Short Communication

The chemical composition of plumbian barite (hokutolite) precipitated from 1981 to 1990 at Tamagawa Hot Springs, Akita Prefecture, Japan

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Introduction

To date precipitating plumbian barite (hokutolite) at Tamagawa Hot Springs, Akita Prefecture, has been consecutively studied (Minami, 1954; Sasaki and Watanuki, 1983, 1988). Their materials were the precipitates on andesite blocks placed under the hot spring water at Yubana Fall in 1953 (Fig. 1a), which is one of the best places for the purpose of consecutive studies. The chemical composition of recent Tamagawa Hot Spring waters has also been consecutively studied (Takano, 1969; Takano and Watanuki, 1972a; Goto, 1982, 1990; Sasaki, 1985, 1991; Sasaki and Watanuki, 1988; Sasaki, Watanuki and Minato, 1991).

The aim of this study is to determine the chemical composition and unit cell parameters of the plumbian barite precipitated from 1981 to 1990, comparing them with the materials of previous recoveries precipitated during the period from 1953 to 1981 (Sasaki and Watanuki, 1983, 1988). The authors endeavour to explain the variation in chemical composition of plumbian barite in relation to the chemical composition of recent Tamagawa Hot Spring waters.

Experiments and results

Material: The plumbian barite (hokutolite) we examined is a light, yellowish brown, thin coating (thickness: < 0.5 mm) composed of an aggregate of minute crystals (size: < 0.3 mm) grown on a sawn tabular andesite block (size: $8\text{cm} \times 10\text{cm} \times 30\text{cm}$) (Fig. 1b)

FIG. 1a. A view of Yubana Fall (Oct., 1983).

FIG. 1b. A view of Yubana Fall when hot spring water is off. The place where the andesite block was laid down is seen (Aug., 1985). It is noticed that the third conduit was shortened.

FIG. 1c. A view of a section of the plumbian barite precipitated on the altered andesite block from 1981 to 1990.

TABLE 1. Chemical composition of plumbian barite (hokutolite) precipitated on andesite blocks at Yubana Fall in Tamagawa Hot Spring.

Sample No.	BaO		PbO		SrO		CaO		Fe ₂ O ₃	SO ₃ *	Sum
	(wt.%)	(mol%)**	(wt.%)	(mol%)	(wt.%)	(mol%)	(wt.%)	(mol%)	(wt.%)	(wt.%)	(wt.%)
S-1	52.66	83.67	13.36	14.58	0.45	1.06	0.16	0.69	0.04	33.23	99.9
S-2	51.20	83.02	13.23	14.73	0.66	1.58	0.15	0.66	0.39	32.58	98.2
S-3	49.86		10.20		0.46		0.19		0.02	30.60	92.1
S-3'	54.10	85.89	11.07	12.07	0.50	1.16	0.21	0.88		33.20	100.0

S-1,2 Data cited from Sasaki and Watanuki (1983, 1988).

S-3 Material recorded in October, 1990.

S-1 (precipitated from 1953 to 1973)

S-2 (precipitated from 1973 to 1981)

S-3 (precipitated from 1981 to 1990)

S-3' (recast of S-3 to 100% after deducting Fe₂O₃)

* Calculated from wt.% values of barium, lead, strontium and calcium oxides.

**Composition in mol % as to barium, lead, strontium and calcium.

Mol % was calculated on the basis of Ba+Pb+Sr+Ca=100%.

which was set under the hot spring water at Yubana Fall in 1981. The plumbian barite had grown by mainly being submerged under the hot spring water (Sasaki, Kayahara and Watanuki, 1991) as mentioned later. The material has strong radioactivity principally due to Ra^{226} and Ra^{224} (ThX). The andesite block under the plumbian barite is peripherally altered by the strongly acidic hot spring water as seen in the sliced surface (Fig. 1c).

Chemical analysis: The hydriodic acid decomposition method (Takano and Watanuki, 1972b) was adopted for the chemical analysis. PbO , SrO , CaO and Fe_2O_3 were measured by atomic absorption spectroscopy (AAS), and BaO content was by both flame photometry and gravimetry. The results are shown in Table 1, where they are compared with those of materials taken from previous recoveries (Sasaki and Watanuki, 1983). The lower summation of the new analysis is to be ascribed to native sulfur (α -sulfur) acting as an impurity. This is because of the fact that the present material was formed by mainly being submerged under the hot spring water after 1984 (Sasaki, Kayahara and Watanuki, 1991). The recalculated figures are also tabulated to enable a direct comparison.

EPMA measurements: EPMA line analysis (Horiba EMAX1770) was made along the direction of crystal growth as seen in the SEM photograph (Hitachi S-510) (Fig. 2a) to demonstrate the substantial homogeneity, which is also reflected in the rather sharp X-ray diffraction peaks as stated below. The results are given in Fig. 2b.

Unit cell parameters: The diffractometer trace given in Fig. 3 consists of sharper peaks suggesting a lesser degree of compositional fluctuation. The unit cell parameters calculated by the least-squares method are given in Table 2, where those of materials of previous recoveries are also tabulated for comparison. Table 2 shows that the unit

FIG. 2a. Scanning electron micrograph of a section of the plumbian barite precipitated on the altered andesite block from 1981 to 1990.

FIG. 2b. Electron microprobe traverses for major and minor elements across the plumbian barite on the andesite block as shown in Fig. 2a.

cell parameters of new plumbian barite are larger than those of the previous recoveries, which correspond well with the decrease in Pb content shown in Table 1 on the basis of Vegard's rule. The relationship between unit cell parameters and the Ba:Pb ratio of

FIG. 3. X-ray diffraction pattern of the plumbian barite (hokutolite) crystallized during the period from 1981 to 1990. Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.5418\text{\AA}$) radiation, with setting 40kV, 25mA, scan rate $1^\circ/\text{min}$ and time const. 1s.

the plumbian barite is shown in Fig. 4, where the tendency of variation is in accordance with the general trend. Note that the unit cell parameters of plumbian barite varies linearly with Pb or Sr contents (Boström *et al.*, 1967; Sugitani *et al.*, 1969; Sasaki and Minato, 1982). The apparent discontinuity of lattice parameters on the Pb:Ba ratio of natural plumbian barite indicated by Takano (1959) was found to be due to the Sr content in the plumbian barite (Sasaki and Minato, 1982).

Rate of precipitation: Provided that the increase in thickness of precipitation is equal each year, the maximum rate of growth of the material is calculated as 0.05 mm per year. This is much the same value as determined for the materials precipitated from 1973 to 1981 (Sasaki and Watanuki, 1983).

Discussion

Compared with the materials of previous recoveries, the present one precipitated from 1981 to 1990 is less plumbian and has larger unit cell parameters. To consider these changes of plumbian barite, we should examine the changes of recent Tamagawa Hot Spring waters from which the plumbian barite was formed (Table 3) (Takano, 1969; Takano and Watanuki, 1972a; Goto, 1982, 1990; Sasaki, 1985, 1991; Sasaki and Watanuki, 1988; Sasaki, Watanuki and Minato, 1991; Sasaki, Yamane and Watanuki, 1991). Sasaki showed that the chemical composition of plumbian barite is not necessarily

FIG. 4. Relationship between unit cell parameters and Ba:Pb ratio of the plumbian barite (S-1, S-2, S-3). (cf. Sasaki and Minato, 1982).

TABLE 2. Unit cell parameters of plumbian barite.

Sample No.	a (Å)	b (Å)	c (Å)	V (Å ³)	Authors (year)
S-1	8.813 (1)	5.451 (1)	7.127 (2)	342.4 (2)	Sasaki and Watanuki (1983)
S-2	8.802 (2)	5.444 (1)	7.110 (2)	340.7 (3)	Sasaki and Watanuki (1983)
S-3	8.823 (1)	5.453 (1)	7.130 (1)	343.0 (1)	The present study (1991)

TABLE 3. Contents of principal dissolved ionic species (including SiO_2) and pH of Tamagawa Hot spring waters ($\text{mg}\cdot\text{dm}^{-3}$).

	1965 ^a	1983	1985	1986	1987	1988	1989
Ba^{2+}	0.82	1.03	1.32	1.58	1.59	1.53	1.77
Pb^{2+}	1.59	0.93	0.78	0.69	0.99	1.03	0.72
Sr^{2+}	0.29	0.36	0.30	0.42	0.40	0.46	0.44
Na^+	110	49.1	47.0	56.1	45.5	48.7	43.1
K^+	21.5	31.9	33.8	37.7	30.4	27.9	29.6
Ca^{2+}	167.8	93.6	89.0	85.0	82.3	83.2	81.3
Mg^{2+}	46.9	32.1	36.0	35.9	33.5	33.2	31.6
ΣFe	85.5	123.0	93.0	85.6	73.7	64.7	59.6
Al^{3+}	151	132.0	104.0	124.0	98.7	96.8	101.0
SiO_2	368.5	257	252	249	239	240	253
SO_4^{2-}	1242	2068	1656	1525	1357	1203	978
Cl^-	3174	3140	2870	2830	2720	2595	2530
pH	1.20	1.13	1.17	1.19	1.23	1.24	1.25

a) Data cited from Takano (1969).

determined by the $\text{Ba}^{2+}:\text{Pb}^{2+}:\text{Sr}^{2+}$ ratio but by the chemical affinities of BaSO_4 , PbSO_4 , SrSO_4 in the solution. Therefore we evaluated the average chemical affinities of BaSO_4 , PbSO_4 , SrSO_4 from the data of chemical compositions of hot spring waters during the period from 1981 to 1989 as given in Table 3. The calculation procedures are given in other papers (Sasaki, 1991; Sasaki *et al.*, 1988, 1991 etc.). The calculated chemical affinities at Yubana Fall (70°C) are as following:

$$A_{\text{BaSO}_4}^0 = 1.253 \quad (1)$$

$$A_{\text{PbSO}_4}^0 = -2.963 \quad (2)$$

$$A_{\text{SrSO}_4}^0 = -4.290 \quad (3)$$

It was noticed that the plumbian barite formed before 1984 was precipitated from the splashing of the hot spring water (Minami, 1954; Sasaki, Kayahara and Watanuki, 1991), while the precipitate after 1984 was formed by being submerged under the hot spring water because of a shortening in length of one of the Yubana conduits (Fig. 1b) through

which the hot spring water falls down and forms plumbian barite on the andesite blocks. From Eqs. 1, 2, 3 we obtain the following phenomenological equations (Sasaki, 1991; Sasaki, Watanuki and Minato, 1991; Sasaki, Kayahara and Watanuki, 1991).

$$v \begin{pmatrix} x_{\text{BaSO}_4} \\ x_{\text{PbSO}_4} \\ x_{\text{SrSO}_4} \end{pmatrix} = \begin{pmatrix} 135.4 & 40.0 & 2.68 \\ 40.0 & 21.7 & 0.85 \\ 2.68 & 0.85 & 0.84 \end{pmatrix} \begin{pmatrix} 1.239 - RT \ln x_{\text{BaSO}_4}/100 \\ -2.963 - RT \ln x_{\text{PbSO}_4}/100 \\ -4.290 - RT \ln x_{\text{SrSO}_4}/100 \end{pmatrix} \quad (4)$$

where, $x_{\text{BaSO}_4} + x_{\text{PbSO}_4} + x_{\text{SrSO}_4} = 100\%$. The solutions of Eq. 4 at 70°C are

$$v = 1.35, x_{\text{BaSO}_4} = 85.5\%, x_{\text{PbSO}_4} = 13.5\%, x_{\text{SrSO}_4} = 1.0\%. \quad (5)$$

These values are nearly coincident with the chemical composition of the plumbian barite present as shown in Table 1.

Sasaki *et al.* showed that the splash yielding the plumbian barite at Yubana Fall is about 60°C and 0~20% concentrated hot spring water (Sasaki, Kayahara and Watanuki, 1991). Hence we can calculate the chemical composition of the plumbian barite of previous recoveries by using phenomenological equations from the data of the hot spring water in 1965 at 60°C. The obtained phenomenological equations are as follows:

$$v \begin{pmatrix} x_{\text{BaSO}_4} \\ x_{\text{PbSO}_4} \\ x_{\text{SrSO}_4} \end{pmatrix} = \begin{pmatrix} 135.4 & 40.0 & 2.68 \\ 40.0 & 21.7 & 0.85 \\ 2.68 & 0.85 & 0.84 \end{pmatrix} \begin{pmatrix} 1.003 - RT \ln x_{\text{BaSO}_4}/100 \\ -2.470 - RT \ln x_{\text{PbSO}_4}/100 \\ -4.364 - RT \ln x_{\text{SrSO}_4}/100 \end{pmatrix} \quad (6)$$

The solutions of Eq. 6 at 60°C are

$$v = 1.18, x_{\text{BaSO}_4} = 84.4\%, x_{\text{PbSO}_4} = 14.8\%, x_{\text{SrSO}_4} = 0.8\%. \quad (7)$$

These values show close agreement with the chemical composition of plumbian barite of a previous recovery crystallized from 1953 to 1972, which is given in Table 1 (Sasaki and Watanuki, 1983, 1988).

If the precipitation condition of plumbian barite had not changed since 1984, in other words, if the present material had been precipitated from the splashing of hot spring water during the period from 1981 to 1991, what composition would the plumbian barite have had? We can estimate the composition in the same manner which has already been mentioned using phenomenological equations. From the average chemical affinities of BaSO_4 , PbSO_4 and SrSO_4 at Yubana Fall at 60°C, we can acquire the following phenomenological equations.

$$v \begin{pmatrix} x_{\text{BaSO}_4} \\ x_{\text{PbSO}_4} \\ x_{\text{SrSO}_4} \end{pmatrix} = \begin{pmatrix} 135.4 & 40.0 & 2.68 \\ 40.0 & 21.7 & 0.85 \\ 2.68 & 0.85 & 0.84 \end{pmatrix} \begin{pmatrix} 1.506 - RT \ln x_{\text{BaSO}_4}/100 \\ -2.711 - RT \ln x_{\text{PbSO}_4}/100 \\ -4.020 - RT \ln x_{\text{SrSO}_4}/100 \end{pmatrix} \quad (8)$$

The solutions of Eq. 8 at 60°C are

$$v = 1.91, x_{\text{BaSO}_4} = 82.4\%, x_{\text{PbSO}_4} = 16.5\%, x_{\text{SrSO}_4} = 1.1\%. \quad (9)$$

Compared with the values of Eqs. 7, Pb, Sr contents of Eqs. 9 are a little large with the change in chemical composition of hot spring waters provided that the precipitation mode is definite. But in fact Pb content decreased with the change of the precipitation mode.

As a result, the authors conclude that the lower Pb content in the present material is principally due to the change of precipitation mode rather than the recent changes in the chemical composition of Tamagawa Hot Spring water.

Acknowledgements—We would like to express our gratitude to Dr. A. Kato (National Science Museum, Japan) for his reading of the manuscript and for his kind and valuable advice for this study. We also wish to thank Y. Matsubara (Asa Elementary School) and M. Iio (Kyowa Junior High School) for our field work.

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Received June 12, 1991; accepted January 16, 1992