THE CHEMICAL FORMULA OF BORACITE

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The chemical formula $Mg_7Cl_2B_{16}O_{30}$ was assigned to boracite almost seventy years ago[1]. In spite of the great attention which this orthorhombic mineral has received on account of its optical behavior and its inversion at 265°C. to the cubic system, no new chemical analyses of boracite seem to have been made[2].

Some months ago the writer started an investigation of the structure of boracite. He is much indebted to Professor E. Schiebold and Professor F. Rinne in Leipzig, in whose laboratories the X-ray work was carried on. It was noticed early in the work that the dimensions of the unit cell, as determined by the oscillation method (Seeman-Schiebold), do not permit the placing of an even number of molecules into the cell. Precision measurements with calcite as standard were made on colorless crystals from Westeregeln and greenish ones from Solvey. The dimensions of the orthorhombic cell of the colorless crystals are: $a_0 = b_0 = 16.97$Å. There is no noticeable difference in the lengths of the a and b axes. Referred to the cubic orientation they are the [110] and [$\bar{1}$10] directions, respectively. c_0 (the [001] direction in the cube) is 12.00Å in length. For the greenish crystals the dimensions are: $a_0 = b_0 = 17.11$Å and $c_0 = 12.10$Å.[3] Density determinations were checked by the writer and found to vary between 2.92 and 2.97 for the colorless and 2.97 to 3.10 for greenish boracite.

The well-known equation,

$$\text{number of molecules} = \frac{\text{volume in Å}^3 \times \text{density}}{\text{molecular weight} \times 1.64 \times 10^{-24}}$$

for the determination of the number of molecules in the unit cell gives values varying from 7.0 to 7.3, when allowance is made for the increase in molecular weight with increase in ferrous iron. Symmetry considerations do not permit the placing of seven molecules into a unit cell. Since the dimensions of the cell and density measurements are correct to within a small limit of error, the writer concluded that the formula might be wrong.

[1] Heintz, W., *Jour. prakt. Chem.*, vol. **77**, p. 338, 1859.
Potyka, J., *Poggendorff Annalen*, vol. **107**, p. 433, 1859.

[2] Doelter, C., *Handbuch der Mineralchemie*, vol. **9**, p. 418, 1922.

[3] Rinne has found the same dimensions in a powder diagram. See "Röntgenographische Untersuchungen an einigen feinzerteilten Mineralien," *Zeitsch. f. Krist.*, vol. **60**, pp. 55-69, 1924.

It was found that former analysts[4] had subjected the boracite to long leaching in order to remove any water soluble chlorides and sulfates. Even then the chlorine found was usually about one half per cent higher than necessary for the formula according to Heintz[5].

The writer wishes to thank Mr. George Ward of the Department of Geology and Mineralogy of the University of Minnesota for a new analysis of boracite. The sample of one gram consisted of about 25 good dodecahedral and cubic colorless crystals from Eime, near Hanover, Germany. The finely ground sample was divided for duplicate analyses. The powders were put into beakers with 100 c.c. of distilled water for 48 hours. Precautions were taken not to contaminate the samples or filtrates by gaseous chlorine or HCl from the air of the laboratory. The water was then carefully decanted through a filter paper. The filtrates were analyzed for chlorine and gave 0.05 per cent and 0.06 per cent Cl, respectively. These almost negligible amounts have been added to the total Cl in the analyses below.

The powder in the beakers was dried at 105°C. for several hours, weighed and fused with sodium carbonate. The chlorine was determined as AgCl volumetrically, as well as gravimetrically for a check. Standard methods were used. The amount of ferrous iron was practically negligible. The trace of it was weighed with the magnesium. Boron was calculated by difference.

TABLE I.

	NEW ANALYSES			THEORETICAL COMPOSITIONS FOR		
	I	II	Average	$Mg_7Cl_2B_{16}O_{30}$	$Mg_3ClB_7O_{13}$ or $Mg_6Cl_2B_{14}O_{26}$	$Mg_{25}Cl_8B_{56}O_{105}$
$MgCl_2$	12.50	12.19	12.35	10.62	12.14	11.99
MgO	26.42	26.36	26.39	26.96	25.70	26.64
B_2O_3	61.08	61.45	61.26	62.42	62.16	61.37
FeO	trace	trace	trace			
	100.00	100.00	100.00	100.00	100.00	100.00

The two analyses and their averages are given in Table 1. The theoretical percentages in the old formula of $Mg_7Cl_2B_{16}O_{30}$ and those in the two new possible ones are found in the three last columns of the table. The last formula $Mg_{25}Cl_8B_{56}O_{105}$, though

[4] *op. cit.*

[5] *op. cit.*

closely approximating the chemical analyses, is of such proportions that it is difficult to believe it correct. Only two of these large molecules could have room in the unit cell. The exact value is 1.936 molecules which is very close to 2. The formula $Mg_6Cl_2B_{14}O_{36}$, while not in such excellent agreement with the MgO of the analyses, gives us a very good value of 7.845 for the unit cell. Eight of these molecules could be accommodated in the unit cell.

This new formula can be written as a combination of a tetraborate and metaborate with $MgCl_2$ as follows:

$$2MgB_4O_7 \cdot 3MgB_2O_4 \cdot MgCl_2$$

or as a double salt of $MgCl_2$ and heptaboric acid $7B(OH)_3$,

$$2\,[7B(OH)_3] - 8H_2O = 2H_5B_7O_{13} \cdot$$

Substituting Mg_5 for $2H_5$ and adding $MgCl_2$ we have the molecule

$$Mg_5B_{14}O_{26} \cdot MgCl_2 \cdot$$

A still simpler formula can be written when $Mg_6Cl_2B_{14}O_{26}$ is divided by 2. $Mg_3Cl\ B_7O_{13}$ could be written as a double salt of metaborate and boron-oxychloride[6], thus:

$$3MgB_2O_4 \cdot BOCl \cdot$$

If boracite is orthorhombic hemimorphic, however, as is claimed, then this formula with 16 molecules in the unit cell will probably have to be doubled. This will be discussed in a paper on the structure of boracite.

Conclusions. X-ray diffraction measurements have shown that boracite can not have the formula $Mg_7B_{16}O_{30}Cl_2$ which has been thought correct for many years.

New analyses and re-examination of the old ones show a larger chlorine content in the mineral than given in the old formula. Two new formulas are possible, $Mg_{25}Cl_8B_{56}O_{105}$ and $Mg_6Cl_2B_{14}O_{26}$. The first has such a large molecule that it does not seem reasonable to assign it to boracite. The second one is more probable. It may be possible to write this formula $Mg_3Cl\ B_7O_{13}$, if boracite is orthorhombic holohedral instead of hemihedral hemimorphic as has been claimed.

[6] For BOCl see: Dammer, O., *Handbuch der anorganischen Chemie*, vol. 3, p. 65, 1893.