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BORON IN TETRAHEDRA OF BORATES AND BOROSILICATES

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Conditions of co-existence and types of condensation of boron and silicon tetrahedra are examined.

It was formerly believed that boron occurred in natural compounds chiefly surrounded by oxygen in triangular co-ordination. Fourfold tetrahedral co-ordination, as determined by Dunbar and Machatschki (1) in danburite, was supposed to be exceptional. More recently, new examples of boron in tetrahedra have been determined, and it seems now that this type of co-ordination is relatively frequent.

Four is an enhanced number of co-ordination of boron towards oxygen, and thus, as was shown by the author in a previous note (2), compounds with boron in tetrahedra can not generally be expected to conform strictly to the Pauling electrostatic valence rule. This had been, in fact, already observed by Berger (3) in the structure of B_2O_3. While the unfavorable radius ratio makes oxygen bridges between aluminum tetrahedra generally unstable, and hence no such bridges occur in any of the structures of Al_2O_3, the favorable radius ratio permits boron tetrahedra in B_2O_3 to be linked to each other in such a way that corners are shared by two and even by three tetrahedra.

The maximum number of tetrahedra which can share one corner without sharing edges is four, since the resulting oxygen configuration is cubic close-packed in the ideal case: one central ion is surrounded by twelve others situated at the centers of the edges of a cube. Four cations are tetrahedrally distributed around the strongly polarized central anion. Such a structure occurs in the well-known basic beryllium acetate, $Be_4O(CH_3CO_2)_6$. A similar configuration, with four boron tetrahedra sharing one corner, was found by Ito, Norimoto and Sadanaga (4) in boracite. The Pauling electrostatic valence rule is fulfilled if a bond-strength as low as $\frac{1}{2}$ is attributed to the boron oxygen bond in this particular case. It may reasonably be expected that also the tetraborate ion has a similar structure, and hence in its completely hydrated form has the composition $[B_4O(OH)_{12}]^{2-}$ or $[B_4O_7 \cdot 6H_2O]^{2-}$. Sharing of corners by the oxygen polyhedra which surround the central oxygen ion should lead to the less hydrated forms of sodium borate.

Boron tetrahedra not only can share corners with each other, but also

with silicon tetrahedra, as in danburite. Since the silicon oxygen bond-strength probably can not be reduced to one half in tetrahedral co-ordination, a sharing of one corner by four tetrahedra should under these conditions be impossible. There are, however, two possibilites for condensation of three tetrahedra: two borons and one silicon, and two silicons and one boron. The latter really occurs in the structure of tourmaline, as determined by Donnay and Buerger (5), and by Ito and Sadanaga (6). This is clearly seen by examining the figures in the papers, though it is not mentioned. Figure 1 shows a model of the tourmaline structure. Only the "molecule" with its continuation in the z-direction is shown;
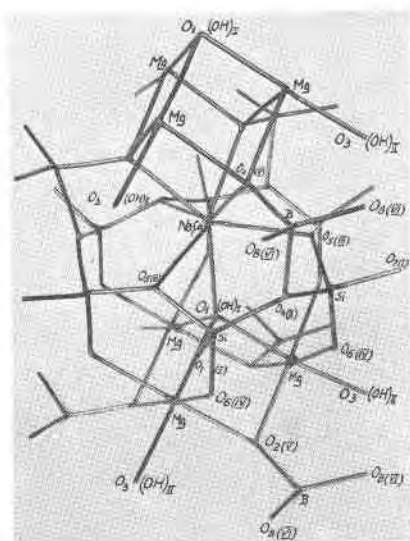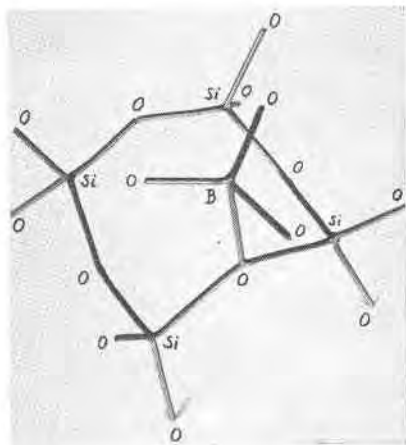

FIG. 1. Model of tourmaline structure.

FIG. 2. $BO_3 \cdot Si_4O_{12}$ group in the structure of axinite.

aluminum atoms are omitted. The boron oxygen $B\text{-}O_{4(II)}$ bond may be expected to have a bond-strength of about $\frac{1}{2}$, and the distance should accordingly be of the order of 2.2 Å, as in B_2O_3 or slightly larger. The bond-strength of the silicon oxygen $Si\text{-}O_{4(II)}$ bond should be about $\frac{3}{4}$, and the distance, accordingly, slightly larger than the normal 1.62 Å. The boron triangles, really bases of $BO_3 \cdot O$ pyramids, as the distorted tetrahedra are called in the description of the boracite structure by Ito, Norimoto and Sadanaga, should be strongly contracted, and the boron atom should lie very close to the plane of these triangles. Sharing of corners of silicon and boron tetrahedra is the explanation why aluminum can not substitute for silicon in the six-membered silicate ring of tourmaline: an oxygen bridge between aluminum and silicon tetrahedra,

already considerably weaker than the silicon-oxygen-silicon bridge, would break down completely under the weakening influence of the boron oxygen bond. Aluminum tetrahedra thus can not be expected to share corners already shared by boron and silicon tetrahedra.

Another example of the same kind is to be found in the structure of axinite, as determined by Ito and Takéuchi (7). Though the description mentions only separate BO_3 and Si_4O_{12} groups, these groups are linked to each other by a boron oxygen bond similar to the one existing in tourmaline. The $BO_3 \cdot Si_4O_{12}$ group is shown in Fig. 2.

It is quite possible that condensation of boron and silicon tetrahedra of the types described is a common feature in the structure of boron silicate glasses, and it may be responsible for some of their properties. It may be expected to occur also in other borosilicates.

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DETERMINATION OF MAGNETITE IN CHRYSOTILE

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During work on the beneficiation of chrysotile, the need developed for a method for estimating quantitatively the magnetite content, either originally present or residual. The procedure evolved is given in detail.

A 1-gram sample of chrysotile is cut up by hand or in a Wiley mill to short lengths ($<\frac{1}{4}$-inch), placed in a Waring blender containing 500 to 600 cc. water, and disintegrated for 3 minutes. A 0.1 molar solution of aluminum formate is added dropwise until further addition causes no marked improvement in dispersion. 1 cc. is the amount recommended in U. S. Patent 2,661,287 (1). Beating in the Waring blender is continued for 3 minutes to give a total of 6 minutes. This treatment largely disperses the chrysotile into its ultimate fibers, which are only some 200 to 300 Å units in diameter, and dislodges most of the magnetite contained therein. Transfer completely to a 1-liter beaker. (The blender used should be in