Hydroxylborite, Mg$_3$(BO$_3$)(OH)$_3$, a New Mineral Species and Isomorphous Series Fluoborate–Hydroxylborite$^1$

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Abstract—Hydroxylborite, a new mineral species, an analogue of fluoborate with OH > F, has been found at the Titovsky deposit (57°41’ N, 125°22’ E), the Chersky Range, Dogdo Basin, Sakha-Yakutia Republic, Russia.

Prismatic crystals of the new mineral are dominated by the {1010} faces without distinct end forms and reach (1–1.5) × (0.1–0.2) mm in size. Radial aggregates of such crystals occur in the mineralized marble adjacent to the boron ore (suaniite–kotoite–ludwigite). Calcite, dolomite, Mg-rich ludwigite, kotoite, zabielyite, clinohumite, magnetite, serpentine, and chlorite are associated minerals. Hydroxylborite is transparent colorless, with a white streak and vitreous luster. The new mineral is brittle. The Mohs’ hardness is 3.5. The cleavage is imperfect on {0001}. The density measured with equilibration in heavy liquids is 2.89(1) g/cm$^3$; the calculated density is 2.872 g/cm$^3$. The wave numbers of the absorption bands in the IR spectrum of hydroxylborite are (cm$^{-1}$; sh is shoulder): 3668, 1233, 742, 630sh, 555sh, 450sh, and 407. The new mineral is optically uniaxial, negative, $\alpha = 1.566(1)$, and $\epsilon = 1.531(1)$. The chemical composition (electron microprobe, wt %) is 18.43 B, 3.03 Mg, 0.55 F, 4.31 O, 70 Ca, 4.13 Si, 0.04 Na, 0.03 K, and 0.04 (alkali). Hydroxylborite is hexagonal, and the space group is $P6_3/m$. The unit-cell dimensions are: $a = 8.912(8)$ Å, $c = 3.112(4)$ Å, $V = 214.05(26)$ Å$^3$, and $Z = 2$. The strongest reflections in the X-ray powder pattern [$d$, Å ($I$, %)] are: 7.69(52)(0110), 4.45(82)(110), 2.573(65)(0310), 2.422(100)(0221), and 2.128(60)(1231). The compatibility index $1 - (K_d/K_C)$ is 0.038 (excellent) for the calculated density and 0.044 (good) for the measured density. The type material of hydroxylborite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (inventory number 91968) and the Geological Museum of the All-Russia Institute of Mineral Resources, Moscow (inventory number M-1663).

INTRODUCTION

Hydroxylborite is an OH-dominant (OH > F) magnesium orthoborate, a member of the isomorphous series fluoborate Mg$_3$(BO$_3$)F$_3$–hydroxylborite Mg$_3$(BO$_3$)(OH)$_3$ with an inferred complete substitution of F for OH. The mineral is named after its chemical composition.

Minerals of the fluoborate group are abundant, although they infrequently form large segregations. These minerals are most typical of ore and mineralized calciphyre at Sn–B and B–Fe magnesian skarn deposits (Tilley, 1951; Gramenitsky, 1966; Pertsiev, 1971, Androkov, 1982; Marinece, 2000). They also occur in skarnified rocks and related ore at Sn deposits (Ahifeld et al., 1938; Sergeev and Novikova, 1969; Kwak and Nicholson, 1988; Štrein et al., 2000); base-metal deposits (Bauer and Berman, 1929); in apodolomitic greisen (Gulyaev, 1971); serpentinite (Oidup and Kudryavtseva, 1999); in metalimestone xenoliths hosted in volcanic tuff (Brisi and Eitel, 1957); and halite–anhdydrite and halite–calcite rocks (Apollonov et al., 1988).

Magnesium fluorhydroxyorthoborate was described for the first time by Geijer (1929) from the Norberg iron deposit (Mine Tallgruvan) in Sweden, and was named fluoborite. The borate was identified in association with magnetite, humite-group minerals, forsterite, and ludwigite and characterized by the significant predominance of OH over F ($h = \text{OH}/(\text{OH} + \text{F})$ ratio is about 70 mol %). The high-fluorine (F > OH) mineral of this group was found in limestone xenoliths in the Nocera volcanic tuff near Naples, Italy by A. Scacchi in 1881 and F. Zambonini in 1919 and originally regarded as a mineral species Mg$_3$Ca$_8$O$_7$F$_8$ named nocaerite. Brisi and Eitel (1957) established that this composition corre-
sponds to a mixture of fluoborite and fluorite. Despite the name nucerite that was initially given to a mineral mixture, Brisi and Eitel kept this name for the identified borate, which is not correct in our opinion.

Fluorine members of the considered mineral group occur in nature more frequently than hydroxyl counterparts; however, OH-dominant minerals are not a mineralogical curiosity (Utekhin, 1960; Kwak and Nicholson, 1988; Šrein et al., 2000; our samples from the Verkhoyansk region). Having studied fluoborite from Sterling Hill, New Jersey, the United States, Bauer and Berman (1929) noted that, under appropriate conditions, it was appropriate to expect an F-free “fluoborite.” While analyzing the chemical composition and properties of the fluoborite-group minerals with the general formula Mg$_3$BO$_3$F$_h$ (Flamini et al., 1988; Rein et al., 2000; our samples from the Titovsky Sn–B deposit that is typical of the Verkhoyansk–Indigirka metallogenic province (Lisitsyn et al., 1995). On the basis of the results obtained and a survey of published data, we propose recognizing hydroxylborite, the hydroxyl mineral species Mg$_3$BO$_3$F$_h$ within a continuous isomorphous series of binary compounds, whereas the name fluoborite is suggested for the Mg$_3$BO$_3$F$_h$ species, which is consistent with the composition of these minerals. The range of compositional variation recommended for definition is the 50% rule. The principal characteristics of the studied hydroxylborite are listed in Table 1.

**EXPERIMENTAL**

The chemical composition of hydroxylborite was studied with a Superprobe-8100 electron microprobe at the All-Russia Institute of Mineral Resources. The accelerating voltage was 5–10 kV for boron, 10 kV for fluorine, and 15 kV for magnesium; the current is 100, 50, and 20 nA, respectively. The following standards have been used: natural danburite CaB$_2$Si$_2$O$_6$ for B and synthetic MgF$_2$ for Mg and F. The LDE2 crystal was used for the detection of boron, and the TAP crystal, for the detection of magnesium and fluorine. Differential discrimination has been applied to measure the intensity of BK$_a$ and FK$_a$. In order to minimize the effect of the chemical bond on the results of the boron and fluoride measurements, the K-ratio ($K = S_{\text{amp}}/S_{\text{standard}}$) was determined by integral intensities. The BK$_a$ and FK$_a$ intensities were measured in the raster regime with an irradiated area of 30 × 30 μm$^2$ to decrease the thermal diffusion of the atoms during analysis. The thermal stability of the new mineral was controlled by the measurement of the MgK$_a$ intensity for a time, which is necessary for obtaining the integral intensity of BK$_a$. The variation in the MgK$_a$ intensity did not exceed 2% at the applied analytical conditions.

The concentrations were calculated with a CITZAF Vers. 3.50 program that is included in the software support for the electron microprobe. The B$_2$O$_3$ content in the mineral (18.15 wt %, average over 3 point analyses) detected at 5 kV was underestimated in comparison with that at 10 kV.

The H$_2$O content was measured using the Penfield method at the Institute of Problems of Chemical Physics, Russian Academy of Sciences (analyst A.S. Astakhova). Ignition was carried out at 1000°C in oxygen flowing with anhydron, magnesium perchlorate Mg(ClO$_4$)$_2$, as an adsorbent.

Infrared spectra were recorded with a SPECORD 75 IR dual-beam spectrophotometer (Carl Zeiss, Jena) within the wave number interval 400–3800 cm$^{-1}$ ranging from 400 to 1400 cm$^{-1}$ at a width of the spectral slit of <2 cm$^{-1}$ and from 1400 to 3800 cm$^{-1}$ at <8 cm$^{-1}$. Polystyrene and gaseous ammonia were used as the standards. The KBr disk with mineral powder was measured. An anhydrous KBr disk without the mineral was placed in a comparison beam during the recording of the spectrum. IR spectroscopy was performed at the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

The density was measured with equilibration in heavy liquids. The optical parameters were determined with immersion liquids. The X-ray powder diffraction pattern of hydroxylborite was recorded with a RIGAKU diffractometer, Cu K$_a$ radiation, at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences.

The X-ray diffraction analysis of hydroxylborite was carried out with a P I SYNTEX automatic single-crystal diffractometer at the Laboratory of X-ray Diffraction Analysis, Department of Crystallography and Crystal Chemistry, Moscow State University. The structure of the new mineral was determined by the direct method using the SHELX-97 software package (Sheldrick, 1997). The model obtained was refined with the least-squares method in an anisotropic fit for Mg, B, and O atoms. The position of the H atom was detected on a differential distribution of the electron density. The absence of additional significant maximums on this distribution confirmed the accuracy of the structure model.

**OCCURRENCE**

Boron mineralization in the Verkhoyansk–Indigirka ore province (Russian Federation, Sakha-Yakutia)