Bornemanite-a new silicophosphate of sodium, titanium, niobium, and barium[1]

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The mineral bornemanite was found in the natrolite zone of the "Jubilee" pegmatoidal body in the Lovozero alkalic massif (Bussen et al., 1972). The name is in honor of Irina Dimitriyevna Borneman-Starynkevich, well-known student of the minerals of the Khibina and Lovozero tundras.

Bornemanite forms yellowish platy deposits up to 10 x 8 x 0.2 mm developed along cleavages and on the surface of large tabular crystals of brown lomonosovite (sample 1), rarely accumulations of curved plates in natrolite (sample 2). It contains small inclusions of lomonosovite and needles of aegirine, and forms intergrowths, parallel to {001}, with lomonosovite. The plates have aggregate structure and consist of very fine leaflets (0.2 x 0.1 x 0.05 mm) elongated along the a axis, or of fibers oriented in subparallel fashion. Sample 1 was studied in the Geological Institute, Kola branch, USSR Academy of Sciences, and sample 2 in the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements. The structural identity of both samples was established on the basis of the identity of the powder patterns.

The powder pattern of sample 1 (table 1) was obtained in the RKD camera (D-57.3) and supplementary lines at small angles on the DRON-0.5 diffractometer (Fe radiation). Indexing of the powder pattern was by means of the EVM "Minsk-22," according to a program worked out by E. M. Medvedeva (Rogachev et al., 1969). The agreement of the calculated and experimental interplanar spacings is excellent. From single crystal X-ray studies, bornemanite is orthorhombic. The unit cell parameters were determined from oscillation X-rays and kforograms on *h0l* (RKOP, KFOR, Cu-radiation) and were made more precise from the powder diagrams: $a_0 = 5.48 \pm 0.05$, $b_0 = 7.10 \pm 0.05$, $c_0 = 48.2 \pm 0.1$ Å;[2] $V_0 = 1875.4$ Å^3; the c axis is perpendicular to the flattening of the crystal. According to the extinction on the kforograms *h0l–h3l* (Cu radiation), preference can be given to the diffraction symbol *mmmIb*, in which are the space groups D_{2h}^{28} = *Ibmm (-Imma)* and C_{2v}^{22} = *Ibm2 (-Ima)*.

The color of the mineral is pale yellow; fine leaflets are nearly colorless. The luster is pearly; translucent; individual areas of the plates are transparent. Cleavage very perfect on (001). The plates are brittle, fibers flexible, sp. gr. 3.47-3.50. Microhardness of the aggregates, measured by S. I. Lebedeva on the PMT-3 apparatus with load 15-30 g, is 257-283 kg/mm^2 (~ 3 1/2-4 on the Mohs scale).

Bornemanite is optically biaxial, positive. The plane of the optic axis is parallel to {010}, Z = a, Y = b, X = c. Indices of refraction, measured in immersion, of samples 1 and 2, respectively are: Ng = 1.720, 1.718; Nm = 1.695, 1.687; Np = 1.682, 1.683. The angle 2V of sample 2, measured conoscopically on the Fedorov stage, is 40°; calculated for 2V is 66° (sample 1), 40° (sample 2). Under the microscope, the mineral is pale yellow, weakly pleochroic from brownish on Z to colorless on X and Y. Absorption Z > Y = X.

The mineral is decomposed by cold 5% HCl and HNO_3, losing its color and depositing plates of silica gel; in H_2SO_4 it is dissolved when heated. Before the blowpipe melts easily to a brown transparent glass. On the thermogram (fig. 1), melting corresponds to the

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[2]The axes of the cell were designated in correspondence with the setting of crystals of lomonosovite, taken from the reference book literature.

TABLE 1. Interplanar spacings of bornemanite.

I	$\frac{d}{n}$	hkl
10	24.1	002
1	12.0	004
10	8.04	006
3	4.82	0.0.10, 105
1	4.26	112, 019, 107
3	4.02	0.0.12
5	3.80	116, 109
1	3.52	118, 022, 0.1.12
10	3.44	0.0.14, 1.0.11
2	3.08	1.1.11, 1.0.13, 0.1.13
10	3.02	0.0.16
1	2.832	1.1.13, 125
1	2.758	1.0.15, 0.1.16, 200
8	2.682	0.0.18, 1.1.14, 128, 204
1	2.586	1.1.15, 206
6	2.413	0.0.20
3	2.152	133, 2.1.12, 222
5	2.012	139, 229, 0.0.24
3	1.970	1.3.10, 2.2.10
1	1.894	2.1.17, 1.1.23
7	1.781	232, 233, 040
3	1.704	216, 239, 048
8	1.610	0.0.30, 149, 324, 323
1	1.570	328, 0.3.23, 3.1.14
1	1.538	3.2.10, 2.3.16, 2.1.25
4	1.507	0.0.32, 1.1.30, 2.2.23, 1.3.23
2	1.491	242, 241, 240, 2.3.18, 1.2.28, 3.2.13
1	1.442	1.3.25, 332, 333, 2.2.25, 331, 330
5	1.420	0.0.34, 051, 052, 050, 1.1.32
1	1.396	339, 2.4.12, 056, 2.1.29
1	1.346	411, 412, 1.1.34, 3.2.20, 3.1.13, 157, 2.2.28, 406, 410
2	1.160	4.1.21, 068, 0.1.41, 2.1.37, 1.1.40, 2.4.26, 3.4.17
3	1.0976	0.0.44, 359, 1.0.43, 1.6.14
1	1.0653	269, 3.5.14, 4.2.25, 518
1	1.0077	0.0.48, 1.0.47, 1.2.45, 5.2.13, 3.5.21, 0.6.25

Note: D = 57.3, FeKα radiation, unfiltered. Analyst, Yu.P. Men'shikov.

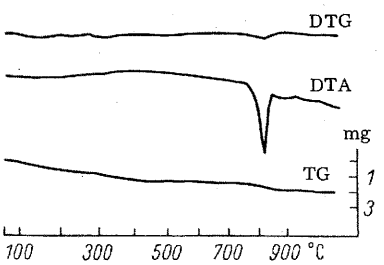

FIGURE 1. Thermogram of bornemanite. Weight of sample 288.9 mg. Loss of weight 2 mg ≈ 0.7% (derivatograph, IGEM AN SSSR).

sharp endothermic break at 720° C. The loss of weight of sample 2, heated in nitrogen to 1000°, was 0.7%, which agrees with the content of water found in the same sample by chemical analysis. An experiment made by A. V. Bykova showed that after 2 hours of boiling ground bornemanite in distilled water, a notable part of the sodium was leached out of it (4.30% Na_2O of 20.00% in the original sample) and also of the phosphorus (3.00% P_2O_5 against 6.80%). The ratio of the atomic amounts of these elements corresponds to their removal from the mineral in the form Na_3PO_4.

The infrared spectrum of bornemanite (fig. 2) is characterized by the presence of a well-resolved maxima of absorption in the bands 1070-870 and 595-440 cm^{-1}, of which the first (according to the conclusion of Ye. S. Rudnitskaya) corresponds to the region of valence oscillation of the tetrahedra SiO_4 and PO_4, and the second the field of deformational vibration of the bonds Si-O and P-O. The weak maxima at 3600 and 1600 cm^{-1} indicate the presence in the mineral of a small amount of hydroxyl-ion and molecular water.

Chemical analyses of two samples of bornemanite, studied in different laboratories,

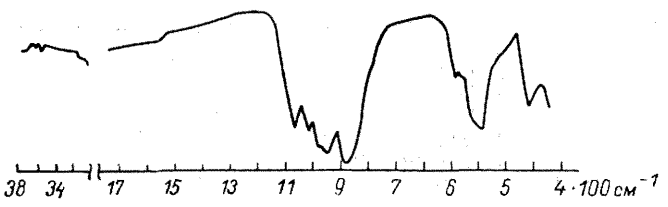

FIGURE 2. Infrared absorption spectrum of bornemanite (UR-10 spectrophotometer, IGEM AN SSSR).

TABLE 2. Chemical composition of bornemanite.

Component	Sample 1		Sample 2	
	wt %	atomic ratios	wt %	atomic ratios
P_2O_5	6.57	0.0926	6.80	0.0958
Nb_2O_5	9.22	0.0694	8.86	0.0667
Ta_2O_5	—	—	0.66	0.0030
TiO_2	18.72	0.2343	18.00	0.2253
ZrO_2	0.20	0.0016	0.25	0.0020
SiO_2	23.96	0.3987	25.00	0.4160
Al_2O_3	0.55	0.0108	0.00	—
Fe_2O_3	—	—	0.30	0.0038
FeO	0.17	0.0024		
MnO	2.97	0.0419	2.48	0.0350
MgO	0.04	0.0010	0.06	0.0015
BaO	12.05	0.0786	13.00	0.0848
SrO	0.70	0.0068	0.68	0.0066
CaO	0.33	0.0059	0.77	0.0137
Na_2O	19.62	0.6331	20.00	0.6454
K_2O	0.65	0.0138	0.67	0.0142
Li_2O	0.10	0.0067		
Rb_2O	0.0025			
Cs_2O	0.002			
H_2O^+	2.44	0.2709	0.70	0.0778
H_2O^-	0.30	—		
F	1.52	0.0800	1.64	0.0863
$-O=F_2$	0.64	—	0.69	
Total	99.47		99.18	
Sp. gr.	3.47		3.50	
Wt. in g	0.460		0.500	
Analyst	N.I. Zabavnikova		A.V. Bykova	

Note. Alkalies and alkali-earth elements in samples 1 and 2 were determined by flame photometry by G.Ye. Kalenchuk.

gave similar results (table 2).[3] Analysis 1, on calculation to the parameters of the unit cell ($Z = 1$) leads to the empirical formula $(Na, Ca)_{14.1}(Ba, K, Sr)_{3.9}(Mn, Fe, Mg, Li)_{2.0}(Ti, Nb, Zr)_{11.9}(Si, Al)_{16.0}O_{68.1}F_{3.1} \cdot 3.6\,Na_3PO_4 \cdot 5.3\,H_2O$. The idealized formula is $Na_{14}Ba_4Mn_2Ti_9Nb_3Si_{16}O_{69}F_3 \cdot 4Na_3PO_4$ (formula weight M = 3957.23, X-ray density calcd. = 3.50). Analysis 2 is calculated as above (with the same sum of cations) to the empirical formula $(Na, K, Mn)_{15.9}(Ba, Sr, Ca)_{4.1}Ti_{8.0}(Nb, Ta, Ti, Zr, Mg, Fe)_{3.8}Si_{16.2}O_{68.0}[F_{3.4}(OH)_{0.6}]_{4.0} \cdot 3.7Na_3PO_4 \cdot 1.2\,H_2O$. The idealized formula with Z = 4, is $Na_4BaTi_2NbSi_4O_{17}F \cdot Na_3PO_4 = Na_7BaTi_2NbPSi_4O_{21}F$ (M = 985.34, ρ = 3.49).

The problem of the formula of the mineral can be solved definitely only after the structure has been solved.

Bornemanite is a late hydrothermal mineral, formed in a highly alkaline medium, later than lomonosovite, possibly by its alteration.

In composition and properties, bornemanite differs sharply from batisite, innelite, shcherbakovite, and other barium titanosilicates; it resembles yoshimuraite, and has close structural similarity to the minerals of the lomonosovite and seidozerite groups. Thus, parameters a_0 and b_0 of bornemanite resemble those of lomonosovite, beta-lomonosovite, murmanite, epistolite, and seidozerite (Strunz, 1970), and parameter c_0 is 4 times that of murmanite and epistolite. The traits of similarity of bornemanite with the minerals of the lomonosovite group are clearly traced in the features of the X-ray powder diagrams and in the infrared absorption spectra [table 3].

In type of chemical formula, bornemanite resembles lomonosovite $Na_{3-4}Ti_4Si_4O_{18} \cdot 2Na_3PO_4$ and vuonnemite $Na_{4-5}TiNb_2Si_4O_{17}F \cdot 2Na_3PO_4$, but the number of sodium phosphate layers in it is half that in lomonosovite and vuonnemite. This especially explains the fact that c_0 of bornemanite is a multiple of the c_0 of murmanite and epistolite, but not of the c_0 of their phosphate analogues, lomonosovite and vuonnemite.

Sodium and phosphorus enter into the water extract of bornemanite in the same form as for lomonosovite and beta-lomonosovite (Borneman-Starynkevich, 1946; Sokolova et al., 1971; Bussen et al., 1973). The ease of leaching the sodium phosphate indicates that in bornemanite, as in minerals of the lomonosovite group, the sodium phosphate network is weakly bonded to the titanosilicate of the main structure. From this one may assume that processes of hydrothermal and supergene alteration of bornemanite ought to lead to its transformation to an unusual barium murmanite.

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Samples of bornemanite are preserved in the Mineralogical Museum, USSR Academy of Sciences, and also in the museum of the Kola Branch of the USSR Academy of Sciences and at IMGRE.

[3]Supplementary to the data of Table 2, Be, Ga, and Cu were found by spectrographic analysis.

[TABLE 3. Infrared absorption spectra of bornemanite, lomonosovite, and beta-lomonosovite.]

Mineral	Maximum absorptions (in cm^{-1})
Bornemanite	1070 strong, 1010 strong, 980 strong, 950 strong, 930 strong, 870 very strong, 590 weak - 580 weak - 570 strong - 545 strong, 460 strong
Lomonosovite	1080 strong, 1045 strong, 1000 strong, 940 very strong, 870 strong, 760 weak, 700 weak, 590 weak - 560 strong, 470 strong - 435 very strong
Beta-lomonosovite	1080 strong, 1040 strong, 920 very strong, 800 weak, 550 strong, 340 strong

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