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Cation occupancies in serendibite: A crystal structure study

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ABSTRACT

Previous refinements of the crystal structure of serendibite, approximately $(Ca,Na)_2(Mg,Fe^{2+})_3(Al,Fe^{3+})_{4.5}B_{1.5}Si_3O_{20}$, a member of the aenigmatite group, left several unanswered questions concerning the metal occupancies. New X-ray data have been refined for Fe-poor serendibite (2 wt% Fe as FeO) from Johnsburg, New York, and two Fe-bearing varieties (5.88 and 13.34 wt% Fe as FeO) from the Tayozhnoye deposit, Siberia, Russia. Cell parameters range as follows: $a = 10.010(3)$–$10.094(3)$, $b = 10.393(3)$–$10.478(3)$, $c = 8.631(2)$–$8.694(2)$ Å, $\alpha = 106.36(1)$–$106.37(1)$, $\beta = 96.00(1)$–$96.10(1)$, $\gamma = 124.38(1)$–$124.40(1)°$, $V = 669.89$–686.43 Å^3, space group $P\bar{1}$, $Z = 2$. Weighted R factors for observed reflections range from 0.028 to 0.033.

Tetrahedral substitutions are constrained to B = Si and Si = Al. One tetrahedral site is nearly fully occupied by B, whereas the other has a B/Si ratio near 1.5. These two tetrahedra are the only ones in serendibite to share three vertices with other tetrahedra, resulting in B-O-B and B-O-Al bridges, as well as B-O-Si bridges. Refinements of the Fe-rich varieties of serendibite indicate that there is little or no Fe^{3+} in the tetrahedral sites.

Fe^{3+} inferred from stoichiometric recalculations of microprobe analyses must reside in the octahedral sites, along with Fe^{2+}. No evidence was found for ordering of the octahedral Fe in the Fe-rich varieties. Mg = Al substitution undoubtedly occurs in some octahedral sites, but specifying Mg and Al occupancies is not possible because of the similarity in the scattering power of these two cations. Mg substitution on the sevenfold-coordinated Ca sites is not verified; instead, a previously overlooked constituent that was discovered in recent electron microprobe analyses, Na, is found to substitute for Ca in the Johnsburg serendibite.

INTRODUCTION

Serendibite, approximately $(Ca,Na)_2(Mg,Fe^{2+})_3(Al,Fe^{3+})_{4.5}B_{1.5}Si_3O_{20}$, is a rare mineral of the aenigmatite group occurring in high-temperature skarn deposits. It was first described by Prior and Coomaraswamy (1903) and to date is known from ten localities worldwide (Grew et al., 1991a; Yaroshchuk et al., 1990). Buerger and Venkatakrishnan (1974) were the first to describe its crystal structure (see also Machin and Süsse, 1974). On the basis of an Fe-poor specimen from Johnsburg, New York, Buerger and Venkatakrishnan (1974) reported Mg = Ca substitution on sevenfold-coordinated sites and B = Al substitution on tetrahedral sites.

However, Buerger and Venkatakrishnan's (1974) refinement leaves several questions unanswered. Firstly, neither of the reported substitutions is common in other silicate minerals. Mg and Ca substitute to a limited extent in a few minerals, such as in the M2 site of clinoenstatite (e.g., Cameron and Papike, 1981), but generally Ca and Mg occupy different sites in a given mineral. Secondly, B = Al substitution in tetrahedral sites has not been conclusively documented in any mineral, and if present, is probably very limited: reedmergnerite-albite is a possible example (Pichavant et al., 1984). Other potential examples are werdingite and kornerupine. However, Niven et al. (1991) reported that in werdingite, B and Al occupy sites that are not identical, although very close together. The "substitution" is better considered as $^{[3]}B = {}^{[4]}Al$. Chemical data suggest B = Al substitution in kornerupine (e.g., Seifert, 1975), but structural refinements indicate that this is a coupled substitution of B for Si and Si for Al on two different sites (Moore and Araki, 1979; Grew et al., 1984; Klaska and Grew, 1991).

Finally, naturally occurring serendibite is commonly Fe-rich. For example, both Fe^{2+} and Fe^{3+} are reported to be present in specimens from the Tayozhnoye deposit, Siberia (Pertsev and Nikitina, 1959; Grew et al., 1991a). In other members of the aenigmatite group, Fe^{3+} occurs in both tetrahedral and octahedral positions (dorrite,

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Table 1. Experimental data for serendibite

Sample location	Low Fe Johnsburg	Intermediate Fe Tayozhnoye 5151	High Fe Tayozhnoye 5152
		Cell data	
Space group		$P\bar{1}$	
Z		2	
μ (mm^{-1})		5.49	
a (Å)	10.010(3)	10.043(3)	10.094(3)
b (Å)	10.393(3)	10.428(3)	10.478(3)
c (Å)	8.631(2)	8.662(2)	8.694(2)
α (°)	106.37(1)	106.37(1)	106.36(1)
β (°)	96.10(1)	96.02(1)	96.00(1)
γ (°)	124.38(1)	124.40(1)	124.40(1)
V (Å^3)	669.89	677.02	686.43
F_{000}	707.39	726.13	747.94
		Intensity measurements	
Diffractometer		Syntex $P2$	
Monochromator		Graphite	
Sinθ/λ(max)		0.7034	
Scan type		ω	
Variable scan		3.91–29.3°/min	
Scan range		±0.5°	
Radiation		Mo$K\alpha$(=0.71069 Å)	
Crystal size (mm)	0.10 × 0.15 × 0.18	0.36 × 0.24 × 0.22	0.20 × 0.17 × 0.15
No. of reflections measured	4251	4281	4198
No. of unique reflections	3914	3934	3978
No. of reflect. with $F_0 > 2.0\sigma(F_0)$	3914	3934	3978
Transm. fact. (min., max.)	1.0, 0.87	1.0, 0.801	1.0, 0.94
Range of h	0–14	0–14	0–14
Range of k	−14–12	−14–12	−14–12
Range of l	−12–11	−12–11	−12–11
		Refinement	
No. of parameters	315	317	320
For significant reflections			
RF	0.030	0.032	0.042
Rw	0.028	0.030	0.033
Goodness of fit	2.319	2.403	1.606
Max. shift or error	0.0005	0.0007	0.0130
Ave. shift or error	0.0001	0.0002	0.0029
Last difference synthesis			
Largest minimum	−0.550e/Å^3	−0.614e/Å^3	−0.721e/Å^3
Highest peak	0.586e/Å^3	0.620e/Å^3	0.694e/Å^3
Secondary ext. coeff.	0.421 × 10^4	0.174 × 10^4	0.063 × 10^4
σ	0.007	0.005	0.003

Cosca et al., 1988; synthetic dorrite or SFCA, Hamilton et al., 1989).

In view of the ambiguities concerning the metal occupancies in serendibite, we undertook a reinvestigation of its crystal structure, including an Fe-poor specimen from Johnsburg and two Fe-rich specimens from Tayozhnoye. Our study resulted in findings differing from those made by previous investigators, namely Na = Ca instead of Mg = Ca substitution, absence of detectable $^{[4]}Fe^{3+}$, and B = Si instead of B = Al substitution. To our knowledge, occupancy of a single site by substantial amounts of both B and Si has been demonstrated to date only in kornerupine, where B = Si substitution is sufficiently extensive to be detected by X-ray diffraction techniques.

Experimental

Three serendibite crystals were selected for X-ray study: (1) an Fe-poor sample (~2 wt% Fe as FeO) from Johnsburg, New York, (2) a sample (designated 5151) intermediate in Fe content (5.8 wt% Fe as FeO) from the Tayozhnoye deposit, Siberia, Russia, and (3) an Fe-rich sample (designated 5152, with 13 wt% Fe as FeO), also from Tayozhnoye. The Johnsburg specimen is a sky blue crystal fragment, about 0.10 × 0.15 × 0.18 mm in size. Johnsburg serendibite occurs in a zoned skarn between marble and a potassium feldspar–rich rock (Grew et al., 1991b). Both crystal fragments from Tayozhnoye are very dark blue (nearly black), the one with intermediate Fe content measuring 0.36 × 0.24 × 0.22 mm, and the high-Fe specimen measuring 0.20 × 0.17 × 0.15 mm. These two specimens come from the magnesian skarns of the Tayozhnoye Fe ore deposit, which is developed in a dolomite marble unit (Grew et al., 1991a).

The crystals were analyzed on a SYNTEX P2 automated diffractometer using Mo$K\alpha$ radiation and a graphite monochromator. Unit-cell parameters were determined by least-squares refinement of the diffraction angles of 15 interplanar spacings in the range $18 < 2\theta < 24°$. The parameters of the Johnsburg crystal are not significantly different from those obtained by Buerger and Venkatakrishnan (1974) and by Machin and Süsse (1974) when all the reported parameters are transformed to the same cell. The cell edges of the intermediate Fe and Fe-rich varieties are slightly longer than those of the Johnsburg serendibite and increase with Fe content (Table 1).

The intensities of reflections with θ values ranging from 1.0 to 30.0° were measured using the ω scan technique. The intensities were corrected for Lorentz, polarization, and absorption factors (the latter using ψ scans). In each case three peaks were selected as intensity standards for monitoring the measurements. During data measurement in each experiment, intensities of these standard peaks varied by less than 2%. Experimental details are listed in Table 1.

STRUCTURE REDETERMINATION AND REFINEMENT

The Fe-poor Johnsburg serendibite sample was studied first. The initial coordinates for B, Si, Al, Ca, and O were taken from Buerger and Venkatakrishnan (1974), and substitutions such as B-Al and Mg-Al were at first ignored. B was dispersed over the Si sites and occupancy was allowed to vary. The scattering factors for Fe, Mg, Ca, Na, Al, Si, O, and B were taken from the *International Tables for Crystallography* (1974). All calculations were performed with the XTAL System (Hall and Stewart, 1989) on a Digital Vax 8820 computer. The final weighted and unweighted *R* factors for the Johnsburg crystal were 0.028 and 0.030, respectively.

For the refinements of the intermediate Fe and Fe-rich specimens, Fe was dispersed over the octahedral sites and proportions were allowed to vary. The final weighted and unweighted *R* factors were 0.030 and 0.032 for the intermediate Fe refinement and 0.033 and 0.042 for the Fe-rich refinement.

Atomic positions and isotropic thermal parameters for the Johnsburg specimen are given in Table 2. These data for the Tayozhnoye specimens may be requested as Table 3[1]. Buerger and Venkatakrishnan (1974) did not carry out an anisotropic refinement or provide structure factors. We present these for all three specimens. Anisotropic thermal parameters and observed and calculated structure factors may be requested as Tables 4 and 5, respectively. In order to facilitate comparison to other aenigmatite group phases, all data reported here have been transformed to the cell and origin used by Machin and Süsse (1974), a cell first used by Kelsey and McKie (1964) for aenigmatite.

TABLE 2. Atom coordinate and isotropic thermal parameters of Johnsburg serendibite

	sof	*x*	*y*	*z*	$\bar{u}$ (Å)
T1	0.652 B 0.348 Si	0.4651(1)	0.2357(1)	0.3304(1)	0.0073(3)
T2	1.0 Si	0.98393(7)	0.22828(7)	0.34086(7)	0.0068(2)
T3	1.0 Al	0.78569(8)	0.34446(7)	0.23325(7)	0.0057(2)
T4	0.980 B 0.020 Si	0.2688(3)	0.3290(3)	0.2197(3)	0.0072(6)
T5	1.0 Si	0.64333(7)	0.94317(7)	0.44362(7)	0.0080(2)
T6	1.0 Si	0.35610(7)	0.55441(7)	0.05422(7)	0.0059(2)
M1	1.0 Al	0	0	½	0.0055(2)
M2	1.0 Al	0	½	0	0.0056(2)
M3	1.0 Al	0.31197(8)	0.85596(8)	0.17246(8)	0.0066(2)
M4	1.0 Al	0.77752(8)	0.82192(8)	0.14551(8)	0.0079(2)
M5	1.0 Mg	0.09481(8)	0.94392(8)	0.06251(8)	0.0044(2)
M6	1.0 Mg	0.59383(9)	0.93901(8)	0.05623(8)	0.0056(2)
M7	1.0 Al	0.99816(8)	0.74020(7)	0.25928(7)	0.0059(2)
M8	0.775 Ca 0.225 Na	0.21564(6)	0.62437(6)	0.39800(6)	0.0088(1)
M9	0.823 Ca 0.177 Na	0.64732(6)	0.60051(6)	0.38263(6)	0.0097(1)
O1	1.0	0.3531(2)	0.0647(2)	0.1736(2)	0.0103(5)
O2	1.0	0.8448(2)	0.0496(2)	0.1682(2)	0.0088(4)
O3	1.0	0.5409(2)	0.9530(2)	0.2890(2)	0.0138(5)
O4	1.0	0.0143(2)	0.9336(2)	0.2775(2)	0.0079(4)
O5	1.0	0.2409(2)	0.8684(2)	0.3818(2)	0.0100(4)
O6	1.0	0.7623(2)	0.8819(2)	0.3830(2)	0.0092(4)
O7	1.0	0.4899(2)	0.2096(2)	0.4948(2)	0.0121(5)
O8	1.0	0.9573(2)	0.7881(2)	0.4825(2)	0.0084(4)
O9	1.0	0.9004(2)	0.3259(2)	0.3802(2)	0.0107(5)
O10	1.0	0.3839(2)	0.3254(2)	0.3450(2)	0.0106(5)
O11	1.0	0.6516(2)	0.1633(2)	0.0462(2)	0.0102(4)
O12	1.0	0.1610(2)	0.1760(2)	0.0618(2)	0.0093(4)
O13	1.0	0.5362(2)	0.7101(2)	0.0488(2)	0.0108(5)
O14	1.0	0.0686(2)	0.7260(2)	0.0646(2)	0.0082(4)
O15	1.0	0.2407(2)	0.6156(2)	0.1168(2)	0.0089(4)
O16	1.0	0.7533(2)	0.6129(2)	0.1350(2)	0.0102(5)
O17	1.0	0.3893(2)	0.4867(2)	0.1931(2)	0.0086(4)
O18	1.0	0.9520(2)	0.5259(2)	0.2158(2)	0.0101(5)
O19	1.0	0.1655(2)	0.3586(2)	0.3125(2)	0.0111(5)
O20	1.0	0.6558(2)	0.3680(2)	0.3333(2)	0.0142(5)

Note: sof = site occupancy factor, $\bar{u}$ = isotropic temperature factor. Standard deviations of the last digit are in parentheses.

DESCRIPTION OF THE STRUCTURE

Buerger and Venkatakrishnan (1974) have described the structure of serendibite, and thus only a brief recapping and highlighting of differences noted in the new studies will be given here. Interleaved octahedral and tetrahedral layers are parallel to the (011) plane. The octahedral layers consist of octahedral walls, parallel to **a**, similar to the octahedral walls in sapphirine described by Moore (1969), but with the protruding wall edge octahedra replaced by sevenfold-coordinated Ca polyhedra (monocapped octahedra). In contrast to Buerger and Venkatakrishnan (1974), we find that adjacent walls are directly linked by corner sharing of the wall edge monocapped octahedra, M8-M9 and M9-M9 (Fig. 1; note that atomic position designations correspond to those used by Cannillo et al., 1971, Machin and Süsse, 1974, and Bonaccorsi et al., 1989, 1990). The monocapped octahedra are arranged such that they alternate with lacunae (i.e., unoccupied octahedral positions) along the **a** direction. The tetrahedra of the tetrahedral layers are found directly above and below the lacunae, with their apices pointing away from the octahedral layer lacunae and their basal face vertices shared with octahedra surrounding the lacunae. The octahedral strip edges of each octahedral layer are in positions corresponding to the strip centers of the next octahedral layer above and below (Fig. 2).

The tetrahedral layers consist of winged (Moore, 1969), kinked chains of tetrahedra cross-linked by two octahe-

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[1] Copies of Tables 3, 4, and 5 may be ordered as Document AM-93-513 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.

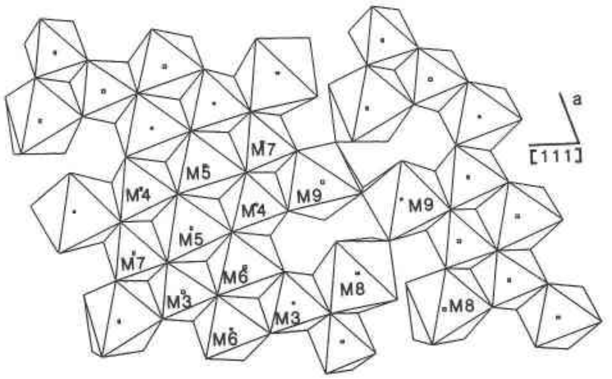

Fig. 1. An octahedral layer parallel to (011), showing the octahedral walls extending infinitely parallel to **a**, the wall edge sevenfold-coordinated Ca sites alternating along **a** with lacunae, and the way that the Ca polyhedra connect adjacent walls.

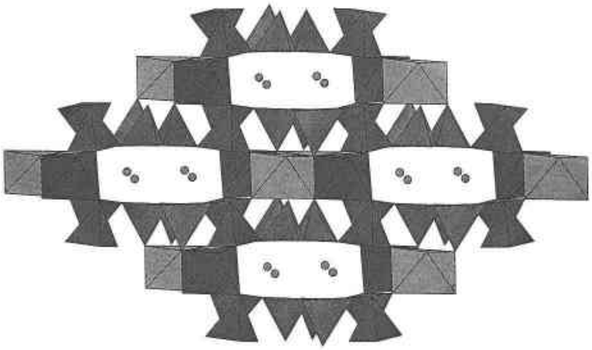

Fig. 2. The structure viewed parallel to **a**, showing the arrangement of the alternating tetrahedral and octahedral layers. The positions of M8 and M9 are indicated by shaded circles.

dral sites, M1 and M2. The chains trend parallel to **a**, and all tetrahedra in a single chain are oriented with their apices pointing in the same direction. Neighboring chains, however, have their apices oriented in opposite directions (Fig. 3).

The structure responds to the substitution of Fe by expanding slightly from a closest-packed arrangement of O atoms (cell constants, Table 1). Fe-poor Johnsburg serendibite has a packing efficiency of 16.7 Å^3/O, whereas Fe-rich Tayozhnoye serendibite has a slightly expanded arrangement with a packing efficiency of 17.2 Å^3/O.

RELATION TO OTHER AENIGMATITE GROUP MINERALS

Perhaps the major structural difference among the aenigmatite group minerals is in the extent of connectedness (i.e., number of shared vertices) between octahedral walls within an octahedral layer parallel to (011). The octahedral wall edge sites in sapphirine are occupied by sixfold-coordinated Mg (Moore, 1969; Merlino, 1980), none of whose vertices is shared with protruding octahedra of adjacent walls. Thus there exist continuous channels trending parallel to **a** between adjacent octahedral walls within an octahedral layer in sapphirine. Aenigmatite and krinovite, in contrast, have eightfold-coordinated Na in the octahedral wall edge sites (Cannillo et al., 1971; Bonaccorsi et al., 1989). Two edges of each Na square antiprism are shared with two Na polyhedra of the opposing octahedral wall, leading to extensive connectedness of octahedral walls within an octahedral layer. Thus in aenigmatite there are no channels between adjacent walls in an octahedral layer.

The situation for serendibite is intermediate between those of sapphirine and aenigmatite. The octahedral wall edge sites in serendibite are occupied by Ca in monocapped octahedral coordination. Unlike aenigmatite, krinovite, and rhönite, the wall edge cation sites of serendibite are each surrounded by seven similarly distant O atoms ($^{[7]}$M-O σ_{n-1} = 0.06 Å; Table 6). There are sharp increases in distance to the eighth nearest O atoms ($^{[8]}$M-O σ_{n-1} = 0.17 Å), the bond valence contributions of the eighth nearest O atoms is minimal (0.09 vu), and the bond valence sums of M8 and M9 are saturated by the contributions of the seven closest O atoms (Table 7). M8 shares a vertex with M9 of the opposing wall, and M9 shares an edge with M9 of the opposing wall, but M8 does not share any vertices with M8 of an adjacent wall in an octahedral layer (Fig. 1). This lends a partially connected aspect to adjacent octahedral walls in the octahedral layers of serendibite.

The cation occupying the wall edge sites does not alone determine the extent of connectedness of the octahedral walls. The sinter phase SFCA, like serendibite, has Ca in the edge sites, but the sites are octahedrally coordinated and are not connected to adjacent walls (Mumme, 1988; Hamilton et al., 1989). The wall edge sites in rhönite are each occupied more than 95% by Ca (the remainder being Na). The M8 and M9 coordination polyhedra in rhönite approximate bicapped octahedra, and each shares two edges with M8 and M9 of an opposing octahedral wall (Bonaccorsi et al., 1990). Cationic constituency of the octahedral and tetrahedral layers must also be important in determining the degree of connectedness of the octahedral walls.

METAL OCCUPANCIES IN SERENDIBITE

Machin and Süsse (1974) left the problem of cation ordering in serendibite for further refinement, and Buerger and Venkatakrishnan (1974) were not wholly satisfied with the metal occupancies derived from their own refinement using a crystal from Johnsburg. On the basis of chemical analyses of the Johnsburg material carried out by Larsen and Schaller (1932), Buerger and Venkatakrishnan calculated that the sevenfold-coordinated sites could not be fully occupied by Ca alone. They concluded that some Mg was also present in these sites. In the course of our studies of Johnsburg serendibite (Grew et al., 1991b) electron microprobe analyses showed that 0.9–1.3 oxide wt% Na is present. In the present refinement, this Na was assumed to reside in the Ca sites. Na is more appropriate than Mg in the Ca sites because it provides both the nec-

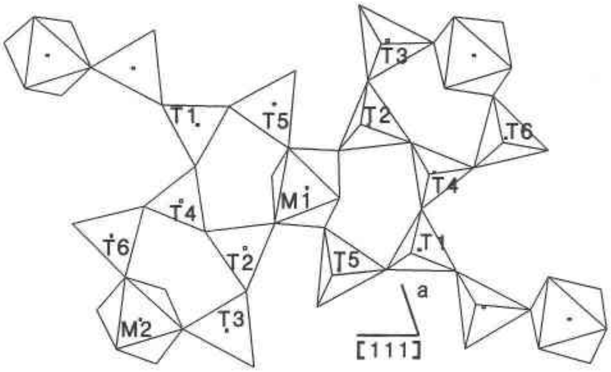

Fig. 3. A tetrahedral layer parallel to (011), showing the tetrahedral chains extending infinitely parallel to **a**, the up and down arrangement of the apices in adjacent chains, and the two octahedral sites which cross-link the tetrahedral chains.

Table 6. Bond lengths (Å) for Johnsburg serendibite

T1-O1	1.524(2)	T2-O9	1.633(2)	T3-O11	1.711(1)
-O10	1.535(2)	-O2	1.640(1)	-O20	1.725(2)
-O7	1.538(2)	-O19	1.643(2)	-O18	1.737(2)
-O20	1.595(3)	-O8	1.664(2)	-O9	1.745(2)
T4-O12	1.442(2)	T5-O3	1.659(2)	T6-O13	1.625(2)
-O19	1.484(3)	-O7	1.678(2)	-O17	1.642(2)
-O17	1.493(3)	-O5	1.689(1)	-O16	1.661(1)
-O10	1.519(3)	-O6	1.702(2)	-O15	1.673(2)
M1-O4	1.900(1)	M2-O14	1.913(2)	M3-O3	1.899(2)
-O4	1.900(2)	-O14	1.913(2)	-O14	1.928(2)
-O6	1.918(2)	-O15	1.949(2)	-O11	1.937(2)
-O6	1.918(2)	-O15	1.949(2)	-O1	1.963(2)
-O8	1.948(2)	-O18	1.956(2)	-O5	2.009(2)
-O8	1.948(2)	-O18	1.956(2)	-O15	2.055(2)
M4-O13	1.933(2)	M5-O1	2.076(2)	M6-O11	2.001(2)
-O12	1.955(2)	-O12	2.078(2)	-O2	2.041(2)
-O4	1.958(2)	-O4	2.105(2)	-O13	2.086(2)
-O2	2.000(2)	-O12	2.112(2)	-O11	2.091(2)
-O6	2.017(2)	-O14	2.133(2)	-O1	2.103(2)
-O16	2.019(2)	-O2	2.149(2)	-O3	2.117(2)
M7-O4	1.882(2)	M8-O7	2.301(2)	M9-O17	2.304(2)
-O14	1.890(2)	-O19	2.373(2)	-O10	2.371(2)
-O18	1.909(2)	-O18	2.376(2)	-O20	2.384(2)
-O5	1.950(2)	-O9	2.424(2)	-O8	2.413(2)
-O16	1.972(2)	-O15	2.447(2)	-O10	2.453(2)
-O8	1.996(2)	-O5	2.449(2)	-O6	2.464(2)
		-O20	2.488(2)	-O16	2.488(2)

Note: Polyhedral bond length averages for all three specimens are in Table 8.

essary scattering material and an ionic radius, $^{[7]}$Na = 1.12 Å, comparable to that of $^{[7]}$Ca, which is 1.06 Å (Shannon, 1976).

Similarly, calculated and observed mean bond lengths (for the latter see Tables 6 and 8) demonstrate Si = B substitution on the tetrahedral sites. With $^{[4]}$B-$^{[4]}$O = 1.49 Å and $^{[4]}$Si-$^{[4]}$O = 1.64 Å (Shannon and Prewitt, 1969; Shannon, 1976) and 0.652 B and 0.348 Si on site T1 (site occupancies shown in Table 2), a bond length of 1.54 Å is calculated. The observed average bond length for this site is 1.55 Å (Table 8). The results for site T4 are similarly favorable. We found no evidence for the B = Al substitution on tetrahedral sites reported by Buerger and Venkatakrishnan (1974).

Satisfactory agreement with the formula calculated from an electron microprobe analysis [7.6 oxide wt% B assumed on the basis of ion microprobe analyses of other samples from Johnsburg (Grew et al., 1991b)], $(Ca_{1.7}Na_{0.2})(Al_{3.2}Mg_{2.7}Fe_{0.2})(Si_{3.1}B_{1.5}Al_{1.4})O_{20}$, was obtained by assigning the non-B-containing tetrahedral sites full occupancy with Si or Al, yielding a structural formula of $(Ca_{1.8}Na_{0.2})(Al_{4.0}Mg_{2.0})(Si_{3.4}B_{1.6}Al_{1.0})O_{20}$. (The grain subjected to probe analysis occurred in the same Johnsburg specimen as the fragment selected for X-ray diffraction work, and within several centimeters of the latter.) Significant undersaturation for the T5 site (Table 7) most probably indicates that Si = Al substitution occurs in this tetrahedral site. This suggestion is supported by the observation that the mean T5-O bond length, in all three refinements, is longer than the mean bond lengths for the other Si sites, T2-O and T6-O (Table 8). Furthermore, in all three refinements the isotropic thermal parameter of T5 is slightly larger than the isotropic thermal parameters of T2 and T6 (Tables 2 and 3). Refined Si = Al occupancies, to be obtained only by setting an ionic radius for Al and back-calculating the amount of Si, were not undertaken.

The thermal vibration parameters (Tables 2, 3, 4) and calculated vs. observed mean bond lengths did not call for additional scattering matter or an ion having a larger ionic radius in any of the tetrahedral sites in the three refinements. Thus we conclude that, even in the Fe-rich specimens of serendibite, there is little or no Fe^{3+} in the tetrahedral positions.

Good agreement between calculated and observed mean bond lengths was obtained for the Johnsburg refinement without assuming significant substitution of Mg and Al in the octahedral positions. In the following comparisons, standard ionic radii for $^{[6]}$Al, $^{[6]}$Mg, $^{[3]}$O, and $^{[4]}$O are from Shannon and Prewitt (1969) and Shannon (1976). The average bond length for M6 is 2.07 Å, and the calculated one is $^{[6]}$Mg-$^{[3]}$O = 2.08 Å. The average bond length for M5 is 2.11 Å, and the calculated value is $^{[6]}$Mg-$^{[4]}$O = 2.10 Å. The average bond lengths of the sites assigned to Al range from 1.92 to 1.98 Å. The calculated bond length is $^{[6]}$Al-$^{[4]}$O = 1.92 Å. Mg undoubtedly substitutes for Al in some sites, as suggested by the bond-valence sums for M3 and M4 (Table 7) and by comparing their mean bond lengths with those of the other octahedral Al positions (Table 7). But, the similarity in scattering power of Mg and Al and the overlapping ranges of their ionic radii, as determined from other structures, precludes a more detailed determination of their octahedral occupancies. As in the case of monoclinic sapphirine (Higgins and Ribbe, 1979), in the octahedral walls of serendibite, sites occupied predominantly by Mg share edges with Mg octahedra in the **a** directions (along an octahedral wall) and with octahedra occupied predominantly by Al in the $[11\bar{1}]$ and $[\bar{1}\bar{1}1]$ directions (across an octahedral wall).

For the intermediate Fe serendibite (Tayozhnoye 5151), acceptable thermal vibration parameters were obtained

TABLE 7. Empirical bond valences in Johnsburg serendibite

Atom	T1	T2	T3	T4	T5	T6	M1
Occup.	0.65 B 0.35 Si	1 Si	1 Al	0.98 B 0.02 Si	1 Si	1 Si	1 Al
O1	0.892						
O2		0.973					
O3					0.923		
O4							2·0.510
O5					0.849		
O6					0.819		2·0.486
O7	0.859				0.875		
O8		0.910					2·0.449
O9		0.992	0.767				
O10	0.866			0.675			
O11			0.838				
O12				0.832			
O13						0.986	
O14							
O15						0.887	
O16						0.917	
O17				0.724		0.887	
O18			0.783				
O19		0.965		0.740			
O20	0.735		0.808				
Calculated cation sum	3.35	3.84	3.20	2.97	3.47	3.76	2.89
Ideal cation sum	3.35	4.00	3.00	3.02	4.00	4.00	3.00

Note: After Brown (1981).

by utilizing the same cation assignments as for the Johnsburg serendibite and then spreading Fe over several of the larger Al sites and over the Mg sites (Tables 3 and 4). In the refinement of the Fe-rich variety (Tayozhnoye 5152), Fe was spread over the octahedral positions, with an initial occupancy in each site of one half, and occupancies were allowed to vary. The site occupancies of Fe after anisotropic convergence suggest that Fe is not ordered into one or two sites but distributed amongst all the octahedral sites (Table 3). Furthermore, the refined Fe occupancies correlate with site size, the sites with larger average M-O distances having higher proportions of Fe. The scattering power of Fe is significantly greater than those of Al and Mg, but in the serendibite specimens that have been studied the Fe content per site is small. Thus our Fe assignments must be considered approximate.

Wet chemical analyses of other Tayozhnoye serendibites and stoichiometric calculations on the microprobe data of the samples studied here suggest the presence of Fe^{2+} and Fe^{3+} in the Tayozhnoye serendibite (Pertsev and Nikitina, 1959; Grew et al., 1991a). If Fe^{3+} is present, it must occur in octahedral coordination because our thermal vibration parameters indicate that there is little or no Fe in the tetrahedral sites. Fe^{3+} is reported or inferred

TABLE 8. Average polyhedral bond and edge lengths (Å), and angles (°)

	Johnsburg			Tayozhnoye 5151			Tayozhnoye 5152		
	Me-O	O-O	O-Me-O	Me-O	O-O	O-Me-O	Me-O	O-O	O-Me-O
T1	1.548	2.526	109.4	1.556	2.546	109.4	1.590	2.593	109.4
T2	1.645	2.684	109.4	1.662	2.711	109.4	1.666	2.717	109.4
T3	1.730	2.819	109.4	1.727	2.814	109.4	1.729	2.818	109.4
T4	1.485	2.422	109.4	1.487	2.425	109.4	1.490	2.431	109.4
T5	1.682	2.743	109.4	1.701	2.774	109.4	1.706	2.782	109.4
T6	1.650	2.693	109.5	1.659	2.708	109.4	1.662	2.713	109.5
M1	1.922	2.716	90.0	1.926	2.721	90.0	1.936	2.736	90.0
M2	1.939	2.740	90.0	1.950	2.754	90.0	1.958	2.766	90.0
M3	1.965	2.762	90.0	1.978	2.799	90.0	1.991	2.795	89.9
M4	1.980	2.812	89.9	1.984	2.819	89.9	2.000	2.796	89.9
M5	2.109	2.975	90.0	2.115	2.983	90.0	2.126	2.999	90.0
M6	2.073	2.926	89.9	2.073	2.926	90.0	2.081	2.938	90.0
M7	1.933	2.733	90.1	1.941	2.743	90.1	1.951	2.759	90.1
M8	2.408	—	—	2.412	—	—	2.416	—	—
M9	2.411	—	—	2.414	—	—	2.418	—	—

TABLE 7—*CONTINUED*

M2	M3	M4	M5	M6	M7	M8	M9	
1 Al	1 Al	1 Al	1 Mg	1 Mg	1 Al	0.77 Ca 0.23 Na	0.82 Ca 0.18 Na	Ideal anion sum = 2.0
	0.432		0.351	0.329				2.004
		0.392	0.295	0.381				2.041
	0.511			0.318				1.752
		0.438	0.327		0.535			1.810
	0.383				0.448	0.240		1.920
		0.375					0.237	1.917
						0.336		2.070
					0.396		0.264	2.019
						0.253		2.012
							0.242	2.073
							0.290	
	0.463			0.338				2.058
				0.419				
		0.441	0.349					1.944
			0.322					
		0.467		0.343				1.796
2·0.493	0.474		0.306		0.523			1.796
2·0.448	0.339					0.241		1.915
		0.373			0.422		0.224	1.936
							0.339	1.950
2·0.440					0.498	0.282		2.003
						0.284		1.989
						0.219	0.282	2.044
2.76	2.60	2.49	1.95	2.13	2.82	1.85	1.88	
3.00	3.00	3.00	2.00	2.00	3.00	1.78	1.82	

to occur in octahedral coordination in other aenigmatite group minerals and compounds, such as sapphirine (Burns and Solberg, 1990; cf. Steffen et al., 1984, who reported $^{[4]}Fe^{3+}$ in synthetic sapphirine, also by Mössbauer spectroscopy), dorrite (Cosca et al., 1988), wilkinsonite (Duggan, 1990), rhönite (Bonaccorsi et al., 1990), and, in the sinter phase, SFCA (Hamilton et al., 1989).

B IN SERENDIBITE

Wet chemical analyses (summarized in Deer et al., 1978, their Table 68) and ion microprobe analyses of serendibite (Grew et al., 1990b, 1991a, 1991b; this paper, Table 9) indicate that the number of B atoms per twenty O atoms ranges from 1.39 to 1.66 in most cases. One exception is the second serendibite from Russell, New York (9.06 oxide wt% B, Table 9). However, its B_2O_3 content exceeds the value for the other Russell serendibite (7.99 wt%) by an amount within the 1σ uncertainty in the ion microprobe analyses (Grew et al., 1990b), i.e., ±1.0 wt%. The high B_2O_3 value for the serendibite from the Melville Peninsula in northern Canada (Table 9) may be due to a systematic error in the ion microprobe analyses, as suggested by the high analytical total. This serendibite also differs from others in its higher CaO and Al_2O_3 contents and low SiO_2 content (see also Hutcheon et al., 1977), the last two possibly through the substitution $Al_2Si_{-1}Mg_{-1}$. Hutcheon et al. (1977) reported cell parameters in good agreement with ours (a = 10.001, b = 10.389, c = 8.622 Å, α = 106.529, β = 95.850, γ = 124.419°, after transformation by the matrix [0$\bar{1}$0/$\bar{1}$10/00$\bar{1}$]). Nonetheless, this serendibite needs further study.

Despite significant variations in Mg, Fe, Al, and Si contents, the above results indicate that on average the occupancy of the two B sites is approximately 1.5 B and 0.5 Si. Refinements of Fe-poor and Fe-rich samples of serendibite demonstrate that B is found in two nonequivalent tetrahedral sites (T1 and T4) in the winged chains of the tetrahedral layer, and the two sites share a vertex (Fig. 3). These are the smallest tetrahedral sites in serendibite. In the refinements described above, the T4 site is nearly fully occupied by B, and the T1 site has a B/Si ratio of about 1.5.

Like the Be site in surinamite (Moore and Araki, 1983), each of the B sites in serendibite is connected to three adjacent tetrahedra. In each case, two of the adjacent tetrahedra are members of the spine of the chain and the third is a wing tetrahedron. The other tetrahedral sites are connected to, at most, two tetrahedra. Sites T1 and T4 each share three of their basal vertices with wall edge Ca sites of one octahedral layer, and the remaining vertex (apex) with wall center octahedra of the neighboring octahedral layer. But the polyhedral connectivities of the two B sites are not equivalent (Table 7). The T1 tetrahedron shares vertices with T3-T4-T5-M3-M5-M6-M9 and edges with M8 and M9′. T4 shares vertices with T1-T2-T6-M4-M5-M8-M9 and an edge with M9′.

Grew et al. (1992) reported chemical data that suggest the possibility of limited solid solution between sapphi-

Table 9. Chemical analyses of serendibite

	Sri Lanka*	Russell, NY**		Melville Penin.
		1872-58	1872-58	
	BM87050	(1)	(2)	136851
	Electron microprobe analyses—wt%†			
SiO_2	23.43	24.05	25.35	21.88
TiO_2	0.12	0.02	0.04	0.03
Al_2O_3	34.11	35.76	34.04	36.69
FeO	5.69	1.94	2.10	3.28
MnO	0.08	0.05	0.09	0.12
MgO	13.90	15.34	15.49	13.71
CaO	15.51	14.22	14.39	16.56
Na_2O	0.23	0.50	0.63	0.00
	Ion microprobe analyses—wt%‡			
B_2O_3	7.31	7.99	9.06	10.76
BeO	0.03	0.01	0.01	0.00
SrO	0.002	0.001	0.001	0.001
Li_2O	0.05	0.03	0.03	0.004
F	0.30	0.03	0.03	0.04
Total	100.64	99.93	101.25	103.06
	Cations per 20 O atoms			
Si	2.751	2.790	2.890	2.465
Al	1.759	1.607	1.324	1.443
B	1.482	1.600	1.783	2.092
Be	0.008	0.003	0.003	0.000
Total	6.000	6.000	6.000	6.000
Ti	0.011	0.002	0.003	0.002
Al	2.962	3.283	3.250	3.428
Fe^{3+}	0.350	—	—	—
Fe^{2+}	0.209	0.188	0.200	0.309
Mn	0.008	0.005	0.009	0.011
Mg	2.433	2.653	2.633	2.302
Li	0.024	0.014	0.014	0.002
Total	5.997	6.145	6.109	6.054
Ca	1.951	1.768	1.758	1.999
Na	0.052	0.112	0.139	0.000
Total	2.003	1.880	1.897	1.999
Total cations	14.000	14.025	14.006	14.053

* Specimen from type locality of Gangapitiya. Fe^{3+}/Fe^{2+} ratio calculated from stoichiometry assuming 14 cations for 20 O atoms.

** Electron microprobe analyses from Grew et al. (1990b).

† Average of several analyses of a single grain (two grains in 136851) by M. G. Yates on a wavelength-dispersive MAC 400s microprobe. Fe_{tot} analyzed as FeO.

‡ Single analysis of a single grain (average of five analyses of two grains in 136851) by N. Marquez (method is given in Grew et al., 1990a). Ranges for 136851 are Li_2O, 0.003–0.007; B_2O_3, 9.9–12.5; F, 0.01–0.09 (all in wt%). Totals corrected for F = O.

rine and serendibite. Electron and ion probe analysis of sapphirine formed from breakdown of serendibite showed that up to 2 oxide wt% B and up to 5.4 oxide wt% Ca is present in localized patches tens of micrometers across. These patches were interpreted as partial exsolution toward serendibite. By analogy with serendibite, any Ca substitution probably occurs on the wall edge octahedra because these are the largest octahedral sites in sapphirine (Moore, 1969; Merlino, 1980). The smallest tetrahedral sites in sapphirine, as in serendibite, are the only two that are connected to three other tetrahedra, and it is on these sites that B substitution would be most likely.

Serendibite is similar to kornerupine in that B substitutes for Si on a single tetrahedral site. However, in contrast to kornerupine, B = Si substitution in serendibite occurs on two adjacent tetrahedral sites such that $^{[4]}$B-O-$^{[4]}$B and $^{[4]}$B-O-$^{[4]}$Al bridges, as well as $^{[4]}$B-O-Si bridges, are present. B-O-B bridges are common in borates [e.g., $CaB_3O_5(OH)$, Clark et al., 1962] and are present in some borosilicates (e.g., cappelenite, Shen and Moore, 1984; danburite, Phillips et al., 1974). However, we are not aware of any previous reports of B-O-Al bridges in borosilicate minerals. Klaska and Grew (1991) proposed a B-Al avoidance, which could explain the absence of B in minerals with a high degree of Al-Si ordering.

Coordination of the bridging O may be a critical factor, and B-Al avoidance may apply only to bridging O atoms in threefold coordination, where saturation is difficult to achieve. In serendibite, O20 is bonded to two $^{[7]}$Ca, as well as to B and Al, and undersaturation is not a problem (Table 7). Another consideration is the T-O-T angle. In serendibite, B-O-T combinations range from 130.5 to 135.4°, i.e., between the optimized values of 128° for B-$^{[3]}$O-Si and 137° for B-$^{[3]}$O-B calculated by Geisinger et al. (1985). In summary, the T1 site must be highly favorable to B incorporation so that the seemingly unfavorable B-O-$^{[4]}$Al configuration is stabilized.

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