Sibirskite from Fuka, Okayama Prefecture, Japan

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Abstract

Sibirskite was found in a vein consisting of borate minerals which developed along the boundary between crystalline limestone and skarns at Fuka, Okayama Prefecture, Japan. Sibirskite occurs as aggregates of prismatic crystals up to 0.1 mm long and 0.02mm wide, in association with takedaite, frolovite and calcite. Wet and microprobe analyses of sibirskite from Fuka give the empirical formula $Ca_{1.004}H_{1.071}B_{0.974}O_3$ on the basis of O=3. The formula, optical properties and X-ray powder data are consistent with those from the type locality. The space group and cell dimensions determined are $P2_1/a$, a=8.643(6), b=9.523(2), c=3.567(3) Å, $\beta=119.23(3)^\circ$ and Z=4. The calculated density is 2.59 g cm⁻³, and agrees with the measured value of 2.58 g cm⁻³.

It is likely that sibirskite at Fuka was formed by late-hydrothermal alteration of takedaite.

Introduction

Sibirskite is a calcium hydrogen borate, CaHBO₃. The mineral was first found in the Urals by Vasilkova (1962). It occurs in datolite-containing garnet-vesuvianite skarns near the contact of Middle Cambrian limestone with granites in close association with calcite, chlorite and pyrite. Subsequently, the mineral was reported from the Novofrolova deposit by Malinko *et al.* (1974), and from the magnesian skarns of the Chersk and Selenyakhsk ridges of Transbaikalia by Aleksandrov and Malinko (1975). The unit-cell parameters and space group for sibirskite from several Russian deposits were reported by Malinko and Dubinchuk (1996).

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

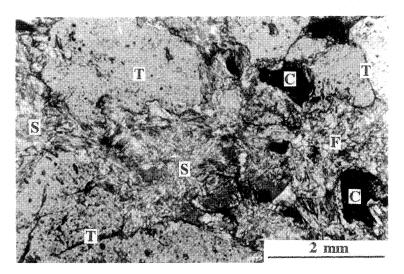


FIG. 1. Photomicrograph of sibirskite. Crossed nicols. Abbreviations: T, takedaite; S, sibirskite; F, frolovite; and C, calcite.

Occurrence

Sibirskite was found in a vein which developed along the boundary between crystalline limestone and gehlenite-spurrite skarns at Fuka. The vein consists of calcium borate minerals such as takedaite (Kusachi *et al.*, 1995a), nifontovite, olshanskyite (Kusachi and Henmi,1994) and frolovite (Kusachi *et al.*, 1995b). Sibirskite occurred as aggregates of prismatic crystals up to 0.1 mm long and 0.02 mm wide in parts formd by late-hydrothermal alteration of takedaite. The altered parts occur up to 2 cm wide along the boundary between takedaite and the crystalline limestone. The associated minerals were takedaite, frolovite, calcite, and as yet, an unidentified mineral. Fig. 1 shows the occurrence of sibirskite. It is likely that sibirskite was formed by alteration of takedaite.

Physical and optical properties

Sibirskite was white with a vitreous luster in hand specimen, and colorless in thin section. Optically, the mineral is biaxial negative with refractive indices α =1.554(2), β =1.638(2) and γ =1.652(2). 2V could not be measured owing to the polysynthetic twinning on (100). The calculated value was 42.6°. The Vickers microhardness was 339 (297~383) kg mm⁻² (25g load) and the density measured by heavy liquid was 2.58 g cm⁻³. In Table 1, these properties are compared with those reported by Vasilkova (1962). The optical properties resemble each other well.

The infrared absorption spectrum of sibirskite was measured by the KBr method for the region 4000 to 250 cm⁻¹, as shown in Fig. 2. The absorption band at 3420 cm⁻¹ is attrib-

TABLE 1. Physical properties of sibirskite.

| | 1. | 2. | |
|----------|-------------------------|-----------|--|
| α | 1.554 | 1.555 | |
| β | 1.638 | 1.643 | |
| γ | 1.652 | 1.658 | |
| 2V | - | 43° | |
| Sign | uniaxial | uniaxial | |
| | negative | negative | |
| D | 2.58 g cm ⁻³ | - | |
| VHN25 | 339 kg mm ⁻² | - | |
| Luster | vitreous | - | |
| Color | white | colorless | |
| | pale gray | | |

^{1.} Fuka, Okayama Prefecture, Japan. Present study.

uted to the OH stretching vibration. Numerous bands observed at 1460 to 310 cm⁻¹ are characteristic of borates.

X-ray study

The X-ray powder data for sibirskite from Fuka was obtained by an Xray diffractometer using Ni-filtered CuKα radiation, and are given in Table 2, comparing with those of the type locality reported by Vasilkova (1962). Twinned crystals were studied using the precession and Weissenberg methods. The diffraction photographs showed sibirskite to be monoclinic with the space group of P2₁/a. The refined unit

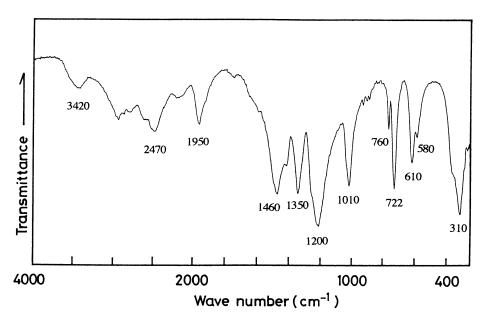


FIG. 2. IR spectrum of sibirskite.

^{2.} Urals. After Vasilkova (1962).

TABLE 2. X-ray powder data for sibirskite from Fuka.

| | 1. | | | 2. | | |
|------------------------|----------|-----------|-----|-------|-----|--|
| hkl | d(calc.) | d(obs.) | I | d | I | |
| 110 | 5.913 | 5.92 | 16 | | | |
| 020 | 4.762 | 4.77 | 33 | 4.65 | 20 | |
| 200 | 3.771 | 3.773 | 13 | 3.74 | 40 | |
| 2 1 0 | 3.506 | 3.515 | 9 | | | |
| 111 | 3.329 | ٦ | | | | |
| | | - 3.329 | 32 | | | |
| $20\overline{1}$ | 3.327 | _ | | | | |
| $21\overline{1}$ | 3.141 | 3.146 | 10 | 3.00 | 20 | |
| 0 1 1 | 2.959 | ٦ | | | | |
| | | 2.955 | 100 | 2.93 | 100 | |
| 220 | 2.956 | J | | | | |
| 1 3 0 | 2.926 | 2.927 | 21 | | | |
| $2 \ 2 \ \overline{1}$ | 2.724 | 2.726 | 14 | 2.69 | 20 | |
| 0 2 1 | 2.606 | 7 | | | | |
| | | - 2.603 | 94 | 2.58 | 100 | |
| 3 1 1 | 2.602 | | | | | |
| $32\overline{1}$ | 2.352 | 2.353 | 12 | 2.33 | 20 | |
| 3 2 0 | 2.223 | 7 | | | | |
| | | - 2.223 | 16 | 2.20 | 40 | |
| 0 3 1 | 2.223 | | | | | |
| $40\overline{1}$ | 2.141 | | | 2.13 | 20 | |
| 3 3 1 | 2.059 | 2.060 | 14 | 2.05 | 40 | |
| 2 4 0 | 2.013 | 2.012 | 8 | | | |
| 3 3 0 | 1.971 | 1.972 | 16 | | | |
| $2 4 \overline{1}$ | 1.936 | 1.936 | 9 | 1.934 | 40 | |
| 041 | 1.891 | 1.891 | 20 | 1.878 | 60 | |
| $31\bar{2}$ | 1.734 | 1.734 | 9 | | | |
| 5 1 1 | 1.701 | 7 | | | | |
| | | 1.700 | 10 | | | |
| 250 | 1.700 | J | | | | |
| a(Å) | | 8.643(| | 3.67 | | |
| b (Å) | | 9.523(2 | | 4.89 | | |
| c (Å) | | 3.567(3) | | 19.30 | | |
| β(°) | | 119.23(3) | | 61 | | |

- 1. Fuka, Okayama Prefecture, Japan. Present study.
- Urals. After Vasilkova (1962). The cell dimensions are values reported by Dubinchuk and Malinko (1974).

cell dimensions are a = 8.643(6), b = 9.523(2), c = 3.567(3)Å, $\beta = 119.23(3)^{\circ}$ and Z = 4. The calculated density is 2.59 g cm⁻³ and agrees with the measured value.

Thermal behavior

DTA and TG curves were obtained by heating sibirskite from room temperature to 900°C at a rate of 10°C/min. in nitrogen flow. The curves are shown in Fig. 3. The DTA curve has an endothermic peak at 375°C and no exothermic peak. The temperature of the endothermic peak is lower than that at 430°C reported by Vasilkova (1962).

Chemical composition

A sibirskite specimen from Fuka was selected for chemical analyses by hand picking separation under a binocular microscope. The concentration of Ca of sibirskite was obtained using an electron microprobe analyzer. The B content was determined by means of wet chemistry, and the H₂O content was determined from ignition loss at 900°C. The results are given in Table 3, and are compared with those reported by Vasilkova (1962) and the theoretical values calculated from the ideal formula of CaHBO₃. The empirical formula of sibirskite from Fuka is Ca_{1.004}H_{1.071}B_{0.974}

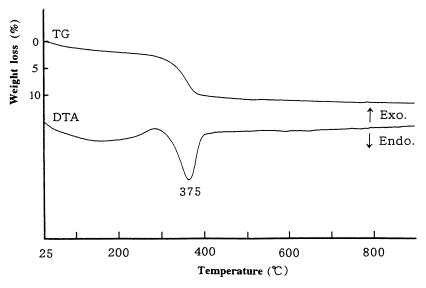


FIG. 3. DTA and TG curves of sibirskite.

TABLE 3. Chemical composition of sibirskite.

| | 1 | 2. | 3. | | | | |
|--------------------------------|----------|--------|--------|--|--|--|--|
| 337.1.1.4.0/ | <u> </u> | | | | | | |
| Weight % | | | 7.73 | | | | |
| SiO ₂ | | | 7.72 | | | | |
| TiO2 | | | 0.03 | | | | |
| Al ₂ O ₃ | | | 2.43 | | | | |
| B ₂ O ₃ | 33.83 | 34.85 | 13.51 | | | | |
| FeO | | | 1.01 | | | | |
| MgO | | | 10.06 | | | | |
| MnO | | | 0.29 | | | | |
| CaO | 56.21 | 56.14 | 41.78 | | | | |
| Na ₂ O | | | 0.04 | | | | |
| CO ₂ | | | 16.72 | | | | |
| H2O(+) | 9.62 | 9.01 | 6.38 | | | | |
| H ₂ O(-) | 0.00 | | 0.36 | | | | |
| C | | | 0.12 | | | | |
| S | | | 0.48 | | | | |
| - O=S | | | 0.24 | | | | |
| Total | 99.66 | 100.00 | 100.69 | | | | |
| Mole ratios (basis : $O = 3$) | | | | | | | |
| Ca | 1.004 | 1 | | | | | |
| В | 0.974 | 1 | | | | | |
| Н | 1.071 | 1 | | | | | |

^{1.} Fuka, Okayama Prefecture, Japan. Present study.

O₃ on the basis of O=3, which is consistent with the ideal formula. Sibirskite was easily soluble in dilute hydrochloric acid.

Discussion

Vasilkova (1962) reported that the symmetry of sibirskite is orthorhombic. Subsequently, Dubinchuk and Malinko (1974) reported that sibirskite from the type locality is monoclinic with the cell dimensions of a=3.67, b=4.89, c=19.30Å and $\beta=61$ °. Malinko and Dubinchuk (1996) also reported that the cell dimensions for sibirskite from several Rissian deposits are a=3.67~3.68, b=4.89, c=19.30~19.32Å and $\beta=62$ ~63°. The single-crystal studies of sibirskite from Fuka showed different cell dimensions from those reported by Dubinchuk and Malinko, and Malinko and Dubinchuk, i.e., a=8.643(6), b=9.523(2),

^{2.} Theoretical CaHBO3.

^{3.} Urals. After Vasilkova (1962).

c = 3.567(3)Å and $\beta = 119.23(3)^\circ$. These parameters are consistent with the X-ray powder data for sibirskite from the type locality.

The X-ray powder pattern of sibirskite from Fuka is distinctly different from that of synthetic CaHBO₃ reported by Lehmann *et al.* (1958). His powder data are similar to those of synthetic 2CaO \cdot B₂O₃ \cdot H₂O reported by Schäfer (1968). The unit cell dimensions of the 2CaO \cdot B₂O₃ \cdot H₂O are monoclinic with a =6.719(2), b =5.434(3), c =3.555(1)Å and β = 92.87(4)°. Sibirskite from Fuka and the type locality, therefore, appear to have a different structure from the synthetic CaHBO₃ and 2CaO \cdot B₂O₃ \cdot H₂O.

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References

- ALEKSANDROV, S. M. and MALINKO, S. V. (1975) Geochemical peculiarities of endogenic and hypergenic alterations of carbonatoborates. *Geokhimiya*, 1, 3–16 (in Russian).
- DUBINCHUK, V. T. and MALINKO, S. V. (1974) Electron-microscopic study of calciborite and sibirskite. *Dokl. Akad. Nauk SSSR*, **216**, 166–168 (in Russian).
- KUSACHI, I. and HENMI, C. (1994) Nifontovite and olshanskyite from Fuka, Okayama Prefecture, Japan. *Mineral. Mag.*, **58**, 279–284.
- KUSACHI, I., HENMI, C. and KOBAYASHI, S. (1995a) Takedaite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineral. Mag.*, **59**, 549–552.
- KUSACHI, I., HENMI, C. and KOBAYASHI, S. (1995b) Frolovite from Fuka, Okayama Prefecture, Japan. *Mineral. J.*, 17, 330–337.
- LEHMANN, H.-A., ZIELFELDER, A. and HERZOG, G. (1958) Die hydrogenmonoborate des calciums. *Zeits. anorg. allgem. Chem.*, **296B**, 199–207.
- MALINKO, S. V., DUBINCHUK, V. T. and MESHCHANKINA, V. I. (1974) Electron microscopic study of the surface changes of endogenous borates. *Dokl. Akad. Nauk SSSR*, **218**, 186–188 (in Russian).
- MALINKO, S. V. and DUBINCHUK, V. T. (1996) New data on calcium borates: sibirskite and korzhinskite. *Zapiski Vses. Mineralog. Obshch*, **125**, 60–71 (in Russian).
- SCHÄFER, U. L. (1968) Synthese und rontgenographische Untersuchung der Borate $3\text{CaO} \cdot \text{B}_2\text{O}_3$, $2\text{CaO} \cdot \text{B}_2\text{O}_3$ und $2\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Neues Jahrb. Mineral. Monatsh., 75–80.
- VASILKOVA, N. N. (1962) A new calcium borate, sibirskite. Zapiski Vses. Mineralog. Obshch, 91, 455–464 (in Russian).

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