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GEOTHERMAL BLUE WATER COLORED BY COLLOIDAL SILICA

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ABSTRACT

Hydrothermal waters in hot pools commonly appear blue in color as a result of the incomplete precipitation of silica sinter. In the case of the Beppu geothermal field, blue thermal waters of the neutral–chloride type initially contain monomeric silica whose concentrations are 2 to 3 times higher than the solubilities of amorphous silica at the water temperatures of the pools. In these pools, aqueous colloidal silica is formed by silica-polymerization. Color measurements using a colorimeter show that the hue of the blue waters in the pools agrees with that of a synthesized colloidal silica solution. Grain size analysis of colloidal silica in natural blue thermal water made before and after the coloration demonstrates that the coloration is caused by Rayleigh scattering of the sunlight by colloidal silica particles somewhat smaller in size than the wavelengths of visible radiation.

1. Introduction

Hydrothermal waters with a blue color are commonly observed in hot pools, bathing pools, and in the pits of geothermal electric power plants. A simplified illustration of such a pool is shown in Fig. 1. Boiling water from springs and/or drilling wells flows into the pool and there is the possibility of a bottom inflow of thermal water. The blue water in the pools often become cloudy with presence of white particulate amorphous silica. Silica sinter is not always totally precipitated so that the pool is sometimes bordered by a silica terrace.

This suggests the presence of aqueous colloidal silica resulting from the polymerization of monomeric and it is proposed that the coloration of the hydrothermal waters could be caused by the Rayleigh scattering of sunlight by aqueous colloidal silica particles of size smaller than the wavelengths in the visible region of the electromagnetic spectrum (0.4 to 0.7μm). The aim of this study is to test this hypothesis on the coloration of hydrothermal water by direct experiment.

2. Locality of blue colored thermal water

Pools of blue waters are found in at least at four places in the Beppu geothermal field, Central Kyushu, Japan. Hot pools in Kamado-Jigoku (Kitchen Range Hell) and Umi-Jigoku (Sea Hell) are located in area A of Fig. 2, and outdoor bathing pools in the Hotel Kannawaen and Restaurant Ichinoidekaikan are situated in areas A and B in Fig. 2, respectively. The thermal waters in the pools of Kamado-Jigoku, Kannawaen and Ichinoidekaikan are typical of neutral–chloride water, whereas water in the Umi-Jigoku hot pool belongs to the acid sulfate–chloride type. Deposits in the Umi-Jigoku include not only amorphous silica but also kaolinite (Ohsawa, unpublished data).

In addition, blue thermal waters of a similar kind of those observed here can be found in Tenchong, China and Waimangu and Rotorua, New Zealand. They also probably exist in the pits of the Ogiri and Hatchobaru geothermal power stations in Japan (Shimada, K. and Kiyota, Y., private communication).

3. Potential for Silica–polymerization

One of most fundamental characteristics of aqueous silica is polymerization. Studies of this chemical reaction are too many to enumerate and include, for example basic studies on the solubility and polymerization of silica, the storage of water samples for silica determination, silica scaling in geothermal pipe lines (e.g., Shimono et al., 1983; Chan, 1989; Yokoyama et al., 1983; Hosoi, M. and Imai, H., 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 which is approximately equal to the steady-state concentration for 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.

The initial degrees of supersaturation of the blue colored thermal waters in the Beppu Geothermal field (described in Section 2) are shown in Table 1. The concentrations of total dissolved silica of the thermal waters in the pools (excluding the Umi-Jigoku hot pool) 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 have the potential for becoming polymeric silica, viz. colloidal silica. In addition, they suggest that silica-polymerization does not take place at the Umi-Jigoku hot pool to any appreciable degree.

4. Color Measurement of Blue Water

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

In this study, a model CS-100 remote colorimeter from Minolta Co., Ltd. was used to objectively measure the colors of both the blue thermal waters and the synthesized colloidal silica solution. The standardization of color for the colorimeter was done with a white color standard plate (Minolta Co., Ltd.) and a xenon lighting system (WACOM R&D Corp.). 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'Eclairage (CIE) in 1931.

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 the Umi-Jigoku hot pool (the arrow at the achromatic point which corresponds to white, gray and black) 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 owing to strong whitish cloudiness resulting from coagulation of the silica colloid. 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 peculiarity of the Umi-Jigoku hot pool is expressed on the x-y diagram; this blue is a little greenish when compared with the others, which might be connected with the degree of supersaturation as mentioned above (see in Section 2).

5. Grain Size Analysis of Silica colloid

Distributions of grain size of the colloidal silica in the thermal waters were examined by the method as follows. 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), 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 0.025μms (obtaoned from Millipore Corp). 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.

The blue colored thermal waters used for these purposes were collected from the two outdoor bathing pools at the Restaurant Ichinoidekaikan (Nos. 1 and 2 in Table 1) and from the hot pools at the Kamado-Jigoku and the Umi-Jigoku (Nos. 4 and 5 in Table 1, respectively). As mentioned in Section 3, the concentrations of total dissolved silica is very high: 324-537mg/l. Therefore the thermal waters were initially supersaturated with respect to amorphous silica. Excluding the Umi-Jigoku hot pool, the proportions of aqueous silica colloids ranging in size from 0.1-0.45μm and over 0.45μm to total dissolved silica are 2-28% and 3-8%, respectively, whereas aqueous polymerized silica in 0.025-0.1μm is absent. The most remarkable result shown by these data is the existence of colloidal silica of particle size a little smaller than wavelengths in the visible region between 0.4 and 0.7μm. This indicates that the blue of the thermal waters is probably due to the colloidal silica of particle size 0.1-0.45 μm. Meanwhile, aqueous silica in the blue water from the Umi-Jigoku hot pool is not polymeric but mostly monomeric (about 95-100% dissolved silica). Consequently, the blue of the Umi-Jigoku hot pool is not from aqueous colloidal silica. In Beppu, the blue thermal water in the Umi-Jigoku hot pool was previously taken to represent a typical 'blue' hot pool, however we now know it represents an exceptional case.

Transparent and colorless thermal water in the outdoor bathing pool of the Hotel Kannawaen turns blue in 2 or 3 days after filling the bath with the thermal water. The water gradually becomes a cloudy whitish blue and then bluish white. We have made a grain size analysis of aqueous silica, chemical analyses of other aqueous components and measurements of water temperature and pH for 7 days. Figure 4 shows variations in the concentrations of aqueous silica of various size, water temperature and pH, and also the contents of Cl and total dissolved silica in the filled thermal water of the pool, with descriptions of the coloration and color changes.

At first, water temperature, pH, concentrations of Cl and total dissolved silica are kept at almost the same values except for the first day when the thermal water was mixed with cold water for reducing temperature of the bathing pool. Although not described in this paper, there are no conspicuous variations on the concentrations of other constituents; e.g. SO_4, Fe. Therefore, it is not thought that these parameters are relevant to the coloration of the thermal water.

A general survey of the variations in grain size of the aqueous silica leads to the conclusion that the concentration of the monomeric silica was always held at a value higher than the solubility of the amorphous silica at the pool temperature for the observation term, and that the silica-polymerization had proceeded in the thermal water in response to the coloration. On the first day, the dissolved silica in the thermal water which is colorless and clear, is almost entirely monomeric. The thermal water begins to tinge blue on the second day; accordingly aqueous silica of 0.1-0.45µm particle size appears in the water. On the third day, the 0.1-0.45µm 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 particle of over 0.45µm size surpassed that of 0.1-0.45µm. Over a one week duration, aqueous polymerized silicas of 0.025-0.1µm particle size and below 0.025µm hardly appeared and were maintained at 20-40 mg/l except the first day.

This observational result demonstrates that small aqueous colloidal silica between 0.1 and 0.45µm are responsible for the blue of the thermal water. In addition, the cloudiness following the blue coloring of the thermal water is caused by the silica colloid particle greater in size than the wavelengths of the visible ray.

6. Conclusions and Remark

The results obtained in this study show that the blue coloration of the hydrothermal 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 particle ranging in size between 0.1 and 0.45µm takes part in the coloration (Fig. 5). Furthermore, colloidal silica formed from particles over 0.45 µm in size would make the thermal water white, and this implies that Mie scattering of the sunlight occurs in whitish thermal pools such as the Shiraike-Jigoku in the Beppu geothermal area (see the lower column of Table 1).

There is every possibility that aqueous colloids will give colors to natural waters under the same principle as the coloring mechanism of the blue hydrothermal water. We propose that the greenish-blue of acid thermal waters (as in active crater lakes) will be due to colloidal sulfur, in agreement with the experimental examination by LaMer and Barnes (1946), and perhaps this colloid is relevant to the coloration in the greenish-blue of the Umi-Jigoku hot pool.

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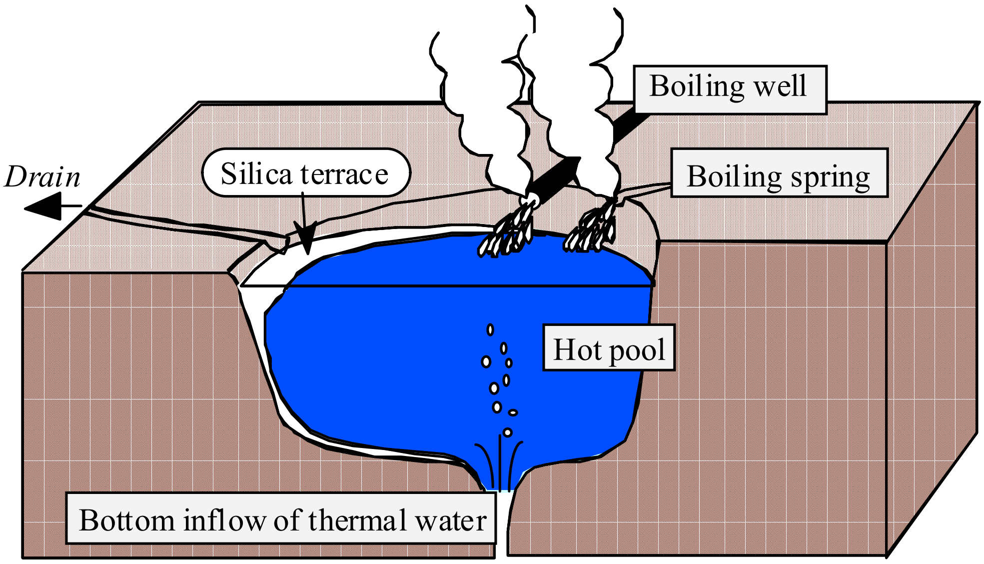

Fig. 1 A simplified illustration of a blue colored pool filled with thermal water.

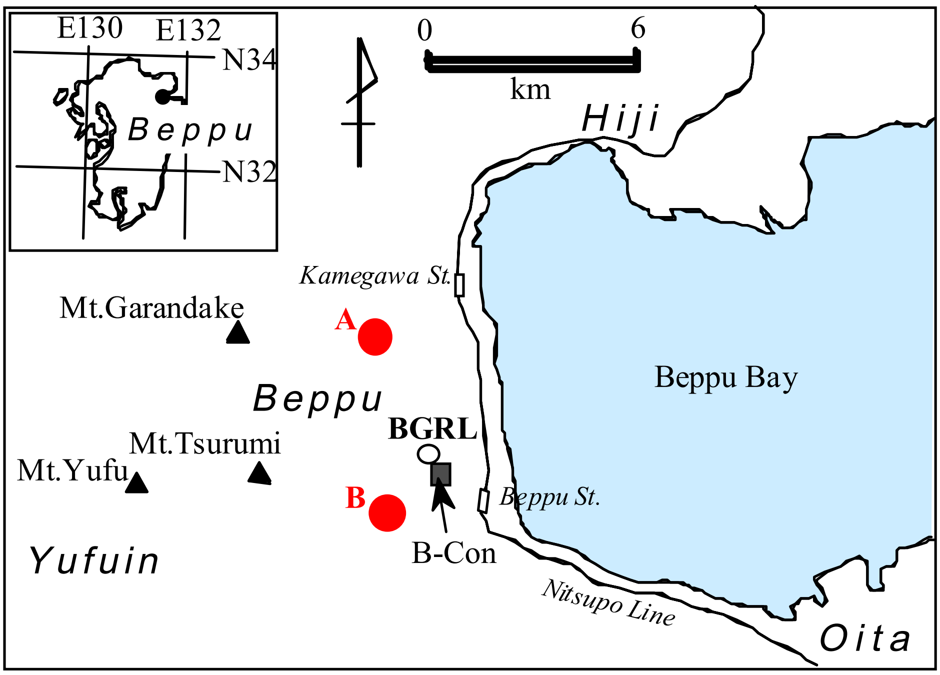

Fig. 2 Localities of blue thermal waters in Beppu geothermal filed, Japan. There are three places : Hotel Kannawaen, Kamado-Jigoku, Umi-Jigoku in area A and one place: Restaurant Ichinoidekaikan in area B. BGRL : Beppu Geothermal Research Laboraory, Kyoto University. B-Con : B-Con Plaza.

Table 1 Potential for silica-polymerization in blue thermal waters of pools .

No.	Name	Location in Fig. 2	Total dissolved SiO_2 (mg/ℓ) *	Water temp. of pool (℃)	pH	Solubility of amorph. SiO_2 at pool temp. (mg/ℓ)	Degree of supersaturation (%) #
1	Ichinoidekaikan (Kinkoyu)	B	366	33	8.1	150	240
2	Ichinoidekaikan (Keikanyu)	B	324	44	8.2	180	180
3	Kannawaen	A	416	43	7.8	180	230
4	Kamado -Jigoku	A	537	59	6.7	240	220
5	Umi-Jigoku	A	328	68	3.2	270	120
White (reference)							
R1	Shiraike -Jigoku	A	546	38		148	370

(Remarks) # Degree of supersaturation (%) = $\frac{\text{(Total dissolved } SiO_2 \text{ in thermal water)}}{\text{(Solubility of amorphous } SiO_2 \text{ at pool temperature)}} \times 100$

* analyzed with ammonium molybdate reagent

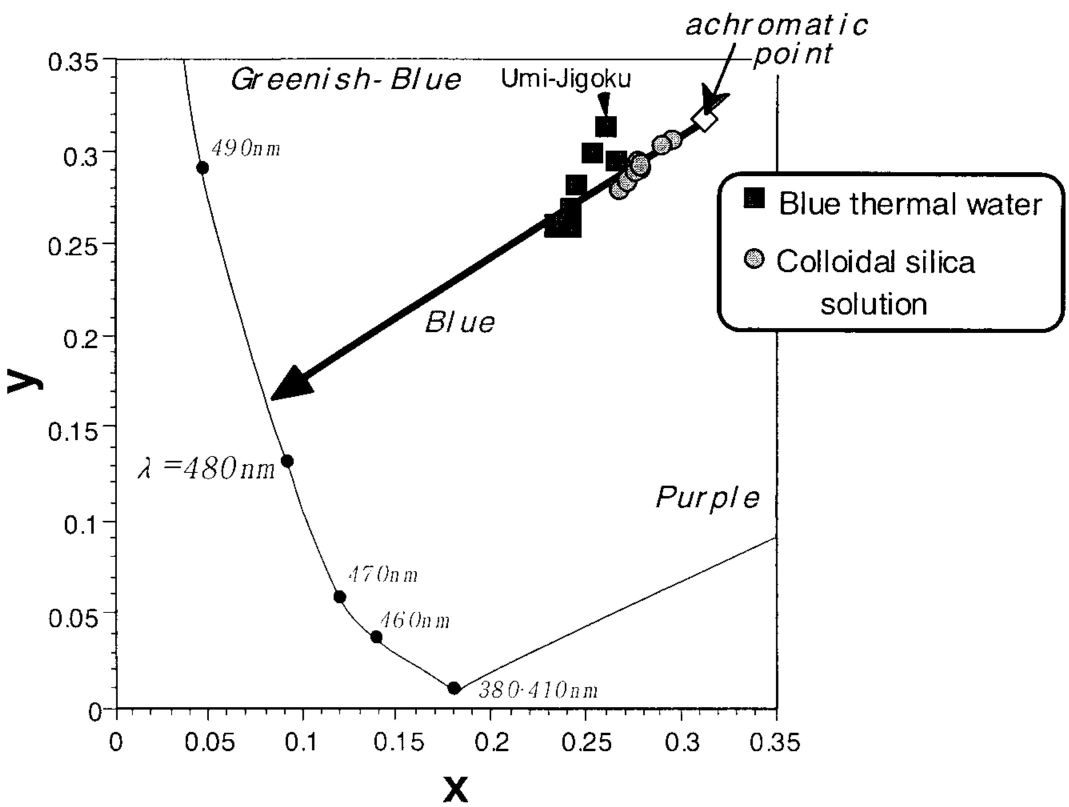

Fig. 3 Colorimetric data of blue thermal waters and synthetic colloidal silica solution plotted on chromaticity diagram of Yxy color space.

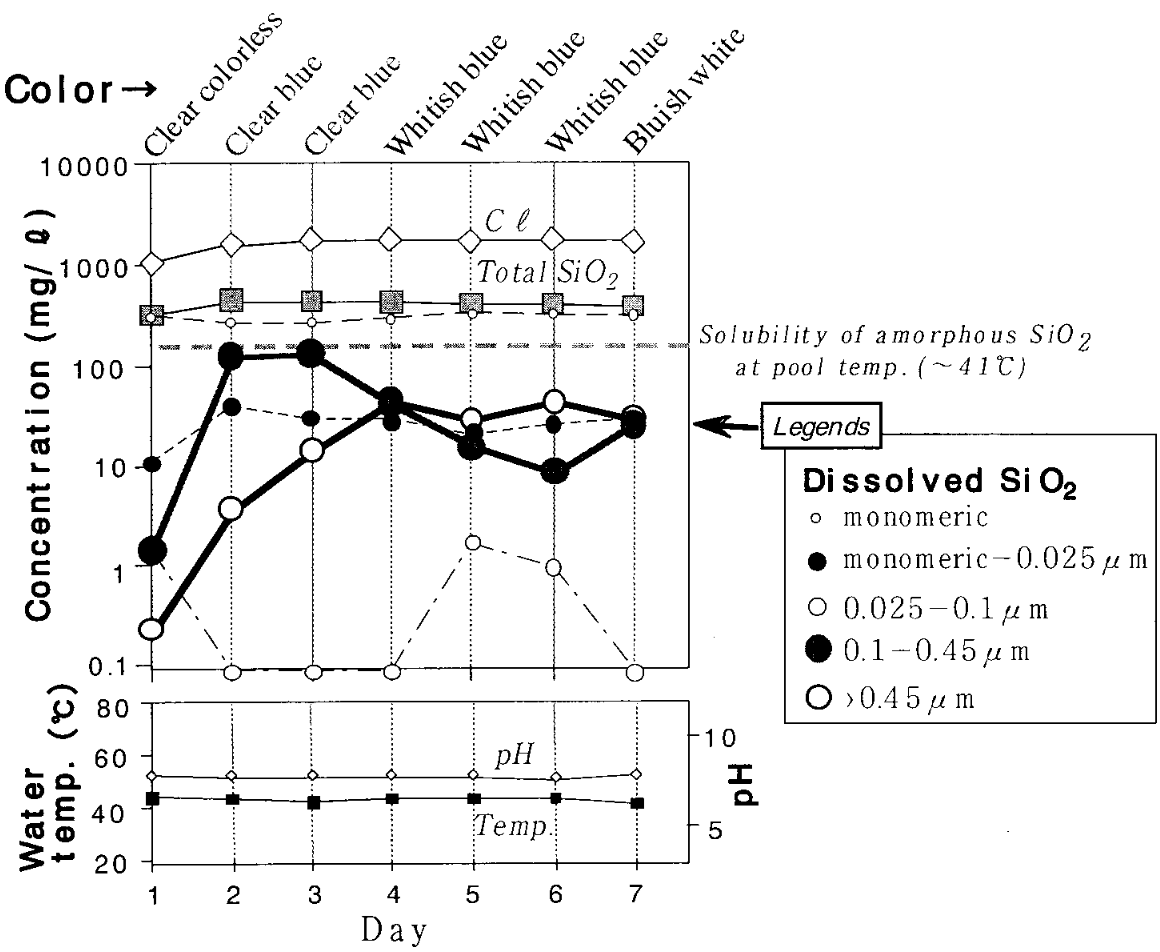

Fig. 4 Changes in concentrations of colloidal silica of various size, pH, water temperature and Cl concentration accompanied by color change of the bathing pool in Kannawaen (northern of Beppu, Japan).

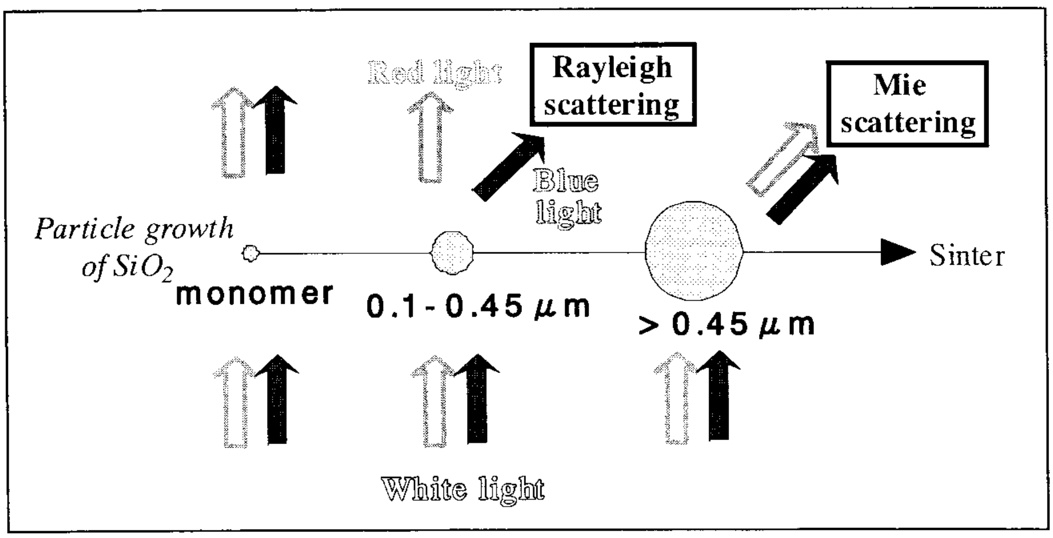

Fig. 5 Summarized mechanism of coloration of blue thermal water.