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REFINEMENT OF THE CRYSTAL STRUCTURE OF A PYROXENE OF FORMULA M_I M_{II} $(Si_{1.5}Al_{0.5})O_6$[1]

DONALD R. PEACOR, *University of Michigan, Ann Arbor, Michigan.*

ABSTRACT

The structure of a pyroxene of approximate formula Ca $(Mg,Fe^{3+},Fe^{2+},Ti,Al)$ $(Si,Al)_2O_6$ having approximately 25 percent of the tetrahedrally coordinated sites occupied by Al has been refined using the least-squares method, and utilizing proportional counter data, to $R=6.7\%$. Ordering of cations is complete within the accuracy of the data with Ca in the M_{II} site and only Al substituting for Si. Isotropic temperature factors fall within the range for structures of this general type where no solid solution occurs.

INTRODUCTION

The crystal structure of diopside was determined by Warren and Bragg (1928) and until recently their approximate determination on diopside comprised the only investigation on the structures of this large family of minerals. Morimoto, Appleman and Evans (1960) refined the structures of clinoenstatite and pigeonite ($P2_1/c$). Prewitt and Burnham (in press) refined the structure of jadeite ($C2/c$), Freed and Peacor (in press) that of johannsenite, and Appleman (personal communication) is currently working on spodumene.

Mr. David Gold brought an unusual pyroxene sample to my attention which he had discovered while investigating the carbonatite complex at Oka, Quebec. He noted that the analysis indicated that at least 25 percent of the tetrahedral sites were occupied by Al. A review of the literature shows that such naturally occurring high Al-containing pyroxenes are unusual. For example, in the compiled pyroxene analyses of Deer, Howie and Zussman (1963) only two analyses show a comparable Al content, and these are described as fassaites or titanaugites. In view of the recent interest in aluminosilicates and in the structures of rock-forming minerals in general it was felt that a refinement of this structure would be of interest, particularly regarding the solid solution relations involving Al.

SPECIMEN DESCRIPTION

The Al-pyroxene occurs as phenocrysts in a nepheline jacupirangite specimen obtained as a drill core from Hessereau Hill, Oka, Quebec, near the border of the carbonatite complex. Dr. Gold (personal communication) reports the following properties in general for pyroxenes from Oka:

"Titanaugite is the main constituent of the jacupirangite, and a minor constituent of the okaite rocks. It occurs as phenocrysts in the alnoite plugs and breccia pipes. Commonly the

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[1] Contribution No. 277, The Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan.

crystals are large (up to 2 cm in length), euhedral and exhibit the hourglass extinction pattern so typical of augite. Zoning is common. The mineral exhibits a weak pleochroism in shades of light brown to pinkish brown, and a biaxial positive figure. The crystals display brilliant interference colours which vary from berlin blue to dark brown, with different segments of the crystal changing at different angles."

Optical data for the Al-pyroxene specimen as kindly provided by Dr. Gold are $\alpha = 1.725$, $\beta = 1.732$, $\gamma = 1.745$, $2V_z = 58$–$64°$, and $Z \wedge c = 33$–$37°$. The analytical data are presented in Table 1. Calculation of absolute unit cell contents yields values slightly greater than those permitted by all equipoint ranks. This is probably caused by inaccuracy in the value of the specific gravity, which is reported as 3.399. Therefore the cell contents relative to 6 oxygen atoms were calculated and are given in Table 1.

Table 1. Analysis of Oka Al-Pyroxene[1]

Oxide	Wt %	Number of ions per six oxygen atoms	Number of ions, calc. free of H_2O and apatite
SiO_2	39.89	1.506	2.000
Al_2O_3	14.94	0.665	1.028
TiO_2	2.30	0.065	
Fe_2O_3	5.62	0.159	
FeO	2.01	0.063	
MgO	10.14	0.570	
MnO	0.21	0.007	0.990
CaO	24.33	0.975	
Na_2O	0.10	0.007	
K_2O	0.03	0.001	
P_2O_5	0.16		
H_2O^+	0.13		
H_2O^-	0.07		
CO_2	*Nil*		
Total	99.87		

The distribution of available atoms per equipoint for the tetrahedral and two octahedral sites is in good agreement with the diopside-type formula as shown by the data of Table 1. Thus the number of Ca ions is near 1.0 (M_{II} site) with minor amounts of the large cations Na, K and Mn substituting for it. The smaller cations (Mg, Fe, Ti and some of the Al) approximately fulfill the equipoint requirements of the smaller octahedral site (M_I site). In view of the variable optical properties for this

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[1] Analyst H. Uik, McGill University Geochemistry Laboratory.

material it is possible that the composition of the specimen chosen for intensity data differed slightly from the bulk composition, although final results confirmed the close compositional relationship.

The occupancy of the tetrahedral site is of prime interest. The assumption was initially made that this site was occupied by 0.494 Al to fulfill equipoint rank requirements. It is usual, when calculating unit cell contents for many silicates, to complete the occupancy of the Si site with Ti^{4+} or Fe^{3+} if the available Al does not suffice. All of the cation distributions initially assumed for this sample involve educated guesses, particularly in the case of Ti^{4+} and Fe^{3+}. One of the principal aims of this study, therefore, was to determine the cation distribution with respect to the occupancy of the tetrahedrally coordinated site.

UNIT CELL AND SPACE GROUP

Series of both precession and Weissenberg photographs were obtained using cleavage fragments from the core specimen used in the chemical analysis. These confirmed that at least this Al-pyroxene has space group $C2/c$ and is therefore of the diopsidic type, as also indicated by the analysis. Most phases having significant substitution of Al for Si show polymorphism, usually involving order-disorder of the Al and Si, at least in part. In this pyroxene and in others, the Al substitutes for Si in a ratio of about 1:3, but apparently is not observed in proportions greater than this in naturally occurring specimens. Ordering of Si and Al should require a symmetry other than $C2/c$. However, several photographs were overexposed to determine if there was even minor variation from this diopside-type symmetry. None was observed.

Unit-cell parameters were determined using least-squares refinement of data from standard 0-level Weissenberg films. The results are presented in Table 2, with values for some other diopsidic pyroxenes for comparison. Clark, Schairer and de Neufville (1962) in a study of the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-SiO_2 determined the variation of a, b, c and β for pyroxenes in the composition range $CaMgSi_2O_6$-$CaAlAlSiO_6$. Sakata (1957) has also obtained similar results. They found that with increasing Al, a decreased from 9.745 Å to 9.615 Å, b decreased from 8.925 to 8.661 Å, and c increased from 5.248 to 5.272. The role of Al with respect to the values of a and b is well known. For example these values for jadeite and spodumene are on the order of magnitude of 0.5 Å less than those for diopside, and both of these minerals have relatively small cations in the M_I and M_{II} sites (Na, Al and Li, Al respectively). However, Clark *et al* note that as Al is added to the tetrahedral site simple expansion of the tetrahedra results in an increase in c (translation parallel to the chains).

With respect to these relations, the values of *a* and *b* of this study are in the range typical of a diopsidic pyroxene. However the average cation radii in the M_I and M_{II} sites are comparable with a phase of the series studied by Clark *et al*, but the values of *a* and *b* are on the order of magnitude of 0.05 Å greater than those for this phase. In addition the value of *c* (5.32 Å) is about 0.04 Å greater than the maximum reported by Clark *et al* in their series, and their maximum value reflects a much higher degree of Al substitution for Si. Thus it appears that the value of *c* increases as Al substitutes for Si with resulting expansion of tetrahedra, but the value of *c* is also related to the cation distribution in the M_I and M_{II} sites. This is illustrated by the magnitude *c* for johannsenite (5.29 Å) which has only Si in the tetrahedral sites, but cations of maximum size (Ca and Mn) for a pyroxene in the M_I and M_{II} sites. Thus the magnitude of *c* cannot be directly and simply used as a function of the degree of substitution of Al for Si in pyroxenes of complex composition, at least until the detailed relations have been determined on material showing a wide range of composition.

TABLE 2. LATTICE PARAMETERS OF OKA AL-PYROXENE AND OTHER SELECTED DIOPSIDIC-TYPE PYROXENES

Specimen	a(Å)	$\sigma(a)$	b(Å)	$\sigma(b)$	c(Å)	$\sigma(c)$	β	$\sigma(\beta)$
Oka Al-pyroxene (this study)	9.794	0.005	8.906	0.005	5.319	0.003	105.90	0.03
Jadeite Burnham and Prewitt (in press)	9.418	.001	8.562	.002	5.219	.001	107.58	.01
Diopside Clark *et al* (1962)	9.745	.001	8.925	.001	5.248	.001	74.13	.01
$CaAlAlSiO_6$ Clark *et al* (1962)	9.615	.003	8.661	.002	5.272	.003	73.88	.03
Johannsenite Freed and Peacor (in press)	9.978	.009	9.156	.009	5.293	.005	105.29	.02

INTENSITY DATA

The specimen used for measurement of intensity data was a cleavage fragment obtained from a phenocryst from the core sample used for the chemical analysis. It was a *c*-axis mounted cleavage prism approximately 0.26 mm long with a triangular cross-section about 0.04 mm in average radius. Data was collected manually using CuKα radiation with a proportional counter mounted on a diffractometer having Weissenberg-like geometry. Direct counting methods were used with background measurements on both sides of each peak. Stability of the instrumentation was regularly monitored both by reference to a standard peak and by determination of pulse-height distribution.

The intensity data for 399 peaks were processed for Lorentz-polarization factors and absorption using the modified programs DFSET3 written by C. T. Prewitt and ABSRP written by C. W. Burnham. Absolute estimated errors of each reflection intensity were calculated as a function of background, peak intensity, time used for the measurement of a peak, the Lp factor and absorption (Freed, personal communication), for use in weighting for least-squares.

REFINEMENT

The structure refinement was carried out using the full matrix least-squares IBM 7090 program SFLSQ3 written by C. T. Prewitt. Form factor curves were used with the assumption of complete ionization throughout all but the final stages of refinement, when half-ionization of all atoms was assumed. The change from full to half ionization resulted only in slight changes in structure parameters, including temperature factors, which were well within their probable errors, indicating that ionization differences in general result in negligible differences in the values of refined parameters. Since accurate values of ionization states of all atoms are not available, the half-ionization assumption was used as the best available approximation. Form factors were calculated assuming the cation distribution given in Table 1 for the initial stages of refinement. However, this ordering model was confirmed by the refinement and it was used throughout.

Beginning with coordinates of the refined johannsenite structure and varying only the scale factor and coordinates, the refinement rapidly converged with $R=7.3\%$. The weighting scheme described above was used, the values of which are a function of the probable error of measurement for a given reflection. At this stage refinement was attempted using weighting schemes with both equal weights for all data and with $\sigma(F) = F_0$. Since no significant parameter changes occurred, refinement was continued with the original weighting scheme.

Refinement of isotropic temperature factors gave values of 0.73, 0.74, 0.17, 0.52, 0.75 and 0.84 for the M_I, M_{II}, (Si, Al), O(1), O(2), and O(3) sites respectively. It has been shown by several investigators that when form factors are in error, due for example to incorrect assumptions regarding solid solution, temperature factors readily refine to unreasonable values. As a further verification of the assumed solid solution relations, scale factors applied to f-curves were refined. All changes were small and within the ranges of the original unit values and their errors. In particular, values for both the M_I and M_{II} sites increased slightly, indicating that no interchange of atoms in these sites would give better values of scattering functions. In addition, the change in the scale factor for the Si site was from 1 to 1.0004. Thus the assumptions on solid solution relations were further verified.

Refinement of both coordinates and temperature factors was carried out with anomalous scattering values obtained from the tables of Dauben and Templeton (1955). Since no significant changes occurred (temperature factors varied within their probable errors), refinement was continued without this correction, which is approximate at best.

Refinement of anisotropic temperature factors yielded some nonpositive-definite values for the Si, O(1), O(2) and O(3) sites. The values became positive only when a new weighting scheme was applied. The scheme recommended by Cruickshank (1965) with $\sigma(F)=2F_{\min}+F+2/F_{\max}\times F^2$ gave reasonable values for all anisotropic temperature factors. Refinement of the scale factor, coordinates and anisotropic temperature factors rapidly converged to $R=6.4\%$ (excluding the few F's with $F=0.0$) and $R=6.7\%$ (including the latter).

TABLE 3. REFINED PARAMETERS OF OKA AL-PYROXENE
(standard deviations in parentheses)

	M_I (Mg)	M_{II} (Ca)	Si	O(1)	O(2)	O(3)
x	0 (0)	0 (0)	0.2129 (2)	0.3870 (4)	0.1379 (4)	0.1482 (4)
y	0.0932 (2)	0.6957 (2)	.4072 (2)	.4122 (4)	.2454 (4)	.4811 (5)
z	3/4 (0)	3/4 (0)	.7728 (3)	.8623 (8)	.6811 (8)	.0083 (8)
$\beta 11$	0.0018 (3)	0.0024 (2)	.0005 (2)	.0010 (5)	.0018 (5)	.0008 (5)
$\beta 22$	0.0010 (3)	0.0012 (2)	.0006 (2)	.0010 (5)	.0017 (5)	.0019 (5)
$\beta 33$	0.0048 (9)	0.0059 (7)	.0031 (7)	.0046 (17)	.0081 (17)	.0074 (19)
$\beta 12$	0 (0)	0 (0)	.0000 (1)	− .0004 (3)	− .0007 (4)	− .0003 (3)
$\beta 13$	−0.0008 (4)	−0.0004 (3)	− .0001 (3)	− .0003 (6)	− .0013 (7)	− .0004 (7)
$\beta 23$	0 (0)	0 (0)	.0000 (2)	.0005 (6)	.0011 (7)	.0007 (7)
B_{equiv}	0.52	.66	.25	.40	.69	.57

RESULTS

The refined parameters with standard deviations are listed in Table 3. A limited portion of the structure is shown in Figure 1B with the corresponding portion of the structure of jadeite in Fig. 1A. These diagrams are projections parallel to a^*, normal to (100) close packed oxygen planes. Only a portion of the structures is shown in detail, since the basic pyroxene structure relations have been diagrammed in several places (*e.g.* Prewitt and Peacor, 1964).

Despite the fact that cation radii and ionic charges are quite different in the Oka Al-pyroxene and jadeite whose structure was refined in detail by Prewitt and Burnham, the structures are essentially the same, the principal apparent difference being only in scale. The polyhedra about the M_I and M_{II} sites appear to have similar geometry, despite some basic differences described below. The chains of tetrahedra are quite similar in both and very close to idealized chains, particularly in the case of jadeite.

Cation ordering. In the discussion of the refinement it was noted that the values of form factor, scale factors and temperature factors confirmed the cation ordering as originally assumed and described in Table 1. Interatomic distances are tabulated in Table 4. All distances and angles and their estimated standard deviations were computed with the function and error program ORFFE written by Busing, Martin and Levy, using the final variance-covariance structure parameter matrix and errors in lattice parameters. The final interatomic distances also are consistent with the assumed ordering scheme. For example, the average M_{II}-O distance is 2.503 Å (8-fold coordination). The four smallest values (2.38 Å) are in the range (2.37–2.38 Å) noted by Prewitt and Peacor (1964) as being quite similar for Ca polyhedra, at least in inosilicates. Ordering of Ca in the M_{II} site is thus complete within the accuracy of the data, while the very small amounts of the large cations Na, K and Mn certainly are included here. The M_I-O distances (ave. 2.069 Å) are in the range expected for occupancy of the M_I site with Mg, Fe^{2+}, Fe^{3+}, Ti and Al.

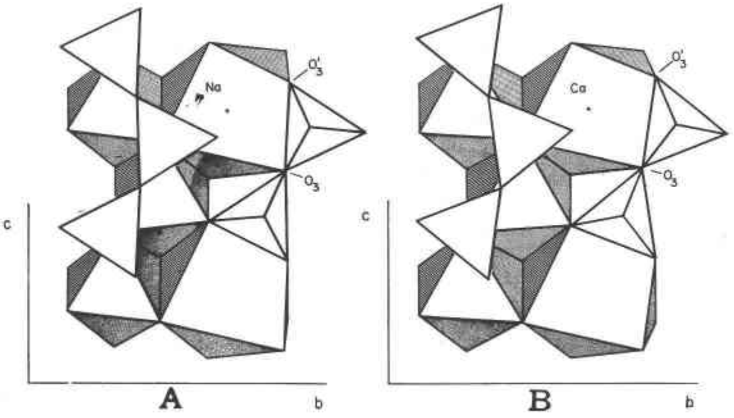

FIG. 1. Representations of portions of the structures of jadeite (Fig. 1A) and the Al-pyroxene of this study (Fig. 1B) projected on (100). The larger relative rotation of tetrahedra in Figure 1B is evident in the nearly equal Ca-O(3) and Ca-O(3)^1 bond lengths.

TABLE 4. INTERATOMIC DISTANCES AND ANGLES

A superscript to an atom symbol denotes a symmetry transformation if the atom coordinates differ from those of Table 3, according to the following key: (1) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ (2) $x, y, -1+z$ (3) $x, 1-y, -\frac{1}{2}+z$ (4) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ (5) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ (6) $-1+x, y, -1+z$ (7) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$ (8) $-x, y, \frac{1}{2}-z$

Si tetrahedron								
Si-O(1)	1.640	(5) Å	O(1)-O_2	2.792	(6)	O(1)-Si-O(2)	117.3°	(0.2)
O(2)	1.629	(4)	O(1)-O(3)^3	2.739	(6)	O(1)-Si-O(3)^3	110.3	(0.2)
O(3)^3	1.697	(5)	O(1)-O(3)^2	2.728	(6)	O(1)-Si-O(3)^2	110.3	(0.2)
O(3)^2	1.685	(5)	O(2)-O(3)^3	2.614	(6)	O(2)-Si-O(3)^3	103.6	(0.2)
av.	1.663		O(2)-O(3)^2	2.711	(6)	O(2)-Si-O(3)^2	109.7	(0.2)
			O(3)^3-O(3)^2	2.681	(2)	O(3)-Si-O(3)^2	104.8	(0.2)
M_I octahedron								
M_I-2O(1)^4	2.057	(5)Å	O(1)^4-O(1)^5	2.779	(8)	O(1)^4-M_I-O(1)^5	83.1	(0.2)
2O(1)^5	2.132	(4)	O(1)^4-O(2)	2.934	(6)	O(1)^4-M_I-O(2)	92.1	(0.2)
2O(2)	2.017	(4)	O(1)^5-O(2)	2.982	(6)	O(1)^5-M_I-O(2)	91.9	(0.2)
av.	2.069		O(1)^5-O(1)^6	3.085	(4)	O(1)^5-M_I-O(1)^6	94.9	(0.2)
			O(1)^5-O(1)^7	2.789	(9)	O(1)^5-M_I-O(1)^7	81.7	(0.2)
			O(2)-O(1)^6	2.873	(6)	O(2)-M_I-O(1)^6	89.7	(0.2)
			O(2)-O(2)^8	2.987	(8)	O(2)-M_I-O(2)^8	95.5	(0.2)
M_{II} polyhedron								
M_{II}-2O(1)^1	2.380	(4)Å						
2O(2)^3	2.379	(5)						
2O(3)^2	2.560	(5)						
2O(3)^3	2.695	(5)						
av.	2.530							

The Si-O distances are particularly interesting. If the average value (1.663 Å) is used in conjunction with the predicted variation of average (Si, Al)-O distances as a function of both the relative Al content and tetrahedral linkage model (Smith and Bailey, 1963) a value of about 28 percent Al is obtained for the occupancy of this site. This compares with a value of 25 percent Al determined from the chemical analysis, as described above. The difference between these two values is well within the probable errors of each. The tetrahedral site is thus occupied on the average by about 25 percent Al, with at most negligible amounts of Ti and Fe^{3+}, despite the presence of the latter two cations in the M_I site.

Coordination polyhedra. The pyroxene structure exhibits significant variations from local charge balance as determined from the classical Pauling electrostatic valency principle. The oxygen atom O(1) is coordinated to

1 Si, 2 M_I, and 1 M_{II}; O(2) to 1 Si, 1 M_I and 1 M_{II}; O(3) to 2 Si and 2 M_{II}. Using the average charges for cations as determined from the ordered model, O(1) is seen to have balanced charge, O(2) a deficiency of 0.4 and O(3) an excess of about 0.4. Thus O(3)-cation distances should be greater than average and O(2)-cation distances consistently less than average. The two Si-O(3) distances (1.70 and 1.68 Å) are about 0.04 Å and 0.02 Å greater than the average Si-O distance, while the two M_{II}-O(3) distances (2.56 and 2.69 Å) are much greater than the M_{II}-O(1) and M_{II}-O(2) distances (both 2.38 Å). Similarly, the Si-O(2) distance (1.63 Å) is about 0.03 Å less than the average and the M_I-O(2) distance (2.02 Å) is the smallest for the M_I polyhedron, while the M_{II}-O(2) distance is equal to the smallest for the M_{II} polyhedron.

The primary differences in pyroxenes occur in the coordination of the M_{II} site. Morimoto *et al* (1960) noted that interatomic distances are consistent with six-fold coordination in clinoenstatite (Mg in M_{II}), eight-fold in diopside (Ca in M_{II}) and seven-fold in pigeonite (Ca, Fe, Mg in M_{II}) although the latter may be considered to be an average of eight-fold in unit cells with Ca in M_{II} and six-fold for those cells with Mg or Fe in the M_{II} site. Prewitt and Burnham (1966) showed that the M_{II} coordination polyhedron in jadeite (Na in M_{II}) is approximately a square antiprism and they noted the correspondence between this site in pyroxenes and the M_4 site in amphiboles. A similar coordination is found for the Ca (M_5) site of rhodonite. In all of these structures the cation occurs at the edge of a band of octahedra (Prewitt and Peacor 1964).

The structural differences arising as a result of differences in the M_{II} polyhedron can be seen in Figures 1A and 1B. In jadeite the two symmetrically different Na-O(3) distances are 2.36 and 2.74 Å for Na-O(2). Thus in terms of distances only, the M_{II} site may be interpreted to approach 6-fold coordination. In the Al pyroxene the two symmetrically different O(3) distances are 2.56 and 2.69 Å, however, as compared to 2.38 Å for both Ca-O(1) and Ca-O(2).

Morimoto *et al* note that one of the significant differences between pyroxenes is in the relative distortion of the chains, caused by rotation of the tetrahedra about an axis passing through Si and O(1) (approximately parallel to *a**, the axis of projection of Fig. 1). Such a rotation changes the two symmetrically different M_{II}-O(3) distances. Thus the difference in M_{II}-O(3) distances in jadeite is partially a reflection of the nearly geometrically ideal silicate chain as shown by the O(3)-O(3)′-O(3)″ angle of 175°. The relative rotation of tetrahedra and subsequent chain distortion in the Al-pyroxene with resulting change in M_{II}-O(3) distances is reflected in a corresponding angle of 166°.

Temperature factors. Both anisotropic temperature factors and their equivalent isotropic temperature factors are listed in Table 3. The calculation of standard errors for the thermal ellipsoids showed that errors in the orientation of the principal axes of vibration are too high to permit interpretation of their values, particularly in the case of the Si-Al ellipsoid, although the standard errors in the magnitudes of the principal axes of vibration are relatively small.

The equivalent isotropic temperature factors are all typical of values found in similar structures (metasilicates) where there is no solid solution in the cation sites. In addition, these equivalent temperature factors, as determined with the weighting scheme suggested by Cruickshank, are quite similar to the isotropic temperature factors which were obtained with other weighting schemes. The value of B_{equiv} for the (Si, Al) site is 0.25, which is quite typical for Si sites in some other metasilicates, as are values of around 0.5 for oxygen atoms and 0.6 for M_I and M_{II} sites. Burnham (1965) has commented at length on temperature factor values for (Si, Al) sites, and notes that, as expected, isotropic temperature factors for some structures increase with substitution of Al for Si. Thus the relatively low value of B_{equiv} for (Si, Al) here appears to be unusual. This may be the result of inaccuracy in the value of the form factor for this site as a function of relative Al content, but the data is in good aggreemet with the values chosen.

The equivalent isotropic temperature factor for the M_I site (0.52) is also quite typical for octahedrally coordinated atoms in metasilicates. Several elements occupy this site so the temperature factor was expected to be relatively high. Since its value is in the range for equivalent sites in other structures this may be a result of an error in the formulation of the form factor curve here too. However, the internal agreement for all data would seem to indicate that the values of temperature factors reflect thermal rather than position disorder arising from solid solution.

Aluminum distribution. Although pyroxenes frequently form in environments where Al is present as the major element, pyroxenes only infrequently have Al present in the tetrahedrally coordinated site in amounts greater than about 5 percent relative to Si. A structure analysis of this pyroxene was undertaken in part because the fraction of Al in the Si site is very close to the maximum reported for naturally occurring pyroxenes. In general the tendency for Al to substitute for Si appears to decrease with a decrease in the tendency for tetrahedra to share vertices. It is therefore tempting, with this structure refinement in hand, to attempt to rationalize the observed relatively low amounts of Al in the Si sites of pyroxene structures. Coupled solid solution of 2Al for M_I^{2+}+Si up to a maximum corresponding to 50 percent substitution in the Si site is a probable mechanism. An analysis of such a structure in terms of the Pauling valency principle shows that the average charge imbalance is similar to that of other pyroxenes. However, for any one unit cell the positive charge deficit on O(2), becomes 4/8 rather than 3/8 as in jadeite. The higher the fraction of Al in tetrahedrally coordinated sites the more likely that adjacent tetrahedra contain Al, resulting in a very high local charge imbalance.

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