Hydroxylborite, Mg$_3$(BO$_3$)(OH)$_3$, a New Mineral Species and Isomorphous Series Fluoborite–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, Yakutia–Sakha 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 (suanite–kotoite–ludwigite). Calcite, dolomite, Mg-rich ludwigite, kotoite, szaibelyite, 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$^{-1}$): 3668, 1233, 742, 630sh, 555sh, 450sh, and 407. The new mineral is optically biaxial, negative, $\alpha = 1.566(1)$, and $\varepsilon = 1.531(1)$. The chemical composition (electron microprobe, H$_2$O measured with the Penfield method, wt %) is 18.43 B$_2$O$_3$, 65.71 MgO, 10.23 F, 9.73 H$_2$O, 4.31 –O = F$_2$, where the total is 99.79. The empirical formula calculated on the basis of 6 anions $pfu$ is as follows: $\text{Mg}_{3.03} \text{B}_{2.03} \text{OH}_{2.00} \text{F}_{1.00} \text{O}_{3.00}$. 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, %)(hkil)] are: 7.69(52) (0110), 4.45(82) (1120), 2.573(65) (0330), 2.422(100) (0221), and 2.128(60) (1231). The compatibility index $1 – (K_d/K_o)$ 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 fluoborite 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; Pertsev, 1971, Androvanov, 1982; Marincea, 2000). They also occur in skarnified rocks and related ore at Sn deposits (Ahifeld et al., 1938; Sergeev and Novikova, 1969; Kwak and


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Nicholson, 1988; Štein et al., 2000); base-metal deposits (Bauer and Berman, 1929); in apodolomitic greisen (Gulyaev, 1971); serpentineite (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 fluorhydroxylorthoborate 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 Zambonini in 1919 and originally regarded as a mineral species Mg$_3$Ca$_8$O$_{23}$F$_8$ named noclere. Brisii and Eitel (1957) established that this composition corre-
sponds to a mixture of fluoborite and fluorite. Despite
the name nocerite 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 counter-
parts; however, OH-dominant minerals are not a miner-
alogical curiosity (Utekin, 1960; Kwak and Nichol-
son, 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 condi-
tions, it was appropriate to expect an F-free “flu-
oborate.” While analyzing the chemical composition and
properties of the fluoborite-group minerals with the
general formula Mg$_3$BO$_3$(F,OH)$_3$, Shaller (1942) and
later Brovkin et al. (1967) demonstrated a wide range
of replacement of F with OH.

In experiments on the hydrothermal synthesis of the
Mg$_3$BO$_3$(F,OH)$_3$ fluoborates, a wide range of varieties
from a fluorine end member ($h = 0$) (Flamini et al.,
1979) to a hydroxyl-rich ($h = 57$ mol %) member were
synthesized. It was revealed that an increasing pressure
favors the synthesis of minerals enriched in hydroxyl
(Nekrasov et al., 1970).

We have studied the OH-dominant mineral species
($h = 67$ mol %) from calciphyre of the Titovsk Sn–B
deposit that is typical of the Verkhovansk–Indigirka
metallocgenic 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$_3$(OH)$_3$ within a con-
tinuous isomorphous series of binary compounds,
whereas the name fluoborite is suggested for the
Mg$_3$BO$_3$F$_3$ species, which is consistent with the com-
position of these minerals. The range of compositional
variation recommended for definition is the 50% rule.
The principal characteristics of the studied hydroxyl-
borite 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 LDEE2 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 inten-
sity of B$K_α$ and F$K_α$. In order to minimize the effect of
the chemical bond on the results of the boron and fluo-
rine measurements, the K-ratio ($K = S_{\text{sample}}/S_{\text{standard}}$) was
determined by integral intensities. The B$K_α$ and F$K_α$
intensities were measured in the raster regime with an
irradiated area of 30 $\times$ 30 $\mu$m$^2$ to decrease the thermal
diffusion of the atoms during analysis. The thermal sta-
bility of the new mineral was controlled by the mea-
surement of the Mg$K_α$ intensity for a time, which is
necessary for obtaining the integral intensity of B$K_α$.
The variation in the Mg$K_α$ intensity did not exceed 2% at
the applied analytical conditions.

The concentrations were calculated with a CITAFA Vers. 3.50 program that is included in the software sup-
port 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 Phys-
ics, Russian Academy of Sciences (analyst A.S. Asta-
khova). 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$^{-1}$ rang-
ing 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$^{-1}$.
Polyesterene and gaseous ammonia were used as the
standards. The KBr disk with mineral powder was mea-
sured. 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.$^2$ The X-ray powder diffraction
pattern of hydroxylborite was recorded with a RIGAKU
diffactometer, Cu$K_α$ radiation, at the Institute
of Geology of Ore Deposits, Petrography, Mineral-
ology, and Geochemistry, Russian Academy of Sciences.

The X-ray diffraction analysis of hydroxylborite
was carried out with a PT SYNTEX automatic single-
crystal diffractometer at the Laboratory of X-ray Diff-
raction Analysis, Department of Crystallography and
Crystal Chemistry, Moscow State University. The
structure of the new mineral was determined by the
direct method using the SHEXL-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 dis-
tribution confirmed the accuracy of the structure model.

**OCCURRENCE**

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

$^2$ Measurements of the density and determination of the optical
parameters were carried out by A.E. Zadov, NPO Regenerator,
Moscow.