Nifontovite and olshanskyite from Fuka, Okayama Prefecture, Japan

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Abstract

Nifontovite and olshanskyite, two rare hydrous calcium borate minerals, have been found in crystalline limestone near gehlenite–spurrite skarns at Fuka, Okayama Prefecture. Nifontovite occurs as aggregates of tabular crystals up to 5 cm long and 1.5 cm wide, and rarely as euhedral crystals up to 1 mm long. Olshanskyite occurs as anhedral masses, or as micro-twinned platy crystals up to 1 cm long. Wet chemical analyses give the empirical formulae $Ca_{3.052}B_{5.991}O_{6.038}(OH)_{12}\cdot 1.96H_2O$ and $Ca_{2.888}B_{3.997}(OH)_{18}$ on the basis of O = 20 for nifontovite and OH = 18 for olshanskyite, respectively. The formulae are consistent with those from type localities.

The X-ray powder data for these minerals were determined with accuracy. The unit cell parameters of nifontovite agree closely with those published previously. X-ray studies show that olshanskyite is triclinic with the possible space group $P\bar{1}$ or $P1$ and a = 9.991(5), b = 14.740(11), c = 7.975(3) Å, α = 94.53(4), β = 69.08(3), γ = 112.44(5)° and Z = 3. The density 2.19 g cm^{-3} (meas.) obtained for olshanskyite agrees with the estimated ideal value 2.31 g cm^{-3} (calc.). Nifontovite was formed by hydrothermal alteration of an anhydrous borate, and olshanskyite was formed by hydrothermal alteration of nifontovite and the anhydrous borate.

KEYWORDS: nifontovite, olshanskyite, borate, skarn, crystalline-limestone, Fuka, Japan

Introduction

NIFONTOVITE, $Ca_3B_6O_6(OH)_{12}\cdot 2H_2O$, was originally found at the Novofrolovo mine of the Turinsk ore deposit in the central Urals by Malinko and Lisitsyn (1961). The mineral occurs in skarn, and is closely associated with grossular-andradite garnet and szaibelyite. Olshanskyite, $Ca_3B_4(OH)_{18}$, was found in magnesian skarn in eastern Siberia by Bogomolov *et al.* (1969). The mineral from the type locality occurs as fibrous aggregates of polysynthetically twinned crystals up to 3 mm in size, and closely associated with limonite, szaibelyite, calcite, etc.

The mineralogical data of nifontovite and olshanskyite from the type localities have been reported only for impure specimens. No other published data are known to the writers.

During our mineralogical survey of the gehlenite–spurrite skarns at Fuka, Okayama Prefecture, nifontovite and olshanskyite were found as pure material. The present paper deals with the modes of occurrence and the mineralogical properties of nifontovite and olshanskyite from Fuka.

Occurrence

In the Fuka district, located about 40 km northwest of Okayama city, many quartz monzonite dykes occur in limestones. Skarn minerals such as gehlenite and spurrite were primarily formed as high-temperature metasomatic products on both sides of the dykes. During the post-metasomatic stage, the skarns were cut by numerous veins which consist of hydrated calcium silicates such as tobermorite (Mitsuda *et al.*, 1972), hillebrandite, foshagite, afwillite, jennite (Kusachi *et al.*, 1989), clino-

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TABLE 1. Optical and physical properties of nifontovite and olshanskyite.

	Nifontovite		Olshanskyite	
	1	2	1	3
α	1.573	1.575	1.553	1.557
β	1.577	1.578	1.562	1.568(calc)
γ	1.585	1.584	1.567	1.570
2V	66°	76°	60°	54°
Sign	positive	positive	negative	negative
VHN_{25}	198~221	-	143~188	-
MHN	4	3.5	3.5	4
D	2.35	2.36	2.19	2.23

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Central Urals. After Malinko and Lisitsyn (1961).
3. Eastern Siberia. After Bogomolov *et al.* (1969).

tobermorite (Henmi and Kusachi,1992), etc.; fluorine-bearing minerals such as bultfonteinite (Kusachi *et al.*, 1984) and fluorite; and boron-bearing minerals such as oyelite (Kusachi *et al.*, 1984) and henmilite (Nakai *et al.*, 1986; Kusachi, 1992).

Nifontovite and olshanskyite were found in an irregular body up to 3 m long and 2 m wide in crystalline limestone in the vicinity of the skarns. At the central part of the body, an unidentified anhydrous borate occurs in association with calcite. At the outer-most skarn side of the body, nifontovite occurs in the area up to 50 cm long and 20 cm wide. Olshanskyite occurs along the boundary between the anhydrous borate and nifontovite. The width ranges from 50 cm to 1 m. The body is cut by calcite veins which contain bultfonteinite, cuspidine and henmilite.

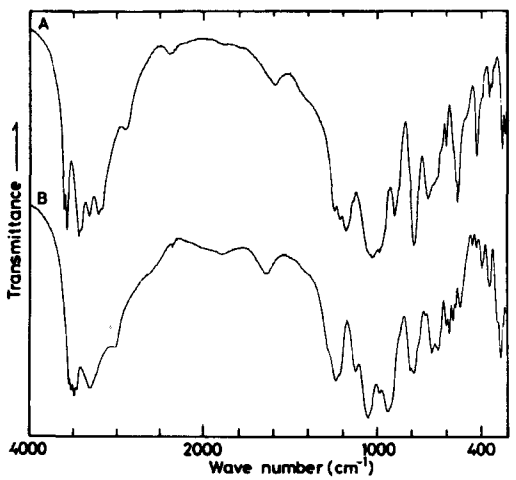

FIG. 1. Infrared absorption spectra of nifontovite (A) and olshanskyite (B).

Nifontovite

Physical and optical properties

Nifontovite from Fuka was found as aggregates of tabular crystals up to 5 cm long and 1.5 cm wide and rarely as euhedral crystals up to 1 mm long. The mineral is grey or colourless with a vitreous lustre in hand specimen, and colourless in thin-section. Optically, the mineral is biaxial positive with refractive indices $\alpha = 1.573$, $\beta = 1.577$, $\gamma = 1.585$, $2V = 66°$, and the elongation is positive. The Vickers microhardness is 198–221 kg mm^{-2} (25 g load). The density measured with a pycnometer is 2.35 g cm^{-3}. In Table 1, the properties are compared with those reported by Malinko and Lisitsyn (1961). They resemble each other well.

The infrared absorption spectrum of nifontovite was measured by the KBr method for the region 4000 to 250 cm^{-1}, as shown in Fig. 1. The absorption bands at 3600 to 3200 cm^{-1} are attributed to the OH and H_2O stretching vibrations. Numerous bands around 1000 cm^{-1} are characteristic of borates.

X-ray study

The X-ray powder data for nifontovite were obtained by X-ray diffractometer using Ni-filtered Cu-$K\alpha$ radiation. The data are shown in Table 2, and they are compared with those of the material from central Urals reported by Shashkin *et al.* (1971). The cell parameters calculated from the powder data are $a = 13.12(1)$, $b = 9.500(5)$, $c = 13.56(1)$ Å and $\beta = 119.62(5)°$. Although some X-ray diffraction lines for nifontovite from Fuka are absent in the pattern of the material from the type locality, the cell parameters agree well with each other.

Chemical composition

The nifontovite specimen from Fuka was purified for chemical analyses by hand picking separation under the binocular microscope. The concentrations of Ca and B were determined by means of wet-chemical analyses. The H_2O content was measured with a Karl-Fisher Moisture meter and ignition loss at 900°C. The result is given in Table

TABLE 2. X-ray powder data for nifontovite.

h k l	1 d(calc.)	1 d(obs.)	1 I	2 d	2 I
$\bar{1}$ 1 1	7.330	7.36	100	7.28	100
1 1 0	7.299				
0 0 2	5.894	5.92	21		
$\bar{2}$ 0 2	5.761	5.77	46	5.75	50
2 0 0	5.702	5.71	28		
$\bar{1}$ 1 2	5.517	5.54	80	5.52	60
0 2 1	4.406	4.42	22	4.42	40
$\bar{1}$ 1 3	4.033	4.04	19		
1 1 2	4.008	4.02	27	4.00	40
$\bar{3}$ 1 2	3.924	3.927	22		
$\bar{2}$ 2 1	3.847	3.857	80	3.84	80
0 2 2	3.698	3.711	30	3.69	50
$\bar{3}$ 1 3	3.561	3.567	11	3.54	40
$\bar{1}$ 1 4	3.093	3.083	28		
$\bar{3}$ 1 4	3.054	3.060	35		
$\bar{1}$ 3 1	3.053				
0 2 3	3.028	3.037	19		
0 0 4	2.947	2.957	52	2.95	60
$\bar{4}$ 0 4	2.881	2.886	6		
2 2 2	2.739	2.743	62	2.75	70
$\bar{4}$ 2 2	2.699	2.699	10		
$\bar{4}$ 2 3	2.636	2.639	18	2.63	40
$\bar{3}$ 1 5	2.583	2.590	8		
$\bar{1}$ 3 3	2.581				
3 1 2	2.555	2.559	20	2.55	40
$\bar{5}$ 1 3	2.518	2.518	7	2.51	20
$\bar{1}$ 1 5	2.485	2.481	36		
4 2 0	2.445	2.449	93		
$\bar{3}$ 3 3	2.443	2.441	71		
$\bar{5}$ 1 4	2.416	2.417	28	2.41	20
0 4 0	2.375	2.382	8	2.38	20
$\bar{2}$ 2 5	2.347	2.353	15	2.35	30
3 3 1	2.246	2.249	19		
$\bar{5}$ 1 5	2.240	2.239	44	2.238	80
5 1 0	2.218	2.217	23	2.214	70
2 0 4	2.210	2.212	24		
0 4 2	2.203	2.204	14		
$\bar{2}$ 4 3	2.091	2.092	6	2.091	20
$\bar{1}$ 1 6	2.068	2.066	34	2.063	80
1 1 5	2.061				
$\bar{2}$ 2 6	2.016	2.022	8	2.023	20
$\bar{5}$ 3 4	1.961			1.958	20
$\bar{2}$ 4 4	1.945	1.942	13	1.946	30
2 4 2	1.938				
$\bar{4}$ 4 2	1.924	1.923	17	1.923	50
6 0 0	1.901	1.902	10	1.900	40
3 1 4	1.878	1.876	12	1.878	50
$\bar{6}$ 2 1	1.876				
5 3 0	1.851	1.852	18	1.854	60
0 4 4	1.849	1.845	25		
$\bar{3}$ 3 6	1.839	1.835	19	1.838	50
0 2 6	1.816			1.815	20
$\bar{7}$ 1 2	1.786	1.783	14	1.783	50
$\bar{2}$ 4 5	1.783				
$\bar{1}$ 1 7	1.768	1.767	9	1.764	30
4 2 3	1.767				
1 5 2	1.746	1.743	10	1.739	50
2 2 5	1.745				
$\bar{7}$ 1 1	1.706	1.705	8	1.706	60
a (Å)		13.12(1)		13.09	
b (Å)		9.500(5)		9.49	
c (Å)		13.56(1)		13.53	
β (°)		119.62(5)		119.47	

1. Fuka, Okayama Prefecture, Japan. Cu/Ni radiation. Diffractometer method. The present work.
2. Central Urals. Unfiltered Fe radiation. Camera method. After Shashkin *et al.* (1971).

3 and it is compared with the values calculated from the ideal formula, $Ca_3B_6O_6(OH)_{12}\cdot 2H_2O$ given by Yegorov-Tismenko *et al.* (1973). The analytical data lead to the empirical formula, $Ca_{3.052}B_{5.991}O_{6.038}(OH)_{12}\cdot 1.96H_2O$, on the basis of O = 20. The chemical composition of nifontovite from Fuka is very close to that of the ideal formula. Nifontovite is easily soluble in dilute hydrochloric acid.

Thermal behaviour

DTA and TG curves were obtained by heating from room temperature to 900°C at a rate of 10°C min^{-1}. The DTA curve has strong endothermic peaks at 208 and 306°C, corresponding to the loss of water, and a sharp exothermic peak at 702°C,

TABLE 3. Chemical analyses of nifontovite and olshanskyite.

	Nifontovite 1	Nifontovite 2	Olshanskyite 1	Olshanskyite 3
CaO	32.31	32.29	34.50	35.84
B_2O_3	39.37	40.08	29.64	29.66
$H_2O(+)$	27.08	27.63	34.54	34.50
$H_2O(-)$	0.83	-	1.21	-
Total	99.59	100.00	99.89	100.00
	(O = 20)		(OH = 18)	
Ca	3.052	3.00	2.888	3.00
B	5.991	6.00	3.997	4.00
OH	12.000	12.00	18.000	18.00
H_2O	1.962	2.00		
O	6.038	6.00		

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Theoretical $Ca_3B_6O_6(OH)_{12}\cdot 2H_2O$.
3. Theoretical $Ca_3B_4(OH)_{18}$.

TABLE 4. X-ray powder data for olshanskyite.

h k l	1 d(calc.)*	d(obs.)	I	2 d	I
1 0 0	8.633	8.63	32		
0 0 1	7.433	7.42	34	7.61	50
1 0 1	6.991	6.98	16		
0 2 0	6.797	6.79	52	6.78	50
1 $\bar{2}$ 0	6.723	6.72	40		
1 $\bar{2}$ 1	5.608	5.61	27		
0 2 1	5.191	5.18	16		
0 2 $\bar{1}$	4.858	4.85	9		
1 0 $\bar{1}$	4.847				
1 2 0	4.564	4.56	28		
2 $\bar{2}$ 1	4.562				
2 $\bar{2}$ 0	4.499	4.49	49	4.50	30
2 0 1	4.488				
1 2 1	4.368	4.36	8		
1 $\bar{2}$ 2	3.588	3.581	24		
1 2 $\bar{1}$	3.540	3.534	20		
0 1 $\bar{2}$	3.526				
2 $\bar{2}$ 2	3.474	3.471	8		
2 $\bar{2}$ $\bar{1}$	3.390	3.388	16		
0 2 2	3.356	3.353	15	3.35	50
2 0 $\bar{1}$	3.264	3.265	19		
2 $\bar{3}$ $\bar{1}$	3.165	3.164	18		
3 $\bar{2}$ 0	3.107	3.104	16		
0 4 $\bar{1}$	3.016	3.015	20	3.05	80
1 $\bar{2}$ $\bar{2}$	2.996	2.990	8		
3 0 0	2.878	2.873	100	2.81	100
2 2 2	2.839	2.838	9		
1 4 1	2.799	2.798	27		
3 $\bar{4}$ 0	2.777	2.775	32		
1 $\bar{5}$ 1	2.774				
3 1 2	2.591	2.586	16		
2 0 3	2.580				
1 1 3	2.573	2.573	35	2.57	40
2 $\bar{2}$ 3	2.549	2.545	22		
4 $\bar{2}$ 1	2.492	2.492	14	2.48	20
3 2 1	2.473	2.470	9		
4 $\bar{3}$ 1	2.473				
2 $\bar{6}$ 0	2.419	2.419	19		
3 $\bar{2}$ 3	2.392	2.388	11	2.37	30
3 $\bar{4}$ $\bar{1}$	2.386				
2 3 $\bar{1}$	2.323	2.322	10		
4 $\bar{3}$ 0	2.321				
0 2 $\bar{3}$	2.280	2.279	23		
2 $\bar{4}$ $\bar{2}$	2.267	2.263	19		
0 6 0	2.266				
3 1 $\bar{1}$	2.247	2.246	17	2.25	30
3 1 3	2.209	2.205	8	2.21	20
0 6 1	2.209				
		2.181	4		
		2.155	11	2.15	10
		2.130	8		
		2.110	7		
		2.079	12	2.09	10
		2.058	14		
		2.020	20	2.02	40
		2.003	14		
		1.982	15		

corresponding to recrystallization. The thermal behaviour of nifontovite from Fuka is similar to that reported by Malinko and Lisitsyn (1961).

Olshanskyite

Physical and optical properties

Olshanskyite from Fuka was found as anhedral masses, and as micro-twinned platy crystals up to 1 cm long. The mineral is white or pale brown with a vitreous lustre in hand specimen and colourless in thin-section. Optically, the mineral is biaxial negative with refractive indices $\alpha = 1.553$, $\beta = 1.562$, $\gamma = 1.567$, $2V = 60°$, and the elongation is negative. The Vickers microhardness is 143–188 kg mm^{-2} (25 g load). The density is 2.19 g cm^{-3}. In Table 1, the properties are compared with those reported by Bogomolov *et al.* (1969). They resemble each other well.

The infrared absorption spectrum was measured by the same method as nifontovite, which is shown in Fig. 1. The absorption bands are similar to those of nifontovite.

X-ray study

Precession and Weissenberg photographs show that olshanskyite is triclinic with the possible space group $P\bar{1}$ or $P1$. The unit cell parameters refined from powder data are a = 9.991(5), b = 14.740(11), c = 7.975(3) Å, α = 94.53(4), β = 69.08(3) and γ = 112.44(5)°. The calculated density is 2.31 g cm^{-3} on the basis of Z = 3. The X-ray powder data for olshanskyite are shown in

TABLE 4. Contd.

1.959	10	1.958	30
1.940	11		
1.916	11	1.917	30
1.909	10		
1.892	13		
1.883	8		
1.875	11	1.872	30
1.860	9		
1.855	8		
1.831	5	1.820	10
1.808	10		
1.799	12	1.800	30
1.791	10		

1. Fuka, Okayama Prefecture, Japan. Cu/Ni radiation. Diffractometer method. The present work.
2. Eastern Siberia. Unfiltered Fe radiation. Camera method. After Bogomolov *et al.* (1969).
* The calculated values are based on $a = 9.991$, $b = 14.740$, $c = 7.975$Å, $\alpha = 94.53$, $\beta = 69.08$, $\gamma = 112.44°$.

Table 4, in which data from the current material are compared with those of the material from eastern Siberia reported by Bogomolov *et al.* (1969). The powder pattern of olshanskyite from Fuka shows more diffraction lines than patterns reported by those authors, but the two patterns resemble each other very closely.

Chemical composition

Olshanskyite from Fuka was analysed by the same methods as nifontovite. The result is given in Table 3 and compared with the values calculated from the ideal formula, $Ca_3B_4(OH)_{18}$reported by Bogomolov *et al.* (1969). The analytical data lead to the empirical formula, $Ca_{2.888}B_{3.997}(OH)_{18}$, on the basis of OH = 18. The empirical formula of olshanskyite from Fuka is consistent with the ideal formula. Olshanskyite is also easily soluble in dilute hydrochloric acid.

Thermal behaviour

DTA and TG curves were obtained by the same methods as nifontovite. The DTA curve shows a strong endothermic peak at 195°C, and weak exothermic peaks at 650 and 706°C. The endothermic peak represents the loss of water. The DTA curve of olshanskyite from Fuka is very close to that reported by Bogomolov *et al.* (1969).

Discussion

Malinko and Lisitsyn (1961) reported the chemical formula of nifontovite to be $CaO{\cdot}B_2O_3{\cdot}2.3H_2O$, after correcting analytical data for small amounts of impurities. Subsequently, Yegorov-Tismenko *et al.* (1973) gave a different formula: $Ca_3B_6O_6(OH)_{12}{\cdot}2H_2O$. This formula was determined by crystal structure analysis of the material from the type locality. This formula may be written as $3CaO{\cdot}3B_2O_3{\cdot}8H_2O$ in oxide form. The CaO/B_2O_3 ratio is the same between these two formulae, and equal to unity. The only difference between the two formulae is their respective water contents. The chemical formula of nifontovite from Fuka shown in Table 3 can be expressed as follows; $3.05CaO{\cdot}3.00B_2O_3{\cdot}7.96H_2O$. Therefore, the present data support the formula given by Yegorov-Tismenko *et al.* (1973).

Bogomolov *et al.* (1969) gave $Ca_3B_4(OH)_{18}$ as the chemical formula of olshanskyite after correcting analytical data for small amounts of impurities. The present data verify this formula.The X-ray powder data for nifontovite and olshanskyite are listed in JCPDS cards No. 27–68 and 22–144, respectively. Some diffraction lines of these two minerals from Fuka are absent in those of the materials from the type localities, as shown in Tables 2 and 4. We consider that some proper diffraction lines must be overlooked when the diffraction lines from coexisting minerals were omitted from the original data. The powder data for olshanskyite are well indexed using the cell parameters which are determined in the present study as shown in Table 4.

Nifontovite and olshanskyite from Fuka occur around an unidentified anhydrous borate phase. From the modes of occurrence, the formation of these minerals may be considered as follows: (1) the unidentified anhydrous borate was formed by reaction of boron-bearing fluids with limestone; (2) nifontovite was formed by hydrothermal alteration of the anhydrous borate; and (3) the late-hydrothermal solution converted nifontovite and the anhydrous borate to olshanskyite.

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