Effect of chlorocomplex of lead on the deposition of lead-bearing barite from hot spring water

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Abstract—The behavior of barium and lead in Tamagawa Hot Spring water has been discussed. Compared with barite of hydrothermal origin, barite from hot spring water is singular in its lead content. This fact was elucidated in terms of lead chlorocomplex formation in the spring water from which barite precipitates. The experimental verification has been attempted on the deposition of this mineral.

INTRODUCTION

Barite is common gangue mineral in hydrothermal ore deposits and is generally almost pure BaSO_4 . Strontium, calcium, magnesium and sometimes lead replace barium and they are usually found as minor constituents. In an extreme case, strontium is present up to 28% as SrO and this mineral is called strontiobarite (PALACHE *et al.*, 1951). According to GRAHMANN (1920), formation of a complete solid solution between BaSO_4 and SrSO_4 is possible. In contrast to the BaSO_4 - SrSO_4 system, however, a solid solution between BaSO_4 and PbSO_4 has been unknown in hydrothermal ore deposits (MINAMI, 1930), until Takano (1959) found it in barite from hot springs.

OKAMOTO (1906) found a radioactive barite containing 30% of PbSO_4 , deposited on rocks in a stream of hot spring water of Hokuto Hot Springs, Formosa. Similar deposits have also been found at Tamagawa Hot Springs, Akita, Japan. These minerals from both hot springs were found to be similar in chemical composition and are considered to deposit through the same mechanism.

Barite from Tamagawa Hot Springs contains lead from 1 to 16% by weight. Lead-poor barite is a large white crystal, while lead-rich one is less crystalline and has a zonal structure of white and brownish layers. The first comprehensive study on hokutolite* was performed by SUGANUMA (1930), who made total chemical analysis of

* The definition of this mineral was somewhat obscure. TAKANO (1959) found that lattice constants of lead-bearing barites do not obey Vegard's rule and their composition is between $\text{A}_{25}\text{B}_{75}$ and $\text{A}_{75}\text{B}_{25}$ ($\text{A}=\text{PbSO}_4$, $\text{B}=\text{BaSO}_4$). He proposed that barite within this range is to be called "hokutolite". According to this, barite from Tamagawa Hot Springs is not "hokutolite". In the present paper, however, the author calls it hokutolite just for convenience.

hokutolite. He also paid attention to its zonal structure of alternative layers and considered that this structure is closely related to the mechanism of formation of this mineral. Furthermore, he noticed that the hokutolite from Tamagawa Hot Springs changes its lead content along with locality, and attributed this to variation in acidity of spring waters.

For the discussion of this phenomenon, it is necessary to know the barium and lead contents of the water in each locality where hokutolite deposits. But available data on the barium and lead contents of the spring water are not enough to discuss this point. In the present paper the variation in lead content of hokutolite will be elucidated in terms of the chlorocomplex formation.

EXPERIMENTAL

(a) *Determination of barium in waters*

Two liters of sample solutions was taken. Five ml of concentrated sulfuric acid and 375 mg of strontium as chloride were added to them. Solutions were left overnight. Precipitates were collected by decantation and brought to laboratory. Barium co-precipitated with SrSO_4 was determined by X-ray fluorescent spectroscopy (TAKANO, 1969).

(b) *Determination of lead in waters and synthesized (Ba, Pb)SO₄*

Lead in hot spring waters was determined colorimetrically by dithizone method (SAITO and TAKEUCHI, 1961). $(\text{Ba, Pb})\text{SO}_4$ was first boiled with 30% Na_2CO_3 solution and converted to carbonate, which was washed several times with dilute Na_2CO_3 solution and then decomposed by nitric acid. Lead in the solution was determined in the same way as described above.

(c) *Preparation of (Ba, Pb)SO₄*

Homogeneous precipitation of BaSO_4 with sulfamic acid was applied in this case from the point of view that the sedimentation rate of hokutolite is very small. Experiments were performed at two temperatures, 60 and 80°C. In the former case 150mg of sulfamic acid, 120mg of Ba^{2+} and 60mg of Pb^{2+} as nitrate and in the latter case 60mg, 100mg and 100mg of each reagent respectively were placed in a 100ml Erlenmeyer flask, and then several aliquots of sodium chloride solution were added to vary the chloride concentration from 0.01 M to 2M. The solution was diluted to 100ml after adding a few drops of nitric acid until the pH value of the solution became 1.2. Then the solution was stirred magnetically and kept at a constant temperature for a day or four days.

RESULTS AND DISCUSSION

Fig.1 shows a sketch map of Tamagawa Hot Springs together with the sampling localities of spring waters for the determination of barium and lead.

Fig.1. Tamagawa Hot Springs.

(a) *Lead content of hokutolite from Tamagawa Hot Springs*

It was noticed by SUGANUMA (1930) and MINAMI (1953) that barite from Tamagawa changes its lead content with its locality. There is a general tendency for the lead content to increase along with the distance from the vent of Obuki Spring (Table 1). This tendency was accounted for by SUGANUMA in terms of the solubility of PbSO_4 . ICHIKUNI (1966) estimated the barium content of the stream water by calculations based on the partition coefficient of lead between solution and barium sulfate precipitates and concluded that the major portion of barium in the original solution precipitates as BaSO_4 within 100m from Obuki Spring. His estimation seems to imply that the increase in the lead content of barite precipitates is attributed to the decrease in the barium concentration in the water, compared with the lead concentration in the water, but in this respect he neglected the effect of the dilution by ground water. The decrease in the barium concentration of the spring water may not directly mean

Table 1. Variation in Pb/Ba weight ratios of barite from Tamagawa Hot Springs with the distance from the vent of Obuki Spring

Distance (meter)	0 ~ 100	200 ~ 400	500 ~ 600	600 ~ 700
Pb/Ba ($\times 10^2$)	1 ~ 8	14 ~ 20	22 ~ 26	28 ~ 31

the precipitation of barium as BaSO_4 . For the further discussion on this point, it is necessary to obtain data on the barium and lead content of the spring water at each locality along the stream.

(b) *Barium and lead content of water*

SUGANUMA (1930) gave the values 0.65 mg Ba/l and 0.61 mg Pb/l for the water issuing from the vent of Obuki Spring. MINAMI and OYAGI (1963) determined the barium content of the water to be 2.9 mg/l (1953) and 5.7 mg/l (1954) by means of flame photometry.

For the lead content of that water, 1.53 mg/l was given by the Iwate Hygiene Laboratory (1953) and 1.1 mg/l by MINAMI *et al.* (1957). To ascertain experimentally the behavior of barium and lead in stream waters, concentrations of both elements were determined at nine sampling locations shown in Fig. 1. Table 2 shows the barium and lead contents of the water collected on July 21, 1965. They apparently decrease,

Table 2. Barium and lead contents of Tamagawa Hot Spring water

Sample point	Ba (mg/l)	Pb (mg/l)	Temperature (°C)
1	0.82	1.59	97.8
2	0.96	1.51	98.2
3	0.85	1.49	82.0
4	0.85	1.50	83.0
5	0.80	1.28	77.0
6	0.80	1.28	—
7	0.16	0.32	27.0
8	0.23	0.35	25.5
9	0.18	0.32	25.5

as the original water flows down, but the mixing of ground water must be taken into consideration. To avoid the effect of dilution, Ba/Cl and Pb/Cl ratios in each water were discussed. Fig. 2 shows that these ratios are almost constant everywhere in the stream studied. The Pb/Ba ratios of the water are apparently constant. In this respect, however, it must be borne in mind that these data show the total quantities of both elements in waters. Barium was determined in very small microcrystals of hokutolite suspended in water as well as dissolved in water. In fact, these microcrystals were recognized under a microscope in sulfurous sinters precipitated on the stream bed, or on the bottom sand of Obuki Spring. As the flow rate of the spring water is considerably high, the major portion of microcrystals is carried away. They are too small to adhere to the surface of bed rocks.

From this point of view, it is impossible to discuss accurately the behavior of

Fig.2. Change in total Ba and Pb content with Cl^- content in spring waters.

barium and lead dissolved in water without the knowledge of solubility of barite under these conditions.

The solubility of hokutolite in the solution, of which composition is similar to that of the water from Obuki Spring, were determined to be $0.50\text{mgBa}^{2+}/\text{l}$ at 83°C and $0.79\text{mgBa}^{2+}/\text{l}$ at the boiling point of the solution (TAKANO, 1969). The original water seems to be slightly supersaturated with barium sulfate.

(c) *Some consideration of the contribution of lead complexes in the spring waters to Pb/Ba ratios of hokutolite*

Pb/Ba ratio of Hokutolite is affected by $a_{\text{Pb}^{2+}}/a_{\text{Ba}^{2+}}$ ratios of spring waters. If the activity ratio of free barium and lead ions increases, Pb/Ba ratio of precipitates will increase proportionally.

The complex formation of lead will decrease the activity of free lead ions which in part coprecipitate with BaSO_4 . The chloro- and thio- complexes are considered generally to be major lead complexes in hot spring water. The formation of thio-complexes, however, could be neglected in the solutions low in H_2S content as in the Tamagawa Hot Spring waters (average H_2S content 2mg/l).

ICHIKUNI (1966) referred to the possibility that the complex formation of lead might modify the activity of free lead ions in the solution, since it contains a considerable amount of chloride ions. Although he neglected this possibility in his calculation, it becomes clear from following calculation that the formation of chlorocomplexes of lead affects Pb/Ba ratios of barite precipitates.

It is well known that lead forms PbCl^+ , PbCl_2^0 , PbCl_3^- and PbCl_4^{2-} in chloride solution. The proportion of the contents of complexes and free lead ions to the total lead content of spring waters are estimated from the next five equations,

$$m_{\text{total Pb}} = m_{\text{Pb}^{2+}} + m_{\text{PbCl}^+} + m_{\text{PbCl}_2^0} + m_{\text{PbCl}_3^-} + m_{\text{PbCl}_4^{2-}} \quad (1)$$

$$\frac{m_{\text{Pb}^{2+}} \gamma_{\text{Pb}^{2+}} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{m_{\text{PbCl}^+} \gamma_{\text{PbCl}^+}} = K_1 \quad (2)$$

$$\frac{m_{\text{PbCl}^+} \gamma_{\text{PbCl}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{m_{\text{PbCl}_2^0} \gamma_{\text{PbCl}_2^0}} = K_2 \quad (3)$$

$$\frac{m_{\text{PbCl}_2^0} \gamma_{\text{PbCl}_2^0} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{m_{\text{PbCl}_3^-} \gamma_{\text{PbCl}_3^-}} = K_3 \quad (4)$$

$$\frac{m_{\text{PbCl}_3^-} \gamma_{\text{PbCl}_3^-} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{m_{\text{PbCl}_4^{2-}} \gamma_{\text{PbCl}_4^{2-}}} = K_4, \quad (5)$$

where m_x is the molality of x-th constituent, γ_x its activity coefficient and K_n its dissociation constant. m_{Cl^-} is considered to be $m_{\text{Cl}^- \text{ total}}$. $m_{\text{Pb total}}$ and $m_{\text{Cl}^- \text{ total}}$ of spring waters are known from analytical data.

HELGESON (1964) summarized the data on the dissociation constants of lead chlorocomplexes and furthermore he estimated the temperature dependence of these constants from the solubility data of PbCl_2 . These constants are available at 25 and 80°C.* Each temperature roughly corresponds to those of Obuki Spring and Yu-daki Fall waters, respectively. Activity coefficients may be calculated by the Debye-Hückel equation, if the ionic strength I of a solution is as much as 0.1. The chemical compositions of spring waters of the two representative localities are given in Table 3, from which the values of the ionic strength are obtained; $I_O = 0.12$ and $I_Y = 0.028$, where the suffix O refers to Obuki Spring and Y to Yu-daki Fall.

From these results, it may be reasonable to apply the D-H equation (6)** for the calculation of activity coefficient, γ_i .

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + \bar{a}_i B \sqrt{I}}, \quad (6)$$

where $\bar{a}_i$ was assumed to be independent of temperature.

* Dissociation constants of lead chlorocomplexes used here are as follows;

at 25°C, $K_1 = 2.69 \times 10^{-2}$, $K_2 = 6.60 \times 10^{-2}$, $K_3 = 1.30$, $K_4 = 2.0$

at 80°C, $K_1 = 1.59 \times 10^{-2}$, $K_2 = 1.41$, $K_3 = 5.6$, $K_4 = 1.2 \times 10^{-1}$.

(After HELGESON (1964))

** For constants in equation (6) were employed the next values:

At 25°C, $A = 0.509$, $B = 0.329$. At 80°C, $A = 0.574$, $B = 0.342$.

$\bar{a}_i = 6$ for PbCl^+ , PbCl_3^- and PbCl_4^{2-} , 5 for Ba^{2+} , 4.5 for Pb^{2+} and 3 for Cl^- .

Table 3. Chemical composition of Tamagawa Hot Spring water (Date: July 21, 1965)

	Locality	
	Obuki Spring	Yu-daki Fall
Na ⁺	110 mg/l	18.5 mg/l
K ⁺	21.5	10.0
Ca ²⁺	168	37.0
Mg ²⁺	46.9	30.7
Fe (total)	85.5	20.0
Al ³⁺	99.1	26.9
Cl ⁻	3174	625
SO ₄ ²⁻	96.1	170
HSO ₄ ⁻	1158	178
pH	1.2	1.7

Table 4. Calculated distribution of the lead chlorocomplexes in the spring waters

Locality Species	Obuki Spring (mole per cent)	Yu-daki Fall (mole per cent)
Pb ²⁺	38	71
PbCl ⁺	60	24
PbCl ₂ ^o	2	5
PbCl ₃ ⁻	< 0.1	< 0.1
PbCl ₄ ²⁻	< 0.1	< 0.1

Using these values, one can obtain activity $a_{\text{Pb}^{2+}}$ for Obuki and Yu-daki Fall, where the total lead contents are 0.725×10^{-5} and 0.159×10^{-5} mol/l and the chloride contents are 89.52×10^{-3} and 17.63×10^{-3} mol/l, respectively. The mole per cent of each complex is given in Table 4. Thus the activity ratios of free lead ions and barium ions for the two representative regions are $(a_{\text{Pb}^{2+}}/a_{\text{Ba}^{2+}})_{\text{Obuki}} = 0.42$, and $(a_{\text{Pb}^{2+}}/a_{\text{Ba}^{2+}})_{\text{Yu-daki Fall}} = 0.81$, respectively. Therefore,

$$\frac{(a_{\text{Pb}^{2+}}/a_{\text{Ba}^{2+}})_{\text{Yu-daki Fall}}}{(a_{\text{Pb}^{2+}}/a_{\text{Ba}^{2+}})_{\text{Obuki}}} = 1.9 \quad (7)$$

This shows that the free lead ion concentration in the Yu-daki Fall region is about twice as much as that in the Obuki Spring region, so that barite in the Yu-daki Fall region is likely to incorporate more lead than does that in the Obuki Spring region.

Furthermore, it may be considered that free lead content of spring waters with respect to barium will become larger than 2 since the free barium content of the Yu-daki Fall region may be less than the determined value.

In Tamagawa Hot Springs, yearly and even daily variations in the chemical composition of original spring water were observed by some authors (SAHARA, 1959, WATANUKI, 1959 and IWASAKI *et al.*, 1963). But in the first approximation, the total salt concentration and the ratio of barium and lead concentrations of the original water can be considered to be constant. Moreover, the considerable variation in temperature of that water was not observed through a year (SUGANUMA, 1930). Consequently, it is presumed that the nature of waters in the Obuki Spring region is similar to that of waters used for the above discussion.

On the other hand, although the ratio of barium and lead concentrations of waters in the Yu-daki Fall region is also considered to be constant, the total salt concentration and temperature of the waters show seasonal variations resulting from confluence of some streamlets. In addition, the topography of Tamagawa Hot Springs was greatly changed on account of repeated constructions for the removal of poisonous spring waters (MIURA, 1964, see Fig.1). Therefore, the nature of the waters in this region is now considerably different from that at the time when hokutolite was deposited.

Taking into account of these two sorts of variations, at the time before the constructions, the temperature and the total salt concentrations of waters in the Yu-daki Fall region are presumed to have been about 40°C and a half of the total salt concentration of the present original water, respectively.* Under these conditions, recalculations were made in the similar way on the γ_i 's of dissolved ions and the proportion of each lead complex to the total lead of water in the Yu-daki Fall region. In this case, a value of 1.8 was obtained from the equation (7).

Experimental results as shown in Fig.3 qualitatively support the above estimation, but lead content of BaSO₄ precipitated at 60°C is smaller than that of BaSO₄ at 80°C. This seemed to be contrary to the general rule in coprecipitation phenomena. It is well known that the amount of coprecipitation is influenced by the speed of formation of the precipitate, which in turn is a function of the concentration of the ion being precipitated and the concentration of the precipitating agent, the presence of foreign substances affecting the solubility and the temperature during the precipitation.

In our experiments, the pH value and the Pb/Ba weight ratio of the original solution were kept constant before each run. The speed of the precipitation, in this case, almost depended upon temperature, since the producing rate of a precipitating agent, SO₄²⁻, was determined by the rate of hydrolysis of sulfamic acid. Therefore, two plots in Fig.3 mean that the amount of coprecipitation increases as the chloride ion concentration of the solution decreases and the speed of precipitation rises. The

* Data used here were obtained by MINAMI *et al.* in 1953 when the drainage of poisonous water was stopped.

Fig.3. Change in Pb content of BaSO₄ with Cl⁻ concentration of solutions.

precipitates were found to be monophasic by X-ray powder diffraction pattern. If, in addition, the Pb/Ba weight ratio of the solution becomes larger, each plot will have a steeper slope. The Pb/Ba ratios of the spring waters are about 1.8 and hence the conditions for the coprecipitation of lead becomes more favorable in the spring waters.

CONCLUSION

The lead content of barite from Tamagawa Hot Springs changes with its locality. This may be due to the three factors, the increase of free lead ions in the spring waters through the dissociation of lead complexes by confluence of some streamlets, the speed of the precipitation and presumably the decrease in concentration of free barium ion resulting from precipitation of microcrystals of barite. In general, barite from hydrothermal ore deposits does not contain an appreciable amount of lead although it is often associated with lead minerals such as galena. This might be accounted for by the similar reasoning since the ore-forming solution is considered to contain usually a few moles of chloride ions.

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