Crystal structure of $2Mg_2SiO_4 \cdot 3Mg(OH)_2$, a new high-pressure structure type

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Abstract

Phase A [$2Mg_2SiO_4 \cdot 3Mg(OH)_2$], a high-pressure hydrous silicate which is a possible H_2O-bearing mineral phase in the mantle, is hexagonal with $a = 7.8603(2)$, $c = 9.5730(2)$Å; $P6_3$ and $Z = 2$. The structure has been determined with 1653 counter-measured intensities and refined by the least-squares method to $R = 0.059$. The structure is based on a slightly distorted ABCB packing of anions (O^{2-}, OH^-) in which one-half of the octahedral sites are filled by Mg and one-fourteenth of the tetrahedral sites by Si. Two types of layers alternate in the structure parallel to (001), one consisting of networks of Mg octahedra and the other of blocks of three Mg octahedra. The first layer is identical to that found in welinite, $Mn^{4+}Mn_3^{2+}SiO_7$, and the second one is similar to a layer observed in hematolite, $(Mn^{2+},Mg,Al)_{15}(OH)_{23}(AsO_3)(AsO_4)_2$. In phase A the chains of Mg octahedra are linked to other similar chains by Mg octahedra to form sheets. Therefore, no isolated chains of Mg octahedra are observed in the structure, though they are important constituents in the humite group minerals of composition $mMg_2SiO_4 \cdot nMg(F,OH)_2$ with $1 \leq m/n \leq 4$.

Introduction

Ringwood and Major (1967) reported synthesis of a new hydrated magnesium silicate, designated phase A, in their investigation of the system Mg_2SiO_4–MgO–H_2O at high pressures and temperatures. Yamamoto and Akimoto (1974) determined the chemical formula of phase A to be $2Mg_2SiO_4 \cdot 3Mg(OH)_2$. The stability diagram of the system MgO–SiO_2–H_2O reported by Yamamoto and Akimoto (1977) indicates that phase A can coexist with forsterite and enstatite up to 800°C at 77 kbar. This suggests that phase A is a possible H_2O-bearing mineral phase in the subduction zone in the mantle.

Yamamoto and Akimoto (1974) reported that phase A has hexagonal symmetry with $a = 7.866(2)$

and $c = 9.600(3)$Å, and its possible space groups are $P6_3$ and $P6_3/m$. However, they reported that the optical interference figure of phase A indicates a biaxial nature, although the X-ray data indicate hexagonal symmetry.

In the system MgO–SiO_2–H_2O, all compounds of composition $mMg_2SiO_4 \cdot nMg(OH)_2$ with $1 \leq m/n \leq 4$ belong to the humite group. However, phase A is the only compound with $m/n < 1$ and has quite different crystallographic characteristics relative to compounds of the humite group. Because of the uniqueness of the crystallographic data and of the possible importance of this compound in the upper mantle, we have determined the structure.

Experimental

The crystals of phase A used in this study were synthesized from mixtures of appropriate amounts of

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$Mg(OH)_2$ and SiO_2 at 700°C and 58 kbar by means of a tetrahedral anvil press.

In spite of the optically biaxial properties, strict hexagonal symmetry of phase A has been confirmed by comparing the X-ray intensities of equivalent reflections from single crystals. X-ray photographs indicate systematic absence of reflections with l odd for $00l$, which is consistent with space group $P6_3$ or $P6_3/m$. Cell dimensions were precisely determined by the least-squares method using 84 high-angle reflections (45 $K\alpha_1$ and 39 $K\alpha_2$ reflections) which were measured on a four-circle diffractometer. The d_{obs} and d_{calc} table has been deposited[2]. The crystal data are summarized in Table 1.

The specimen used for intensity measurement is a hexagonal prism with edges of $110\mu m$ and a height of $200\mu m$. $MoK\alpha$ radiation monochromatized by pyrolytic graphite was used. The intensities of 2188 independent reflections within the range $0° < 2\theta \leq 107.9°$ were obtained using a four-circle diffractometer (Rigaku AFC-3) employing the $2\theta-\omega$ scan technique. Of all reflections measured, 156 had zero intensity and 379 had high standard deviations ($3\sigma_{hkl} > F_o$). Conventional polarization and Lorentz corrections were carried out in the process of the data collection. No absorption correction was applied.

Structure analysis

A closest-packed arrangement of O^{2-} and OH^- anions parallel to (001) was predicted from the composition and crystallographic data. This arrangement was confirmed in the three-dimensional Patterson synthesis. Since the structure has hexagonal symmetry and there are four oxygen-atom layers along the c direction, only two kinds of the closest-packing arrangements of oxygen atoms, ABAB and ABCB (= ABAC), are possible. These two arrangements are easily distinguished in the $z = \frac{1}{2}$ section of the Patterson synthesis, and the ABCB arrangement was confirmed in this structure.

There are four Si atoms in the unit cell. If space group $P6_3/m$ is assumed for the structure, only the $4f(\frac{1}{3},\frac{2}{3},z; \frac{2}{3},\frac{1}{3},\bar{z}; \frac{2}{3},\frac{1}{3},\frac{1}{2} + z; \frac{1}{3},\frac{2}{3},\frac{1}{2}-z)$ or the $4e(0,0,z; 0,0,\bar{z}; 0,0,\frac{1}{2}+z; 0,0,\frac{1}{2}-z)$ crystallographic position is available for Si atoms, resulting in an unreasonable face-sharing arrangement of Si tetrahedra. Therefore, the space group $P6_3$ was adopted for this structure.

[2] The table is deposited with the F_a and F_c table. To obtain a copy of these tables, order Document AM-79-098 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 1. Crystal data

$2Mg_2SiO_4 \cdot 3Mg(OH)_2$	$\underline{V} = 512.22\text{A}^3$
Hexagonal	$\underline{Z} = 2$
Space group $\underline{P6}_3$	$\underline{D}_m = 2.96(2)$ gcm^{-3} *)
$\underline{a} = 7.8603(2)$A	$\underline{D}_c = 2.959$ gcm^{-3}
$\underline{c} = 9.5730(2)$	$\mu(MoK\alpha) = 8.45$ cm^{-1}

*) Data from Yamamoto and Akimoto (1974).

From the Patterson synthesis diagram, only a limited number of structure models is possible. They were differentiated by comparing their calculated structure factors with the observed ones. The best structure was confirmed by Fourier and difference-Fourier syntheses. The atomic parameters have been refined by least-squares refinement using 1653 reflections with $F_o \geq 3\sigma_{hkl}$, and an R value of 0.061 was obtained with isotropic temperature factors. Unit weights were applied to all reflections. The final R value is 0.059 for the refinement with anisotropic temperature factors for all atoms. The R values for all 2188 reflections including undetectable intensities and for 2032 reflections omitting the undetectable intensities are 0.095 and 0.078, respectively. Hydrogen atoms were not detected experimentally. The F_o and F_c table has been deposited[2]. The final atomic parameters are given in Table 2. Fully-ionized scattering factors were taken from the *International Tables for X-ray Crystallography, Vol. IV (1974)* for Mg^{2+} and Si^{4+} and from Tokonami (1965) for O^{2-} ions. All computations of Patterson and Fourier syntheses, least-squares refinement of the structure, and interatomic distances were carried out using the programs 3DFR (Iitaka, private communication), RSFLS (Sakurai, 1967), and BADTEA (Finger, 1968) at the Computation Center of Osaka University.

Discussion of the structure

The structure of $2Mg_2SiO_4 \cdot 3Mg(OH)_2$ is based on the ABCB closest packing of O^{2-} and OH^- (see Fig. 1). All Mg atoms are in octahedral sites, and Si atoms are in tetrahedral sites. There are three symmetrically independent Mg and two Si atoms in the structure. Mg(3) and Si(1) are on the three-fold axis, and Si(2) is on the 6_3 axis.

The Mg(2) octahedron shares edges with other symmetrically equivalent Mg(2) octahedra and forms an Mg_3O_{13} group around the 6_3 axis. This group is linked to others like it by sharing edges with the Mg(3) octahedron, resulting in a layer parallel to (001) (Fig. 1a). The Si(1) tetrahedra are located in the interstices of the network, and they share their cor-

Table 2a. Atomic coordinates and thermal parameters of phase A

atom	position	multipl.	x	y	z	B/Å²
Mg(1)	6c	1	.3722(1)	.4547(1)	.3857(4)	.56(1)
Mg(2)	6c	1	.2252(1)	.2438(1)	.1127(4)	.49(1)
Mg(3)	2b	1/3	1/3	2/3	.1029(4)	.50(2)
Si(1)	2b	1/3	2/3	1/3	.1741(4)	.33(1)
Si(2)	2a	1/3	0	0	.4018(4)	.36(1)
O(1)	6c	1	.2001(3)	.0274(3)	-.0240(4)	.46(2)
O(2)	6c	1	.4766(3)	.0988(3)	.4844(4)	.51(2)
O(3)	6c	1	.4538(3)	.2947(3)	.2320(4)	.54(2)
O(4)	6c	1	.1704(3)	.4367(3)	.2398(5)	.54(2)
O(5)	2b	1/3	2/3	1/3	0	.53(3)
O(6)	2a	1/3	0	0	.2323(6)	.52(3)

B: Isotropic temperature factors in the form $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations are given in parentheses.

Fig. 1. Crystal structure of phase A projected along the c axis. Oxygen atoms are at the corners of octahedra. Solid and open circles represent Mg and Si atoms, respectively. (a) Atoms between $z \simeq 0$ and $z \simeq 1/4$. (b) Atoms between $z \simeq 1/4$ and $z \simeq 1/2$.

ners with Mg(2) octahedra. Like the Mg(2) octahedra, Mg(1) octahedra form an Mg_3O_{13} group around the three-fold axis by sharing edges with symmetrically equivalent Mg(1) octahedra. The $Mg(1)_3O_{13}$ groups are isolated, but this group is linked to others by sharing corners with Si(2) tetrahedra, resulting in another layer parallel to (001) (Fig. 1b).

The two types of layers described above alternate along the c axis. The Mg(1) octahedron shares edges with the Mg(2) and Mg(3) octahedra, and the Si(2) tetrahedron shares edges with the Mg(2) octahedra. However, the Si(1) tetrahedron does not share edges with Mg octahedra. In the structures of the humite group minerals, $m\mathrm{Mg_2SiO_4} \cdot n\mathrm{Mg(F,OH)_2}$, where $1 \le m/n \le 4$), shared edges between Si tetrahedra and Mg octahedra in the same layer are common. Absence of shared edges between Si tetrahedra and Mg octahedra in the same layer is one of the characteristics of the structure of phase A.

Note that the structure of phase A is constructed

Table 2b. Anisotropic temperature factors in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values are multiplied by 10^5

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B_{eq}/\text{Å}^2$
Mg(1)	289(15)	292(14)	145(7)	125(12)	-47(11)	5(10)	.53
Mg(2)	291(15)	242(14)	126(6)	127(13)	-39(9)	-33(9)	.47
Mg(3)	283(16)	283(16)	133(14)	142(8)	0	0	.49
Si(1)	196(11)	196(11)	73(9)	98(6)	0	0	.31
Si(2)	204(10)	204(10)	70(9)	102(5)	0	0	.32
O(1)	251(23)	240(23)	118(12)	115(20)	-6(14)	-10(15)	.43
O(2)	320(26)	268(25)	136(12)	149(22)	4(17)	-12(16)	.50
O(3)	219(24)	401(27)	136(13)	164(22)	-16(16)	-7(17)	.51
O(4)	293(26)	280(26)	176(14)	145(23)	21(18)	23(17)	.54
O(5)	279(27)	279(27)	120(23)	139(14)	0	0	.47
O(6)	366(26)	366(26)	55(18)	183(13)	0	0	.49

B_{eq}: Equivalent isotropic temperature factors computed according to the relation $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$
Estimated standard deviations are given in parantheses.

from two different layers of Mg octahedra rather than chains of Mg octahedra which are common in the structures of the humite group. The Mg octahedral chains in the humite group are shown in Figures 2a and 2b, for norbergite $\mathrm{Mg_2SiO_4} \cdot \mathrm{Mg(F,OH)_2}$ and chondrodite $2\mathrm{Mg_2SiO_4} \cdot \mathrm{Mg(F,OH)_2}$ (Ribbe *et al.,* 1968), respectively. Similar Mg octahedral chains, and their attendant bridging Si tetrahedra, can be found in the structures of other humite-group minerals. A schematic representation of the octahedral and tetrahedral arrangements in phase A is shown in Figure 2c. Alternating slabs of olivine-like and brucite-like structures in the humite-group structures (Bragg and Claringbull, 1965, p. 173–178; Ribbe *et al.,* 1968) cannot be found in the structure of phase A. Lack of these structural features indicates that phase A should not be grouped with the humite-group structures, though its chemical formula belongs to the compositional series $m\mathrm{Mg_2SiO_4} \cdot n\mathrm{Mg(OH)_2}$.

Moore and Araki (1978) have shown that hematolite, $(\mathrm{Mn^{2+},Mg,Al})_{15}(\mathrm{OH})_{23}(\mathrm{AsO_3})(\mathrm{AsO_4})_2$, has five different layers: (1) isolated octahedra; (2) octahedral and tetrahedral sheet; (3) octahedral and trigonal pyramidal sheet; (4) insular octahedra and tetrahedra; and (5) octahedral sheet. Among them, the octahedral and tetrahedral sheet (2) is identical to that shown in Figure 1a, and the octahedral and trigonal pyramidal sheet (3) is similar to that shown
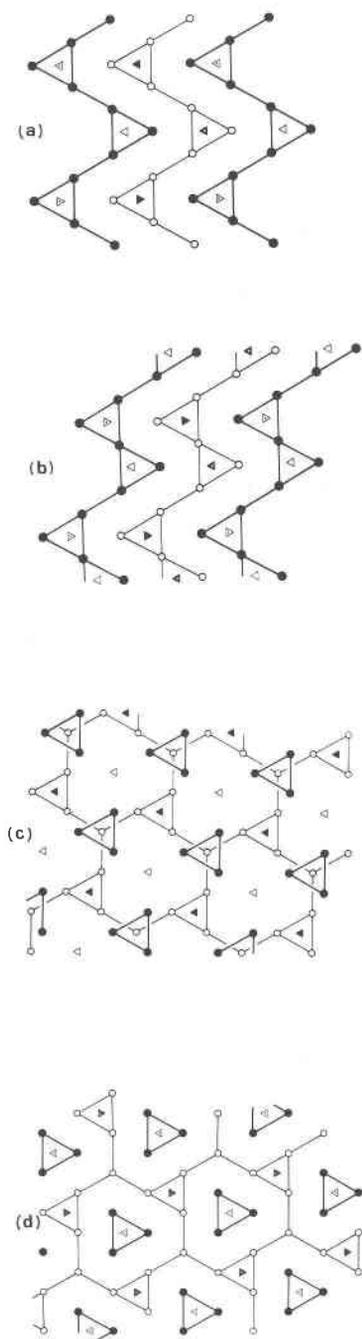
Fig. 2. Schematic representations of the arrangements of Mg octahedra. Open and solid circles are octahedral cations at the lower and upper levels, respectively. Open and solid triangles represent tetrahedral cations at the lower and upper levels, respectively. Solid lines indicate edge-shared relationship between octahedra. This relationship between the lower and upper level octahedra is not depicted. Dotted triangles indicate the apical corner of the tetrahedron points upwards. (a) Norbergite; (b) chondrodite; (c) phase A; (d) projection of sheets (2) and (3) along c axis in hematolite. Shaded triangles represent AsO_3 pyramids.

in Figure 1b. The only difference between sheet (3) and that shown in Figure 1b is that the As trigonal pyramid in hematolite is replaced by the Si tetrahedra in phase A. There is an edge-shared relationship between two layers in phase A but only a corner-sharing relationship between two sheets [sheet (2) and (3)] in hematolite. The relationship between sheets (2) and (3) of hematolite is schematically shown in Figure 2d. The main difference between the two arrangements of Figure 2c and Figure 2d is the location of Mg_3O_{13} groups in the upper level. The shaded triangles of the upper level show AsO_3 pyramids in Figure 2d.

There are several minerals structurally related to hematolite: welinite (Moore, 1968), dixenite (Wickman, 1951), kraisslite (Moore and Araki, 1978), and mcgovernite (Wuensch, 1960; Moore and Araki, 1978). They belong to hexagonal or rhombohedral systems with a common a periodicity. Phase A also has the a periodicity in common with these minerals and is made up of four layers along the c axis. The four layers are formed by the alternation of two sheets, (2) and (3). Welinite, $Mn^{4+}Mn_3^{2+}SiO_7$, is the simplest of the above structures and is built up from two layers of type (2) along the c axis. Structures of the minerals listed seem more complicated than welinite, phase A, and hematolite. However, their structures are still unknown. Thus, phase A can be structurally classified with the group of minerals including welinite and hematolite.

Interatomic distances and angles for phase A are given in Table 3. The mean Si–O distance, 1.635A, of the $Si(2)O_4$ tetrahedron, which shares edges with MgO_6 octahedra, is comparable with those of SiO_4 tetrahedra in humite-group minerals [hydroxylchondrodite: 1.634A (Yamamoto, 1977), clinohumite: 1.626A and 1.638A (Robinson et al., 1973), chondrodite: 1.634A (Gibbs et al., 1970), norbergite: 1.631A (Gibbs and Ribbe, 1969)]. The bond distances from Si to apical oxygens of tetrahedra of humite-group minerals and $Si(2)O_4$ in phase A are in the range of 1.612 (norbergite) to 1.626A (clinohumite). These distances are smaller than those to basal oxygens which are involved in edge sharing, except for one of two SiO_4 tetrahedra of clinohumite, in which the distance to the apical oxygen is 1.626A while those to basal oxygens are 1.622 to 1.632A. In contrast, the $Si(1)O_4$ tetrahedron of phase A, which shares no edges with MgO_6 octahedra, has a silicon to apical oxygen distance of 1.666A, and a silicon to basal oxygen distance of 1.641A. The mean Si–O distance of the $Si(1)O_4$ tetrahedron is 1.647A.

The O(1)–O(1) bond, which forms a shared edge

Table 3. Interatomic distances (A) and angles (degrees)

Mg(1) Octahedron			Mg(2) Octahedron		
	Distance			Distance	
Mg(1)-O(1^i)	2.018(3)		Mg(2)-O(1)	2.076(4)	
-O(2^{ii})	1.996(4)		-O(1^{iv})	2.204(4)	
-O(3)	2.229(4)		-O(2^v)	2.025(2)	
-O(4)	2.065(4)		-O(3)	1.993(4)	
-O(4^{iii})	2.392(4)		-O(4)	2.149(4)	
-O(5^i)	2.139(2)		-O(6)	2.173(3)	
mean	2.140		mean	2.103	
	O-M-O angle			O-M-O angle	
O(3) -O(4)	2.950(4)^o	86.7(2)	O(1) -O(1^{iv})	2.558(4)^t	73.3(2)
O(4) -O(4^{iii})	2.789(3)^o	77.1(2)	-O(6)	2.864(4)^o	84.7(1)
-O(5^i)	2.967(4)^o	89.7(1)	O(1^{iv})-O(6)	2.864(6)^o	81.7(1)
O(4^{iii})-O(5^i)	2.967(4)^o	81.6(1)	O(2^v)-O(4)	2.867(5)^o	86.7(1)
O(1^i)-O(2^{ii})	3.158(4)	103.7(2)	O(3) -O(4)	2.950(4)^o	90.7(2)
-O(3)	3.041(5)	91.3(1)	O(1) -O(2^v)	3.081(3)	97.4(2)
-O(4)	2.934(5)	91.8(1)	-O(3)	3.194(5)	103.4(2)
-O(5^i)	3.235(2)	102.2(2)	O(1^{iv})-O(2^v)	2.873(4)	85.4(2)
O(2^{ii})-O(3)	2.906(5)	86.8(1)	-O(4)	3.142(5)	92.4(1)
-O(4^{iii})	3.033(5)	87.0(2)	O(2^v)-O(3)	2.978(5)	95.7(1)
-O(5^i)	3.001(2)	93.0(2)	O(3) -O(6)	3.134(2)	97.5(2)
O(3) -O(4^{iii})	3.112(4)	84.6(2)	O(4) -O(6)	2.997(2)	87.8(2)
mean	3.008		mean	2.959	

Mg(3) Octahedron			Si(1) Tetrahedron		
Mg(3)-O(2^v)	2.040(4) [3]		Si(1)-O(3)	1.641(3) [3]	
-O(4)	2.076(4) [3]		-O(5)	1.666(4)	
mean	2.058		mean	1.647	
O(2^v)-O(4)	2.867(5)^o [3]	88.3(1)	O(3) -O(3^{ii})	2.675(4) [3]	109.2(2)
O(4) -O(4^{iii})	2.789(5)^o [3]	84.4(2)	-O(5)	2.705(4) [3]	109.7(2)
O(2^v)-O(4^{vi})	2.937(3) [3]	92.1(2)	mean	2.690	
-O(4^{iii})	3.039(5) [3]	95.2(1)			
mean	2.908		Si(2) Tetrahedron		
			Si(2)-O(1^i)	1.639(3) [3]	
			-O(6)	1.623(7)	
			mean	1.635	
			O(1^i)-O(1^i)	2.558(4)^t [3]	102.6(2)
			-O(6)	2.761(6) [3]	115.2(2)
			mean	2.660	

Symmetry codes			
none	x	y	z
i	x-y	x	1/2+z
ii	1-x+y	1-x	z
iii	1-y	1+x-y	z
iv	-y	x-y	z
v	x-y	x	-1/2+z
vi	y	1-x+y	-1/2+z
vii	-x	-y	1/2+z

Estimated standard errors are given in parantheses and refer to last decimal place.
t: Edge shared between tetrahedron and tetrahedron
o: Edge shared between two octahedra.
Numbers in square brackets are multiplicity factors.
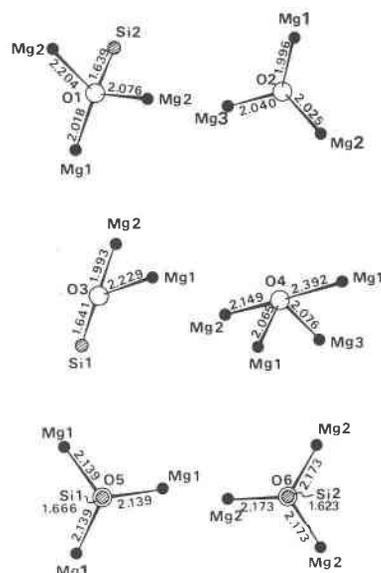
Fig. 3. The coordination of cations around oxygen atoms.

2.573A, the mean distances of shared edges between octahedra are 2.857, 2.837, and 2.851A, and those of unshared edges are 3.192, 3.086, and 3.040A, respectively, for three octahedra in the structure. The shortening of shared edges of octahedra is also found in hematolite. The shortening of distances between oxygens involved in edge sharing has been explained by Pauling (1960) as the result of cation–cation repulsion. This phenomenon was also discussed for olivine and spinel by Kamb (1968).

The distribution of hydrogen atoms was not determined in the present study. To predict the position of the hydrogen atoms in the structure, the cation environment around oxygen atoms has been scrutinized (Fig. 3). O(1), O(5), and O(6) are in tetrahedral coordination with one Si and three Mg atoms, and these cations contribute a total charge of +2 to the oxygen atoms. O(3) is coordinated by one Si and two Mg with total charge of +1.67. On the other hand, O(2) and O(4) are coordinated by only Mg atoms, and their total charges are +1 and +1.33, respectively. Therefore, one may assume that O(2) and O(4) atoms are hydroxyl ions (Donnay and Allmann, 1970).

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between an octahedron and a tetrahedron, is the shortest, 2.558A, of all O–O distances in phase A. The mean distances of the shared edges between octahedra, 2.918, 2.886, and 2.827A for Mg(1)O$_6$, Mg(2)O$_6$ and Mg(3)O$_6$ respectively, are smaller than the mean distances of unshared octahedral edges which are 3.053, 3.057, and 2.988A respectively. This finding is similar to the characteristics of octahedra in humite-group minerals discussed above. For example, in hydroxyl-chondrodite, the shared edges between octahedra and tetrahedra are 2.562, 2.562, and

mal Ellipsoids with Error Analysis).

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