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The crystal structure of B-free kornerupine: Conditions favoring the incorporation of variable amounts of B through $^{[4]}B \rightleftharpoons {}^{[4]}Si$ substitution in kornerupine

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Abstract

B-free kornerupine from the Limpopo Belt, southern Africa, $a = 16.117(4)$, $b = 13.728(3)$, $c = 6.749(2)$ Å, space group *Cmcm*, $Z = 4$, has been refined to $R = 0.034$ and $R_w = 0.028$ for 1550 observed reflections. The formula for one eightfold, five octahedral, and three tetrahedral sites based on the structure refinement (F from the chemical analysis), $(\square_{0.71}Mg_{0.16}Fe_{0.13})(Mg_{1.64}Fe_{0.20}\square_{0.16})(Mg)(Al_{1.64}Mg_{0.36})(Al)_4(Si)_2(Al_{1.12}Si_{0.88})(Si_{0.68}Al_{0.32})O_{20.55}(OH)_{1.2}F_{0.25}$, is in good agreement with wet chemical analyses for H_2O and electron microprobe analyses of the other constituents. The (OH + F) content of 1.5 per formula unit determined by wet chemical analysis exceeds the theoretical maximum of 0.67(OH) predicted by P. B. Moore and colleagues for kornerupine with 33% occupancy of the eightfold X site. Protons are bound to only one O atom, and thus two-thirds of these O sites must be bound to two protons. Comparison with three kornerupine samples having B contents of 0.41–0.69 B atoms per formula unit indicates coupled substitution of B for Si and Al in T3 and Si for Al in T2, and it implies that T3 in kornerupine with low B contents (possibly 0–0.5 atoms) contains Al as well as Si and B. We suggest that the following factors enable kornerupine to incorporate variable amounts of B: (1) flexibility of the structure in the vicinity of the triad of T2 and T3 tetrahedra, allowing the structure to adjust to the size differences between B, Si, and Al, (2) a low T3-O7-T2 angle, which leads to a minimum-energy situation for a B-O-Si bridge, and (3) compositional disorder on T2 and T3, so that B-O-Al bridges are avoided.

Introduction

Kornerupine, a relatively rare magnesium iron aluminum silicate of aluminous upper-amphibolite and granulite-facies rocks, generally contains B in amounts up to 4 wt% B_2O_3 (e.g., Grew et al., 1990). However, kornerupine from the Limpopo Belt in Zimbabwe is B free (Schreyer and Abraham, 1976; Windley et al., 1984; Droop, 1989), and B-free kornerupine has an extensive field of stability in the MgO-Al_2O_3-SiO_2-H_2O system at $T > 735$ °C, $P_{H_2O} \geq 4.5$ kbar (Seifert, 1975). In contrast to the other borosilicate minerals in aluminous metamorphic rocks, namely tourmaline, dumortierite, grandidierite, and werdingite, the B in kornerupine is entirely in fourfold coordination. A point of particular mineralogical interest in kornerupine is the mechanism enabling variable amounts of B to be incorporated.

The crystal structure of B-bearing kornerupine was first determined by Moore and Bennett (1968), who refined the structure of ferrian kornerupine from Mautia Hill, Tanzania (1.92 wt% B_2O_3, McKie, 1965). Moore and Bennett's structure is consistent with Bartl's (1965) suggestion that B substitutes for Si on a tetrahedral site, thus allowing for a variable B content in kornerupine. Moore and Bennett (1968) determined that a quarter of the kornerupine unit cell includes 22 O atoms (of which one is OH) and 14 cations on three distinct tetrahedral and five distinct octahedral sites. Moore and Araki (1979) carried out a more precise refinement of a B-bearing kornerupine sample (2.72 wt% B_2O_3) synthesized by Werding and Schreyer (1978). Moore and Araki confirmed the basic features of the Moore and Bennett structure, conclusively demonstrated B substitution for Si on one tetrahedral site, and located an additional, partially occupied cation site with distorted eightfold coordination. Subsequently, Finger and Hazen (1981) refined the structure of a natural Fe-rich kornerupine sample (3.09 wt% B_2O_3 from the crystal structure refinement) from a specimen of quartzofeldspathic gneiss that Lonker (1988) had collected in the Grenville Province of Ontario (locality is erroneously given as Rangeley Quadrangle, Maine, by Finger and Hazen, 1981). Ion microprobe data on kornerupine in another sample collected by Lonker (1988) at the same locality gave 3.20 wt% B_2O_3 (Grew et al., 1990).

Moore et al. (1989) redetermined the crystal structure of the Mautia Hill specimen to take advantage of improved methods of X-ray diffraction and the information

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TABLE 1. Composition of B-free kornerupine

Wt%		Formula for 22 (O,OH,F)	
SiO_2	28.62	Si	3.551
Al_2O_3	48.20	$^{[4]}$Al	1.449
		$^{[6]}$Al	5.600
TiO_2	0.13	Ti	0.012
Fe_2O_3	0.18	Fe^{3+}	0.017
FeO	3.06	Fe^{2+}	0.317
MnO	0.05	Mn	0.005
MgO	17.23	Mg	3.187
CaO	0.07	Ca	0.009
Na_2O	0.04	Na	0.010
F	0.63	F	0.247
H_2O	1.52	OH	1.254
Total	99.46	Total (cations only)	14.157

Note: Sample no. 9365 (Collection of the Institut für Mineralogie, Ruhr-Universität, Bochum, Germany) from the Limpopo Belt, Zimbabwe. Total corrected for F = O. Cr_2O_3, Li_2O, B_2O_3 = 0; BeO = 0.0003 wt%. Analysis by electron microprobe, except for Fe_2O_3/FeO ratio from Mössbauer data (Amthauer, personal communication), H_2O by Karl-Fischer titration, B by colorimetry, and Li, Be by atomic absorption (from Grew et al., 1990).

TABLE 2. Experimental details for the Limpopo belt B-free kornerupine

(A) Crystal cell data		
a (Å)	16.117(4)	
b (Å)	13.728(3)	
c (Å)	6.749(2)	
V (Å^3)	1493.2(1)	
Reflections	25	
Space group	*Cmcm*	
Z	4	
ρ_{calc} (g/cm^3)	3.298	
μ (cm^{-1})	12.3	
(B) Intensity measurements		
Crystal size (μm)	50 × 75 × 60	
Diffractometer	Syntex R3 automated four-circle diffractometer	
Radiation	Mo*Kα* (λ = 0.70926)	
Monochromater	graphite	
Scan type	θ-2ω	
2θ range	70° (sin θ/λ = 0.8 Å^{-1})	
Maximum scan time (s)	240	
Orientation monitors	three orientation standards checked every 50 reflections	
Number of reflections measured	5696	
Number of unique reflections (merging *R* value 2.15%)	1801	
Independent reflections	1550 above 4σ, used in final refinement	
(C) Final refinement		
	1550 F_{obs}	1801 F_{obs}
R	0.034	0.042
R_w	0.028	0.030

obtained in the Moore and Araki (1979) study. As a result, crystal structure information is available on three kornerupine samples varying in B content from 0.41 to 0.69 B per formula unit of 22 O atoms, that is, 41–69% occupancy of one site by B.

To understand better the variations in the kornerupine structure as a function of B content, we refined the crystal structure of the naturally occurring, B-free kornerupine found by Schreyer and Abraham (1976). In the present paper, we present the results of our refinement of B-free kornerupine from the Limpopo Belt and compare the structures of the B-free and B-bearing kornerupine.

EXPERIMENTAL PROCEDURE

Description of the crystal

The crystal fragment used in this study was broken from sample 9365 (housed in the mineral collection of the Institut für Mineralogie, Ruhr-Universität, Bochum, Germany) collected by W. Schreyer at Sinyoni Claims in the Limpopo Belt near Beit Bridge, Zimbabwe (Schreyer and Abraham, 1976). This sample consists of randomly oriented, decimeter-sized kornerupine crystals, together with corundum and sapphirine, in a matrix of coarse cordierite. The kornerupine is largely replaced by a sapphirine-cordierite-gedrite symplectite described in detail by Schreyer and Abraham. Of the several crystal fragments that were picked from the sample and ground, a spheroid apparently free of inclusions was selected for X-ray study.

Chemical composition

The crystal fragment was analyzed by K. Abraham at Bochum in 1984 with the electron microprobe at 20 spots along two traverses at right angles to one another. No systematic variations in composition were detected. Thus the crystal appears to be homogeneous with respect to the major constituents of atomic mass greater than 11 (Na) (Table 1 from Grew et al., 1990).

H_2O was analyzed by Karl-Fischer titration (see Werding and Schreyer, 1978) under different conditions as follows: (1) after drying overnight at 135 °C, total H_2O = 1.43, 1.50 wt%; (2) no drying prior to analyses, H_2O^+ = 1.55, 1.58 wt% and H_2O^- = 0.07, 0.05 wt%, respectively; and (3) total H_2O = 1.57, 1.62 wt%. The value of 1.52 wt% in Table 1 is an average of the two values for the dried kornerupine and the two H_2O^+ values; the uncertainty is estimated to be ±0.1% H_2O from these four values.

Refining the crystal structure

Unit-cell dimensions and diffraction intensities were measured on the unoriented crystal and the cell dimensions obtained by least-squares regression (Table 2). Diffraction intensities of 5696 reflections, including *hkl* and $\bar{h}\bar{k}l$, were measured with variable-speed, θ-2ω scans and scaled by comparison with repeatedly measured standard reflections. Because of the favorable shape and low absorption of the crystal, no absorption correction was applied. After applying Lp corrections, symmetrically equivalent reflections were averaged (merging *R* value 2.15%) yielding 1801 unique reflections. A total of 1550 reflections were considered to have nonzero intensities using the criterion $F > 4\sigma_F$. Systematic absences were consistent with the space group *Cmcm* determined by Moore and Bennett (1968).

The calculations were performed with the computer program for crystal structure analysis SHELXTL (1979 version) developed by G. M. Sheldrick. The structure was solved in *Cmcm* by automated centrosymmetric direct

TABLE 4. Atomic coordinates for B-free kornerupine

Atom	Site	Occupancies	*x*	*y*	*z*
H	8f	0.30(3)	½	0.550(3)	0.141(6)
XFe	4a	0.0330(4)	0	0	0
XMg	4a	0.0400(10)	0	0	0
M1Mg	8g	0.4095(14)	0.1223(1)	0.1364(1)	¼
M1Fe	8g	0.0502(6)	0.1223(1)	0.1364(1)	¼
M2Mg	4c	0.25	½	0.1447(1)	¼
M3Al	8e	0.5	0.2161(0)	0	0
M4Al	8g	0.4100(13)	0.3145(0)	0.1401(1)	¼
M4Mg	8g	0.0900(13)	0.3145(0)	0.1401(1)	¼
M5Al	8e	0.5	0.4059(0)	0	0
T1Si	8g	0.5	0.4016(0)	0.3519(0)	¼
T2Si	8g	0.2200(13)	0.1825(0)	0.3317(1)	¼
T2Al	8g	0.2800(14)	0.1825(0)	0.3317(1)	¼
T3Si	4c	0.1700(8)	0	0.3404(1)	¼
T3Al	4c	0.0800(9)	0	0.3404(1)	¼
O1	8g	0.5	0.2258(1)	0.0446(1)	¼
O2	8g	0.5	0.4022(1)	0.0459(1)	¼
O3	8g	0.5	0.4019(1)	0.2335(1)	¼
O4	16h	1.0	0.1390(1)	0.0998(1)	−0.0529(2)
O5	8g	0.5	0.2386(1)	0.2337(1)	¼
O6	16h	1.0	0.3161(1)	0.0959(1)	−0.0437(2)
O7	8g	0.5	0.0864(1)	0.2764(1)	¼
O8	8f	0.5	½	0.0883(1)	−0.0479(2)
O9	4c	0.25	0	0.1159(2)	¾
O10	4c	0.25	0	0.0874(2)	¼

Note: Standard errors are given in parentheses.

methods. In our initial input, the hand-picked signs of 12 *E* values were fixed. The program searched out 12 additional *E* values by varying their signs, and through permutation the number of *E* values was expanded to 189. The best *E* map showed the positions of eight cations and three of the O atoms. After refining the coordinates of these atoms ($R = 36\%$), a difference synthesis showed all ten O atoms and the partially filled X site. The scattering power of this site is similar to that of an O atom. Refinement without temperature factors reduced the *R* index to 11%. From the bond distances in this initial model and from comparison of the coordinates in the initial model with those reported by Moore and Araki (1979), we could assign scattering factors to each of the cation sites without knowing the actual site occupancies. Our only assumption was that the X position was 20% occupied by Fe. The weighted refinement ($w = 1/\sigma_F^2$) proceeded to $R_w = 8\%$. A refinement with isotropic temperature factors for all atoms gave $R = 5.5\%$ ($R_w = 4.7\%$). After a refinement with anisotropic temperature factors, we were able to estimate the site occupancies from consideration of polyhedral distortion and M-O and T-O distances, as well as from the form of anisotropic ellipsoids. After several trials with different Fe contents of the M and X sites, we selected the refinement with (1) Fe and Mg on X and M1, (2) Mg only on M2 and M4, and (3) total Si, Al, Fe, Mn equal to the values given in the chemical analysis (Table 1). This refinement gave the most reasonable temperature factors and is consistent with G. Amthauer's (personal communication) Mössbauer data suggesting two sites for Fe.

At this stage, the difference-Fourier synthesis showed the position of one H atom. The final *R* is 3.4%, $R_w = 2.8\%$ for 1550 observed reflections (Table 3; $R = 4.2\%$, $R_w = 3.0\%$ for all 1801 reflections).[1] Throughout the calculations in the refinement, nonionized form factors of Fe, Si, Al, Mg, and O were used, as provided by volume IV of the *International Tables for X-ray Crystallography.* Tables 4 and 5 give the final positional parameters and anisotropic temperature factor coefficients, respectively, and Table 6 gives bond lengths and angles.

TABLE 5. Thermal parameters of B-free kornerupine

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H		$\bar{U}_{equ} = 0.024(14)$				
X	0.0368(17)	0.0130(14)	0.0132(12)	−0.0012(10)	0	0
M1	0.0203(4)	0.0177(4)	0.0137(4)	0	0	0.0082(3)
M2	0.0090(5)	0.0111(6)	0.0116(5)	0	0	0
M3	0.0119(3)	0.0126(4)	0.0096(3)	−0.0007(3)	0	0
M4	0.0075(3)	0.0088(3)	0.0127(3)	0	0	0.0005(3)
M5	0.0113(3)	0.0121(3)	0.0097(3)	−0.0006(3)	0	0
T1	0.0093(3)	0.0109(3)	0.0109(3)	0	0	0.0007(3)
T2	0.0104(3)	0.0115(3)	0.0101(3)	0	0	0.0004(3)
T3	0.0100(4)	0.0114(5)	0.0111(5)	0	0	0
O1	0.0112(7)	0.0128(8)	0.0100(7)	0	0	0.0005(7)
O2	0.0123(7)	0.0113(8)	0.0105(7)	0	0	−0.0002(7)
O3	0.0128(8)	0.0114(8)	0.0167(8)	0	0	0.0007(7)
O4	0.0153(6)	0.0144(6)	0.0124(5)	−0.0003(4)	−0.0014(5)	0.0031(5)
O5	0.0169(9)	0.0212(10)	0.0173(8)	0	0	0.0054(8)
O6	0.0122(6)	0.0152(6)	0.0143(6)	−0.0015(5)	−0.0006(5)	0.0008(5)
O7	0.0138(8)	0.0119(8)	0.0160(7)	0	0	−0.0017(7)
O8	0.0120(8)	0.0118(9)	0.0130(8)	−0.0003(7)	0	0
O9	0.0099(11)	0.0135(13)	0.0273(14)	0	0	0
O10	0.0158(12)	0.0179(14)	0.0232(13)	0	0	0

Note: The thermal parameters U_{ij} are defined by the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*\cos\gamma^*)]$. Standard deviations are given in parentheses.

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[1] To receive a copy of the list of observed and calculated structure amplitudes (Table 3), order Document AM-91-481 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 6. Polyhedral interatomic distances and angles of B-free kornerupine.

Bond	Distance (Å)	Angle (°)
	Configuration around H	
2 O10-H1	0.90(4)	
1 O9-H1	2.39(5)	
H1-O10-H1		110(1)
O10-H1-O9		107(3)
	Polyhedron around X	
2 X-O10	2.070(2)	
2 X-O9	2.319(2)	
4 X-O4	2.650(1)	
Average	2.422	
X-H	1.17(4)	
X-H	2.52(4)	
	Octahedron around M1	
1 M1-O7	2.007(2)	
1 M1-O10	2.083(1)	
1 M1-O1	2.091(2)	
2 M1-O4	2.123(1)	
1 M1-O5	2.302(2)	
Average	2.122	
1 O7-O5*	2.522(3)	71.3(1)
2 O1-O4**	2.591(2)	75.9(0)
1 O1-O5**	2.604(2)	72.6(1)
1 O7-O10	2.945(2)	92.1(1)
2 O10-O4	3.038(1)	92.5(0)
2 O4-O5	3.185(2)	92.0(0)
2 O7-O4	3.283(2)	105.3(0)
1 O10-O1	3.686(2)	124.0(1)
Average	2.996	91.0
	Octahedron around M2	
2 M2-O3	1.997(2)	
2 M2-O2	2.080(2)	
2 M2-O8	2.155(2)	
Average	2.077	
2 O3-O2**	2.576(2)	78.3(1)
4 O2-O8**	2.621(2)	76.5(1)
1 O2-O2	3.153(2)	98.6(1)
1 O3-O3	3.162(3)	104.7(1)
4 O3-O8	3.243(2)	102.7(1)
Average	2.910	89.7
	Octahedron around M3	
2 M3-O1	1.802(1)	
2 M3-O4	1.884(1)	
2 M3-O6	2.101(1)	
Average	1.929	
2 O1-O6**	2.558(2)	81.5(1)
2 O1-O4**	2.591(2)	89.3(1)
1 O6-O6**	2.698(2)	79.9(1)
2 O1-O4	2.766(2)	97.3(1)
2 O1-O6	2.789(2)	90.9(1)
1 O4-O4	2.830(2)	97.4(1)
2 O4-O6	2.856(2)	91.4(1)
Average	2.716	89.8
	Octahedron around M4	
1 M4-O5	1.775(2)	
1 M4-O3	1.904(2)	
1 M4-O2	1.915(2)	
1 M4-O1	1.940(2)	
2 M4-O6	2.073(1)	
Average	1.947	
2 O2-O6**	2.515(2)	78.1(0)
2 O1-O6**	2.558(2)	79.1(0)
1 O3-O2**	2.576(2)	84.8(1)
1 O5-O1**	2.604(2)	88.9(1)
1 O5-O3	2.631(3)	91.2(1)
1 O2-O1	2.843(3)	95.0(1)
2 O5-O6	3.012(2)	102.7(0)
2 O3-O6	3.067(2)	100.8(0)
Average	2.747	90.1
	Octahedron around M5	
2 M5-O2	1.802(1)	
2 M5-O8	1.968(1)	
2 M5-O6	1.978(1)	
Average	1.916	
1 O8-O8**	2.509(3)	79.2(1)
2 O2-O6**	2.515(2)	83.3(1)
2 O2-O8**	2.621(2)	87.9(1)
1 O6-O6**	2.698(2)	86.0(1)
2 O2-O6	2.766(2)	94.0(1)
2 O2-O8	2.782(2)	95.0(1)
2 O8-O6	2.965(1)	97.4(1)
Average	2.709	90.0
	Tetrahedron around T1	
2 T1-O4	1.624(1)	
1 T1-O3	1.626(2)	
1 T1-O9	1.647(1)	
Average	1.630	
1 O3-O9	2.603(3)	105.4(1)
2 O4-O9	2.615(1)	106.2(1)
1 O4-O4	2.660(2)	110.0(1)
2 O4-O3	2.728(2)	114.2(1)
Average	2.658	109.4
	Tetrahedron around T2	
1 T2-O5	1.621(2)	
2 T2-O6	1.711(2)	
1 T2-O7	1.725(2)	
Average	1.692	
1 O5-O7*	2.522(3)	97.8(1)
2 O6-O7	2.735(2)	105.5(1)
1 O6-O6	2.785(2)	108.9(1)
2 O5-O6	2.862(2)	118.4(1)
Average	2.750	109.1
	Tetrahedron around T3	
2 T3-O7	1.646(2)	
2 T3-O8	1.679(2)	
Average	1.663	
4 O7-O8	2.692(2)	108.1(0)
1 O8-O8	2.727(3)	108.7(1)
1 O7-O7	2.785(3)	115.5(1)
Average	2.713	109.4
	T-O-T angles	
T2-O7-T3		121.6(1)
T1-O9-T1		148.9(2)

Note: Standard errors are given in parentheses.
* Shared edge between M and T polyhedra.
** Shared edge between M and M′ polyhedra.

According to this refinement, M1 is 8% vacant and the other M sites (also T sites) are 3% vacant. The 3% vacancies are not considered significant in view of the high correlations among occupancy factors, scale factor, and temperature factors, a conclusion generally accepted by other investigators (e.g., Moore and Araki, 1978). Our structural refinement (Table 4, except F from Table 1) yields the following structural formula in terms of the sites X, M1, M2, M4, M3, M5, T1, T2, and T3 (notation for cation sites from Moore and Araki, 1979): $(\square_{0.71}Mg_{0.16}Fe^{2+}_{0.13})(Mg_{1.64}Fe^{2+}_{0.20}\square_{0.16})Mg(Al_{1.64}Mg_{0.36})Al_2Al_2Si_2(Al_{1.12}Si_{0.88})(Si_{0.68}Al_{0.32})O_{20.55}(OH)_{1.2}F_{0.25}$ (total positive charges = 42.46, total negative charges = 42.55).

On the basis of average bond lengths for Si-O equal to 1.63 Å and Al-O equal to 1.74 Å, the tetrahedral site occupancies were calculated to be $(Al_{1.13}Si_{0.87})$ for T2 and $(Si_{0.71}Al_{0.29})$ for T3, in good agreement with the refinement constrained by the chemical analysis.

DESCRIPTION OF THE STRUCTURE

The structure of B-free kornerupine has the same general features as that of B-bearing kornerupine refined by

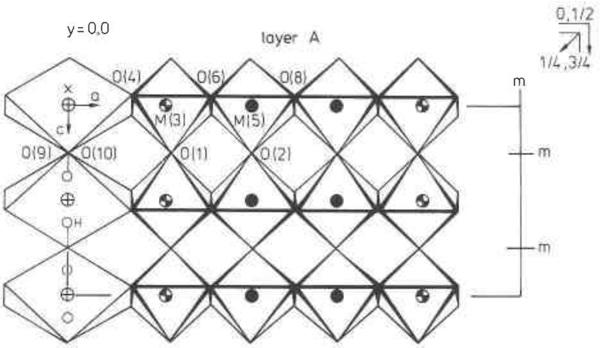

Fig. 1. Projection parallel to [010] of the A layer in kornerupine at $y = 0$.

Moore and Araki (1979), who recommended viewing the structure in terms of two layers parallel to (010), A and B (Figs. 1 and 2, respectively). Layer A consists of a wall of M3 and M5 octahedra extending parallel to [001] and alternating with a chain of the partially occupied, highly distorted cubic X site. Layer B consists of chains of M1-M4-M2 octahedra and alternating T_2O_7 and T_3O_{10} groups in [100]. Layer B is joined to layer A through shared edges between octahedra and vertices between tetrahedra and octahedra. An exception is the tetrahedron T2, which shares an edge with the octahedron M1 (Fig. 3).

The M1 octahedron is the most distorted of the M polyhedra, whereas the M5 and M3 octahedra are the most symmetrical. Thus the M3 + M5 wall is the most compact unit in the structure. The degree of distortion increases roughly with polyhedron and cation size: M3 and M5 are occupied only by Al, M4 by Al and subordinate Mg, M2 by Mg, and M1 by Mg, Fe, and vacancies. The X position is 29% occupied and has the highest Fe/Mg ratio. The three T positions are occupied only by Si and Al.

A unique feature of the B-free kornerupine is the 8% vacancy on M1. None of the other investigators reported vacancies on any of the sites except X in the B-bearing kornerupine samples. In the chemical analysis, the cation total per 22 (O,OH,F) is 14.16. Given that X is 29% occupied, the other sites are left with 13.87 cations, which is close to the 13.84 cations calculated by assuming M1 is 92% occupied.

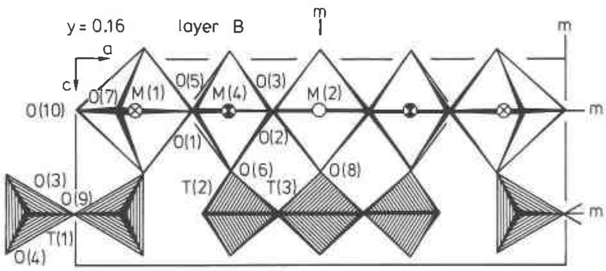

Fig. 2. Projection parallel to [010] of the B layer in kornerupine at $y = 0.16$.

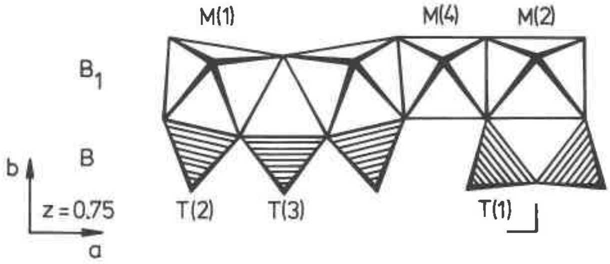

Fig. 3. Projection parallel to [001] of a portion of the kornerupine structure at $z = 0.75$.

ANION COMPOSITION

The proton located by difference-Fourier analysis is situated in the polyhedron surrounding the X site (Figs. 1 and 4). The 1.2 (1) H per formula unit calculated in the refinement is in good agreement with the chemical analysis (1.254 H). The H-O10-H angle is 110(1)°, which is close to the H-O-H angle of 104.5° in H_2O (Pauling, 1960, p. 111). The two possible O10-H···O9 configurations are highly asymmetric. The O10-H bond is 0.90 Å long, whereas the H···O9 distances are 2.39 Å long in a direction roughly parallel to **b** and 2.79 Å long in a direction roughly parallel to **c** (Fig. 4). These distances are too long for there to be H bonding (cf. Moore et al., 1989); such bonding appears unlikely because O9 is electrostatically saturated (Table 7).

Only one proton site was found, which is consistent with the findings of previous investigators. There is no indication of a second site in the bond strengths (Table 7) calculated for O atoms in the B-free kornerupine from the parameters in Brown (1981, his Table A-1). These bond strengths range from 1.87 to 2.16, except for O10, whose bond strength was calculated to be 0.87, assuming that only O is present on this site.

A. Beran (personal communication, 1984, 1985, 1991) obtained polarized infrared spectra on (011) plates from the same B-free kornerupine specimen from which we selected our crystal. A major absorption feature at 3550 cm^{-1} with a shoulder at 3350 cm^{-1} and minor features at 3000 cm^{-1} and 1570 cm^{-1} are most intense perpendicular to **a** and virtually absent parallel to **a**. Thus the O-H bonds

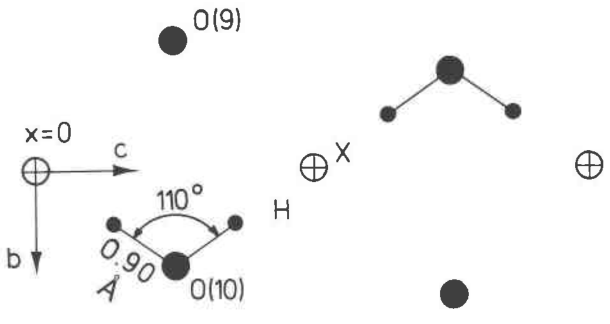

Fig. 4. Projection parallel to [100] of the H and O positions in the vicinity of the X site at $x = 0$.

TABLE 7. Bond strengths of O atoms in B-free kornerupine

	X	M1	M2	M3	M4	M5	T1	T2	T3	Total
O1	—	0.317	—	1.320	0.464	—	—	—	—	2.101
O2	—	—	0.347	—	0.495	1.320	—	—	—	2.162
O3	—	—	0.423	—	0.509	—	1.011	—	—	1.943
O4	0.028	0.293	—	0.532	—	—	1.017	—	—	1.870
O5	—	0.191	—	—	0.710	—	—	1.046	—	1.947
O6	—	—	—	0.300	0.329	0.415	—	0.821	—	1.865
O7	—	0.388	—	—	—	—	—	0.790	0.969	2.147
O8	—	—	0.291	—	—	0.853	—	—	0.885	2.029
O9	0.121	—	—	—	—	—	1.908	—	—	2.029
O10	0.222	0.646	—	—	—	—	—	—	—	0.868
								Average without O10		2.010

Note: Calculated from parameters in Brown (1981).

must lie in the (100) plane. Beran reported that the major feature at 3550 cm^{-1} is indicative of nearly free OH groups and that the two minor features could be attributed to H_2O molecules. Aines and Rossman (1984) stated that features near 1620 cm^{-1} are diagnostic of H_2O molecules. Interaction with other constituents could shift the features to lower wavenumbers, such as the 1570 cm^{-1} observed in our pattern. Although preliminary, Beran's infrared spectra confirm the orientation of OH bonds deduced from the X-ray refinement.

The main question concerning the anion composition is that the number of protons determined by wet chemical analyses and the X-ray refinement, 1.2–1.25 H per formula unit, exceeds the number of O10 sites, of which there is but one per formula unit. Given the presence of 0.25 F per formula unit, only 0.75 O atoms per formula unit are available for bonding to H. If only one proton is bonded to an O atom at O10 as an OH group, then the composition of this site would be 0.25 F + 0.75 OH, and not all of the analyzed H_2O would be accommodated. On the other hand, if all the 1.25 H found by wet chemical analysis is assumed to be bonded to the O10 site, then its composition would be 0.25 F + 0.25 OH + 0.5 OH_2, that is, one half of the O10 site is occupied by H_2O molecules. In this case, an average of 1.67 H is bonded to O at the O10 site, and the total bond strength for O10 increases to 2.26 (vs. 1.56 for 0.75 H). As F is also present at O10, the actual bond strength may be less than the calculated value because the F ion is smaller than the O ion. Moreover, the presence of two protons attached to O10 is consistent with the (001) mirror plane passing through O10. Symmetry requires that a single proton be disordered over the two potential sites, although ordering of the proton might escape detection because of its small scattering volume and because of the symmetry of the X-ray scattering experiment (Laue symmetry *mmm*).

Even with 1.25 H per formula unit, there are not too many occupants for the X site in the B-free kornerupine. This site could be filled either by two protons, one proton with F replacing O on O10, or by a cation (Mg,Fe) with F or O on O10, that is, a disordered distribution of 0.625 H pairs and 0.29 (Mg,Fe) in X and a disordered distribution of F and O in O10. In the absence of F, the maximum number of protons that could theoretically be accommodated in kornerupine would be two per formula unit. Seifert (1975) reported 2.13–2.15 H in synthetic B-free kornerupine. Moore and Araki (1979) calculated that in Seifert's (1975) kornerupine the X site would be vacant and the M1 site 93% occupied. Moore and Araki (1979) also considered the possibility of H_2O molecules at O10 in Seifert's (1975) kornerupine but dismissed this possibility as unlikely given the high temperatures and pressures of synthesis.

In summary, the wet chemical, X-ray diffraction, and infrared data all point to the possibility that H_2O molecules, as well as F and OH, are lodged in the O10 site in the B-free kornerupine analyzed in this study. We admit that our evidence for molecular H_2O is not conclusive. However, the detailed and systematic X-ray and infrared investigation needed to ascertain the presence of molecular H_2O is beyond the scope of the present study. F. C. Hawthorne and G. R. Rossman have begun a systematic study of kornerupine that will involve structural refinements and infrared studies of a large number of kornerupine specimens. It is hoped that the results of their investigation will clarify the anion composition of kornerupine.

COMPARISON WITH B-BEARING KORNERUPINE

Compositions of the tetrahedral sites

The major differences among the structures of the B-free kornerupine and those of the B-bearing Mautia Hill, synthetic, and Grenville kornerupine refined by Moore et al. (1989), Moore and Araki (1979), and Finger and Hazen (1981), respectively, are in the compositions of the cation sites. Of the three tetrahedral sites, only T1 has the same composition, 100% Si, and same size (Fig. 5) in the four kornerupine samples. Among the sites showing variable composition, T3 in the B-free kornerupine is occupied by Al as well as Si, whereas no Al was reported in T3 in the three boron kornerupine samples. Moreover, T2 in the B-free kornerupine contains more Al than Si, in contrast with the B-bearing kornerupine samples but consistent with Moore and Araki's (1979) prediction for T2 composition in Seifert's (1975) synthetic B-free kornerupine.

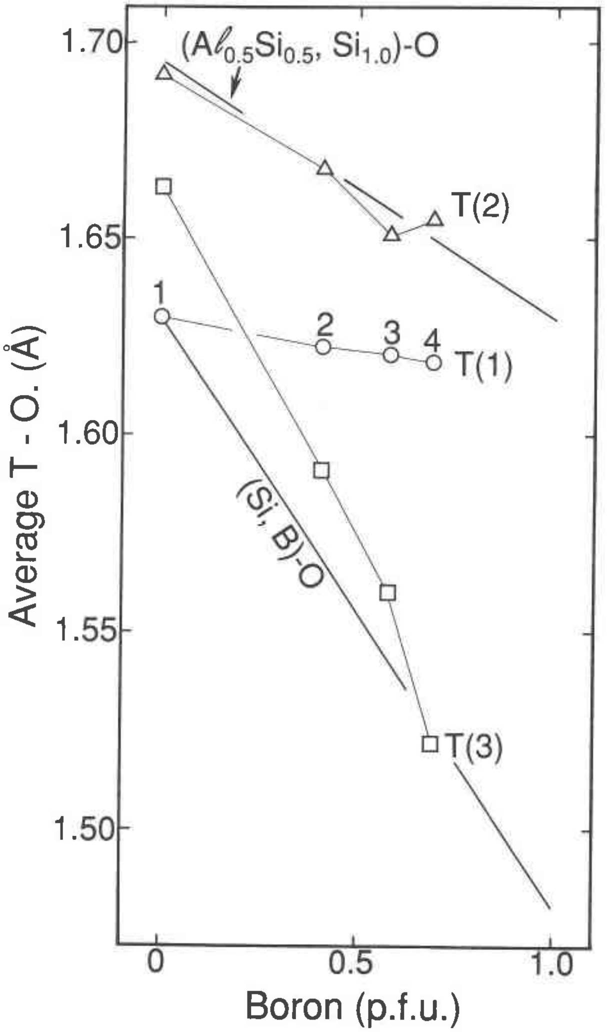

Fig. 5. Average tetrahedral distances are plotted as a function of B content (in atoms B per formula unit from chemical analysis) of the four kornerupine samples for which the crystal structure has been refined. Lines join average $^{[4]}$Si-O = 1.63 Å and $^{[4]}$B-O = 1.48 Å and average $^{[4]}$Si-O and $^{[4]}(Al_{0.5}Si_{0.5})$-O = 1.695 Å calculated for an average O coordination of 3.5 from data of Shannon (1976). Sources of chemical and crystallographic data are as follows: (1) B = 0, Limpopo Belt, southern Africa, Grew et al. (1990), this paper; (2) B = 0.41, Mautia Hill, Tanzania, McKie (1965), Moore et al. (1989); (3) B = 0.58, synthetic, Werding and Schreyer (1978), Moore and Araki (1979); and (4) B = 0.69, Grenville Province, Canada, Finger and Hazen (1981).

The *Cmcm* space group requires complete cation disorder on T2 and T3, and no investigator has reported any violations of the symmetry due to cation ordering in these sites. Thus, there is no evidence for different structural states among the four kornerupine samples, although their thermal histories differ considerably.

Average T3-O lengths decrease from 1.66 Å in the B-free kornerupine to 1.52 Å in that richest in B, a decrease greater than that predicted for B → Si substitution (Fig. 5). Substitution on T3 must be B → (Si,Al) because T3 in the B-free kornerupine contains 32% Al. This suggests that in kornerupine containing between 0 and 0.5 B per formula unit, B and Al, as well as Si, are present in T3. No Al has been reported in T3 in any of the three B-bearing kornerupine samples, probably because of the difficulty of finding small amounts of Al on a site with dominant Si as well as B.

Average T2-O lengths decrease with increasing B content of T3 and Si content of T2 along a trend corresponding to the substitution Si → 0.5 Si + 0.5 Al (Fig. 5). This trend suggests that the substitutions on the two sites are coupled, and consequently B appears to substitute for Al, as has been reported by Seifert (1975) and many other investigators. However, the coupling is not one-to-one: Si and Al vary with B in a more complex fashion, which is discussed in the next section.

Compositions of the octahedral and X sites

The possibilities for compositional variations in the octahedral sites are considerable, given the presence of substantial Mg, $^{[6]}$Al, Fe^{2+}, and Fe^{3+} in most kornerupine. Among the four kornerupine samples for which structure refinements are available, only M3 and M5 are compositionally invariant: 100% Al. In the B-free kornerupine sample, M4 is occupied by Al and subordinate Mg, and no more than 5% Fe is present on either M4 or M2. M4 is occupied by substantial Fe^{3+} in the Mautia Hill kornerupine sample (Moore et al., 1989), whereas M2 is occupied by substantial Fe in the Grenville kornerupine sample (Finger and Hazen, 1981); Fe in M2 is presumably Fe^{2+} (Moore et al., 1989). M1 and X contain Mg and Fe^{2+} in the B-free and Grenville kornerupine samples.

The structural role of Fe determined by X-ray diffraction is consistent with Mössbauer data on the B-free kornerupine. Amthauer (personal communication) found that 95% of the Fe in the B-free kornerupine is divalent and is present in roughly equal amounts on two sites. Thus the amount of Fe^{3+} that would occupy M4 is too small to be detected by X-ray analysis. Moreover, our refinement converged to 0.13 Fe per formula unit on X and 0.20 Fe per formula unit on M1, a distribution consistent with the Mössbauer results as well as with Moore and Araki's (1979) predictions.

Finger and Hazen (1981) reported that Fe^{2+} and Mg are disordered among the M2, M1, and X sites in the Grenville kornerupine, that is, $X_{Fe} = Fe^{2+}/(Fe^{2+} + Mg) = 0.30$, 0.36, and 0.35 in M2, M1, and X, respectively. In contrast, the B-free kornerupine has a partially ordered Fe^{2+}-Mg distribution, namely, X_{Fe} = 0, 0.11, and 0.45 in M2, M1, and X, respectively.

Given the large number of constituents, four specimens are too few to assess properly compositional variations of the three octahedral sites M1, M2, and M4 with B content. Any statement based on the trends illustrated in Figure 6 must be considered tentative at best. Nonetheless, a few comments are in order, if only as a guide to future studies of kornerupine crystal chemistry.

Only two sites vary significantly in size among the four kornerupine samples: M4 and M2. Variations in the size of M4 are due both to Fe^{3+} ⇌ Al substitution and to Al ⇌ Mg substitution. The sizes of M4 and T2 vary inversely, which suggests that a coupled substitution of the Tschermak type, namely $^{[4]}Al + ^{[6]}Al \rightleftharpoons ^{[4]}Si + ^{[6]}Mg$, applies to kornerupine, whereas Fe^{3+} ⇌ Al plays a secondary role. Combining this substitution with variations in T3 composition, we get an overall substitution $^{[4]}Si + ^{[6]}Mg \rightleftharpoons ^{[4]}(B,Al) + ^{[6]}Al$ that involves concomitant substitutions on T2, T3, and M4. Compositional variations in highly magnesian natural kornerupine (where ambiguities concerning Fe valence do not arise) can be rationalized in terms of this overall substitution (Grew et al., 1987; Grew, 1988).

M2 increases in size with B content and thus becomes a more favorable site for Fe → Mg substitution in B-rich kornerupine. On the other hand, M1 may become a less favorable site for Fe → Mg substitution because of increasing electronegativity of the O atoms coordinated both to B,Al and Si in T3 and T2 and to Fe and Mg in M1 (Grew et al., 1990). These two factors together could explain the disordered Fe-Mg distribution between M1 and M2 that Finger and Hazen (1981) reported for the Grenville kornerupine, which contrasts with the partially ordered distribution in the B-free kornerupine.

Composition of the O10 site

Substitutions involving anions on the O10 site appear to be indirectly related to B content but not with occupancy of the neighboring X and M1 sites (kornerupine specimens are numbered as in Figs. 5 and 6):

Kornerupine sample no.	1	2	3	4
B per formula unit	0	0.41	0.58	0.69
F + OH per formula unit	1.50	0.25	0.82	—
X occupancy	0.29	0.37	0.32	0.20
M1 occupancy	0.92	1.00	1.00	1.00

McKie's (1965) OH value of 0.25 for sample 2 seems too low: it is significantly less than the lowest values reported for synthetic kornerupine (Werding and Schreyer, 1978: OH = 0.5) and the OH needed to balance the formulae calculated from the crystal structure (Moore et al., 1989: OH = 0.76). For kornerupine samples 1 and 3, (OH + F) content appears to be independent of the occupancy of X and may only affect occupancy of M1 when (OH + F) contents exceed 1. Thus, more crystal structure refinements, together with high-quality analyses of H$_2$O and F, are needed to assess the applicability to kornerupine of the series by Moore and Araki (1979) and Moore et al. (1989): $X^{2+}O^{2-} - X^{2+}_{0.33}\square_{0.67}OH^{-}_{0.67}$.

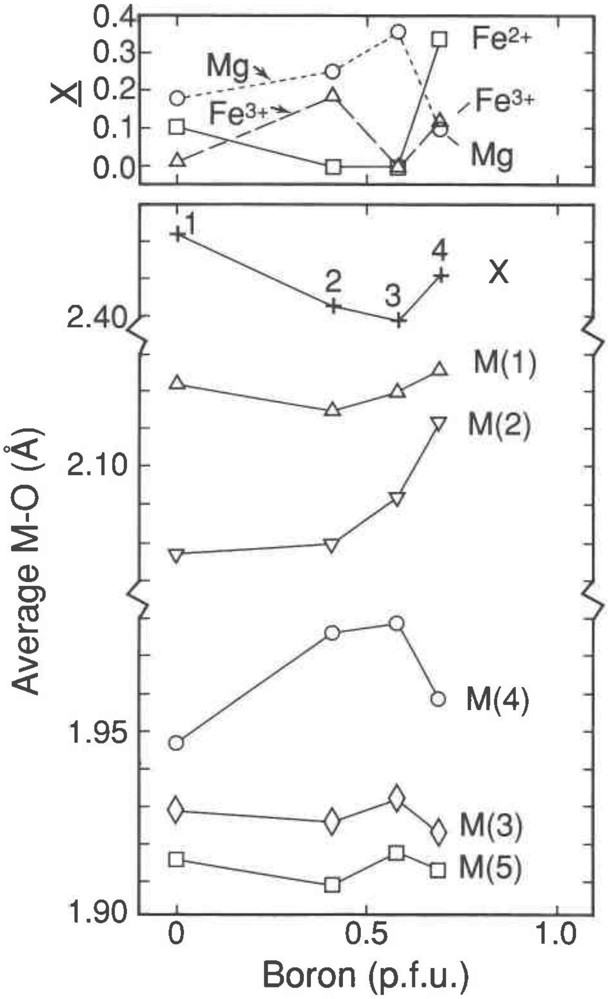

Fig. 6. Average octahedral and X-site distances are plotted as a function of B content (in atoms B per formula unit from chemical analysis) of the four kornerupine samples for which the crystal structure has been refined (sources of data are given in Fig. 5). The following mole fractions X are plotted: $X_{Fe^{2+}} = Fe^{2+}/(Fe^{2+} + Mg)$ in M1, M2, and X (solid line), $X_{Fe^{3+}} = Fe^{3+}/(Fe^{3+} + Mg + Al)$ in M4 (long-dashed line), and $X_{Mg} = Mg/(Fe^{3+} + Mg + Al)$ in M4 (short-dashed line). The mole fractions were calculated from the chemical analyses and site occupancies; X_{Mg} in no. 3 was calculated from the average M4-O distance, assuming Al-O = 1.91 Å and Mg-O = 2.10 Å (see Moore et al., 1989).

Werding and Schreyer (1978) reported an inverse relation having a slope of −1.7 between B and H in synthetic kornerupine, which is equivalent to the exchange $BH_{-1.7}$. Data on kornerupine samples 1 and 3, above, give an exchange of $BH_{-1.2}$ (combining F with OH). The inverse relation was inferred by Werding and Schreyer (1978) to result from a chain of substitutions in which occupancy of X increases with B content, resulting in a decrease of H content. However, there is no correlation of X occupancy and B content among the four kornerupine samples listed above.

Dimensional variations with B content

The substitution of B for Si results in a 1.7% decrease in cell volume among the four kornerupine samples (1493 Å^3 to 1468 Å^3), most of which is due to a 1% decrease in the *a* cell parameter (16.117–15.960 Å) and to a lesser extent the *c* parameter (6.749–6.706 Å), consistent with the results reported by Werding and Schreyer (1978) for synthetic kornerupine and Grew et al. (1990) for natural kornerupine. The decrease is concentrated in the T3 tetrahedron; T2 also decreases but much less and not consistently (Fig. 5). As the edges of T2 and T3 are parallel to **c** and **a** (Fig. 2), variations in their compositions would be expected to have the largest effect on the *c* and *a* parameters.

For example, the decrease in the O7-O7 edge (oriented parallel to **a**) of T3 from 2.785 to 2.506 Å (from B = 0 to B = 0.69 per formula unit) is not much greater than the decrease in the O8-O8 edge (oriented parallel to **c**) from 2.727 to 2.523 Å. However, the decrease in the O8-O8 edge of T3 is partly offset by an increase in the O8-O8 length of the M2 octahedron, resulting in a marked increase in the size of M2 (Fig. 6). The sum of these two O8-O8 distances, equal to the *c* parameter, thus decreases much less with B content than does the O8-O8 edge length of T3. The changes in the edge O7-O5, which is shared by M1 and T2, and in the edge O7-O7 are accommodated by the pair of M1 octahedra (Fig. 3). In the line of M1-M4-M2 octahedra of the B layer, the greatest and most consistent changes are in the M1-M1 distance, which decreases with increasing B content, whereas the M4-M2 distance is unchanged. Overall, the pair of M1 octahedra seems to be highly flexible. Its ability to adjust to the marked changes in the dimensions of the T2-T3-T2 triad is probably due to the octahedra sharing a vertex (O10) rather than an edge (making for looser articulation), to the irregular form and variable occupancy of the individual octahedra, and to the variable number of protons attached to O10.

The A sheet adjusts to the changes in the B sheet through kinking of the octahedra wall and distortion of the Al octahedra. The line of M3-M5 octahedra rotates around twofold symmetry axes parallel to [100] as the O8-O8 distance across M2 increases with increasing B content. The O6-O6 distance across M4 increases as the Al content of T2 decreases, but to a lesser extent than O8-O8. The O4-O4 distance is least affected. Most of the contraction along [100] is taken up by the M5-M5 distance, which decreases 0.126 Å as B content increases to 0.69 per formula unit; the M3-M5 distance increases 0.033 Å, and X-M3 decreases 0.049 Å.

One might expect that the X site would play a critical role in variable B incorporation because it could offer a flexibility to the A sheet of kornerupine that is not possible in a more homogeneous sheet such as the octahedral ("brucite") sheet in micas. However, this role is not evident in the available information; for example, the average size of the X site does not vary systematically with B content (Fig. 6).

MECHANISMS FOR B → (Si,Al) SUBSTITUTION

The ability of kornerupine to incorporate a variable amount of B is unusual in a silicate mineral. B in the borosilicates tourmaline, grandidierite, dumortierite, and axinite is in triangular coordination and its content is fixed, as is the B content of reedmergnerite, danburite, and datolite, where B is in fourfold coordination. Other than such borosilicates, few silicate minerals contain more than 0.1% B_2O_3 (e.g., Harder, 1959; Oftedal, 1964). Examples of minerals in which significant and variable amounts of B substitute for Si or Al are sapphirine (e.g., Grew et al., 1990), serendibite (Buerger and Venkatakrishnan, 1974; Sen Gupta et al., 1989), olivine and humite-group minerals (Hinthorne and Ribbe, 1974; Grew et al., 1991), B-rich cookeite (Černý et al., 1971), authigenic potassium feldspar (Smith and Brown, 1988), and sillimanite (Grew and Hinthorne, 1983). Examples of synthetic materials with such substitution are albite that possibly contains as much as 10 mol% reedmergnerite in solid solution (Pichavant et al., 1984) and ZSM-5 zeolite, in which replacement of $^{[4]}$Al by $^{[4]}$B was demonstrated using ^{27}Al and ^{11}B magic-angle sample spinning NMR (Derouane et al., 1985). Except in the case of sillimanite, available structural and compositional data imply that B is substituting for Si or Al on a tetrahedral site. Incorporation of B in sillimanite involves rearrangement of the structure, and the coordination of B is closer to triangular than to tetrahedral (Grew and Rossman, 1985; Niven et al., 1991).

The mechanism of B substitution for Si and Al in silicate minerals has received little attention to date, and thus the scarcity of B → Si and B → Al substitution has not been fully explained. Many investigators simply assume B → Al substitution in minerals such as feldspars and micas. Christ (1965) suggested that B substitution for Si would be possible in minerals lacking Al if one of the O atoms were not coordinated to another tetrahedron and could accept a proton, that is, BO_3OH for SiO_4 as in the series datolite-bakerite-garrelsite. Hinthorne and Ribbe (1974) suggested that B substitution for Si in chondrodite was balanced by additional OH or F substitution for O, and this additional OH or F could be coordinated to the B-bearing tetrahedron.

However, neither the substitution proposed by Christ (1965) nor a simple B → Al substitution is applicable to kornerupine, sapphirine, serendibite, or to other aluminosilicates. In the present discussion, we will consider some of the factors involved in B → Si and B → Al substitution in an attempt to explain the substantial B substitution in kornerupine, sapphirine, and serendibite and its absence in most other minerals.

The difference in average bond lengths between $^{[4]}$B-O (1.48 Å) and $^{[4]}$Al-O (1.76 Å) is too large to allow simple miscibility of B and Al on a single site. Christ (1965) suggested that disordered silicate structures would be more favorable than ordered structures for B → Al substitution. The large difference in bond lengths between Al and B could be more readily accommodated in sites where Si, as well as B and Al, is present. The difference in bond lengths between B-O (1.48 Å) and Si-O (1.63 Å) is not so large and is comparable to the difference between Al-O and Si-O. Thus B → Si seems more likely than B → Al. This is consistent with the situation in kornerupine, where the dominant substitution on T3 is B → Si, in serendibite (Sen Gupta et al., 1989), and probably in sapphirine, in which the T2 and T3 sites are dominantly Si (Moore, 1969; Higgins and Ribbe, 1979; Merlino, 1980). Thus mechanisms for B → Si substitution, rather than B → Al substitution, are probably more important in controlling the incorporation of B in silicates. Even allowing for the scarcity of B relative to Al in nature, B → Si substitution is much less common and less extensive than Al → Si substitution, which is all the more surprising because the size differences are comparable and the charge difference identical. Clearly, the size difference between B-O and Si-O is not the only factor constraining B → Si substitution.

An important factor restricting B → Si substitution may be the T-O-T angle over the bridging O atom (Geisinger et al., 1985; Navrotsky et al., 1985). Geisinger et al. (1985) calculated from molecular orbital theory that Si-O-B angles should on the average be much smaller than either Si-O-Si or Si-O-Al angles in cases where the bridging O atom is in twofold coordination, that is, 125° compared with 144° and 139°, respectively. Moreover, the range of angles for Si-O-Si and Si-O-Al would be relatively unrestricted, whereas Si-O-B would be energetically stable only over a narrower range. In the case where the bridging O atom is in threefold coordination (as is O7 in kornerupine), the optimized Si-O-Si (132°) and Si-O-Al (132°) angles and possible range of angles would decrease, whereas the stable configurations for Si-O-B would be less affected (128°). In B-free kornerupine, the T2-O7-T3 angle is 121.6(1)°, and in the three B-bearing kornerupine samples this angle is 123(1)° (Mautia Hill, Moore et al., 1989), 124° (synthetic, Moore and Araki, 1979), and 124.6(2)° (Grenville, Finger and Hazen, 1981), all of which are less than the T1-O9-T1 of 148.9(2)° in the B-free kornerupine and 150.8(3)° in the Grenville kornerupine. The T2-O7-T3 angles are near the predicted minimum-energy angles for Si-O-B. The T-O-T angles for the tetrahedra T2 and T3 in sapphirine, where B → Si substitution may occur, are also low, 117–120° (Higgins and Ribbe, 1979).

Other structural units with T-O-T angles favorable to B → Si substitution are the four-membered rings in cordierite (T-O-T angles 127–133°, Cohen et al., 1977), as suggested by Geisinger et al. (1985), and sheets in micas with high α angles such as paragonite (T-O-T at 125–134°, Lin and Bailey, 1984), margarite (T-O-T at 119–126°, Guggenheim and Bailey, 1975), and clintonite (T-O-T = 120–121°, S. W. Bailey, personal communication, 1991, calculated from data in Joswig et al., 1986; MacKinney et al., 1988). However, cordierite associated with B-bearing kornerupine contains ≤0.01% B_2O_3 (Grew et al., 1990), margarite and paragonite associated with tourmaline contain 0.02–0.03% B_2O_3 (Grew et al., 1986), and clintonite associated with serendibite contains 0.01 wt% B_2O_3 (Grew et al., 1991). Evidently these minerals do not incorporate substantial B, even in B-rich environments including minerals rich in $^{[4]}$B. Moreover, their B contents do not exceed that of muscovite, which has a low α angle (Bailey, 1984); for example, phengitic muscovite is reported to contain 0.010–0.064 wt% B_2O_3 (ion microprobe analyses, Domanik et al., 1991).

We suggest that an additional factor is involved. The structure must not only accommodate B → Si on one site, but it must also accommodate Si → Al on an adjacent tetrahedral site, as implied in the substitutional schemes proposed by Werding and Schreyer (1978) and by Moore and Araki (1979). In kornerupine, these substitutions are partially coupled on the T3 and T2 sites. In sapphirine, Si → Al is possible on the other three T sites, which are Al rich and share vertices with T3 and T2 (Moore, 1969; Higgins and Ribbe, 1979; Merlino, 1980). This coupling could be due to the instability of B-O-$^{[4]}$Al bridges ["B-Al avoidance," although B-O-B bridges are reported in danburite (Phillips et al., 1974), and in cappelenite (Shen and Moore, 1984)]. This "B-Al avoidance" may explain the absence of significant B in cordierite and margarite, in which Si and Al are highly ordered. In both minerals, each Si tetrahedron shares corners with two Al tetrahedra, so that coupled substitutions of B → Si and Si → Al in adjacent tetrahedra still result in B tetrahedra sharing corners with Al tetrahedra. In minerals with Si-Al disorder, such as paragonite and clintonite, this problem should not arise. However, B → Si coupled with Si → Al will reduce the size of the tetrahedral sheet, resulting in a mismatch with the octahedral sheet (see Bailey, 1984, for a review). Thus rotation of the tetrahedra would be required to restore the match, increasing α and T-O-T angles. Indeed, the required match between the tetrahedral and octahedral sheets in micas may be the main factor limiting B → Si substitution in this mineral group. In this regard, structures of the B-rich cookeite described by Černý et al. (1971) and manandonite $Li_2Al_4Si_2AlBO_{10}(OH)_8$, a member of the 7 Å serpentine-kaolinite group (Ranorosoa et al., 1989), would be of interest.

CONCLUSIONS

In summary, we suggest the following mechanisms facilitating B incorporation in kornerupine and other aluminosilicate minerals:

1. The structure in the vicinity of the T2-T3-T2 triad is flexible, which allows the structure to adjust to the size differences between B, Si, and Al tetrahedra. Moreover, the variable occupancies of M1 and X give kornerupine extra degrees of freedom for compositional variation, which may be necessary for B incorporation involving a chain of several substitutions, such as the chain suggested by Werding and Schreyer (1978). In sapphirine, linear gaps between the walls of octahedra (Moore, 1969) could provide the flexibility of size variations in the tetrahedra, which form chains parallel and adjacent to the gaps.

2. The T-O-T angular configuration is favorable; specifically, the low T3-O7-T2 angle results in a minimum energy situation for a B-O-Si bridge.

3. There is compositional disorder on T2 and T3. As T2 can accommodate a variable amount of Si and Al, B-O-Al bridges are avoided by means of coupling the

substitutions of B → Si on T3 and Si → Al on T2. The coupling of these substitutions appears to be possible only in minerals with disorder on the sites involved, such as kornerupine, sapphirine, and possibly also serendibite. Highly ordered minerals such as cordierite and margarite are not expected to incorporate significant B, even in B-rich environments and despite energetically favorable T-O-T angles.

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