Eclogitic Pyroxenes, Ordered with P2 Symmetry

Abstract. *X-ray diffraction crystal-structure analysis of omphacite from eclogite, Tiburon Peninsula, Marin County, California, shows that this clinopyroxene has* P2 *symmetry with a nearly ordered distribution of the multiple cation content defined by its approximate formula:* $(Na_{0.5}Ca_{0.5})(Mg_{0.4}Fe^{2+}_{0.1}Al_{0.4}Fe^{3+}_{0.1})Si_2O_6$. Na^+ *and* Ca^{2+} *tend to assume alternate locations in the structure, and* (Mg,Fe^{2+}) *octahedra alternate with* Al^{3+} *or* (Al,F^{3+}) *octahedra in chains along* c.

Single-crystal, x-ray diffraction examination of the clinopyroxene, omphacite, from eclogite, Tiburon Peninsula, Marin County, California, was initiated to refine the crystal structure and thus to obtain information about the degree of ordering of the multiple cation content. Omphacite was assumed to have a structure similar to that originally described for diopside (*1*), $CaMgSi_2O_6$, and recently confirmed and refined for jadeite (*2*), $NaAlSi_2O_6$. The *C*-centered *C*2/*c* space-group symmetry characteristic of these structures has been reported by Warner (*3*), and subsequently confirmed by us, for omphacite from Norwegian eclogite.

X-ray diffraction powder patterns of a number of different omphacite samples from California and New Caledonia eclogites associated with glaucophane schists (*4*) can be indexed completely with *hkl* indices compatible with *C*2/*c* symmetry (*hkl* present for $h + k = 2n$ only; *h*0*l*, for $h = 2n$ and $l = 2n$). However, single-crystal patterns reveal the presence of weak reflections violating the *C*2/*c* criteria and lowering the symmetry to a choice between the primitive space-groups, *P*2/m or *P*2. Because the intensity distribution indicates similar structures for jadeite and omphacite, and atomic coordinates related to those of the jadeite structure cannot be assigned in the presence of mirror planes (*P*2/*m*), the omphacite space group must be *P*2.

The monoclinic unit-cell constants for the omphacite crystal selected for structural study (*4*, sample 100-RGC-58) are: *a* 9.596 Å, *b* 8.771 Å, *c* 5.265 Å, *β* 106°56′; the cell volume is 423.9 Å^3. The composition of the crystal, according to an analysis of the bulk sample (*4*), is $(Na_{0.48}Ca_{0.51})(Mg_{0.44}Fe^{2+}_{0.10}Al_{0.39}Fe^{3+}_{0.10})Si_2O_6$. No evidence of any inhomogeneity was found during electron-microprobe scans across several crystals in various orientations.

Three-dimensional counter-measured intensities for 1297 reflections were collected on the single-crystal goniostat using molybdenum radiation; 836 of these intensities are greater than twice the background value and were used in the refinements that were carried out by Fourier and by full-matrix, least-squares methods. The initial atomic coordinates were appropriately converted from those found for jadeite (*2*), and, once the locations of silicon and oxygen atoms were determined, various models for ordering the six cations, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, and Fe^{3+}, among the eight available sites, as well as a model with complete disorder, were tested. Among the 299 weak reflections violating *C*2/*c* symmetry, the *h*0*l* with *h* and *l* odd are found to occur with measurable intensities only for a particular ordered distribution of Na^+ and Ca^{2+}. Therefore, such an ordered model was assigned, and site-occupancy refinements were carried out by least-squares methods (*5*); full occupancy of each site was assumed. The residual factor dropped from an initial value of 0.43 to a final value of 0.07 for all the data. The final atomic coordinates, individual isotropic temperature factors, and site-occupancy values are given in Table 1.

The omphacite structure is illustrated in Fig. 1. The structure contains two distinct pyroxene-type chains, formed by joining in pairs four different Si—O tetrahedra, in contrast to jadeite, which contains only one kind of chain, formed by repetition of only one symmetrically distinct tetrahedron (*2*). Whereas the *C*2/*c* structure has one crystallographic site for Na^+ and a second for Al^{3+}, the omphacite structure has eight different sites among which the variable cation content can be distributed. The larger cations, Na^+ and Ca^{2+}, tend to occupy alternate sites, although the ordering is not complete.

On the level at $x = 0$, one site is wholly occupied by Ca^{2+}, and the other has a 2 : 1 Na : Ca ratio. Similarly, the two sites at $x = ½$ alternate in contents, one having 2 : 1 Na : Ca, and the next, 1 : 2 Na : Ca. The smaller cations are surrounded by oxygen octahedra which share edges to form chains parallel to *c*, and on each level the octahedra alternate within the chain, one being (Mg,Fe^{2+}), and the next, either Al or (Al,Fe^{3+}). The total values for each cation species, determined from the site occupancy refinement, agree reasonably well with those of the bulk analysis: Ca 0.59 (0.51 analysis); Na 0.41 (0.48 analysis); Fe 0.16 (0.20 analysis); Mg 0.40 (0.44 analysis); Al 0.44 (0.39 analysis). Furthermore, the Al^{3+}, (Al,Fe^{3+}), and (Mg,Fe^{2+}) site assignments are confirmed by comparison of the average cation-oxygen distances for each site with known values

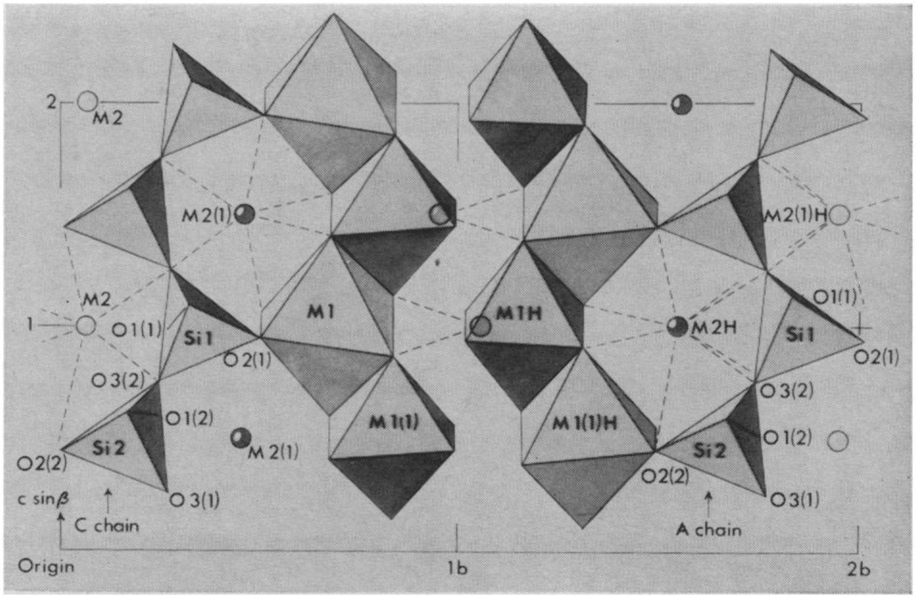

Fig. 1. View along *a* of the omphacite structure, showing the four distinctive chains, two tetrahedral and two octahedral (Table 1). H designates the cations at $x = ½$. Shadings indicate site contents: dark octahedra, Al/Fe^{3+}; pale octahedra, Mg/Fe^{2+}; dark circles, Ca^{2+}; pale circles, Na^+. Dashed lines indicate some of the oxygen bonds to Ca^{2+} or Na^+ cations.

(*6*): 1.942 Å and 1.948 Å, respectively, for the Al^{3+} and (Al,Fe^{3+}) sites; 2.060 Å and 2.104 Å respectively, for the (Mg,Fe^{2+}) sites. There is no evidence shown on electron-density or difference Fourier sections for segregation of Fe^{2+} in any site.

Similarly alternating octahedral chains are present in the structure of the sodium amphibole, glaucophane (*7*), and the reported pseudomorphism of omphacite by glaucophane (*8*) may be partially explained by this feature common to the two structures.

Table 1. Atomic coordinates, temperature factors, and cation site occupancy factors for omphacite from Tiburon Peninsula, Marin County, Calif.

Atom*; site occupancy†	Coordinates‡			Isotropic B (Å^2) §
	x	y	z	
O1(1)A	0.111	0.833	0.861	0.8
O1(2)A	.110	.673	.406	.5
O1(1)C	.384	.314	.102	.3
O1(2)C	.383	.160	.618	(.3)
O2(1)A	.365	.013	.063	.3
O2(2)A	.348	.497	.553	(.3)
O2(1)C	.133	.499	.942	.3
O2(2)C	.137	.994	.442	.3
O3(1)A	.356	.772	.754	.4
O3(2)A	.350	.744	.251	.4
O3(1)C	.153	.265	.258	.2
O3(2)C	.147	.237	.751	.2
Si 1 A	.2876	.8469	.9768	.23
Si 2 A	.2873	.6633	.4804	.25
Si 1 C	.2136	.3384	.0196	.20
Si 2 C	.2104	.1521	.5244	.15
M 1	0	.6619	0	.3
Mg^{2+} 0.81				
Fe^{2+} 0.19				
M 1(1)	0	0.8500	0.500	.4
Al^{3+} 0.95				
Fe^{3+} 0.05				
M 1 H	0.500	.1545	0	.4
Al^{3+} 0.82				
Fe^{3+} 0.18				
M 1(1) H	.500	.3451	0.500	.3
Mg^{2+} 0.80				
Fe^{2+} 0.20				
M 2	0	.0538	0	.8
Na^+ 0.64				
Ca^{2+} 0.36				
M 2(1)	0	.4515	0.500	.7
Na^+ 0.36				
Ca^{2+} 0.64				
M 2 H	0.500	.5507	0	.8
Na^+ 0.03				
Ca^{2+} 0.97				
M 2(1) H	.500	.9497	0.500	.8
Na^+ 0.64				
Ca^{2+} 0.36				

* Atom designations assigned by analogy to jadeite (*2*), according to nomenclature described by Burnham *et al.* (*10*). Different tetrahedral chains are designated A and C; the small, octahedrally coordinated cations, M 1; the large eightfold coordinated cations, M 2. † Approximate standard errors in site occupancy factors, ±0.02. A total occupancy of 1.0 for each site was assumed. ‡ Approximate standard errors: Si x, y, z and M 1, M 2 y, ±0.0005; oxygen x, y, ±0.001, z ±0.002. Transformation to compare with jadeite coordinates, $y + 1/4$, $z + 1/4$. § Approximate standard errors in B: Si ± 0.05 Å^2; oxygen, M 1, M 2 ± 0.1 Å^2. Temperature factors in parentheses were fixed.

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Crystal Structure of the Zeolite Paulingite

Abstract. *Paulingite, a zeolite, has a framework structure consisting of 2016 atoms (672 silicon or aluminum and 1344 oxygen) which are in a cubic cell with an edge of length 35.093 Å. The framework has several features in common with the synthetic zeolites Linde A and ZK-5; the main channels are of similar size. We have also located most of the cations and water molecules inside the framework.*

The mineral Paulingite was identified by Kamb and Oke (*1*) as a zeolite exhibiting a cubic structure with $a = 35.10 \pm 0.02$ Å and probable space group $Im3m$ $(O_h{}^9)$.

Our x-ray studies have led to a structure determination of the zeolite framework. We have also located most of the water molecules and metal ions inside the cages. The structure is consistent with space group $Im3m$. A more accurate value of the length of the cube edge, $a = 35.093 \pm 0.002$ Å, was determined.

The crystal used for our x-ray studies was one-half of a rhombic dodecahedron 0.2 mm in size. Intensities of the diffracted x-rays were measured with a Datex automated, General Electric XRD-5 diffractometer (nickel-filtered CuK_α radiation) equipped with the one-quarter-circle Goniostat. We examined 4185 symmetrically independent reflections out to a diffraction angle of $2\theta = 155°$ by scanning 2θ. Of these, 1190 were too weak to be measured.

The structure of the zeolite framework was determined by fitting the most prominent Patterson vectors into Samson's (*2*) packing maps for the (100) and (110) planes. The framework consists of 2016 atoms (672 silicon and aluminum, 1344 oxygen) and constitutes enough scattering matter to allow calculation of valid Fourier syntheses. Electron-density maps thus showed the locations of 88 metal ions (K, Ca, Na, Ba) and 452 water molecules. Because of difficulty in discriminating between the metal ions or mixture thereof they shall be called $M_{1,2,3}$, and so forth.

The parameters of these 2556 atoms and water molecules, distributed among the 45 different positions listed in Table 1, were refined by full-matrix, least-squares calculations with the use of data from the reflection range $14° < 2\theta < 155°$. The agreement index

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$$

for the 3900 reflections used is 0.14 and establishes confidence in the correctness of the basic structure.

The x-ray structure analysis gives the number of silicon-aluminum atoms (672) and the corresponding framework-oxygen atoms (1344) in the unit cell. The Si/Al ratio and the cation content were determined approximately by electron-microprobe analysis, and the water content, by weight loss on heating. The unit cell thus contains 520 Si, 152 Al, 1344 O, 68 K, 36 Ca, 13 Na, 1.5 Ba, and 705 H_2O.

Accordingly, about 250 more water molecules and about 30 more cations have yet to be located by x-ray structure analysis. Difference-Fourier maps indicate that these are arranged in a