

SUBSTITUTION OF BORON IN
SILICATE CRYSTALS¹

By

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Abstract. The concentration of boron as a non-essential constituent in silicate minerals is explained on a crystal-structure basis as due to the replacement of an SiO_4 , in which there is at least one unshared oxygen, by a $\text{BO}_3(\text{OH})$. It is unlikely that B proxies directly for Al; boron-analogue structures of aluminosilicates are either end members or disordered structures.

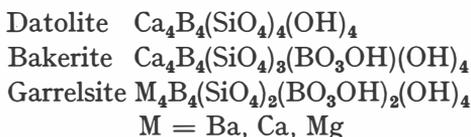
In recent publications, OFTEDAL (1964 a, b, c) presents some very useful spectrochemical results obtained on the concentration of boron as a non-essential constituent in a number of silicate and metamict rare-earth oxide minerals. He found, for example, a maximum of 2.5 per cent B_2O_3 (by weight) in gadolinite and vesuvianite, values of B_2O_3 ranging up to 0.5 per cent in a variety of other silicates, and values of B_2O_3 up to 0.8 per cent (in euxenite), for several metamict rare-earth oxides. In addition to providing these valuable basic chemical data, OFTEDAL (1964 a, b) also tentatively discussed possible mechanisms of substitution of boron for silicon in the silicate structures. Oftedal's suggestions are not altogether in accord with our present knowledge of borate and silicate crystal chemistry, and because of the importance of the general problem, it is of interest to explore it further.

A basis for discussion of the problem is provided through consideration of the crystal structure of datolite, $\text{CaB}(\text{SiO})_4(\text{OH})$. As shown by ITO and MORI (1953), and later verified by PAVLOV and BELOV (1957), datolite contains infinite sheets of composition $[\text{BSiO}_4(\text{OH})]_n^{-2n}$ in which SiO_4 tetrahedra and $\text{BO}_3(\text{OH})$ tetrahedra link at corners so

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that each SiO_4 shares three corners and has one unshared corner, and each $\text{BO}_3(\text{OH})$ shares three corners, with the unshared (OH) at the fourth corner (see Fig. 5 of the paper of ITO and MORI 1953). Christ (1959) showed that successive replacement of the SiO_4 groups containing the unshared O by BO_3OH would yield the minerals bakerite and garrelsite (MILTON, AXELROD, and GRIMALDI 1955). Thus,



FRONDEL (p. 363 in PALACHE, BERMAN, and FRONDEL 1951) had previously postulated a common structural basis for datolite, bakerite, homilite $[(\text{Ca,Fe})\text{B}(\text{SiO}_4)(\text{OH})]$, and herderite $[\text{CaBe}(\text{PO}_4)(\text{F,OH})]$, because of their similar powder patterns.

These results suggest a definite mechanism by which boron can proxy for silicon, namely the replacement of an SiO_4 , in which the O does not make a second tetrahedral bond, by a BO_3OH . The average Si-O bond length in silicates is about 1.61 Å (SMITH and BAILEY 1963), and the average tetrahedral B-OH bond length in hydrated borates is 1.47 Å (CLARK, APPLEMAN, and CHRIST 1964). Thus, the replacement of an SiO_4 by a BO_3OH would cause a nominal linear reduction of only 8.7 per cent, which seems feasible. The presence of the proton in the BO_3OH group not only leads to the correct charge for the substitution but is also in agreement with the crystal-chemical principle that an oxygen bonded to only one boron usually has a great tendency to attach a proton (CHRIST 1960).

Of the silicates analyzed by OFTEDAL (1964 a, b), gadolinite and vesuvianite contained the highest maximum weight percentages of B_2O_3 , 2.5 per cent in each case. Gadolinite, $\text{Y}_2\text{FeBe}_2(\text{SiO}_4)_2\text{O}_2$, has the same type of sheet structure (ITO and MORI 1953) as datolite. In gadolinite, SiO_4 tetrahedra and BeO_4 tetrahedra link at corners so that each SiO_4 shares three corners and has one unshared corner (each BeO_4 shares three corners and has one unshared corner). Thus, unshared-corner SiO_4 groups would be available for replacement by BO_3OH groups, in accordance with our postulated proxying mechanism. For a content of 2.5 per cent B_2O_3 , the calculated formula for gadolinite would be $\text{Y}_2\text{Be}_2\text{Fe}(\text{SiO}_4)_{1.7}(\text{BO}_3\text{OH})_{0.3}\text{O}_2$.

Vesuvianite, according to WARREN and MODELL (1931), has the unit-cell content $\text{Ca}_{10}(\text{Mg,Fe})_2\text{Al}_4\text{Si}_9\text{O}_{34}(\text{OH,F})_4$, and in the structure four of the Si form Si_2O_7 groups and the other five form independent SiO_4 groups. Thus, in this mineral, most of the oxygens are bonded to only one silicon, so that the postulated substitution of BO_3OH for SiO_4 is possible. OFTEDAL (1964 a) correlated the optic sign of a number of vesuvianite specimens with the B_2O_3 content. He found that the sign was negative for low B_2O_3 , and positive for high B_2O_3 , the rule being that vesuvianites containing less than about 0.5 per cent B_2O_3 are optically negative, while those containing 1 per cent or more are optically positive. DEER, HOWIE, and ZUSSMAN (1962) have reported a correlation between the optics of vesuvianites and their hydroxyl contents. They state (p. 115): 'The birefringence appears to be related to the amount of (OH) in the structure, an increasing hydroxyl content reducing the birefringence. In some vesuvianites, the decrease in birefringence (and in the ϵ index [ω index?]) is sufficient to make them almost isotropic or even optically positive as in the variety wiluite, which was reported to contain some boron and which is in addition often biaxial and has a low to moderate $2V$.' Thus, the two separate correlations, namely the decrease of birefringence with increasing B_2O_3 content, and the decrease of birefringence with increasing (OH) content, are, taken together, consistent with the postulation that BO_3OH can proxy for SiO_4 in these vesuvianites.

Of the other boron-containing silicates discussed by OFTEDAL (1964 b), all contain at least some oxygens bonded to only one silicon, and most contain discrete SiO_4 groups, so that the substitution of BO_3OH for SiO_4 is feasible.

It seems fruitless to attempt any discussion of the mode of boron substitution in a metamict mineral. The atomic architecture of a substance in a metamict state must be sufficiently far removed from crystallinity that we can hardly apply the same kind of thinking about mechanisms of substitutions as we do to crystals.

HEIER (1965) has suggested that the relative boron enrichment of metamict specimens, noted by OFTEDAL (1964 c) in his study of the distribution of boron in pegmatite minerals, is due to preferential adsorption by these 'amorphous' metamict materials. With this view, no structural considerations need be invoked. Heier also discusses the possibility that this excess boron is ^{10}B , resulting from the radioactive

decay of ^{10}Be , and hence, that Be plays a key role in the metamictization of minerals, and their boron enrichment.

The possibility of substituting boron for tetrahedral aluminum, in aluminosilicate structures, must also be considered. The mineral reedmergnerite, NaBSi_3O_8 , is the boron analogue of albite, $\text{NaAlSi}_3\text{O}_8$ (MILTON, CHAO, AXELROD, and GRIMALDI 1960). CLARK and APPLEMAN (1960) have shown that reedmergnerite is isostructural with low-temperature albite, and that the AlO_4 tetrahedron of low albite, with average Al–O bond length of 1.74 Å (RIBBE, FERGUSON, and TAYLOR 1962), is replaced by a BO_4 tetrahedron, with average B–O bond length of 1.47 Å (APPLEMAN and CLARK 1965) in reedmergnerite. The average reduction in bond length effected here is 15.5 per cent. The existence of these analogous structures suggests that under some conditions B may proxy for tetrahedral Al, but offers no direct evidence of this. EUGSTER and MCIVER (1959) have reported very briefly on the existence of a solid solution between NaBSi_3O_8 and $\text{NaAlSi}_3\text{O}_8$ extending to at least 20 mole per cent of NaBSi_3O_8 . This result would seem to offer more convincing evidence for the substitution of B for Al. However, it is not known whether these solid-solution compounds are disordered, as is the case in high-temperature albite. In high albite the four crystallographically non-equivalent tetrahedra each contain approximately 0.75 Si and 0.25 Al, and have approximately equal (Si,Al)–O bond lengths of average value 1.64 Å (FERGUSON, TRAILL, and TAYLOR 1958). A disordered structure would seem to be more favorable than an ordered structure for the substitution of B for Al, because of the smaller nominal adjustment in bond length required. D. E. Appleman (oral communication, 1965) has suggested that a possible distribution of Si, Al, and B in four tetrahedral sites of the 20 per cent NaBSi_3O_8 solid solution might be: 1) 0.75 Si, 0.25 Al; 2) 0.75 Si, 0.25 Al; 3) 0.75 Si, 0.25 Al; 4) 0.75 Si, 0.05 Al, 0.20 B, with 4) being the $T_1(\text{O})$ tetrahedron.

Other boron-analogue structures have been synthesized. EUGSTER and WRIGHT (1960) have prepared aluminum-free boron phlogopite, $\text{KMg}_3\text{BSi}_3\text{O}_{10}(\text{OH})_2$, and boron annite, $\text{KFe}_3\text{BSi}_3\text{O}_{10}(\text{OH})_2$; NODA, DAIMON, and TOYODA (1944) have made a boron fluoro-phlogopite $\text{KMg}_3\text{BSi}_3\text{O}_{10}\text{F}_2$.

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