11. *Arsenic and Arsenic-lead Sulfides Sediments from Tamagawa Hot Springs, Akita Prefecture*

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On the middle slope of Volcano Yakeyama in Akita Prefecture are found strong acid springs called Tamagawa Hot Springs. The springs are well known for the highest content of acid in Japan and for the occurrence of a radioactive mineral, hokutolite (Ba, Pb)SO_4 deposited from the acid thermal water. As is shown in Fig. 1, a sketch map of Tamagawa Hot Springs, the acid river Yukawa starts at the Obuki Spring located in the central part of the valley. A large amount of water flows out of the orifice of Obuki Spring and runs down as Yukawa River. On the bed of the river are found various fresh deposits colored white, yellow, brown, and red. Chemical analyses were made of these spring waters and sediments. The details of the analytical methods will be given elsewhere (Jour. Chem. Soc. Japan).

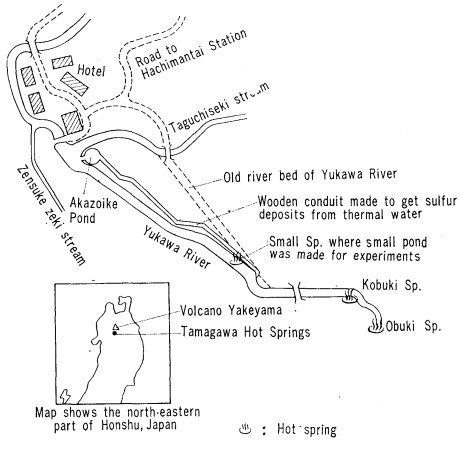

Fig. 1. Sketch map of Tamagawa Hot Springs. (Scale: 1/6000.)

Partial composition of water. A partial analysis of water collected from Obuki Spring and Akazoike Pond on Nov. 3, 1964 was carried out with the results shown in Table I. Kobuki Spring is a boiling spring and has the highest contents in chloride and sulfate. Akazoike Pond is mainly supplied with the water flowing down from Obuki Spring. The waters of Tamagawa Hot Springs are richer in

Table I. Chemical analyses of the waters collected from Obuki Spring, Kobuki Spring and Akazoike Pond on November 3, 1964

Number	Name of spring or pond	Temperature °C	pH	H_2S mg/l	Cl^- mg/l	SO_4^{2-} mg/l	As mg/l	Pb mg/l
1	Obuki Spring	98.0	1.2	1.9	3081	1191	2.6	1.6
2	Kobuki Spring	98.0	1.2	1.6	3392	1476	2.6	1.5
3	Akazoike Pond	71.5	1.4	0.6	2982	1203	2.3	1.3

hydrochloric acid than in sulfuric acid.

Analytical results of yellow and red sediments. On Nov. 3, 1964, fresh yellow, orange and red sediments were collected from the present river bed of Yukawa River and analyzed, with the results shown in Table II. The contents of free sulfur in these deposits are remarkably high and have no relationship with their colors. The deposits from which free sulfur was extracted with carbon disulfide, were analyzed for arsenic, sulfur combined with arsenic, and lead; then sulfur combined with arsenic to arsenic atom ratio and lead to arsenic atom ratio were calculated. As shown in Table II, the As/S atom ratios of the arsenic sulfide in fresh yellow, orange and red sediments are always about 2.0.

These values are much greater than those both of orpiments (1.5) and realgar (1.0), and coincide well with that of amorphous arsenic disulfide (2.0), reported in 1955 by N. Ikeda on the arsenic sulfide deposits from Yumoto Hot Springs in Nasu district. Moreover, it was found that the lead arsenic atom ratios of the deposits increase with the color change from yellow through orange to red. Analyses of arsenic sulfide deposits collected from the old river bed where the water of the Yukawa River flowed down about 43 years ago are shown in Table III. The contents of free sulfur in old sediments are distinctly smaller than those in the fresh deposits collected from the present river bed of Yukawa River. The S/As atom ratios of the arsenic sulfide in the old yellow or red deposits are about 1.5. These values correspond to that in orpiment. Moreover, the old yellow deposits are crystalline, very poor in lead, and show distinctly the X-ray diffraction patterns of orpiment. Therefore, the old yellow deposits are considered to be orpiment as reportd formerly. Fresh yellow deposits are amorphous and do not show any X-ray diffraction pattern. Their chemical composition is AsS_2. It is not correct to consider them to be orpiment. The following explanation is offered: Arsenic in the solution of thermal water was deposited first as arsenic disulfide AsS_2. Since arsenic disulfide is not stable, it gradually changed to the stable form of orpiment by aging for about forty years.

Table II. Analyses of fresh yellow, orange and red deposits collected from the present bed of Yukawa R.

Sample number	Color of sediments	Free sulfur in deposits wt%	Composition of the deposits from which free sulfur was extracted with carbon disulfide						
			Sulfur* wt%	Arsenic wt%	Lead wt%	Total wt%	S/As atom ratio	Pb/As atom ratio	Solid state determined by X-ray
1	Reddish brown	5.81	14.86	18.90	8.33	42.09	1.90	0.159	Amorphous
2	Red	71.33	18.66	23.23	12.03	53.92	1.88	0.187	Amorphous
3	Reddish orange	82.19	15.05	18.87	11.96	45.88	1.86	0.288	Amorphous
4	Reddish orange	81.52	35.34	39.29	9.09	83.72	2.04	0.083	Amorphous
5	Reddish brown	56.60	33.11	44.30	6.59	84.00	1.99	0.054	Amorphous
6	Orange	68.71	32.57	39.92	10.74	83.23	1.91	0.097	Amorphous
7	Orange-yellow	59.88	11.42	12.99	2.22	26.63	2.06	0.062	Amorphous
8	Orange-yellow	63.21	17.78	19.00	2.96	39.74	2.18	0.055	Amorphous
9	Yellow	74.03	5.28	6.35	0.62	12.25	1.90	0.035	Amorphous

* Sulfur combined with arsenic.

Table III. Analyses of arsenic-lead sulfide deposits collected from the old river bed of Yukawa R.

Sample number	Color of sediments	Free sulfur in deposits wt%	Composition of the deposits, from which free sulfur was extracted with carbon disulfide						
			Sulfur* wt%	Arsenic wt%	Lead wt%	Total wt%	S/As atom ratio	Pb/As atom ration	Solid state by X-ray
1	Yellow	15.68	35.53	55.53	0.38	91.45	1.50	0.003	Orpiment
2	Yellow	13.30	33.47	51.94	1.21	86.62	1.51	0.008	Orpiment
3	Yellow	14.81	38.53	55.41	0.34	94.28	1.63	0.002	Orpiment
4	Yellow	24.77	37.95	57.50	0.88	96.33	1.54	0.005	Orpiment
5	Red	12.88	35.39	56.12	8.49	100.00	1.47	0.054	Amorphous
6	Red	7.13	32.80	47.18	5.51	85.49	1.62	0.042	Amorphous
7	Red	11.27	33.81	45.17	6.27	85.25	1.74	0.053	Amorphous
8	Red	5.31	37.10	54.93	6.42	98.45	1.57	0.042	Amorphous
9	Red	8.07	37.70	49.22	12.07	98.99	1.59	0.088	Amorphous

* Sulfur combined with arsenic.

The Pb/As atom ratio of the old sediments shows remarkable color change from yellow to red. Moreover, the old deposits collected from the old bed of the Yukawa River are distinctly lower in Pb/As atom ratio than the fresh sediments collected from the present river bed. The contents of free sulfur in the fresh sediments also are remarkably higher than those in the old sediments. This may be explained by supposing that while the arsenic disulfide changed to the stable form of As_2S_3 by aging for more than forty years, a considerable amount of free sulfur and some parts of lead sulfide were oxidized by air to the soluble compounds of sulfur and lead. It seems unreasonable to suppose that the above-mentioned difference in sediments was caused by the change of chemical composition of the hot spring waters during these periods.

Field experiments on the formation of arsenic and arsenic-lead sulfide sediments. On Nov. 3, 1964, the authors found red, orange and yellow fresh sediments around the orifice of a small spring which was overrun with strong acid water, of higher temperature, flowing down the Yukawa River from Obuki Spring etc. As shown in Fig. 2-1 and Fig. 2-2, the authors made a tiny pond of 30 cm in length, 20 cm in bredth and 4 cm in depth around the spring. The amount of a strong acid water flowing into the pond was controlled by closing or opening the small water inlet with gravel and clay. The experiments were made in the following order: (1) Chemical analyses were carried out both of spring water and strong acid water from Obuki Spring; and the following results were obtaned: As to the

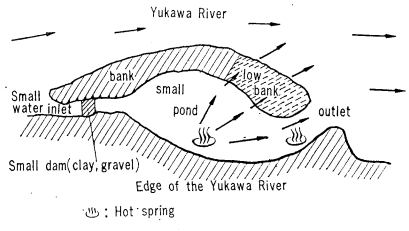

Fig. 2-1. Small pond made for experiments near the bank of the Yukawa River, the water inlet to pond being closed completely with clay and gravel. No precipitation of yellow or red arsenic sulfides took place on the pebbles which were placed in the pond just before experiment. Arrows indicate flow direction of water.

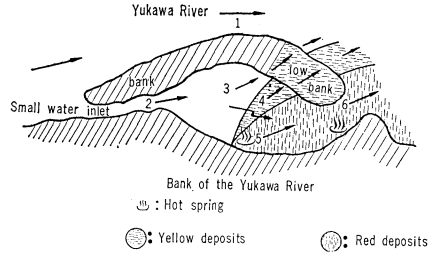

Fig. 2-2. Small pond made for experiments near the bank of the Yukawa River, the water inlet to the pond being open. Yellow or red arsenic sulfide quickly precipitated on the pebbles which were placed in the pond just before experiment. Arrows indicate flow direction of water.

former: temperature 66.3°C, pH 2.2, As 0.003 mg/l, Pb 0.00 mg/l, H_2S 233 mg/l, Cl 547 mg/l, SO_4 441 mg/l. As to the latter: temperature 84.0°C, pH 1.3, As 2.6 mg/l, Pb 1.6 mg/l, H_2S 7.6 mg/l, Cl 3026 mg/l, SO_4 1274 mg/l. (2) The water inlet to the pond was closed completely with gravel and clay. Then the entire bottom of the pond was covered with fresh andesitic gravel. The water from the spring flowed over the gravel to the main stream of Yukawa River. Under such conditions no deposit precipitated on the fresh andesitic gravel placed around the orifice of the spring for one night. (3) As soon as the water inlet was opened, strong acid water, rich in arsenic and lead, but poor in hydrogen sulfide, flowed into the pond and mixed with spring water, very rich in hydrogen sulfide, but poor in arsenic and lead. Under such conditions, on the gravel placed at the area indicated with No. 5 and No. 6 in Fig. 2-2 red sediments accumulated remarkably during one night, while on the gravel at the area indicated with No. 4 in Fig. 2-2, yellow sediments accumulated. The pH-value of the water, from which red sulfides precipitated, was found to be about 2.0, and that of the water, from which yellow sulfides were precipitated, about 1.6, as shown in Table IV. At the water inlet, where the strong acid water entered the pond, and the part near the inlet, indicated with No. 3 in Fig. 2-2, no sediment deposited, because no mixing of water occurred there.

Table IV. Chemical analyses of waters collected on November 4, 1964, from the small experimental pond, when the water inlet to the pond was open

Spots where the samples were collected (Fig. 2-2)	Water temperature °C	pH	H_2S mg/l	Cl^- mg/l	SO_4^{2-} mg/l	As mg/l	Pb mg/l	Remarks
1	82.5	1.3	7.6	3081	1274	2.6	1.5	Yukawa River
2	79.2	1.3	3.4	3161	1230	2.3	1.5	No deposit
3	78.2	1.3	3.4	3151	1175			No deposit
4	73.4	1.6	67.2	2799	1027	0.14	0.52	Yellow deposits
5	66.3	2.0	233.0	547	441	0.003	0.01	Red deposits
6	69.7	2.0	95.2	1463	737	0.01	0.61	Red deposits

Comparison between the new arsenic-lead sulfides and known lead-arsenic sulfide minerals. As lead-arsenic sulfide minerals, the following minerals are known: jordanite $4PbS.As_2S_3$, gratonite $9PbS.As_2S_3$, guitermanite $10PbS.3As_2S_3$, dufrenoysite $2PbS.As_2S_3$, rathite $13PbS.9As_2S_3$, baumhauerite $4PbS.3As_2S_3$, liveingite $5PbS.4As_2S_3$ and sartorite $PbS.As_2S_3$ (Palache, C., Barman, H., and Frondel, C., 1944; Rösch, H., and Hellner, E., 1959; and Hellner, E., 1959). Lead to arsenic atom ratios of these minerals are 0.50–2.25.

Of arsenic-lead sulfides of Tamagawa Hot Springs, Pb/As atoms ratios are 0.159–0.228 in the fresh red sediments, 0.055–0.097 in the fresh orange sediments, and 0.042–0.088 in the old red sediments.

Conclusion. Yellow, orange and red sediments are found on the bed of the Yukawa River which starts at Obuki Spring. The old yellow sediments found on the bed of Yukawa River are orpiment, as stated in the previous reports, but the composition of fresh yellow sediments collected from the present river bed of Yukawa River is AsS_2, not As_2S_3. Red sediments from which free sulfur was extracted with carbon disulfide, were found to be arsenic disulfide which contains lead sulfide in a small amount. Therefore, it is not correct to call them realgar. The fresh red and orange sediments are approximately $5AsS_2PbS$ and $10AsS_2(PbS)$ respectively. The old red sulfide is expressed with formula $5As_2S_3(PbS)$ and the old yellow sulfide with As_2S_3 (orpiment). It was found by field experiments that yellow, orange and red sediments were formed by mixing of a strong acid water, rich in arsenic and lead, but poor in hydrogen sulfide, which flows down as Yukawa River from Obuki Spring, and a weak acid spring water, poor in arsenic and lead, but very rich in hydrogen sulfide. If a large amount of the former mixes with a small amount of the latter, the mixed solution shows 1.6 pH and yellow arsenic sulfide is formed. If the amount relation is reverse, the pH-value of the mixture is about 2.0, and red arsenic-lead sulfide is formed.

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