Parasibirskite, a new mineral from Fuka, Okayama Prefecture, Japan

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ABSTRACT

Parasibirskite, with the ideal formula $Ca_2B_2O_5$ ·H₂O, is a new mineral species found at Fuka, Okayama Prefecture, Japan. It is a polymorph of sibirskite, CaHBO₃, and occurs as subparallel aggregates of tabular crystals up to $40 \times 20 \times 3 \mu m$ in size. Associated minerals are takedaite, olshanskyite, sibirskite, frolovite and calcite. The mineral is white, and has a weak pearly luster. Optically, the mineral is biaxial positive, α 1.556(2), β 1.593(2), γ 1.663(2) (λ 589 nm). The Vickers microhardness of aggregates is 121 kg mm⁻². The mineral is monoclinic with space group of $P2_1/m$, *a* 6.722(4), *b* 5.437(2), *c* 3.555(2) Å, β 93.00(5)°, V 129.8(2) Å³. The strongest lines in the X-ray powder pattern [*d* in Å (*I*)(*hkl*)] are 2.237(100)(300), 6.73(70)(100), 2.975(60)(011), 3.354(30)(200), 2.855(20)(210) and 1.776(20) (002). Wet chemical analysis, electron-microprobe analysis and ICP emission spectrometry give the values CaO 56.06 %, B₂O₃ 34.10 %, H₂O 9.97 % and total 100.13%. The empirical formula calculated on the basis of O = 6 is Ca_{1.985}B_{1.945}O_{4.901}·1.099H₂O, for Z = 1, D_{calc} 2.54 and D_{meas} 2.50(1) g cm⁻³. Parasibirskite is formed by hydrothermal alteration of takedaite.

KEYWORDS: parasibirskite, sibirskite, gehlenite-spurrite skarns, borate, Fuka, Japan.

Introduction

DURING a mineralogical survey of the gehlenitespurrite skarns at Fuka, Okayama Prefecture, Japan, Kusachi *et al.* (1997) reported the occurrence of an unidentified hydrous borate mineral associated with sibirskite and frolovite. Subsequent study has shown the mineral to be a natural analogue of synthetic 2CaO·B₂O₃·H₂O reported by Schäfer (1968). The new mineral has been named parasibirskite as a polymorph of sibirskite, CaHBO₃. The mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The type mineral of parasibirskite is deposited at the National

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Science Museum, Tokyo, Japan. The present paper deals with its mode of occurrence and mineralogical properties.

Occurrence

At Fuka, Okayama Prefecture, primary skarn minerals such as gehlenite and spurrite were formed as pyrometasomatic products of limestone. In subsequent retrograde hydration reactions, most of the gehlenite crystals were altered to retrograde minerals such as vesuvianite, hydrogrossular and bicchulite (Henmi *et al.*, 1973). Retrograde changes of spurrite crystals, on the other hand, are not extensive.

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FIG. 1 Photomicrograph of parasibirskite. Crossed nicols. Abbreviations: P = parasibirskite, F = frolovite and C = calcite.

During the post-metasomatic stage, an irregular vein consisting of borate minerals penetrated along the boundary between crystalline limestone and the skarns. In the vein, an anhydrous borate, takedaite (Kusachi *et al.*, 1995*a*), was primarily formed by the reaction of boron-bearing fluids with limestone. At the circumference of the vein, hydrous borates such as nifontovite, olshanskyite (Kusachi and Henmi, 1994), frolovite (Kusachi *et al.*, 1995*b*) and sibirskite (Kusachi *et al.*, 1997) were secondarily formed by late-hydrothermal alteration of takedaite.

Parasibirskite was found in the altered part of takedaite, and occurred as subparallel aggregates of tabular crystals up to 40 μ m long, 20 μ m wide and 3 μ m thickness, in association with takedaite, olshanskyite, frolovite, sibirskite and calcite. The occurrence of parasibirskite from Fuka is shown in Fig. 1. It is likely that parasibirskite was formed by hydrothermal alteration of takedaite.

Physical and optical properties

Parasibirskite was white with a weak pearly lustre in hand specimen, and colourless in thin-section. The cleavage is perfect on (100). Optically, the mineral was biaxial positive with refractive indices



FIG. 2. IR spectrum of parasibirskite.

PARASIBIRSKITE, A NEW MINERAL

		2				
Ī	d _(meas)	d _(calc)	h k l	d	Ι	
70	6.73	6.7128	1 0 0	6.71	70	
10	4.23	4.2250	1 1 0	4.23	10	
		3.5501	0 0 1	3.55	<5	
30	3.354	3.3564	2 0 0	3.36	30	
		3.0725	1 0 1	3.076	5	
60	2.975	2.9727	0 1 1	2.973	60	
20	2.855	2.8560	2 1 0	2.857	20	
		2.7632	Ī 1 1	2.760	<5	
10	2.721	2.7185	0 2 0	2.715	10	
		2.6749	1 1 1	2.676	<5	
		2.3776	2 0 1	2.378	<5	
100	2.237	2.2376	3 0 0	2.237	100	
		2.1784	2 1 1	2.181	<5	
		2.1584	0 2 1	2.158	<5	
		2.1125	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.112	<5	
10	2.075	2.0742	$\bar{1} 2 1$			
			}	2.071	10	
		2.0692	3 1 0			
10	2.036	2.0360	1 2 1	2.035	10	
		1.9393	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1.936	<5	
5	1.842	1.8424	$\bar{2}$ 2 1	1.840	5	
10	1.826	1.8267		1.825	10	
10	1.790	1.7897	2 2 1	1.790	10	
20	1.776	1.7752	0 0 2	1.776	20	
		1.7512	3 1 1	1.752	5	
5	1.750	1.7497	1 3 0	1.749	5	
a (Å) =	6.722(4)			6.7	6.719(2)	
b (Å) =	5.437(2)			5.4	5.434(3)	
c(Å) =	3.555(2)			3.5	3.555(1)	
β (°) =	93.00(5)			92.	92.87(4)	

TABLE 1. X-ray powder data for parasibirskite

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

2. Synthetic Ca₂B₂O₅·H₂O (Schäfer, 1968)

α 1.556(2), β 1.593(2), γ 1.663(2), 2V 74.8° (calc.). 2V could not be measured due to the thinness of crystals. The Vickers microhardness of aggregates was 121(109–155) kg mm⁻² (25 g load). The measured density by heavy liquids was 2.50(1) g cm⁻³, the calculated density being 2.54 g cm⁻³. The measured density was lower than that of synthetic 2CaO·B₂O₃· H₂O reported by Schäfer (1968), which was found to be 2.60 g cm⁻³.

The infrared absorption spectrum of parasibirskite was measured by the KBr method for the region 4000 to 250 cm⁻¹, as shown in Fig. 2. The absorption band at 3350 cm⁻¹ is attributed to the OH stretching vibration. Numerous bands observed at 1420 to 305 cm^{-1} are characteristic of borates.

Chemical composition

Chemical analysis using an electron-microprobe analyser revealed the presence of Ca, B and O, and the absence of any other element. The concentration of Ca was obtained by an electron-microprobe analyser, the B content was determined by ICP, and the H₂O content was determined from ignition loss and TGA at 900°C. Chemical analysis gave the values CaO 56.06%, B₂O₃ 34.10%, H₂O 9.97% and total 100.13%. The empirical formula calculated on the basis of O = 6is therefore $Ca_{1.985}B_{1.945}O_{4.901} \cdot 1.099H_2O$ which gives the ideal formula $Ca_2B_2O_5 \cdot H_2O$. Parasibirskite easily alters to calcium borate hydrate ($CaB_2O_4 \cdot 6H_2O$) and calcite in water, and is also easily soluble in dilute hydrochloric acid with no effervescence.

X-ray studies

The X-ray powder data for parasibirskite were obtained by an X-ray diffractometer using Ni-filtered Cu- $K\alpha_1$ radiation. Single crystal studies could not be carried out because of the small crystal size. Reflections of parasibirskite from Fuka were indexed on the monoclinic cell, *a* 6.719, *b* 5.434, *c* 3.555 Å and β 92.87°, reported for synthetic 2CaO·B₂O₃·H₂O (Schäfer, 1968). Unit cell dimensions, refined by least squares from the present powder diffraction data for parasibirskite, were *a* 6.722(4), *b* 5.437(2), *c* 3.555(2) Å and β 93.00(5)°. The X-ray powder data are given in Table 1, and compared with those of synthetic 2CaO·B₂O₃·H₂O reported by Schäfer.

Thermal behaviour

DTA and TG curves were obtained by heating parasibirskite from room temperature to 900° C at a rate of 10° C min⁻¹, as shown in Fig. 3. The DTA curve has endothermic peaks at 371 and 414°C corresponding to the loss of water. An exothermic peak was not observed. On heating the mineral at 900° C, calcium borate (Ca₂B₂O₅) appeared as a crystalline phase.

Discussion

Schäfer(1968) synthesized single crystals of $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ from Ca(OH)₂ and H₃BO₃ at temperatures between 100 and 300°C under saturated water pressure. The chemical composition and X-ray powder data for parasibirskite from Fuka agree well with those for the synthetic 2CaO·B₂O₃·H₂O. Therefore, parasibirskite from Fuka is a natural analogue of the synthetic 2CaO·B₂O₃·H₂O. 2CaO·B₂O₃·H₂O in an oxide form may be written as Ca₂B₂O₃·H₂O and can also be expressed as 2(CaHBO₃). The mineral



FIG. 3. DTA and TG curves of parasibirskite.

with the chemical formula of CaHBO₃ is known as sibirskite. Kusachi et al. (1997) reported that chemical data of sibirskite from Fuka are consistent with the ideal formula of CaHBO₃. The chemical composition of parasibirskite agrees with that of sibirskite from Fuka, and their infrared absorption spectrum and thermal behaviour are similar. X-ray powder data for parasibirskite, however, are different from those for sibirskite from Fuka. The unit cell parameters for parasibirskite are a 6.722(4), b 5.437(2), c 3.555(2) Å and β 93.00(5)° although those for sibirskite from Fuka are *a* 8.643(6), *b* 9.523(2), c 3.567(3) Å and β 119.23(3)° (Kusachi *et al.*, 1997). From these data, it is considered that there is a polymorphic relationship between parasibirskite and sibirskite.

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