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THE CRYSTAL STRUCTURE OF SAPPHIRINE

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ABSTRACT

Sapphirine is monoclinic, space group $P2_1/a$, with $a=11 \cdot 266(12)$, $b=14 \cdot 401(7)$, $c=9 \cdot 929(10)$ Å, $\beta=125 \cdot 46(5)°$. The asymmetric unit contains $Mg_{3.5}Al_{9.0}Si_{1.5}O_{20}$ comprised of eight octahedra and six tetrahedra incorporated in a cubic close-packed array of oxygen atoms. Three-dimensional refinement with 2800 independent reflections from a Fiskenaesset, West Greenland, crystal, gave $R_{hkl}=0.055$.

The structure consists of octahedral walls running parallel to z, which are connected along y by a new kind of $[T_6O_{18}]_\infty$ tetrahedral chain. The crystallochemical formula is $M_7(M)O_2[T_6O_{18}]$ with the parenthetical octahedra between the walls.

Average M-O and T-O distances are M(1)-O 1.926, M(2)-O 1.930, M(3)-O 1.988, M(4)-O 2.078, M(5)-O 2.120, M(6)-O 2.115, M(7)-O 1.921, M(8)-O 1.930, T(1)-O 1.771, T(2)-O 1.658, T(3)-O 1.700, T(4)-O 1.733, T(5)-O 1.755, T(6)-O 1.736 Å. The cation distributions are assigned as follows: M(1), M(2), M(7), M(8), T(1), T(5), and T(6)$=Al_{1.0}$; M(3)$=Mg_{0.5}Al_{0.5}$; M(4), M(5), M(6)$=Mg_{1.0}$; T(2)$=Al_{0.25}Si_{0.75}$; T(3)$=Al_{0.5}Si_{0.5}$: T(4) $=Al_{0.75}Si_{0.25}$.

The site preferences appear to be a compromise between conditions of electro-neutrality and minimization of cation-cation repulsions.

INTRODUCTION

Sapphirine has been a crystallochemical enigma since it was first announced as a distinct mineral species some 150 years ago. As recorded by Bøggild (1953), it was originally found by Gieseke in 1809 who called it cyanite, later renaming it emery. Eventually, many mineralogists considered it to be merely an impure spinel and its validity as a species was uncertain until Lorenzen (1893) placed sapphirine on firm ground. The sapphirine problem continued during the series of X-ray studies undertaken on the mineral. Gossner and Mussgnug (1928) offered a long discussion on the crystal cell, concluding with the proposed formula $Mg_2Al_4SiO_{10}$, $Z=8$, with a bounded coupled substitution of SiMg by AlAl. They did not determine a space group.

Kuzel (1961) was able to obtain more precise cell data using modern techniques. He proposed the space group $P2_1/c$ and his results are summarized in Table 1. McKie (1963) offered new data on an anomalous yellow sapphirine from Mautia, Hill, Tanganyika with a doubled b-repeat, and extra sharp as well as diffuse reflections which require a C-centered cell (Table 1). Fleet (1967), noting non-space group absences in sapphirine, proposed a structure of cubic close-packed oxygen atoms with the cations in both octahedral and tetrahedral coordination, as indicated by Patterson projections. The latest paper on sapphirine is a note by

TABLE 1. SAPPHIRINE CRYSTAL DATA

	1	2	3
a	11.266 (12) Å	11.29	11.26
b	14.401 (7)	28.6	14.42
c	9.929 (10)	9.96	9.93
β	125.46 (5)°	125.25°	125.33°
V	1311 (3) A^3	2×1313	1319
Z	4	8	4
S. G.	$P2_1/a$	A-centered	$P2_1/c$

1. Crystal from Fiskenaesset, West Greenland, used in this study. The formula is $Mg_{3.5}Al_{9.0}Si_{1.5}O_{20}$.

2. Crystal from Mautia Hill, Tanganyika. McKie (1963) gave a 9.85 Å, b 28.6, c 9.96, β 110½°. His cell has been transformed by $[101/0\bar{1}0/00\bar{1}]$. The A-centered cell is the extreme structural state. The formula is $Mg_{3.67}Mn_{0.04}Fe^{2+}_{0.17}Ti_{0.01}Fe^{3+}_{0.33}Al_{8.07}Si_{1.75}O_{20.00}$ (McKie, 1963).

3. Data of Kuzel (1961). The space group is apparently in error. The crystal was from Fiskenaesset, West Greenland.

Moore (1968) which offers atomic coordinates and a short discussion on its crystal structure. This paper, an extension of that study, presents very accurate atomic coordinates and interatomic distances, and a site preference scheme for the cations.

Sapphirine is an uncommon rock-forming mineral but it occurs as a major phase in certain aluminum-rich and silicon-poor high grade upper amphibolite to lower granulite facies rocks. The noteworthy localities and a discussion of sapphirine parageneses were presented by Sørensen (1955). Typical associations include gedrite, hornblende, biotite (and phlogopite), anorthite, cordierite, spinel, corundum, and rarely kornerupine. Kornerupine, long a crystallochemical puzzle, was recently shown by Moore and Bennett (1967) to have a very complex crystal structure.

Sapphirine occupies a small stability field in the system $MgO–Al_2O_3–SiO_2$ (Keith and Schairer (1952)). Its compositional variation has resulted in several proposed formulae, and considerable confusion regarding the interpretation of wet chemical analyses. On the basis of six available analyses, Vogt (1947) proposed the general cell formula $Mg_{16-n}Al_{32+2n}Si_{8-n}O_{80}$ where n varies from 0 to about 2.5. Departures in n from these values, as noted by Deer, Howie, and Zussman (1962) are slight. This appears to be the most reasonable formula to assign the mineral.

EXPERIMENTAL

The entire study was undertaken on a sample from Fiskenaesset harbor, West Greenland, the type locality. The specimen, collected and donated by Dr. Brian Windley, shows abundant pale blue sapphirine oriented with {010} parallel to phlogopite cleavage planes. Often, grains appear with laminated intergrowths of sapphirine and phlogopite. Minor corundum and cordierite also occur in the specimen.

A nearly equant fragment of 0.3 mm mean dimension was selected for crystal structure analysis. 6000 independent spectra of the *h*0*l* to *h*.20.*l* levels were collected up to $2\theta = 70°$ on a Pailred automatic diffractometer using monochromatized MoKα radiation. After processing to obtain $|F_{obs}|$, 3600 reflections proved to be 'nonzero' and were the only spectra used in the ensuing analysis. The remainder included reflections with asymmetric backgrounds, systematic extinctions, or with non-positive intensities.

The cell data in Table 1 were obtained by least-squares refinement based on 26 powder lines which could be indexed with certainty. This proved to be a difficult task since the large cell resulted in many overlapping spectra. 34 of the 200 strongest spectra from the single crystal data gave uniquely indexed lines for the powder pattern, obtained from a scintillation counter-diffractometer using Ni-filtered Cu radiation, a scanning speed of 1/4° per minute, and silicon ($a = 5.4301$ Å) as an internal standard. The space group, $P\,2_1/a$, consistent with the extinction criteria recorded on long exposure films, is uniquely determined. The powder data for the Fiskenaesset material are given in Table 2 with indices for

TABLE 2. SAPPHIRINE POWDER DATA[a]

I/I_0	*d*(obs)	*d*(calc)	*hkl*
5	7.728	7.738	110
10	7.062	7.052	011[b]
5	5.378	5.378	021
5	4.586	4.587	200
8	4.039	4.047	$\bar{1}22$
5	3.869	3.869	220[b]
10	3.600	3.600	040
20	3.361	3.351	140
10	3.277	3.270	$\bar{3}22$[b]
65	2.990	2.991	310
50	2.844	2.844	122
25	2.762	2.763	$\bar{4}12$
10	2.695	2.697	231[b]
		2.696	003[b]
10	2.647	2.650	013
5	2.606	2.603	$\bar{4}11$[b]
30	2.576	2.570	$\bar{3}42$
5	2.525	2.525	023[b]
5	2.488	2.484	$\bar{4}21$[b]
100	2.447	2.449	$\bar{2}52$
	2.447	2.447	$\bar{2}04$
35	2.347	2.347	142
	2.347	2.346	052
5	2.248	2.243	$\bar{1}14$[b]
12	2.127	2.127	260
11	2.072	2.069	$\bar{5}14$[b]
60	2.023	2.022	004
90	2.015	2.013	$\bar{4}52$
10	1.5517	1.5520	$\bar{6}06$[b]
25	1.5403	1.5399	$\bar{6}52$
30	1.4401	1.4401	0.10.0
65	1.4353	1.4348	$\bar{4}56$
65	1.4192	1.4186	452
30	1.4073	1.4079	$\bar{8}04$

[a] CuKα; silicon standard $a = 5.4301$ Å.

[b] Reflections excluded from cell refinement.

unambiguous lines. The indexed powder patterns recorded in the literature and in files are largely incorrect and should be abandoned.

No chemical analysis was undertaken on this sapphirine as the analysis quoted by Bøggild (1953) for Fiskenaesset material was considered adequate and agrees with the crystal structure.

STRUCTURE ANALYSIS

Several noteworthy features influenced the crystal structure analysis. Sapphirine has 14 cations and 20 oxygen atoms in the asymmetric unit. Only two scattering curves were applied initially, Si^{2+} for the cations and O^- for oxygen, obtained from International Tables for X-ray Crystallography, Vol. 3 (1962). The spectra for $hkl, l \neq 2n$, were relatively weak with unitary structure factors less than 0.6. Furthermore, the powder pattern is similar to that of spinel, in keeping with Fleet's suggestion that the oxygen atoms are cubic close-packed. These facts imply a strong subperiodicity in the sapphirine crystal structure, which proved to hinder rapid solution by direct methods involving statistical procedures. Thus, the structure was solved in several stages.

The first stage consisted of processing the 3600 spectra in the programmed symbolic addition procedure MAGIC, written by E. B. Fleischer, R. B. K. Dewar, and A. L. Stone (1967). Sign determination, based on seven starting symbols, was applied to 500 of the strongest spectra. Several iterations resulted in only 15 determinations, whereupon the run was abandoned. These proved to be the 'spinel' substructure reflections. It may be stated that sapphirine is a substructure-within-a-substructure problem, the former being the spinel-like reflections, and the latter being the $l=2n$ reflections. The 15 'spinel' spectra were omitted in the second MAGIC run, and processing the remaining data led to 490 sign determinations, all for $l=2n$. Only one sign combination had no contradictions and its E-map showed that the oxygen atoms were indeed cubic close-packed, with the layers parallel to $\{100\}$.

The cation populations were not as straightforward to decipher. Since the analysis had to be confined to the $l=2n$ reflections only, atoms periodic only over c should appear but their densities would be approximately half those for the atoms periodic over $c/2$. Eight octahedrally coordinated cations, seemingly periodic over $c/2$, were assigned to high E-densities. Unfortunately, other cations were masked by the appearance of many false peaks.

The next stage included least squares refinement on the $l=2n$ reflections for eight octahedral cations and twenty oxygen atoms in the full asymmetric unit. A difference synthesis, performed when R_{hkl} had converged to 0.43, showed seven prominent densities within an asymmetric unit of the $c/2$ subunit. One of these showed anomalously low density and required removal of an incorrectly assigned octahedrally coordinated cation. Two others, tetrahedrally coordinated, were believed to be truly periodic over $c/2$ on the basis of their high densities. Remaining were two octahedrally coordinated cations and two tetrahedrally coordinated cations which were assumed periodic over c only. Excluding these four atoms from ensuing refinement, $R_{hkl}(l=2n)$ converged to 0.32.

The final stage of the analysis was confined to the $l \neq 2n$ reflections and it was initially assumed that these reflections were dominated by the four cations which were periodic only over c. Much labor and computation expense was saved by simply testing the various ordered possibilities for just these four atoms The total number of distinct configurations is

$$\sum_{r=0,s=4}^{s=0,r=4} \frac{4!}{r!s!} = 16.$$

Several appeared untenable from electrostatic arguments. Of the few remaining, one model gave $R_{hkl}(l \neq 2n) = 0.35$ whereas the others gave $R_{hkl}(l \neq 2n) > 0.50$. The atomic coordinates periodic over $c/2$ were not used in the refinement. All 34 atoms in the sapphirine full asymmetric unit using 2000 low-angle reflections gave $R_{hkl} = 0.11$ after several cycles of coordinate refinement.

Sapphirine appears to be the most complex mineral structure solved to date with the assistance of direct methods. Despite the pronounced subperiodicity in sapphirine, information was obtained for atoms which were periodic over the $c/2$ subunit and for those which were not. The latter appeared on the E-maps as attenuated peaks. Since the aperiodic atoms were few, the analysis was straightforward, involving a test of the various possible configurations until the correct arrangement was found.

REFINEMENT

Initially, all cations were referred to the scattering curve of Si^{2+} and oxygen to O^{-}. One cycle of isotropic temperature factor refinement and one cycle of atomic coordinate refinement led to $R_{hkl} = 0.09$ using all 3600 non-zero reflections. The 32 strongest low-angle reflections suffered severe extinction effects, and were removed. Many weak reflections—defined herein with F_{obs} less than three times the absolute average difference between F_{obs} and F_{calc} for the 3600 reflections—were substantially affected by the expected background error and they were omitted. The background errors were assessed by examining the F_{obs} in the Pailred data which belonged to systematically extinct reflections. For the conditions mentioned, this was approximately greater than 25 percent of the

TABLE 3. CHEMICAL ANALYSIS FOR SAPPHIRINE (USSING IN BØGGILD, 1953)

	Weight percent	Moles in cell (80 oxygens)	Ideal[a]
SiO_2	12.83	5.96	6.00
Al_2O_3	65.29	35.76 }36.08	36.00
Fe_2O_3	0.93	0.32	
FeO	0.65	0.25 }13.95	14.00
MgO	19.78	13.70	
	99.48		
$\rho = 3.486$ gm/cm^3		$\sum O = 79.06$	

[a] For $Mg_{3.5}Al_{9.0}Si_{1.5}O_{20}$ in the asymmetric unit.

mean background error. Further refinement of the 2800 reflections remaining led to $R_{hkl} = 0.082$.

The chemical analysis for Fiskenaesset sapphirine, recorded by Bøggild (1953), is given in Table 3. The asymmetric formula unit is almost ideally $Mg_{3.5}Al_{9.0}Si_{1.5}O_{20}$, and it was assumed that Si distributed over the tetrahedral sites and Mg over the octahedral sites. Tetrahedral distributions, derived from mean T–O polyhedral distances, were obtained from the tables of Smith and Bailey (1963). Assuming average values of 1.92 Å for Al–O and 2.10 Å for Mg–O, the octahedral distributions were obtained in a similar manner. Good agreement is found if the following asymmetric formula is used:

$$[Mg_{3.0}(Mg_{0.5}Al_{0.5})Al_{4.0}]^{VI}[Al_{3.0}(Al_{0.25}Si_{0.75})(Al_{0.5}Si_{0.5})(Al_{0.75}Si_{0.25})]^{IV}O_{20.0}.$$

The appropriate scattering curves were obtained by averaging the fractions of Mg^{+}, $Al^{3/2+}$, and Si^{2+} for each site; curves for the pure atomic species were obtained from *International Tables for X-ray Crystallography, Vol. 3* (1962). The final full-matrix atomic coordinate and isotropic temperature factor refinement (136 varied parameters) gave $R_{hkl} = 0.055$ for 2800 reflections and 0.073 for all 3600 non-zero reflections, excluding those substantially affected by extinction. Tests for anisotropic thermal motion were not performed due to the large number of parameters. The close-packed nature of the structure in combination with consistently reasonable values for isotropic temperature factors suggest that this correction would be slight. Table 4 lists the final cation distributions, atomic coordinates, and isotropic temperature factors, and Table 5[1] are the $|F_{obs}| - F_{calc}$ values.

DISCUSSION OF THE STRUCTURE

Topology. The essential features of the sapphirine crystal structure were stated by Moore (1968). Figure 1 is a polyhedral diagram for the sapphirine asymmetric unit. Oxygen atoms are cubic close-packed, with the layers stacked parallel to $\{100\}$. The volume per oxygen atom is 16.4 Å^3.

The crystal structure is difficult to visualize, but it may be considered in terms of three structural components which, when fitted together, result in the three-dimensional arrangement. The first component consists of octahedral walls which run parallel to the z-axis and which are oriented parallel to the $\{100\}$ plane. The term 'wall' is reserved for that arrangement which is intermediate between the 'chain' and the 'sheet'; a chain

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[1] To obtain a copy of Table 5, order NAPS Document #00227 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies payable to ASIS-NAPS.

TABLE 4. ATOMIC DISTRIBUTIONS, ATOMIC COORDINATES, AND ISOTROPIC TEMPERATURE FACTORS FOR SAPPHIRINE (ESTIMATED STANDARD ERRORS IN PARENTHESIS)

		x	y	z	B (Å^2)
M(1)	$Al_{1.00}$	0.0078 (2)	0.1584 (1)	0.1375 (2)	0.27 (2)
M(2)	$Al_{1.00}$	−0.0089 (2)	0.1560 (1)	0.6136 (2)	0.40 (2)
M(3)	$Al_{0.50}Mg_{0.50}$	−0.0043 (3)	0.0567 (1)	0.3726 (3)	0.20 (2)
M(4)	$Mg_{1.00}$	−0.0013 (3)	0.0576 (1)	0.8728 (4)	0.38 (2)
M(5)	$Mg_{1.00}$	0.0081 (3)	0.3667 (1)	0.1425 (3)	0.31 (3)
M(6)	$Mg_{1.00}$	−0.0084 (3)	0.3649 (1)	0.6079 (3)	0.26 (3)
M(7)[a]	$Al_{1.00}$	0.0000 (2)	0.2569 (1)	0.8754 (2)	0.33 (2)
M(8)[a]	$Al_{1.00}$	0.2510 (2)	0.2496 (1)	0.8755 (2)	0.33 (2)
T(1)	$Al_{1.00}$	0.1963 (2)	0.5559 (1)	0.2442 (2)	0.42 (2)
T(2)	$Al_{0.25}Si_{0.75}$	0.2018 (2)	0.5536 (1)	0.7552 (2)	0.44 (2)
T(3)	$Al_{0.50}Si_{0.50}$	0.2026 (2)	0.4502 (1)	0.5072 (2)	0.20 (2)
T(4)	$Al_{0.75}Si_{0.25}$	0.1993 (2)	0.4420 (1)	0.0051 (2)	0.19 (2)
T(5)[a]	$Al_{1.00}$	0.1878 (2)	0.7552 (1)	0.7553 (2)	0.21 (2)
T(6)[a]	$Al_{1.00}$	0.1872 (2)	0.2458 (1)	0.5041 (2)	0.20 (2)
O(1)		0.1205 (4)	0.2556 (3)	0.1174 (4)	0.26 (4)
O(2)		0.1281 (4)	0.2524 (3)	0.6315 (4)	0.54 (5)
O(3)		0.1170 (4)	0.0555 (3)	0.1244 (5)	0.39 (5)
O(4)		0.1091 (4)	0.0533 (3)	0.6176 (5)	0.54 (5)
O(5)		0.1146 (4)	0.1547 (3)	0.3658 (5)	0.49 (5)
O(6)		0.1052 (4)	0.1667 (3)	0.8467 (5)	0.58 (5)
O(7)		0.1124 (5)	−0.0540 (3)	0.3754 (5)	0.72 (5)
O(8)		0.1114 (5)	−0.0611 (3)	0.8692 (5)	0.55 (5)
O(9)		0.3726 (4)	0.2503 (3)	0.1123 (4)	0.35 (5)
O(10)		0.3771 (4)	0.2472 (3)	0.6261 (5)	0.64 (6)
O(11)		0.3596 (4)	0.0389 (3)	0.1255 (5)	0.54 (5)
O(12)		0.3696 (4)	0.0408 (3)	0.6287 (5)	0.60 (5)
O(13)		0.3898 (5)	0.3425 (3)	0.3866 (5)	0.63 (6)
O(14)		0.3943 (4)	0.3320 (3)	0.9009 (4)	0.23 (4)
O(15)		0.3620 (4)	0.1486 (3)	0.3507 (5)	0.36 (4)
O(16)		0.3736 (4)	0.1568 (3)	0.8751 (5)	0.53 (5)
O(17)		0.1415 (4)	0.4556 (3)	0.1246 (5)	0.35 (5)
O(18)		0.1482 (4)	0.4618 (3)	0.6330 (5)	0.42 (5)
O(19)		0.1332 (4)	0.3500 (3)	0.3961 (5)	0.62 (5)
O(20)		0.1244 (4)	0.3449 (3)	0.8697 (4)	0.28 (5)

[a] Atoms without a pseudo-period over c/2.

is usually described as running parallel to some axis and a sheet is always considered oriented parallel to some plane. A wall is a chain with finite thickness; that is, it can be considered running parallel to some axis as well as being situated in some plane. The octahedral walls are separated along the y-axis in sapphirine and they are made up of seven non-equivalent octahedra. These walls are of three and four octahedra in width, and are idealized in Figure 2a.

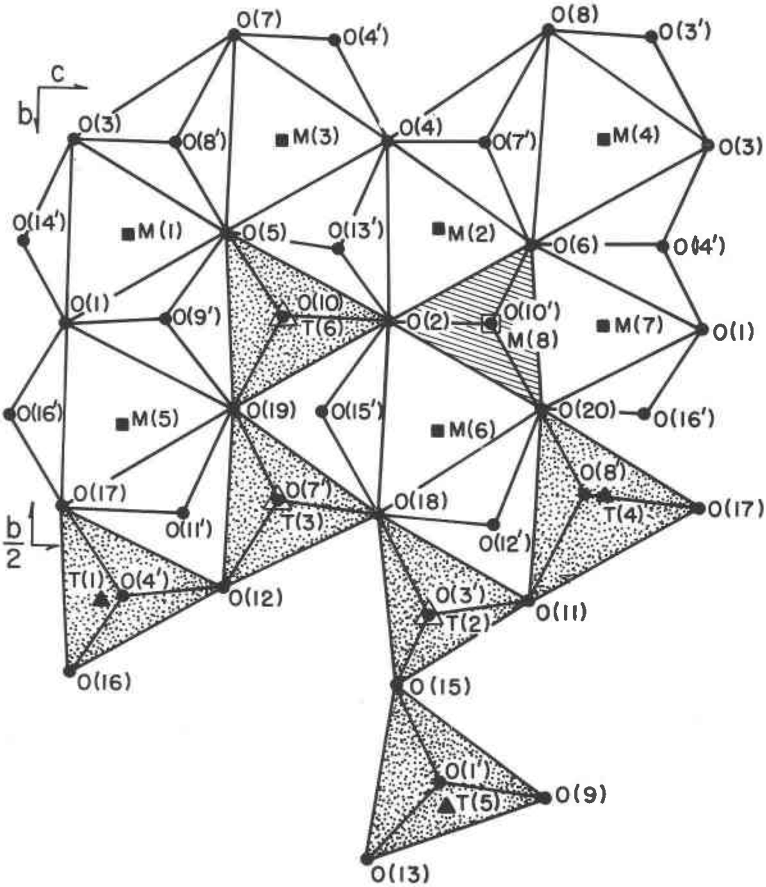

FIG. 1. The asymmetric unit of sapphirine crystal structure down x^*. The actual polyhedral distortions are shown. Octahedra in the walls are unshaded and the tetrahedra are stippled. The octahedron between the walls resides above the ruled region.

The second component includes all six nonequivalent tetrahedra in the crystal structure which are linked by corner-sharing to form a $[T_6O_{18}]_\infty$ chain running parallel to the *z*-axis. This interesting chain consists of a pyroxene-like member with additional 'wings' of corner-sharing tetrahedra. Thus, two tetrahedra share three corners each, two share two corners and two share only one corner. The tetrahedral chains connect the separated walls along the *y*-axis by sharing corners with them. This tetrahedral chain is shown in Figure 2b.

The third component consists of the remaining octahedron in the asymmetric unit which is situated between the walls along the x^*-axis, sharing six of its edges with the walls above and below.

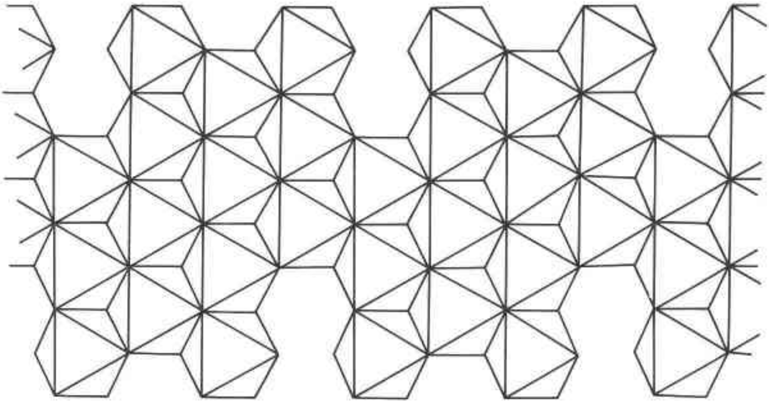

FIG. 2a. Idealized polyhedral diagram of the octahedral walls in sapphirine which run along the z-axis and lie parallel to {100}.

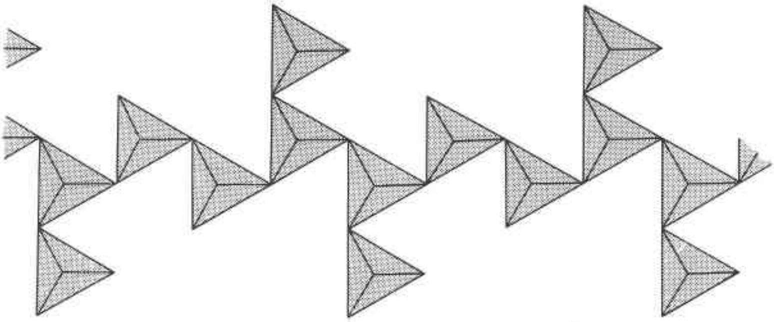

FIG. 2b. Idealized polyhedral diagram of the tetrahedral chains in sapphirine. These chains run along the z-axis.

The three-dimensional arrangement is obtained by connecting symmetry equivalent octahedral walls, obtained by the axial glide operation, upon the tetrahedral vertices. Thus, if the structure is visualized along the z-axis, the walls are stacked along the x^*-axis like brick-work with the tetrahedral populations in between. The sapphirine crystallochemical formula can be written $M_7(M)O_2[T_6O_{18}]$, where M are the octahedra and T are the tetrahedra and the parentheses include the remaining octahedron between the walls. Placing the three components together results in the idealized polyhedral diagram of the sapphirine crystal structure in Figure 3.

The spinel arrangement, on the other hand, consists of unbroken octahedral sheets, with octahedra and insular tetrahedra between the sheets. Its crystallochemical formula may be written $M_4(M_2)[TO_4]_3$ with the parenthetical octahedral species between the sheets (Fig. 4). The asymmetric unit of sapphirine can be written as $M_8T_6O_{20}$, in comparison to the

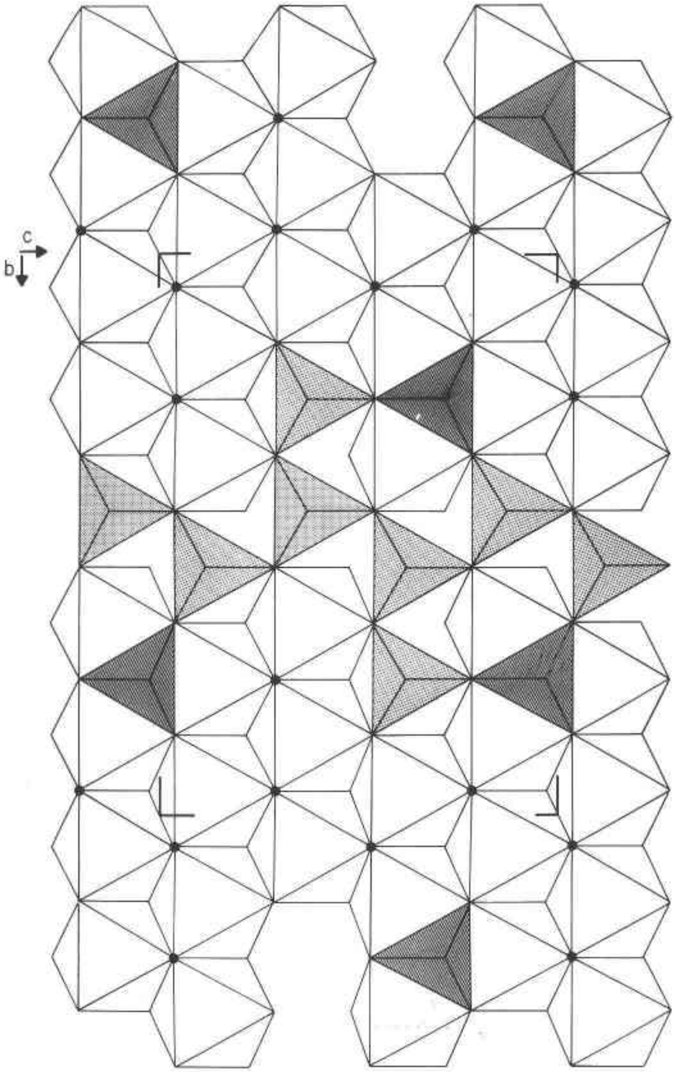

FIG. 3. Idealized polyhedral diagram of the sapphirine crystal structure down x^*. The octahedral walls are unshaded, the tetrahedra are stippled, and the octahedra between the walls reside above the ruled regions. Black disks denote junction of octahedra with the tetrahedral vertices above the walls. Tetrahedra below the walls are not shown. The sapphirine cell is outlined.

same oxygen aliquot of spinel which is $M_{10}T_5O_{20}$. Though both structures have cubic close-packed oxygens, spinel is crystallochemically denser since it has one more cation per twenty oxygens than does sapphirine.

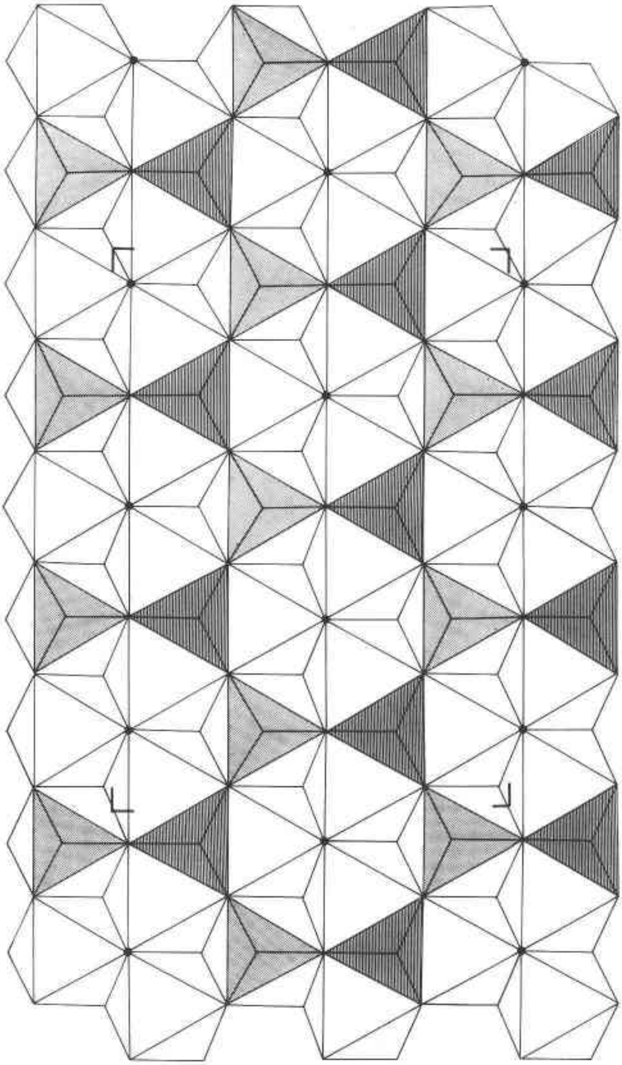

FIG. 4. Idealized polyhedral diagram of the spinel structure type down [111]. Octahedra in the sheets are unshaded, tetrahedra are stippled, and octahedra between the sheets reside above the ruled regions. Black disks denote junction of octahedra with the tetrahedral vertices above the sheets. Tetrahedra below the sheets are not shown. The sapphirine cell is outlined.

Cation site populations. Site populations were estimated from M–O and T–O average interatomic distances, which are known to a high level of reliability (±0.005 Å). The unique M–O, T–O, O–O′, O–M–O′, and O–T–O′ interatomic distances and angles and their errors are given in

TABLE 6. OCTAHEDRAL AND TETRADHEDRAL INTERATOMIC DISTANCES AND ANGLES IN SAPPHIRINE[a]

$M(1) = Al_{1.00}$		$M(2) = Al_{1.00}$		$M(3) = Mg_{0.50}Al_{0.50}$	
M(1)-O(5)	1.850 Å	M(2)-O(13)	1.842	M(3)-O(13)	1.935
M(1)-O(8)	1.915	M(2)-O(6)	1.891	M(3)-O(8)	1.964
M(1)-O(9)	1.916	M(2)-O(7)	1.918	M(3)-O(5)	1.973
M(1)-O(14)	1.920	M(2)-O(10)	1.947	M(3)-O(4)	1.986
M(1)-O(3)	1.977	M(2)-O(4)	1.975	M(3)-O(4′)	2.012
M(1)-O(1)	1.977	M(2)-O(2)	2.007	M(3)-O(7)	2.057
average	1.926		1.930		1.988
a O(1)-O(14′)	2.520	a O(10′)-O(6)	2.532	b O(7)-O(4′)	2.537
a O(9′)-O(14′)	2.536	b O(4)-O(7′)	2.537	b O(5)-O(8′)	2.618
c O(8′)-O(3)	2.612	a O(2)-O(6)	2.604	b O(13′)-O(4)	2.654
b O(8′)-O(5)	2.618	b O(4)-O(13′)	2.654	O(13′)-O(5)	2.658
c O(3)-O(14′)	2.718	c O(7′)-O(6)	2.691	d O(4)-O(4′)	2.682
O(8′)-O(9′)	2.721	O(2)-O(13′)	2.724	e O(7)-O(8′)	2.811
c O(1)-O(9′)	2.766	c O(10′)-O(2)	2.798	O(7)-O(4)	2.875
O(9′)-O(5′)	2.772	O(13′)-O(7′)	2.804	O(13′)-O(8′)	2.885
O(8′)-O(14′)	2.783	O(10′)-O(13′)	2.818	O(4)-O(5)	2.925
O(3)-O(5)	2.802	O(4)-O(6)	2.819	O(8′)-O(4′)	2.978
O(1)-O(3)	2.883	O(10′)-O(7′)	2.865	O(7)-O(5)	3.007
O(1)-O(5)	2.894	O(4)-O(2)	2.874	O(13′)-O(4′)	3.035
	2.719		2.727		2.805
O(5)-M(1)-O(8)	88.1°	O(13)-M(2)-O(7)	96.4	O(13)-M(3)-O(8)	95.5
O(5)-M(1)-O(9)	94.8	O(13)-M(2)-O(10)	96.0	O(13)-M(3)-O(5)	85.7
O(5)-M(1)-O(3)	94.0	O(13)-M(2)-O(4)	88.0	O(13)-M(3)-O(4)	85.2
O(5)-M(1)-O(1)	98.3	O(13)-M(2)-O(2)	90.0	O(13)-M(3)-O(4′)	100.5
O(8)-M(1)-O(9)	90.5	O(6)-M(2)-O(7)	89.9	O(8)-M(3)-O(5)	83.4
O(8)-M(1)-O(14)	93.0	O(6)-M(2)-O(10)	82.5	O(8)-M(3)-O(4′)	97.0
O(8)-M(1)-O(3)	84.3	O(6)-M(2)-O(4)	93.6	O(8)-M(3)-O(7)	88.7
O(9)-M(1)-O(14)	82.8	O(6)-M(2)-O(2)	83.8	O(5)-M(3)-O(4)	95.2
O(9)-M(1)-O(1)	90.5	O(7)-M(2)-O(10)	95.7	O(5)-M(3)-O(7)	96.4
O(14)-M(1)-O(3)	88.4	O(7)-M(2)-O(4)	81.3	O(4)-M(3)-O(4′)	84.3
O(14)-M(1)-O(1)	80.6	O(10)-M(2)-O(2)	90.1	O(4)-M(3)-O(7)	90.6
O(3)-M(1)-O(1)	93.6	O(4)-M(2)-O(2)	92.3	O(4′)-M(3)-O(7)	77.2
	89.9		90.0		90.0
O(5)-M(1)-O(14)	177.3	O(13)-M(2)-O(6)	173.7	O(13)-M(3)-O(7)	175.5
O(8)-M(1)-O(1)	173.4	O(7)-M(2)-O(2)	170.8	O(8)-M(3)-O(4)	178.3
O(9)-M(1)-O(3)	169.5	O(10)-M(2)-O(4)	175.2	O(5)-M(3)-O(4′)	173.6

[a] Estimated standard errors: Me-O ± 0.005 Å, O-O′ ± 0.007 Å, O-Me-O′ ± 0.3°
Edges shared between octahedral pairs: a = $Al_{1.0}$-$Al_{1.0}$, b = $Mg_{0.5}Al_{0.5}$-$Al_{1.0}$, c = $Mg_{1.0}$-$Al_{1.0}$,
d = $Mg_{0.5}Al_{0.5}$-$Mg_{0.5}Al_{0.5}$, e = $Mg_{0.5}Al_{0.5}$-$Mg_{1.0}$, f = $Mg_{1.0}$-$Mg_{1.0}$.

Table 6. The averages are M(1)–O 1.926, M(2)–O 1.930, M(3)–O 1.988, M(4)–O 2.078, M(5)–O 2.120, M(6)–O 2.115, M(7)–O 1.921, M(8)–O 1.930, T(1)–O 1.771, T(2)–O 1.658, T(3)–O 1.700, T(4)–O 1.733, T(5)–O 1.755 and T(6)–O 1.736 Å. Assignment of cation site populations on the basis of these average distances can at best be only approximate since the distances are dependent on the kind of polyhedral linkage as well as the cation species. The errors associated with the proposed site distribution are probably around 10 percent. Assuming Si–O 1.63 and Al–O 1.77 Å, the distribution which best fits the average distances and the chemical

TABLE 6. (*Continued*)

M(4) = $Mg_{1.00}$		M(5) = $Mg_{1.00}$		M(g) = $Mg_{1.00}$	
M(4)-O(7)	2.015	M(5)-O(17)	2.059	M(6)-O(12)	2.027
M(4)-O(3)	2.038	M(5)-O(19)	2.065	M(6)-O(15)	2.088
M(4)-O(6)	2.083	M(5)-O(11)	2.085	M(6)-O(20)	2.136
M(4)-O(14)	2.089	M(5)-O(1)	2.143	M(6)-O(10)	2.138
M(4)-O(3′)	2.097	M(5)-O(9)	2.176	M(6)-O(18)	2.148
M(4)-O(8)	2.143	M(5)-O(16)	2.189	M(6)-O(2)	2.151
	2.078		2.120		2.115
c O(8)-O(3′)	2.612	c O(4′)-O(16′)	2.711	c O(2)-O(20)	2.733
c O(6)-O(7′)	2.691	c O(1)-O(16′)	2.713	c O(20)-O(10′)	2.749
c O(14′)-O(3)	2.718	c O(1)-O(9′)	2.766	c O(2)-O(10′)	2.798
c O(14′)-O(6)	2.724	O(1)-O(17)	2.887	O(12′)-O(20)	2.952
e O(18)-O(7′)	2.811	O(1)-O(19)	3.009	O(12′)-O(10′)	2.974
f O(3)-O3′)	2.838	O(19)-O(9′)	3.009	O(10′)-O(15′)	2.995
O(3′)-O(7′)	2.973	O(17)-O(16′)	3.033	O(2)-O(15′)	3.017
O(8)-O(3)	3.008	O(11′)-O(9′)	3.054	O(2)-O(18)	3.022
O(6)-O(3)	3.121	O(11′)-O(16′)	3.087	O(18)-O(20)	3.025
O(14′)-O(7′)	3.158	O(11′)-O(19)	3.111	O(12′)-O(18)	3.115
O(14′)-O(3′)	3.225	O(17)-O(19)	3.141	O(12′)-O(15′)	3.122
O(8)-O(6)	3.286	O(11′)-O(17)	3.178	O(18)-O(15′)	3.209
	2.930		2.975		2.975
O(7)-M(4)-O(6)	82.1	O(17)-M(5)-O(19)	99.2	O(12)-M(6)-O(15)	98.7
O(7)-M(4)-O(14)	100.6	O(17)-M(5)-O(11)	100.3	O(12)-M(6)-O(20)	90.3
O(7)-M(4)-O(3′)	92.6	O(17)-M(5)-O(1)	86.8	O(12)-M(6)-O(10)	91.1
O(7)-M(4)-O(8)	85.0	O(17)-M(5)-O(16)	91.1	O(12)-M(6)-O(18)	96.5
O(3)-M(4)-O(6)	98.5	O(19)-M(5)-O(11)	97.1	O(15)-M(6)-O(10)	90.2
O(3)-M(4)-O(14)	82.4	O(19)-M(5)-O(1)	91.2	O(15)-M(6)-O(18)	98.5
O(3)-M(4)-O(3′)	86.7	O(19)-M(5)-O(9)	90.3	O(15)-M(6)-O(2)	90.7
O(3)-M(4)-O(8)	92.0	O(11)-M(5)-O(9)	91.5	O(20)-M(6)-O(10)	80.1
O(6)-M(4)-O(14)	81.5	O(11)-M(5)-O(16)	92.5	O(20)-M(6)-O(18)	89.8
O(6)-M(4)-O(8)	102.1	O(1)-M(5)-O(9)	79.7	O(20)-M(6)-O(2)	79.2
O(14)-M(4)-O(3′)	100.8	O(1)-M(5)-O(16)	77.6	O(10)-M(6)-O(2)	81.4
O(3′)-M(4)-O(8)	76.1	O(9)-M(5)-O(16)	77.0	O(18)-M(6)-O(2)	89.3
	90.0		89.5		89.6
O(7)-M(4)-O(3)	177.0	O(17)-M(5)-O(9)	163.6	O(12)-M(6)-O(2)	168.0
O(6)-M(4)-O(3′)	174.5	O(19)-M(5)-O(16)	164.3	O(15)-M(6)-O(20)	166.9
O(14)-M(4)-O(8)	173.8	O(11)-M(5)-O(1)	167.9	O(10)-M(6)-O(18)	167.4

composition is as follows: M(1), M(2), M(7), M(8), T(1) and T(5) = $Al_{1.0}$; M(3) = $Mg_{0.5}Al_{0.5}$; M(4), M(5), M(6) = $Mg_{1.0}$; T(2) = $Al_{0.25}Si_{0.75}$; T(3) = $Al_{0.5}Si_{0.5}$; T(4) = $Al_{0.75}Si_{0.25}$. T(6) is enigmatic since its average distance suggests $Al_{0.75}Si_{0.25}$, but this would require an excess of silicon over that allowed by the analysis. It has been assigned $Al_{1.0}$ with the added reservation that some Si may be present. Perhaps T(4) has less Si than it is allotted, with the remainder added to T(6).

The average O–O′ distances (Table 6) further substantiate this ordering scheme. O–O′ averages for their appropriate octahedra and tetrahedra are as follows: $Al_{1.0}$ 2.71–2.73, $Mg_{0.5}Al_{0.5}$ 2.80, $Mg_{1.0}$ 2.93–2.98 for the octahedra, and $Al_{1.0}$ 2.83–2.89, $Al_{0.75}Si_{0.25}$ 2.83, $Al_{0.5}Si_{0.5}$ 2.77, and $Al_{0.25}Si_{0.75}$ 2.71 Å for the tetrahedra.

TABLE 6. (*Continued*)

$M(7)=Al_{1.00}$		$M(8)=Al_{1.00}$	
M(7)-O(14)	1.863	M(8)-O(14)	1.899
M(7)-O(6)	1.888	M(8)-O(6)	1.913
M(7)-O(16)	1.889	M(8)-O(9)	1.914
M(7)-O(20)	1.915	M(8)-O(16)	1.924
M(7)-O(1)	1.956	M(8)-O(20)	1.956
M(7)-O(10)	2.017	M(8)-O(2)	1.973
	1.921		1.930
a O(1)-O(14′)	2.520	a O(16)-O(14)	2.532
a O(16′)-O(14′)	2.532	a O(9)-O(14)	2.536
a O(6)-O(10′)	2.532	a O(20)-O(6)	2.574
a O(6)-O(20)	2.574	a O(2)-O(6)	2.604
c O(16′)-O(1)	2.713	c O(9)-O(16)	2.711
c O(6)-O(14′)	2.724	c O(2)-O(20)	2.733
c O(20)-O(10′)	2.749	O(2)-O(16)	2.765
O(1)-O(20)	2.798	O(9)-O(20)	2.769
O(16′)-O(10′)	2.812	O(2)-O(14)	2.855
O(16′)-O(20)	2.857	O(16)-O(6)	2.874
O(14′)-O(10′)	2.887	O(9)-O(6)	2.876
O(6)-O(1)	2.888	O(14)-O(20)	2.879
	2.716		2.726
O(14)-M(7)-O(6)	93.1	O(14)-M(8)-O(9)	83.4
O(14)-M(7)-O(16)	84.9	O(14)-M(8)-O(16)	83.0
O(14)-M(7)-O(1)	82.6	O(14)-M(8)-O(20)	96.6
O(14)-M(7)-O(10)	96.2	O(14)-M(8)-O(2)	95.0
O(6)-M(7)-O(20)	85.2	O(6)-M(8)-O(9)	97.4
O(6)-M(7)-O(1)	97.4	O(6)-M(8)-O(16)	97.0
O(6)-M(7)-O(10)	80.8	O(6)-M(8)-O(20)	83.4
O(16)-M(7)-O(20)	97.4	O(6)-M(8)-O(2)	84.2
O(16)-M(7)-O(1)	89.7	O(9)-M(8)-O(16)	90.1
O(16)-M(7)-O(10)	92.0	O(9)-M(8)-O(20)	91.3
O(20)-M(7)-O(1)	92.4	O(16)-M(8)-O(2)	90.3
O(20)-M(7)-O(10)	88.7	O(20)-M(8)-O(2)	88.2
	90.0		90.0
O(14)-M(7)-O(20)	174.5	O(14)-M(8)-O(6)	179.2
O(6)-M(7)-O(16)	172.3	O(9)-M(8)-O(2)	178.3
O(1)-M(7)-O(10)	177.7	O(16)-M(8)-O(20)	178.4

Distortions. The polyhedral diagram of the sapphirine asymmetric unit in Figure 1 shows that the octahedra and tetrahedra are substantially distorted. These distortions, a consequence of partial cation ordering and cation-cation repulsions, are most pronounced whenever the octahedra share edges with each other. Since the structure is based on cubic close-packed oxygens, the tetrahedra cannot share edges with the octahedra. Table 6 shows that, as expected, the shortest distances are for the shared edges; these increase with the increasing size of the polyhedron, from Al–Al polyhedra to the Mg–Mg polyhedra. The average edge-shared distances of each kind with their frequency in parentheses are: $Al_{1.0}$–$Al_{1.0}$ 2.55 (12), $Mg_{0.5}Al_{0.5}$–$Al_{1.0}$ 2.60 (6), $Mg_{0.5}Al_{0.5}$–$Mg_{0.5}Al_{0.5}$ 2.68 (1),

TABLE 6. (*Continued*)

T(1) = Al$_{1.00}$		T(2) = Al$_{0.25}$Si$_{0.75}$		T(3) = Al$_{0.50}$Si$_{0.50}$	
T(1)-O(17)	1.738	T(2)-O(15)	1.617	T(3)-O(18)	1.687
T(1)-O(16)	1.747	T(2)-O(18)	1.653	T(3)-O(7)	1.701
T(1)-O(4)	1.790	T(2)-O(3)	1.665	T(3)-O(12)	1.706
T(1)-O(12)	1.809	T(2)-O(11)	1.696	T(3)-O(19)	1.706
	1.771		1.658		1.700
O(17)-O(12)	2.804	O(18)-O(11)	2.688	O(12)-O(18)	2.733
O(17)-O(4′)	2.847	O(18)-O(3′)	2.690	O(18)-O(7′)	2.756
O(12)-O(4′)	2.878	O(15)-O(3′)	2.698	O(19)-O(12)	2.757
O(17)-O(16)	2.902	O(18)-O(15)	2.701	O(19)-O(18)	2.772
O(12)-O(16)	2.940	O(15)-O(11)	2.723	O(19)-O(7′)	2.781
O(16)-O(4′)	2.967	O(3′)-O(11)	2.739	O(12)-O(7′)	2.851
	2.890		2.707		2.775
O(17)-T(1)-O(16)	112.7	O(15)-T(2)-O(18)	111.4	O(18)-T(3)-O(7)	108.9
O(17)-T(1)-O(4)	107.4	O(15)-T(2)-O(3)	110.5	O(18)-T(3)-O(19)	109.5
O(17)-T(1)-O(12)	104.4	O(15)-T(2)-O(11)	110.6	O(18)-T(3)-O(12)	107.3
O(16)-T(1)-O(4)	114.1	O(18)-T(2)-O(3)	108.3	O(7)-T(3)-O(19)	109.5
O(16)-T(1)-O(12)	111.4	O(18)-T(2)-O(11)	106.7	O(7)-T(3)-O(12)	113.7
O(4)-T(1)-O(12)	106.2	O(3)-T(2)-O(11)	109.2	O(19)-T(3)-O(12)	107.8
	109.4		109.4		109.4
T(4) = Al$_{0.75}$Si$_{0.25}$		T(5) = Al$_{1.00}$		T(6) = Al$_{1.00}$	
T(4)-O(17)	1.663	T(5)-O(13)	1.703	T(6)-O(5)	1.724
T(4)-O(8)	1.739	T(5)-O(15)	1.759	T(6)-O(19)	1.736
T(4)-O(11)	1.752	T(5)-O(1)	1.760	T(6)-O(2)	1.738
T(4)-O(20)	1.777	T(5)-O(9)	1.797	T(6)-O(10)	1.744
	1.733		1.755		1.736
O(11)-O(17)	2.749	O(15)-O(1′)	2.799	O(19)-O(2)	2.754
O(17)-O(8′)	2.760	O(15)-O(13)	2.809	O(19)-O(10′)	2.772
O(20)-O(11)	2.798	O(15)-O(9)	2.842	O(2)-O(10′)	2.835
O(11)-O(8′)	2.848	O(9)-O(1′)	2.871	O(5)-O(19)	2.848
O(20)-O(17)	2.899	O(13)-O(1′)	2.918	O(5)-O(10′)	2.888
O(20)-O(8′)	2.909	O(13)-O(9)	2.931	O(5)-O(2)	2.913
	2.827		2.862		2.835
O(17)-T(4)-O(8)	108.4	O(13)-T(5)-O(15)	108.5	O(5)-T(6)-O(19)	109.4
O(17)-T(4)-O(11)	107.2	O(13)-T(5)-O(1)	114.8	O(5)-T(6)-O(2)	114.5
O(17)-T(4)-O(20)	114.9	O(13)-T(5)-O(9)	113.7	O(5)-T(6)-O(10)	112.7
O(8)-T(4)-O(11)	109.4	O(15)-T(5)-O(1)	105.4	O(19)-T(6)-O(2)	104.8
O(8)-T(4)-O(20)	111.7	O(15)-T(5)-O(9)	106.1	O(19)-T(6)-O(10)	105.6
O(11)-T(4)-O(20)	104.9	O(1)-T(5)-O(9)	107.6	O(2)-T(6)-O(10)	109.1
	109.4		109.3		109.4

Mg$_{1.0}$–Al$_{1.0}$ 2.72 (20), Mg$_{0.5}$Al$_{0.5}$–Mg$_{1.0}$ 2.81 (2), and Mg$_{1.0}$–Mg$_{1.0}$ 2.84 (1) Å. Again, the proposed site preference scheme is supported since the increase in the O–O′ shared edge distances follows the order of expected increasing polyhedral size.

Distortions are also reflected in the O–Me–O′ angles (Table 6), but the averages of these angles for each of the polyhedra are very close to the values expected for the ideal octahedron and tetrahedron, a result of the restrictions placed on polyhedral distortions by the cubic close-packed anionic frame.

Reasons for cation ordering in sapphirine. The unusual sapphirine composition appears to be a consequence of its structure type. Two simple arguments are known to work adequately for silicates, aluminosilicates and aluminates and have been used by Bragg (1930) and Pauling (1929) to explain polyhedral arrangements in these systems. The first argument, the electrostatic valence rule, (Pauling, 1929) stipulates electro-neutrality about the anions and should ideally hold for purely ionic systems. Substantial deviations from saturation should be reflected in overall shortening in Me–O distances for cation undersaturation about the anion in question, and lengthening in Me–O distances for cation oversaturation. The second argument, a consequence of cation-cation repulsions is the tendency of high charge, low ligancy cations *not* to share polyhedral edges with each other.

The cation populations in sapphirine assure the best compromise of the electrostatic valence bond strengths (ζ) for all but two of the twenty oxygen atoms in the asymmetric unit (Table 7). The two oxygen atoms, O(5) and O(13), are highly undersaturated ($\zeta = 1.66$) and their Me–O interatomic distances are among the shortest for their polyhedra, as clearly shown in Table 6. It is further seen that hypothetically disordered sapphirine (Table 7) has not two but four highly undersaturated anions and would be less favorable crystallochemically.

This argument is extended further for other hypothetical sapphirine compositions. Two extreme compositions are given in Table 7, representing hypothetical silicon-free sapphirine and hypothetical aluminum-free sapphirine (magnesium-free sapphirine cannot exist since some divalent cations must be present for charge balance). The ζ-values for silicon-free sapphirine are either considerably low or considerably high; for the aluminum-free sapphirine, extreme undersaturation results. These arguments are too qualitative to place hypothetical limits which are reliable, but reasonable limits appear to be close to those suggested by the general sapphirine formula of Vogt (1947).

The second argument holds very well for sapphirine. As stated earlier, there are twenty Mg–Al edge-sharing O–O′ distances in the asymmetric unit whereas there are only twelve Al–Al edge-sharing O–O′ distances. Thus, ordering in sapphirine appears to be a reasonable compromise between nearest neighbor electro-neutrality and minimization of cation-cation repulsion effects.

TABLE 7. ELECTROSTATIC VALENCE BOND STRENGTH COMPUTATIONS (ζ) FOR SAPPHIRINE

(Extreme values of bond strength are italicized)

	$Mg_2Al_6O_2[Al_6O_{18}]$[a]	$Mg_{3.5}Al_{4.5}O_2[Al_{4.5}Si_{1.5}O_{18}]$		$Mg_8O_2[Si_6O_{18}]$
		normal[b]	*disordered*[c]	
O(1)	2.14	2.08	2.10	1.99
O(2)	2.14	2.08	2.10	1.99
O(3)	2.14	2.27	2.10	1.99
O(4)	2.25	2.07	2.10	1.99
O(5)	*1.75*	*1.66*	*1.67*	*1.66*
O(6)	1.89	1.83	*1.72*	*1.32*
O(7)	2.14	2.11	2.10	1.99
O(8)	2.14	2.06	2.10	1.99
O(9)	2.14	2.08	2.10	1.99
O(10)	2.14	2.08	2.10	1.99
O(11)	1.89	2.09	2.05	*2.33*
O(12)	1.89	1.96	2.05	*2.33*
O(13)	*1.75*	*1.66*	*1.67*	*1.66*
O(14)	1.89	1.83	*1.72*	*1.32*
O(15)	1.89	2.02	2.05	*2.33*
O(16)	2.14	2.15	2.10	1.99
O(17)	1.89	1.90	2.05	*2.33*
O(18)	1.89	2.15	2.05	*2.33*
O(19)	1.89	1.96	2.05	*2.33*
O(20)	2.14	2.15	2.10	1.99

[a] M(4), M(5), M(6) = (Mg_2,Al_1).

[b] Site populations proposed in this study.

[c] M = (Al,Mg), T = (Al,Si).

OTHER STRUCTURES POSSIBLY RELATED TO SAPPHIRINE

It is not possible to predict *a priori* the sapphirine structure type on the basis of its chemical stoichiometry nor is it possible to systematically list other hypothetical arrangements which could equally well satisfy the conditions of electro-neutrality discussed above. These interesting questions must await more sophisticated calculations than presently available. I would like to suggest, however, that other new structure types based on complex population schemes of Mg, Al, and Si cations in cubic close-packed oxygen atoms may actually exist.

Two compounds are particularly intriguing and have been considered to be spinel-like phases on the basis of their X-ray powder data. It may be remarked that a close correspondence between the strongest diffraction spectra for these 'spinel-like' phases and spinel does not necessarily mean topological equivalence; indeed, sapphirine is topologically quite distinct from spinel even though the fifteen strongest spectra are 'spinel-like' reflections.

One phase is the metastable intermediate structure of Saalfeld and Jagodzinski (1957) that they obtained by tempering $MgO:Al_2O_3$-spinels in excess of 1:2.5 at temperatures above 850°C. It has a 9.76, b 5.64, c 12.71 Å, $\beta = 110°46'$. They further note that the indices of refraction of this material are very similar to the index of refraction for $MgAl_2O_4$ spinel. Thus, if the same density of 3.55 gm/cm^3 is assumed, the cell contents can be calculated. A good fit ($Z = 2.02$) is obtained if the composition $Mg_2Al_{12}O_{20}$ is selected, a composition analogous to the hypothetical Si-free sapphirine.

The other phase is a high-pressure polymorph of olivine, synthesized and described by Ringwood and Major (1966). It was obtained above 170 kb from a starting mix of $(Mg_{0.85},Fe_{0.15})_2SiO_4$ composition. The powder data indicate a complex cell, perhaps of low symmetry; very small grain size of this phase precludes further study by single crystal X-ray methods.

These phases, like sapphirine, have relatively complex cells with low symmetry, strong 'spinel-like' spectra, and a preponderance of small octahedral and tetrahedral cations over larger ones. Presumably, the larger cations are extensively ordered, like Mg in sapphirine, resulting in distortions leading to complex cells with low symmetry. Like sapphirine, the large cations may be ordered in such a manner to minimize the overall cation-cation repulsion effects.

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