Short Communication

Variation in chemical composition of naturally occurring lead-bearing barite (hokutolite) having crystallized since 1953 at Tamagawa Hot Spring. Nobuyuki SASAKI* and Kunihiko WATANUKI,**

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Abstract

Natural hokutolite from Tamagawa Hot Spring was examined in its chemical composition and lattice constant. There are appreciable changes in the chemical composition and the lattice constants of the mineral along the direction of crystal growth. These changes well correspond to the changes in the concentrations of sulfate and iron ions in the hot spring water.

Introduction

Tamagawa Hot Spring in the western part of Hachimantai district in the Northern Japan is probably the only place in the world where lead-bearing barite (hokutolite) is crystallizing at present.

Minami (1954) and his co-workers started the experimental growth of hokutolite from the hot spring water at this place. They set an andesite rock under the Yudaki fall at the end of Yubana conduits in 1953. After that a small piece of the andesite rock was once taken out in 1969 by Takano and Watanuki, and chemical composition of that hokutolite was determined (Takano and Watanuki, 1972a). The lattice constants were measured by Sasaki and Minato (1982).

In 1981 we took out the andesite rock and set new blocks of andesite rock at the same place. It was clearly observed that the collected sample was covered by another newly grown crystal layer, which had a different color (ocher yellow) from the crystals examined before (light brown).

Recently Yoshiike and Iwasaki (1979) and Goto (1982) pointed out that the chemical composition of hot spring water at Tamagawa Hot Spring had changed noticeably since about 1973 and that the concentration of sulfate and iron ions in the hot spring water have been increasing since then. It is assumed that the newly-added crystal layer have grown from the hot spring water of changing composition.

In this study, the chemical composition and lattice constants are examined for the collected hokutolite samples with new layer. And the relationship between these values and the recent change in the chemical compositions of the hot spring water at Tamagawa is discussed.

Experimental and results

Material

The hokutolite layer covering the andesite host rock is about 1.5 to 3.0 mm in thickness. The crystal layer grown on the upper side is thicker than that grown on the bottom side of the rock. The hokutolite shows strong radioactivity measured by means of a survey meter. The section of the hokutolite grown on the andesite rock is shown in Fig. 1.

FIG. 1. A view of a section of the hokutolite grown on the andesite rock since 1953 to 1981 in Tamagawa Hot Spring.

Chemical analysis

EPMA analysis. Chemical analysis of the hokutolite was done by the scanning technique along the direction of crystal growth with an electron probe micro-analyzer (JXA-50A). The measurements were made for three elements Ba, Pb and Sr. Electron beam of 2 μm in diameter was used at 15 kV and 0.02 μA . It was found, however, that the electron beam irregularly drifted and measurements were nearly impossible.

For comparing with this sample, lead-bearing barites collected at Kawarage Hot Spring (Shiikawa and Yamaguchi, 1956), which have almost no radioactivity, were also examined. The Kawarage samples showed no electron beam drift, which made normal measurements possible.

Therefore, it is supposed that the beam drift observed for Tamagawa hokutolite may be due to its strong radioactivity, perhaps β -ray from Ra^{228} .

Wet analysis. Chemical analyses were conducted on two bulk crystal layers which are apparently different in color, light brown and ocher yellow. The samples were decomposed by hydriodic acid (Takano and Watanuki, 1972b). Calcium and iron contents were determined by means of the atomic absorption spectroscopy, and strontium content was by both the flame photometry and the atomic absorption spectroscopy. Barium content was determined by the gravimetric method, and lead content was by both the atomic absorption and the gravimetric method.

The results of chemical analysis are shown in Table 1. It is found that the newly grown ocher yellow crystals contain more strontium and iron than formerly grown light brown crystals. The lead and calcium contents show nearly the same values between these two crystals. The cationic mole fractions of barium, lead, strontium and calcium are given in Table 1(b). From Table 1(b), it is found that lead content is also higher in the newly grown crystal than in the formerly grown crystal. According to Deer *et al.* (1965), barite forms a continuous solid solution with PbSO_4 and SrSO_4 , and a partial solid solution with CaSO_4 . And in BaSO_4 - PbSO_4 - SrSO_4 series, it is clarified that lattice constants vary continuously with cationic mole ratio (Boström *et al.*, 1968; Sasaki and Minato, 1982). Therefore it is presumed with considering the ionic radii that the newly grown crystal has smaller lattice constants than the formerly grown one.

TABLE 1. Chemical compositions of lead-bearing barite crystals precipitated in different period of time at the end of Yubana conduit at Tamagawa Hot Spring.

(a) Composition in weight percent.

Crystallization period	BaO (wt. %)	PbO (wt. %)	SrO (wt. %)	CaO (wt. %)	FeO (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 mole % as to 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

X-ray diffraction

The lattice constants of the two crystal layers mentioned above were determined by X-ray diffractometry with Ni filtered $\text{CuK}\alpha$ radiation. The diffraction data were corrected by using silicon as an internal standard, then the lattice

constants were determined by the least-square procedure from fifteen 2θ values in the range from 18° to $50^\circ(2\theta)$. The results are shown in Table 2. The numbers in parentheses denote the standard deviations. It is revealed that the newly grown crystal shows a lattice constant a little smaller than the formerly grown light brown crystal. This result is consistent with the result of the chemical analysis.

TABLE 2. Lattice constants and unit cell volumes of lead-bearing barite in Table 1.

Crystallization period	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
1953~1972	8.813(1)	5.451(1)	7.127(2)	342.4(2)
1973~1981	8.802(2)	5.444(1)	7.110(2)	340.7(3)

Discussion

The change in chemical composition of the hot spring water from Obuki vent in Tamagawa Hot Spring since 1953 was presented by Goto (1982), who stated that sulfate and iron ions remarkably increased since 1973. As it is supposed that the change in the chemical composition of the crystal corresponds to the change in the chemical composition of the hot spring water, the reason of the change in the crystal composition is explained in the following two ways.

1) In the Obuki vent, if the spring water is nearly saturated with barium sulfate, barium concentration decreases with an increase of the sulfate concentration because the ion product of barium and sulfate should be constant. Note that lead and strontium concentrations are nearly invariable because the solution is undersaturated with respect to lead sulfate and strontium sulfate. So with decreasing barium concentration, the ratios Pb/Ba and Sr/Ba in the solution increase, then Pb/Ba and Sr/Ba in the crystal also increase.

2) If the change of sulfate concentration in the hot spring water is an independent geochemical incident and barium concentration is invariable notwithstanding the increase of sulfate ions, the ion product of barium and sulfate increase, and at the same time the degree of supersaturation also increases. Then the apparent partition coefficient of minor elements, which is the function of the crystal growth rate that are determined by the degree of supersaturation of the solution (Sunagawa, 1981), increases and approaches to the partition coefficient at the adsorption layer (Kitamura and Sunagawa, 1977).

In the case of 1) the crystal growth would be slower after the change of chemical composition of hot spring water. While, in the case of 2) the crystal growth, on the contrary, must be faster after the change of hot spring water.

Then the crystal growth rates of the two crystal layers, which are light brown and ochre yellow, were examined from the thickness of the crystal layers. Assuming that each crystal layer has grown at a constant growth rate, following results are obtained.

$$R_{\text{former}} = 2.0(\text{mm})/20(\text{years}) = 0.10 \text{ mm/year (light brown crystal)}$$

$$R_{\text{latter}} = 0.40(\text{mm})/8(\text{years}) = 0.05 \text{ mm/year (ochre yellow crystal)}$$

It is shown that the newly grown crystals had grown at a smaller rate than the formerly grown ones. Hence the explanation 1) is acceptable for this case.

Saito *et al.* (1963) evaluated the rate of crystal growth of hokutolite by using the radioactive elements. Their values measured for the newly grown hokutolite are in the range from 0.09 to 0.25 mm/year. In comparison with their values, the values obtained from the present samples seem a little smaller, but nearly of the same order.

Conclusion

Changes in the chemical composition and lattice constants, which occurred perhaps in about 1973, were observed in the natural lead-bearing barite that had been crystallized since 1953. There are appreciable differences in color and luster, between the crystal layers which perhaps grew before and after 1973. The former is light brown and the latter is ochre yellow in color. The latter crystals contain more Sr and Fe ions than the former. The lattice constants and cell volume of the latter crystals are smaller than those of the former ones.

Since the growth rate of the latter crystals ($\cong 0.05$ mm/year) is smaller than that of the former ($\cong 0.10$ mm/year), the changes in the chemical composition and the lattice constants of the crystals mentioned above are supposed to be brought about by the decrease in barium concentration of the hot spring water owing to the increase in sulfate ions since 1973 at Tamagawa Hot Spring.

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