THE CRYSTAL STRUCTURES OF THE HUMITE MINERALS. II. CHONDRODITE

G. V. Gibbs, P. H. Ribbe and C. P. Anderson,[1]
Department of Geological Sciences,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061.

Abstract

The crystal structure of chondrodite, $Mg_{4.95}Fe_{0.05}(SiO_4)_2F_{1.3}(OH)_{0.7}$, from Hangleby, Sibbo, Finland ($a = 4.7284[3]$, $b = 10.2539[3]$, $c = 7.8404[2]$ Å; $\alpha = 109.059[2]°$; $P2_1/b$, $\rho = 3.177$ g/cm) was refined by least-squares methods to $R = 0.039$ using 660 F_0's weighted so that $(w\Delta F^2)$ is essentially independent of F_0. The structure is based on a slightly distorted hcp (O, OH, F) anion array in which one-half of the octahedral sites are filled by Mg, Fe and one-tenth the tetrahedral sites are filled by Si. As in norbergite, bond angle strains produced by cation-cation repulsions measure the distortion of the hcp anion array from ideality. There are three chemically and geometrically distinct octahedra in the array: $M(1)O_6$ is analogous to the M(1) octahedron in olivine; $M(2)O_5(F,OH)$ is chemically different but geometrically similar to the M(2) octahedron in olivine, and $M(3)O_4(F,OH)_2$ is chemically and geometrically similar to the $M(3)$ octahedron common to all humites. The small amount of Fe in the specimen is ordered in the $M(1)O_6$ octahedron whereas the larger $M(2)O_5(F,OH)$ and the smaller $M(3)O_4(F,OH)_2$ octahedra contain only Mg. This ordering scheme is consistent with crystal field theory which predicts a greater crystal-field stabilization energy when Fe^{2+} is bonded to oxygen than when it is bonded to (F,OH).

Introduction

The structural similarities of the humite minerals, $nMg_2SiO_4 \cdot Mg(F, OH)_2$, and forsterite were recognized by Bragg and West (1927) and demonstrated by Taylor and West (1928, 1929) using X-ray methods. Ribbe, Gibbs and Jones (1968) emphasized that the key structural units of both the humites and the olivines are zigzag chains of edge-sharing M^{2+} octahedra running along c and linked laterally by Si-tetrahedra between the layers of hexagonal close-packed anions (*cf.* Birle, Gibbs, Moore, and Smith, 1968).

A detailed study of the structure of norbergite, $Mg_2SiO_4 \cdot Mg(F,OH)_2$ (Gibbs and Ribbe, 1969; Paper I of this series), indicates that cation-cation repulsion across shared polyhedral edges produces strains in bond angles which are a measure of the distortion of the hexagonal close-packed anion array from an ideal arrangement. Chondrodite, $2Mg_2SiO_4 \cdot Mg(F,OH)_2$, is similarly distorted but has three chemically and geometrically distinct octahedra: MO_6 is analogous to the $M(1)$ octahedron in forsterite, sharing two edges with tetrahedra and four with octahedra;

[1] Present address: Department of Geological Sciences, University of California at Riverside.

MO_5F_1, chemically different from octahedra in either fosterite or norbergite but geometrically similar to the $M(2)$ octahedra of these structures, shares two edges with an octahedron and one with a tetrahedron; MO_4F_2 is chemically and geometrically identical to $M(3)$ in norbergite and shares one F—F and two O—O edges with octahedra and one O—O edge with the Si-tetrahedron. The small amount of iron in this specimen is concentrated in the $M(1)$ site (the MO_6 octahedron), whereas the $M(2)O_5(F,OH)$ and the $M(3)O_4(F,OH)_2$ octahedra contain only Mg. This is predictable from crystal field considerations because the ordering of Fe^{2+} into octahedra with six oxygen ligands lowers the potential energy more than if it were ordered into octahedra with both oxygen and (F,OH) ligands (Lever, 1969).

EXPERIMENTAL PROCEDURES

The chondrodite specimen used in this study was chosen for its low iron content from a suite of thirty chondrodites chemically analyzed with the electron microprobe by Jones (1968) and reported by Jones, Ribbe and Gibbs (1969). It is from Hangleby, Sibbo, Finland and was kindly contributed by Professor Th. G. Sahama (Sahama, 1953). The microprobe analysis, unit cell parameters, density and optical properties (Sahama, 1953) are listed in Table 1. The space group $P2_1/b$ (α obtuse) is consistent with that initially determined by Taylor and West (1928) and is preferred over the more conventional settings because it permits direct comparison of the cell parameters and crystal structures of orthorhombic norbergite and humite with their monoclinic morphotropes, chondrodite

TABLE 1. MICROPROBE ANALYSIS AND PHYSICAL PROPERTIES OF CHONDRODITE
FROM HANGLEBY, SIBBO, FINLAND

Microprobe analysis (Jones *et al.*, 1969)

SiO$_2$	35.17 wt. %	CaO	0.01 wt. %
FeO	0.71	ZnO	0.05
MnO	0.17	F	6.97
MgO	59.92	OH (calc.)	3.61
TiO$_2$	0.03	Total, corrected for F, OH: 100.01 wt. %	

Chemical formula, normalized to two Si:

$Mg_{3.95}Fe_{0.034}Mn_{0.008}Ca_{0.01}Zn_{0.002}(SiO_4)_2 \cdot Mg_{0.999}Ti_{0.0013}F_{1.5}OH_{0.732}O_{0.2003}$

Unit cell parameters (Jones *et al.*, 1969)

Estimated standard deviations [in parentheses] refer to the last decimal place.

a	4.7284(3) Å	Space Group $P2_1/b$
b	10.2539(3) Å	$Z = 2$
c	7.8404(2) Å	
α	109.059(2)°	
V	359.30 Å³	

Refractive indices and density (Sahama, 1953)

α	1.600	$2V = 72°$
β	1.609	$\rho = 3.177$ gm/cc.
γ	1.628	

and clinohumite (see Fisher, 1951; Jones, 1969). Cell parameters were measured by Dr. N. W. Jones with a precision back-reflection Weissenberg camera and refined using 91 reflections with a least-squares program written by Burnham (1962).

Six-hundred-and-sixty non-zero intensities from five levels about a were collected by C. P. Anderson on a Weissenberg single-crystal diffractometer equipped with a scintillation counter. Niobium-filtered molybdenum radiation was used to collect all the diffraction data ($\sin \theta / \lambda < 0.65$) which were recorded on a strip-chart, integrated with a planimeter and corrected for Lp effects and absorption. The resulting F_0's were then submitted to an isotropic least-squares calculation (Busing, Martin and Levy, 1962) using coordinates obtained by Taylor and West (1928) as starting parameters. The form-factor curves were taken from the International Tables, Vol. III, and all Fe^{2+} was assumed to be concentrated in the $M(1)$ site for reasons discussed later.

TABLE 3. POSITIONAL PARAMETERS, ISOTROPIC TEMPERATURE FACTORS AND R.M.S. EQUIVALENTS FOR CHONDRODITE.

(Estimated standard deviations are in parentheses and refer to the last decimal place)

Atom	x	y	z	$B(\text{Å}^2)$	$\langle\mu\rangle^a(\text{Å})$
$M(1)$	$\frac{1}{2}$	0	$\frac{1}{2}$	0.49 (2)[b]	0.079 (2)[b]
$M(2)_5$	0.0091	0.1731	0.3055	.45 (2)	.075 (2)
$M(3)$	.4915	.8867	.0791	.43 (2)	.074 (2)
Si	.0768	.1441	.7038	.20 (1)	.050 (1)
O(1)	.7787	.0009	.2937	.36 (3)	.067 (3)
O(2)	.7280	.2404	.1252	.40 (3)	.071 (3)
O(3)	.2255	.1682	.5275	.35 (3)	.067 (3)
O(4)	.2649	.8546	.2943	.42 (3)	.073 (3)
F,OH	.2656	.0582	.1018	.50 (2)	.080 (2)

[a] The e.s.d. listed for the root-mean square displacements $\langle\mu\rangle$ were computed using the expression $\hat{\sigma}\langle\mu\rangle = \hat{\sigma}(B)/16\pi^2\langle\mu\rangle$.

[b] Refined values with 0.05 Fe in this site.

The F_0's were weighted according to a scheme proposed by Hanson (1965) which gives the less weight to the small and large F_0's and more to those of intermediate magnitude. As the refinement progressed the weighting function was adjusted to give approximately equal $\langle w\Delta F^2\rangle$ for ten equal-sized groups of increasing F_0's thereby making $\langle w\Delta F^2\rangle$ essentially independent of F_0. The final residual was 0.039 (weighted $R=0.035$). To test the assignment of Fe at $M(1)$, the data were submitted to a site refinement using the Finger program (1969) which calculated 0.05 Fe at $M(1)$, 0.00 at $M(2)_5$ and 0.00 Fe at $M(3)$, all with estimated standard deviations (e.s.d.'s) of 0.01.

Observed and calculated structure amplitudes and weights are listed in Table 2.[1] Atomic positional and isotropic vibrational parameters are in Table 3, and interatomic distances and bond angles are recorded in Tables 4 and 5. The e.s.d.'s are given in parentheses and apply to the last decimal place.

[1] To obtain a copy of Table 2, order NAPS Document No. 01048 from National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Ave., New York, New York 10001; remitting $2.00 for microfiche or $5.00 for photocopies, payable to CCMIC-NAPS.

TABLE 4. Si–O, *M*–O AND O–O DISTANCES, O–Si–O AND O–*M*–O ANGLES
AND BOND-ANGLES STRAINS IN CHONDRODITE

(Estimated standard deviations are in parentheses and refer to the last decimal place).

Si tetrahedron, SiO_4

		Angles at Si[a]	Strain[b]
Si—O (4)[A]	1.617 (2) Å		
—O (2)	1.636 (2)		
—O (3)	1.640 (2)		
—O (1)	1.642 (2)		
mean	1.634 Å		
O (1)—O (3)	2.562 (2)[t]	102.7°	− 6.7°
O (1)—O (2)	2.565 (2)[t]	103.0	− 6.4
O (2)—O (3)	2.575 (2)[t]	103.6	− 5.8
O (1)—O (4)	2.747 (3)	114.9	+ 5.5
O (2)—O (4)	2.748 (3)	115.3	+ 5.9
O (3)—O (4)	2.756 (3)	115.6	+ 6.2
mean	2.659 Å	109.2°	

$M(1)$ octahedron, MO_6

		Angles at M (2)[a]	Strain[b]
$M(1)$—O (1) [2]	2.090 (2) Å		
—O (3) [2]	2.114 (2)		
—O (4) [2]	2.119 (2)		
mean	2.108 Å		
O (1)—O (3) [2]	2.562 (2)[t]	75.1°	−14.9°
O (3)—O (4) [2]	2.833 (3)[o]	84.0	− 6.0
O (1)—O (4) [2]	2.857 (3)[o]	85.5	− 4.5
O (1)—O (4)′ [2]	3.090 (2)	94.5	+ 4.5
O (3)—O (4)′ [2]	3.144 (2)	96.0	+ 6.0
O (1)—O (3)′ [2]	3.332 (3)	104.9	+14.9
mean	2.970 Å	90.0°	

$M(2)_5$ octahedron, $MO_5(F, OH)$

$M(2)_5$—O (3)[A]	2.033 (2) Å
—O (1)[A]	2.049 (2)
—O (4)	2.173 (2)
—O (3)′	2.184 (2)
—O (2)	2.210 (2)
—(F, OH)	2.045 (2)
mean	2.116 Å

TABLE 4 (*continued*)

		Angles at $M(2)_5$[a]	Strain[b]
O (2)—O (3)'	2.575 (2)[t]	71.7°	−18.3°
O (2)—O (4)	2.804 (3)[o]	79.5	−10.5
O (3)'—O (4)	2.833 (3)[o]	81.1	− 8.9
O (1)—O (3)	2.951 (3)	92.6	+ 2.6
O (3)—O (3)'	3.010 (2)	91.0	+ 1.0
O (3)—O (4)	3.046 (2)	99.7	+ 2.7
O (1)—O (2)	3.154 (2)	95.5	+ 5.5
O (1)—O (3)'	3.229 (2)	99.4	+ 9.4
(F, OH)—O (1)	2.913 (3)	90.7	+ 0.7
(F, OH)—O (4)	2.922 (2)	87.6	− 2.4
(F, OH)—O (2)	3.125 (2)	94.4	+ 4.4
(F, OH)—O (3)	3.162 (2)	101.7	+11.7
mean	2.977 Å	89.8°	

$M(3)$ octahedron, $MO_4(F, OH)_2$

$M(3)$—O (2)[A]	1.994 (2) Å		
—O (4)	2.113 (2)		
—O (2)'	2.120 (2)		
—O (1)	2.182 (2)		
—(F, OH)	2.016 (1)		
—(F', OH)	2.042 (2)		
mean	2.078 Å		

		Angles at $M(3)$[a]	Bond-angle strain[b]
O (1)—O (2)'	2.565 (2)[t]	73.2°	−16.8°
O (2)'—O (4)	2.804 (3)[o]	83.0	− 7.0
O (1)—O (4)	2.857 (3)[o]	83.4	− 6.6
(F, OH)—(F, OH)	2.764 (3)[o]	85.8	− 4.2
(F', OH)'—O (2)	2.842 (2)	89.5	− 0.5
(F, OH)—O (4)	2.950 (2)	91.2	+ 1.2
(F', OH)—O (1)	2.965 (2)	89.1	− 0.9
(F, OH)—O (2)	2.997 (2)	96.8	+ 6.8
(F, OH)—O (1)	3.013 (3)	91.7	+ 1.7
(F', OH)'—O (2)'	3.140 (2)	97.9	+ 7.9
O (2)'—O (4)	3.110 (2)	98.4	+ 8.4
O (2)'—O (2)	3.119 (2)	98.6	+ 8.6
mean	2.927 Å	89.9°	

[A] Indicates bond to apical cation.
[t] Edge shared between tetrahedron and octahedron.
[o] Edge shared between two octahedra.
[a] Estimated standard error of all angles is 0.1°.
[b] Bond-angle strain = observed minus ideal angle.

TABLE 5. DETAILS OF ANION COORDINATION IN CHONDRODITE

	Inter-cation distance	Angle at anion	Ideal angle	Bond-angle strain
O (1)				
$M(2)_A$—Si_B	3.253 Å	124.6°	125.3°	− 0.7°
—$M(1)_B$	3.610	121.4	131.8	−10.4
—$M(3)_B$	3.789	127.1	131.8	− 4.7
$M(1)_B$—$M(3)_B$	3.120	93.8	90.0	+ 3.8
—Si_B	2.683	91.1	79.5	+11.6
$M(3)_B$—Si_B	2.741	90.4	79.5	+10.9
O (2)				
$M(3)_A$—Si_B	3.189 Å	122.7°	125.3°	− 2.6°
—$M(2)_B$	3.724	124.6	131.8	− 7.2
—$M(3)_B$	3.566	120.1	131.8	−11.7
$M(2)_B$—$M(3)_B$	3.239	96.8	90.0	+ 6.8
—Si_B	2.792	91.8	79.5	+12.3
$M(3)_B$—Si_B	2.741	92.8	79.5	+13.3
O (3)				
$M(2)_A$—Si_B	3.248 Å	124.0°	125.3°	− 1.3°
—$M(2)_B$	3.773	126.9	131.8	− 4.9
—$M(1)_B$	3.553	117.9	131.8	−13.9
$M(2)_B$—$M(1)_B$	3.199	96.2	90.0	+ 6.2
—Si_B	2.792	92.7	79.5	+13.2
$M(1)_B$—Si_B	2.683	90.3	79.5	+10.8
O (4)				
Si_A—$M(2)_B$	3.289 Å	119.7°	125.3°	− 5.6°
—$M(1)_B$	3.261	121.0	125.3	− 4.3
—$M(3)_B$	3.251	120.7	125.3	− 4.6
$M(2)_B$—$M(1)_B$	3.199	96.4	90.0	+ 6.4
—$M(3)_B$	3.239	98.2	90.0	+ 8.2
$M(1)_B$—$M(3)_B$	3.120	95.0	90.0	+ 5.0
(F, OH)				
$M(2)$—$M(3)$	3.684 Å	130.2°	131.8°	− 1.6°
—$M(3)'$	3.720	131.1	131.8	− 0.7
$M(3)$—$M(3)'$	2.972	94.2	90.0	+ 4.2

DISCUSSION

The structure of chondrodite, $M_5(SiO_4)_2(F,OH)_2$ is based on a slightly distorted hexagonal close-packed (O,F,OH) anion array with half the available octahedral sites occupied by divalent metal cations M and one-tenth the tetrahedral sites occupied by Si. As in forsterite oxygen is bonded to three M and one Si, whereas (F,OH) is ordered in the anion

array and bonded to three M cations, as in norbergite. The same type of anion substitution is observed in chondrodite and norbergite: the replacement of four oxygens by four (F,OH) in the close-packed array of forsterite is balanced by the replacement of one tetrahedrally coordinated Si by a tetrahedral void, according to the general formula $M_{2x}Si_{x-1}O_{4x-4}(F,OH)_4$, where $x = 5$ for chondrodite. This results in the
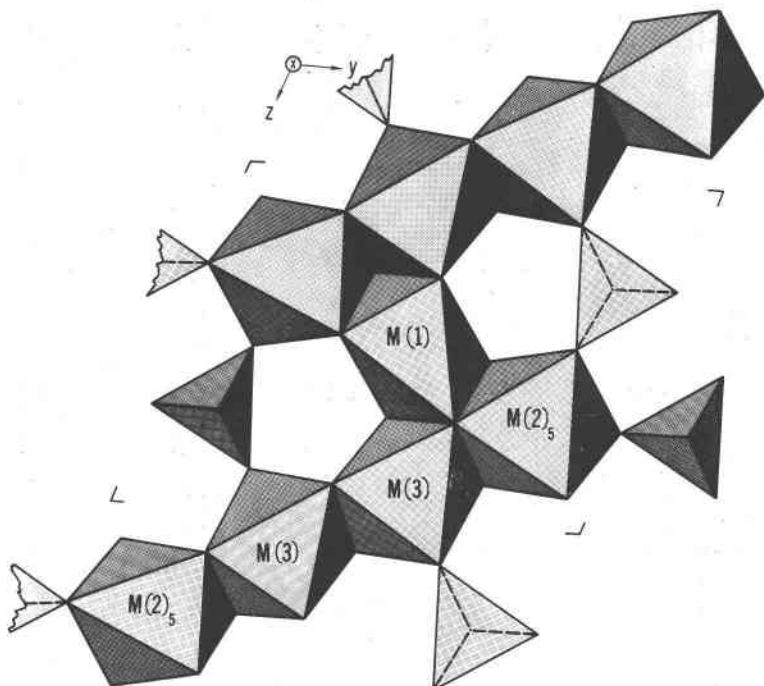

FIG. 1. The chains of edge-sharing M-octahedra in chondrodite, cross-linked by Si tetrahedra. Compare with Fig. 1, Gibbs and Ribbe (1969) and Figs. 1 and 3, Ribbe *et al.* (1968).

zigzag chains of edge-sharing M-octahedra shown in Fig. 1. In chondrodite the periodic repeat in the chains is five octahedra, producing monoclinic unit-cell geometry, whereas in forsterite with four and norbergite with six octahedra in the periodic repeat, the geometry is orthorhombic.

ANION COORDINATION

Fluorine and OH. The site of the monovalent anion in this chondrodite is occupied on the average by 0.63F and 0.37(OH). As in norbergite, (F,OH) is nearly coplanar with three M cations to which it is bonded

(*cf.* Fig. 5a, Paper I). The $M(2)$—(F,OH)—$M(3)$ angles (Table 5) are less than 2° smaller than the 131.8° expected to an ideal close-packed array, whereas the $M(3)$—(F,OH)—$M(3)'$ angle is 4.2° greater than the ideal angle of 90° because of repulsion between the $M(3)$ cations which are only 2.972 Å distant. However, these angles also imply that the orbitals on (F,OH) form hybrid bonds (intermediate between sp^2 and sp^3) with the three coordinating M-cations rather than forming p^3 bonds. As in norbergite, the root-mean-square displacement $<\mu> = 0.08$ Å calculated for the smaller, three-coordinated (F,OH) is somewhat greater than those calculated for the larger, four-coordinated oxygen atoms. This can be attributed to the substitutional disorder of F and OH as well to their lower coordination number (Burnham, 1964)

Oxygen. Each oxygen in olivine, norbergite, chondrodite and the other humite minerals is coordinated by one Si and three M cations in a "tetrahedral" array suggesting that the orbitals on oxygen form second order sp^3 hybrid bonds with adjacent cations (Fyfe, 1954). The angles that the cations subtend at each oxygen are very similar, although there are two distinct types of "tetrahedral" arrays. One has Si as the apical (A) cation and three M's as the basal (B) cations. The other has M as the apical cation, with one Si and two M's in the basal array. (See Fig. 2).

The cation array around O(4) is the most regular: Si is the apical cation and the Si_A—O(4)—M_B angles are within a degree of 120°, while the M_B—O(4)—M_B angles are within 2° of 96°. (Data are in Table 5; *cf.* Fig. 2 with Figs. 5 and 6 of Paper I). However, when Si is in the basal array, the Si_B—M_B distances are relatively short ($\sim$2.7 Å) and the Si_B—O(1,2,3)—M_B angles are 11° to 13° larger than the ideal 79.5° expected in a close-packed array. As in the case of M_B—O(4)—M_B angles the M_B—O(1,2,3)—M_B angles are within a few degrees of the 125.3° ideal angle, but the M_A—O(1,2,3)—M_B angles are 5°–14° smaller than the 131.8° ideal angle due to repulsion between Si and M in the basal array. Figure 3a is a graphical presentation of the relationships between basal and apical bond-angle strains at the oxygen atoms.

Figure 2 shows that the bond-angle strains in chondrodite can be explained by cation-cation repulsion across shared polyhedral edges. The O(1,2,3)—O(4) edges in the upper right diagram are shared between octahedra, whereas the O(1)—O(2,3) and O(2)—O(3) edges in the lower diagram are shared between the Si-tetrahedron and M-octahedra. As expected from electrostatic considerations, the bond-angle strains at the basal cations are negative and those at the oxygens are positive. The relationships amongst these bond-angle strains are depicted in Fig. 3b.
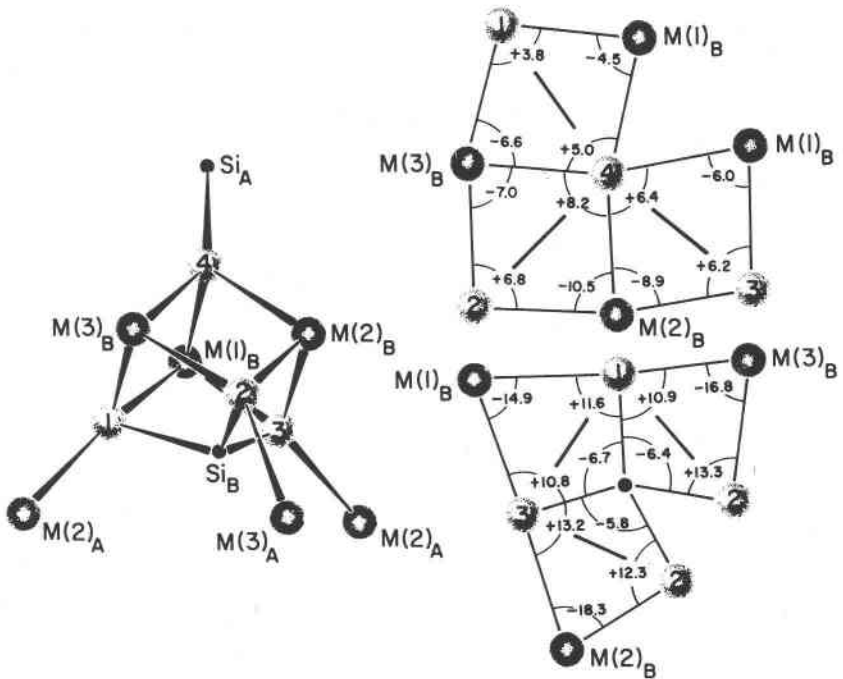
Fig. 2. The ball and spoke figure on the left shows the cation coordination about each oxygen atom (labeled 1, 2, 3, 4). The subscripts A (apical) and B (basal) apply to the relative position of the cation in the anion coordination array (see text and Table 5). On the right are drawings of the faces of the distorted "cube" whose corners are the four oxygen anions, the three basal M cations and Si_B. The unlabeled heavy lines between anions signify shared edges. The values (in degrees) given at the vertices are basal bond angle strains. Compare Fig. 6, Gibbs and Ribbe (1969).

Cation Coordination

SiO₄ Tetrahedron (Fig. 4a). The dimensions of the SiO_4^{4-} ion in chondrodite are statistically identical with those in norbergite despite the fact that its point symmetry is C_s in norbergite and C_1 in chondrodite. The three edges shared with M-octahedra average 2.568 Å; the O–Si–O angles opposite them average 103.1°, whereas the unshared edges average 2.70 Å and the angles opposite them average 115.1°. The Si–O bonds to the three oxygens comprising the shared edges average 1.639 Å and that to remaining oxygen is 1.617 Å (see Table 4).

M(1) Octahedron (Fig. 4b). The $M(1)$ octahedron is geometrically and chemically similar to $M(1)$ in forsterite, humite and clinohumite. In
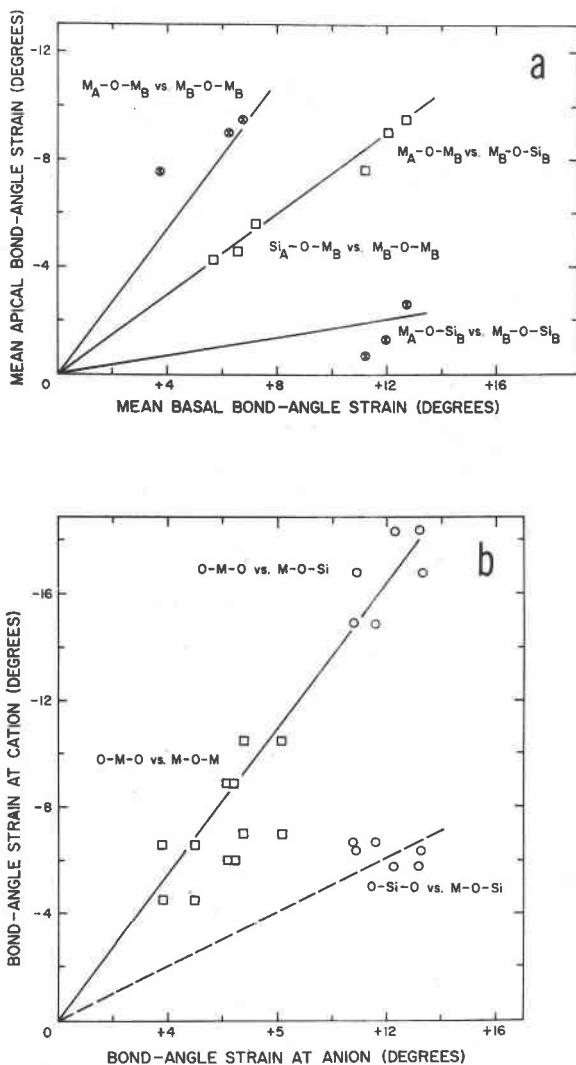
Fig. 3. (a) Basal *vs.* apical bond-angle strains at the oxygens. (b) Bond-angle strains at the anions plotted against strains at the cations. The data points are from Tables 4 and 5; the lines are the same as those for norbergite, Figs. 7b and 7a, respectively, Gibbs and Ribbe (1969).

chondrodite $M(1)$ exhibits point symmetry C_i, shares four edges with octahedra (2.83–2.86 Å), two with tetrahedra (2.56 Å) and has six oxygen ligands at a mean distance of 2.108 Å. The M–O distances have a range

Fig. 4. The cation coordination polyhedra. Edges shared between octahedra are heavy weight, those shared between the tetrahedron and octahedra are double. For selected edges the bond angle strains are shown. See Tables 4 and 5 and compare with Figs. 2 and 3, Gibbs and Ribbe (1969).

of 0.03 Å which is significantly less than that recorded for any other cation-containing octahedra in either forsterite, norbergite, humite or chondrodite.

$M(2)_5$ *Octahedron* (Fig. 4c). By convention $M(2)$ octahedra are those which share two edges with other octahedra and one with a tetrahedron. There are three chemically different $M(2)$ octahedra in the forsterite-humite mineral series—$M(2)_6$ with six oxygen ligands (in forsterite, clinohumite and humite), $M(2)_5$ with one (F,OH) and five oxygen ligands (in chondrodite, humite, and clinohumite), and $M(2)_4$ with two (F,OH) and four oxygen ligands (in norbergite only). Thus the $M(2)$ octahedron in chondrodite is an $M(2)_5$ octahedron. Its location at the "elbow" of the serrated chain of octahedra gives it its distorted appearance (see Fig. 1 and Fig. 4c): all three shared edges are on one end of the octahedron, and the cation is repelled toward the opposite end. Bonds from the M-cation

to oxygens involved in the shared edges range from 2.173 to 2.210 Å; those to the other two oxygens and (F,OH) range between 2.033 and 2.049 Å. The total range of bond lengths is 0.177 Å, about six times as great as that found in the $M(1)$ octahedron.

The $M(3)$ Octahedron (Fig. 4d). The $M(3)$ octahedron, $MO_4(F,OH)_2$, is directly comparable to $M(3)$ in norbergite, humite and clinohumite in which it shares its (F,OH)—(F,OH) edge with an adjacent $M(3)$ octahedron, one edge with an SiO_4 tetrahedron, and two O—O edges with other octahedra. In chondrodite these octahedra are $M(1)$ and $M(2)_5$. The bonds to oxygens involved in shared edges are longer (2.120–2.182 Å) than those to the (F,OH) ions involved in a shared edge (2.016 and 2.042 Å) and even longer than that to the only oxygen not involved in a shared edge (1.996 Å). The 0.188 Å range of bond lengths for $M(3)$ is greater than those of the other octahedra in chondrodite.

Mg/Fe Ordering

Although less than one percent of the divalent metal cations in this chondrodite is iron, there is evidence that all the iron is ordered into one site.[1] In the initial least-squares refinement Fe^{2+} was assumed to be disordered in $M(1)$, $M(2)_5$ and $M(3)$, and the isotropic temperature factors calculated at 0.35, 0.50 and 0.48 Å^2, respectively. Ordinarily there would be no reason to investigate this further, but the refinement of humite (Ribbe and Gibbs, 1969) had shown that more than 70 percent of its Fe^{2+} was concentrated in the octahedra with no (F,OH) ligands. An assignment of 0.05 Fe, 0.95 Mg to the $M(1)$ site (with six oxygen ligands) and 1.00 Mg in the $M(2)_5$ and the $M(3)$ octahedra resulted in more nearly equal temperature factors (see Table 3). Furthermore, the Finger (1969) site-refinement program produced the same Mg/Fe distribution with e.s.d.'s of 0.01 Fe at all three sites.

The ordering of Fe^{2+} into the $M(1)$ site is expected from a consideration of the Fajans-Tsuchida spectrochemical series which predicts a greater crystal field stabilization energy when Fe^{2+} is bonded to oxygen than when it is bonded to fluorine or OH, other things being equal. However, as the $M(1)$ octahedron (mean M—$O = 2.108$ Å) is significantly smaller than the $M(2)$ octahedron (mean M—$O = 2.116$ Å), the ordering scheme in chondrodite cannot be rationalized in terms of ionic size. Further discussion of the ordering phenomenon in the humite minerals in terms of ligancy and octahedral distortions is forthcoming in a study of humite, $Mg_{6.6}Fe_{0.4}(SiO_4)_3F(OH)$, which contains a significant amount

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[1] The small amounts of Mn, Ca, Zn and Ti were included in the scattering factor as Fe. See formula in Table. 1.

of Fe^{2+} and a greater diversity of octahedra $M(1)$, $M(2)_6$, $M(2)_5$ and $M(3)$.

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