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A proposed crystallographic nomenclature for clinopyroxene structures

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Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Um die Strukturdaten der Klinopyroxene besser vergleichen zu können, wird eine einheitliche kristallographische Nomenklatur, die auf alle Klinopyroxene mit Strukturen ähnlich der des Diopsids anwendbar ist, vorgeschlagen und erläutert.

Abstract

In order to facilitate comparison of clinopyroxene structural data, a uniform crystallographic nomenclature applicable to all clinopyroxenes having structures similar to that of diopside is proposed and illustrated.

1. Introduction

The need for precise crystal-chemical data for a wide variety of pyroxene minerals has led to several recent studies using x-ray diffraction methods, infrared-absorption spectroscopy, Mössbauer spectra, nuclear-magnetic resonance and electron-spin resonance techniques. In large part such studies have been designed to examine the problems of cation distribution, and related polymorphism and order-disorder phenomena. Collation and comparison of results would be simplified by adoption of a systematic nomenclature scheme for the clinopyroxene structures, just as the treatment of structural problems in feldspars has been made easier by general use of the nomenclature scheme proposed by Megaw (1956). In the present paper, we outline a scheme suitable for all clinopyroxene structures similar to that of diopside, and designed to meet three major objectives. First, it is easy to become acquainted with, and hence, to use. Second, it is applicable to any monoclinic or triclinic space-group symmetry. Third, it is compatible with computer operations, because it contains no superscripts, subscripts or lower-case letters. The latter feature also reduces the likelihood of errors occurring during typesetting.

2. Description of the clinopyroxene structure

The crystal structure of diopside, $CaMgSi_2O_6$, was determined in 1928 by Warren and Bragg. Its basic features are well known, and general descriptions are given by Deer, Howie and Zussman (1963),

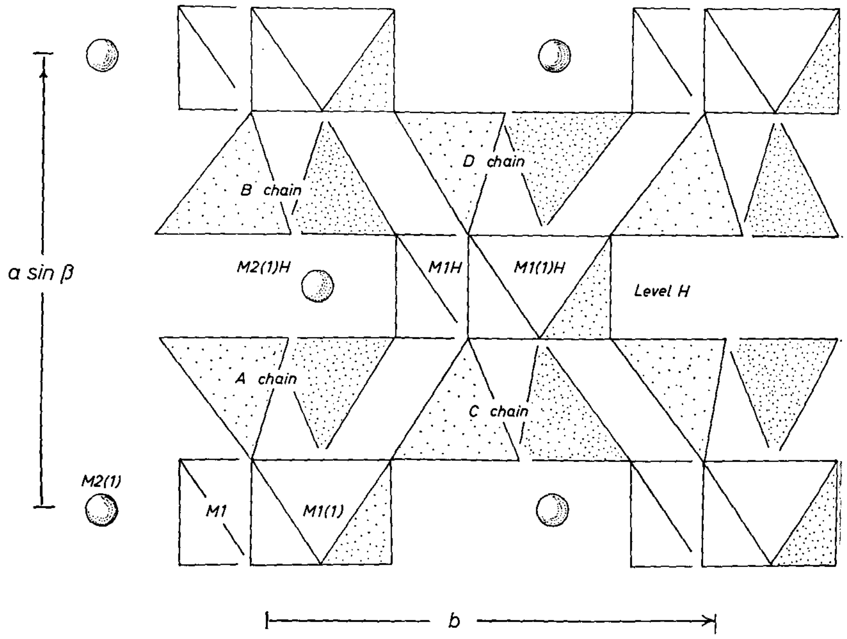

Fig. 1. Schematic view along c of the jadeite structure from coordinates by Prewitt and Burnham (1966), illustrating the alternation of tetrahedral chain layers with polyhedral cation layers. The origin lies at the lower left of the figure between the M1 and M1(1) octahedra. Tetrahedral chains A, B, C, D are identified (Table 3), and some M1 and M2 sites are shown (Table 2)

and by Bragg and Claringbull (1965); a comparison of various pyroxene and pyroxenoid structures has been made by Prewitt and Peacor (1964). The single silicate chains run parallel to the c axis, and have a repeat length of approximately 5.2 Å. These tetrahedral chains line up to form layers parallel to (100), and the Ca and Mg cations are sandwiched between, so that cation layers alternate with the tetrahedral chain layers (Fig. 1). The Mg cations are coordinated octahedrally by three oxygen atoms from the layer above and three from the layer below; the octahedra share edges to form chains parallel to c (Fig. 2). The distance separating octahedral chains in one layer corresponds to the b dimension of the unit cell. The Ca

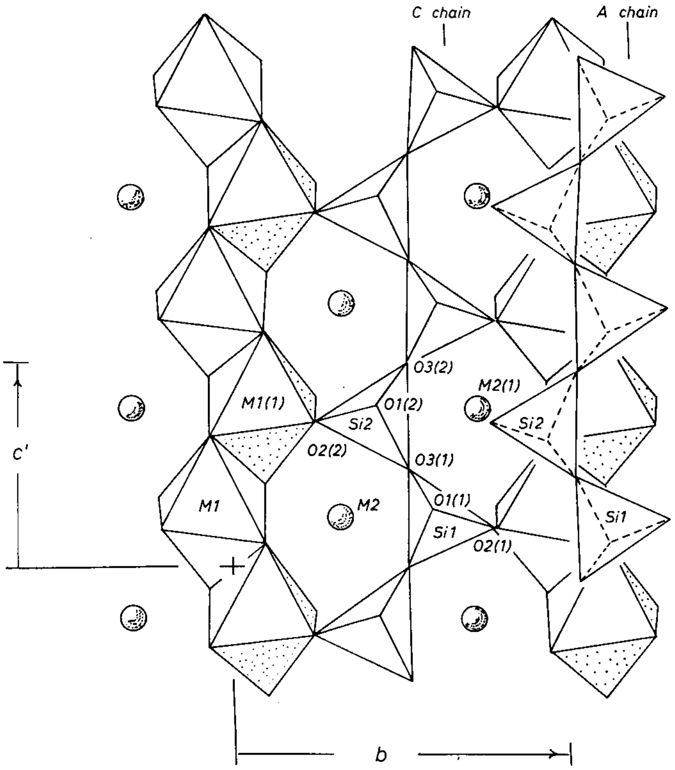

Fig. 2. View of jadeite structure along a line near a, adapted from Prewitt and Burnham (1966), Fig. 1. Cell contents shown from 0 to $\frac{1}{2}a$ only; origin is indicated by a cross near the M 1 octahedron. A and C chains and individual atomic sites are labelled as in Table 3; M 1 and M 2 sites, as in Table 2

Table 1. *Unit-cell parameters and chemical formulas for some clinopyroxenes**

	Diopside NOLAN and EDGAR (1963)	Jadeite PREWITT and BURNHAM (1966)	Acmite NOLAN and EDGAR (1963)	Clinoenstatite MORIMOTO *et al.* (1960)	Omphacite CLARK and PAPIKE (1966)	Spodumene APPLEMAN and STEWART (1966)
a (Å)	9.748	9.418 ± 1	9.658	9.620 ± 5	9.596 ± 5	9.449 ± 3
b (Å)	8.924	8.562 ± 2	8.795	8.825 ± 5	8.771 ± 4	8.386 ± 1
c (Å)	5.251	5.219 ± 1	5.294	5.188 ± 5	5.265 ± 6	5.215 ± 2
β	105° 40.4′	107° 34.8′ ± 0.6′	107° 25.2′	108° 20′ ± 10′	106° 56′ ± 4′	110° 06′ ± 1.7′
Cell volume (Å^3), $Z = 4$	(439.8)**	401.2	429.1	(418.1)**	423.9	(388.1)**
Space group	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$	$P2$	$C2$
Chemical formula	$CaMgSi_2O_6$	$NaAlSi_2O_6$	$NaFeSi_2O_6$	$Mg_2Si_2O_6$	$Ca_{0.5}Na_{0.5}(Mg, Fe^{2+})_{0.5}(Al,Fe^{3+})_{0.5}Si_2O_6$	$LiAlSi_2O_6$

* Errors apply to the last digit given, i.e. 9.418 ± 1 means 9.418 ± 0.001 Å. The unit cell contains four formula units.

** Values in parentheses calculated by present authors. NOLAN and EDGAR (1963) give 439.5 Å^3 for diopside cell volume.

cations are coordinated by eight oxygen atoms, and each Ca polyhedron shares edges with three adjacent Mg octahedra located in the same chain. The distance required for four alternating tetrahedral and cationic layers corresponds to the *a* unit-cell dimension (Fig. 1).

Diopside has $C2/c$ symmetry. WARREN and BRAGG (1928) chose a monoclinic cell with β acute, following the description given by WYCKOFF and MERWIN (1925). Since then, however, the use of a right-handed axial system with β obtuse has become conventional (*International tables for x-ray crystallography,* 1959); a discussion of problems resulting from the earlier choice of cell is given by WHITTAKER (1961) for amphiboles. We urge that the modern convention be followed in all future studies of clinopyroxenes. Some representative unit-cell parameters and chemical formulas are given in Table 1.

3. Space-group symmetries of clinopyroxenes

Single-crystal x-ray diffraction studies of a number of clinopyroxenes were carried out by WARREN and BISCOE (1931), who correctly concluded that jadeite, acmite, hedenbergite, augite, clinoenstatite, and spodumene had structures similar to that of diopside. For the next thirty years, these clinopyroxenes were all assumed to have the $C2/c$ symmetry characteristic of diopside. However, MORIMOTO (1956) showed that the symmetry of clinoenstatite and pigeonite is actually $P2_1/c$, and BURNHAM (1967) found that clinoferrosilite also had this symmetry. Spodumene was found to have $C2$ symmetry (APPLEMAN and STEWART, 1966) and the eclogitic clinopyroxene, omphacite, to have $P2$ symmetry (CLARK and PAPIKE, 1966). The reflections violating the $C2/c$ symmetry criteria (hkl with $h + k = 2n$ only, $h0l$ with $l = 2n$ only) are always weak and usually observed only on long-exposure, single-crystal, x-ray diffraction photographs — not on powder patterns.

Recent single-crystal photographs of diopside, acmite and jadeite do not reveal any reflections incompatible with assignment of $C2/c$ symmetry, and the crystal structure of jadeite has been successfully refined using that symmetry (PREWITT and BURNHAM, 1966). Diopside, acmite and jadeite may therefore be safely considered $C2/c$ clinopyroxenes and, by analogy, hedenbergite may also. Because refined atomic coordinates are available for jadeite, and its unit cell has been chosen in accordance with modern conventions, we shall use jadeite as the type example for the proposed nomenclature.

Theoretically, a structure similar to that of jadeite might fit the symmetry requirements of any monoclinic space group that does not contain mirror planes. Either of the two triclinic space groups is also theoretically possible. Not yet observed, but possible, therefore, are $P1$, $P\bar{1}$, $P2_1$, Pc, Cc and $P2/c$. The proposed nomenclature fits these space groups as well as the observed ones: $P2$, $C2$, $P2_1/c$ and $C2/c$.

4. Choice of origin

A single origin cannot be chosen that satisfies the conventions in *International tables for x-ray crystallography* (1952) for all the known pyroxene space-groups. We recommend, therefore, that priority be given to selecting the origin so as to satisfy the conventions while moving the least possible distance from the origin defined by the jadeite coordinates. The conversion necessary to return to the jadeite origin point from the origin selected for another space group should be given; in $P2$, for example, the conversion to the $C2/c$ origin is $0\ 0\ \frac{1}{4}$. For space groups such as $P2$, in which the origin must be fixed arbitrarily, we suggest fixing the coordinates of one of the heaviest cations so that, with the appropriate conversion, they are the same as those of one Na or Al cation in jadeite (Table 2).

Table 2. *Proposed nomenclature applied to the* Na *and* Al *atomic sites in jadeite* (See Figs. 1 and 2)

Atom	Site designation	Coordinates			Equivalent positions 4(*e*) in $C2/c$
		x	y	z	
Al	M1	0	0.9060	0.25	$0, y, \frac{1}{4}$
	M1(1)	0	0.0940	0.75	$0, 1-y, \frac{3}{4}$
	M1H	0.50	0.4060	0.25	$\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}$
	M1(1)H	0.50	0.5940	0.75	$\frac{1}{2}, \frac{1}{2}-y, \frac{1}{4}$
Na	M2	0	0.3009	0.25	$0, y, \frac{1}{4}$
	M2(1)	0	0.6991	0.75	$0, 1-y, \frac{3}{4}$
	M2H	0.50	0.8009	0.25	$\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}$
	M2(1)H	0.50	0.1991	0.75	$\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4}$

y coordinates from PREWITT and BURNHAM (1966).

5. Atomic notation

The pyroxene unit cell contains eight cations such as Mg, Al, Fe, Ca, Na, etc., plus 24 oxygen and eight tetrahedrally coordinated (Si, Al, Fe) atoms, the latter two kinds joined to make four tetrahedral

Table 3. *Proposed nomenclature applied to the sites of tetrahedral chain atoms in jadeite*
(See Figs. 1 and 2)

Atom	Site designation	Tetrahedral chain											
		A			B			C			D		
		x	y	z	x	y	z	x	y	z	x	y	z
Si	T1	0.2906	0.0934	0.2277	0.7094	0.0934	0.2723	0.2094	0.5934	0.2723	0.7906	0.5934	0.2277
	T2	0.2906	−0.0934	0.7277	0.7094	−0.0934	0.7723	0.2094	0.4066	0.7723	0.7906	0.4066	0.7277
O1	O1(1)	0.1090	0.0763	0.1275	0.8910	0.0763	0.3725	0.3910	0.5763	0.3725	0.6090	0.5763	0.1275
	O1(2)	0.1090	−0.0763	0.6275	0.8910	−0.0763	0.8725	0.3910	0.4237	0.8725	0.6090	0.4237	0.6275
O2	O2(1)	0.3608	0.2630	0.2929	0.6392	0.2630	0.2071	0.1392	0.7630	0.2071	0.8608	0.7630	0.2929
	O2(2)	0.3608	−0.2630	0.7929	0.6392	−0.2630	0.7071	0.1392	0.2370	0.7071	0.8608	0.2370	0.7929
O3	O3(1)	0.3533	0.0070	0.0058	0.6467	0.0070	0.4942	0.1467	0.5070	0.4942	0.8533	0.5070	0.0058
	O3(2)	0.3533	−0.0070	0.5058	0.6467	−0.0070	0.9942	0.1467	0.4930	0.9942	0.8533	0.4930	0.5058
		Equivalent positions $8f$ in $C2/c$											
	1	x, y, z			$1-x, y, \frac{1}{2}-z$			$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$			$\frac{1}{2}+x, \frac{1}{2}+y, z$		
	2	$x, -y, \frac{1}{2}+z$			$1-x, -y, 1-z$			$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$			$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$		

x, y, z coordinates from PREWITT and BURNHAM (1966).

chains. The $C2/c$ structure has only one crystallographically distinct chain, formed by repetition of only one distinct tetrahedron. However, a triclinic structure might have four symmetrically distinct chains, so the chains are assigned letter designations as follows: the chain nearest the jadeite origin is A, the one in the same basal layer but about a half over in *b* is C, and the two in the tetrahedral layer near $\frac{1}{2}a$ are called B, directly above A, and D, directly above C. These chains are all identified in Fig. 1, and the atomic coordinates for every atom in each chain of jadeite are given in Table 3. Each chain contains two tetrahedral cations which may, in certain space groups, be crystallographically independent. These cations should be designated T, Si, Al or Fe as required, and numbered 1 and 2 plus the chain letter. Thus, the tetrahedral cations in a triclinic structure might be T1A, T2A, T1B, T2B, etc.

The oxygen atoms are numbered as in jadeite O1, O2 and O3, the latter being the tetrahedron-linking (bridging) oxygen, and the two former, the external oxygens. When a chain has two distinct tetrahedra, requiring assignment of T1 and T2, the oxygen atoms are keyed to the tetrahedral cation to which they are bonded, using the notation O1(1) for an O1 bonded to T1, O1(2) for an O1 bonded to T2, etc. If the chains are also distinct, the chain letter is added, e.g. O1(1)A, O2(1)B, etc. (Fig. 2, Table 4). Thus O3(2)D would refer to the bridging oxygen atom in the second tetrahedron of the D chain.

The source of the greatest confusion in the literature is the notation used for the larger cations which occupy special positions on the two-fold axes in the $C2/c$ structure. WARREN and BISCOE (1931) referred to these cations as X and Y, and other authors have used variants of M1 and M2. Unfortunately, the atoms associated with M1 and M2, respectively, are not always the same ones. For example, M1 is associated with Ca and M2 with (Mg, Fe) by MORIMOTO *et al.* (1960), whereas these associations are reversed by DEER *et al.*, (1963). We have somewhat arbitrarily decided to fix M2 for the four larger, eight-coordinated sites (that attain irregular six coordination in some pyroxenes), and M1 for the four smaller octahedrally coordinated sites. In jadeite, therefore, the M2 sites contain Na, the M1 sites, Al.

The cation site nearest the location of the Na atom whose coordinates are cited by PREWITT and BURNHAM (1966) in jadeite is called M2, and the notation for designating other M2 cations is as follows. The parenthetically enclosed numeral one, (1), indicates a shift of

$\frac{1}{2}$ in the z coordinate of M2, and the letter H ("half"), a shift of $\frac{1}{2}$ in the x coordinate of M2. The four sites are therefore M2, M2(1), M2H and M2(1)H. Similar considerations govern the notation for the four M1 cations. The Al coordinates given by PREWITT and BURNHAM (1966) have been converted to a set with $z = \frac{1}{4}$, so that the notation can be identical for both M1 and M2 sites. The jadeite coordinates

Table 4

Independent crystallographic sites named in observed clinopyroxene space groups

Diopside, jadeite	Clinoenstatite, pigeonite, clinoferrosilite	Spodumene	Omphacite
$C2/c$	$P2_1/c$	$C2$	$P2$
O1	O1A O1B	O1(1) O1(2)	O1(1)A O1(2)A O1(1)C O1(2)C
O2	O2A O2B	O2(1) O2(2)	O2(1)A O2(2)A O2(1)C O2(2)C
O3	O3A O3B	O3(1) O3(2)	O3(1)A O3(2)A O3(1)C O3(2)C
Si	SiA SiB	Si1 Si2	Si1A Si2A Si1C Si2C
M1	M1	M1 M1(1)	M1 M1(1) M1H M1(1)H
M2	M2	M2 M2(1)	M2 M2(1) M2H M2(1)H

References: diopside, WARREN and BRAGG (1928); jadeite, PREWITT and BURNHAM (1966); clinoenstatite, pigeonite, MORIMOTO *et al.* (1960); clinoferrosilite, BURNHAM (1967); spodumene, APPLEMAN and STEWART (1966); omphacite, CLARK and PAPIKE (1966).

for all the M1 and M2 cations are listed in Table 2. Finally, the crystallographically distinct atoms in each of the presently known structures are labelled in Table 4 according to the proposed nomenclature scheme. In general, the use of more symbols than are required by the space-group symmetry should be avoided unless the additional notation is needed for some special reason.

6. Summary

The atomic sites in any clinopyroxene structure related to diopside and jadeite can be readily compared by using the nomenclature scheme outlined here. The following procedure is recommended: First, choose the correct unit cell (Table 1), using a right-handed axial system. Second, select the correct origin for the particular space group (*International tables for x-ray crystallography*, 1952), and make the appropriate conversion to obtain the jadeite origin. Third, assign atoms and names to each site in accordance with those assigned to the corresponding sites in jadeite, as shown in Tables 2 and 3, and illustrated in Figs. 1 and 2.

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