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Effects of Compositional Changes of Hot Spring Water upon Mineral Precipitate. I. Changes in Chemical Composition and Crystal Growth Rate of Pb-Bearing Barite (Hokutolite) from Tamagawa Hot Spring Waters

Nobuyuki SASAKI* and Kunihiko WATANUKI†
Department of Chemistry, Faculty of Education, Kagawa University, Saiwai-cho, Takamatsu 760
†Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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Changes in the chemical compositions of Tamagawa Hot Spring waters and Pb-bearing barite (hokutolite) were examined. Samples were obtained from various locations and various time in Tamagawa Hot Spring. The relationships between the hot spring waters and the minerals were expressed as partition equations and phenomenological equations; then, the partition coefficients and phenomenological coefficients were calculated. The apparent partition coefficients of Pb^{2+} and of Sr^{2+} between the two phases were found to have increased, from 0.14 to 0.30(0.31) and from 0.023 to 0.035(0.042) respectively, with the decrease in the hokutolite growth rate since 1973. The reaction rate of hokutolite as calculated from the phenomenological equations was, however, about 2 times higher in 1983 than in 1965. These results were ascribed to the rise in the degree of the supersaturation of barium sulfate and also to the increase in the nucleation rate in the hot spring water.

The partition formula of a chemical element between an aqueous solution and a solid solution is often useful in expressing the relationship between these two phases. There are, however, some problems with this manner. One is the remarkable dispersion of partition coefficients[1)] caused by the effect of the chemical nonequilibrium of each ion between the two phases, and the other is the difficulty of expressing the partition of the multicomponent system.[2)] For the measurement of the partition coefficient of trace elements between an aqueous solution and an insoluble salt like barium sulfate, it needs a long time to reach a chemical equilibrium, so it is sometimes convenient for getting an equilibrium value to use the data of the chemical compositions of natural minerals and hot spring waters instead of the data from synthetic solids and solutions in a laboratory.[3)]

As to the partition of a multicomponent system, Takano[2)] proposed a formulation of a three-component system on the basis of an ion-exchange reaction, but there have been very few actual applications to experimental and natural data.

Sasaki[4)] proposed a formulation of partition by utilizing phenomenological equations and applied it to the data of Tamagawa Hot Spring. To solve these phenomenological equations, however, several sets of data obtained under different conditions are needed.

In recent years conspicuous changes in chemical composition have been observed in several hot springs, including Tamagawa Hot Spring[5—7)] and Kusatsu Hot Spring,[8,9)] in Japan. Tamagawa Hot Spring showed remarkable increases in the SO_4^{2-} and Fe^{2-} concentrations from 1973 to 1978, from about 1200 ppm to 2600 ppm, and from about 90 ppm to 170 ppm, respectively. Sasaki[4,10)] reported that these increases caused the changes in the Ba^{2+}, Pb^{2+}, and Sr^{2+} concns, of the hot spring waters. These cations are the main components of the Pb-bearing barite (hokutolite) precipitated from the hot spring waters in this district.[11)] Hokutolite is a famous radioactive mineral and has been designated as a special natural monument in Japan since 1952.

The present authors[12)] observed and examined the hokutolite which had been growing at Yubana fall (the end of the Yubana conduits in Tamagawa Hot Spring; shown in Fig. 1) after 1953; they also observed increases in the Pb, Sr, and Fe[a)] contents (Table 1) with the decrease in the crystal growth rate (0.10 mm y^{-1} to 0.05 mm y^{-1}) after 1973. They supposed that the changes in the mineral were attributable to the decrease in the Ba^{2+} concn in the hot spring water, which might have been caused by the increase in the SO_4^{2-} concn, judging from the ionic equilibria.

The aims of present work are to ascertain the truth of this supposition formerly proposed by the present authors[12)] and to clarify the relationship between the

Table 1. Chemical Composition of Pb-Bearing Barite (Hokutolite) Precipitated at Different Times at the End of the Yubana Conduit at Tamagawa Hot Spring

(a) Composition in weight percentages

Crystallization period	BaO wt%	PbO wt%	SrO wt%	CaO wt%	FeO[a)] wt%
1953—1972	52.66	13.36	0.45	0.16	0.04
1973—1981	51.20	13.23	0.66	0.15	0.35

(b) Composition in mol% as barium, lead, strontium, and calcium

Crystallization period	Ba mol %	Pb mol %	Sr mol %	Ca mol %
1953—1972	83.67	14.58	1.06	0.69
1973—1981	83.02	14.73	1.58	0.66

Data cited from Sasaki and Watanuki (1983)[12)] a) Iron is not situated in the crystal lattice of $BaSO_4$ (Sasaki and Watanuki, 1984).[13)]

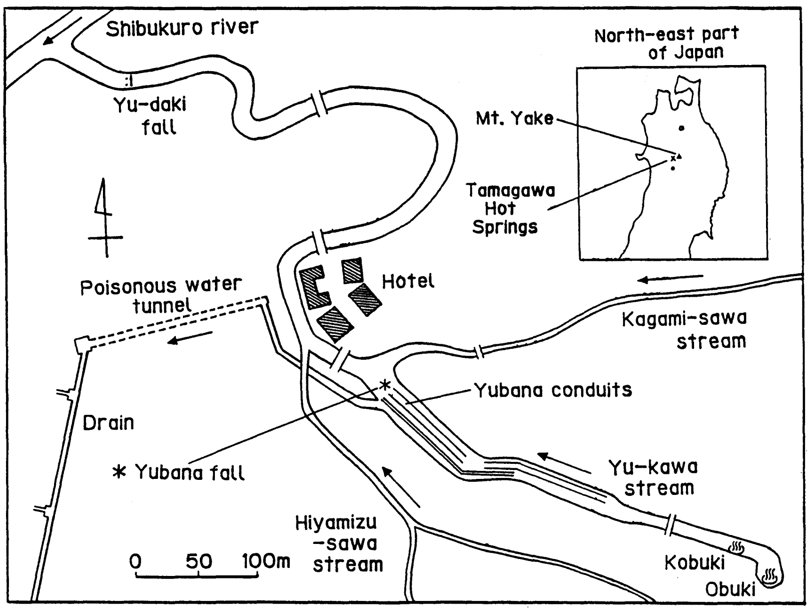

Fig. 1. Location map of Tamagawa Hot Springs. The mark * indicates Yubana fall.

changes in the chemical composition of the hot spring waters and those in the chemical composition and the crystal growth rate of mineral (hokutolite) occurring in this area.

Experimental

The hot spring water samples were collected in October, 1983, in August, 1985, and in August, 1986, at four sites, Obuki Spring and Kobuki Spring (1983, 1985, 1986), Yubana fall (1985, 1986), and the so-called poisonous water tunnel (1986) (Fig. 1).

Analytical Procedures. 1) Barium and Lead: After sampling, the Ba^{2+} and Pb^{2+} were separated immediately in situ from the other elements by coprecipitation with strontium sulfate.[14)] The precipitate was brought to the laboratory, decomposed by means of hydriodic acid,[15)] and analyzed. The Ba^{2+} and Pb^{2+} were determined by flame photometry and atomic-absorption spectroscopy (AAS) respectively.

2) Strontium: The Sr^{2+} was preconcentrated using Pb^{2+} and fuming nitric acid, and was determined by the use of AAS.[11)]

3) Sulfate and Chloride: The SO_4^{2-} concentration was determined by the use of the gravimetric method.[16)] The Cl^- concentration was measured by means of chloride-ion electrode using an ion meter (DKK, IOC-10).

Results and Discussion

The analytical results of the hot spring water are shown in Table 2. The analytical data given by Takano[14)] and by Takano and Watanuki[11)] for the waters sampled in 1965 are also listed in Table 2. It may be seen that the SO_4^{2-} concns in the Obuki vent were about 2100—2300 ppm in 1983, about 1600 ppm in 1985, and 1200 ppm in 1986, indicating a decrease in the SO_4^{2-} from the maximum value (ca. 2600 ppm)[6,17)] in 1978.

Table 2. Barium-, Lead-, Strontium-, Sulfate-, and Chloride-Ion Concentrations of Tamagawa Hot Spring Waters (mg·dm^{-3})

	Obuki Spring						
	1965	1983		1985		1986	
		I[c)]	II[d)]	III[e)]	IV[f)]	V[g)]	VI[h)]
Ba^{2+}	0.82[a)]	1.03	1.20	1.32	1.30	1.58	1.57
Pb^{2+}	1.59	0.93	1.03	0.78	0.77	0.69	0.69
Sr^{2+}	0.29	0.36	0.35	0.30	0.29	0.42	0.40
SO_4^{2-}	1242[b)]	2068	2335	1577	1614	1222	1237
Cl^-	3174	3140	3160	2870	2870	2880	2780
pH	1.20	1.13	1.13	1.17	1.17	1.19	1.19

	Kobuki Spring						
	1965	1983		1985		1986	
		I[c)]	II[d)]	III[e)]	IV[f)]	V[g)]	VI[h)]
Ba^{2+}	0.96[a)]	1.42	1.65	1.55	1.63	1.48	1.61
Pb^{2+}	1.51	1.16	1.27	1.36	1.23	0.67	0.78
Sr^{2+}	0.33	0.48	—	0.39	0.42	0.41	0.39
SO_4^{2-}	—	2144	2341	1751	1713	1443	1465
Cl^-	—	3420	3470	3150	3150	3150	3090
pH	—	1.11	1.10	1.14	1.14	1.15	1.14

a) Data cited from Takano and Watanuki (1972). b) Data cited from Takano (1969). c) I. Sampled at 8:00 a.m. on Oct. 24, 1983. d) II. Sampled at 5:00 p.m. on Oct. 24, 1983. e) III. Sampled on Aug. 3, 1985. f) IV. Sampled on Aug. 4, 1985. g) V. Sampled on Aug. 7, 1986. h) VI. Sampled on Aug. 8, 1986.

The Ba^{2+} concentrations in 1983 and in 1985 are at levels similar to or a little higher than those in 1965. This result is contrary to our estimation[12)] previously mentioned. On the other hand, the Pb^{2+} concentrations have decreased, and the Sr^{2+} concns have increased, in both spring waters. The Cl^- concns are nearly invariable during the 1965—1986 period,

Table 3. Weight Ratios of Lead and Barium and of Strontium and Barium in Tamagawa Hot Spring Waters

	Obuki Spring					Kobuki Spring				
Point No.	1965	1983		1985		1965	1983		1985	
		I	II	III	IV		I	II	III	IV
Pb^{2+}/Ba^{2+}	1.94	0.90	0.86	0.59	0.59	1.57	0.82	0.77	0.88	0.75
Sr^{2+}/Ba^{2+}	0.35	0.35	0.29	0.23	0.22	0.34	0.34	—	0.25	0.26

Table 4. Apparent Partition Coefficients of Lead and Strontium between Hokutolite and Thermal Solution at Yubana Fall

	1965	1983	
		I	II
D_{Pb}	0.14	0.30	0.31
D_{Sr}	0.023	0.035	0.042

though the 1978 value (ca. 3300 ppm)[6] was a little high.

As compared with the Obuki Spring, the Kobuki Spring shows a slightly low pH value, slightly high Ba^{2+}, Pb^{2+}, and Sr^{2+} values (1983, 1985), and or Cl^- and SO_4^{2-} concns, very similar Sr^{2+}, Pb^{2+}, and Ba^{2+} (1986) concns.

The relationship between the chemical composition of a Pb-bearing barite crystal and that of Tamagawa Hot Spring water can be expressed by the following equation:

$$(M/Ba)_{crystal} = D_M\ (M/Ba)_{solution}, \qquad (1)$$

where D_M denotes an apparent partition coefficient of M between the $BaSO_4$ crystal and the thermal solution on the basis of the surface equilibrium and where M refers to Pb, Sr or other minor elements. (M/Ba) indicates the weight ratio or mole ratio of two elements in each phase.

The partition of an element between the binary solid phase and the aqueous phase was formulated by Takano[2] on the basis of the ion exchange equilibrium as an example of treating a multicomponent chemical equilibrium system, but farther experimental study has not been carried out.

In this paper Eq. 1 is used.

If D_M is constant for the Tamagawa water, the chemical composition of hokutolite, (Ba, Pb, Sr)SO_4, can be calculated from the (Pb^{2+}/Ba^{2+}) and (Sr^{2+}/Ba^{2+}) ratios of the thermal solution (Obuki Spring water). Both ratios are shown in Table 3. It can clearly be seen that the (Pb^{2+}/Ba^{2+}) ratios of I in 1983 are lower than in 1965, while the (Sr^{2+}/Ba^{2+}) ratios are at similar levels between I in 1983 and in 1965 in both springs. Actually, however, the Pb/Ba and Sr/Ba ratios in hokutolite clearly increased[12] (see Table 1(b)). The apparent partition coefficients were calculated from the data in Tables 1 and 2; they are shown in Table 4. In this case, the solutions in 1965 and in 1983 were assumed to be the solutions from which the Pb-bearing barite crystals of 1953—1972 and of 1973—1981 were formed. It was found that the apparent partition coefficients of Pb and Sr both nearly doubled.

The reasons for these rises in the apparent partition coefficients seem to be profoundly interesting.

Takano[14] interpreted the variation in the Pb content of barite in terms of Pb-chloro complex formation. However, the chloro complex effect is a nondecisive factor in this case because the Cl^- concns in 1965 and in 1983 are nearly equal.

Ichikuni[18] noted that the major portion of the barium in the spring water might have been precipitated as barium sulfate within 100 m of the vent of the Obuki Spring; he also explained the increase in the Pb content in Pb-bearing barite collected at various points of the stream of Tamagawa Hot Spring. He used the homogeneous partition coefficient of Kolthoff and Noponen,[19] which is based on the solid-liquid equilibrium, as a first approximation. He calculated the crystal growth rate as 0.86 $mm\,y^{-1}$, which was considerably higher than the results of crystal growth rate obtained by Saito et al.[20] (0.09—0.25 $mm\,y^{-1}$) and by the present authors[12] (0.05—0.10 $mm\,y^{-1}$). He considered that the barium sulfate (barite) precipitates mainly in the form of minute crystals and that part of them are buried in sulfurous sinter, as was also observed by Saito et al.[20]

Takano (private communication) thought that nearly pure $BaSO_4$ is already formed as fine particles (clusters) in the upper part of the vents. To examine these ideas, the ion-activity products (IAP) of barium sulfate at several points were calculated as follows:

$$IAP = a_{Ba^{2+}} \cdot a_{SO_4^{2-}} = \frac{a_{Ba^{2+}} \cdot a_{HSO_4^-}}{a_{H^+}} K_2, \qquad (2)$$

$$\begin{aligned} &\text{Obuki vent } (100\,^\circ C) && IAP(1965)=2.70\times10^{-10}, \\ & && IAP(1983)=4.70\times10^{-10}, && (3) \end{aligned}$$

$$\begin{aligned} &\text{Yubana fall } (70\,^\circ C) && IAP(1965)=6.15\times10^{-10}, \\ & && IAP(1983)=10.8\times10^{-10}, && (4) \end{aligned}$$

$$\text{Yudaki fall } (25\,^\circ C) \quad IAP(1965)=6.35\times10^{-10}, \qquad (5)$$

where K_2 is the second dissociation constant of sulfuric acid, K_2: $10^{-3.0}$ at 100 °C, $10^{-2.6}$ at 70 °C, and $10^{-2.0}$ at 25 °C.[21]

These IAP values show that Obuki Spring water is nearly saturated, or even a little supersaturated, while

Yubana fall and Yudaki fall are supersaturated with $BaSO_4$, whose solubility product, K_{sp}, is 2.82×10^{-10} (100 °C), 2.56×10^{-10} (70 °C), or 1.12×10^{-10} (25 °C).[22]

Liu et al.[23] and Sasaki and Minato[24] have shown that the rise in the degree of supersaturation, shown by the value of $IAP/K_{sp}-1$, causes the formation of many fine nuclei in the cases of $BaSO_4$ and $(Ba, Pb)SO_4$ crystallization. Now we can postulate that numerous barite microcrystals, which are hardly visible, are formed from three-dimensional nuclei, that they flow, drifting downstream from the upper stream, and that a large part of them no longer adhere to the crustal hokutolite crystals. This image suggests the decrease in the dissolved free Ba^{2+} concn and, therefore, the increase in Pb^{2+}/Ba^{2+} and Sr^{2+}/Ba^{2+} in the solution and the resulting increase in Pb/Ba and Sr/Ba in hokutolite crystals; at the same time, it explains the reduction of the hokutolite growth rate.

To verify this idea, the following experiments were carried out. The hot spring waters collected at Obuki and Kobuki Springs (1985) and at Yubana fall (1986) were immediately filtered with 0.1 μm membrane filters before the coprecipitation of Ba^{2+} and Pb^{2+} with strontium sulfate; then, the Ba^{2+} and Pb^{2+} concentrations were determined. The results are shown in Table 5. It was found that the Ba^{2+} and Pb^{2+} concns were nearly invariable by filtration for Obuki hot spring water, but were reduced in the Yubana fall water. These results obviate the possibility of barite microcrystals or, at least, obviate the possibility of crystals over 0.1 μm in diameter around the Obuki vent. At the Yubana fall, however, at least 20% of the Ba^{2+} had already become barite particles over 0.1 μm in diameter, although the SO_4^{2-} concn in 1986 had returned to nearly the same value as in 1965.

According to the crystal-growth (precipitation) theory, an increase in the degree of supersaturation brings about an acceleration of the crystal growth.[25] It is known that the rise in the growth rate brings about an increase in the apparent partition coefficient of a minor element in a depletion system:[26,27]

$$\lambda = \frac{I/M - k_1}{I/M - k_2}\,. \tag{6}$$

Table 5. Barium and Lead Concentrations of Filtered Tamagawa Hot Spring Water Compared with Non-Filtered Water ($mg\cdot dm^{-3}$)

Locality	Treatment	Ba^{2+}	Pb^{2+}
Obuki Spring (1985)[a]	non-filtered	1.32	0.78
	filtered	1.34	0.81
Kobuki Spring (1985)[b]	non-filtered	1.63	1.23
	filtered	1.63	1.20
Yubana fall (1986)[c]	non-filtered	1.56	0.68
	filtered	1.25	0.54

a) Sampled on Aug. 3, 1985. b) Sampled on Aug. 4, 1985. c) Sampled on Aug. 9, 1986.

Sasaki,[4] treated the partition of a multicomponent-system using the matrix formula of phenomenological equations[28,29] and assuming that the precipitation reaction proceeds under conditions close to those of chemical equilibrium. The case of a three-component system may be formulated as follows:

$$\begin{pmatrix} v_{r1} \\ v_{r2} \\ v_3 \end{pmatrix} = k_r \begin{pmatrix} x_{r1} \\ x_{r2} \\ x_{r3} \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix} \begin{pmatrix} A_{r1} \\ A_{r2} \\ A_{r3} \end{pmatrix} \quad (r=1, 2, 3), \tag{7}$$

$k_r x_{ri}$ (i=1, 2, 3) is the precipitation rate of each end member, where x_{ri} (i=1, 2, 3) expresses the chemical composition (mol%) and where k_r is the reaction-rate parameter of the r'th solid phase (k_1=1 is the standard value). L_{ij} (i=1, 2, 3; j=1, 2, 3) is the phenomenological coefficient, and A_{ri} (i=1, 2, 3) is the chemical affinity of each end-member component of the r'th solid solution in the precipitation reaction.[30]

For example, A_{BaSO_4} is calculated by means of:

$$A_{BaSO_4} = RT\ln S_{BaSO_4}, \tag{8}$$

where S_{BaSO_4} is the supersaturation ratio: $S_{BaSO_4}=IAP(BaSO_4)/K_{sp}(BaSO_4)$, where $IAP(BaSO_4)$ is an ion-activity product of Ba^{2+} and SO_4^{2-} in the spring water and where $K_{sp}(BaSO_4)$ is the solubility product of $BaSO_4$ at each temperature.

Using the data in Tables 1 and 2 and other sources,[11,14] following reaction-rate equations are obtained:

Yubana fall:

1965

$$k_1 \begin{pmatrix} 83.67 \\ 14.58 \\ 1.06 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix} \begin{pmatrix} 0.615 \\ -2.298 \\ -5.150 \end{pmatrix}, \tag{9}$$

1983

$$k_2 \begin{pmatrix} 83.02 \\ 14.73 \\ 1.58 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix} \begin{pmatrix} 0.724 \\ -2.425 \\ -4.762 \end{pmatrix}, \tag{10}$$

Yudaki fall:

1965

$$k_3 \begin{pmatrix} 81.41 \\ \\ 16.55 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ & & \\ L_{21} & L_{22} & L_{23} \end{pmatrix} \begin{pmatrix} 1.027 \\ -1.886 \\ -4.399 \end{pmatrix}. \tag{11}$$

The solution is given as follows:

L_{11}=1078.4, $L_{12}=L_{21}$=200.7, $L_{13}=L_{31}$=23.0, L_{22}=39.7, $L_{23}=L_{32}$=3.4, L_{33}=1.0, k_2=2.2, k_3=7.5.

These calculations indicate that the precipitation rate of hokutolite was higher in 1983 (k_2=2.2) than in 1965 (k_1=1.0), and that it was higher in the Yudaki fall (k_3=7.5) than in the Yubana fall (k_1=1.0) in 1965 with an increase in the chemical affinity of the $BaSO_4$-formation reaction. However, the actual growth rate of hokutolite was lower in 1983 (0.05 mm y^{-1}) than in 1965 (0.10 mm y^{-1}).[12] Also the growth rate in the

Yudaki fall was lower (0.09 mm y^{-1}) than in the Yubana fall (0.25 mm y^{-1}).[20]

This discrepancy seems to be explicable by taking account of the nucleation rate of lead-bearing barite, as has already been mentioned. That is, at the Yubana fall or the Yudaki fall, numerous fine (three-dimensional) nuclei of hokutolite are formed because of the high supersaturation with regard to $BaSO_4$, but a large part of them cannot adhere to the crustal hokutolite crystals in an open-flow system like Tamagawa, so the actual crystal-growth rate decreases in spite of the increase in the total precipitation rate. These relations may be roughly formulated as following:

$$v = m_1 A - m_2 \exp(-\Delta G^*/RT), \qquad (12)$$

$$\Delta G^* = \frac{16\pi\gamma^3 V^2}{3A^2}, \qquad (13)$$

where v: apparent growth rate, A: chemical affinity of the $BaSO_4$ formation reaction, γ: surface energy of $BaSO_4$, V: mole volume of $BaSO_4$, ΔG^*: critical free enegy of nucleus formation, m_1, m_2: constants.

The first term in Eq. 12 indicates the total precipitation rate, while the second term expresses the elimination rate of small nucleus crystals of hokutolite. It is, however, questionable whether or not nucleation formation rate of $BaSO_4$ is expressed as the second term in Eq. 12.[30] More quantitative and precise analyses will be needed to confirm this inference.

Finally, we must consider the reason for the recent changes in the Tamagawa hot spring waters mentioned above. Considering the changes in the pH, and in the Fe^{2+} and SO_4^{2-} concentrations, we can guess that a reaction like the following one might have occurred in the deep places under the Obuki vent:

$$FeS_2 + 10H_2O + 15SO_2 \rightarrow Fe^{2+} + 10H^+ + 10HSO_4^- + 6S + S^{2-}. \qquad (14)$$

This reaction proceeds toward the right side with an increase in the SO_2, indicating an increase in volcanic activity.[8,31] Moreover, with the rise in the S^{2-} concn in Eq. 14, the decrease in the Pb^{2+} concn can be explained as the next reaction of PbS (galena) formation:

$$Pb^{2+} + S^{2-} \rightarrow PbS. \qquad (15)$$

These reactions explain the rise in the HSO_4^- and Fe^{2+} concns and also the fall in the pH and the Pb^{2+} concn nearly quantitatively. Of course, this is only one possible reaction process to explain the compositional changes in Tamagawa hot spring waters in recent years. The presence of FeS_2 and PbS and the reaction temperature and the reaction depth have, in fact, not yet been established. Further experimental research and discussion are needed.

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