CRYSTAL-CHEMICAL CHARACTERIZATION OF OMPHACITES[1]

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Abstract

The clinopyroxene, omphacite, can be defined compositionally within the system Jd-Ac-Di-He-Tsch, the chemical formula being expressed as $(M2)(M1)(Si,Al)_2O_6$; $M2$ represents Ca and Na, the ratio of $Na/(Na+Ca)$ being between 0.2 and 0.8, and $M1$ represents the octahedrally coordinated cations, Mg, Fe^{2+}, Al, Fe^{3+}, the ratio of $Al/(Al+Fe^{3+})$ being greater than 0.5. Omphacites are found to have space-group symmetries $C2/c$ or $P2$, although this distinction cannot be made by examination of X-ray diffraction powder data. The $P2$ omphacites have a restricted compositional range.

The results of a crystal-structure refinement of California $P2$ omphacite show that the cation distribution is largely ordered, (Mg,Fe^{2+})-octahedra alternating with (Al,Fe^{3+})-octahedra in the octahedral chains, and the larger polyhedra alternating in contents between major Na and major Ca. The presence of sufficient octahedrally coordinated Al to initiate the ordering process is considered necessary to obtain $P2$ omphacite. Appearance of $P2$ omphacites in blueschist facies at widely separated localities along the Circumpacific mountain belt suggests that these omphacites form at the low temperature-high pressure conditions considered characteristic of this facies of metamorphism.

Introduction

Modern X-ray diffraction techniques can be used to obtain crystal-structure refinements of numerous rock-forming silicates, each sample being selected for its chemical and petrological significance. Such studies taken singly provide data on the chemical bonding and cation distribution in individual crystals, and, when considered jointly, give valuable information on phase characterization, which is useful in the studies of mechanisms, energetics and kinetics of mineral reactions. A systematic research program of this kind is in progress at this laboratory, and the subject of the present paper, one of a series, is the eclogitic clinopyroxene, omphacite. A definition of this mineral is proposed that is based on its chemical composition and removes the requirement of association with eclogite; a brief review of the occurrence and composition of omphacites and aegirine-augites is included. The results of single-crystal, X-ray diffraction studies of various omphacites and aegirine-augites are presented, and a crystal-structure refinement of an omphacite from eclogite associated with glaucophane schists in California is reported. Finally, the implications of this research for pyroxene crystal chemistry and for eclogite formation are considered.

Historical and Geological Background

Omphacite in mineralogy. The name *omphax* in connection with a mineral first appears in the treatise *De Lapidibus* by Theophrastus (*circa* 315 B.C.). In their commentary on the text, Caley and Richards (1956) suggest that *omphax* may be prehnite, or possibly chrysoprase, since the name indicates that the stone resembled an unripe grape, *i.e.* that it was green in color and botryoidal in its natural state; Theophrastus refers to it as a stone from which seals are cut. Unfortunately, there are apparently no *omphax* seals surviving, and so identification of the classical *omphax* must remain conjectural.

Probably Werner (1812, as cited by Dana, 1892) was familiar with the classical names and thought *omphazit* appropriate to the green pyroxene he found near Beireuth. We have been unable to ascertain whether he believed *omphazit* to be the same as the *omphax* mentioned by Theophrastus. At any rate, the name *omphazit* or *omphacite* has been used by mineralogists for nearly 150 years to designate "a green clinopyroxene occurring in eclogites and related rocks" (Deer, Howie and Zussman, 1963). In 1865, Breithaupt remarked that omphacite is a mineral that not enough is known about as yet. Nearly one hundred years later, this remark was still valid, despite a large number of publications on the mineral.

Other mineral names have been used for clinopyroxenes of compositions similar to those assigned to omphacites (Deer *et al.*, 1963), such as diopside-jadeite, and chloromelanite. This complication is discussed by Hashimoto (1964), and we agree with his conclusion that retention of the name omphacite appears desirable (especially in view of its classical significance), provided the restriction of eclogitic association is removed.

Omphacite and eclogites. Eclogite was defined by Haüy in 1822 as a rock with the essential components *"la diallage, le grenat, et le disthène"* (pyroxene, garnet, and kyanite, respectively). Sometime in the next half-century, omphacite became accepted as the characteristic eclogitic pyroxene even while remaining itself ill-defined. In fact, a circular definition evolved, so that eclogite is described as the rock containing omphacite and garnet, and omphacite is described as the pyroxenic constituent of the garnet-rock eclogite (Rice, 1954). Confusion is further compounded because the assemblage garnet-clinopyroxene occurs in rocks other than eclogites, a point discussed by White (1964). Some of the problems associated with formation of eclogites have been described by Yoder (1950), Yoder and Tilley (1962), Coleman *et al.* (1965), Forbes (1965) and Green and Ringwood (1966). We prefer not to enter controversies concerning

eclogites; for the present paper we shall adopt the definition given by Green and Ringwood (1966), which is in harmony with much modern usage of the rock name, and use the classification of eclogites into three groups according to Coleman *et al.* (1965).

Green and Ringwood (1966) define eclogite as " . . . a rock of basaltic chemistry consisting mineralogically of garnet (almandine-pyrope solid solution) plus clinopyroxene with or without quartz, kyanite, hypersthene or olivine as minor minerals. Plagioclase is absent as a primary phase from rocks strictly classifiable as eclogites and in addition the clinopyroxene of eclogites contains jadeite solid solution and a high jadeite/Tschermak's silicate ratio (White, 1964)." As we shall show, the chemical composition of omphacite can be defined so that it is essentially compatible with this definition of the clinopyroxene associated with eclogite.

Coleman *et al.* (1965) refer to eclogites as Group A, B or C types. The Group A eclogites are defined as "inclusions in kimberlites, basalts, or layers in ultramafic rocks . . . . . . [having] a very deep-seated igneous or metamorphic origin." Omphacites associated with such eclogites are not considered in the present paper, but will be the subject of a later study. The Group B eclogites are "bands or lenses within migmatic gneissic terrains", and Group C eclogites are "bands or lenses within the metamorphic rocks of the alpine-type orogenic zones . . . . locally forming isolated blocks when associated with glaucophane schists." Most of the omphacites considered in the present paper are from Group C eclogites but some data are also given for omphacites from Group B eclogites.

Clinopyroxene crystal structure. The original determination of this structure was reported nearly forty years ago by Warren and Bragg (1928) for diopside, $CaMgSi_2O_6$, which has the space group $C2/c$. Other clinopyroxenes were examined by Warren and Biscoe (1931), who concluded that hedenbergite, augite, clinoenstatite, acmite, jadeite, and spodumene are all similar to diopside in structure. This conclusion remains valid insofar as gross structural features are concerned, but clinoenstatite was shown by Morimoto (1956) to have the space group $P2_1/c$, and spodumene has been found to have space group $C2$ (Appleman and Stewart, 1966). Recent refinements of the crystal structures of jadeite, $NaAlSi_2O_6$, by Prewitt and Burnham (1966), and of johannsenite, $CaMnSi_2O_6$, by Freed and Peacor (1967), confirm $C2/c$ symmetry for these clinopyroxenes. An omphacite from Group B eclogite (Warner, 1964) has $C2/c$ symmetry, but the Group C omphacites are found to have space group $P2$, and a preliminary note on the $P2$ structure has been published (Clark and Papike, 1966).

DEFINITION OF OMPHACITE

The compositions of most omphacites, as the term is now used, can be represented within the system $NaAlSi_2O_6$-$NaFe^{3+}Si_2O_6$-$CaMgSi_2O_6$-$CaFe^{2+}Si_2O_6$. However, some omphacites have been reported to contain significant amounts of Al in tetrahedral coordination (White, 1964; Velde, 1966). Although such omphacites do not fit the definition quoted from Green and Ringwood (1966) for the eclogitic clinopyroxene, nevertheless this feature must be considered in arriving at a satisfactory definition of omphacite. In order to represent such pyroxenes compositionally, a fifth component, $CaAl(SiAl)O_6$, must be added and we must therefore consider the system Jd-Ac-Di-He-Tsch. We suggest that within this system the omphacite compositional field be defined as lying between the boundary planes $0.2 \leq Na/(Na+Ca) \leq 0.8$ and limited to the region where the ratio, $Al/(Al+Fe^{3+}) > 0.5$ (Fig. 1; octahedrally coordinated Al only). The portion of this volume with $Al/(Al+Fe^{3+}) < 0.5$ is occupied by the aegirine-augites. Considering tetrahedrally coordinated Al, the volume bounded by the planes having a ratio of $Na/(Na+Ca)$ between 0 and 0.2 can be divided into two regions. One region locates the aluminous diopside-hedenbergites with $Al/(Al+Si) < 0.2$, and the second locates fas-
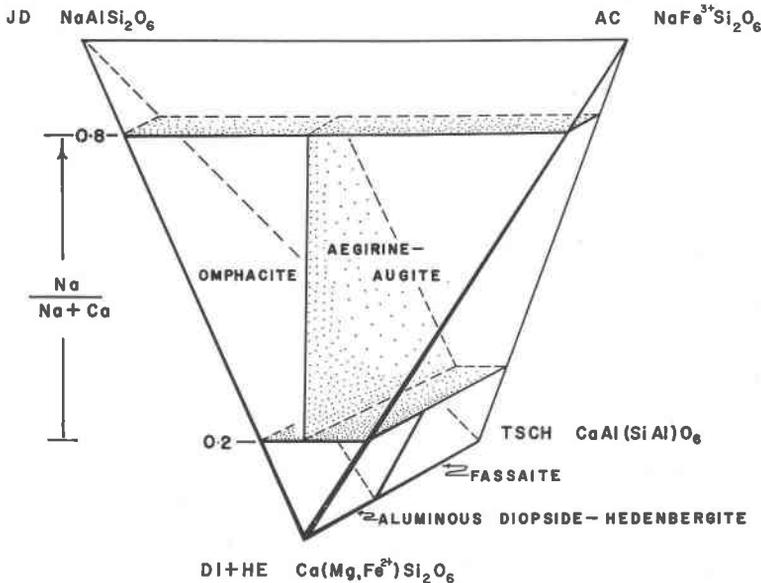

FIG. 1. Schematic view of the omphacite compositional field (shaded region) within the system Jd-Ac-Di+He-Tsch, showing its relationship to the fields for aegirine-augite, fassaite, and aluminous diopside-hedenbergite.
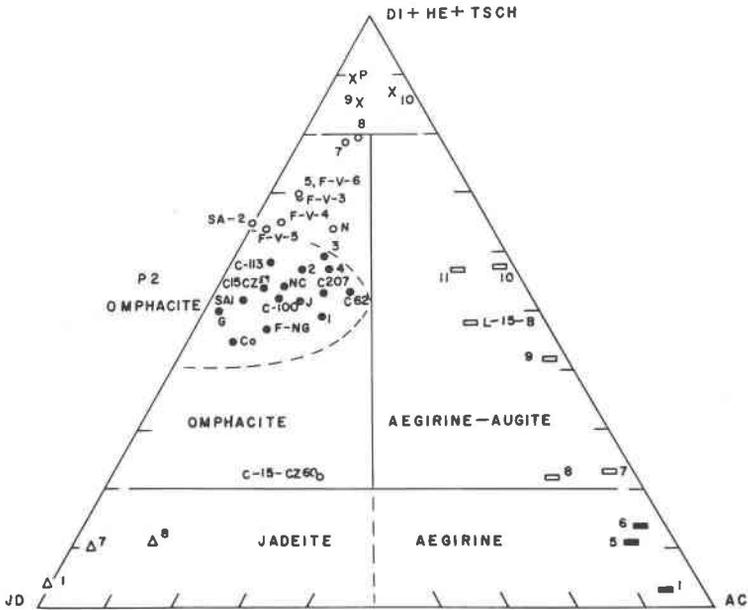
Fig. 2. Compositions of omphacites, jadeites, aegirine-augites and some diopside-hedenbergites plotted on the plane Jd-Ac-Di+He+Tsch. *P2* omphacites are indicated by dots, others, by circles; diopsidic pyroxenes, by crosses; jadeitic pyroxenes, by triangles; aegirines, by solid rectangles; and aegirine-augites, by open rectangles. The field of *P2* omphacites is indicated by dashed lines. Numbers correspond to analyses in Deer *et al.* (1963) for jadeites, omphacites and aegirines (aegirine-augites), respectively; other symbols as follows: C and NC, Coleman *et al.* (1965); Co, D. H. Green and J. P. Lockwood, written communication (see Table 1); F-NG, Nicholas and Gagny (1964) F-V, Velde (1966); G. Foshag (1955); J, Hashimoto (1964); L, Klein (1966); N, Warner (1964); P, W. R. Church, written communication (see Table 1); SA, Williams (1932). Total amounts of components other than those shown are minor. See Table 1 for analytical data on some of these samples.

saites with $Al/(Al+Si) > 0.2$. These divisions are in accordance with modern usage.

Some natural compositions of clinopyroxenes falling within this system and between the boundary planes $0.2 \leq Na/(Na+Ca) \leq 0.8$ are plotted in projection on a triangular plane diagram (Fig. 2). The clustering of omphacites in the portion of the diagram selected for the omphacite field by the present definition shows that the definition agrees with most current usage. There clearly exists a distinct separation between the naturally occurring omphacites and aegirine-augites. Projection of natural compositions on a plane quadrilateral omitting the Tschermak's component illustrates the range of variations natually found in Mg and Fe^{2+} (Fig. 3).
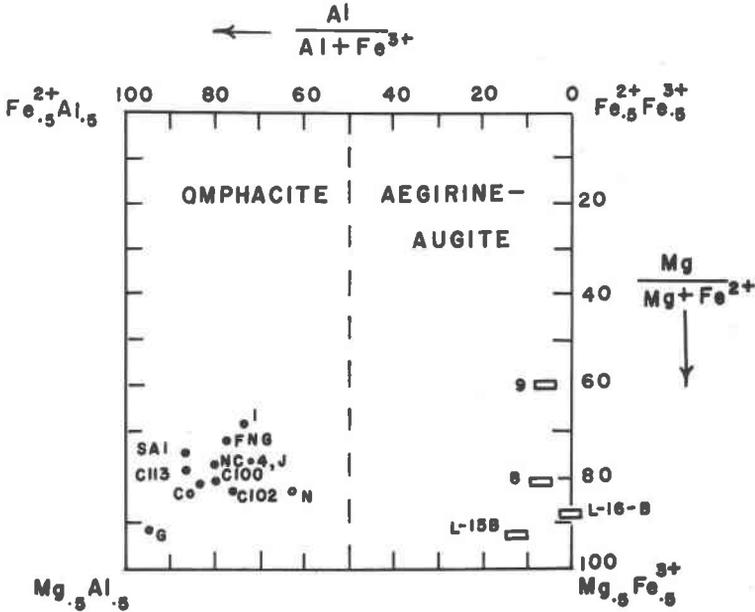
FIG. 3. Compositions of omphacites (dots, $P2$ omphacites; circles, $C2/c$ omphacites) and aegirine-augites (rectangles) plotted on the plane $Di_{50}Jd_{50}$-$Hd_{50}Jd_{50}$-$Hd_{50}Ac_{50}$-$Di_{50}Ac_{50}$. Only analyses with tetrahedral Al<0.05 atoms per formula unit are shown. Numbers are keyed to analyses in Deer *et al.* (1963) for omphacites and aegirine-augites, respectively; others, as follows: C and NC, Coleman *et al.* (1965); Co, D. H. Green and J. P. Lockwood, written communication (see Table 1); F-NG, Nicholas and Gagny (1964); G, Foshag (1955); J, Hashimoto (1964); L, Klein (1966); N, Warner (1964); SA, Williams (1932). Analytical data for some are given in Table 1.

The $P2$ omphacites to be described in the following sections of this paper are expected to be restricted to a fairly narrow compositional range with the ratio $Na/(Na+Ca) \approx 0.5$, and the ratio for the octahedrally coordinated cations, $Al/(Al+Fe^{3+})>0.6$ (Figs. 2, 3). Substitutions among octahedrally coordinated cations may occur in natural systems by elements such as Mn^{2+}, Cr^{3+}, and V^{3+}, among others. Adjectival qualifications, such as chromian omphacite, are preferable to assignment of new mineral names, and Ca- or Na-rich omphacites may conveniently be designated calcic or sodic omphacites, respectively.

STUDIES OF VARIOUS OMPHACITES AND AEGIRINE-AUGITES

Experimental techniques. Analyzed samples were available for most of the minerals studied, and the analytical results are given in other publications. Therefore, only the formula contents, in terms of six oxygen atoms

per formula unit, are given in Table 1. Electron-probe examinations of a few selected crystals were carried out during the present study and verified the homogeneity and the bulk analysis figures. Single crystals were examined with Zr-filtered Mo radiation on the Buerger precession camera, and powder samples were studied both by diffractometer and film methods using Ni-filtered Cu radiation. Preliminary unit-cell parameters were obtained from measurements of the precession patterns. The powder data, obtained from measurements of diffractometer patterns prepared with CaF_2 or Si as an internal standard, were used in a computer least-squares refinement program (Evans, Appleman and Handwerker, 1963), starting with the preliminary unit-cell parameters, to arrive at the final values given in Table 2.

Omphacites. The single-crystal patterns of some omphacites reveal the presence of weak reflections violating the $C2/c$ space-group criteria that require hkl to be present only if $h+k=2n$, and $h0l$, only if $l=2n$ (and $h=2n$). The $h0l$ photograph of such an omphacite is illustrated in Figure 4; the weak reflections are sharp and precisely aligned, so the diffraction pattern is representative of a single, well crystallized phase. Assignment of $P2/m$ or $P2$ symmetry is required to fit the observations, but atomic coordinates for a structure closely analogous to the known $C2/c$ structure (Warren and Bragg, 1928), as indicated by the intensity distribution, cannot be assigned in $P2/m$. The true symmetry of these omphacites must therefore be $P2$. Although there are few such reflections on the precession photographs, an appreciable number can be measured for a single crystal by the greater sensitivity of scintillation counting, and these data were available for the structure refinement. However, reflections with $h+k$ odd have not been observed on X-ray diffraction powder patterns of these omphacites (see Table 3, especially footnote 1) and the powder data for all omphacites are satisfactorily indexed using the $C2/c$ symmetry. Therefore, X-ray diffraction powder data cannot be used to distinguish between $C2/c$ and $P2$ omphacites.

Crystals from six different samples described by Coleman *et al.* (1965) from Group C eclogites associated with glaucophane schists in California, U.S.A., and in New Caledonia all proved to be $P2$ omphacites. Because the chemical analyses are similar for the six samples, data are given in Tables 1 and 2 only for sample 100–RGC-58, from which the crystal selected for structural analysis was taken. X-ray diffraction powder data for this same sample are listed in a paper by Coleman and Clark (1968), in which the relationships of jadeite, jadeitic pyroxenes, and omphacites in the blueschist facies of California are considered. Geological features of the California localities were discussed by Coleman and Lee (1963).

Some crystals of a diopside-jadeite from a boulder tomb, Kaminaljuyú, Guatemala, Central America, which were described by Foshag (1955) and were obtained from his samples at the U.S. National Museum, are very nearly pure $Na_{0.5}Ca_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$, and are found to be $P2$ omphacite. The results of electron-probe analysis of two crystals of this diopside-jadeite agree well with the values obtained from the bulk analysis (Table 1). Because the sample contains so little iron, it is virtually a corner member on the plane $Na_{0.5}Ca_{0.5}$ in the Jd-Ac-Di-He system (Fig. 3), and therefore the indexed X-ray diffraction powder data for this sample are given in Table 3. A crystal-structure refinement of this mineral is in progress.

Other crystals that proved to be $P2$ omphacites came from Group C eclogite cobbles, Guajira Peninsula, Colombia, South America, (D. H. Green and J. P. Lockwood, written communication, 1966) and from Group B eclogite (Duen type) described by Eskola (1921) from Vanelvsdalen, Norway.

An omphacite with $C2/c$ symmetry was studied by Warner (1964), who gave single-crystal and X-ray diffraction powder data for the mineral. This omphacite came from Group B eclogite in the Eiksundsdal Complex, Hareidland, Sunmøre, Norway (Schmitt, 1963), and, unlike the other omphacites mentioned above, is associated with orthopyroxene. We examined crystals from this sample and confirm Warner's results. Electron-probe analysis of a crystal of this omphacite also checks the values obtained from the bulk analysis (Table 1). A possible igneous "omphacite," from garnet-bearing ariégites of the French Pyrenees (Church, 1966), also has $C2/c$ symmetry; however, it is not an omphacite according to the present definition and should preferably be called a sodium-rich aluminous diopside (Table 1; Fig. 2).

Aegirine-augites. An aegirine-augite sample from the Wabush Iron Formation, Labrador, Newfoundland, Canada (Klein, 1966) has a composition very nearly $Na_{0.5}Ca_{0.5}Mg_{0.5}Fe^{3+}_{0.5}Si_2O_6$ and it is therefore approximately a corner member on the plane $Na_{0.5}Ca_{0.5}$ in the Jd-Ac-Di-He system (Fig. 3). The crystals were examined to determine whether they would exhibit the $P2$ symmetry, but no weak reflections violating $C2/c$ symmetry were found. A similar result was obtained for another aegirine-augite sample of different composition from the same formation.

Summary of general studies. All of these results considered together with published chemical analyses of omphacites which have been included in Figures 2 and 3, constitute the evidence for the chemical definition of omphacite and the distinction between $P2$ and $C2/c$ omphacites. The

TABLE 1. CHEMICAL DATA[a] FOR SELECTED OMPHACITES AND AEGIRINE-AUGITES

Atoms	Aluminous diopside[b] France Pyrenees Church (1966)	C2/c Omphacite Norway Hareidland, Sunmøre 1725 Warner (1964)	C2/c Omphacite Norway Hareidland, Sunmøre 1725 Present study[d]	P2 Omphacites California Tiburon Peninsula 100-RGC-58 Coleman et al. (1965)	P2 Omphacites New Caledonia Boulder, 36-NC-62 Coleman et al. (1965)	P2 Omphacites Guatemala Tomb, Kaminaljuyú Foshag (1955)[e]	P2 Omphacites Guatemala Tomb, Kaminaljuyú Present study[d]	P2 Omphacites Colombia Cobble, Guajira Peninsula 2833 Green and Lockwood[f]	P2 Omphacites Norway Vanelvs-dalen[e] Eskola (1921)	Aegirine-Augites Labrador Wabush Iron Formation 15 B Klein (1966)	Aegirine-Augites Labrador Wabush Iron Formation 16 B Klein (1966)
Si	1.88	2.00	2.00	1.96	1.96	1.98	2.00	1.95	1.95	2.02	2.02
Al	0.12	—	—	0.04	0.04	0.02	—	0.05	0.05	—	—
Σ Tetrahedral	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.02	2.02
Al	0.15	0.24	0.20	0.39	0.40	0.48	0.48	0.38	0.44	0.05	—
Fe^{3+}	0.03	0.12	0.11	0.10	0.10	0.02	0.02	0.07	0.15	0.41	0.64
Σ $Al+Fe^{3+}$	0.18	0.36	0.31	0.49	0.50	0.50	0.50	0.45	0.59	0.46	0.64
Mg	0.80	0.59	0.57	0.44	0.40	0.47	0.41	0.45	0.28	0.49	0.22
Fe^{2+}	0.08	0.12	0.12	0.10	0.11	0.04	0.04	0.10	0.12	0.04	0.03
Σ $Mg+Fe^{2+}$	0.88	0.71	0.69	0.54	0.51	0.51	0.45	0.55	0.40	0.53	0.25
Ca	0.85	0.59	0.58	0.51	0.52	0.48	0.45	0.55	0.46	0.42	0.20
Na	0.10	0.32	0.38	0.48	0.45	0.47	0.56	0.45	0.48	0.45	0.67
Σ $Ca+Na$	0.95	0.91	0.96	0.99	0.97	0.95	1.01	1.00	0.94	0.87[g]	0.87[h]

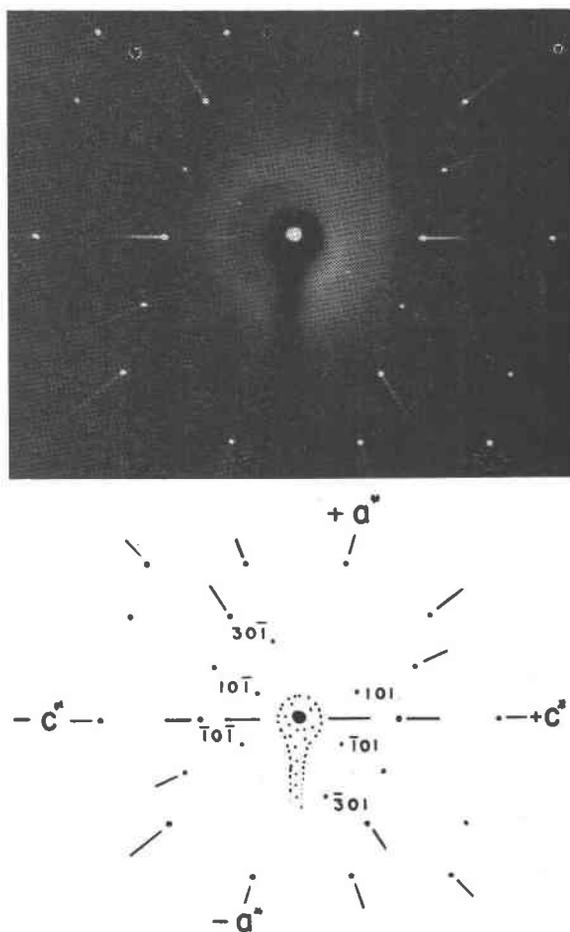(Footnotes for table 1 on following page)

FIG. 4. (a) Precession photograph taken with Zr-filtered Mo radiation for the *h0l* net of a *P2* omphacite from Guajira Peninsula, Colombia (see Table 1 for analytical data). (b) Schematic diagram showing indexing of the precession photograph.

^a Analytical data available in given references, converted on the basis of six oxygen atoms per formula unit; tetrahedral contents made up to 2.00 by addition of Al.

^b A possible "igneous omphacite"; analysis figures from W. R. Church (written communication, 1967).

^c Analysis for a "chloromelanite" (Eskola, 1921, p. 32); conversion as given in Deer *et al.* (1963, p. 156, no. 1). Sample examined during present study is from the same locality, was obtained from the University of Cambridge, and electron-probe scans of single crystals show that it is comparable in chemistry to the Eskola sample.

^d Average of electron-probe analyses for two crystals. Total Fe divided between Fe^{2+} and Fe^{3+} as found in chemical analysis.

^e Conversion of analytical data as given in Deer *et al.* (1963, p. 103, no. 9).

^f Written communication, 1966.

^g Sample contains 0.09 atoms Mn^{2+}.

^h Sample contains 0.19 atoms Mn^{2+}.

TABLE 2. UNIT-CELL PARAMETERS, SPACE GROUPS, AND DENSITIES OF OMPHACITES AND AEGIRINE-AUGITES

	Omphacites					Aegirine-Augites	
	California[a]	New Caledonia[b]	Guatemala[b]	Colombia[c]	Norway[d]	Labrador[e]	
	Tiburon Peninsula	Boulder, near Amos Stream	Tomb, Kaminaljuyú	Cobble, Guajira Peninsula	Hareidland, Sunmøre	Wabush Iron Formation	
	Coleman et al. (1965)		Foshag (1957)	Green and Lockwood	Warner (1964)	Klein (1966)	
	100-RGC-58	36-NC-62	6	2833	1725	15B	16A
a (Å)	9.596±0.005	9.595±0.006	9.559±0.006	9.596±0.005	9.662±0.003	9.694±0.002	9.689±0.003
b (Å)	8.771±0.004	8.786±0.009	8.762±0.006	8.786±0.004	8.819±0.004	8.855±0.001	8.843±0.002
c (Å)	5.265±0.006	5.260±0.006	5.245±0.006	5.267±0.006	5.228±0.002	5.260±0.005	5.286±0.008
β	106°56'±4'	106°52'±6'	106°55'±4'	106°55'±4'	106°33'±1'	106°50'±1'	107°15'±2'
Cell Volume (Å³)	423.9±0.4	424.4±0.6	420.3±0.4	424.4±0.4	[427.0]	432.2±0.3	432.5±0.6
Space Group	P2	P2	P2	P2	C2/c	C2/c	C2/c
Density (g/cm³) obs.	3.34	3.32	3.196	3.32	3.39 ±0.07	3.40 ±0.02	3.51 ±0.02

[a] Unit-cell parameters measured for a single crystal on the goniostat and space-group determination are by the present authors; obs. density from Coleman et al. (1965).

[b] Unit-cell parameters from refinement of powder data (see text) and space-group determination are by the present authors; obs. density from given reference.

[c] Unit-cell parameters from refinement of powder data and density are by D. H. Green and J. P. Lockwood (written communication, 1966). Space-group determination by present authors.

[d] Cell volume calculated by present authors; all other data from Warner (1964), checked during the present study (except density).

[e] Space-group determination by present authors; other data from Klein (1966), checked during the present study (except density).

TABLE 3. X-RAY DIFFRACTION POWDER DATA FOR $P2$ OMPHACITE,
$Na_{0.5}Ca_{0.5}Al_{0.5}Mg_{0.5}Si_2O_6$, FROM KAMINALJUYÚ, GUATEMALA

Monoclinic, true space-group $P2$, pseudo space-group for indexing of powder patterns, $C2/c$: $a = 9.559$, $b = 8.762$, $c = 5.245$ Å, $\beta = 106°55'$, $V = 420.3$ Å³

hkl	Calculated[a]			Observed[b]	
	2θ, $CuK\alpha_1$ (degrees)	d_{hkl}(Å)	I	d_{hkl}(Å)	Peak height
110	13.98	6.330	0.7		
200	19.37	4.577	0.0		
$\bar{1}$11	20.23	4.385	0.7		
020	20.25	4.381	8.0	4.371	10
111	24.74	3.596	0.2		
021	26.99	3.300	10.7	3.299	7
220	28.17	3.165	19.7	3.162	20
$\bar{2}$21	30.18	2.959	100.0	2.956	100
310	31.00	2.882	33.8	2.877	45
$\bar{3}$11	31.23	2.862	33.4	2.861	30
130	32.14	2.782	0.1		
$\bar{2}$02	35.41	2.533	3.0		
$\bar{1}$31	35.45	2.530	22.5	2.527	20
$\bar{1}$12	35.71	2.512	0.4		
002	35.76	2.509	42.2	2.511	30
221	36.45	2.463	39.3	2.462	25
131	38.32	2.347	1.3		
400	39.33	2.289	0.1		
311	40.10	2.247	16.4	2.247	10
112	41.25	2.187	12.8	2.186	7
022	41.44	2.177	9.9		
330	42.82	2.110	8.2		
$\bar{3}$31	42.99	2.102	17.0	2.102	15
$\bar{4}$21	43.56	2.076	7.8	2.074	5
041	45.12	2.008	21.1⎫	2.007	20
$\bar{4}$02	45.15	2.006	10.2⎭		
202	45.99	1.972	5.3		
$\bar{1}$32	46.50	1.951	5.8		
510	50.90	1.792	7.1	1.790	5B
132	51.08	1.786	3.0		
150	53.17	1.721	11.3	1.721	10
$\bar{3}$13	55.37	1.658	7.1⎫	1.655	5B
042	55.65	1.650	5.2⎭		
$\bar{2}$23	56.79	1.620	16.6	1.622	7
$\bar{5}$32	57.66	1.597	16.9	1.597	10
440	58.25	1.583	7.0	1.582	7
600	60.64	1.526	3.4⎫	1.522	5B
350	60.91	1.520	5.4⎭		
$\bar{6}$02	61.17	1.514	5.4		
$\bar{1}$33	62.11	1.493	13.9	1.495	7
402	62.31	1.489	6.7		
060	63.67	1.460	5.2		
$\bar{3}$52	67.18	1.392	11.9⎫	1.391	10B
531	67.38	1.389	18.5⎭		
223	68.45	1.369	5.5		

[a] Intensities (I) calculated using the atomic coordinates of Table 6, assuming Mg in M1, M1(1)H, Al in M1(1), M1H, Na in M2, M2(1)H, and Ca in M2(1), M2H. No absorption corrections were made. Intensities are normalized with $I(\bar{2}21) = 100$. All hkl for $C2/c$ are listed for $2\theta \leq 40°$; thereafter only those with calculated $I \geq 3.0$ are given. The largest calculated I for a $P2$ reflection is 5.7 for $\bar{1}01$; this reflection should be at $2\theta = 17.49°$ (5.065 Å) and was not observed on any powder patterns. All other $P2$ type reflections have calculated $I < 2.0$.

[b] Measurements from diffractometer patterns with NaF as internal standard; $CuK\alpha_1$, $\lambda = 1.5405$ Å. Broad peaks are marked B.

petrologic significance of these results is discussed in another section of this paper.

CRYSTAL STRUCTURE ANALYSIS

Experimental details. The omphacite crystal selected for structural study was from Group C eclogite associated with glaucophane schist on the Tiburon Peninsula, Marin County, California (Sample 100-RGC-58, Coleman *et al.*, 1965; see present Table 1 for chemical data). The pale green prismatic crystal was about $0.2 \times 0.07 \times 0.04$ mm with {010} the dominant form. For collection of the diffraction data, the crystal was mounted with b parallel to the ϕ axis of the single-crystal, manually operated goniostat. Three-dimensional intensities for reflections with $2\theta \leq 60°$ were measured with a scintillation counter using the 2θ-scan technique; the scan range was calculated according to the equation for $MoK\alpha$ radiation suggested by Alexander and Smith (1964). Background counts of 50 seconds duration were made for each reflection at the beginning and end of the scan range. Unfiltered Mo radiation was used for most of the measurements, but approximately 60 reflections were also measured with Nb-filtered Mo radiation (0.002″ thick Nb foil used). A total of 1297 independent reflections were recorded; 830 of these had scan counts greater than twice the background standard deviation, and only this group was used in the refinement. The measurements were corrected for Lorentz and polarization effects, and for absorption ($\mu = 22$ cm^{-1}), using computer programs listed in an appendix. None of the reflections appears to be affected by extinction.

Refinement of the structure. The refinement calculations were handled by computer methods which are described in an appendix. In the $C2/c$ structure of jadeite, the unit cell contains four formula units, NaAlSi$_2$O$_6$. The asymmetric unit consists of one Si and three oxygen atoms, all in the general positions $8f$, plus two cations, Al($M1$) and Na($M2$), each located on the twofold axes in special positions $4e$. The unit cell of omphacite also contains four units of similar formula, although with varying kinds of cations, but the general positions in $P2$ are of twofold multiplicity ($2e$), so that four Si and twelve oxygen atoms must be located in these positions. The special positions on the twofold axes of $P2$ are single ($1a$, $1b$, $1c$), $1d$, so that one $M1$ and one $M2$ cation must be assigned to each of these four special positions. The initial atomic coordinates for $P2$ omphacite were derived from those for corresponding equivalent positions in jadeite, using the asymmetric set given by Prewitt and Burnham (1966). These derived coordinates were then modified in two ways, first by adding

+0.250 to all z coordinates in order to place the $P2$ origin on a twofold axis, and second, by arbitrarily altering the x, y, z values slightly (± 0.010) in order to avoid the exact centrosymmetric model. The co-ordinates of one $M2$ position were fixed to locate the $P2$ origin. As a first approximation, all $M1$ and $M2$ cations were assigned the Na^0 scattering factor. The initial residual R was 0.43, but the value dropped rapidly after a few cycles of least-squares refinement, becoming 0.21 with fixed, individual, isotropic temperature factors, and 0.16 after refinement of individual, isotropic temperature factors.

The silicon and oxygen atoms were then assumed to be reasonably well located, and attention was directed to the problem of cation distribution among the eight available sites. Some trial structure-factor and bond-length calculations showed that division of the eight sites into four of $M2$ type, suitable for the large cations Na and Ca, and four of $M1$ type, suitable for the smaller cations Mg, Fe^{2+}, Al, Fe^{3+}, was reasonable. Because a site refinement program was not immediately available, two other approaches were tried. First, some individual structure factor contributions were examined to determine the effect of various cation distributions. A number of models were tested, and during this study, the calculations for $h0l$ structure factors with h and l odd revealed that Na and Ca must be

TABLE 4. INDIVIDUAL ATOMIC CONTRIBUTIONS TO THE $\overline{1}01$ STRUCTURE
FACTOR OF $P2$ OMPHACITE

Atoms		$e^{-B_j s^2}(f_j + \Delta f_j')$	$\cos 2\pi(-x_j + z_j)$	F' (calc.)[a]
Oxygens (24)		7.24	−0.788	−5.71
Silicons (8)		12.29	−0.152	−1.87
M Cations (4)				+0.68
$M1$	$0.8Mg+0.2Fe$	13.26	+1.000	
$M1(1)$	$0.95Al+0.05Fe$	11.96	−1.000	
$M1H$	$0.8Al+0.2Fe$	13.87	−1.000	
$M1(1)H$	$0.8Mg+0.2Fe$	13.25	+1.000	
$M2$ Cations (4)				−7.12
$M2$	$0.64Na+0.36Ca$	12.50	+1.000	
$M2(1)$	$0.36Na+0.64Ca$	14.67	−1.000	
$M2H$	$1.00Ca$	17.45	−1.000	
$M2(1)H$	$0.64Na+0.36Ca$	12.50	+1.000	
Calculated F				−14.0
Observed F				12.9

[a] $F'(\text{calc.}) = \sum e^{-B_j s^2}(f_j + \Delta f_j') \cos 2\pi(-x_j + z_j)$; atomic parameters as in Table 6, $s(\overline{1}01) = 0.0097 \text{Å}^{-1}$.

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TABLE 5. VARIOUS NA-CA ORDERING MODELS TESTED

Cation Site	Model						Final site refinement	
	1	2	3	4	5	6	Na	Ca
$M2$	Na	Ca	Ca	Ca	Na	Na	0.64	0.36
$M2(1)$	Na	Ca	Na	Na	Ca	Ca	0.36	0.64
$M2$H	Ca	Na	Ca	Na	Na	Ca	—	1.00
$M2(1)$H	Ca	Na	Na	Ca	Ca	Na	0.64	0.36
			Residual Factors[a]					
Initial	0.34	0.38	0.35	0.50	0.35	0.34		
Final	0.25	0.28	0.22	0.29	0.24	0.16	0.11	

[a] For 299 hkl having $h+k \neq 2n$; initial coordinates after 12 cycles of least-squares refinement using all hkl. Final residual factors after six cycles of refinement varying x, y, z for all atoms but using fixed isotropic temperature factors.

largely ordered if these reflections are to have observable intensities. The individual atomic contributions to the $\bar{1}01$ reflection, calculated using the final atomic parameters and site occupancies, illustrate this feature (Table 4). Various models having ordered Na and Ca were then subjected to least-squares refinement using only the 299 data having $h+k$ odd. The results (Table 5) unambiguously favored one model, which was then adopted for further refinement using all data. However, the temperature factors of the cations and of some oxygen atoms persistently became negative when all parameters were refined together. This effect was attributed to the large correlations (0.85 and up) that were found among various pairs of atoms. Accordingly, when the site refinement program became available, the atoms were divided into two groups, and refinement of parameters was carried out within one group at a time; parameters of the other group were held fixed. High correlations between the site occupancy and temperature factor for the same cation were also found, so the final site refinement, assuming full occupancy of each site by two atomic species, was carried out with fixed isotropic temperature factors, using only the data having $h+k$ odd. The full data set was then used with the site occupancies fixed during successive refinement of the other atomic parameters.

By these gradual methods a successful refinement was achieved, and the final atomic parameters and site-occupancy figures are given in Table 6, where they are compared with the corresponding parameters in the jadeite structure. The atomic designations used in Table 6 and in the description of the structure follow the scheme outlined by Burnham et al.

TABLE 6. ATOMIC PARAMETERS AND CATION SITE-OCCUPANCY FACTORS FOR $P2$
OMPHACITE, COMPARED WITH SIMILAR DATA FOR JADEITE

Atom[c]	Site occupancy[d]		Omphacite[a] present study			Jadeite[b] Prewitt and Burnham (1966)		
			x	y	z	x	y	z
O1(1)A	1.0		0.112	0.088	0.864	0.1090	0.0763	0.8775
O1(2)A			.110	.922	.405	.1090	.9237	.3775
O1(1)C			.386	.567	.103	.3910	.5763	.1225
O1(2)C			.385	.411	.620	.3910	.4237	.6225
O2(1)A	1.0		.364	.263	.066	.3608	.2630	.0429
O2(2)A			.347	.747	.551	.3608	.7370	.5429
O2(1)C			.133	.749	.939	.1392	.7630	.9571
O2(2)C			.135	.244	.446	.1392	.2370	.4571
O3(1)A	1.0		.360	.022	.757	.3533	.0070	.7558
O3(2)A			.350	.994	.252	.3533	.9930	.2558
O3(1)C			.154	.515	.255	.1467	.5070	.2442
O3(2)C			.147	.489	.750	.1467	.4930	.7442
Si1A	1.0		.2890	.0972	.9774	.2906	.0934	.9777
Si2A			.2881	.9135	.4820	.2906	.9066	.4777
Si1C			.2137	.5880	.0196	.2094	.5934	.0223
Si2C			.2103	.4027	.5232	.2094	.4066	.5223
M1	Mg^{2+}	0.81	0	.9122	0	0	.9060	0
	Fe^{2+}	0.19						
M1(1)	Al^{3+}	0.95	0	.1002	.500	0	.0940	.500
	Fe^{3+}	0.05						
M1H	Al^{3+}	0.82	.500	.4045	0	.500	.4060	0
	Fe^{3+}	0.18						

[a] Coordinates for space group $P2$. Standard errors in coordinates: oxygen x, $y \pm 0.001$, $z \pm 0.002$; silicon x, y, z and M1, M2 $y \pm 0.0005$. Individual isotropic temperature factors as follows: oxygens 0.4 ± 0.1 Å^2; silicon 0.17 ± 0.05 Å^2; M1 and M1(1)H 0.2 ± 0.1 Å^2; M1(1) and M1H 0.3 ± 0.1 Å^2; M2(1) 0.7 ± 0.1 Å^2; other M2 0.8 ± 0.1 Å^2.

[b] Coordinates converted by present authors from those of basic atom set; M1 is Al, M2 is Na. Individual isotropic temperature factors as follows: O1, 0.36 Å^2; O2, 0.48 Å^2; O3, 0.49 Å^2; Si, 0.41 Å^2; Al, 0.40 Å^2; Na, 0.95 Å^2.

[c] Nomenclature according to Burnham *et al.* (1967).

[d] Total occupancy of 1.00 assumed. The method does not distinguish between Fe^{2+} and Fe^{3+}; assignment of Fe^{3+} with Al and Fe^{2+} with Mg is arbitrary.

TABLE 6 (continued)

Atom[c]	Site occupancy[d]		Omphacite[a] present study			Jadeite[b] Prewitt and Burnham (1966)		
			x	y	z	x	y	z
$M1(1)H$	Mg^{2+} 0.80	Fe^{2+} 0.20	.500	.5957	.500	.500	.5940	.500
$M2$	Na^+ 0.64	Ca^{2+} 0.36	0	.3036	0	0	.3009	0
$M2(1)$	Na^+ 0.36	Ca^{2+} 0.64	0	.7017	.500	0	.6991	.500
$M2H$	Na^+ 0.03	Ca^{2+} 0.97	.500	.8009	0	.500	.8009	0
$M2(1)H$	Na^+ 0.64	Ca^{2+} 0.36	.500	.1996	.500	.500	.1991	.500

(1967). The final R is 0.08 for the 830 observed structure factors, and the observed and calculated structure factors are compared in Table 7.[1]

Description of structure. There are two characteristic features of the omphacite structure that distinguish it from other pyroxene structures. First, the octahedral chains along c, formed by $M1$ octahedra sharing edges, alternate (Al,Fe³⁺)-octahedra and (Mg,Fe²⁺)-octahedra. Similar octahedral chains occur in the structure of the amphibole, glaucophane (Papike and Clark, 1966). Second, the large $M2$ polyhedra that link the octahedral chains into layers are alternately occupied dominantly by either Na or Ca (Fig. 5). Layers adjacent along the a direction stack so that the (Mg,Fe²⁺)-octahedra of one layer have (Al,Fe³⁺)-octahedra above in the next layer, and a similar staggered arrangement prevails for

[1] Table 7 has been deposited as Document No. 9896 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C. 20540. A copy may be secured by citing the Document number and by remitting in advance $2.50 for photoprints or $1.75 for 35 mm microfilm. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE 8. BOND DISTANCES IN THE SILICATE TETRAHEDRA OF *P*2 OMPHACITE

Atoms	Distances[a] (Å), tetrahedron			
	Si1A	Si2A	Si1C	Si2C
Si-O1	1.63	1.64	1.59	1.60
Si-O2	1.63	1.57	1.60	1.57
Si-O3(1)	1.65	1.70	1.64	1.67
Si-O3(2)	1.66	1.66	1.63	1.68
Average	1.64	1.64	1.62	1.63
O1-O2	2.80	2.66	2.82	2.73
O1-O3(1)	2.66	2.72	2.61	2.66
O1-O3(2)	2.71	2.73	2.58	2.64
O2-O3(1)	2.66	2.63	2.61	2.66
O2-O3(2)	2.57	2.69	2.51	2.61
O3(1)-O3(2)	2.65	2.64	2.65	2.64
Average	2.67	2.68	2.63	2.66
Si1-Si2	3.06, 3.11		3.07, 3.12	

[a] Si-O distances ± 0.02Å, O-O distances ± 0.03 Å, Si-Si distances ± 0.01 Å.

the $M2$ cations. The four crystallographically distinct silicate tetrahedra are joined in pairs to form the two different tetrahedral chains. Within the restrictions of the structure, this relative freedom permits the best possible oxygen coordination for the variable cation content. Adherence to $C2/c$ symmetry would preclude such accommodation, and the lowering of the symmetry restrictions to $P2$ is thus reasonable.

Silicon-oxygen bonding. The sodium metasilicate structure (Grund and Pizy, 1952), which contains single silicate chains comparable to those in the pyroxenes, was recently refined by McDonald and Cruickshank (1967) with particular attention given to the Si-O bonding. In a discussion of π-bonding in second-row elements, Cruickshank (1961) suggested that there should be observable differences between the lengths of bridging and non-bridging atoms in chain silicates. Noll (1961) discussed the same feature from the viewpoint of electronic theory. The Si-O distances in omphacite (Table 8) are thus most meaningful when considered according to whether the oxygens are bridging (designated $03xx$ according to the nomenclature scheme of Burnham *et al.*, 1967) or non-bridging ($01xx$, $02xx$), and comparison with the corresponding values from the recent structural refinements of jadeite (Prewitt and Burnham, 1966), Na_2SiO_3 (McDonald and Cruickshank, 1967), and an ordered hyper-

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TABLE 9. BOND ANGLES IN THE SILICATE TETRAHEDRA AND
CHAINS OF *P*2 OMPHACITE

Oxygen atoms of O-Si-O angles	O-Si-O Angles,[a] tetrahedron			
	Si1A	Si2A	Si1C	Si2C
O1-O2	118°	112°	124°	119°
O1-O3(1)	109°	109°	108°	108°
O1-O3(2)	111°	112°	107°	106°
O2-O3(1)	109°	107°	107°	110°
O2-O3(2)	103°	113°	102°	107°
O3(1)-O3(2)	106°	104°	109°	103°

Oxygen atom	Si-O-Si Angles[a]	
	Chain A	Chain C
O3(1)	132°	137°
O3(2)	139°	130°

[a] Angles ± 1°.

sthene (Ghose, 1965) shows that the observed differences are indeed significant. For bridging Si-O, the following average values are found: omphacite, chain A, 1.67 Å; chain C, 1.65 Å; jadeite 1.632 Å, somewhat lower than the others; Na_2SiO_3, 1.672 Å; and hypersthene 1.66 Å. The average non-bridging Si-O values are appreciably smaller: omphacite, chain A, 1.62 Å, chain C, 1.59 Å; jadeite 1.614 Å; Na_2SiO_3, 1.592 Å; and hypersthene 1.60 Å. The differences between the two kinds of bonds range from about 0.02 Å in jadeite to 0.08 Å in omphacite and Na_2SiO_3. For the oxygen-oxygen distances within the tetrahedra (Table 8), the difference is smaller and in the reverse direction, probably as a result of the angular distortions described below. The average O-O distances in omphacite are 2.64 Å for the bridging pairs and 2.75 Å for the external pairs.

The variation among average O-Si-O angles also becomes significant when considered in the same way. All the O-Si-O angles for omphacite are given in Table 9, and the average for the sixteen angles containing both a bridging and a non-bridging oxygen is 108°, close to the tetrahedral value as might be expected. However, considering the O-Si-O angles containing bridging oxygen atoms only, we find in the various structures the following values: omphacite 105°, jadeite 106.3°, Na_2SiO_3 103.1°, and hypersthene 108.2°. The average values for the non-bridging O-Si-O angles are higher by about 10 to 13°: omphacite 118°, jadeite 118.5°, Na_2SiO_3 116.9°,

and hypersthene 117.5°. The suggestion by McDonald and Cruickshank (1967) that the angular distortion in the latter case results in part from charge repulsion that is greater between the nonbridging oxygen atoms appears to be a reasonable explanation of these observations.

The four distinct Si-O-Si angles in omphacite (Table 9) range from 130° to 139°, each chain alternating one smaller and one larger angle along the chain. The range is in accord with other observations: in jadeite, the single Si-O-Si angle is 139.3°; in Na_2SiO_3, 133.7°; and the two in hypersthene are 139.5° and 132.2°, respectively.

Cation-oxygen bonding. The assignment of cations to the $M1$ sites from the site refinement is confirmed by the $M1$-oxygen bond distances (Table 10). The averages for the two sites containing (Al,Fe^{3+}) are 1.94 Å and 1.95 Å, in reasonable agreement with the average Al-O distance in jadeite, 1.928 Å. Fe^{3+}-O distances are less well established, but apparently average about 1.99 Å, e.g. 1.989 Å in krausite (Graeber *et al.*, 1965) and in laueite (Moore, 1965). The averages for the two $M1$ sites containing (Mg,Fe^{2+}) are 2.06 Å and 2.10 Å, significantly higher than the (Al,Fe^{3+})-O average values, and in good agreement with the reported average value of 2.092 Å for the $Mg_{0.85}Fe_{0.15}^{2+}$-oxygen distance in hypersthene (Ghose, 1965).

Each $M2$ cation is coordinated by six oxygens at distances of about 2.4 Å, and two more at about 2.7 Å. The average distance for all eight taken over all four sites is 2.50 Å, with a range of 2.34 Å to 2.80 Å (Table 9). Such values are well established in numerous structures for both Na^+ and Ca^{2+}; the average Na-O distance in jadeite is 2.469 Å.

Charge balance and overall bonding features. Consideration of all the bond distances and angles in the omphacite structure, compared with values for related structures, shows that whereas the averages are generally the expected ones, the range of variation within each average is greater than for other metasilicates. To some extent, the presence of Ca in the structure may be responsible for this variation, and refinement of the structure of diopside, now in progress, will permit appropriate comparison and evaluation of this factor. However, another factor undoubtedly enters also. Omphacite appears to represent a natural triumph of chemical-bonding compromises within the framework of the pyroxene structure, and the range of observed distances and angles is indicative of these compromises.

Because of the differences observed between the distances to bridging and non-bridging oxygen atoms, it is evident that an evaluation of charge balance in the structure based on a simple ionic model will not be entirely

satisfactory. In fact, such a model provides the external O1 oxygens with a $+2.00$ charge received from two $M1$ neighbors, one $M2$ neighbor, and Si, but leaves the external O2 oxygens, each having one $M1$ neighbor, one $M2$ neighbor, and one Si, deficient by about 0.4, whereas the bridging O3 oxygens, with two $M2$ neighbors and two Si, receive an excess 0.4 charge. The variations in the bond distances are in the right direction to offset this apparent imbalance: long Si-O distances for the bridging oxygens and short Si-O distances for the more electronegative external O2 oxygens. Although the simple ionic model fails to explain the details of the bond variations, it does provide an indication of the direction in which the variations will occur.

CRYSTAL CHEMISTRY OF CLINOPYROXENES

Prewitt and Peacor (1964) have reviewed the general structural features of pyroxenes and pyroxenoids; all clinopyroxenes have these features, whatever the individual symmetry. In particular, all clinopyroxenes contain the metasilicate chains (*zweierketten*), arranged so that eight locations per unit cell are available for cations other than those in the tetrahedral chains. Some of the distinctions that may affect the symmetry were pointed out by Morimoto *et al.* (1960). The results of recent studies suggest that these and other distinctions are caused by variations in the chemical compositions.

In the $C2/c$ structures, the metasilicate chain is formed by repetition of one tetrahedron by the c glide plane (the bridging oxygen, O3, lying very nearly in this plane), a layer of like chains parallel to (100) is built up by the operation of 2_1 axes, and other identical layers are formed by the C-centering. This symmetrical arrangement leaves spaces of two different sizes, surrounding twofold axes. Small cations such as Mg fit into the regular, octahedrally coordinated $M1$ spaces, and larger ones such as Ca fit into the eight-cornered, polyhedral $M2$ spaces. The maximum symmetry possible to clinopyroxenes is thus achieved, and compounds of the following compositions are known to have this symmetry: $CaMgSi_2O_6$, diopside; $CaFe^{2+}Si_2O_6$, hedenbergite; $CaMnSi_2O_6$, johannsenite; $NaAlSi_2O_6$, jadeite; $NaFe^{3+}Si_2O_6$, acmite, and $NaCr^{3+}Si_2O_6$, ureyite (Kosmochlor). Mean cation-oxygen distances for most of these cations are given in Table 11, and the difference between pairs in all of the above compounds is about 0.4 to 0.6 Å.

When the size difference diminishes, as in $LiAlSi_2O_6$, spodumene, to about 0.2 Å, or vanishes, as in $MgSiO_3$, clinoenstatite, and $FeSiO_3$, clinoferrosilite (Burnham, 1967), the larger polyhedra can no longer be adequately filled. The structure must shift somewhat to obtain smaller spaces for the $M2$ cations, and this is accomplished either by rearranging

the chain linkages within a chain or by altering the packing sequence. In spodumene, Appleman and Stewart (1966) found rearrangement of the chain linkages, each chain being formed with two crystallographically distinct tetrahedra, so the *c* glide symmetry is lost. Other symmetry elements remain, however, because the layers and their stacking are still related by the 2_1 axes and the *C*-centering, respectively, so the spodumene space-group is *C*2. For clinoenstatite, Morimoto *et al.* (1960) found that the packing sequence was shifted, each layer still being made up of 2_1 related chains, but the chains of one layer differing from those in the next, thus eliminating the *C*-centering. In order to achieve the best coordination, the cations move away from the former twofold axes, and the symmetry of clinoenstatite reduces to $P2_1/c$.

Clinopyroxenes with space-groups $P2_1$, *Pc*, *Cc*, and $P2/c$ have not yet been reported, but they appear to be structurally feasible for various rearrangements of the metasilicate chains, and their observation would not be surprising, especially in naturally occurring clinopyroxenes of variable compositions. The basic pyroxene structure cannot accommodate to the symmetry of a mirror plane, and observation of any such monoclinic space groups would mean the occurrence of a new structure type.

The omphacite, with its *P*2 symmetry, has nearly the maximum freedom possible for rearrangement of the chains, a feature undoubtedly necessitated by the requirements of the multiple cation contents. However, if the cation distribution were random within each of the *M*1 and *M*2 site groups respectively, small deviations of the chain oxygens might not be observed, and $C2/c$ symmetry would be reported for such dis-

TABLE 10. CATION-OXYGEN DISTANCES[a] IN *P*2 OMPHACITE

Oxygen atoms	M1 Cations				M2 Cations			
	M1 Mg 0.81 Fe 0.19	M1(1)H Mg 0.80 Fe 0.20	M1(1) Al 0.95 Fe 0.05	M1H Al 0.82 Fe 0.18	M2 Na 0.64 Ca 0.36	M2(1)H Na 0.64 Ca 0.36	M2(1) Na 0.36 Ca 0.64	M2H Na 0.03 Ca 0.97
O1(1)A	2.12 Å		1.91 Å		2.39 Å		2.32 Å	
O1(2)A	2.09		2.03					
O1(1)C		2.07		1.97 Å				2.46 Å
O1(2)C		2.16		1.99		2.33 Å		
O2(1)A				1.91		2.35		
O2(2)A		2.06						2.44
O2(1)C	2.01						2.33	
O2(2)C			1.88		2.39			
O3(1)A						2.67		2.49
O3(2)A						2.43		2.79
O3(1)C					2.51		2.76	
O3(2)C					2.73		2.48	
Average	2.07 Å	2.10 Å	1.94 Å	1.95 Å	2.50 Å	2.44 Å	2.47 Å	2.55 Å

[a] Distances ± 0.02 Å; each distance occurs twice in the same polyhedron.

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TABLE 11. MEAN CATION-OXYGEN DISTANCES FOR OCTAHEDRAL COORDINATION

Atoms	Average distances (Å)	References
Al-O	1.93	Prewitt and Burnham (1966)
Fe^{3+}-O	2.03	Graeber *et al.* (1965); Moore (1965); Blake *et al.* (1966)
Fe^{2+}-O	2.14	Burnham (1967)
Mg-O	2.09	Ghose (1965)

Atoms	Differences in average distances (Å)	Compositional joins
$(Fe^{2+}$-O)-(Mg-O)	0.05	He-Di
(Mg-O)-$(Fe^{3+}$-O)	0.06	Di-Ac
$(Fe^{3+}$-O)-(Al-O)	0.10	Ac-Jd
$(Fe^{2+}$-O)-$(Fe^{3+}$-O)	0.11	He-Ac
(Mg-O)-(Al-O)	0.16	Di-Jd
$(Fe^{2+}$-O)-(Al-O)	0.21	He-Jd

ordered clinopyroxenes. The ordered $P2$ structure probably results because the size requirements of the Al-O octahedron (Tables 10, 11) force ordering into the octahedral chains, thus encouraging segregation of Na and Ca in the $M2$ sites to achieve, insofar as possible, univalent cation polyhedra near the trivalent cation octahedra and divalent cation polyhedra near the divalent cation octahedra (Fig. 5). The $P2$ structure is not observed for the aegirine-augites, such as $Na_{0.5}Ca_{0.5}Mg_{0.5}Fe_{0.5}^{+3}Si_2O_6$ (Klein, 1966), partly because the ferric iron octahedra are nearly the same size as the Mg octahedra (Tables 10, 11) so ordering is not encouraged. The higher temperatures of formation (about 600°C, Klein, 1966) for these clinopyroxenes also tend to inhibit ordering. Solid solutions between jadeite and diopside-hedenbergite appear to be logical candidates for $P2$ ordering (Table 11), and such omphacites are therefore expected to be restricted to a narrow compositional range in the Jd-Ac-Di-He system (Figures 2 and 3), characterized by having $Na/(Na+Ca) \approx 0.5$ and an octahedral cation ratio, $Al/(Al+Fe^{3+}) > 0.6$.

PETROLOGICAL IMPLICATIONS OF $P2$ OMPHACITES

Evidence available to date suggests that $P2$ omphacites are characteristic of rocks of basaltic composition that have been metamorphosed under glaucophane schist facies conditions, *i.e.* temperatures 200° to 300°C with pressures of 6 to 9 kbars, according to evidence presented by several authors (*e.g.* Coleman and Lee, 1963; Ernst, 1963; Coleman, 1966;
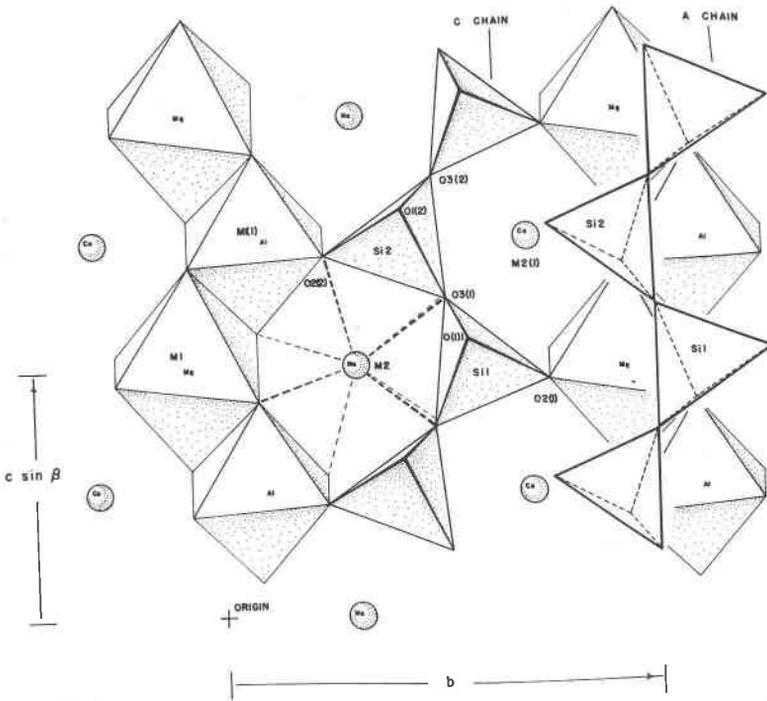
Fig. 5. View along a of selected portions of the omphacite structure. The octahedral chains near $x=0$ are shown, together with the A and C tetrahedral chains, and the larger cations at $x=0$. Dashed lines indicate the oxygen coordination around an $M2$ cation.

Fyfe and Turner, 1966; Coleman and Clark, 1968; Coleman and Papike, 1968; Essene and Fyfe, 1967). Experimental studies of the reaction

$$CaMgSi_2O_6 + xNaAlSi_3O_8 = CaMgSi_2O_6 \cdot xNaAlSi_2O_6 + xSiO_2$$

diopside   albite   omphacite
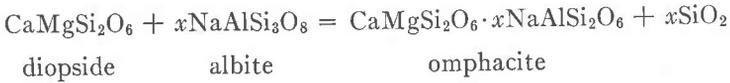
by Kushiro (1965) support this hypothesis by demonstrating that the high concentration of $NaAlSi_2O_6$ in $P2$ omphacite is consistent with physical conditions of the glaucophane schist facies. Green and Ringwood (1966) suggest that eclogites may form under physical conditions realized within the earth's crust, and we suggest further that eclogites so formed will be characterized by the presence of $P2$ omphacites which have the highly ordered cation distributions necessary to minimize volume under high pressure-low temperature conditions of formation.

Synthesis of $P2$ omphacites may be difficult to achieve experimentally because of the slow reaction rates associated with the formation of such highly ordered compounds at low temperatures. Nevertheless, synthetic

studies at low temperature in the natural omphacite compositional range are necessary if the phase diagrams are to be correctly related to the natural occurrences. Meanwhile, the occurrence of $P2$ omphacites is established in Type C eclogites along the Pacific from California through Guatemala into Colombia, and again in New Caledonia; the omphacite from Japan (Hashimoto, 1964) is expected to have $P2$ symmetry, according to its composition. These occurrences thus provide additional evidence that physical conditions of metamorphism and eclogite genesis have been similar throughout the Circumpacific belt.

Summary

The principal conclusions of this study may be summarized as follows. First, omphacite is defined within the system Jd-Ac-Di-He-Tsch as having the composition $(M2)(M1)(Si,Al)_2O_6$, where $M2$ represents Na $+$ Ca in the range $0.2 \leq Na/(Na+Ca) \leq 0.8$, and $M1$ is divided among the octahedral cations Mg, Fe^{2+}, Al and Fe^{3+} such that $Al/(Al+Fe^{3+}) \geq 0.5$. The amount of tetrahedrally coordinated Al is expected to be small. According to this definition, omphacites may occur within any kind of rocks and are no longer restricted to eclogites. Second, those omphacites having space group $P2$ are called $P2$ omphacites and are expected to lie within a narrow compositional range, having $Na/(Na+Ca) \approx 0.5$, and octahedrally coordinated Al contents greater than those of Fe^{3+}. Third, the crystal structures of $P2$ omphacites contain ordered cation distributions, with (Mg,Fe^{2+})-octahedra alternating with (Al,Fe^{3+})-octahedra to form $M1$ octahedral chains. Fourth, the bonding within the $P2$ omphacite structure accords with the distinctions proposed by Cruickshank (1961) between bridging and nonbridging oxygen atoms, the average Si-O distance for the bridging oxygens being 1.66 Å compared with 1.60 Å for the nonbridging oxygens. Fifth, $P2$ omphacites have so far been found only in environments where low temperature-high pressure formation conditions are otherwise indicated, so these omphacites may be useful indicators of these formation conditions.

grams and information about the jadeite structure in advance of publication. Mr. Larry W. Finger, University of Minnesota, Minneapolis, Minnesota, kindly arranged calculations for the powder intensities (Table 3).

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APPENDIX ON COMPUTATIONS

The IBM 7094 computer programs used in the crystal structure refinement were principally from X-ray 63 Program System for X-ray Crystallography by James M. Stewart and Darrell High. This is an unpublished program system of the University of Maryland, College Park, Maryland, and the University of Washington, Seattle, Washington. A special program written by D. E. Appleman, U. S. Geological Survey, was incorporated into the system to convert the measured diffraction data into structure amplitudes. Absorption corrections were made following a program incorporated into this program system, and written by Dr. C. W. Burnham, Geophysical Laboratory, Carnegie Institution, Washington D. C.[1] Atomic scattering factors are reproduced from the tables in *International Tables for X-ray Crystallography*, Vol. III, 1962 (The Kynoch Press: Birmingham, England); values for neutral atoms were selected. Dispersion corrections for MoKα radiation were taken from this same source. The least-squares program uses the full matrix of the normal

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equations and was adapted from the FORTRAN coding of W. R. Busing, K. O. Martin, and H. A. Levy (ORNL-TM-305, Oak Ridge National Laboratory). Unit weights were used exclusively after some trial cycles with a weighting scheme based on the counter statistics proved unsatisfactory, because it maximized the contributions of the strong reflections (those corresponding to the pseudo-$C2/c$ structure) and minimized the contributions of the weak reflections (important in defining the $P2$ structure).

For the site occupancy refinements, a program developed by Drs. C. T. Prewitt, E. I. duPont de Nemours Corp., Wilmington, Delaware, and C. W. Burnham was used. This program requires scattering factors calculated as described by Silverman and Simonsen (1960); coefficients appropriate to ionized atoms were used, Fe^{3+} being taken for all Fe atoms. The residual R quoted in the text is calculated according to the relation, $R = \Sigma |\Delta F| / \Sigma |F_{obs.}|$.

The powder pattern intensities (Table 3) were calculated using a computer program written by D. K. Smith (Report U.C.R.L. 7196, Lawrence Radiation Laboratory, 1963) and revised by Mr. Cyrus Jahanbagloo, University of Minnesota.