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The Barium Content of Barite-forming Hydrothermal Waters as Exemplified by Tamagawa Hot Spring Waters

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An estimation of the barium concentration in Tamagawa Hot Spring water was made on the basis of the partition of lead between spring waters and barite deposits precipitated from the waters. As the lead content of the waters and the chemical composition of the deposits are already known, the barium concentration can be computed by the use of the following relation:

$$D=\left(\frac{\mathrm{Pb}}{\mathrm{Ba}}\right)_{\mathrm{S}}\bigg/\left(\frac{\mathrm{Pb}}{\mathrm{Ba}}\right)_{\mathrm{L}}$$

where D is the partition coefficient of lead, and where S and L denote the solid and liquid phases respectively. A value of 2±1 mg./l. was obtained for the barium concentration in the water issuing from the vents. It was pointed out that the water is supersaturated with barium sulfate. This supersaturation may be due to the addition of a considerable amount of sulfates, probably formed by supergene processes, to the original thermal water. The genesis of hydrothermal barite deposits was also discussed.

The determination of the barium content of thermal waters presents a considerable difficulty, its concentration being in general very small. The accumulation of data on the barium concentration in natural waters, especially of hydrothermal origin, will therefore provide useful information on the genesis of ore deposits containing barium minerals. It is of particular importance to define the range of its concentration in various hydrothermal waters producing barite or related minerals.

As one spring indicating a high barium content, we may refer to the Tamagawa Hot Springs, where a continuous deposition of plumbian barite, or so-called hokutolite, occurs on the bed of the stream. The barite originates from the principal spring, called "Obuki," and from other small springs located nearby.

In the studies of the genesis of plumbian barite, Suganuma[1] gave a value of 1.1 mg./l. as the barium sulfate content of Obuki Spring water. This value is, however, very questionable, as compared with the lead content of the same spring water, which has recently been reported by Minami et al.[2] Admittedly, Watanuki,[3] assuming the saturation of the spring water with barium sulfate, recommended a value of 1 mg./l. as its barium concentration. However, this value is possibly a lower limit of barium content, because the water issuing from the vents may be supersaturated with barium sulfate. On the other hand, Minami et al.[4] gave the following values for the barium concentration in the same spring water: 2.9 mg./l.

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[1] I. Suganuma, This Bulletin, **3**, 69 (1928).

[2] E. Minami, G. Sato and K. Watanuki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 1096 (1957).

[3] K. Watanuki, *Onsen Kagaku*, **14**, 88 (1963).

[4] E. Minami, Y. Oyagi and M. Suzuki, reference cited in E. Minami, G. Sato and K. Watanuki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **79**, 860 (1958).

(sample collected on May 5, 1954) and 5.7 mg./l. (collected on July 14, 1956). It is obvious that more extensive works must be done in order to obtain a reliable value for the barium content.

This report will propose another approach to estimating the concentration of this element. It is a method developed on the basis of the partition equilibrium of a minor element between the liquid and solid phases. As we have a useful review on this subject,⁵⁾ it would be unnecessary to give the full details of this method. Minami et al.⁶⁾ outlined the same approach, but they did not make any accurate calculations.

Method of Calculation

From the experiments on the partition of lead between the solution and the barium sulfate precipitate, Kolthoff and Noponen⁷⁾ determined the partition coefficient, D, to be as follows: 0.027 at 95°C, and 0.026 at 26°C. The coefficient D is defined by Eq. 1:

$$D=\left(\frac{\mathrm{Pb}}{\mathrm{Ba}}\right)_{\mathrm{S}}\Big/\left(\frac{\mathrm{Pb}}{\mathrm{Ba}}\right)_{\mathrm{L}} \qquad (1)$$

where (Pb/Ba) designates the weight ratio of the two elements, and the subscripts S and L refer to the solid and liquid phases respectively. They examined the precipitates with compositions ranging from 0.025 to 0.302 in a Pb/Ba ratio. The composition of plumbian barites from the Tamagawa Hot Springs falls entirely within this range. It was also shown that perchloric acid had no effect upon the partition coefficient; thus, the value is not affected by a high acidity of spring water. The presence of chloride ions in spring water may modify the coefficient slightly as a result of the complex-formation of lead, but as a first approximation, the reported value can be used here without correction.

In the Tamagawa Hot Springs, the plumbian barite precipitates from waters ranging in temperature from 90°C to 40°C; therefore, a partition coefficient of 0.027 may be accepted in this calculation. Special emphasis must be placed on a small variability of the coefficient with the temperature. From Eq. 1, the barium concentration in the solution $(\mathrm{Ba})_{\mathrm{L}}$ is given by the following equation:

$$(\mathrm{Ba})_{\mathrm{L}}=\frac{0.027(\mathrm{Pb})_{\mathrm{L}}}{\left(\dfrac{\mathrm{Pb}}{\mathrm{Ba}}\right)_{\mathrm{S}}} \qquad (2)$$

where $(\mathrm{Pb})_{\mathrm{L}}$ is the lead concentration in the stream water from which the plumbian barite is precipitating. Since the lead concentration appears to be roughly constant in the stream, a value of 1.2 mg./l. for the stream water²⁾ is inserted into Eq. 2. In reality this is not true, however, it will be seen later that the correction due to a decrease in lead concentration does not affect the results of calculation. The lowering of the lead concentration resulting from the confluence of some streamlets with the main stream can be equally neglected, their discharge being small compared with that of the latter.

Results and Discussion

Table I indicates the chemical composition of several plumbian barites⁸,⁹⁾ and the calculated barium contents of the waters which are in equilibrium with these minerals. Figure 1 represents the locality of the barites. It is well known that the deposits formed in the lower course of the stream are rich in lead, while those formed in the upper course are deficient in this element. The change in chemical composition can be attributed to the selective incorporation of barium into the deposits. Thus, the Pb/Ba ratio in the

TABLE I. COMPOSITION OF SOME PLUMBIAN BARITES AND CALCULATED BARIUM CONCENTRATIONS IN SOLUTION

No.	Locality (distance from Obuki spring, m.)	PbO %	BaO %	$(\mathrm{Pb/Ba})_{\mathrm{S}}$	$(\mathrm{Ba})_{\mathrm{L}}$ mg./l.
1	30	—	—	0.035*	0.92
2	50	0.75	64.25	0.0121	2.68
3	50	4.61	62.18	0.0768	0.42
4	100	7.17	53.57	0.139	0.23
5	700	15.17	48.14	0.327	0.10
6	700	16.83	47.67	0.366	0.088

* Estimated from the refractive index α.

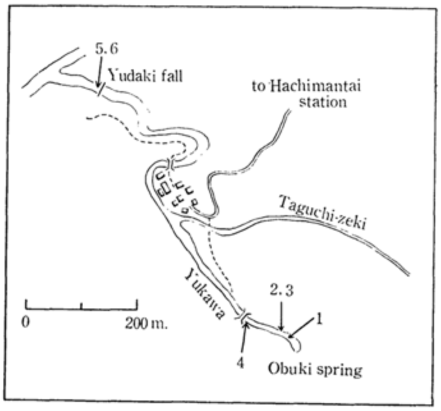

Fig. 1. General map of the Tamagawa Hot Springs and localities of barite samples

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5) W. L. McIntire, *Geochim. et Cosmochim. Acta*, **27**, 1209 (1963).

6) E. Minami, G. Sato and K. Watanuki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **79**, 860 (1958).

7) I. M. Kolthoff and G. E. Noponen, *J. Am. Chem. Soc.*, **60**, 197 (1938).

8) E. Minami, "Geochemistry of the Tamagawa Hot Springs," Tokyo (1963), p. 108.

9) S. Misumi, ibid., p. 146.

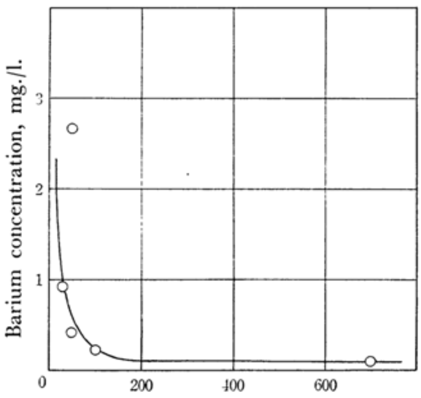

Fig. 2. Plot of calculated barium concentrations against distance from Obuki Spring.

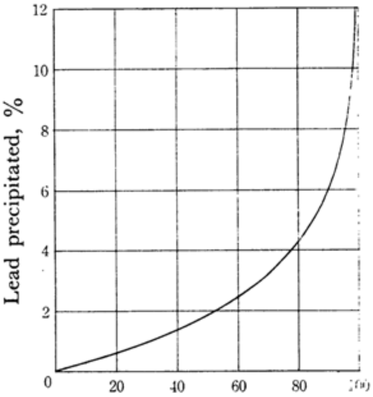

Fig. 3. Relation between the portion of barium precipitated and that of lead precipitated.

waters is evidently the lowest at the vents of the springs, and increases gradually with the flowing of the stream. In Fig. 2, the calculated barium concentration in the stream water is plotted against the distance from the Obuki Spring. The figure shows that 2±1 mg./l. may be a reasonable value for the barium concentration in the water issuing from the vent of the Obuki Spring. This leads to the rather surprising conclusion that the major portion of the barium contained in the original water precipitates within 100 m. of the Obuki Spring.

The quantity of lead coprecipitated with barium can be computed if we assume that the precipitate once formed has no further interaction with the solution. Starting from Eq. 1, we have:

$$\frac{-(\varDelta\mathrm{Pb})}{-(\varDelta\mathrm{Ba})} = D\frac{(\mathrm{Pb})}{(\mathrm{Ba})} \tag{3}$$

where $(\varDelta\mathrm{Pb})$ and $(\varDelta\mathrm{Ba})$ represent small portion of these elements incorporated into the precipitate, and where (Pb) and (Ba) refer to their concentrations in the solution from which the precipitate was formed. The integration of the above equation gives:

$$\frac{(\mathrm{Pb})}{(\mathrm{Pb})_0} = \left\{\frac{(\mathrm{Ba})}{(\mathrm{Ba})_0}\right\}^{\mathrm{D}} \tag{4}$$

where $(\mathrm{Pb})_0$ and $(\mathrm{Ba})_0$ denote their initial concentrations. Equation 4 indicates the relation between lead and barium concentrations in the solution during the formation of the precipitate. From Eq. 4, the portion of lead coprecipitated is given by:

$$1-\frac{(\mathrm{Pb})}{(\mathrm{Pb})_0} = 1-\left\{\frac{(\mathrm{Ba})}{(\mathrm{Ba})_0}\right\}^{\mathrm{D}}$$

Figure 3 shows the relation between the portion of barium precipitated and the corresponding value for lead. In order to calculate the total amount of plumbian barite deposited on the bed of the stream extending over 700 m. from the Obuki Spring to the Yudaki Fall, we need only the lead and the barium concentrations in the water at both points and the discharge of the stream in this area. As is shown in Fig. 2, the amount of barium precipitated on the bed under consideration corresponds to approximately 95% of its initial amount. In this case, a value of 8% may be expected for the coprecipitated portion of lead. Consequently, one liter of spring water may precipitate 1.9 mg. of barium and 0.096 mg. of lead, or 3.37 mg. of mixed sulfate (Ba, Pb) SO_4. Using a discharge value of 75.4 l./sec. or 2.4×10^9 l./yr. (both as given by Miura[10]), we can estimate the annual production of deposits as 8.09×10^9 g.

If the bed of the stream between the Obuki Spring and the Yudaki Fall were covered with crustal deposits of a uniform thickness, the rate of the growth of the crustal deposits would be of 0.86 mm./yr.* This value is extremely high compared with the results obtained by Saito et al.[11] A spectrochemical investigation by Nakagawa[12] showed that some sulfurous sinters occuring in the Tamagawa Hot Springs contain a considerable amount of barium and lead, so the above-mentioned disagreement means simply that the precipitate exists mainly in the form of minute crystals buried in sulfurous sinters, and not in the form of crustal deposits.

The formation of abundant microcrystals of plumbian barite presents a direct evidence that the spring water issuing from the vents is supersaturated with barium sulfate. It is well known that the greater the degree of supersaturation,

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* This calculation was made on the assumption that the bed occupies an area of 2100 m^2 and that the barite deposits have a density of 4.5 g./cm^3.

[10] H. Miura, "Geochemistry of the Tamagawa Hot Springs," Tokyo (1963), p. 83.

[11] N. Saito, Y. Sasaki and H. Sakai, ibid., p. 182.

[12] R. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 46 (1965).

the greater will be the number of nuclei formed. We will discuss here briefly the possible causes of this phenomenon. It may be attributed to a rapid decrease in the temperature or to an abrupt change in the chemical composition of the original thermal water. As a cause of the decrease in the temperature, the mixing of the original water with some groundwater of a low temperature may be considered. However, the addition of groundwater of a low mineralization cannot always result in the precipitation of barium sulfate, for the water may be effective not only in cooling the original solution, but also in diluting it. Therefore, no separation of solid barium sulfate takes place unless the water is accompanied by a considerable quantity of sulfates. It may be generally admitted that the increase in sulfate concentration is indispensable for the formation of barite deposits. This hypothesis is in accord with the present author's interpretation of the formation of the Tamagawa Hot Springs.[13]

From the foregoing discussion, we can schematize the genesis of hydrothermal barite deposits as follows: the original ore solutions are relatively deficient in sulfate ions and contain at least 1 mg. of barium per liter. When the ore solutions encounter some subsurface waters which are rich in sulfates, the precipitation of barite will take place because of the decrease in the solubility of the barium sulfate. The sulfates may be formed by the oxidation of sulfides contained in the same ore solutions or by some other supergene processes.

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13) M. Ichikuni, *Geochim. et Cosmochim. Acta*, **17**, 6 (1959).