"N	130°49'00.60"E	759	light brown
9	31°54'37.70"N	130°49'00.60"E	759	gray
10	31°54'37.80"N	130°49'00.20"E	759	light gray
13	31°54'36.70"N	130°48'59.90"E	757	light gray
14	31°55'05.10"N	130°48'42.30"E	892	light gray
15	31°55'04.50"N	130°48'41.00"E	885	gray
16	31°55'05.00"N	130°48'41.10"E	884	light gray
17	31°55'04.80"N	130°48'40.90"E	884	light gray
18	31°55'05.10"N	130°48'41.20"E	885	light gray
19	31°55'05.20"N	130°48'40.80"E	884	gray
20	31°55'05.30"N	130°48'41.80"E	889	light gray
21	31°55'06.10"N	130°48'42.70"E	896	gray
22	31°55'05.80"N	130°48'42.50"E	894	gray
23	31°55'05.80"N	130°48'42.20"E	892	light gray

with Fe/Si, S/Si, Al/Si, Mg/Si, P/Si, Rb/Si, and Cs/Si. The pH values were strongly and positively correlated with Ca/Si, Na/Si, and As/Si. Temperature was statistically correlated with Mg/Si and Cs/Si with a significance level of $\alpha = 0.10$.

3.3　Principal component analysis

Principal component analysis was performed to distinguish the 21 ponds based on environmental variables. Some variables characterizing the sites were explained by three principal factors : Factor 1, Factor 2, and Factor 3 (Table 5). The first factor explained 45% of the total variance ; Factor 2 and Factor 3 accounted for 22% and 11% of the total variance,

Table 2　Temperature, pH, and chemical components of water samples from 21 ponds in the Kirishima geothermal area.

Station	Temp.	pH	Fe	S	Al	Mg	Si	Ca	P	Na	K	As	Rb	Cs	Total conc.
1	80	2.8	1.173	3.019	4.331	N.D.	2.022	0.063	0.059	N.D.	N.D.	0.014	0.647	0.934	12.26
2	66	2.0	20.57	21.91	10.67	1.924	1.620	0.271	0.152	N.D.	N.D.	0.015	14.05	2.223	73.41
3	91	2.5	10.14	20.50	2.387	N.D.	1.241	0.153	0.132	N.D.	N.D.	0.012	6.169	0.219	40.95
4	90	2.2	4.895	13.35	8.562	0.917	1.585	0.218	0.107	0.043	N.D.	0.013	2.796	1.773	34.26
5	93	4.0	N.D.	3.944	0.865	1.458	0.646	5.950	0.041	0.569	N.D.	0.011	0.047	0.401	13.93
6	69	2.8	0.658	2.617	0.699	N.D.	2.716	0.061	0.058	1.213	N.D.	0.013	0.371	0.156	8.562
7	94	2.9	1.012	4.866	3.338	1.975	1.316	2.698	0.044	0.227	N.D.	0.012	0.571	0.775	16.83
8	93	2.6	6.964	20.68	16.07	3.568	1.704	1.367	0.092	N.D.	N.D.	0.014	4.130	3.341	57.93
9	91	2.2	3.569	34.40	22.39	3.662	2.129	1.336	0.144	0.039	N.D.	0.016	9.950	4.775	82.40
10	94	1.9	4.173	19.37	15.27	2.497	1.633	0.516	0.229	N.D.	N.D.	0.014	2.407	3.224	49.33
13	88	2.4	4.262	27.23	18.04	4.808	3.846	3.704	0.075	0.326	N.D.	0.015	2.585	3.908	68.79
14	90	2.5	1.608	2.782	3.921	N.D.	1.961	0.177	0.053	N.D.	N.D.	0.015	0.846	0.840	12.20
15	67	2.3	0.487	1.930	0.075	1.783	5.285	0.979	0.041	0.367	0.189	0.011	0.288	0.047	11.48
16	88	2.4	0.172	1.863	0.540	N.D.	3.700	0.187	0.041	N.D.	N.D.	0.012	0.092	0.118	6.725
17	63	2.3	0.271	2.166	0.945	0.757	4.358	0.665	0.043	0.203	0.005	0.012	0.152	0.208	9.784
18	94	2.4	0.490	2.215	2.358	N.D.	4.047	0.183	0.046	N.D.	N.D.	0.012	0.265	0.504	10.12
19	93	1.8	0.279	5.991	1.994	0.005	4.133	0.261	0.043	N.D.	N.D.	0.012	0.157	0.422	13.30
20	82	2.3	0.073	1.804	0.313	N.D.	1.160	0.131	0.040	N.D.	N.D.	0.012	0.016	0.070	3.619
21	78	2.4	0.026	1.541	0.263	N.D.	1.049	0.057	0.039	N.D.	N.D.	0.011	0.021	0.059	3.067
22	75	2.3	0.172	1.623	0.747	N.D.	2.143	0.235	0.041	N.D.	N.D.	0.012	0.108	0.167	5.248
23	65	2.5	0.049	1.523	0.307	N.D.	1.086	0.077	0.040	N.D.	N.D.	0.012	0.032	0.068	3.191
mean	83	2.5	2.906	9.301	5.433	1.112	2.351	0.919	0.074	0.142	0.009	0.013	2.176	1.154	25.59
SD	11	0.45	4.875	10.29	6.889	1.481	1.327	1.490	0.051	0.292	0.041	0.001	3.703	1.461	25.75
VC	0.14	0.18	1.677	1.106	1.268	1.331	0.564	1.622	0.689	2.054	4.446	0.115	1.702	1.266	1.006

Temperature is expressed in °C. The concentrations of each chemical component are expressed in mmol L^{-1}. The concentrations of each chemical component are the means of values measured three times. The detection limits of the elements that were not detected are shown as N.D. The detection limit was 0.001 mg L^{-1}. Temp., Total conc., SD, and CV indicate temperature, total concentration of measured chemical components, standard deviation, and coefficient of variation, respectively.

Table 3　Temperature, pH, and the percentage of each chemical component with respect to total concentrations of measured chemical components of water from 21 ponds in the Kirishima geothermal area.

Station	Temp.	pH	Fe	S	Al	Mg	Si	Ca	P	Na	K	As	Rb	Cs
1	80	2.8	9.6	25	35	N.D.	16	0.51	0.48	N.D.	N.D.	0.11	5.3	7.6
2	66	2.0	28	30	15	2.6	2.2	0.37	0.21	N.D.	N.D.	0.021	19	3.0
3	91	2.5	25	50	5.8	N.D.	3.0	0.37	0.32	N.D.	N.D.	0.029	15	0.54
4	90	2.2	14	39	25	2.7	4.6	0.64	0.31	0.13	N.D.	0.038	8.2	5.2
5	93	4.0	N.D.	28	6.2	10	4.6	43	0.29	4.1	N.D.	0.081	0.34	2.9
6	69	2.8	7.7	31	8.2	N.D.	32	0.72	0.67	14	N.D.	0.16	4.3	1.8
7	94	2.9	6.0	29	20	12	7.8	16	0.26	1.3	N.D.	0.069	3.4	4.6
8	93	2.6	12	36	28	6.2	2.9	2.4	0.16	N.D.	N.D.	0.025	7.1	5.8
9	91	2.2	4.3	42	27	4.4	2.6	1.6	0.18	0.048	N.D.	0.019	12	5.8
10	94	1.9	8.5	39	31	5.1	3.3	1.0	0.46	N.D.	N.D.	0.029	4.9	6.5
13	88	2.4	6.2	40	26	7.0	5.6	5.4	0.11	0.47	N.D.	0.021	3.8	5.7
14	90	2.5	13	23	32	N.D.	16	1.4	0.43	N.D.	N.D.	0.12	6.9	6.9
15	67	2.3	4.2	17	0.65	16	46	8.5	0.36	3.2	1.6	0.10	2.5	0.41
16	88	2.4	2.6	28	8.0	N.D.	55	2.8	0.61	N.D.	N.D.	0.18	1.4	1.8
17	63	2.3	2.8	22	9.7	7.7	45	6.8	0.44	2.1	0.052	0.12	1.6	2.1
18	94	2.4	4.8	22	23	N.D.	40	1.8	0.45	N.D.	N.D.	0.12	2.6	5.0
19	93	1.8	2.1	45	15	0.040	31	2.0	0.32	N.D.	N.D.	0.089	1.2	3.2
20	82	2.3	2.0	50	8.7	N.D.	32	3.6	1.1	N.D.	N.D.	0.32	0.44	1.9
21	78	2.4	0.83	50	8.6	N.D.	34	1.9	1.3	N.D.	N.D.	0.36	0.68	1.9
22	75	2.3	3.3	31	14	N.D.	41	4.5	0.78	N.D.	N.D.	0.22	2.1	3.2
23	65	2.5	1.5	48	9.6	N.D.	34	2.4	1.2	N.D.	N.D.	0.36	0.99	2.1
mean	83	2.5	7.6	34	17	3.5	22	5.1	0.50	1.2	0.081	0.12	4.9	3.7
SD	11	0.45	7.5	10	10	4.7	18	9.4	0.34	3.2	0.36	0.11	5.1	2.
VC	0.14	0.18	0.99	0.30	0.60	1.3	0.82	1.8	0.69	2.6	4.4	0.89	1.0	0.58

Temperature is expressed in °C. The amounts of each chemical component are expressed as percentages. The concentrations of each chemical component are the means of values measured three times. The detection limits of the elements that were not detected are shown as N.D. The detection limit is 0.001 mg L^{-1}. Temp., SD, and CV indicate temperature, standard deviation, and coefficient of variation, respectively.
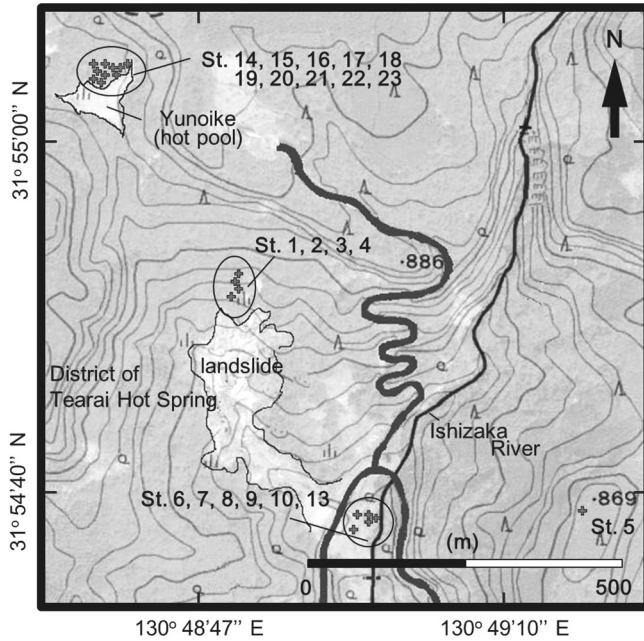
Fig. 2　Location of pond-water sampling stations in the Kirishima geothermal area.
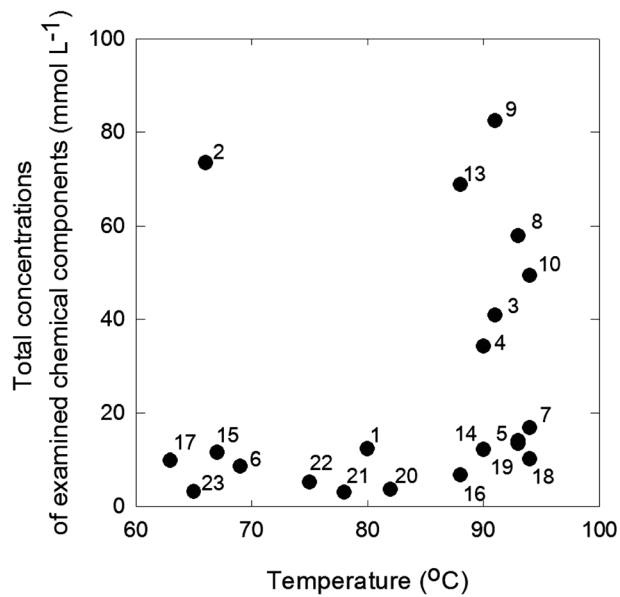

Fig. 3　The relationship between temperature and total concentrations of measured chemical components in water from 21 ponds in the Kirishima geothermal area ; N = 21.　The numbers denote each pond name.　Arabic figures denote sampling stations as shown in Fig. 2 and Table 1.

Table 4　Correlation matrix showing r values for Pearson's correlation among 14 environmental variables in the pond waters of the Kirishima geothermal area : N = 21.

Variables	Temp.	pH	Fe/Si	S/Si	Al/Si	Mg/Si	Ca/Si	P/Si	Na/Si	K/Si	As/Si	Rb/Si	Cs/Si	Total conc./Si
Temp.	—	0.13	-0.05	0.34	0.37	0.40	0.28	0.27	0.07	-0.34	0.18	-0.02	0.38	0.29
pH		—	-0.24	-0.12	-0.23	0.33	**0.82**	-0.09	**0.83**	-0.08	**0.56**	-0.27	-0.15	-0.06
Fe/Si			—	**0.74**	**0.47**	0.25	-0.12	**0.66**	-0.19	-0.12	0.23	**0.93**	0.42	**0.79**
S/Si				—	**0.82**	**0.62**	0.10	**0.83**	-0.06	-0.20	0.36	**0.83**	**0.79**	**0.97**
Al/Si					—	**0.73**	-0.01	**0.66**	-0.17	-0.19	0.19	**0.61**	**0.99**	**0.85**
Mg/Si						—	**0.61**	**0.48**	0.41	-0.08	**0.46**	0.35	**0.79**	**0.71**
Ca/Si							—	0.14	**0.87**	-0.06	**0.64**	-0.10	0.10	0.18
P/Si								—	0.01	-0.23	**0.56**	**0.65**	**0.64**	**0.81**
Na/Si									—	-0.02	**0.48**	-0.19	-0.07	0.02
K/Si										—	-0.32	-0.13	-0.19	-0.19
As/Si											—	0.22	0.24	0.41
Rb/Si												—	**0.56**	**0.86**
Cs/Si													—	**0.84**
Total conc./Si														—

Values in bold are different from 0 with a significance level of $\alpha = 0.05$ ($r > 0.43$). Temp. and Total conc. denote the temperature and total concentration of measured chemical components, respectively. Each chemical component was standardized with respect to silicon (/Si).

respectively. The cumulative variance of these three factors explained 79% of the total variance ; three extracted factors did not show all variables. Factor 1 was strongly loaded by Fe/Si, S/Si, Al/Si, Mg/Si, P/Si, As/Si, Rb/Si, and Cs/Si (positively) ; Factor 2 was strongly loaded by Ca/Si, Na/Si, and As/Si (positively) ; and Factor 3 was strongly loaded by temperature (negatively) and Fe/Si (positively) (Table 6). Only K/Si was not explained by any of the three factors.

The cumulative variance of principal components 1 and 2 (PC1 and PC2), which affected Factor 1 and 2, explained 67% of the total variance (Fig. 4a). Strong contributions to PC1 were made by S/Si, Al/Si, Cs/Si, P/Si, Mg/Si, Rb/Si, Fe/Si, and As/Si and a moderate contribution was made by temperature. Ca/Si, Na/Si, and As/Si strongly contributed to PC2, and Ca/Si showed a stronger contribution to PC2 than did Na/Si. As/Si had a similar influence on both PC1 and PC2, but the contribution to PC2 was slightly higher. The site distributions corresponding to loadings on PC1 and PC2 are shown in Fig. 4b. The sites that were strongly and negatively correlated to PC1 are shown on the left side of horizontal axis (F1). These sites

Table 5　Factor analysis of 12 environmental variables in 21 ponds of the Kirishima geothermal area.

Factor	Eigenvalue	Total variance (%)	Cumulative eigenvalue	Cumulative variance (%)
Factor 1	5.39	44.9	5.39	44.9
Factor 2	2.69	22.4	8.07	67.3
Factor 3	1.37	11.4	9.44	78.7

Table 6　Factor loadings for 12 environmental variables in 21 ponds of the Kirishima geothermal area.

Variables	Factor 1	Factor 2	Factor 3
Temperature	0.40	0.29	**0.66**
Fe/Si	**0.70**	-0.42	**-0.47**
S/Si	**0.94**	-0.17	-0.05
Al/Si	**0.88**	-0.19	0.33
Mg/Si	**0.77**	0.43	0.17
Ca/Si	0.25	**0.92**	-0.16
P/Si	**0.85**	-0.06	-0.18
Na/Si	0.06	**0.89**	-0.27
K/Si	-0.29	-0.11	-0.24
As/Si	**0.51**	**0.58**	-0.34
Rb/Si	**0.77**	-0.42	-0.38
Cs/Si	**0.88**	-0.08	0.34

Values in bold differ from 0 with a significance level of $\alpha = 0.05$ ($r > 0.43$).

were thickly scattered around the vertical axis (F2＝0). Therefore, the 21 ponds could be classified into three types based on the two principal components that were defined only by chemical components : Type 1, hot springs for which both PC1 and PC2 were relatively higher (St. 5, 7, and 13) ; Type 2, hot springs for which PC1 was relatively higher and PC2 was relatively
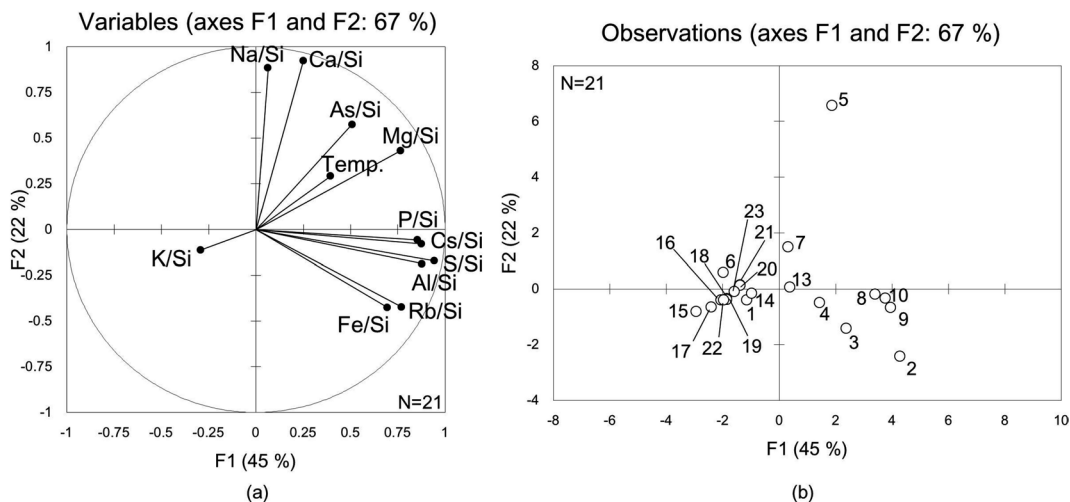

Fig. 4 Principal component analysis showing the environmental variables of the 21 ponds.
　(a) Factor loadings for principal components 1 and 2. (b) Relationships between the 21 ponds and the principal components.
　F1 and F2 indicate Factor 1 and Factor 2, respectively. Arabic figures in (b) denote sampling stations as shown in Fig. 2 and Table 1.
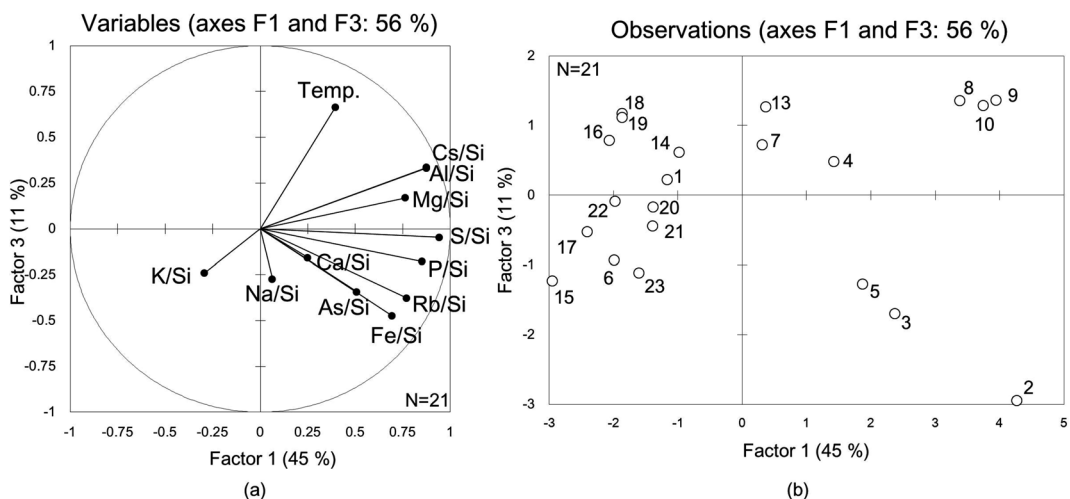
Fig. 5 Principal component analysis showing the environmental variables of the 21 ponds.
　(a) Factor loadings on principal components 1 and 3. (b) Relationships between the 21 ponds and the principal components.
　F1 and F3 indicate Factor 1 and Factor 3, respectively. Arabic figures in (b) denote sampling stations as shown in Fig. 2 and Table 1.

lower (St. 2, 3, 4, 8, 9, and 10) ; and Type 3, hot springs for which PC1 was relatively lower (St. 1, 6, 14, 15, 16, 17, 18, 19, 20, 21, 22, and 23).

The cumulative variance of principal components 1 and 3 (PC1 and PC3), which affected factors 1 and 3, explained 56% of the total variance (Fig. 5a). Strong contributions to PC1 were made by S/Si, Al/Si, Cs/Si, P/Si, Mg/Si, Rb/Si, Fe/Si, and As/Si and moderate contributions were made by temperature. Strong contributions to PC3 were made by temperature (positively) and Fe/Si (negatively). The site distributions corresponding to loadings on PC1 and PC3 were widely scattered in four compartments (Fig. 6b). Therefore, the chemical characteristics and temperature values could be used to classify the 21 ponds into four types : Type A, hot springs in which both PC1 and PC3 were relatively higher (St. 4, 7, 8, 9, 10, and 13) ; Type B, hot springs in which PC1 was relatively higher and PC3 was relatively lower (St. 2, 3, and 5) ; Type C, hot springs in which PC1 was relatively lower and PC3 was relatively higher (St. 1, 14, 16, 18, and 19) ; and Type D, hot springs in which PC1 and PC3 were relatively lower (St. 6, 15, 17, 20, 21, 22, and 23).

4.　Discussion

The highly acidic 21 ponds distributed in a $1 \, km^2$ field within the Kirishima geothermal area were chemically characterized by statistical analysis and classification of the pond waters based on their environmental variability. The 21 ponds could be classified into three types based on the two principal components (PC1 and PC2) that were defined only by chemical components. However, the only site that was explained well by PC2 was St. 5. This pond was located away from other ponds investigated in this study. Additionally, PC2 was most strongly affected by Ca/Si. The percentage of Ca in the total concentration of the measured chemical components accounted for a high value of 43% compared to the other sites. Thus, the water chemistry in St. 5 was considered to be hydrologically different from that in other ponds. Conversely, the 21 ponds could be classified into four types on the basis of PC1 and PC3, which were defined by chemical factors and temperature. As major environmental variables affecting the prokaryotic communities in the terrestrial highly acidic hot springs are expected to be temperature and chemistry, it might be possible to detect different prokaryotic communities in the four types of ponds of the Kirishima geothermal area classified by temperature and chemical components. Prokaryotes are divided into two domains, Bacteria and Archaea, based on 16S rRNA gene phylogenetic analysis (Woese and Fox, 1977 ; Woese *et al.*, 1990). Investigations of both bacterial and archaeal communities in representative ponds in the field area using 16S rRNA gene phylogenetic analysis detected a total of 61 phylotypes (35 Bacteria and 26 Archaea ; Satoh *et al.*, 2013a, b). It was additionally demonstrated that the bacterial and archaeal biodiversity and species composition were clearly different between the ponds.

The concentrations of rubidium and cesium, which are mobile alkaline elements, were measured by ICP-AES in this study. Some mobile elements (including Cs and Rb) are efficiently extracted from basalts by high-temperature hydrothermal fluids and do not show a strong affinity for secondary mineral phases (Bowers *et al.*, 1985, 1988 ; Palmer and Edmond, 1989). Therefore, their concentrations in hydrothermal fluids can yield information concerning the

nature of the primary mineral assemblage that reacted with the fluids. The concentrations of Cs and Rb in 20 submarine hydrothermal vent fluids from the East Pacific Rise, southern Juan de Fuca Ridge, and Mid-Atlantic Ridge showed positive linear relationships with a significance level of $\alpha = 0.01$ (Fig. 6). The concentrations of Cs and Rb in submarine hydrothermal vent fluids were determined by isotope dilution and thermal ionization mass spectrometry (Palmer and Edmond, 1989). On the other hand, the concentrations of Cs and Rb in the pond waters of the Kirishima geothermal area also showed positive linear relationships with a significance level of $\alpha = 0.01$ (Fig. 6). The rocks in the study area are predominantly andesitic lava and pyroclastic rocks produced by the Younger Kirishima volcano (Imura *et al.*, 2001). The relationship between the concentrations of Cs and Rb were compared for the terrestrial hot spring waters of this study and submarine hydrothermal vent fluids. The samples derived from terrestrial hot springs plotted higher
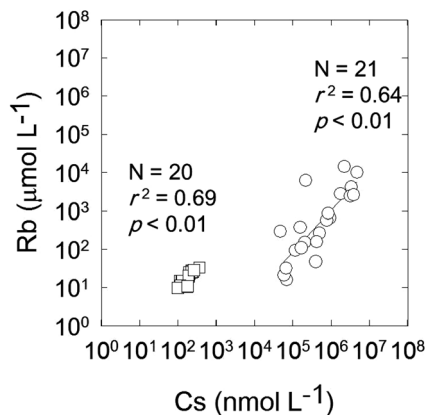

Fig. 6   The positive linear relationships between the concentrations of cesium and rubidium in terrestrial, highly acidic, hot-spring waters and submarine hydrothermal vent fluids. The samples derived from this study are shown as open circles and the samples derived from submarine hydrothermal vent fluids are shown as open squares.

than those of submarine hydrothermal vents. This could be explained by the samples from the terrestrial hot springs having been concentrated by evaporation, whereas the samples derived from submarine hydrothermal vents plotted in the lower side because the fluid was diluted by exposure to seawater. The relationship between the concentrations of Cs and Rb in terrestrial hot spring waters might be elucidated by focusing on the Kirishima geothermal area.

5.   Conclusion

In this study, we investigated the chemical characteristics of the solfataric-acidic hot spring waters in the Kirishima geothermal area, Kagoshima Prefecture, Japan. Temperature, pH, and the chemical components of pond waters were quantitatively measured as being representative of major environmental factors affecting the biodiversity of prokaryotic communities. The trends of relationships among the environmental variables of the highly acidic 21 ponds were discussed in detail. The 21 ponds were statistically classified into four types based on their environmental variability in terms of certain chemical components and temperature using principal component analysis. The concentrations of eight elements (Fe, S, Al, Mg, P, As, Rb, and Cs) were the major influences on principal component 1 (PC1) and temperature was the major contribution to principal component 2 (PC2). The four types of hot spring are as follows. Type A is hot springs in which both PC1 and PC2 were relatively higher (St. 4, 7, 8, 9, 10, and 13). Type B is hot springs in which PC1 was relatively higher and PC2 was relatively lower (St. 2, 3, and 5). Type C is hot springs in which PC1 was relatively lower and PC2 was relatively higher (St. 1, 14, 16, 18, and 19). Type D is hot springs in which both PC1 and PC2 were

relatively lower (St. 6, 15, 17, 20, 21, 22, and 23). These chemical data will be helpful for improving our understanding of the ecology in the solfataric-acidic hot springs by linking with the biological data.

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