

## Hexahydroborite from Fuka, Okayama Prefecture, Japan

Isao KUSACHI\*<sup>1</sup>, Yasushi TAKECHI\*<sup>2</sup>, Shoichi KOBAYASHI\*<sup>3</sup>, Junji YAMAKAWA\*<sup>4</sup>, Yoshihiro NAKAMUTA\*<sup>5</sup>, Kyue-Hyung LEE\*<sup>6</sup> and Shoji MOTOMIZU\*<sup>6</sup>

\*<sup>1</sup> Department of Earth Sciences, Faculty of Education, Okayama University, Okayama 700-8530, Japan

\*<sup>2</sup> Kurashiki Museum of Natural History, Kurashiki 710-0046, Japan

\*<sup>3</sup> Division of Earth Sciences, Kurashiki University of Science and the Arts, Kurashiki 712-8505, Japan

\*<sup>4</sup> Department of Earth Science, Faculty of Science, Okayama University, Okayama 700-8530, Japan

\*<sup>5</sup> Department of Earth and Planetary Science, Faculty of Science, Kyushu University, Fukuoka 812-8581, Japan

\*<sup>6</sup> Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

### Abstract

Hexahydroborite was found in a vein consisting of borate minerals which developed along the boundary between crystalline limestone and skarns at Fuka, Okayama Prefecture, Japan. Hexahydroborite occurred as aggregates of pyramidal crystals up to 2mm wide on the cavity wall, in association with olshanskyite and calcite. Wet analyses and ICP-MS gave the empirical formula  $\text{Ca}_{1.001}\text{B}_{2.102}\text{O}_{4.154} \cdot 5.846\text{H}_2\text{O}$  on the basis of  $\text{O}=10$ , which was consistent with the ideal formula  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$ . The reflections of X-ray powder data for hexahydroborite from Fuka were indexed on the monoclinic cell,  $a=16.011(2)$ ,  $b=6.688(1)$ ,  $c=7.954(2)\text{\AA}$ ,  $\beta=103.81(1)^\circ$ , determined by single crystal method. The mineral was optically biaxial positive with refractive indices  $\alpha=1.502(2)$ ,  $\beta=1.505(2)$ ,  $\gamma=1.509(2)$  and had a Mohs hardness of 2.5 and a density of  $1.84\text{gcm}^{-3}$ . It is likely that hexahydroborite at Fuka was formed by a reaction of ground water with sibirskite and/or parasibirskite at a low temperature around  $25^\circ\text{C}$ .

### Introduction

Hexahydroborite,  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$ , was originally found in drill cores at the Solongo deposit, Buryat USSR by Simonov *et al.* (1977). It occurred as aggregates of flattened colorless prismatic crystals up to 0.5mm in veinlets associated with pentahydroborite. The mineralogical data of hexahydroborite from the type locality was reported for only impure specimens, and no other published data are known to the writers.

During a mineralogical survey of the gehlenite-spurrite skarns at Fuka, Okayama Prefecture, Japan, hexahydroborite was found. This is the first occurrence of hexahydroborite to be reported in Japan. The present paper deals with its mode of occurrence and mineralogical properties.

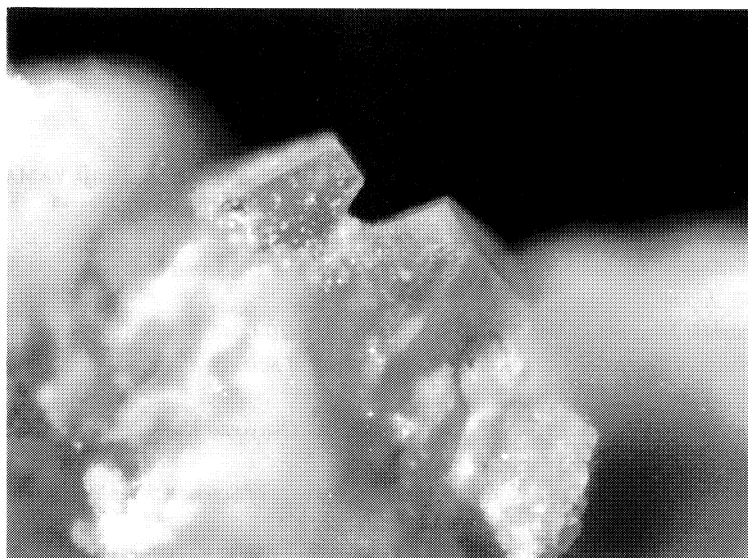


FIG. 1. Photograph of hexahydroborite crystals. Scale bar indicates 1 mm.

### Occurrence

Hexahydroborite was found in a vein which develops along the boundary between crystalline limestone and gehlenite-spurrite skarns at Fuka. The vein is approximately 10 cm in thickness, although in one part expands to 3m. Takedaite (Kusachi *et al.*, 1995a) occurs at the central part of the expanded area, which was primarily formed by a reaction of boron-bearing fluids with limestone. Along the boundary between takedaite and the crystalline limestone, hydrous borates such as sibirskite (Kusachi *et al.*, 1997a) and parasibirskite (Kusachi *et al.*, 1998) occur up to 2 cm wide. At the outer skarn side of the expanded area, hydrous borates such as nifontovite and olshanskyite (Kusachi *et al.*, 1994) occur from 20 cm to 50 cm in thickness. All the hydrous borates appear to be formed by late-hydrothermal alteration of takedaite. Other constituent minerals of the vein are frolovite (Kusachi *et al.*, 1995b), borcarite (Kusachi *et al.*, 1997b), pentahydroborite, vivianite, brucite and calcite.

Hexahydroborite occurs as aggregates of pyramidal crystals up to 2 mm wide on the cavity wall in the vicinity of the calcite vein, in association with olshanskyite and calcite. Figure 1 shows the occurrence of hexahydroborite crystals.

### Physical and Optical Properties

Hexahydroborite was transparent with a vitreous luster in hand specimen. Optically, the mineral was biaxial positive with refractive indices  $\alpha=1.502(2)$ ,  $\beta=1.505(2)$ ,  $\gamma=1.509(2)$

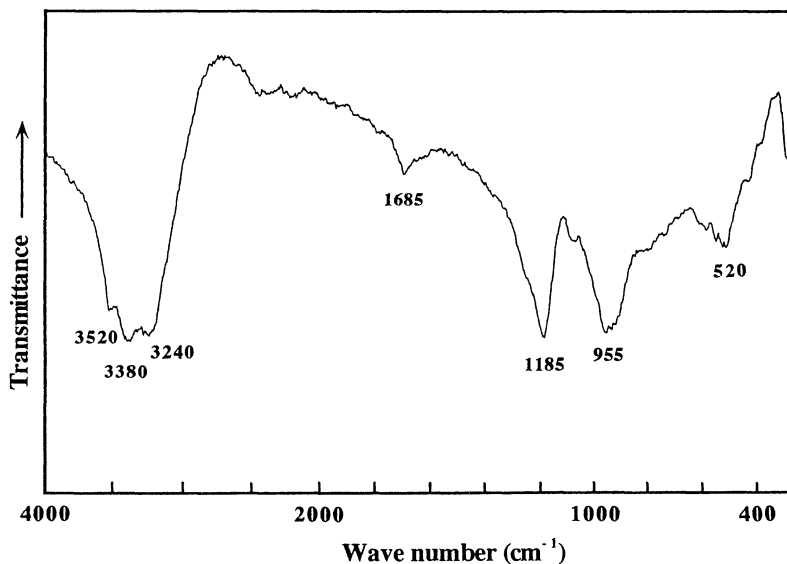


FIG. 2. Infrared absorption spectrum of hexahydroborite.

and calculated  $2V=82^\circ$ . The Mohs hardness was 2.5 and the density measured by heavy liquid was  $1.84 \text{ gm cm}^{-3}$ . The properties show a close resemblance to those from the type locality reported by Simonov *et al.* (1977). Hexahydroborite was easily soluble in dilute hydrochloric acid and slowly soluble in water at room temperature, but not in alcohol. The mineral decomposed during preparation of normal thin sections.

The infrared absorption spectrum of hexahydroborite was measured by the KBr method for the region  $4000$  to  $250 \text{ cm}^{-1}$ , as shown in Figure 2. The absorption bands at  $3240$  to  $3520 \text{ cm}^{-1}$  are attributed to the OH stretching vibration. Numerous bands observed at  $1185$  to  $280 \text{ cm}^{-1}$  are characteristic of borates.

### X-ray Study

The X-ray powder data for hexahydroborite from Fuka was obtained by an X-ray diffractometer using Rigaku RINT 2500V monochromated  $\text{Cu-K}\alpha_1$  radiation operated at 40kV and 200mA. The reflections of hexahydroborite from Fuka were indexed on the monoclinic  $C2/c$ ,  $a=16.011(2)$ ,  $b=6.688(1)$ ,  $c=7.954(2)\text{\AA}$ ,  $\beta=103.81(1)^\circ$ , determined by single crystal method using a Rigaku AFC-5R four-circle automated diffractometer operated at 50 kV and 200 mA, with graphite- monochromatized  $\text{Mo-K}\alpha$  radiation.

The data are given in Table 1, and are compared with those of the type locality reported by Simonov *et al.* (1977) and the synthetic phase reported by Gode and Kuka (1970). The cell parameters of the mineral from Fuka agree well with those from the type locality, except for an  $a$  dimension twice that reported by Simonov *et al.*

TABLE 1. X-ray powder data for hexahydroborite.

h k l	1.		I	2.		3.		I	I
	d(calc.)	d(obs.)		d	I	d	I		
2 0 0	7.775	7.78	100	7.73	10	7.80	100		
1 1 0	6.145	6.15	22	(6.97)	1	6.16	80		
1 1 1	4.602	4.60	10	4.58	4	4.65	50		
3 1 0	4.097	4.10	14	4.09	1	4.17	40		
3 1 1	3.940	3.943	12	3.895	4	3.97	50		
4 0 0	3.887	3.890	4						
1 1 2	3.419	3.420	12			5.27	10		
3 1 1	3.366	3.368	22	3.37	9b	3.40	80		
0 2 0	3.345	3.346	8						
4 0 2	3.140	3.141	14	3.118	9	3.18	60		
3 1 2	3.120	3.123	6						
2 2 0	3.072	3.073	6						
5 1 1	2.856	2.857	4						
5 1 0	2.820	2.821	18	2.792	8	2.85	40		
2 2 1	2.767	2.767	6						
6 0 0	2.592	2.592	4						
3 1 2	2.578	2.579	2						
2 2 2	2.523	2.525	20	2.550	9	2.54	100		
5 1 1	2.482	2.481	16	2.469	8	2.48	80		
1 1 3	2.459	2.460	12						
3 1 3	2.393	2.394	2	2.381	1				
4 2 2	2.289	2.290	10	2.283	8	2.31	60		
7 1 1	2.162	2.162	6	2.141	3	2.17	30		
1 3 1	2.141	2.142	2						
7 1 0	2.108	2.109	6	2.098	1				
6 2 1	2.080	2.080	2						
5 1 2	2.074	2.073	2						
6 2 0	2.049	2.049	4	2.024	2				
0 2 3	2.040	2.041	2						
3 3 1	2.028	2.028	2						
4 2 2	1.983	1.982	8					1.961	7
6 2 2	1.970	1.971	4						
8 0 0	1.944	1.944	18					1.931	7
0 0 4	1.931	1.932	4						
3 1 4	1.890	1.890	4					1.881	2
7 1 3	1.849	1.850	2						
5 3 1	1.821	1.822	6					1.810	2
5 3 0	1.812	1.813	2						
1 1 4	1.795	1.795	2						
5 1 4	1.784	1.784	4					1.787	1
2 0 4	1.778	1.778	4					1.774	6
6 0 4	1.763	1.764	2						
3 3 2	1.743	1.743	2						
5 3 2	1.736	1.736	2						
5 3 1	1.712	1.712	2						
6 2 2	1.683	1.683	4					(1.702)	1
0 2 4	1.673								
8 2 2	1.672	1.672	4					1.674	5
0 4 0	1.672								
2 4 0	1.635	1.635	4					1.625	4
8 2 1	1.576	1.576	2						
8 0 4	1.570	1.571	2						
8 2 3	1.563	1.563	2						
10 0 0	1.555	1.555	4					1.549	5
3 1 5	1.545	1.545	2						
3 3 3	1.534	1.534	2						
a(Å)	16.012(2)							8.006	
b(Å)	6.689(1)							6.649	
c(Å)	7.955(2)							8.012	
b(°)	103.81(1)							104.21	

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Solongo. After Simonov *et al.* (1977).
3. Synthetic. After Gode and Kuka (1970).

### Thermal Behavior

DTA and TG curves were obtained by heating hexahydroborite from room temperature to 900°C at a rate of 10°C/min. The curves are shown in Figure 3. The DTA curve has an endothermic peak at 102°C and an exothermic peak at 699°C. The curve is similar to that from the type locality, except for the absence of two endothermic peaks at 123°C and 160°C reported by Simonov *et al.* (1977). On heating hexahydroborite from Fuka at 800°C, calcium borate (Ca<sub>2</sub>B<sub>2</sub>O<sub>4</sub>) appeared as a crystalline phase.

### Chemical Composition

A hexahydroborite specimen from Fuka was selected for chemical analyses by hand picking separation under a binocular microscope. The concentration of Ca was determined by ICP, and the content of B was determined by ICP-MS. The H<sub>2</sub>O content was determined from ignition loss at 900°C. The results are given in Table 2, and are compared with those reported by

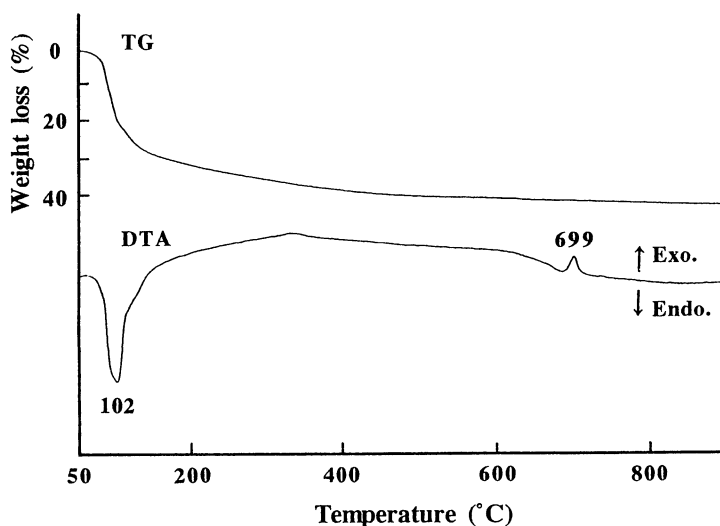


FIG. 3. DTA and TG curves of hexahydroborite.

TABLE 2. Chemical composition of hexahydroborite.

	1.	2.	3.
Weight percentages			
SiO <sub>2</sub>	-		1.56
B <sub>2</sub> O <sub>3</sub>	31.49	29.78	26.91
FeO	-		0.22
MgO	-		0.89
CaO	24.15	23.99	20.51
CO <sub>2</sub>	-		1.76
H <sub>2</sub> O	45.28	46.23	43.45
Total	100.92	100.00	101.30
Mole ratio (basis : O=10)			
B	2.102	2	
Ca	1.001	1	
H	11.692	12	

1. Fuka, Okayama Prefecture, Japan. The present work.

2. Theoretical Ca[B(OH)<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O.

3. Solongo. After Simonov *et al.* (1977).

Simonov *et al.* (1977) and the theoretical values calculated from the ideal formula, Ca[B(OH)<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O. The empirical formula of hexahydroborite from Fuka was calculated as Ca<sub>1.001</sub> B<sub>2.102</sub> O<sub>4.154</sub> · 5.846 H<sub>2</sub>O on the basis of O=10, which is consistent with the ideal formula.

## Discussion

The cell parameters of synthetic calcium borate dihydrate, Ca[B(OH)<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O, have been reported by Ghose (1963), Ozol *et al.* (1964) and others. Subsequently, Simonov *et al.* (1976) determined the cell parameters using a natural specimen. In the present work,

we determined the cell parameters by single crystal method using a four-circle diffractometer;  $a=16.011$ ,  $b=6.688$ ,  $c=7.954\text{\AA}$ ,  $\beta=103.81^\circ$ . Comparing these results, the lattice constants  $b$ ,  $c$  and  $\beta$  are almost equal in all cases, and  $a$  is either approximately  $16\text{\AA}$  or half this length.

Sedlacek and Dornberger-Schiff (1971) reported that apparently different modifications of calcium monoborate dihydrate described by many authors are based on the same structure unit with  $a=4.0\text{\AA}$ . According to their results, it may be considered that the synthetic calcium borate dihydrate reported by many authors, and the natural specimens from

Solongo and Fuka have the same structure.

Hexahydroborite from Fuka occurs as a late stage product, and is closely associated with calcite. Sibirskite and parasibirskite from Fuka are easily decomposed to hexahydroborite and calcite by reaction with water at room temperature. Gode and Kuka (1970) reported that calcium borate hexahydrate,  $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$  is synthesized at 25°C. From this experiment, it is likely that hexahydroborite was formed as a secondary mineral by the reaction of ground water with sibirskite and/or parasibirskite at a low temperature around 25°C.

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