# Ammonioborite: New Borate Polyion and Its Structure

Abstract. *The mineral ammonioborite is monoclinic with unit cell dimensions (in angstroms)*: $a = 25.27$, $b = 9.65$, and $c = 11.56$; $\beta = 94°17'$, *and the space group is* C 2/c. *Analysis of the crystal structure revealed the crystallochemical formula* $(NH_4)_3B_{15}O_{20}(OH)_8 \cdot 4H_2O$, *with four such formula units in the unit cell. The basic structural unit is the double ring consisting of one* $BO_4$ *tetrahedron and four* $BO_3$ *triangles: in ammonioborite three of these units are connected to give trimeric ions* $[B_{15}O_{20}(OH)_8]^{3-}$.

Ammonioborite was identified as a new mineral phase by Schaller (*1*), who found it in a specimen of natural borate from Larderello, Italy. In his original description of the new mineral Schaller distinguished it from the associated ammonium borate larderellite through the examination of its habit and the study of its optical properties. The x-ray crystallography of a sample of synthetic ammonioborite supplied by Schaller was studied by Clark and Christ (*2*); on the basis of their single-crystal x-ray data and the experimentally observed density combined with the results of unpublished chemical analyses by Schaller, these authors derived the formula $NH_4B_5O_8 \cdot 2\frac{2}{3}H_2O$ as the most probable for ammonioborite.

The following crystal data were given by Clark and Christ: $a = 25.27 \pm 0.05$ Å; $b = 9.65 \pm 0.03$ Å; $c = 11.56 \pm 0.03$ Å; $\beta = 94°17' \pm 5'$; space group, $C\ 2/c$ (or, less likely, $Cc$); measured density, $D_m = 1.765 \pm 0.004$ g $cm^{-3}$; cell contents, $12(NH_4B_5O_8 \cdot 2\frac{2}{3}H_2O)$.

We report here the results of our study of the crystal structure of ammonioborite; this study has been undertaken in order to establish definitively the composition of this mineral and to fix its position in the crystallochemical classification of borates.

Intensity data were collected from a suitable, small, single crystal (*3*) by means of Weissenberg photographs made with Ni-filtered CuK$\alpha$ radiation; nine layers with $b$ as the rotation axis ($k = 0$ through 8) and the zero layer with $c$ as the rotation axis were recorded. The intensities were visually estimated and corrected for Lorentz and polarization factors. Then the magnitudes of the normalized structure factors $E$ were calculated: their statistical averages ($\langle |E| \rangle = 0.746$, $\langle |E^2 - 1| \rangle = 1.087$, $\langle |E^2| \rangle = 1.000$) and distribution ($|E| > 3$, 1.0 percent; $|E| > 2$, 5.4 percent; $|E| > 1$, 27.0 percent) confirmed the choice of the $C\ 2/c$ space group.

The symbolic addition method of Karle and Karle (*4*), used in conjunction with a computer program written by Hall for the National Research Council crystallographic programs (*5*), yielded directly the phases of 275 of the largest normalized structure factors. On the basis of this set of determined phases a three-dimensional $E$-map, which revealed the positions of all but one of the nonhydrogen atoms, was calculated. A subsequent three-dimensional Fourier synthesis, computed with all the observed structure factors, showed that the missing atom, corresponding to the oxygen atom of a water molecule, is distributed on two positions. Refinement of atomic coordinates and of individual isotropic temperature factors was carried out by means of three full-matrix, least-squares cycles; then one least-squares cycle was

Table 1. Positional coordinates and anisotropic thermal parameters with their standard deviations (in parentheses) (both × $10^4$); O* andO** represent, respectively, hydroxyl ions and water molecules. Temperature factors are given in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The occupancy factors for **O(16)**** and **O(17)**** are 0.65 and 0.35, respectively.

| Atom | Coordinates | | | Temperature factors | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| O(1) | 0.3466(2) | 0.2150(5) | 0.0167(3) | 10(1) | 92(6) | 50(3) | 5(1) | 4(1) | 2(3) |
| O(2) | .4097(1) | .0372(4) | .0334(3) | 10(1) | 74(5) | 54(3) | 5(1) | 3(1) | −2(3) |
| O(3) | .4713(1) | −.1402(4) | .0035(3) | 10(1) | 74(5) | 53(3) | 5(1) | 1(1) | −1(3) |
| O(4) | .3091(2) | .3119(5) | .1831(4) | 10(1) | 90(6) | 62(3) | 6(1) | 5(1) | −5(3) |
| O(5) | .3783(2) | .1382(4) | .2052(3) | 11(1) | 76(5) | 57(3) | 6(1) | 3(1) | 2(3) |
| O(6) | .4577(2) | −.0675(4) | .1951(3) | 10(1) | 73(5) | 61(3) | 4(1) | 2(1) | −3(3) |
| O(7) | .3128(2) | .1550(4) | .3447(3) | 10(1) | 59(5) | 61(3) | −3(1) | 1(1) | −3(3) |
| O(8) | .3792(2) | .3346(4) | .3323(4) | 12(1) | 75(5) | 61(3) | −7(1) | 4(1) | 6(3) |
| O(9) | .4777(2) | −.2456(4) | .3378(3) | 10(1) | 69(5) | 62(3) | −6(1) | 3(1) | −2(3) |
| O(10) | .3536(2) | .2609(5) | .5155(3) | 14(1) | 92(6) | 48(3) | −7(1) | 3(1) | −2(3) |
| O(11)* | .2830(2) | .3961(5) | −.0029(4) | 13(1) | 100(6) | 60(3) | 9(2) | 2(1) | 3(3) |
| O(12)* | .2908(2) | .0914(5) | .5356(4) | 15(1) | 118(6) | 60(3) | −9(2) | 6(1) | −1(3) |
| O(13)* | .4124(2) | .4478(5) | .5020(4) | 16(1) | 88(6) | 64(3) | −9(2) | 5(1) | −5(3) |
| O(14)* | .4707(2) | −.3207(5) | .5304(3) | 14(1) | 95(6) | 50(3) | −9(2) | 3(1) | −5(3) |
| O(15)** | .2868(2) | .5900(5) | .2672(4) | 14(1) | 112(6) | 66(3) | 4(2) | 1(1) | −11(4) |
| O(16)** | .4105(3) | .5702(8) | .2277(5) | 14(1) | 108(10) | 59(5) | −8(2) | −1(2) | 7(5) |
| O(17)** | .4354(5) | .5267(14) | .2223(10) | 20(2) | 62(16) | 56(9) | −9(4) | 4(3) | −2(5) |
| B(1) | .3132(2) | .3083(8) | .0673(6) | 9(1) | 73(9) | 62(5) | 1(2) | −1(1) | 4(4) |
| B(2) | .3782(2) | .1271(7) | .0902(5) | 8(1) | 66(8) | 58(5) | −1(2) | 2(1) | 1(4) |
| B(3) | .4465(2) | −.0555(7) | .0818(5) | 8(1) | 68(8) | 54(4) | −1(2) | 3(1) | 5(4) |
| B(4) | .3448(2) | .2352(7) | .2659(5) | 11(1) | 72(8) | 43(4) | −2(2) | 3(1) | 1(4) |
| B(5) | ½ | −.1575(9) | ¼ | 10(1) | 72(11) | 42(5) | 0 | 3(2) | 0 |
| B(6) | 0.3181(2) | .1674(7) | 0.4615(6) | 10(1) | 53(8) | 60(5) | −1(2) | 1(1) | 8(4) |
| B(7) | .3816(3) | .3481(7) | .4476(6) | 11(1) | 75(9) | 55(5) | 1(2) | 4(1) | 3(4) |
| B(8) | .4916(2) | −.2377(7) | .4506(5) | 9(1) | 56(8) | 54(4) | −2(2) | 4(1) | 1(4) |
| N(1) | .3508(2) | .8438(7) | .2686(5) | 17(1) | 117(8) | 75(5) | 1(2) | 7(2) | 14(5) |
| N(2) | ½ | .2211(9) | ¼ | 15(1) | 110(11) | 57(6) | 0 | −1(2) | 0 |

Table 2. Ammonium-oxygen distances (less than 3.4 Å) and hydrogen bond lengths (estimated standard deviations, 0.007 Å).

| Atom pair | Distance (Å) | Hydrogen-bonded pair | Distance (Å) |
|---|---|---|---|
| N(1)–O(1) | 2.933 | O(15) . . . O(4) | 2.924 |
| N(1)–O(15) | 2.934 | O(15) . . . O(7) | 2.813 |
| N(1)–O(6) | 3.016 | O(11) . . . O(15) | 2.670 |
| N(1)–O(5) | 3.028 | O(12) . . . O(11) | 2.658 |
| N(1)–O(12) | 3.055 | O(16) . . . O(8) | 2.720 |
| N(1)–O(16) | 3.095 | O(16) . . . O(9) | 2.709 |
| N(1)–O(10) | 3.101 | O(13) . . . O(16) | 2.619 |
| N(1)–O(7) | 3.293 | O(14) . . . O(13) | 2.683 |
| N(1)–O(9) | 3.359 | O(17) . . . O(8) | 2.709 |
| N(2)–O(14) | 2.763* | O(17) . . . O(9) | 2.746 |
| N(2)–O(6) | 3.033* | O(13) . . . O(17) | 2.581 |
| N(2)–O(3) | 3.169* | | |
| N(2)–O(5) | 3.182* | | |
| N(2)–O(17) | 3.374* | | |

* The distance is repeated by the twofold axis.

carried out in which anisotropic temperature factors were introduced and the occupancy factors for the disordered oxygen atom were allowed to vary.

The present reliability index is $R = 0.131$ for the 2103 observed reflections (*6*). Scattering factors for boron and oxygen atoms in neutral states reported in the *International Tables for X-Ray Crystallography* (*7*) and for ammonium ion calculated by Davis and Whitaker (*8*) were used. Positional coordinates and temperature factors at the present stage of refinement are shown in Table 1.

The basic structural unit is the double ring built up from one $BO_4$ tetrahedron and four planar $BO_3$ triangles: it was first found by Zachariasen as an isolated ion in $KB_5O_6(OH)_4 \cdot 2H_2O$ (*9*). In ammonioborite three of these structural units are connected to give trimeric ions with symmetry $C_2$-2. Assignment of the hydrogen atoms was carried out on the assumption, according to Christ's (*10*) third rule, that the oxygen atoms linked to only one boron in the polyion represent hydroxyl groups and that the unattached oxygen atoms represent water molecules. Thus the trimeric ions in ammonioborite are: $[B_{15}O_{20}(OH)_8]^{3-}$; these trimeric ions are linked to each other through ammonium-oxygen bonds and hydrogen bonds (Fig. 1). Table 2 gives the bond lengths of the ammonium-oxygen bonds and hydrogen bonds. From Table 2 the system of the hydrogen bonds can be deduced unequivocally: the oxygen atoms O(4) and O(7) are proton acceptors from O(15), and the oxygen atoms O(8) and O(9) are proton acceptors from O(16) [or from O(17)]; O(12) and O(14) are proton donors to O(11) and O(13), respectively; O(11) and O(13), in turn, are proton donors to O(15) and O(16) [or O(17)], respectively. Moreover, an examination of the bond lengths listed in Table 2 indicates the reason for the different

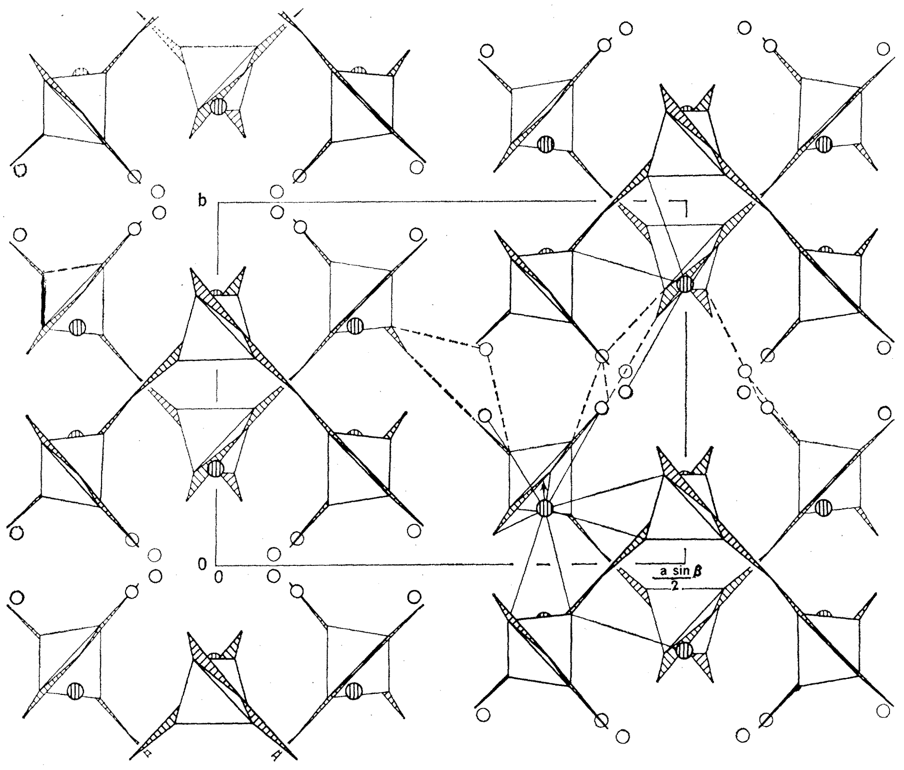

Fig. 1 (middle left). The crystal structure of ammonioborite viewed along the [001] direction. Only the crystallographically independent hydrogen bonds (dashed lines) and ammonium-oxygen bonds (unbroken lines) are represented. The line ending with an arrow indicates that the bond is associated with an oxygen atom translated one unit in the [001] direction.

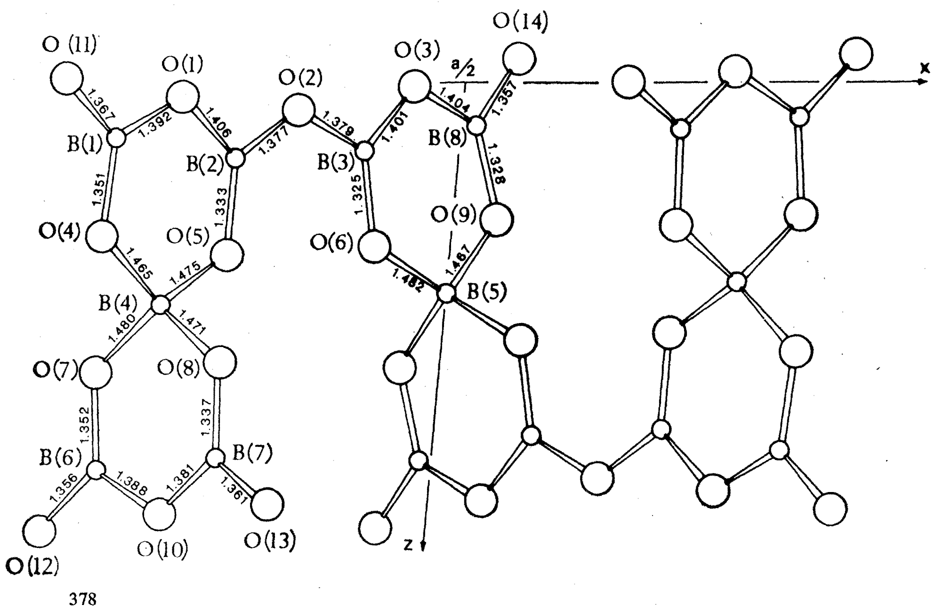

Fig. 2 (bottom left). Projection of the borate polyion $[B_{15}O_{20}(OH)_8]^{3-}$ viewed along the *b*-axis. Boron-oxygen bond lengths (in angstroms) are indicated; standard deviations, 0.007 Å.

occupancy factors for O(16) and O(17): in fact, the O(16) water molecule (whose occupancy factor is 0.65) appears firmly linked to the N(1) ammonium ion (bond length, 3.095 Å), whereas the O(17) water molecule (whose occupancy factor is 0.35) appears more loosely bound to the N(2) ammonium ion (bond length, 3.374 Å).

The structural formula for ammonioborite is: $(NH_4)_3B_{15}O_{20}(OH)_8 \cdot 4H_2O$, with four such formula units per unit cell.

The infinite chains found in larderellite $NH_4B_5O_7(OH)_2 \cdot H_2O$ (*11*) can be regarded as the polymerization product of the trimeric polyions $[B_{15}O_{20}(OH)_8]^{3-}$, according to the schematic reaction:

$$n[B_{15}O_{20}(OH)_8]^{3-} = [B_5O_7(OH)_2]_{3n}^{-3n} + nH_2O$$

Bond lengths in the polyion are given in Fig. 2: in ammonioborite the average B–O distance in the triangles is 1.366 Å and in the tetrahedra is 1.473 Å; these values correspond to those found in larderellite (1.373 Å and 1.466 Å, respectively) and in $\beta = NH_4B_5O_6(OH)_4 \cdot 2H_2O$ (*12*) (1.364 Å and 1.479 Å, respectively) and are in excellent agreement with the values found by several workers in other borates (*13*).

As regards the B–O bonds in the triangles, there are significant differences between those involving oxygen atoms linked to two boron atoms in the trigonal state (mean bond length, 1.391 Å) and those involving oxygen atoms linked to only one boron in the trigonal state (mean bond length, 1.347 Å). Such differences can be explained in terms of differences in π-bond order (*14*).

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# Magnetoglow: A New Geophysical Resource

Abstract. *Evidence has been found that the earth is immersed in a large volume of glowing helium ions. This ionic glow, at 304 angstroms, is similar to the geocoronal hydrogen glow in that it extends to very high altitudes, but it is unique in that it is largely confined to the closed field line portion of the magnetosphere. Because of its magnetic containment, this ionic radiation is called the "magnetoglow." Observations of the magnetoglow from inside and outside the magnetospheric cavity promise to provide a valuable means of studying the structural dynamics of the magnetosphere.*

In August 1967, two far ultraviolet photometers with thin-film filters were flown aboard an Aerobee rocket into the night sky (*1*). The major portion of the signal from the indium filter photometer (770- to 1080-Å passband) was identified as solar Lyman-β radiation resonantly backscattered from the hydrogen geocorona. The aluminum filter instrument (150- to 800-Å passband) measured radiation that was absorbed mainly between 160 and 140 km in altitude. This absorption characteristic is similar to that for He+ (304 Å) radiation (*2*). However, the wide bandwidth of the aluminum filter, the large view angle of the collimator, small light leaks through the thin film, and high background noise in the photomultiplier detector rendered it impossible to identify positively the radiation as 304 Å and to exclude the possibility that some of the signal within the detector passband may have been due to 584-Å photons resonantly scattered by the neutral helium within the earth's atmosphere.

On 13 October 1969, new photometers, which were insensitive to visible light, which used low-noise Channeltron detectors, and each of which had a 0.1-steradian field of view, were flown into the night sky above White Sands, New Mexico. An additional photometer with an aluminum-carbon thin-film filter (150- to 400-Å passband) flew this time in order to isolate the 304-Å from the 584-Å nightglow. The existence of He+ (304 Å) radiation was substantiated by the fact that the signal from both the aluminum and aluminum-carbon photometers followed each other closely both in phase and amplitude excursions. Within the limits of experimental error, subtraction of the aluminum-carbon signal from that of the aluminum photometer left a noisy signal from which we could not identify a nightglow at 584 Å.

Figure 1 shows isophotes of He+ (304 Å) intensity from the night sky hemisphere centered on the zenith above the rocket. The data are derived from the aluminum filter photometer as the rolling rocket scanned the sky from above 207-km altitude. No atmospheric attenuation corrections have been made to the data in Fig. 1. No He+ (304 Å) albedo was observed below the optical horizon.

For contrast, Fig. 2 displays the hydrogen Lyman-α (1216 Å) night sky radiation measured with a magnesium fluoride filter photometer above 178 km on the same rocket flight. Scattered from the neutral hydrogen geocorona, the Lyman-α radiation is most intense in the general direction of the sun, which at the time lay 44 deg below the horizontal.

From the many rocket and satellite observations of hydrogen Lyman-α radiation (*3*), it has been concluded that the earth's blanket of neutral hydrogen has an optical thickness greater than 1 —that is, on the average, each photon is scattered more than once before it reaches the lower atmosphere where it is absorbed by molecular oxygen. Thus, when viewed from inside the "thick" hydrogen geocorona, nonuniformities in the initially scattered Lyman-α radiation pattern are diffused by the subsequent scattering process. Figure 2 shows a Lyman-α intensity variaiton of less than 2 : 1 over the night sky.

On the other hand, the intensity of the He+ (304 Å) radiation (Fig. 1) is