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CRYSTAL-CHEMICAL CHARACTERIZATION OF CLINOPYROXENES BASED ON EIGHT NEW STRUCTURE REFINEMENTS[1]

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ABSTRACT

Comparison of new crystal-structure refinements for spodumene, $LiFe^{3+}Si_2O_6$, synthetic ureyite, acmite, diopside, augite, a *C*2/*c* omphacite, and a *P*2 omphacite with published refinements for jadeite, johannsenite, $NaIn^{3+}Si_2O_6$, fassaite, and another *P*2 omphacite indicates that the structures are strikingly similar throughout the range of chemical compositions. The "end-member" clinopyroxenes are ordered within the limits of resolution. Bonding can be satisfactorily explained in terms of an essentially ionic model without invoking additional covalent effects. Except for *P*2 omphacites, the charge and size of the *M*2 cations determine the structure type: if *M*2 is Ca or Na, *C*2/*c* is expected; if *M*2 is Li, *C*2; and if *M*2 is Mg or Fe^{2+}, $P2_1/c$ or orthorhombic. Precise bond distances for ordered "end-member" clinopyroxenes can be used in determining *T* and *M*1 site contents of intermediate-composition clinopyroxenes, and ferrous iron is disordered in such clinopyroxenes. "Ideal" *P*2 omphacite, $Ca_{0.5}Na_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$, is expected to have Mg and Al fully ordered in the *M*1 octahedral chains, but in the *M*2 sites the maximum amount of order in alternating sites is $\frac{1}{3}$ Ca, $\frac{2}{3}$ Na, and $\frac{1}{3}$ Na, $\frac{2}{3}$ Ca.

INTRODUCTION

In a recent review of the crystal chemistry of pyroxenes, Zussman (1968) pointed out that before 1959 very few details of the crystal structures were known. Since then, although the results of several modern refinements have been published, the structures of a number of "end-member" pyroxenes, including diopside, $CaMgSi_2O_6$, have not been examined by modern methods. We have therefore carried out precise structure refinements of diopside, acmite $NaFe^{3+}Si_2O_6$, ureyite $NaCr^{3+}Si_2O_6$, spodumene $LiAlSi_2O_6$, and synthetic $LiFe^{3+}Si_2O_6$ (Table 1). The results of these refinements are presented here and are compared with those previously reported for jadeite, $NaAlSi_2O_6$ (Prewitt and Burnham, 1966), johannsenite, $CaMn^{2+}Si_2O_6$ (Freed and Peacor, 1967), and synthetic $NaIn^{3+}Si_2O_6$ (Christensen and Hazell, 1967). In addition, results of refinements for three clinopyroxenes of intermediate compositions (Table 2: a *C*2/*c* omphacite, a nearly Fe-free *P*2 omphacite, and a *C*2/*c* augite) are also given here and are compared with those for another *P*2 omphacite (Clark and Papike, 1968) and for an Al-rich pyroxene that approximates fassaite (Peacor, 1967). In the discussion to follow, the crystallographic nomenclature for clinopyroxenes is essentially that proposed by Burnham *et al.* (1967). The "end-member" clinopyroxene crystals that we have studied are fully ordered within the limits of the X-ray diffraction method (except for the $LiFe^{3+}Si_2O_6$, as explained later), and in the following discussion they are all referred to as *ordered* clinopyroxenes.

EXPERIMENTAL DATA

Crystallographic, chemical and X-ray diffraction powder data. Crystallographic data and information about the source of the crystals used for the structural studies are given in Table 1 for eight ordered clinopyroxenes and in Table 2 for five clinopyroxenes of intermediate compositions. The relationship of the cell parameters to chemical composition and structure is discussed at the end of the paper. In most cases, the cell parameters were obtained by least-squares refinement of powder X-ray data derived from diffractometer measurements taken with Ni-filtered Cu radiation (Cu $K\alpha_1$, $\lambda = 1.5405$ Å). The refinement program for the IBM 360/65 is described by Appleman and Evans (1967). Bulk chemical and electron-microprobe analyses (Tables 2, 3) indicate that the ordered clinopyroxenes and the Venezuelan *P*2 omphacite have compositions close to ideal. A trace amount of Ca was detected in the synthetic ureyite crystals and is attributed to impurity of a reagent used in the synthesis (L. Fuchs, oral commun., 1968). The synthetic $LiFe^{3+}Si_2O_6$ crystals contain about 0.10 atom of Fe^{2+} per formula unit, a point discussed later, and this occurrence is due to partial reduction of iron during the quench process (D. B. Stewart, oral commun., 1968).

Determination of the space groups was confirmed during the present study by examination of single-crystal precession photographs and by checking individual reflections manually on the single-crystal diffractometer. The spodumenes have from two to ten weak reflections of the type *h*0*l* with $l = 2n + 1$, violating the *c*-glide symmetry. The *P*2 omphacites each have from 200 to 300 weak reflections of the types *hkl* with $h + k = 2n + 1$ and *h*0*l* with $l = 2n + 1$. Reflections violating *C*2/*c* symmetry requirements were sought but not observed for any of the other clinopyroxenes. A number of the crystals, including spodumene, were checked for piezoelectricity but no response was observed. A powdered sample of a known *P*2 omphacite was studied by the harmonic oscillator method (Kurtz and Perry, 1968) and showed no indication of any second harmonic generation (S. K. Kurtz and K. Nassau, written commun., 1968). This result is not surprising in view of the nearly centrosymmetric nature of the *P*2 structure.

Observed X-ray diffraction powder data for most of these clinopyroxenes are available in the XRDF, and calculated patterns are soon to be published (Borg and Smith, in press). However, powder data for synthetic $LiFe^{3+}Si_2O_6$ have never been given before, so these data are listed in Table 4, together with data for the Newry (Maine) spodumene. Similar data are also given for the Kakanui (New Zealand) augite in Table 5.

Single-crystal X-ray diffraction data. The information on data collection (crystal size, number of independent reflections, final *R* values, *etc.*) is summarized for the eight ordered clinopyroxenes in Table 6 and for the five intermediate composition pyroxenes, in Table 7. For this study the scan range was computed according to the equation for Mo $K\alpha$ X radiation suggested by Alexander and Smith (1964), with constants ad-

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[1] Studies of silicate minerals (13). Publication authorized by the Director, U. S. Geological Survey.

Table 1. Crystal Data for Eight Ordered Clinopyroxenes[a]

	Spodumene		Jadeite	Ureyite[b]	Acmite[c]		Diopside	Johannsenite
	$LiAlSi_2O_6$	$LiFe^{3+}Si_2O_6$	$NaAlSi_2O_6$	$NaCr^{3+}Si_2O_6$	$NaFe^{3+}Si_2O_6$	$NaIn^{3+}Si_2O_6$	$CaMgSi_2O_6$	$CaMn^{2+}Si_2O_6$
	Present study	Present study	Prewitt and Burnham (1966)	Frondel and Klein (1965); present study	Nolan and Edgar (1963); present study	Christensen and Hazell (1967)	Present study	Freed and Peacor (1967)
a (Å)	9.449 (3)	9.666 (2)	9.418 (1)	9.550 (16)	9.658 (2)	9.916	9.746 (4)	9.978 (9)
b (Å)	8.386 (1)	8.669 (1)	8.562 (2)	8.712 (7)	8.795 (2)	9.132	8.899 (5)	9.156 (9)
c (Å)	5.215 (2)	5.294 (2)	5.219 (1)	5.273 (8)	5.294 (1)	5.371	5.251 (6)	5.293 (5)
β (°)	110.10 (2)	110.15 (2)	107.58 (1)	107.44 (16)	107.42 (2)	107.0	105.63 (6)	105.48 (3)
Cell volume (Å^3)	388.1 (1)	416.4 (1)	401.20 (15)	418.6 (1.4)	429.1 (1)	*465.1[a]	438.6 (3)	*466.0[a]
Space group	$C2$	$C2$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
Z	4	4	4	4	4	4	4	4
Calc. density, g cm^{-3}	3.184	3.427	*3.345[a]	3.603	3.577	4.13	3.278	*3.522[a]
Source of material	natural	synthetic	natural	synthetic	natural	synthetic	natural	natural
Locality or method of synthesis	Newry, Maine	d	Santa Rita peak area, New Idria Peak District, California	e	Green River Formation, Wyoming	f	Gouverneur talc district, Gouverneur, New York	Schio-Vincenti mine, Venetia, Italy

[a] Values in parentheses are one standard deviation, *i.e.*, for 9.449 (3) read 9.449 ± 0.003 Å. An asterisk marks values not given in reference and calculated by present authors.

[b] Cell parameters obtained by refinement during present study of selected data from Frondel and Klein (1965).

[c] Cell parameters and volume from Nolan and Edgar (1963); other data from present study.

[d] Hydrothermal, 700° C, 2 kbar for 16 hrs, using Fe_2O_3 and $Li_2Si_4O_9$ in the $LiFe^{3+}Si_2O_6$ ratio.

[e] From melt of $NaCr^{3+}Si_2O_6$ plus 10 wt % Na_2SiO_3 in air at 1000° C for 2 days.

[f] Obtained as impurity from a hydrothermal preparation of rhombohedral indium oxide.

Table 2. Crystallographic and Chemical Data[a] for Five Clinopyroxenes of Intermediate Compositions

		Omphacites			Augite	Fassaite[c]
		Present study	Clark and Papike (1968)	Warner (1964); present study[b]	Present study	Peacor (1967)
a (Å)		9.551 (8)	9.596 (5)	9.646 (6)	9.699 (1)	9.794 (5)
b (Å)		8.751 (5)	8.771 (4)	8.824 (5)	8.844 (1)	8.906 (5)
c (Å)		5.254 (4)	5.265 (6)	5.270 (6)	5.272 (1)	5.319 (3)
β (°)		106.87 (8)	106.93 (8)	106.59 (8)	106.97 (2)	105.90 (3)
Cell volume (Å^3)		420.2 (4)	423.9 (4)	429.9 (5)	432.5 (1)	446.2
Space group		$P2$	$P2$	$C2/c$	$C2/c$	$C2/c$
Cations per 6 oxygen atoms						
Tetrahedral	Si	1.98	1.96	1.995	1.83	1.506
	Al	0.02	0.04	0.005	0.17	0.494
	Σ	2.00	2.00	2.000	2.00	2.000
M cations	Ca	0.47	0.51	0.583	0.61	0.975
	Na	0.48	0.48	0.325	0.09	0.007
	Mg	0.42	0.44	0.582	0.90	0.570
	Fe^{2+}	0.05	0.10	0.116	0.11	0.063
	Fe^{3+}	0.02	0.10	0.123	0.10	0.159
	Al	0.51	0.39	0.233	0.16	0.171
	Ti	0.01	0.01	0.002	0.02	0.065
	Σ	1.96	2.03	1.964	1.99	2.010
Z		4	4	4	4	4
Calc. density, g cm^{-3}		3.32	3.37	3.36	3.31	3.35
Locality of mineral		Puerto Cabello, Venezuela	Tiburon Peninsula, California	Hareidland, Sunmøre, Norway	Kakanui, New Zealand	Hessereau Hill, Oka, Quebec, Canada
Reference for chemical analysis, mineralogy		Morgan (1967), sample Ca-1059	Coleman *et al.* (1965), sample 100-RGC-58	Schmitt (1963), sample 1725	Mason (1966)	Peacor (1967)

[a] Values in parentheses are one standard deviation; for 9.551(8) read 9.551 ± 0.008 Å.

[b] Cell constants obtained by refinement during present study of selected data from Warner (1964). The value for Si of 1.973 (Warner 1964) is incorrect; recalculation yields 1.995.

[c] M cations include 0.007 atom Mn. Cell volume calculated by present authors.

justed when necessary to increase the range slightly. Background counts of 20 seconds duration were made for each reflection at the beginning and end of the scan range. The take-off angle was 3°. A standard reflection was recorded after each 30 measurements, and a number of equivalent reflections were collected; agreement in all cases was excellent.

Computer programs, written by Dr. C. T. Prewitt, E. I. du Pont de Nemours and Co., Wilmington, Delaware, and modified by D. E. Appleman for the IBM 360/65, were used to obtain the diffractometer settings and to reduce the ·raw· data, including corrections for the total background count, absorption, Lorentz and polarization factors (program ACACA). Reflections for which the |F| was less than four (five for ureyite) times the standard deviation in |*F*| as determined by the counting statistics were coded as "less-thans" and were not used in the refinment.

Refinement procedures. Computer programs used for the initial refinements were taken from *X-Ray 67, Program System for X-Ray Crystallography*, by J. M. Stewart, University of Maryland, adapted by D. E. Appleman for the IBM 360/65. The initial atomic parameters were those reported for jadeite (Prewitt and Burnham, 1966), except for the *P*2 omphacite, for which the coordinates were taken from the published *P*2 omphacite parameters (Clark and Papike, 1968). In the latter stages of the refinements, the data for each structure were refined with programs written by Dr. L. W. Finger, Geophysical Laboratory, Washington, D.C. Final cycles of least-squares refinement were carried out using anisotropic temperature factors with the form

$$\exp\left\{-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right\}$$

for each atom, except for the *P*2 omphacite, for which only individual isotropic temperature factors were refined. Corrections for anomalous dispersion (Cromer, 1965) were also applied, and site occupancies were refined where necessary and possible. The site occupancy refinements were based on a fixed total chemical composition, assigned from the results of the chemical analyses (Table 2, 5); the principles governing the calculations are discussed by Finger (1969). No large correlations between parameters were noted except for the *P*2 omphacite, described in that section of this paper. A trial refinement of Mg *vs* Ca between *M*1 and *M*2 sites in diopside confirmed the assumption of complete ordering within the limits of the data. No corrections were made for extinction, either primary or secondary; the data appeared to be relatively unaffected by primary extinction. A few reflections were strong enough to swamp the scintillation counter, and these data were not used in the final refinements.

TABLE 4. X-RAY DIFFRACTION POWDER DATA FOR SPODUMENE FROM NEWRY, MAINE, AND FOR SYNTHETIC $LiFe^{3+}Si_2O_6$[a]

Spodumene				$LiFe^{3+}Si_2O_6$[b]			
Calculated[c]		Observed[d]		Observed[d]		Calculated[c]	
hkl	d_{hkl}(Å)	d_{hkl}(Å)	Peak height	Peak height	d_{hkl}(Å)	d_{hkl}(Å)	*hkl*
110	6.095	6.08	60	90	6.28	6.268	110
200	4.436	4.44	30			4.537	200
$\bar{1}11$	4.352	4.35	20	35	4.44	4.443	$\bar{1}11$
020	4.193	4.20	80	70	4.33	4.334	020
111	3.442	3.437	20	25	3.510	3.509	111
021	3.185	3.187	30	5	3.268	3.267	021
220	3.047	3.046	5			3.134	220
$\bar{2}21$	2.914	2.914	85	100	2.992	2.992	$\bar{2}21$
$\bar{3}11$	2.854	2.853	15			2.920	$\bar{3}11$
310	2.789	2.790	100	85	2.854	2.856	310
130	2.666	2.665	30	15	2.753	2.753	130
$\bar{2}02$	2.546	2.545	5			2.587	$\bar{2}02$
$\bar{1}12$	2.484					2.525	$\bar{1}12$
				35	2.523		
$\bar{1}31$	2.450					2.523	$\bar{1}31$
		2.449	20				
002	2.449			35	2.484	2.485	002
221	2.351	2.350	20	40	2.405	2.405	221
131	2.246			2	2.308	2.308	131
$\bar{3}12$	2.234					2.277	$\bar{3}12$
400	2.218	2.222	15			2.268	400
$\bar{2}22$	2.176			2	2.221	2.221	$\bar{2}22$
311	2.143	2.145	10			2.188	311
022	2.115			2	2.167	2.167	040
112	2.107	2.108	10			2.156	022
040	2.096			5	2.143	2.142	112
$\bar{3}31$	2.056	2.054	20	20	2.115	2.114	$\bar{3}31$
$\bar{4}21$	2.048			10	2.100	2.099	$\bar{4}21$
330	2.032	2.032	10	2	2.089	2.089	330
$\bar{4}02$	2.027			5	2.067	2.067	$\bar{4}02$
420	1.961					2.010	420
041	1.927	1.927	20	5	1.987	1.987	041
$\bar{1}32$	1.904					1.956	240
240	1.896					1.949	$\bar{1}32$
202	1.887					1.919	$\bar{2}41$
				25	1.919		
$\bar{2}41$	1.862	1.863	30			1.919	202
$\bar{5}11$	1.843	1.847	15	10	1.886	1.886	$\bar{5}11$
$\bar{4}22$	1.825		2	2	1.866	1.866	$\bar{4}22$
$\bar{3}32$	1.784			5	1.829	1.828	$\bar{3}32$
						1.781	331
				5	1.779		
						1.776	510
		1.738	10	2	1.734		
		1.724	5	15	1.703		
		1.681	2	5	1.692		
		1.647	15	10	1.634		
				10	1.630		
		1.608	15	40	1.606		
		1.593	5				
		1.566	35				
		1.523	20				

[a] See Table 1 for crystallographic data, Table 3 for spodumene chemical analysis. C2/c

[b] Actual composition close to $Li_{0.95}Fe^{+2}_{0.10}Fe^{+3}_{0.95}Si_2O_6$.

[c] All calculated values down to $2\theta(CuK\alpha_1) \leq 52°$ are given for *C*2/*c hkl* only.

[d] Measurements from diffractometer patterns taken with Ni-filtered Cu radiation, $CuK\alpha_1$ $\lambda = 1.5405$ Å. Peak heights are normalized to 100 for the largest observation and are approximate only; patterns may be subject to preferred orientation effects.

TABLE 3. CHEMICAL DATA FOR FOUR CLINOPYROXENES

Element	Atoms per six atoms of oxygen			
	Spodumene[a]	Ureyite[b]	Acmite[b]	Diopside[b]
Li	1.00	—	—	—
Na	0.01	1.00	0.95	0.02
Ca	—	0.05	—	0.99
Mg	—	0.04	0.01	1.01
Al^{VI}	1.00	—	0.01	0.01
Cr^{3+}	—	0.97	—	—
Fe^{3+}	—	—	0.99	0.01
Mn^{2+}	—	0.01	—	—
ΣM	2.01	2.07	1.96	2.04
Si	1.99	1.97	2.00	1.97

[a] Values converted from chemical analysis of bulk sample (Newry, Maine), wt. % as follows: Li_2O 8.0, Na_2O 0.18, Al_2O_3 27.40, Fe_2O_3 0.03, SiO_2 64.18. Analyst, J. J. Fahey, U.S.G.S., Li by flame photometer, Joseph I. Dinnin, U.S.G.S.

[b] Electron microprobe analyses of selected single crystals by A. T. Anderson, U.S.G.S.; locality or method of synthesis are given in Table 1.

The atomic scattering factors used during the final cycles of refinement were calculated from a nine-coefficient analytical function (Cromer and Waber, 1965), using the coefficients of Cromer and Mann (1968) for O^{-1} and fully ionized cations. At the end of the refinement, the magnitudes and orientations of the thermal ellipsoids were calculated. The final bond lengths

TABLE 5. X-RAY DIFFRACTION POWDER DATA FOR AUGITE FROM KAKANUI, NEW ZEALAND[a]

Calculated[b]		Observed[c]		Calculated[b]		Observed[c]	
hkl	d_{hkl} (Å)	d_{hkl} (Å)	Peak height	hkl	d_{hkl} (Å)	d_{hkl} (Å)	Peak height
110	6.401			330	2.134	2.135	20
200	4.638			$\bar{3}31$	2.124	2.125	40
020	4.422			$\bar{4}21$	2.101	2.101	10
$\bar{1}11$	4.415			420	2.054		
111	3.622			$\bar{4}02$	2.026	2.025	35
021	3.324	3.325	10	041	2.025		
220	3.201	3.204	55	240	1.996		
$\bar{2}21$	2.988	2.989	100	202	1.985	1.985	5
310	2.919	2.917	100	$\bar{1}32$	1.964	1.965	15
$\bar{3}11$	2.895	2.897	25	$\bar{2}41$	1.941		
130	2.810			$\bar{5}11$	1.889		
$\bar{1}31$	2.552	2.550	35	$\bar{4}22$	1.842		
$\bar{2}02$	2.548			331	1.837		
$\bar{1}12$	2.525					1.816	15
002	2.520	2.520	25			1.811	20
221	2.485	2.485	35			1.738	20
131	2.367					1.666	10
400	2.319					1.628	10
311	2.270	2.269	25			1.616	30
$\bar{3}12$	2.236					1.600	5
040	2.211					1.535	10
$\bar{2}22$	2.208					1.531	10
112	2.199	2.194	10			1.501	20
022	2.190					1.474	5
						1.404	40

[a] See Table 2 for crystallographic and chemical data.

[b] Calculated values complete to $2\theta \leq 50.0°$ ($CuK\alpha_1$, $\lambda = 1.5405$ Å).

[c] Measurements from diffractometer patterns with NaF as internal standard, $CuK\alpha_1$. Peak heights normalized to 100 using 310, $\bar{2}21$.

and angles with associated standard deviations (s.d.) were obtained from the full matrices of the errors in atomic and cell parameters, using program BADTEA written by Finger.

Both unit weights and statistical weights were tried in the course of the refinements. Statistical weights were computed from the formula $w^{1/2} = 1/\sigma(F)$, where $\sigma(F)$ is one s.d. in $|F_o|$ determined from the counting statistics. For unit weights a weight of 1.0 was assigned to all reflections. The statistical weighting scheme was not suitable for the $P2$ omphacites because of the large difference in average intensity between the group of reflections with $h + k = 2n$ and the much weaker group with $h + k = 2n + 1$. For ordered $C2/c$ pyroxenes such as diopside, the two weighting schemes yielded virtually identical results. For consistency, unit weights were used for *all* final refinements. In Tables 6 and 7 we list both the conventional $R =$

$$\sum ||F_o| - |F_c|| / \sum |F_o|,$$

and the so-called weighted $R =$

$$[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

We emphasize that $w = 1$ in all cases.

Refinement results. Atomic parameters and their standard deviations are compared with published values in Table 8 for ordered clinopyroxenes, in Table 9 for $C2/c$ intermediate composition clinopyroxenes, and in Table 10 for $P2$ omphacites. The anisotropic temperature factor tensors for ordered clinopyroxenes are given in Table 11. Observed and calculated structure factors obtained from the atomic parameters of Tables 8–10 are listed in Table 12.[1]

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[1] Table 12 may be ordered as NAPS Document #00454 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N.Y. 10001; remitting in advance $1.00 for microfiche or $3.00 for photocopies, payable to ASIS-NAPS.

TABLE 6. DATA-COLLECTION INFORMATION FOR EIGHT ORDERED CLINOPYROXENES

	Spodumene		Jadeite	Ureyite	Acmite		Diopside	Johannsenite
	$LiAlSi_2O_6$	$LiFe^{3+}Si_2O_6$	$NaAlSi_2O_6$	$NaCr^{3+}Si_2O_6$	$NaFe^{3+}Si_2O_6$	$NaIn^{3+}Si_2O_6$	$CaMgSi_2O_6$	$CaMn^{2+}Si_2O_6$
	Present study	Present study	Prewitt and Burnham (1966)	Present study	Present study	Christensen and Hazell (1967)	Present study	Freed and Peacor (1967)
Size of crystal (mm)	0.07×0.16 ×0.23	0.10×0.10 ×0.16	0.04×0.08 ×0.22	0.03×0.07 ×0.13	0.07×0.10 ×0.20	0.06×0.06 ×0.3	0.07×0.13 ×0.20	0.074×0.033 ×0.173
Radiation/filter	Mo/Nb	Mo/Nb	Cu/Ni	Mo/Nb	Mo/Nb	Mo/not given	Mo/Nb	Not given
Collection method	a	a	b	a	b	c	a	d
Crystal axis (ϕ) for data collection	$[hh0]^*$	$[hh0]^*$	not given	$[\bar{h}0h]^*$	$[hh0]^*$	not given	$[\bar{h}0h]^*$	[001]
Absorption correction	no	yes	yes	yes	yes	no	no	yes
μ, cm^{-1}	11.	42.	108.	34.	42.	56.	20.	not given
No. of $\|F_o\| > 0$	850	866	348	711	834	534	918	398
Isotropic R	0.037	0.050	0.045	0.056	0.054	0.055	0.043	0.066
Isotropic wtd R[e]	0.044	0.058	—	0.062	0.057	—	0.047	—
Anisotropic R	0.031	0.035	0.037	0.040	0.035	0.049	0.023	—
Anisotropic wtd R[e]	0.039	0.046	—	0.047	0.039	—	0.030	—
Standard deviation in $\|F\|$ (anisotr.)	4.34	7.04	—	3.01	3.76	—	3.80	—

[a] Normal-beam, equatorial geometry, 4-circle automatic diffractometer, scintillation counter, 2θ scans.

[b] Equiinclination Weissenberg, scintillation detector, balanced filters.

[c] Inclination geometry, linear diffractometer, scintillation counter, balanced filters.

[d] Equi-inclination diffractometer, proportional detector.

[e] See text for definition of R and wtd R (so-called weighted R); w=1 in all refinements.

TABLE 7. DATA-COLLECTION INFORMATION FOR FIVE CLINOPYROXENES OF INTERMEDIATE COMPOSITIONS

	Omphacites			Augite	Fassaite
	Venezuela Present study	California Clark and Papike (1968)	Norway Present study	New Zealand Present study	Quebec Peacor (1967)
Size of crystal (mm)	0.20×0.20×0.07	0.20×0.07×0.04	0.16×0.13×0.03	0.30×0.23×0.13	0.04×0.04×0.26
Radiation/filter	Mo/Nb	Mo/none	Mo/Nb	Mo/Nb	Cu/not given
Collection method	Normal beam, equatorial diffractometer, scintillation counter, 2θ scans				a
Diffractometer	4-circle automatic	manual	4-circle automatic	4-circle automatic	manual
Crystal axis (ϕ) for data collection	[001]*	[010]*	[010]*	[010]*	c
Absorption correction	no	yes	yes	yes	yes
μ, cm^{-1}	18.	22.	24.	23.	239.
No. of $\|F_0\|>0$	1150	830	724	944	about 390
Isotropic R	0.047	0.080	0.056	0.089	0.073
Isotropic wtd R[b]	0.045	—	0.060	0.085	—
Anisotropic R	not done	not done	0.046	0.049	0.064
Anisotropic wtd R[b]			0.052	0.054	—
Standard deviation in $\|F\|$ (final)	4.96	—	4.44	11.03	—

[a] Equiinclination diffractometer, proportional counter, direct counting methods with background measurements.
[b] See text for definition of R and wtd R (so-called weighted R); $w=1$ in all refinements.

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The clinopyroxene crystal structure. The basic structure of the clinopyroxenes was first determined by Warren and Bragg (1928) for diopside. The distinctive features of the structure are well described and illustrated in papers by Prewitt and Peacor (1964) and Zussman (1968), as well as in the published refinements of jadeite and johannsenite, already cited. The oxygen atom O3 links between two Si atoms (Fig. 1) and is referred to as "bridging." The other two crystallographically distinct oxygen atoms O1 and O2 are each linked to only one Si (Fig. 1) and are referred to as "nonbridging." The $M1$ site (Fig. 2) is octahedrally coordinated and is occupied by the cations Mg, Al^{VI}, Cr, Mn, Fe^{2+} and Fe^{3+}; the $M2$ site (Fig. 3) is larger than $M1$ and is usually occupied by Ca, Na and Li. In the following discussion, we assume the reader's familiarity with the structure and concern ourselves with specific details of the crystal chemistry.

The ordered clinopyroxenes. Some features of the ordered $C2/c$ clinopyroxenes have been described elsewhere (Appleman and Stewart, 1966; Clark, Appleman

TABLE 8. ATOMIC PARAMETERS COMPARED FOR EIGHT ORDERED CLINOPYROXENES[a]

Atom	Parameter	Spodumene $LiAlSi_2O_6$		$LiFe^{3+}Si_2O_6$	Jadeite $NaAlSi_2O_6$	Ureyite $NaCr^{3+}Si_2O_6$	Acmite $NaFe^{3+}Si_2O_6$	$NaIn^{3+}Si_2O_6$	Diopside $CaMgSi_2O_6$		Johannsenite $CaMn^{2+}Si_2O_6$
		Warren and Biscoe (1931)	Present study	Present study	Prewitt and Burnham (1966)	Present study	Present study	Christensen and Hazell (1967)	Warren and Bragg (1928)	Present study	Freed and Peacor (1967)
SiA1	x	0.29	0.29411 (6)	0.29626 (9)	0.2906 (1)	0.2921 (1)	0.29051 (8)	0.2922 (3)	0.290	0.28623 (5)	0.2871 (2)
	y	.09	0.09349 (7)	.0895 (1)	.0934 (1)	.0918 (1)	.08940 (9)	.0869 (3)	.090	.09331 (5)	.0917 (2)
	z	.25	0.2560 (1)	.2663 (2)	.2277 (2)	.2333 (2)	.2351 (1)	.2477 (5)	.236	.22928 (9)	.2363 (4)
	B	—	0.15 (1)	.29 (1)	.41	.36 (2)	.29 (1)	—	—	.228 (7)	.26 (3)
O1A1	x	.11	0.1099 (2)	.1168 (2)	.1090 (2)	.1140 (3)	.1141 (2)	.1194 (7)	.124	.1156 (1)	.1203 (6)
	y	.09	0.0823 (2)	.0851 (3)	.0763 (3)	.0791 (3)	.0784 (2)	.0800 (7)	.099	.0873 (1)	.0930 (5)
	z	.14	0.1402 (3)	.1503 (4)	.1275 (4)	.1374 (5)	.1380 (4)	.1538 (13)	.139	.1422 (2)	.1541 (11)
	B	—	0.24 (2)	.42 (3)	.36	.42 (4)	.39 (2)	—	—	.33 (2)	.39 (8)
O2A1	x	.37	0.3646 (2)	.3671 (3)	.3608 (2)	.3599 (3)	.3582 (2)	.3578 (8)	.358	.3611 (1)	.3632 (5)
	y	.25	0.2673 (2)	.2576 (3)	.2630 (3)	.2583 (3)	.2558 (2)	.2467 (8)	.251	.2500 (1)	.2431 (6)
	z	.32	0.3009 (3)	.3290 (5)	.2929 (4)	.3037 (6)	.3001 (4)	.3149 (12)	.320	.3180 (3)	.3295(10)
	B	—	0.44 (2)	.69 (3)	.48	.55 (4)	.53 (3)	—	—	.46 (2)	.47 (9)
O3A1	x	.36	0.3565 (2)	.3558 (3)	.3533 (2)	.3531 (3)	.3518 (2)	.3472 (7)	.345	.3505 (1)	.3482 (7)
	y	.01	−0.0129 (2)	.0000 (3)	.0070 (3)	.0105 (3)	.0079 (2)	.0112 (8)	.022	.0176 (1)	.0206 (6)
	z	.000	0.0578 (3)	.0539 (5)	.0058 (4)	.0066 (6)	.0118 (4)	.0195 (11)	.000	−.0047 (2)	−.0043 (12)
	B	—	0.41 (2)	.72 (3)	.49	.53 (3)	.52 (3)	—	—	.39 (2)	.40 (10)
$M1$	y	.91	0.9066 (1)	.89867 (7)	.9060 (1)	.9076 (1)	.89890 (7)	.8948 (1)	.917	.90823 (9)	.9053 (2)
	B	—	0.17 (1)	.31 (1)	.40	.42 (1)	.37 (1)	—	—	.26 (1)	.48 (3)
$M2$	y	.31	0.2752 (9)	.2685 (6)	.3009 (2)	.3008 (3)	.2999 (2)	.3034 (8)	.305	.30154 (5)	.3019 (2)
	B	—	1.1 (1)	.6 (1)	.95	.77 (4)	.98 (3)	—	—	.514 (7)	.58 (3)

[a] x, y, z in cycles, equivalent B (Å^2) from anisotropic refinement, except for johannsenite (isotropic refinement only). In $C2/c$ oxygen, Si positions $8f$, $M1$ and $M2$ positions $4e$ with $x=0$, $z=0.25$. Previously published values converted as necessary to obtain the same asymmetric set for all (Burnham *et al.*, 1967). Errors in parentheses are one standard deviation; for 0.2922 (3) read 0.2922 ± 0.0003.

TABLE 9. ATOMIC PARAMETERS AND SITE OCCUPANCIES FOR THREE $C2/c$ CLINOPYROXENES OF INTERMEDIATE COMPOSITIONS[a]

Atom	Parameters, atomic contents	Omphacite	Augite	Fassaite
		Norway	New Zealand	Quebec
		Present study		Peacor (1967)
T	x	0.2881 (1)	0.2896 (1)	0.2871 (2)
	y	0.0924 (1)	0.0924 (1)	0.0928 (2)
	z	0.2308 (2)	0.2353 (1)	0.2272 (3)
	B	0.40 (1)	0.52 (1)	0.25
	Si	2.00	1.82	1.506
	Al	0.	0.16 (+.02 Ti)	0.494
O1	x	0.1140 (3)	0.1150 (2)	0.1130 (4)
	y	0.0829 (4)	0.0865 (3)	0.0878 (4)
	z	0.1387 (6)	0.1402 (4)	0.1377 (8)
	B	0.73 (4)	0.77 (3)	0.40
O2	x	0.3604 (4)	0.3647 (3)	0.3621 (4)
	y	0.2531 (4)	0.2530 (3)	0.2546 (4)
	z	0.3136 (6)	0.3260 (5)	0.3189 (8)
	B	0.83 (4)	1.13 (3)	0.69
O3	x	0.3513 (3)	0.3526 (2)	0.3518 (4)
	y	0.0147 (4)	0.0185 (3)	0.0189 (5)
	z	−0.0002 (6)	0.0013 (4)	−0.0083 (8)
	B	0.63 (3)	1.03 (3)	0.57
$M1$	y	0.9048 (2)	0.9063 (1)	0.9068 (2)
	B	0.55 (3)	0.51 (2)	0.52
	Al	0.240	0.182	0.171
	Mg	0.543	0.715	0.570
	Fe	0.217 (7)	0.103 (5)	0.222
	Σ	1.000	1.000	1.028
$M2$	y	0.2999 (2)	0.2952 (1)	0.3043 (2)
	B	0.85 (3)	1.23 (2)	0.66
	Ca	0.590	0.616	0.975
	Na	0.320	0.090	0.007
	Mg	0.057	0.187	—
	Fe	0.033	0.107	—
	Σ	1.000	1.000	0.982

[a] x, y, z in cycles; equivalent isotropic B (Å^2) taken from anisotropic refinement. In $C2/c$, T and O, positions $8f$; $M1$ and $M2$, positions $4e$ with $x=0$, $z=0.25$. Errors in parentheses are one standard deviation; for 0.2881 (1) read 0.2881 ± 0.0001. Atomic contents based on six oxygen atoms; tetrahedral site filled to 2.00 with Si and Al (also Ti for augite). For omphacite and augite, Ca, Na were fixed in $M2$, Al in $M1$ and Fe/Mg occupancy refined. Site occupancies were assumed for the fassaite with 0.065 atom Ti also in $M1$; its coordinates have been converted to the standard set (Burnham *et al.*, 1967) by the present authors.

and Papike, 1968). For the silicate tetrahedra in these clinopyroxenes, the final bond lengths and angles obtained from the present study are compared in Table 13 with the values published for jadeite, johannsenite and $NaIn_3Si_2O_6$.

Comparison of interatomic distances and angles for ordered clinopyroxenes of greatly differing compositions shows that certain features of the silicate chains remain constant throughout the series (Table 13). For example, the Si-O2 bond is the shortest of the four Si-O bond lengths for all eight compounds and varies only between 1.585 and 1.598 Å, with a mean of 1.591 Å. The O1-Si-O2 angle is the largest O-Si-O angle in each compound, subtending the longest tetrahedral edge, O1-O2. In addition, the $M1$-O2 distance is the shortest $M1$-O distance in each compound (Table 14). These constant features all involve O2. As shown in Table 15 under bond strengths in the columns headed "Ideal ionic model", O2 has an unsatisfied charge of from 0.3 to 0.4 electrons that is by far the largest charge imbalance of the three independent oxygen atoms in these clinopyroxenes. This apparent excess negativity is compensated for by the shorter O2-Si and O2-$M1$ bonds and may also be responsible for the relative constancy of the Si-O2 distances throughout the series. The relationships between bond lengths and strengths are discussed in detail later in this section. The large O1-Si-O2 angles may also be due in part to the greater repulsion between the more negatively charged nonbridging oxygen atoms, a point made by McDonald and Cruickshank (1967) in connection with the refinement of Na_2SiO_3, which has a metasilicate chain comparable to the clinopyroxene chain.

There has been considerable discussion recently about the influence of d-p π bonding in causing the increase in length of Si-O bridging bonds over the value observed for nonbridging bonds (Cruickshank, 1961; McDonald and Cruickshank, 1967; Pant and Cruickshank, 1967, 1968). In sodium metasilicate, the bridging Si-O bonds average 1.672 Å but the nonbridging Si-O bonds average only 1.592 Å. These values are similar to those observed in the clinopyroxenes with Ca in the $M2$ position, which have mean values of 1.682 Å for bridging and 1.596 Å for nonbridging Si-O bonds. There is much less difference between the bridging and nonbridging Si-O distances in the clinopyroxenes with univalent cations in the $M2$ position (Table 13).

In the clinopyroxene series the increase in bridging Si-O bond distance can be directly related to the strength of the $M2$-O bonds. Each O3 bridging oxygen coordinates two $M2$ cations (except when $M2$ is Li), and assuming the electrostatic attraction between O3 and Ca^{2+} to be greater than that between O3 and Na^+, and Si-O3 bridging bonds would be expected to lengthen in the Ca clinopyroxenes. In the Na_2SiO_3 structure, Na is coordinated by only five oxygens instead of eight as in the clinopyroxenes, but each bridging oxygen still has two Na neighbors. Bond-strength calculations based on a simple ionic model show that the O-Na bonds in Na_2SiO_3 have strengths of about 0.2 valence unit, very close to the strengths of the O-Ca bonds in Ca clinopyroxenes (Table 15), so the bridging oxygens in each case receive about 0.4 electron from this source. The nearly identical lengthening of the bridging Si-O bonds in Na_2SiO_3 and Ca clinopyroxenes is thus explained on the basis of local charge balance, providing further evidence for the validity of an essentially ionic model for the bonding in chain silicates.

The value of the Si-O3-SiA2 angle differs but little throughout the series of compounds (Table 13); the average for the six phases with univalent $M2$ is 140.1°, and for the two with Ca^{2+}, 136.3°. Again the effect of Ca^{2+} is apparent. Comparison of a related feature, the linearity of the chain "backbone", O3A2-O3A1-O3A2 (+1 in c), demonstrates that the straightest chains are found in jadeite, acmite and synthetic $LiFe^{3+}Si_2O_6$ (Table 13); in

TABLE 10. ATOMIC PARAMETERS AND SITE OCCUPANCIES COMPARED FOR TWO *P*2 OMPHACITES

	Venezuela Present study					California Clark and Papike (1968)				
Atom[a]	Site occupancy[b]	*x*	*y*	*z*	B (Å²)	Site occupancy[c]	*x*	*y*	*z*	B (Å²)
*M*1	Fe 0.10 (1) Mg 0.82 Al 0.08	0	0.914 (1)	0	0.5 (1)	Fe 0.19 Mg 0.81	0	0.9122 (5)	0	0.2 (1)
*M*1(1)	Al 1.00	0	0.099 (1)	0.5	0.37 (9)	Al 0.95 Fe 0.05	0	0.1002 (5)	0.5	.3 (1)
*M*1 H	Fe 0.08 Al 0.92	0.5	.404 (1)	0	0.4 (1)	Fe 0.18 Al 0.82	0.5	0.4045 (5)	0	.3 (1)
*M*1(1)H	Fe 0.10 Mg 0.90	0.5	.595 (1)	0.5	0.25 (9)	Fe 0.20 Mg 0.80	0.5	0.5957 (5)	0.5	.2 (1)
*M*2	Na 0.76 (9) Ca 0.24	0	.303 (1)	0	1.1 (3)	Na 0.64 Ca 0.36	0	0.3036 (5)	0	.8 (1)
*M*2(1)	Na 0.25 (8) Ca 0.75	0	.7018 (3)	0.5	0.8 (2)	Na 0.36 Ca 0.64	0	0.7017 (5)	0.5	.7 (1)
*M*2 H	Na 0.31 (8) Ca 0.69	0.5	.8009	0	0.7 (2)	Na 0.03 Ca 0.97	0.5	0.8009	0	.8 (1)
*M*2(1)H	Na 0.68 Ca 0.32	0.5	.199 (1)	0.5	0.6 (2)	Na 0.64 Ca 0.36	0.5	0.1996 (5)	0.5	.8 (1)
Si 1A	1.0 for all Si, O	0.2892 (5)	.0987 (8)	0.9775 (9)	0.28 (6)	1.0 for all Si, O	.2890 (5)	0.0972 (5)	0.9774 (5)	0.17 (5)
Si 2A		.2872 (5)	.9131 (8)	.4784 (10)	0.43 (7)		.2881 (5)	0.9135 (5)	0.4820 (5)	
Si 1C		.2123 (4)	.5882 (8)	.0175 (9)	0.13 (6)		.2137 (5)	0.5880 (5)	.0196 (5)	
Si 2C		.2104 (5)	.4033 (8)	.5245 (9)	0.27 (6)		.2103 (5)	0.4027 (5)	.5232 (5)	
O1 A1		.110 (1)	.092 (1)	.864 (2)	0.3 (1)		.112 (1)	0.088 (1)	.864 (2)	0.4 (1), for all O
O1 A2		.108 (1)	.931 (1)	.399 (2)	0.2 (1)		.110 (1)	0.922 (1)	.405 (2)	
O1 C1		.386 (1)	.574 (2)	.104 (2)	0.6 (2)		.386 (1)	0.567 (1)	.103 (2)	
O1 C2		.384 (1)	.415 (1)	.622 (2)	0.5 (2)		.385 (1)	0.411 (1)	.620 (2)	
O2 A1		.363 (1)	.264 (1)	.056 (2)	0.4 (2)		.364 (1)	0.263 (1)	.066 (2)	
O2 A2		.350 (1)	.751 (1)	.556 (2)	0.7 (2)		.347 (1)	0.747 (1)	.551 (2)	
O2 C1		.139 (1)	.755 (1)	.945 (2)	0.3 (1)		.133 (1)	0.749 (1)	.939 (2)	
O2 C2		.133 (1)	.245 (2)	.438 (3)	0.6 (2)		.135 (1)	0.244 (1)	.446 (2)	
O3 A1		.356 (1)	.021 (2)	.751 (3)	0.5 (2)		.360 (1)	0.022 (1)	.757 (2)	
O3 A2		.351 (1)	.996 (1)	.253 (2)	0.3 (1)		.350 (1)	0.994 (1)	.252 (2)	
O3 C1		.155 (1)	.515 (1)	.259 (2)	0.6 (2)		.154 (1)	0.515 (1)	.255 (2)	
O3 C2		.143 (1)	.489 (2)	.742 (3)	0.3 (2)		.147 (1)	0.489 (1)	.750 (2)	

[a] *M* atoms in positions 1*a*, 1*b*, 1*c*, 1*d* of *P*2; *M*2 H *y* fixed to assign origin. Other atoms in positions 2*e* of *P*2. Errors in parentheses are one standard deviation; for 0.2892 (5) read 0.2892 ± 0.0005.

[b] Total occupancy fixed at 1.0; chemical contents fixed from adjusted analysis for Venezuelan omphacite (see text). The errors in parentheses (one standard deviation) indicate those parameters refined.

[c] Total occupancy fixed at 1.0, but chemical contents allowed to vary during refinement.

the latter the angle is 180° within the error of measurement. The chains in the two Ca clinopyroxenes, however, have the largest departures from linearity, with an average angle of 165°.

The *M*1 octahedral chains (Fig. 2) are a dominant structural feature in the clinopyroxenes. The average *M*1-O distances obtained in this study for the various *M*1 cations (Table 14) agree in general with values previously reported (*cf.* MacGillavry and Rieck, 1962). The angles of the Mg octahedron in diopside closely approximate those of a regular octahedron. The other *M*1 octahedra are also fairly regular, the average angular distortion being about 5° and the largest distortion, about 13°. Zussman (1968) suggested that the Mn^{2+} cation represents the upper size limit for *M*1 occupancy; the In^{3+} cation appears to be very nearly the same size as Mn^{2+}, so that the clinopyroxenes which have been studied confirm this size limitation. The In-In closest approach is, however, appreciably longer (by about 0.1 Å) than any other *M*1-*M*1 contact observed. The Si-O-*M*1 angles, as well as the Si-O-*M*2 angles (Table 16), vary little across the series and show no apparent dependence on the kind of *M*1 or *M*2 cation. Comparison of acmite with synthetic $NaFe^{3+}Ge_2O_6$, which has the clinopyroxene structure (Solov'eva and Bakakin, 1967), would be interesting to show the effects on the structure of substituting Ge for Si,

TABLE 11. ANISOTROPIC TEMPERATURE FACTOR TENSOR VALUES COMPARED FOR ORDERED CLINOPYROXENES[a]

Atom	ij of β_{ij}	Spodumene $LiAlSi_2O_6$ Present study	$LiFe^{3+}$-Si_2O_6 Present study	Jadeite NaAl-Si_2O_6 Prewitt and Burnham (1966)	Ureyite $NaCr^{3+}$-Si_2O_6 Present study	Acmite $NaFe^{3+}$-Si_2O_6 Present study	Diopside CaMg-Si_2O_6 Present study
Si	11	4.2 (5)	13.3 (8)	11 (1)	15 (1)	4.9 (6)	5.5 (4)
	22	6.0 (6)	10.9 (8)	17 (2)	13 (1)	7.3 (7)	7.0 (4)
	33	15 (2)	14 (2)	36 (5)	15 (3)	38 (2)	25 (1)
	12	−1.8 (5)	−1.6 (6)	0 (1)	−1 (1)	−0.8 (5)	−0.2 (3)
	13	3.0 (7)	9 (1)	6 (2)	2 (1)	−2.9 (9)	2.6 (5)
	23	−1.0 (8)	−1 (1)	−1 (2)	−2 (1)	0 (1)	−0.9 (6)
O1	11	6 (1)	15 (2)	4 (3)	16 (2)	6 (2)	6.3 (9)
	22	11 (2)	17 (2)	20 (3)	18 (3)	12 (2)	12 (1)
	33	18 (4)	31 (6)	32 (9)	19 (7)	46 (6)	35 (3)
	12	−1 (1)	−1 (2)	−4 (2)	−1 (2)	−1 (1)	0.6 (8)
	13	0 (2)	11 (3)	0 (4)	3 (3)	−5 (2)	1 (1)
	23	0 (2)	−3 (3)	−7 (4)	4 (4)	1 (3)	2 (2)
O2	11	14 (1)	28 (2)	10 (3)	22 (3)	14 (2)	15 (1)
	22	12 (2)	15 (2)	20 (3)	15 (3)	8 (2)	9 (1)
	33	64 (5)	82 (8)	47 (9)	38 (8)	75 (6)	49 (4)
	12	−6.5 (1)	−10 (2)	−4 (2)	−6 (2)	−5 (2)	−5.6 (8)
	13	15 (2)	28 (4)	0 (4)	4 (4)	2 (3)	3 (2)
	23	−3 (2)	−10 (3)	2 (4)	−4 (4)	0 (3)	−1 (2)
O3	11	10 (1)	22 (2)	13 (3)	18 (2)	11 (2)	9 (1)
	22	24 (2)	37 (3)	22 (3)	24 (3)	19 (2)	16 (1)
	33	23 (4)	37 (7)	41 (10)	25 (7)	51 (6)	35 (3)
	12	2 (1)	0 (2)	−3 (2)	0 (3)	2 (2)	0 (1)
	13	2 (2)	12 (3)	9 (4)	4 (3)	0 (3)	5 (2)
	23	−12 (2)	−25 (4)	0 (4)	−12 (5)	−8 (3)	−7 (2)
*M*1	11	5.3 (8)	14.2 (6)	13 (2)	17 (1)	8.1 (5)	7.5 (7)
	22	7.2 (9)	9.9 (6)	15 (2)	15 (1)	8.6 (5)	7.5 (8
	33	14 (3)	20 (2)	35 (6)	23 (2)	46 (2)	25 (2)
	13	2 (1)	8.1 (8)	5 (3)	4 (1)	−2.0 (7)	1 (1)
*M*2	11	30 (7)	25 (6)	35 (2)	35 (3)	34 (2)	18.1 (4)
	22	38 (8)	22 (7)	26 (3)	17 (3)	20 (2)	11.4 (4)
	33	134 (24)	27 (18)	74 (8)	34 (7)	84 (6)	42 (1)
	13	20 (11)	14 (8)	−2 (3)	−11 (4)	−11 (3)	−3.0 (6)

[a] $\beta_{ij} \times 10^4$; for $M1$ and $M2$, $\beta_{12} = \beta_{23} = 0$. Errors in parentheses are 1 standard deviation; for 4.2 (5) read 0.00042 ± 0.00005. Temperature factor form:

$$\exp\left\{-\sum_{i=1}^{3}\sum_{j=1}^{3} \mathbf{h}_i\,\mathbf{h}_j\,\beta_{ij}\right\}$$

but unfortunately the errors in bond distances for the Ge compound are so large that the comparison would be meaningless at present.

The *M2* coordination polyhedron in the ordered clinopyroxenes is typified by the one in diopside (Fig. 3). When *M2* is occupied by Na^+ or Ca^{2+} cations, the coordination is irregularly eightfold, with six oxygen neighbors nearby at distances averaging 2.4 Å, and two further away at an average distance of 2.8 Å (Table 16). In spodumene and $LiFe^{3+}Si_2O_6$, where *M2* is occupied by Li^+, the two most distant oxygen atoms (O3C2, O3D2) are removed from the coordination polyhedron, so Li^+ is irregularly coordinated by only six oxygen atoms. The average *M2*-O distances for Na^+ and Ca^{2+} do not differ significantly, but those for Li^+ are appreciably smaller. The average Li-O distances obtained in this study are in good agreement with the few reliable values in the literature for octahedrally coordinated Li^+. For example, the average Li-O distance in lithium dihydrogen citrate (Glusker *et al.*, 1965) is 2.18 Å, compared to 2.21 Å in spodumene.

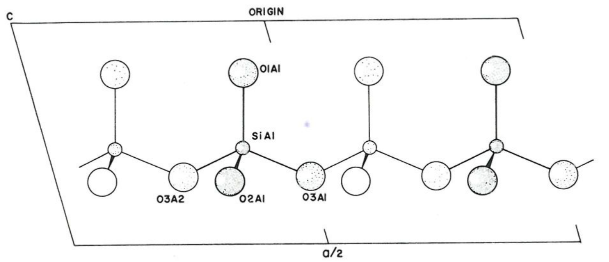

Fig. 1. The clinopyroxene tetrahedral chain as it appears in diopside. Atoms labelled according to nomenclature used in Tables 13, 21, 24.

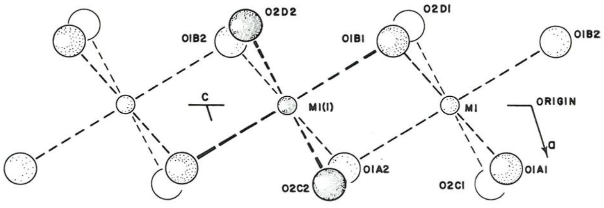

Fig. 2. The *M*1 octahedral chain as it appears in acmite. Atoms labelled according to nomenclature used in Tables 14, 20, 22.

Relationships for the bond strengths (*n*) associated with the various bond lengths in these clinopyroxenes can be developed following the empirical method used by Zachariasen (1963) for B-O bonds. Taking the principles established by Pauling (1929), Zachariasen assumed that the sum of bond strengths for each atom could be set equal to its valence, and that the bond lengths observed could be related empirically to the bond strengths. The method is independent of the bonding model. The Zachariasen curve for B-O bond lengths *vs* B-O bond strengths, which has been tested by numerous structure determinations and found successful, is compared in Figure 4 with a similarly developed curve for the Si-O bond in clinopyroxenes.

To obtain the Si-O curve, the bridging bonds in the Ca clinopyroxenes were assumed to have strengths of about 0.8 valence units, and the short Si-O2 bond was assumed to

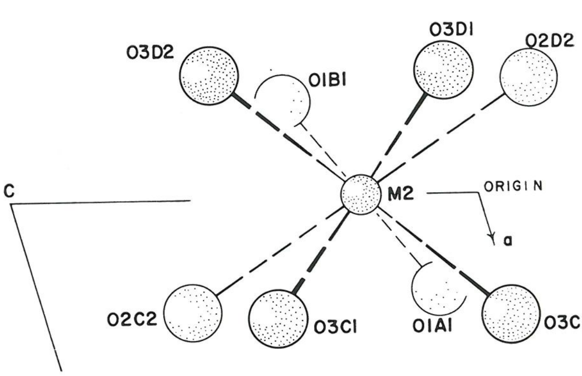

Fig. 3. The *M*2-O coordination polyhedron as it appears in diopside. Atoms labelled according to nomenclature used in Tables 16, 20, 23.

TABLE 13. BOND LENGTHS (Å) AND ANGLES (°) FOR SILICATE TETRAHEDRA IN EIGHT ORDERED CLINOPYROXENES

Atoms[a]	Spodumene $LiAlSi_2O_6$	$LiFe^{3+}Si_2O_6$	Jadeite $NaAlSi_2O_6$	Ureyite $NaCr^{3+}$-Si_2O_6	Acmite $NaFe^{3+}$-Si_2O_6	$NaIn^{3+}Si_2O_6$	Diopside $CaMgSi_2O_6$	Johannsenite $CaMn^{2+}Si_2O_6$
Source	Present study	Present study	Prewitt and Burnham (1966)[b]	Present study	Present study	Christensen and Hazell (1967)[b]	Present study	Freed and Peacor (1967)[b]
Si-O1	1.638 (2)	1.629 (2)	1.637 (2)	1.626 (4)	1.629 (2)	1.641 (7)	1.602 (2)	1.604 (6)
-O2	1.586 (2)	1.596 (3)	1.590 (2)	1.586 (3)	1.598 (2)	1.595 (8)	1.585 (1)	1.594 (6)
mean, non-brg.	1.612	1.612	1.613	1.606	1.614	1.618	1.594	1.599
Si-O3A1	1.622 (2)	1.626 (2)	1.628 (2)	1.640 (4)	1.637 (2)	1.633 (8)	1.664 (2)	1.683 (7)
-O3A2	1.626 (2)	1.627 (2)	1.636 (2)	1.645 (4)	1.646 (2)	1.664 (7)	1.687 (2)	1.693 (7)
mean, brg.	1.624	1.626	1.632	1.642	1.642	1.648	1.676	1.688
mean of 4	1.618	1.620	1.623	1.624	1.628	1.633	1.634	1.644
O1-O2	2.742 (2)	2.722 (2)	2.773 (3)	2.736 (5)	2.742 (3)	2.731	2.735 (2)	2.725 (8)
O1-O3A1	2.635 (2)	2.637 (3)	2.633 (3)	2.644 (5)	2.650 (3)	2.640	2.678 (2)	2.708 (8)
O1-O3A2	2.651 (3)	2.654 (3)	2.638 (3)	2.636 (7)	2.654 (3)	2.657	2.695 (3)	2.707 (9)
O2-O3A1	2.658 (2)	2.648 (3)	2.644 (3)	2.657 (4)	2.651 (3)	2.656	2.658 (2)	2.675 (8)
O2-O3A2	2.535 (2)	2.551 (3)	2.575 (3)	2.583 (4)	2.585 (3)	2.614	2.570 (2)	2.588 (8)
O3A1-O3A2	2.616 (1)	2.647 (1)	2.612 (4)	2.643 (5)	2.651 (1)	2.693	2.644 (3)	2.673 (3)
mean of 6	2.640	2.643	2.646	2.650	2.656	2.665	2.663	2.679
Si-SiA2	3.043 (1)	3.068 (1)	3.061 (1)	3.084 (4)	3.079 (1)	3.119	3.107 (2)	3.134 (3)
O1-Si-O2	116.5 (1)	115.1 (1)	118.5 (1)	116.8 (2)	116.4 (1)	115.17 (39)	118.25 (7)	116.84 (27)
O1-Si-O3A1	107.9 (1)	108.2 (1)	107.5 (1)	108.1 (2)	108.5 (1)	107.51 (37)	110.11 (8)	110.92 (31)
O1-Si-O3A2	108.6 (1)	109.2 (1)	107.4 (1)	107.4 (2)	108.3 (1)	107.10 (40)	109.99 (8)	110.32 (31)
O2-Si-O3A1	111.9 (1)	110.6 (1)	110.5 (1)	110.9 (2)	110.1 (1)	110.68 (44)	109.78 (7)	109.37 (29)
O2-Si-O3A2	104.2 (1)	104.6 (1)	105.9 (1)	106.1 (2)	105.6 (1)	106.70 (36)	103.46 (10)	103.80 (30)
O3A1-Si-O3A2	107.3 (1)	108.9 (1)	106.3 (1)	107.1 (2)	107.7 (1)	109.55 (40)	104.17 (9)	104.71 (24)
mean of 6	109.4	109.4	109.4	109.4	109.4	109.5	109.29	109.3
Si-O3-SiA2	139.0 (1)	141.2 (2)	139.3 (1)	139.7 (2)	139.4 (2)	142.24 (40)	135.93 (9)	136.37 (41)
O3A2-O3A1-O3A2 (+1 in *c*)	170.5 (2)	180 (2)	174.7 (2)	172.1 (2)	174.0 (2)	171.3	166.38 (11)	163.78 (47)

[a] Nomenclature adapted from Burnham *et al.*, 1967. Atoms are in the basic set unless otherwise designated (see Fig. 1). Errors in parentheses are one standard deviation; for 1.638 (2) read 1.638±0.002 Å.

[b] Values not given in the reference were calculated by present authors.

have a strength of about 1.25 valence units. Because the clinopyroxenes do not give many points in an intermediate range, the bond strength 1.0 was assigned at the length of 1.613 Å, an average value for the amphibole bridging distance Si-O7 taken from the refinements of glaucophane (Papike and Clark, 1968) and tremolite (Papike, Ross and Clark, 1969, this volume). Least-squares fitting of the empirical points to polynomials of degrees one to five was tried, and the best fit, both for our Si-O *vs* *n* points and for Zachariasen's B-O *vs* *n* points, was found for a third-degree polynomial. For the Si-O *vs* *n* data points, the following regression equation applies: Si-O (Å) $= 3.6 - (4.8 \pm 1.6)\, n + (4.0 \pm 1.6)\, n^2 - (1.1 \pm 0.5)\, n^3$.

Similar relationships were developed for the $M1$ and $M2$ cations (Table 17) and the results for the clinopyroxenes, divided into three groups according to $M2$, are compared in Table 15 with the values for the ideal ionic model, obtained from use of Pauling's second rule (Pauling, 1929). The improvement is evident, but obviously further improvement of these empirical relationships would be desirable, in view of the large errors associated with the equation given above.

Spodumene and its synthetic iron analogue were refined in space group $C2/c$, although a few weak reflections in both crystals violate the *c*-glide criterion. Their true space-group must be $C2$, because a mirror plane is incompatible

Table 14. Bond Lengths (Å) and Angles (°) for the $M1$ Octahedra in Eight Ordered Clinopyroxenes[a]

Atoms[b]	Spodumene $\mathrm{LiAlSi_2O_6}$	$\mathrm{LiFe^{3+}Si_2O_6}$[c]	Jadeite $\mathrm{NaAlSi_2O_6}$	Ureyite $\mathrm{NaCr^{3+}Si_2O_6}$	Acmite $\mathrm{NaFe^{3+}Si_2O_6}$	$\mathrm{NaInSi_2O_6}$	Diopside $\mathrm{CaMgSi_2O_6}$	Johannsenite $\mathrm{CaMn^{2+}}$-$\mathrm{Si_2O_6}$
	Present study	Present study	Prewitt and Burnham (1966)[d]	Present study	Present study	Christensen and Hazell (1967)[d]	Present study	Freed and Peacor (1967)[d]
$M1$-O1A1, B1	1.997 (2)	2.139 (2)	1.996 (2)	2.039 (3)	2.109 (2)	2.211 (7)	2.115 (1)	2.231 (6)
-O1A2, B2	1.943 (2)	2.034 (2)	1.933 (2)	2.009 (6)	2.029 (2)	2.158 (6)	2.065 (3)	2.155 (6)
-O2C1, D1	1.818 (2)	1.921 (2)	1.856 (2)	1.947 (3)	1.936 (2)	2.056 (8)	2.050 (1)	2.134 (6)
mean of 6	1.919	2.031	1.928	1.998	2.025	2.142	2.077	2.173
O1A1-O1B1	2.694 (4)	2.803 (4)	2.726 (4)	2.775 (6)	2.798 (4)	2.85	2.781 (3)	2.845
O2C1-O2D1	2.787 (4)	2.963 (5)	2.790 (4)	2.897 (7)	2.941 (4)	3.10	2.981 (3)	3.064
(2) O1A1-O2C1	2.661 (2)	2.843 (3)	2.716 (4)	2.815 (5)	2.860 (3)	3.05	3.013 (2)	3.208
(2) O1A1-O1A2	2.951 (2)	3.030 (2)	2.918 (2)	2.975 (5)	2.985 (2)	3.06	3.051 (3)	3.147
(2) O1A2-O2C1	2.705 (2)	2.931 (3)	2.677 (3)	2.797 (5)	2.819 (3)	3.04	2.878 (3)	3.009
(2) O1A2-O2D1	2.697 (2)	2.784 (3)	2.818 (4)	2.904 (6)	2.964 (3)	3.13	2.979 (3)	3.071
(2) O1A1-O1B2	2.504 (3)	2.708 (5)	2.458 (4)	2.617 (7)	2.639 (4)	2.86	2.813 (3)	3.039
mean of 12	2.710	2.863	2.724	2.824	2.856	3.02	2.936	3.041
$M1$-$M1$ (1)	3.042 (1)	3.177 (1)	3.066 (1)	3.089 (4)	3.189 (1)	3.302	3.092 (2)	3.164
$M1$-SiA1	3.181 (1)	3.282 (1)	3.306	3.242 (3)	3.289 (1)	3.484	3.267 (1)	3.352
$M1$-SiA2	3.106 (2)	3.208 (1)	3.205	3.165 (8)	3.188 (1)	3.390	3.214 (3)	3.301
O-$M1$-O Angles								
O1A2, O1B2	174.5 (1)	172.1 (1)	170.1 (1)	173.4 (2)	168.7 (1)	167.74 (25)	177.8 (1)	179.2
(2) O1A1, O2D1	167.8 (1)	169.7 (1)	166.1 (1)	169.2 (1)	167.3 (1)	169.63 (26)	171.3 (1)	172.9
O1A1, O1B1	84.8 (1)	81.9 (1)	86.2 (1)	85.8 (2)	83.1 (1)	80.15 (28)	82.2 (1)	79.2
O2C1, O2D1	100.0 (1)	100.9 (2)	97.5 (2)	96.1 (2)	98.9 (1)	97.7	93.3 (1)	91.8
(2) O1A1, O2C1	88.3 (1)	88.7 (1)	89.6 (1)	89.8 (2)	89.9 (1)	91.33 (29)	92.6 (1)	94.6
(2) O1A1, O1A2	97.0 (1)	93.1 (1)	95.9 (1)	94.6 (1)	92.3 (1)	88.82 (25)	93.8 (1)	91.7
(2) O1A1, O1B2	78.9 (1)	80.9 (1)	77.4 (1)	80.6 (1)	79.2 (1)	81.78 (25)	84.6 (1)	87.7
(2) O1A2, O2C1	92.0 (1)	95.6 (1)	89.9 (1)	89.8 (2)	90.6 (1)	92.22 (26)	88.8 (1)	89.1
(2) O1A2, O2D1	91.6 (1)	89.4 (1)	96.1 (1)	94.4 (2)	96.7 (1)	95.84 (26)	92.8 (1)	91.5
Si-O1A1-$M1$	121.9 (1)	120.6 (1)	123.5	124.0 (2)	122.7 (1)	122.7	122.4 (1)	121.0
Si-O1A2-$M1$	120.1 (1)	121.9 (1)	120.0	120.6 (2)	120.9 (1)	121.5	122.0 (1)	122.1
Si-O2C1-$M1$	148.2 (1)	143.8 (2)	147.2	145.8 (2)	145.8 (1)	144.9	145.7 (1)	145.2

[a] Errors in parentheses are one standard deviation; for 1.997 (2) read 1.997 ± 0.002 Å.

[b] When atoms for only one of the two symmetrically related distances or angles are designated, reference to Fig. 2 will aid identification of the other pair; *e.g.*, O1A1-O1C1=O1B1-O1D1, *etc.*

[c] Actual $M1$ occupancy close to $\mathrm{Fe^{3+}_{0.95}Fe^{2+}_{0.05}}$.

[d] Values not given in the reference were calculated by present authors.

with the clinopyroxene structure. The refinements presented in this paper thus represent average structures, and these are almost identical, even in detail, to those of the true $C2/c$ clinopyroxenes. The major difference is, of course, the change in $M2$ coordination from eight to six, discussed above. Because the synthetic compound contained some $\mathrm{Fe^{2+}}$, as previously mentioned, the occupancy of $\mathrm{Fe^{2+}}$ against $\mathrm{Li^+}$ in $M2$ was refined, and the true formula for the crystal studied is $(\mathrm{Li}_{1-x}\mathrm{Fe}_x^{2+})$ $(\mathrm{Fe}_{1-x}^{3+}\mathrm{Fe}_x^{2+})\mathrm{Si_2O_6}$, where $x = 0.048 \pm 0.05$. This substitution affects the bond lengths because the average $M2$-O distance for the synthetic is slightly longer than the Li-O in spodumene (Table 16) and the average $M1$-O is slightly longer than the $\mathrm{Fe^{3+}}$-O in acmite (Table 14).

Only pyroxenes with eight-coordinated $M2$ cations have the $C2/c$ (diopside type) pyroxene structure; all those with six-coordinated $M2$ sites are in different space-groups: $P2_1/c$ (clinoenstatite type), $Pbca$ (enstatite type), $Pbcn$ (proposed protoenstatite type), or $C2$ (spodumene type.) The differences in detail among these structure types have been summarized by Appleman *et al.* (1966), and specific references to structure determinations are given in Table 18.

In the spodumene $C2$ structure, as in the diopside $C2/c$

TABLE 15. BOND STRENGTHS IN ORDERED CLINOPYROXENES

Bond	$M2 = Li^+$			$M2 = Na^+$			$M2 = Ca^{2+}$		
	Average distance (Å)	Bond strength		Average distance (Å)	Bond strength		Average distance (Å)	Bond strength	
		Ideal ionic model	Present study		Ideal ionic model	Present study		Ideal ionic model	Present study
O1-Si	1.634	1.000	0.93	1.635	1.000	0.93	1.603	1.000	1.12
O1-*M*1	1.996 to 2.138	0.500	0.42	1.996, 2.111	0.500	0.40	2.119, 2.231	0.333	0.21
O1-*M*1	1.942 to 2.033	0.500	0.50	1.933, 2.158	0.500	0.50	2.061, 2.155	0.333	0.40
O1-*M*2	2.112	0.167	0.15	2.405	0.125	0.16	2.374	0.250	0.28
Σ		2.167	2.00		2.125	1.99		1.916	2.01
O2-Si	1.591	1.000	1.26	1.593	1.000	1.25	1.591	1.000	1.26
O2-*M*1	1.817, 1.921	0.500	0.58	1.856 to 2.056	0.500	0.59	2.053, 2.134	0.333	0.40
O2-*M*2	2.223	0.167	0.15	2.402	0.125	0.16	2.332	0.250	0.34
Σ		1.667	1.99		1.625	2.00		1.583	2.00
O3-SiA1	1.625	1.000	0.90	1.634	1.000	0.93	1.675	1.000	0.82
O3-SiA2	1.625	1.000	0.90	1.648	1.000	0.89	1.690	1.000	0.80
O3-*M*2	2.357	0.167	0.20	2.435	0.125	0.11	2.606	0.250	0.22
O3-*M*2	[3.159]	—	—	2.812	0.125	0.07	2.746	0.250	0.16
Σ		2.167	2.00		2.250	2.00		2.500	2.00

structure, all the tetrahedral chains are equivalent. However, in spodumene two crystallographically distinct tetrahedra alternate along this chain, whereas in diopside all tetrahedra are of the same kind. Thus the chains in spodumene have more freedom to adapt to the coordination requirements of the small Li^+ cation. Table 8 shows that the principal differences in atomic coordinates between the spodumene and the other ordered clinopyroxenes are in the *M*2 coordination polyhedra (*M*2 and O3). This is additional evidence that accommodation to the small size of the Li^+ cation is chiefly responsible for the degradation in symmetry from *C*2/*c* to *C*2. Note

TABLE 16. BOND LENGTHS (Å) AND SOME ANGLES (°) FOR THE *M*2 CATIONS IN EIGHT ORDERED CLINOPYROXENES[a]

Atoms[b] Oxygen of *M*2-O	Spodumene $LiAlSi_2O_6$ Present study	$LiFe^{3+}Si_2O_6$ Present study[c]	Jadeite $NaAlSi_2O_6$ Prewitt and Burnham (1966)[d]	Ureyite $NaCr^{3+}Si_2O_6$ Present study	Acmite $NaFe^{3+}Si_2O_6$ Present study	$NaIn^{3+}Si_2O_6$ Christensen and Hazell (1967)[d]	Diopside $CaMgSi_2O_6$ Present study	Johannsenite $CaMn^{2+}Si_2O_6$ Freed and Peacor (1967)[d]
O1A1, O1B1	2.105 (6)	2.120 (5)	2.357 (3)	2.378 (4)	2.398 (3)	2.487 (9)	2.360 (1)	2.384 (6)
O2C2, O2D2	2.278 (2)	2.167 (3)	2.413 (2)	2.389 (7)	2.415 (2)	2.394 (6)	2.353 (3)	2.316 (6)
O3C1, O3D1	2.251 (6)	2.459 (5)	2.363 (3)	2.424 (4)	2.430 (3)	2.517 (9)	2.561 (2)	2.651 (7)
O3C2, O3D2	[3.144 (5)]	[3.178 (4)]	2.741 (2)	2.764 (4)	2.831 (3)	2.922 (9)	2.717 (1)	2.771 (6)
mean of 6	2.211	2.249	2.378	2.397	2.414	2.466	2.425	2.450
mean of 8	—	—	2.469	2.489	2.518	2.580	2.498	2.530
Angles								
Si-O1A1-*M*2	114.6 (1)	118.5 (1)	109.8	112.4 (2)	112.9 (1)	115.0	115.5 (1)	119.6
Si-O2C2-*M*2	93.8 (2)	100.3 (2)	94.1	95.9 (2)	95.8 (1)	97.5	102.2 (1)	104.6
Si-O3C1-*M*2	116.4 (1)	112.4 (1)	103.6	102.4 (2)	103.8 (1)	103.6	101.1 (1)	100.4
Si-O3D1-*M*2	93.7 (1)	88.4 (1)	94.7	93.0 (2)	94.0 (1)	91.2	91.4 (1)	89.2
Si-O3C2-*M*2	—	—	114.7	116.3 (2)	115.9 (1)	117.5	117.8 (1)	118.8
Si-O3D2-*M*2	—	—	89.0	89.5 (2)	88.5 (1)	87.8	94.6 (1)	95.7

[a] Errors in parentheses are one standard deviation; for 2.105 (6) read 2.105±0.006 Å.

[b] See Fig. 3.

[c] Actual *M*2 occupancy close to $Li_{0.95}Fe^{2+}_{0.05}$.

[d] Values not given in reference were calculated by present authors.

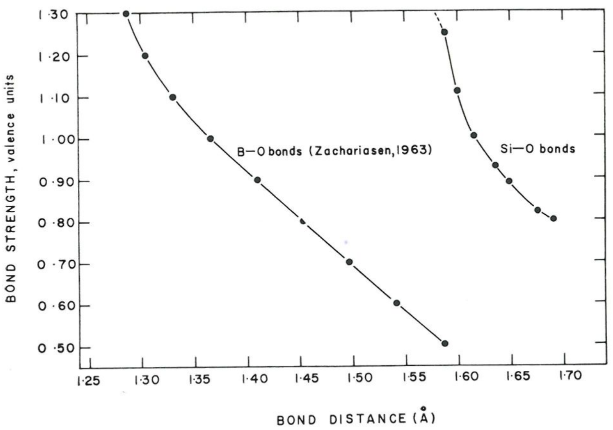

Fig. 4. Empirical curves for bond strengths *vs.* bond distances for boron-oxygen bonds (Zachariasen, 1963) and silicon-oxygen bonds in clinopyroxenes.

that the deviations from $C2/c$ symmetry are very small; in fact, even the temperature factors for the spodumenes refined in $C2/c$ are entirely comparable to those found in the other ordered clinopyroxenes.

One must also explain why spodumene and $LiFe^{3+}Si_2O_6$ do not crystallize with the enstatite or clinoenstatite structures. The closely related enstatite and clinoenstatite structure types contain two kinds of tetrahedral chains, A and B, segregated by layers. Comparison of the O3-O3-O3 angles shows that the Si A chains are very like those in the diopsidic pyroxenes, but the Si B chains are much more strongly kinked (Table 18). This distortion, discussed by Morimoto, Appleman and Evans (1960), is primarily due to a rotation of the tetrahedra around a line connecting Si B with O1 B (*cf.* Fig. 1). The result, in the enstatite and clinoenstatite structures, is to decrease markedly the $M2$-O2 bond distances and increase the $M2$-O3 distances, relative to those in spodumene, although the average $M2$-O distances are very similar in all of the structures listed in Table 18. This effect is exactly what would be expected, on the basis of a simple ionic charge-balance model, when doubly charged Mg^{2+} or Fe^{2+} rather than singly charged Li^+ is present in the $M2$ site.

Table 17. Strength and Length of $M1$-O and $M2$-O Bonds in Clinopyroxenes[a]

$M1$ cations[b]				$M2$ cations[c]		
Bond strength	Bond lengths (Å)			Bond strength	Bond lengths (Å)	
	Al	Fe^{3+}	Mg		Na	Ca
0.20			2.125	0.05	2.930	
.30	2.080		2.087	.10	2.630	
.40	2.005	2.135	2.055	.15	2.305	2.850
.50	1.922	2.030	2.020	.20		2.625
.60	1.842	1.920		.25		2.480
				.30		2.375
				.35		2.285

[a] Values taken from best-fit curve through empirical points.
[b] Six-coordinated.
[c] Eight-coordinated.

On the basis of the evidence considered above, we conclude that the size and charge of the cations occupying the $M2$ site chiefly determine the structure type of a pyroxene. Large singly or doubly charged $M2$ cations lead to a diopside structure, small singly charged $M2$ cations to a spodumene structure, and small doubly charged $M2$ cations, with much stronger $M2$-O bonds, to a clinoenstatite or enstatite structure. The more complex $P2$ omphacite pyroxene structure type represents an exception and is discussed later.

Thermal ellipsoids were obtained for the atoms of those ordered clinopyroxenes for which comparable anisotropic refinements were carried out (Table 19). As might be expected, the largest rms amplitudes of about 0.13 Å are observed for Li; for Si and the oxygen atoms, rms amplitudes range from about 0.04 to 0.11 Å. The atoms in these ordered structures show relatively little anisotropy in their thermal motion, so the errors in the orientation of the thermal ellipsoids are rather high. For the same reason, it is difficult to make a general interpretation of the anisotropy. However, the results are compatible with the bonding environment of the atoms. The relative lack of anisotropy in the thermal ellipsoids is consistent with the predominantly ionic character of these structures.

The equivalent individual isotropic temperature factors for Si and O (Table 8) agree so well for all the structures that they can be taken as values representative for ordered pyroxenes, *i.e.*, Si, 0.3 ± 0.1 Å^2, and oxygen, 0.4 ± 0.1 Å^2. There is a tendency for O2 to have a slightly higher value than the other two oxygens, undoubtedly because it bonds to only three cations instead of four (Table 15).

$C2/c$ clinopyroxenes of intermediate compositions. In order to refine the structures of the two intermediate $C2/c$ clinopyroxenes, their chemical analyses (Table 2)

Table 18. Variation in O3-O3-O3 Angles with $M2$ Occupancy in Pyroxenes

$M2$ occupancy	O3A2-O3A1-O3A2 angle (°)	O3B2-O3B1-O3B2 angle (°)	Reference
Li^+	175.2	—	Average of 2 structures (Table 13)
Na^+	173.0	—	Average of 4 structures (Table 13)
Ca^{2+}	165.1	—	Average of 2 structures (Table 13)
Fe^{2+}	167.	142.	Clinoferrosilite (Burnham, 1967)
Fe^{2+}	169.	145.	Orthoferrosilite (Burnham, 1967)
Fe^{2+} (approximately)	168.	144.	Hypersthene (Ghose, 1965)
0.77 Fe^{2+}, 0.05 Mg^{2+}, 0.18 Ca^{2+}	167.	142.	Pigeonite (Morimoto and Güven, 1968)
Mg^{2+}	161.	134.	Clinoenstatite (Morimoto, Appleman and Evans, 1960)

were used to constrain the total amount of each cation present. However, the values from Table 2 were slightly altered in some cases by recalculation to bring the total occupancies of both *M1* and *M2* to 1.0. The cell contents actually used are given in Table 9 in terms of occupancies resulting from the refinements. On the basis of size considerations, we assumed that all the Na^+ and Ca^{2+} are in *M2* and all the Al^{3+} in *M1*. We then refined the occupancy of Fe and Mg between *M1* and *M2*, assuming each site to be completely filled and using the chemical constraints.

During the site refinement, no distinction was made between Fe^{2+} and Fe^{3+}, and the scattering factors used for iron were those for Fe^{2+}. However, assuming the cell contents given in Table 9 to be correct, total charge balance in the structure enables us to calculate the amounts of Fe^{3+} and Fe^{2+} present, on the basis of six oxygen atoms and four cations. For the omphacite this process gives 0.08 atom of Fe^{3+} and 0.17 atom of Fe^{2+}; the chemical analysis (Warner, 1964) yields approximately 0.12 atom of Fe^{3+} and 0.12 atom of Fe^{2+}. For the augite, the charge balance calculation gives 0.06 atom of Fe^{3+} and 0.15 of Fe^{2+}, whereas the chemical analysis (Mason, 1966) yields approximately 0.10 atom of Fe^{3+} and 0.11 of Fe^{2+}. In view of these discrepancies, both in the same direction, other methods of determining the ratio and distribution of ferrous and ferric iron seemed warranted. Two methods were tried: (1) the use of Mössbauer resonance spectra, and (2) the use of bond distances.

Dr. Stefan S. Hafner, Department of Geophysical Sciences, University of Chicago, kindly examined the New Zealand augite by means of Mössbauer spectra, both at room temperature and at liquid nitrogen temperature. The detailed results of his work will appear elsewhere, but the conclusions pertinent to this paper (S. S. Hafner, written comm., 1969) are as follows: first, there is very little Fe^{3+} present, and interpretation of the spectra suggests that it is in the *M1* site, with Fe^{3+}/total Fe $\approx$ 0.10 (about 0.02 atom Fe^{3+}); second, there is no doubt that Fe^{2+} is present in both the *M1* and *M2* sites; third, the ratio (Fe in *M1*)/(Fe in *M1*+*M2*) $\approx$ 0.40. By comparison, the calculation based on charge balance, discussed in the preceding paragraph, gives Fe^{3+}/total Fe $\approx$ 0.28, and the site occupancy refinement gives (Fe in *M1*)/(Fe in *M1*+*M2*) $=$ 0.49±0.02.

Another method of checking site occupancies in intermediate pyroxenes is based on the use of the accurate and consistent values for average *M1*-O distances obtained from the refinements of ordered clinopyroxenes. From Table 14, we may take the following average distances: Al-O = 1.923 Å (jadeite and spodumene), Mg-O = 2.077 Å (diopside) and Fe^{3+}-O = 2.025 Å (acmite). From clinoferrosilite and orthoferrosilite (C. W. Burnham, 1967, and oral comm., 1968) we take the average Fe^{2+}-O = 2.137 Å. If we assume that the average *M1*-O distance in disordered *M1* sites (Table 20) is simply a linear combination of the average *M1*-O distances for the various ions present, in the ratios obtained from the site-occupancy refinements, we can calculate average *M1*-O to be expected for any particular model.

Let us first assume that in the augite all the Fe^{3+} is in the *M1* site, from size considerations and the Mössbauer results. Then if Fe^{3+} = 0.06 (the value obtained from the charge balance calculation), *M1*-O (ave.) = 2.048 Å (calc.) as compared with 2.054 Å observed (Table 20). The lower calculated value indicates that too much Fe^{3+} has been assigned to *M1*. In order for the bond-distance method to yield the observed average distance of 2.054 Å, the amount of Fe^{3+} in *M1* must be reduced to approximately 0.01 atom. Using this value, a ratio Fe^{3+}/ total Fe $\approx$ 0.1 is found, in excellent agreement with the Mössbauer results, but substantially less than that obtained from the chemical analysis.

It has been observed (B. Mason, oral commun., 1969) that Fe^{3+}/Fe^{2+} values from chemical analyses are frequently too high in this type of mineral, due to oxidation during the analysis (*cf.* also Bancroft and Burns, 1969, this volume). Considering all evidence presented above, we conclude, first that there is very little ferric iron in this augite and the ratio Fe^{3+}/total Fe is probably between 0.1 and 0.3 (*i.e.*, 0.02 to 0.06 atom Fe^{3+}), and second, that virtually all the ferric iron is in the *M1* site and that the ferrous iron is disordered between *M1* and *M2*, with approximately 0.09 atom in *M1* and 0.11 atom in *M2* (Table 9).

No Mössbauer spectral analysis has been done for the *C2/c* omphacite. Using the bond lengths in the same way as for the augite, we calculate an average *M1*-O distance of 2.044 Å compared to the observed 2.040 Å, assuming the Fe^{3+} value of 0.08 atom from the charge-balance calculation with all Fe^{3+} in *M1*. In order to obtain the observed distance, Fe^{3+} must be approximately 0.12 atom, in excellent agreement with the chemical analysis. As in the augite, the evidence is consistent with the assignment of all Fe^{3+} to the *M1* site and Fe^{2+} disordered between the *M1* and *M2* sites, with approximately 0.10 atom in *M1* and 0.03 atom in *M2* (Table 9). Considering the very small amounts of iron present in these minerals, it is hardly surprising that there are some discrepancies between the values for Fe^{3+}/total Fe obtained by different methods.

The present study is the first, to our knowledge, in which detailed structure determinations have been made of *C2/c* clinopyroxenes of intermediate compositions, close to augite. The site occupancies found in these minerals are somewhat unexpected. The small Al^{3+} cation is apparently well ordered in *M1*, and the large Ca^{2+} and Na^+ cations, in *M2*. However, there is a considerable degree of Mg^{2+}/Fe^{2+} disorder between the two sites; in both the omphacite and the augite the Mg^{2+}/Fe^{2+} ratio in *M2* is greater than 1.0, within the error of our

TABLE 19. MAGNITUDES AND ORIENTATIONS OF THERMAL ELLIPSOIDS COMPARED FOR SIX ORDERED CLINOPYROXENES[a]

Pyroxene, reference	Ellipsoid axis, r_i r	Si				O1				O2			
		rms amplitude, Å	Angle (°) of r_i with			rms amplitude, Å	Angle (°) of r_i with			rms amplitude, Å	Angle (°) of r_i with		
	i	r_i	a	b	c	r_i	a	b	c	r_i	a	b	c
Spodumene, $LiAlSi_2O_6$, present study	1	0.034 (3)	36 (8)	55 (6)	99 (14)	0.042 (6)	61 (14)	86 (12)	49 (15)	0.045 (6)	132 (6)	138 (6)	76 (5)
	2	.042 (2)	77 (14)	96 (12)	171 (14)	.057 (5)	40 (23)	64 (29)	134 (18)	.079 (8)	52 (8)	125 (8)	136 (12)
	3	.051 (2)	57 (7)	144 (6)	89 (11)	.064 (4)	115 (25)	27 (29)	73 (22)	.092 (3)	66 (9)	111 (8)	50 (12)
$LiFe^{3+}Si_2O_6$ present study	1	.035 (4)	111 (3)	89 (5)	1 (4)	.057 (7)	115 (13)	82 (12)	10 (11)	.062 (7)	62 (8)	28 (6)	95 (11)
	2	.062 (3)	110 (7)	159 (7)	89 (5)	.076 (5)	141 (32)	124 (40)	90 (15)	.086 (5)	55 (8)	104 (10)	159 (6)
	3	.076 (2)	30 (6)	111 (7)	89 (3)	.082 (5)	63 (36)	145 (40)	80 (11)	.122 (4)	48 (5)	114 (4)	69 (6)
Jadeite, $NaAlSi_2O_6$, Prewitt and Burnham (1966)[b]	1	.067 (4)	113 (16)	83 (11)	9 (8)	.035 (16)	34 (14)	75 (8)	77 (14)	.056 (9)	36 (11)	73 (12)	75 (15)
	2	.068 (4)	163 (16)	92 (20)	107 (15)	.067 (9)	57 (15)	102 (13)	160 (14)	.079 (7)	75 (17)	52 (19)	142 (18)
	3	.080 (4)	92 (9)	173 (9)	83 (9)	.090 (7)	83 (9)	160 (9)	75 (12)	.094 (7)	122 (11)	43 (18)	55 (17)
Ureyite, $NaCr^{3+}Si_2O_6$, present study	1	.043 (5)	89 (4)	83 (6)	20 (4)	.047 (10)	92 (10)	101 (11)	19 (8)	.062 (9)	72 (10)	48 (22)	57 (24)
	2	.071 (3)	78 (13)	14 (12)	100 (7)	.079 (7)	133 (32)	135 (31)	87 (15)	.076 (7)	75 (13)	51 (22)	141 (23)
	3	.081 (3)	12 (13)	102 (13)	107 (5)	.088 (6)	137 (32)	47 (31)	71 (9)	.106 (6)	156 (8)	66 (8)	73 (9)
Acmite, $NaFe^{3+}Si_2O_6$, present study	1	.040 (3)	36 (3)	77 (10)	73 (3)	.041 (8)	37 (5)	82 (11)	71 (5)	.045 (8)	61 (6)	30 (7)	89 (4)
	2	.054 (3)	99 (8)	13 (10)	97 (5)	.069 (5)	90 (10)	12 (10)	102 (9)	.081 (5)	132 (7)	61 (7)	109 (8)
	3	.081 (2)	125 (3)	87 (4)	18 (3)	.092 (4)	127 (5)	80 (9)	22 (6)	.107 (4)	124 (7)	81 (5)	19 (8)
Diopside, $CaMgSi_2O_6$, present study	1	.049 (2)	27 (17)	72 (20)	85 (9)	.051 (4)	30 (9)	98 (9)	77 (8)	.050 (4)	62 (3)	30 (4)	87 (5)
	2	.053 (2)	67 (20)	155 (17)	106 (11)	.069 (3)	65 (14)	45 (35)	132 (34)	.079 (3)	103 (7)	72 (6)	146 (8)
	3	.059 (1)	105 (8)	107 (11)	17 (11)	.073 (3)	105 (17)	46 (35)	44 (34)	.094 (3)	149 (5)	67 (4)	56 (8)

[a] Errors in parentheses are one standard deviation; for 77 (14) read 77 ± 14°.

[b] Orientations recalculated to conform to those of present study using β_{ij} values and rms amplitudes given by Prewitt and Burnham (1966).

determinations. These results differ from the Fe^{2+}-Mg^{2+} distributions in enstatite-like structures such as hypersthene (Ghose, 1965) and pigeonite (Morimoto and Güven, 1968), in which there is a high degree of order and the Mg^{2+}/Fe^{2+} ratios in $M2$ are very low. It is evident that the structures of more $C2/c$ clinopyroxenes of augitic or near-augitic compositions must be investigated to determine whether a pattern of Fe^{2+}-Mg^{2+} distribution exists in these minerals.

The Si-O bonds and O-Si-O angles of $C2/c$ omphacite (Table 21), which has no tetrahedral aluminum, agree closely with those found for diopside (Table 13). The augite, which has 0.16 atom of tetrahedral Al per six oxygen atoms, has longer T-O distances reflecting this occupancy, as does the fassaite with 0.49 atoms of tetrahedral Al per six oxygen atoms (Peacor, 1967). By using the T-O2 distances for these three intermediate composition clinopyroxenes, a linear relationship between T-O2 distance and the tetrahedral Al contents can be constructed for clinopyroxenes, following the general method developed by Smith (1954) and refined by Smith and Bailey (1963). We have already shown that the T-O2 distance is a better indicator of the amount of Al in a pyroxene tetrahedron than is the average T-O distance (Clark, Appleman, and Papike, 1968). Results from further refinements of intermediate clinopyroxenes will be needed to test the general applicability of the relationship.

These refinements all indicate that very little distortion occurs in intermediate $C2/c$ clinopyroxene structures because of the multiple cation contents. The silicate chains are closely comparable to those in the most nearly corresponding ordered clinopyroxene (usually diopside), and the other features are also those that would be predicted from knowledge of the cation contents. Details of the cation distribution in the disordered structures can be inferred only indirectly from our results. There is no evidence of streaking or diffuse reflections on X-ray diffraction photographs of these minerals, so whatever short-range order exists is below the threshold of the usual X-ray diffraction analysis. The anisotropic temperature factors are larger in all directions in the disordered structures than in the ordered ones for the $M1$ and $M2$ cations. The rms displacements of the oxygen atoms along the $M1$-O bonds are about 50 percent greater in the disordered structures, and displacements along the $M2$-O bonds are about 20 percent greater. These effects are precisely those to be expected around disordered cation sites (Burnham, 1965).

P2 omphacites. The structure of the Venezuelan omphacite is similar in all respects to that reported for the Californian omphacite (Clark and Papike, 1968), despite the appreciably lower Fe content (0.07 atom of Fe per six oxygen atoms, instead of 0.20). The excellent agreement between these independent refinements of data from different specimens lends confidence to the results, which can be assumed applicable in general for $P2$ omphacites. Because of large correlations (aboout 0.9) between certain parameters, the initial refinement of

O3				M1				M2			
rms amplitude, Å	Angle (°) of r_i with			rms amplitude, Å	Angle (°) of r_i with			rms amplitude, Å	Angle (°) of r_i with		
r_i	a	b	c	r_i	a	b	c	r_i	a	b	c
0.043 (6)	96 (12)	68 (5)	26 (5)	0.041 (4)	80 (22)	90	30 (22)	0.11 (1)	17 (27)	90	93 (27)
.061 (5)	161 (6)	76 (6)	83 (12)	.048 (3)	10 (22)	90	120 (22)	.12 (1)	90	180	90
.101 (3)	108 (4)	153 (4)	66 (3)	.051 (3)	90	0	90	.13 (1)	107 (27)	90	3
.040 (10)	106 (5)	65 (3)	25 (3)	.046 (2)	107 (3)	90	3 (3)	.05 (2)	106 (12)	90	4 (12)
.095 (5)	162 (6)	89 (6)	88 (6)	.061 (2)	90	180	90	.09 (1)	90	180	90
.129 (4)	98 (6)	155 (3)	65 (3)	.077 (2)	17 (3)	90	93 (3)	.10 (1)	16 (12)	90	94 (12)
.067 (9)	146 (53)	105 (17)	43 (61)	.066 (6)	80 (29)	90	27 (29)	.089 (5)	69 (4)	90	38 (4)
.073 (8)	117 (58)	102 (20)	133 (61)	.074 (6)	90	180	90	.097 (5)	90	180	90
.093 (6)	71 (13)	161 (14)	93 (13)	.074 (6)	8 (29)	90	115 (29)	.136 (4)	159 (4)	90	52 (4)
.047 (10)	92 (8)	70 (7)	26 (7)	.054 (3)	91 (3)	90	16 (3)	.057 (8)	75 (3)	90	33 (3)
.088 (6)	164 (22)	76 (20)	80 (13)	.075 (2)	90	180	90	.080 (6)	90	180	90
.102 (6)	106 (22)	155 (13)	67 (7)	.086 (2)	1 (3)	90	106 (3)	.140 (5)	165 (3)	90	57 (3)
.064 (6)	41 (16)	87 (19)	67 (15)	.054 (2)	38 (2)	90	69 (2)	.086 (5)	90	0	90
.074 (5)	63 (20)	140 (8)	125 (13)	.058 (2)	90	180	90	.086 (5)	118 (3)	90	134 (3)
.101 (4)	118 (6)	130 (7)	44 (7)	.088	128 (2)	90	21 (2)	.149 (3)	152 (3)	90	44 (3)
.058 (4)	113 (27)	59 (6)	33 (8)	.052 (3)	56 (10)	90	49 (10)	.066 (1)	66 (1)	90	39 (1)
.064 (3)	156 (26)	96 (15)	98 (23)	.055 (3)	90	180	90	.068 (1)	90	180	90
.085 (3)	97 (6)	148 (5)	59 (5)	.065 (2)	146 (10)	90	41 (10)	.103 (1)	156 (1)	90	50 (1)

atomic parameters had to be handled as described by Clark and Papike (1968) by alternately fixing the parameters for one set of atoms and refining those of the other set. However, once the coordinates were close to the final values, it was possible to refine all the parameters together, including positions, occupancies, and isotropic temperature factors.

The site occupancy refinement was handled differently from the previous study (Clark and Papike, 1968), because the constraints imposed by the chemical composition were used (Finger, 1969). During initial refinements of positional parameters, site occupancies were taken from the previous *P2* omphacite study. Consideration of the average *M*1-O distances and *M*1 temperature factors derived from the initial refinement showed that *M*1(1) was entirely occupied by Al^{3+} within the limits of resolution. Using average *M*1-O distances from the ordered clinopyroxenes, as described above, it was also possible

TABLE 20. BOND LENGTHS (Å) COMPARED FOR THE *M*1 AND *M*2 CATIONS IN SOME *C*2/*c* PYROXENES OF INTERMEDIATE COMPOSITIONS

*M*1 octahedron				*M*2 polyhedron			
	Omphacite Present study[b]	Augite Present study[b]	Fassaite Peacor (1967)[c]		Omphacite Present study[b]	Augite Present study[b]	Fassaite Peacor (1967)[c]
*M*1 occupancy				*M*2 occupancy			
Mg	0.543	0.715	0.570	Ca	0.590	0.616	0.975
Al	0.240	0.182	0.171	Na	0.320	0.090	0.007
Fe	0.217 (7)	0.103 (5)	0.222	Fe	0.033	0.107	—
Ti	—	—	0.065	Mg	0.057	0.187	—
				Mn	—	—	0.007
*M*1-O lengths				*M*2-O lengths			
O1A1, O1B1	2.095 (3)	2.120 (2)	2.132 (4)	O1A1, O1B1	2.364 (3)	2.316 (2)	2.380 (4)
O1A2, O1B2	2.032 (4)	2.035 (2)	2.057 (5)	O2C2, O2D2	2.356 (5)	2.278 (3)	2.379 (5)
O2C1, O2D1	1.994 (3)	2.007 (3)	2.017 (4)	O3C1, O3D1	2.512 (3)	2.563 (3)	2.560 (5)
				O3C2, O3D2	2.747 (3)	2.760 (3)	2.695 (5)
Mean of six	2.040	2.054	2.069	Mean of six	2.411	2.386	2.440[d]
				Mean of eight	2.495	2.479	2.504[d]

[a] Errors in parentheses are one standard deviation; for 2.095 (3) read 2.095±0.003 Å.

[b] Al, Ca, Na occupancies fixed from chemical analysis (Table 2 and text); occupancy of Mg/Fe refined.

[c] Assigned from chemical analysis and size considerations; no site-occupancy refinement.

[d] Calculated by present authors; the 2.530 Å average value (Peacor, 1967) appears to be a misprint.

TABLE 21. BOND LENGTHS (Å) AND ANGLES (°) COMPARED FOR THE TETRAHEDRA IN SOME *C2/c* PYROXENES OF INTERMEDIATE COMPOSITIONS

Atoms[a]	Omphacite, present study	Augite, present study	Fassaite,[b] Peacor (1967)
T-O1	1.612 (3)	1.621 (2)	1.640 (5)
T-O2	1.585 (3)	1.604 (3)	1.629 (4)
mean, non-brg.	1.598	1.612	1.634
T-O3	1.657 (3)	1.662 (2)	1.685 (5)
T-O3A2	1.668 (3)	1.674 (2)	1.697 (5)
mean, brg.	1.662	1.668	1.691
mean of 4	1.630	1.640	1.663
O1-O2	2.739 (4)	2.758 (3)	2.792 (6)
O1-O3	2.663 (4)	2.682 (3)	2.728 (6)
O1-O3A2	2.667 (5)	2.689 (3)	2.739 (6)
O2-O3	2.661 (4)	2.670 (3)	2.711 (6)
O2-O3A2	2.570 (4)	2.588 (3)	2.614 (6)
O3-O3A2	2.648 (3)	2.656 (1)	2.681 (6)
mean of 6	2.658	2.674	2.711
T-*T*A2	3.099 (3)	3.102 (1)	3.131
O1-*T*-O2	117.9 (2)	117.6 (1)	117.3 (2)
O1-*T*-O3	109.1 (2)	109.6 (1)	110.3 (2)
O1-*T*-O3A2	108.8 (2)	109.4 (1)	110.3 (2)
O2-*T*-O3	110.3 (2)	109.7 (1)	109.7 (2)
O2-*T*-O3A2	104.4 (2)	104.3 (1)	103.6 (2)
O3-*T*-O3A2	105.6 (1)	105.6 (1)	104.8 (2)
mean of 6	109.4	109.4	109.3
T-O3-*T*A2	137.5 (2)	136.8 (2)	135.6
O3A2-O3-O3A2 (+1 in *c*)	168.7 (2)	165.8 (2)	166

[a] Nomenclature after Burnham *et al.* (1967); atoms of basic set unless otherwise designated. Errors in parentheses are one standard deviation; for 1.612 (3) read 1.612±0.003 Å. For tetrahedral contents, see Table 9.

[b] Values not given in reference were calculated by present authors.

to estimate the Mg, Al, and Fe^{2+} contents in the three remaining *M*1 sites. These occupancy values were used as starting parameters for a least-squares refinement of occupancies in which (Mg + Al) content was assigned the scattering factor of Mg and refined against Fe^{2+}, using appropriate constraints. Finally, Mg contents were fixed in three *M*1 type sites on the basis of this refinement plus consideration of the bond distances, and Fe^{2+} was then refined against Al.

Bond distances are not helpful in assigning Na and Ca contents among *M*2 type sites, because these two cations have similar average *M*2-O distances. Therefore, *M*2 occupancies were refined from an initial model assigning to each *M*2 site a composite (0.5Na + 0.5Ca) atom with an individual isotropic temperature factor of 0.8 Å². Final parameters obtained for the Venezuelan omphacite from these refinements are compared in Table 10 with those of the Californian omphacite, and the bond distances and angles are given in Tables 22 to 24.

The refined *P2* omphacite structures are characterized by a high degree of order in the *M*1 octahedral chains, which consist essentially of alternating Al^{3+} and Mg^{2+} octahedra. Clark and Papike (1968) suggested that ordering of the *M*1 chains due to the large size difference between Al^{3+} and Mg^{2+} was the chief reason for the formation of clinopyroxenes with the *P2* structure and that the partial order in the *M*2 sites (alternating Ca-rich and Na-rich) was a response to the charge distribution in the ordered *M*1 chains. This conclusion is confirmed by the present results for the Venezuelan omphacite, in which *M*2 occupancies are similar to those observed in the Californian omphacite.

The "ideal" *P2* omphacite may thus be considered as a clinopyroxene in which the *M*1 octahedrally coordinated cations are one-half Mg and one-half Al, and the *M*2 cations are one-half Ca and one-half Na, *i.e.* $Ca_{0.5}Na_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$. The *M*1 chains are required by size and charge considerations to be highly ordered, so that the Al octahedra are as far as possible from each other, both along the chains and from chain to chain. Each *M*2 polyhedron shares oxygen atoms with three consecutive *M*1 octahedra from one *M*1 chain. Hence, if one *M*2 polyhedron has one Al^{3+} and two Mg^{2+} neighbors, the next *M*2 polyhedron will have one Mg^{2+} and two Al^{3+} neighbors. If all *M*1 sites contain Al^{3+}, as in jadeite, then all *M*2 sites must have Na^+; similarly, if all *M*1 sites contain Mg^{2+}, as in diopside, all *M*2 sites must have Ca^{2+}. In the "ideal" *P2* omphacite, then, the *M*2 polyhedron with one Al^{3+} and two Mg^{2+} neighbors must have on the average $\frac{1}{3}$ Na^+ and $\frac{2}{3}$ Ca^{2+}; the *M*2 polyhedron with one Mg^{2+} and two Al^{3+} neighbors must have on the average $\frac{2}{3}$ Na^+ and $\frac{1}{3}$ Ca^{2+}. This is the *maximum* degree of order to be expected, even in "ideal" omphacite. The Californian and Venezuelan omphacites do have a degree of order approaching this maximum.

X-ray diffraction studies cannot distinguish between Fe^{2+} and Fe^{3+} except on the basis of observed bond distances and charge considerations. For the Californian omphacite (Clark and Papike, 1968), Fe was allocated among the four *M*1 sites by assuming Fe^{2+} to be associated with Mg^{2+} and Fe^{3+}, with Al. The Venezuelan omphacite has so little Fe^{3+} that only Fe^{2+} was considered during refinement, and it is allocated among three *M*1 sites (Table 10). Mössbauer spectral studies (Bancroft, Williams, and Essene, 1969) of samples comparable to those from which our omphacite crystals were selected indicate for both samples the presence of Fe^{2+} in four sites that are assumed to be the *M*1 type sites. The differences between the X-ray diffraction and Mössbauer results are minor but suggest that further investigation of the partitioning of Fe in a number of *P2* omphacites is necessary in order to determine the nature and significance of the Fe distribution.

Relationship of cell parameters to chemical composition and structure. On the basis of the cell parameters

TABLE 22. COMPARISON OF DISTANCES FOR $M1$ TYPE OCTAHEDRA IN TWO $P2$ OMPHACITES

Oxygen of M-O	Bond distances (Å)[a]							
	Venezuela Present study[b]				California Clark and Papike (1968)[c]			
	$M1$	$M1$ (1)H	$M1$ (1)	$M1$H	$M1$	$M1$ (1)H	$M1$ (1)	$M1$H
	Mg 0.82 Fe 0.10 Al 0.08	Mg 0.90 Fe 0.10	Al 1.00	Al 0.92 Fe 0.08	Mg 0.81 Fe 0.19	Mg 0.80 Fe 0.20	Al 0.95 Fe 0.05	Al 0.82 Fe 0.18
O1A1	2.12		1.90		2.12		1.91	
O1A2	2.06		1.96		2.09		2.03	
O1C1		2.06		2.01		2.07		1.97
O1C2		2.13		1.97		2.16		1.99
O2A1				1.88				1.91
O2A2		2.06				2.06		
O2C1	2.00				2.01			
O2C2			1.89				1.88	
Mean	2.06	2.08	1.92	1.96	2.07	2.10	1.94	1.95

[a] Each bond occurs twice.

[b] 1 standard deviation, 0.01 Å.

[c] 1 standard deviation, 0.02 Å.

known at that time, Whittaker (1960) suggested that the ionic size of both $M1$ and $M2$ cations affects the β value, the major influence being that of $M2$ and a "disturbing influence" being due to $M1$. The refined cell parameters currently available (Table 1) indicate that this suggestion is correct. The eight ordered clinopyroxenes can be divided neatly into three $M2$ groups: Li clinopyroxenes with β near 110°, Na clinopyroxenes with β near 107.5°, and Ca clinopyroxenes with β near 105.5°.

TABLE 23. COMPARISON OF DISTANCES FOR $M2$ TYPE POLYHEDRA IN TWO $P2$ OMPHACITES

Oxygen of $M2$-O	Bond distances (Å)[a]							
	Venezuela Present study[b]				California Clark and Papike (1968)[c]			
	$M2$	$M2$(1)H	$M2$(1)	$M2$H	$M2$	$M2$(1)H	$M2$(1)	$M2$H
	Na 0.76 Ca 0.24	0.68 0.32	0.25 0.75	0.31 0.69	0.64 0.36	0.64 0.36	0.36 0.64	0.03 0.97
O1A1	2.34				2.39			
O1A2			2.38				2.32	
O1C1				2.40				2.46
O1C2		2.37				2.33		
O2A1		2.39				2.35		
O2A2				2.40				2.44
O2C1			2.38				2.33	
O2C2	2.34				2.39			
O3A1		2.67		2.51		2.67		2.49
O3A2		2.41		2.80		2.43		2.79
O3C1	2.51		2.75		2.51		2.76	
O3C2	2.72		2.44		2.73		2.48	
Mean of 6 shortest	2.40	2.39	2.40	2.44	2.43	2.37	2.38	2.46
Mean of 8	2.48	2.46	2.49	2.53	2.50	2.44	2.47	2.55

[a] Each bond occurs twice.

[b] 1 standard deviation, 0.01 Å.

[c] 1 standard deviation, 0.02 Å.

The "disturbing influence" of $M1$ is slight (less than one degree) within the groups of ordered clinopyroxenes presented here. The intermediate composition clinopyroxenes (Table 2), which all have appreciable Na + Ca in the $M2$ site, have β angles of 106.5 to 107°, very nearly halfway between the values found for the ordered Na and Ca groups.

Surprisingly, the length of the c dimension in the ordered clinopyroxenes (Table 1) appears to be correlated with the kind and size of the cation occupying the $M1$ site. The c values range from 5.22 Å for Al in $M1$ to 5.29 Å for Fe^{3+} and Mn^{2+} in that site and attain a high of 5.37 Å for the In^{3+} compound. Brown (1960) suggested that the c-dimension was unlikely to be affected by factors other than substitution of tetrahedral aluminum for silicon, but the present observations indicate otherwise.

The equation proposed by Clark, Appleman, and Papike (1968) to relate the b-dimension to the average $M1$-O distance fits fairly well for the ordered clinopyroxenes, but rather poorly for the intermediate $C2/c$ clinopyroxenes. Perhaps this means the equation is applicable only when $M2$ is filled with Na and Ca.

CONCLUSIONS

The most important results of the present study are as follows:

1. The bonding in chain silicates is largely ionic in character, and the details of the structures can be explained in terms of an essentially ionic model without invoking additional covalent effects.

2. The charge and size of the $M2$ cation are considered responsible for determining the structure type of most pyroxenes, the $P2$ omphacites excepted. Large singly or doubly charged $M2$ cations lead to the $C2/c$ diopside-type

Table 24. Comparison of Bond Distances (Å) and Bond Angles (°) for the Tetrahedra of Two *P*2 Omphacites[a]

Atoms	A1 tetrahedron		A2 tetrahedron		C1 tetrahedron		C2 tetrahedron	
	Venezuela[b]	California[c]	Venezuela[b]	California[c]	Venezuela[b]	California[c]	Venezuela[b]	California[c]
	Si-O distances							
Oxygen								
O1	1.64	1.63	1.65	1.64	1.59	1.59	1.59	1.60
O2	1.61	1.63	1.55	1.57	1.62	1.60	1.58	1.57
mean, non-brg.	1.62	1.63	1.60	1.60	1.60	1.60	1.59	1.58
O3 (1)	1.65	1.65	1.65	1.66	1.65	1.64	1.65	1.68
O3 (2)	1.66	1.66	1.68	1.70	1.65	1.63	1.66	1.67
mean, brg.	1.65	1.66	1.67	1.68	1.65	1.64	1.65	1.68
mean of 4	1.64	1.64	1.63	1.64	1.63	1.62	1.62	1.63
	O-O distances							
O1-O2	2.77	2.80	2.72	2.66	2.76	2.82	2.75	2.73
O1-O3 (1)	2.65	2.66	2.71	2.72	2.61	2.61	2.60	2.66
O1-O3 (2)	2.73	2.71	2.67	2.73	2.64	2.58	2.64	2.64
O2-O3 (1)	2.65	2.66	2.58	2.63	2.65	2.61	2.58	2.66
O2-O3 (2)	2.58	2.57	2.67	2.69	2.56	2.51	2.66	2.61
O3 (1)-O3 (2)	2.66	2.65	2.61	2.64	2.58	2.65	2.69	2.64
mean of 6	2.67	2.67	2.66	2.68	2.63	2.63	2.65	2.66
	Si-Si distances							
Si (1)—Si (2)	3.080	3.06	3.098	3.11	3.049	3.07	3.121	3.12
Oxygens	O-Si-O angles							
O1, O2	117.2	118	116.6	112	119.0	124	120.5	119
O1, O3 (1)	107.6	109	110.5	112	107.4	108	109.2	106
O1, O3 (2)	111.6	111	106.4	109	109.2	107	106.3	108
O2, O3 (1)	108.9	109	113.3	113	108.2	107	110.8	107
O2, O3 (2)	104.1	103	105.5	107	103.4	102	105.6	110
O3 (1), O3 (2)	107.1	106	103.3	104	109.4	109	102.8	103
mean of 6	109.4	109.3	109.3	109.5	109.4	109.5	109.2	108.8
	Si-O3-Si angles							
Si (1), Si (2)	135.1	132	139.0	139	141.2	137	135.2	130
	O3 (1)-O3 (2)-O3 (1) angles							
	A chain				C chain			
	Venezuela 107.3		California 165		Venezuela 169.1		California 165	

[a] Nomenclature after Burnham *et al.* (1967).

[b] Present study; one standard deviation, Si-O, 0.01 Å, O-O, 0.02 Å, Si-Si, 0.007 Å, O-Si-O, 0.6°, Si-O-Si, 0.7°.

[c] Clark and Papike (1968); one standard deviation, Si-O and O-O, 0.02 Å, Si-Si, 0.01 Å, angles, 1°.

structure, small singly charged *M*2 cations to the *C*2 spodumene-type structure, and small doubly charged *M*2 cations to the *P*2_1/*c* clinoenstatite-type or orthorhombic structures.

3. The average *M*1-O bond distances found for the ordered clinopyroxenes can be used in linear combination with the ratios of the various *M*1 ions present in a disordered clinopyroxene to arrive at expected average *M*1-O values for any particular compositional model.

4. The *T*-O2 distance in disordered *C*2/*c* clinopyroxenes containing tetrahedral Al appears to vary linearly with the amount of Al and is a more sensitive indicator than the average *T*-O distance.

5. Ferrous iron is disordered between *M*1 and *M*2 in two *C*2/*c* clinopyroxenes of intermediate composition, but ferric iron is ordered entirely in the *M*1 site.

6. "Ideal" *P*2 omphacite has the formula $Ca_{0.5}Na_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$; Mg and Al are fully ordered in *M*1 sites, but (Na + Ca) are partially ordered in *M*2 sites, the maximum partial ordering being in the Ca/Na ratio of 1:2 or 2:1, alternating between sites.

7. The *c* dimensions of "end-member" clinopyroxenes re-

flect the nature of the chemical species in the $M1$ octahedral chains.

8. The silicon and oxygen atoms in "end-member" clinopyroxenes have individual isotropic temperature factors of 0.3 ± 0.1 Å^2 and 0.4 ± 0.1 Å^2, respectively; these atoms have higher temperature factors in intermediate compositon clinopyroxenes.

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Note added in proof: The crystal-structure refinement of a synthetic diopside (L. Schröpfer, 1968, *Neues. Jahrb. Mineral. Monatsh.* **1968,** 441–453), containing 2.13 ± 0.05 weight percent Ti (0.06 atom Ti per six oxygen atoms) yields T-O bond distances identical within 2 s.d. of those reported here for diopside; agreement for M-O distances is not as close. Schröpfer concluded that Ti is located in the tetrahedral sites. Comparison with results of our study shows that the observed T-O distances cannot be used to support this conclusion, although his site-occupancy refinement is consistent with the assignment.

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