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Rayleigh scattering by aqueous colloidal silica as a cause for the blue color of hydrothermal water

Shinji Ohsawa^{a,*}, Takao Kawamura^b, Nobuki Takamatsu^b, Yuki Yusa^a

^a *Beppu Geothermal Research Laboratory, Kyoto University, Noguchibaru, Beppu 874-0903, Japan*

^b *Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi 274-8510, Japan*

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Abstract

Thermal waters in hydrothermal ponds, bathing pools and the brines of geothermal electric power plants commonly have a characteristic blue color. Although many researchers have assumed that the blue color is due to a colloidal suspension and/or absorption by dissolved ferrous iron or by water itself, there has been no specific effort to identify the physical nature of this phenomenon. We have tested, in synthetic and natural solutions, whether aqueous colloidal silica is responsible for the blue color. Aqueous colloidal silica is formed by silica polymerization in thermal waters of the neutral-chloride type which contain initially monomeric silica in concentrations up to three times above the solubilities of amorphous silica. The hue of the blue thermal waters in the pools tested agrees with that of a synthesized colloidal silica solution. Grain-size analyses of aqueous colloidal silica in the blue-colored thermal waters demonstrate that the color is caused by Rayleigh scattering from aqueous colloidal silica particles with diameters (0.1–0.45 μm) smaller than the wavelengths of visible radiation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: thermal water; blue color; colloidal silica; Rayleigh scattering

1. Introduction

Thermal waters with a blue color are commonly observed in hydrothermal ponds, bathing pools and in the pits of geothermal electric power plants all over the world. Such blue-colored thermal waters have a strong visual appeal and most workers in this field are aware of this phenomenon. Although many researchers have assumed that the blue color is due to a colloidal suspension

and/or absorption by dissolved ferrous iron or by water itself, there has been no specific effort to identify the physical nature of the phenomenon.

We have observed the blue thermal waters in hydrothermal ponds and bathing pools in the Beppu area (Central Kyushu, Japan), and in hydrothermal ponds in Waimangu and Rotorua (New Zealand) and Tenchong, Yunnan Province (China). In addition, blue thermal waters of a similar kind have been reported from Svartsengi ('the Blue Lagoon'; Iceland; Ehara and Gislason, personal communication) and from the pits of the Ogiri and Hatchobaru geothermal power stations in Japan (Shimada and Kiyota, private communi-

* Corresponding author. Tel.: +81-977-22-0713; Fax: +81-977-22-0965.

E-mail address: ohsawa@bep.vgs.kyoto-u.ac.jp (S. Ohsawa).

cation). Most of the blue-colored thermal waters are of the neutral-chloride water type, except for the thermal waters in Umi-jigoku (Beppu) and Inferno Crater (Waimangu), which belong to the acid sulfate-chloride type.

Thermal pools filled with the blue waters have several characteristics in common. Boiling water from springs and/or drilling wells flows into the pools, sometimes with additional bottom inflow of thermal water. The blue water in the pools often becomes cloudy due to the presence of white particulate amorphous silica. Silica sinter is not always totally precipitated, and the pool is sometimes bordered by a silica terrace.

These common features suggest the presence of aqueous colloidal silica resulting from the polymerization of monomeric silica. We proposed that the blue color of the thermal waters is caused by Rayleigh scattering of sunlight on aqueous colloidal silica particles, which are smaller in size than the wavelengths in the visible region of the electromagnetic spectrum (0.4–0.7 μm) (Ohsawa and Yusa, 1997).

The aim of this study is to test this hypothesis for the blue color of thermal waters by direct experiments: color measurements of natural thermal waters and synthetic silica solutions, grain-size analysis of aqueous silica of natural blue thermal water, and the detection of aqueous colloidal silica related to the blue color in natural blue thermal waters. We present here the test results and their relation to the occurrence of the blue color in thermal waters.

2. Behavior of silica in thermal waters

One of the most fundamental characteristics of aqueous silica is the occurrence of polymerization. Studies of this chemical reaction are too numerous to list here, but include, for example, basic studies on the solubility and polymerization of silica, the storage of water samples for silica determination, and silica scaling in geothermal pipe lines (e.g. Shimono et al., 1983; Chan, 1989; Yokoyama et al., 1983; Hosoi and Imai, 1982).

According to Ellis and Mahon (1977), in freshly discharged thermal waters from high-temperature

hot springs and geothermal wells, aqueous silica is almost always present in a reactive monomeric form as H_4SiO_4 . Cooled thermal waters show concentrations of monomeric silica, which decrease with time and approach a value approximately equal to the steady-state concentration at equilibrium with amorphous silica at the holding temperature. The silica present in the water in excess of the amorphous silica solubility polymerizes through a series of reactions involving linear, cyclic and three-dimensional polymeric silica (e.g. Ellis and Mahon, 1977; Iler, 1979).

The initial degrees of super-saturation as defined by the ratio of total dissolved silica concentration and amorphous silica solubility of the blue-colored thermal waters in Beppu (Fig. 1) are shown in Table 1. The amorphous silica solubilities were calculated through the use of a silica geothermometer equation for amorphous silica (Nicholson, 1993). It is well known that not only temperature but also pH and salinity of solution affect the amorphous silica solubility (e.g. Tarutani, 1956), however in this case, there is no necessity to consider the pH and salinity effects (for pH values and molal NaCl concentrations of the thermal waters, see Table 1). The concentrations of total dissolved silica of the thermal waters in the pools are initially in excess of the amorphous silica saturation at the water temperatures of the pools. These results indicate that the monomeric silica in the thermal waters has the potential to form aqueous colloidal silica. However, low pH around between 2 and 3 is well known for delaying the polymerization of silica (e.g. Tarutani, 1956; Ichikuni, 1968; Yokoyama et al., 1983), so little polymerization would be expected in the Umi-jigoku hot pool (pH 3.2, see Table 1). It is reasonable to believe this since the analytical results for total and colorimetric silica in the Umi-jigoku thermal water are identical at 328 and 329 mg/l, respectively.

3. Test methods and description of field tests

3.1. Synthesis of colloidal silica solution

In order to confirm the fact that colloidal silica



Fig. 1. Natural blue thermal waters in Beppu, Central Kyushu, Japan. (1) Kinko-yu and (2) Keikan-yu in Restaurant Ichinoide-kaikan (outdoor bathing pools; depth, ca. 50–90 cm); (3) outdoor bathing pool in Hotel Kannawa-en (depth, ca. 50 cm); (4) No. 3 pond in Kamado-jigoku and (5) Umi-jigoku (hydrothermal pond). The last photograph (6) shows a synthesized colloidal silica solution (right) and distilled water (left) under pseudo-sunlight with a xenon lighting system (WACOM R&D).

Table 1
Potential for silica polymerization in blue thermal water of pool

Name	T_w (°C)	pH TDS (mg/l)	SAS (mg/l)	TDS/SAS	NaCl concentration (mol/l)	No. in Fig. 1
Kinko-yu (Ichinoide-kaikan)	33	8.1 366	150	2.4	0.03	1
Keikan-yu (Ichinoide-kaikan)	44	8.2 324	180	1.8	0.03	2
Kannawa-en	43	7.8 416	180	2.3	0.05	3
No. 3 pond, Kamado-jigoku	59	6.7 537	240	2.2	0.06	4
Umi-jigoku	68	3.2 328	270	1.2	0.03	5

T_w , water temperature of pool.

TDS, total dissolved silica (expressed as SiO_2), analyzed by spectrophotometry with ammonium molybdate reagent; SAS, solubility of amorphous silica (expressed as SiO_2) at pool temperature. Each SAS was calculated through the use of the amorphous silica geothermometer equation (Nicolson, 1993): $t = [731/(4.52 - \log \text{SiO}_2)] - 273$ where T is in °C and SiO_2 is concentration (mg/kg).

solution colors blue, it was synthesized in accordance with the method by Kitahara and Furusawa (1979). A 4% sodium silicate solution was prepared from water glass dissolved in distilled water, and Na^+ in the solution was removed by cation-exchange chromatography in H^+ form. One-fifth of this solution was heated to 100°C for 10 min after being adjusted to pH 9 with 1.5% sodium hydroxide solution. Over 6 h, the remainder of the desalted solution was trickled into the prepared solution held at $80\text{--}90^\circ\text{C}$ while compensating for evaporation of the mixed solution by adding distilled water. Several attempts of this synthesis provided six colloidal silica solutions for color measurement and grain-size analysis as described below.

3.2. Color determination

Colorimetry is generally used in color quality control operations for a wide range of industrial products, and also for geological studies. Color measurements using a colorimeter can sensitively detect color differences impossible to detect by the naked eye in weathered rocks and marine sediments (Nagao and Nakashima, 1989; 1991).

In this study, a model CS-100 remote colorimeter from Minolta was used to objectively measure the colors of both natural blue thermal waters and synthesized colloidal silica solution. The standardization of color for the colorimeter was carried out with a white color standard plate (Minolta) and a xenon lighting system (WACOM R&D). By using this instrument together with a data processor (Minolta DP-101), colors can be described in terms of the values of standard color systems such as the Yxy color space established by the Commission Internationale d'Éclairage (CIE) in 1931.

3.3. Grain-size analysis of aqueous silica

Distributions of grain size of the colloidal silica in the thermal waters were examined using the following method:

(1) When the samples were collected, their pH value was immediately adjusted to 2 with hydrochloric acid in the field in order to stop polymerization of the aqueous silica (Yokoyama et al., 1983).

(2) The samples were filtered in the laboratory with mixed cellulose-ester type membrane filters whose pore sizes were 1.2, 0.45, 0.1, 0.05 and $0.025\ \mu\text{m}$ (obtained from Millipore).

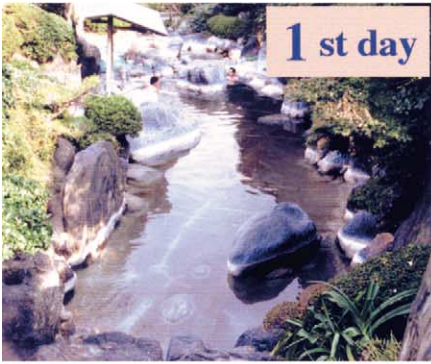
(3) The composition of each colloidal silica sample divided by the filtration was determined by spectrophotometry with ammonium molybdate reagent after resolving the polymerized silicas into monomeric silica using sodium bicarbonate solution.

If hydrothermal-alteration minerals, such as montmorillonite and chlorite, suspend together with the colloidal silica, there is no proof that determinable silica by the spectrophotometry may be generated as a result of decomposition of the almino-silicates by the sodium bicarbonate solution. Accordingly, in order to find out whether the colloidal suspension is really silica, qualitative analysis by X-ray fluorescence (XRF) analysis was conducted for the filtrate on the smallest pore-size membrane filter ($0.025\ \mu\text{m}$). The XRF analysis was carried out by the use of a model JSX-3220 energy dispersive X-ray spectrometer from JEOL with Rh target X-ray tube. This spectrometer is capable of detecting the elements of atomic numbers greater than 10.

3.4. Time series of blue coloration of natural thermal water

Transparent and colorless thermal water in the

Fig. 2. Coloration and color changes of thermal water in outdoor bathing pool in Hotel Kannawa-en, northern of Beppu, Japan (Nov. 4–10, 1997). On the first day, the water in the pool was colorless and clear, and began to tinge blue on the second day. On the third day, the water became distinctly blue, and the color changed to whitish blue or bluish white from the fourth day onwards.



outdoor bathing pool (water depth is about 50 cm) of Hotel Kannawa-en in Beppu turns blue in 2 or 3 days after filling the bath with thermal water (Fig. 2). From the fourth day onwards, the water gradually becomes a cloudy whitish blue and then bluish white. One week after filling up, the now white-cloudy thermal water is removed during the cleaning of the pool. The sequence of these phenomena (color change of the thermal water) occurs routinely.

This place is well suited for the test of our hypothesis of the cause for the blue color in thermal waters. We carried out grain-size analysis of aqueous silica together with chemical analyses of other aqueous components and measurements of water temperature and pH over 7 days.

4. Results and discussion

4.1. Synthetic colloidal silica solution

The colloidal silica solution made by the procedure as described in Section 3.1 is shown in photograph No. 6 in Fig. 1. Results of grain-size analyses of the synthetic solutions listed in Table 2 clearly show that aqueous colloidal silica particles below 0.45 μm in size are formed in large quantities.

One of the colloid solutions in the bottle on the right illuminated from below by pseudo sunlight from a xenon lighting system (see Section 3.2) shows a color similar to that of natural blue thermal waters, standing in sharp contrast to the distilled water in the bottle on the left. In addition, sunlight radiation passing through the colloidal

silica solution turns red, implying that blue light is selectively scattered from aqueous colloidal silica in the solution. This indicates that aqueous colloidal silica is capable of causing Rayleigh scattering.

4.2. Color measurement

Colorimetric data plotted on a chromaticity diagram (x - y) in Yxy color space are shown in Fig. 3. All of the data points, except for Umi-jigoku, indicate that the natural blue thermal waters have almost the same shade of blue as the synthesized colloidal silica solutions. The data points of the synthesized solutions are plotted somewhat near the achromatic point, which corresponds to white, gray and black, owing to strong whitish cloudiness resulting from an abundance of coagulated silica colloid larger than 0.45 μm . The agreement in hue of both solutions strongly suggests that the blue of the thermal waters in the pools is caused by colloidal silica. The different behavior of Umi-jigoku is visible on the x - y diagram: its blue is shifted somewhat to a greenish color, which might be related to a slight amount of super-saturation and also delaying of the silica polymerization in this pool as mentioned in Section 2.

4.3. Chemistry of colloidal suspension in blue-colored thermal water

Results of the qualitative X-ray analysis by the energy dispersive X-ray spectrometer for the filtrates by the smallest pore-size membrane filter (0.025 μm) from the blue-colored thermal waters (see in Fig. 1 and Table 1) are shown in Fig. 4.

Table 2
Distributions of aqueous silica of various sizes in synthetic colloidal silica solutions

Run product No.	Aqueous silica (mg/l)					
	< 0.025 μm	0.025–0.05 μm	0.05–0.1 μm	0.1–0.45 μm	0.45–1.2 μm	> 1.2 μm
1	5710	650	2300	3640	n.d.	600
2	8810	n.d.	3740	1910	150	n.d.
3	4520	1710	3180	1130	n.d.	n.d.
4	3880	2000	4340	170	230	n.d.
5	5740	5480	n.d.	2250	460	n.d.
6	5050	3240	2280	500	100	n.d.

n.d.: not detected.

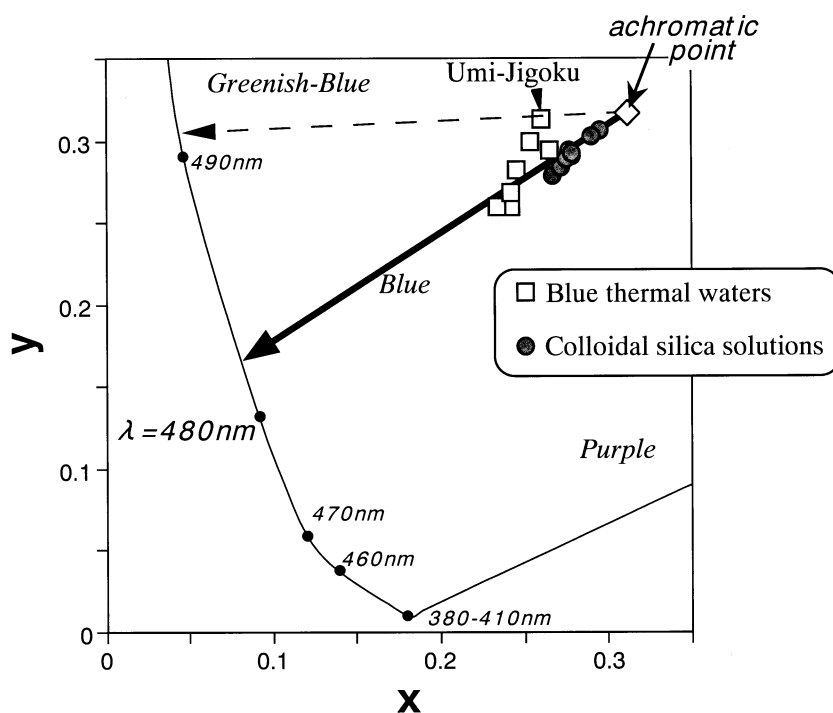


Fig. 3. Colorimetric data of blue thermal waters and synthetic colloidal silica solution plotted on chromaticity diagram of Yxy color space.

Only silicon (Si) is detected in the filtered materials from the blue thermal waters, excluding the Umi-jigoku hot pool; consequently, it is indicated chemically that the suspending particle in the blue waters is really silica. In geothermal waters at temperatures in excess of about 150°C the solubility of quartz controls the concentration of silica, and when discharged at atmospheric pressure, the cooled geothermal waters are usually supersaturated with respect to amorphous silica solubility (Ellis and Mahon, 1977). Accordingly, it is concluded that the suspending particle is not quartz cristobalite but amorphous silica.

On the other hand, not only silicon (Si) but also aluminum (Al) is only just detected in the filtrate from the Umi-jigoku water. This result is not contradictory to the opinion presented in Section 2; little polymerization of monomeric silica would be expected in the Umi-jigoku hot pool. Therefore, there is little likelihood that the color of the Umi-jigoku hot pool (greenish blue) is caused by aqueous colloidal silica.

4.4. Time series tests

Fig. 5 shows variations in the concentrations of aqueous silica of various size, water temperature and pH, and also the contents of chloride ion and total dissolved silica in the thermal water pool of the Hotel Kannawa-en, with descriptions of the coloration and color changes.

Water temperature, pH, concentrations of chloride ion and total dissolved silica remained almost at the same values except for the first day when the thermal water was mixed with cold water to reduce the temperature of the bathing pool. Incidentally, the water temperature of the pool had been kept at almost the same values (42–44°C; Table 2) over 1 week by adding more thermal water a little at a time for the purpose of bathing.

There are also no remarkable variations in the concentrations of other constituents except for drastic changes of Na, K, Ca and SO₄ concentrations from the first day to the second day (see

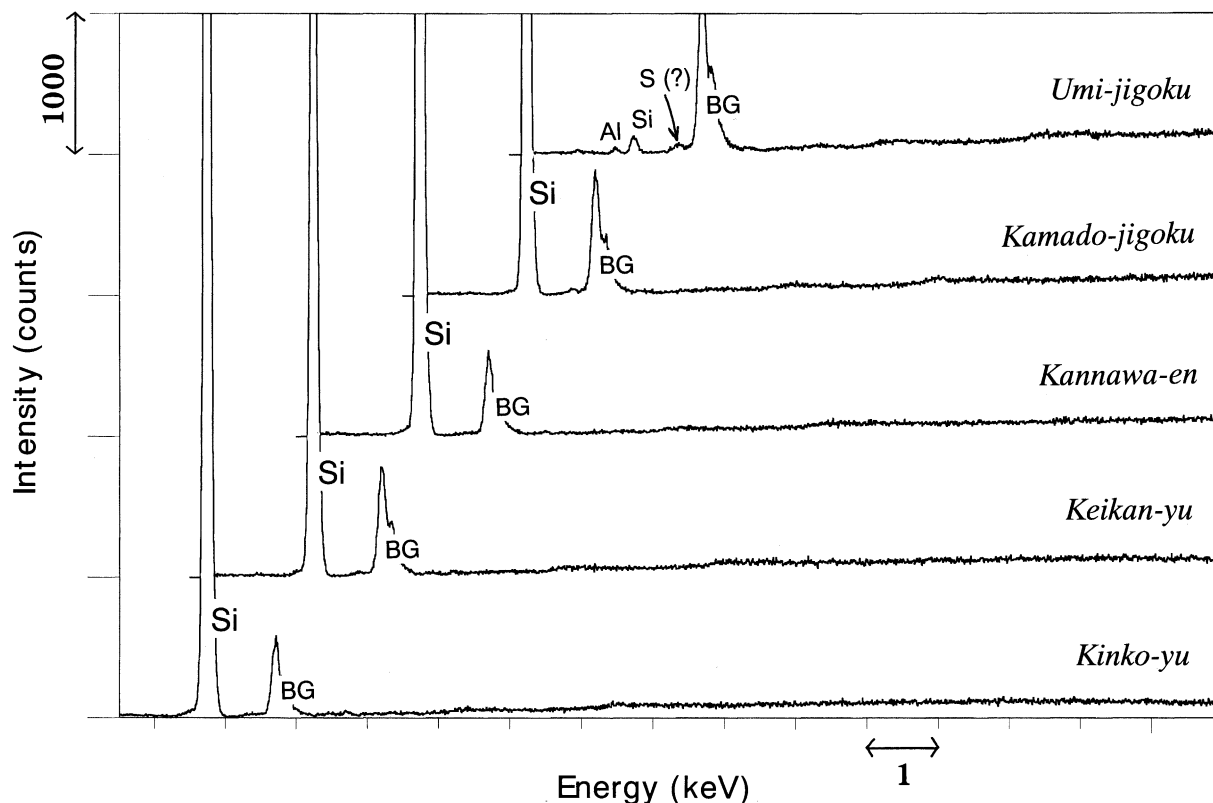


Fig. 4. Results of the qualitative XRF for the filtrates from the blue-colored thermal waters (Fig. 1) by membrane filter of pore size $0.025\ \mu\text{m}$. BG presents background signal caused from X-ray tube (Rh target). Si; silicon, Al; aluminum, S; sulfur.

Table 3). These constituents excluding Fe must form colorless ions in aqueous solution, and Fe which has the possibility of causing coloration of the water is a minor constituent and besides its concentration did not change drastically during the observation term. Therefore, these parameters are probably not relevant to the coloration of the thermal water.

The concentration of the monomeric silica was always at a value higher than the solubility of the amorphous silica at the pool temperature (the thick broken line marked by [S] in Fig. 5) throughout the observation term, so that the silica polymerization could proceed in the thermal water. On the first day, the dissolved silica in the thermal water, which was colorless and clear, was almost entirely monomeric. As the thermal water began to tinge blue on the second day, aqueous colloidal silica of $0.1\text{--}0.45\text{-}\mu\text{m}$ particle

size appeared in the water. On the third day, the $0.1\text{--}0.45\text{-}\mu\text{m}$ size silica reached maturity and the water became distinctly blue. From the fourth day onwards, the color changed into whitish blue or bluish white resulting from formation of particulate silica when the aqueous silica concentration for particles of over $0.45\text{-}\mu\text{m}$ size surpassed that of $0.1\text{--}0.45\ \mu\text{m}$. Over the 1-week duration, aqueous colloidal silica below $0.025\ \mu\text{m}$ remained at $20\text{--}40\ \text{mg/l}$ except for the first day, and aqueous colloidal silica of $0.025\text{--}0.1\text{-}\mu\text{m}$ particle size hardly appeared.

The survey of the variations in grain size of the aqueous silica shows that the blue color of the thermal water is closely related to aqueous colloidal silica of particle size $0.1\text{--}0.45\ \mu\text{m}$, and the milky white color is caused by the occurrence of aqueous colloidal silica with particles over $0.45\ \mu\text{m}$ in size.

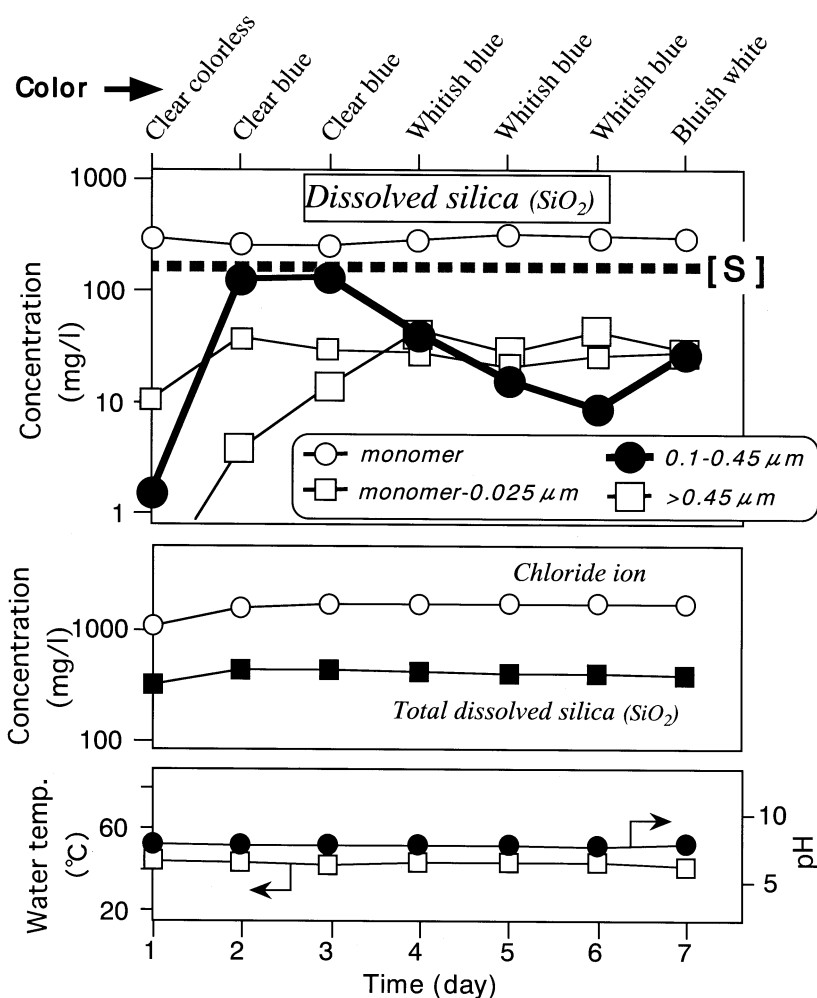


Fig. 5. Changes in concentrations of colloidal silica of various size, pH, water temperature, and concentrations of chloride ion and total dissolved silica accompanied by color changes of the bathing pool in Hotel Kannawa-en (Beppu, Japan). Thick dashed line marked by [S] represents solubility of amorphous silica at the pool temperature. Aqueous polymerized silica below 0.025 μm hardly appeared over 1-week duration.

4.5. Abundance of aqueous colloidal silica of particle size 0.1–0.45 μm

Aqueous colloidal silica of particle size 0.1–0.45 μm , which is inferred to be the cause of the blue color, was analyzed for the water samples from the blue-colored thermal waters listed in Table 1. Excluding Umi-jigoku, concentrations of the colloidal silica of this size were between 7 and 104 mg/l, constituting between 2 and 28% of total dissolved silica (Table 4). Almost the same concen-

tration of the silica particle of size 0.1–0.45 μm exists in these blue pools as in the blue-colored bathing pool in Hotel Kannawa-en (9–137 mg/l; Fig. 5). The percentage of total dissolved silica is also in the same range for these cases (2–31%). These observations indicate that, at least in thermal waters of neutral-chloride type, colloidal silica of particle size 0.1–0.45 μm is the cause for the blue color observed in the sunlight.

On the other hand, aqueous silica of particle size 0.1–0.45 μm is not detected in the blue ther-

Table 3
Concentrations of dissolved constituents in the blue-colored thermal waters with alkalinity, pH and water temperature

Name (date)	Water temp. (°C)	pH	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Al (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	Alkalinity (meq)
Kinko-yu (Ichinoide-kaikan) (Oct. 30, 1997)	33	8.1	685	81.8	26.6	3.5	0.24	0.08	999	208	1.40
Keikan-yu (Ichinoide-kaikan) (Oct. 30, 1997)	44	8.2	691	82.9	28.9	2.8	0.21	0.02	1030	211	1.38
No. 3 pond, Kamado-jigoku (Oct. 30, 1997)	59	6.7	1360	177	39.9	9.9	0.36	0.06	2170	307	0.13
Umi-jigoku (Oct. 30, 1997)	68	3.2	659	128	53.1	10.3	0.59	0.38	973	508	
Hotel Kannawa-en 1st day (Nov. 4, 1997)	44	7.9	710	95.6	34.5	5.5	0.30	0.05	1070	244	0.63
2nd day (Nov. 5, 1997)	44	7.8	1060	146	43.2	8.2	0.39	0.06	1590	371	0.51
3rd day (Nov. 6, 1997)	42	7.8	1140	153	47.3	7.3	0.41	0.07	1700	400	0.47
4th day (Nov. 6, 1997)	44	7.8	1160	161	47.5	7.4	0.38	0.04	1710	407	0.46
5th day (Nov. 8, 1997)	44	7.8	1160	159	46.0	8.1	0.39	0.03	1710	405	0.46
6th day (Nov. 9, 1997)	44	7.7	1170	158	47.9	7.2	0.37	0.03	1700	421	0.47
7th day (Nov. 10, 1997)	42	7.9	1170	158	48.3	6.8	0.39	0.06	1710	421	0.47

mal water from Umi-jigoku at all. This result also shows that the blue of Umi-jigoku is not from aqueous colloidal silica. In Beppu, the blue thermal water in Umi-jigoku hot pool was previously taken to represent a typical 'blue' hot pool, but it actually represents an exceptional case.

4.6. Relation to occurrence of blue color

The test results lead to the conclusion that the blue coloration of thermal water is caused by Rayleigh scattering of sunlight by an aqueous silica colloid of particles smaller than wavelengths in the visible region; moreover, aqueous silica particles ranging in size between 0.1 and 0.45 μm take part in the coloration. Furthermore, colloidal silica formed from particles over 0.45 μm in size makes the thermal water milky white, and this

implies that Mie scattering of the sunlight occurs in whitish thermal ponds such as Shiraike-jigoku in Beppu. The summarized coloration mechanism of the blue and milky white thermal waters of the neutral-chloride type is illustrated in Fig. 6. Seem-

Table 4
Abundance of aqueous silica colloid of particle size 0.1–0.45 μm in blue-colored thermal water

Name	CS _{0.1–0.45} (mg/l)	CS _{0.1–0.45} /TDS (%)
Kinko-yu (Ichinoide-kaikan)	104	28
Keikan-yu (Ichinoide-kaikan)	7	2
No. 3 pond, Kamado-jigoku	27	5
Umi-jigoku	n.d.	0

TDS, total dissolved silica (expressed as SiO₂); CS_{0.1–0.45}, colloidal silica of particle size 0.1–0.45 μm (expressed as SiO₂; n.d., not detected).

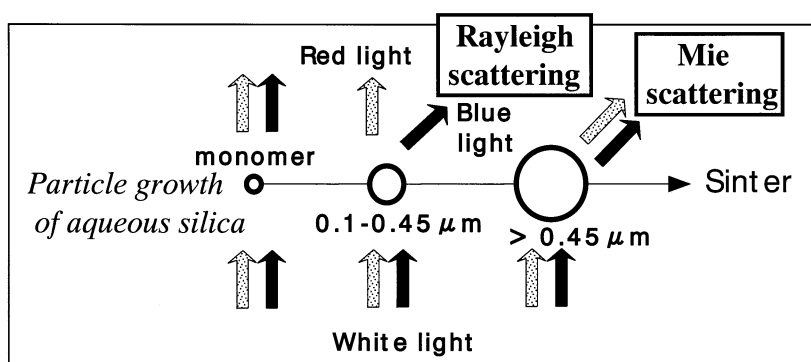


Fig. 6. Summarized mechanism of coloration of the blue (and milky white) thermal water(s). Full arrows and stippled arrows show blue and red portions of sunlight spectrum, respectively.

ingly the blue and milky white colors are not connected, but there is a close connection between them from the point of view of the particle growth of aqueous silica.

There is a good possibility that aqueous colloids will give colors to natural waters following the same principle as the coloring mechanism of the blue thermal water. We propose that the greenish-blue of acid waters such as in active crater lakes, e.g. Yugama of Mt. Kusatsu-Shirane (Japan) and Crater Lake of Mt. Ruapehu (New Zealand), might be due to colloidal sulfur which is formed by the reaction between $\text{SO}_2(\text{aq})$ and $\text{H}_2\text{S}(\text{aq})$ (Ohsawa, 1992), in agreement with the experimental examination by LaMer and Barnes (1946).

5. Conclusion and remarks

Detailed physical measurements and chemical analyses of synthetic and natural solutions to establish whether aqueous colloidal silica is responsible for the blue color of the thermal waters lead to the following conclusions:

(1) The blue color of the thermal waters of the neutral-chloride type is caused by Rayleigh scattering from aqueous colloidal silica particles with diameters (0.1–0.45 μm) smaller than the wavelengths of visible radiation.

(2) Aqueous colloidal silica formed from particles over 0.45 μm in size in the neutral-chloride type thermal waters make the thermal water milky

white, implying that Mie scattering of the sunlight occurs in whitish thermal ponds.

(3) The blue of Umi-jigoku in Beppu is not from aqueous colloidal silica. The blue thermal water in the Umi-jigoku hot pool was previously taken to represent a typical 'blue' hot pool in Beppu, but it actually represents an exceptional case. It is thought that the color of the Umi-jigoku pool might be due to colloidal sulfur and perhaps polysulfides formed by the oxidation of H_2S (Brown, personal communication), and/or very small particulates of almino-silicate (Hangai, 1999). Further investigation is required in order to explain this exceptional blue color.

(4) It is very likely that aqueous colloids are the cause for colors in natural waters under the same principle as the coloring mechanism of the blue thermal water. We propose that the greenish-blue and/or bluish-green of acid waters such as in active crater lakes is due to colloidal sulfur which is formed by the reaction between $\text{SO}_2(\text{aq})$ and $\text{H}_2\text{S}(\text{aq})$.

For an advanced understanding of the blue coloration of the thermal water of the neutral-chloride type, we are planning microscopic observation to reveal detailed particle-size distribution of aqueous colloidal silica and also calculation using the Rayleigh-scattering equation to explain perfectly the blue coloration and aqueous colloidal silica. For the purpose of this calculation, especially in order to specify the polarizability of the colloidal silica, it is necessary to precisely measure

the particle size distribution of the aqueous colloidal silica as mentioned above.

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Appendix I. Addresses of test fields in this study

Restaurant Ichinoide-kaikan (Kinko-yu and Keikan-yu): Kamihara 14-2, Beppu 874-0829, Japan.

Hotel Kannawa-en: Miyuki 6, Beppu 874-0045, Japan.

Kamado-jigoku: Miyuki 5, Beppu 874-0045, Japan.

Umi-jigoku: Kannawa 559-1, Beppu 874-0046, Japan.

Appendix II. Analytical methods for dissolved components in the blue thermal waters

Chemical analyses of the water samples collected from the blue-colored thermal pools were carried out by the following methods:

Na, K: atomic absorption spectrophotometry.

Ca, Mg: EDTA chelatometric titration.

Fe, Al: inductively coupled plasma mass spectrometry.

Cl: Mohr's titration.

SO₄: ion chromatography.

Alkalinity: neutralization titration.

Results of the chemical analyses are shown in

Table 3 together with pH values and water temperatures.

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