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THE CRYSTAL STRUCTURE OF A TITANIFEROUS CLINOHUMITE

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ABSTRACT

The crystal structure of a titaniferous clinohumite from Cargill Lake, Ontario, $Mg_{7.34}Fe_{1.45}Ti_{0.26}(SiO_4)_4(OH,F,O)$, $a = 4.753(4)$, $b = 10.269(6)$, $c = 13.724(7)$ Å, $\alpha = 100.90°$, $P2_1/b$, (unique axis a) has been refined by full matrix anisotropic least squares calculations to a residual of $R = 0.036$ for 1644 observed reflections. Structural details are similar to those of other members of the humite series, norbergite, chondrodite and humite, being based on a hexagonal closest packing of anions, containing chains of octahedrally coordinated M ions. There are five distinct types of octahedra: $M(1)O_6$ (2 types) and $M(2)O_6$, similar to those of the same nomenclature in olivine; and $M(2)O_5(OH,F)$ and $M(3)O_4(OH,F)_2$, like those in chondrite and humite. The cation distribution suggests that Ti is exclusively concentrated in, and Fe almost completely absent from the $M(3)O_4(OH,F)_2$ octahedron, and that there is significant Mg enrichment in the $M(2)O_5(OH,F)$ octahedron.

INTRODUCTION

The humite minerals have recently been the subject of detailed study by Gibbs, Ribbe and co-workers (1968-1971) and the structural analogies of the humites with the olivine group have been amply demonstrated. The humite minerals may be represented by the formula

$$n[M_2SiO_4] \,.\, [M_{1-x}Ti_x(F,OH)_{2-2x}]$$

where n takes integral values from 1 to 4 for norbergite, chondrodite, humite and clinohumite respectively, and M is predominantly Mg with lesser Fe. The formula thus presented is seen to combine olivine units with 'brucite-sellaite' units ($Mg(OH)_2$,MgF_2), though Ribbe *et al.* (1968) have shown that this description of unit blocks is a misleading way of regarding the structure. Ti, when present, has been assumed to substitute in the 'brucite-sellaite' part of the formula, since natural olivines contain very little TiO_2, and by analogy the olivine part of the structure of the humite minerals may be expected to behave similarly. The substitution of Ti^{4+} for M^{2+} involves anion substitution of O^{2-} for $(F,OH)^-$, as indicated in the general formula. Clinohumite is the only humite mineral which contains high TiO_2, and values as high as 5.6% have been recorded (McGetchin *et al.* 1970; Jones *et al.* 1969). It is therefore of interest to study the role of Ti in the clinohumite structure.

A rather unusual occurrence of clinohumite has been found in a carbonatite complex at Cargill Lake, Ontario, (Gasparrini *et al.* 1971) and as it contains 3 to 5 per cent TiO_2 it was considered a suitable candidate for the study.

The cell orientation and atomic nomenclature used in this paper are the same as those adopted by Ribbe and Gibbs in their work on the humite minerals. In clinohumite there are two types of $M(1)O_6$ octahedra, of which the central atom $M(1)$ has been given the subscript A to designate the centrosymmetric variety sharing edges with $M(1)$ and $M(2)$ types only, or B to designate that sharing edges with $M(1)$, $M(2)$ and $M(3)$ types.

The material was analysed by electron microprobe, ARL model EMX. Operating conditions were 15 kv, 0.05 μa sample current, and standards were synthetic forsterite for Si and Mg, synthetic ferrosilite for Fe, synthetic tephroite for Mn, rutile for Ti and NaF for F. Data were processed by EMPADR 7 (Rucklidge & Gasparrini 1969) which corrects for background, dead time, absorption, atomic number and fluorescence effects according to the scheme of Sweatman & Long (1969). A representative analysis of the material is shown in Table 1.

For single-crystal x-ray study a crystal was selected with overall dimensions 0.12 × 0.15 × 0.10 mm. Cell parameters and standard deviations were determined by least squares fit of 25 high-angle reflections carefully centred on a Picker four-circle diffractometer FACS-1 using Ni-filtered Cu$K\alpha$ radiation. Zr-filtered Mo$K\alpha$

TABLE 1. ELECTRON MICROPROBE ANALYSIS OF TITANIFEROUS CLINOHUMITE (Analyst E.L. Gasparrini)

SiO_2	36.1 wt.%
TiO_2	3.14
FeO	14.6
MnO	0.62
MgO	44.7
F	1.15
H_2O (calc.)	1.46
	101.9
Less O=F	0.48
	101.4

Chemical formula normalised to 4 Si:

$(Mg_{.82}Fe_{.17}Mn_{.01})_{8.05}(SiO_4)_4 \cdot$

$Mg_{0.74}Ti_{0.26}F_{0.40}OH_{1.08}O_{0.52}$

radiation was used for actual data collection to decrease absorption by the crystal (for Cu$K\alpha$, $\mu = 209.4$ cm^{-1}; for Mo$K\alpha$, $\mu = 24.6$ cm^{-1}).

The crystal data for the sample used in this study are as follows: Monoclinic space group $P2_1/b$ (unique axis a), a = 4.753(4), b = 10.269(6), c = 13.724(7)Å, α = 100.90(1)°, V = 657.76Å^3, measured density 3.390 g/cc, calculated density 3.404 g/cc, $Z = 2$.

A total of 1937 symmetry-independent reflections were measured by $\theta - 2\theta$ scan technique up to sin $\theta/\lambda = 0.70$. Of these, 1644 reflections were above the background level. The scan rate was 1° per minute, and two 20-second background counts were taken on each side of the peak. Two reflections (001 and 002) were excluded from the data because they were suspected to be incorrectly collected. To check for the absorption of the crystal several Φ sweep runs at $\chi = 90°$ were made, and the intensities of an additional 40 high-angle symmetry-related reflections were measured. The intensity variation of the Φ sweeps was less than 4% in the whole range, and the intensity variation between symmetry-related pairs of reflections was less than 1.5%; thus no absorption corrections were necessary. Data were reduced to structure amplitudes in the normal way, using $2\sigma(F^2)$ as the threshold level for unobserved reflections. The weighting function used for (F^2) was

$$\sigma^2(F^2) = (I/[Lp]^2 + CF^4 \quad \text{with } C = 0.008$$

where $\sigma^2(F^2)$ is the standard deviation of corrected (F^2), Lp is the Lorentz and polarization correction and C is an estimated 'instrument factor' to allow for diffractometer instability.

An initial least squares refinement, using the coordinates of Taylor & West (1928) for clinohumite, was carried out by the computer program XFLS (Ellison 1962) making the assumption that all M sites contain the same cation distribution. The R value after scale refinement was 0.47, and six additional cycles of positional and scale refinement lowered R to 0.12. Two more cycles of isotropic refinement brought the residual to 0.08. The isotropic temperature factors of the $M(1)_A$, $M(1)_B$, $M(2)_5$ and $M(3)$ sites were of the same order of magnitude in the range B = 0.40 – 0.52Å^2, but the temperature factor of the $M(2)_6$ site refined to an unusually low value of 0.24Å, indicating a predominance of Fe^{2+} in the $M(2)_6$ position. A computer programme to refine site occupancy (Finger 1967) was used to determine the distribution of Fe and Mg in the various M sites. The isotropic temperature factors were fixed at B = 0.45A^2 for all the M sites which were assumed to contain Fe and Mg, with the only restriction that Fe + Mg = 1.0 for each site. The small amounts of Mn and Ti in the analysis were regarded as Fe, thus giving an Fe equivalent atomic proportion of 1.71 atoms per formula unit. The true effect of the contribution of Ti will be discussed later. Three cycles of Finger's refinement varying scale, site occupancy, positional parameters and isotropic temperature factors of the remaining atoms decreased the R value to 0.057. At this point the Fe occu-

TABLE 2. ATOMIC POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B(Å^2)
$M(1)_A$	0.5	0.0	0.5	0.48(2)
$M(1)_B$	0.00294(14)	0.44596(6)	0.27424(5)	0.47(2)
$M(2)_5$	0.01258(15)	0.13989(7)	0.16997(5)	0.47(2)
$M(2)_6$	0.98872(15)	0.75089(7)	0.38792(6)	0.47(2)
$M(3)$	0.00599(15)	0.38156(8)	0.04182(6)	0.48(2)
Si(1)	0.42699(15)	0.56673(6)	0.38952(5)	0.24(2)
Si(2)	0.57563(14)	0.32317(6)	0.16460(5)	0.23(2)
O(1,1)	0.76733(40)	0.56471(16)	0.38786(12)	0.50(3)
O(1,2)	0.28089(38)	0.42086(16)	0.38774(13)	0.52(3)
O(1,3)	0.27872(37)	0.61312(17)	0.29395(13)	0.59(3)
O(1,4)	0.27941(38)	0.65899(16)	0.48633(13)	0.56(3)
O(2,1)	0.23539(39)	0.32279(17)	0.16273(13)	0.52(3)
O(2,2)	0.72116(37)	0.46805(17)	0.16273(13)	0.58(3)
O(2,3)	0.72219(39)	0.27913(17)	0.26181(13)	0.61(3)
O(2,4)	0.72579(38)	0.22776(17)	0.06969(13)	0.63(3)
OH,F	0.24213(39)	0.54469(17)	0.05394(13)	0.63(3)

Numbers in parentheses are the e.s.d. for coordinates x10^5, for B x10^2.

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$M(1)_A$	392(43)	191(9)	51(5)	0	0	44(5)
$M(1)_B$	454(35)	163(7)	41(4)	-9(9)	-12(7)	15(4)
$M(2)_5$	509(33)	135(7)	56(4)	9(10)	-3(7)	33(4)
$M(2)_6$	565(31)	135(7)	54(4)	9(9)	6(7)	29(4)
$M(3)$	357(33)	201(7)	34(4)	-64(9)	28(7)	-11(4)
Si(1)	159(29)	103(6)	22(4)	4(8)	-5(6)	22(3)
Si(2)	175(28)	95(6)	22(4)	6(9)	7(6)	19(3)
O(1,1)	431(70)	183(15)	58(8)	-3(23)	-23(17)	33(8)
O(1,2)	603(68)	106(14)	80(8)	-24(24)	-30(19)	24(8)
O(1,3)	518(68)	214(15)	67(8)	-16(25)	-8(19)	54(7)
O(1,4)	486(67)	158(15)	80(8)	39(24)	17(18)	1(8)
O(2,1)	411(67)	178(15)	71(8)	-10(23)	-3(17)	50(8)
O(2,2)	677(69)	163(15)	67(8)	-34(25)	-26(19)	34(8)
O(2,3)	587(70)	220(16)	63(8)	31(25)	20(19)	59(9)
O(2,4)	651(69)	179(15)	73(8)	-14(25)	41(20)	3(8)
OH,F	536(67)	207(15)	77(8)	-25(25)	-91(20)	2(8)

*The form of the thermal ellipsoids is exp $-\left[h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23}\right]$

Nos. in parentheses are e.s.d. All numbers are x10^5.

pancies of each M site were 0.194 in $M(1)_A$, 0.197 in $M(1)_B$ 0.160 in $M(2)_5$, 0.241 in $M(2)_6$ and 0.155 in $M(3)$. Two additional isotropic cycles of refinements using these M site occupancies resulted in a further reduction of R to 0.048, and there was little change in the isotropic temperature factors, (see Table 2). This result appears to confirm that the correct amount of scattering matter was given by the Finger programme. Final anisotropic refinement, varying 140 parameters and applying full shifts, produced an ultimate residual of 0.036 ($R_W = 0.060$) for 1644 observed reflections. The R-factor for all 1925 hkl reflections was 0.044. The value of

$$(\Sigma w_{hkl} \cdot \Delta F^2_{hkl}/(m-n))^{1/2}$$

TABLE 4. INTERATOMIC DISTANCES, AND ANGLES IN CLINOHUMITE

Si(1) tetrahedron, SiO_4	Q.E.=1.0103	
Si(1)-O(1,1)^A	1.617(2)	
O(1,2)	1.647(2)	
O(1,3)	1.637(2)	
O(1,4)	1.636(2)	
Mean	*1.634*	
		Angle at Si
O(1,3)-O(1,2)^t	2.552(3)	102.0
O(1,4)-O(1,2)^t	2.561(3)	102.5
O(1,4)-O(1,3)^t	2.593(3)	104.7
O(1,1)-O(1,2)	2.743(3)	114.3
O(1,1)-O(1,3)	2.746(3)	115.1
O(1,1)-O(1,4)	2.765(3)	116.4
Mean	*2.660*	*109.2*

Si(2) tetrahedron, SiO_4	Q.E.=1.0102	
Si(2)-O(2,1)^A	1.617(2)	
O(2,2)	1.645(2)	
O(2,3)	1.642(2)	
O(2,4)	1.638(2)	
Mean	*1.636*	
		Angle at Si
O(2,4)-O(2,2)^t	2.555(3)	102.2
O(2,3)-O(2,2)^t	2.571(3)	102.9
O(2,4)-O(2,3)^t	2.589(3)	104.2
O(2,1)-O(2,4)	2.746(3)	115.1
O(2,1)-O(2,2)	2.748(3)	114.8
O(2,1)-O(2,3)	2.763(3)	115.9
Mean	*2.662*	*109.2*

$M(1)_A$ octahedron, MO_6	Q.E.=1.0286	
$M(1)_A$-O(1,2)	[2]2.084(2)	
O(1,1)	[2]2.102(2)	
O(1,4)	[2]2.140(2)	
Mean	*2.109*	
		Angle at M
O(1,2)-O(1,4)^t	[2]2.561(3)	74.6
O(1,2)-O(1,1)^o	[2]2.853(3)	85.9
O(1,1)-O(1,4)^o	[2]2.862(3)	84.7
O(1,2)-O(1,1)	[2]3.063(3)	94.1
O(1,1)-O(1,4)	[2]3.132(3)	95.2
O(1,2)-O(1,4)	[2]3.359(3)	105.4
Mean	*2.972*	*90.0*

$M(1)_B$ octahedron, MO_6	Q.E.=1.0296	
$M(1)_B$-O(2,2)	2.078(2)	
O(1,2)	2.095(2)	
O(2,1)	2.105(2)	
O(1,1)	2.110(2)	
O(1,3)	2.136(2)	
O(2,3)	2.153(2)	
Mean	*2.113*	
		Angle at M
O(1,2)-O(1,3)^t	2.552(3)	74.2
O(2,2)-O(2,3)^t	2.571(3)	74.8
O(1,1)-O(1,3)^o	2.834(3)	83.9
O(1,2)-O(1,1)^o	2.853(3)	85.4
O(2,2)-O(2,1)^o	2.863(3)	86.4
O(2,1)-O(2,3)^o	2.868(3)	84.7
O(1,2)-O(2,1)	3.069(3)	93.9
O(2,2)-O(1,1)	3.069(3)	94.2
O(1,1)-O(2,3)	3.118(3)	94.0
O(2,1)-O(1,3)	3.184(3)	97.4
O(1,2)-O(2,3)	3.347(3)	104.0
O(2,2)-O(1,3)	3.387(3)	106.9
Mean	*2.976*	*90.0*

$M(2)_6$ octahedron, MO_6	Q.E.=1.0300	
$M(2)_6$-O(1,4)	2.054(2)	
O(1,2)	2.060(2)	
O(2,3)	2.067(2)	
O(1,1)	2.182(2)	
O(1,3)	2.207(2)	
O(1,4)'	2.259(2)	
Mean	*2.138*	
		Angle at M
O(1,3)-O(1,4)^t	2.593(3)	71.0
O(1,1)-O(1,3)^o	2.834(3)	80.6
O(1,1)-O(1,4)^o	2.862(3)	80.2
O(1,2)-O(2,3)	2.924(3)	90.2
O(1,4)'-O(1,2)	2.926(3)	90.7
O(1,4)'-O(1,4)	3.002(3)	88.1
O(2,3)-O(1,3)	3.009(3)	89.4
O(1,4)'-O(1,1)	3.030(3)	91.3
O(2,3)-O(1,1)	3.047(3)	91.6
O(1,2)-O(1,3)	3.191(3)	96.7
O(1,2)-O(1,4)	3.243(3)	97.2
O(1,4)'-O(2,3)	3.394(3)	110.9
Mean	*3.005*	*89.8*

$M(2)_5$ octahedron, MO_5(OH,F)	Q.E.=1.0235	
$M(2)_5$-O(1,3)	2.033(2)	
O(2,2)	2.072(2)	
O(2,1)	2.175(2)	
O(2,3)	2.204(2)	
O(2,4)	2.244(2)	
OH,F	2.064(2)	
Mean	*2.132*	
		Angle at M
O(2,3)-O(2,4)^t	2.589(3)	71.2
O(2,1)-O(2,4)^o	2.824(3)	79.4
O(2,1)-O(2,3)^o	2.868(3)	81.9
OH,F -O(2,2)	2.911(3)	89.5
OH,F -O(2,1)	2.964(3)	88.7
O(1,3)-O(2,2)	2.978(3)	93.0
O(1,3)-O(2,3)	3.002(3)	90.1
O(1,3)-O(2,1)	3.058(3)	93.2
OH,F -O(2,4)	3.134(3)	93.2
O(2,2)-O(2,4)	3.177(3)	94.7
O(2,2)-O(2,3)	3.237(3)	98.4
OH,F -O(1,3)	3.240(3)	104.5
Mean	*2.999*	*89.8*

$M(3)$ octahedron, $MO_4(OH,F)_2$	Q.E.=1.0198	
$M(3)$-O(2,4)'	2.010(2)	
O(2,4)	2.155(2)	
O(2,1)	2.165(2)	
O(2,2)	2.195(2)	
OH,F'	1.997(2)	
OH,F	2.017(2)	
Mean	*2.090*	
		Angle at M
O(2,4)-O(2,2)^t	2.555(3)	71.9
OH,F' -OH,F^o	2.796(3)	88.3
O(2,4)-O(2,1)^o	2.824(3)	81.7
O(2,1)-O(2,2)^o	2.863(3)	82.1
OH,F -O(2,4)	2.894(3)	91.9
OH,F' -O(2,1)	2.951(3)	90.2
OH,F -O(2,2)	2.957(3)	89.1
OH,F' -O(2,4)'	2.986(3)	96.3
OH,F' -O(2,2)	3.069(3)	94.0
O(2,4)'-O(2,1)	3.134(3)	97.2
O(2,4)-O(2,4)'	3.137(3)	97.7
OH,F -O(2,4)	3.140(3)	97.6
Mean	*2.942*	*89.8*

t = edge shared between tetrahedron and octahedron

Q.E. = Quadratic elongation

o = edge shared between two octahedra

superscript prime distinguishes two similar anions in the same polyhedron - see Fig. 2

superscript A indicates apical oxygen

numbers in parentheses are the e.s.d. for bond lengths x10^3. E.s.d. of all bond angles 0.1

[2] indicates multiplicity factor for bonds in centrosymmetric octahedron

was 1.17, further confirming the validity of the weighting scheme. No corrections for anomalous dispersion were made. The final atomic coordinates and isotropic temperature factors for all atoms in the asymmetric unit are listed in Table 2, and the corresponding anisotropic temperature factors are to be found in Table 3. The significant bond lengths and angles, with standard deviations as calculated by the computer programme ORFFE (1962), are summarized in Table 4. The scattering curves used in the refinements were those of Cromer & Mann (1968). A comparison of the observed structure amplitudes and calculated structure factors is available in Table 6*.

Discussion of Crystal Structure

An exploded (100) projection of the five octahedra and two tetrahedra which comprise the structure is shown in Figure 1. Bond lengths and atomic nomenclature are also given in this diagram. Figure 2 shows a (100) projection of the octahedral chain which extends through the structure parallel to z, and which is linked laterally above and below to similar chains, through SiO_4 tetrahedra. This projection also shows two pseudohexagonal planes of anion closest packing. The octahedral chain is the principal feature involved in understanding the structure, and agrees with the schematic representation of Ribbe, Gibbs & Jones (1968) for clinohumite.

We have argued the likelihood of Ti being associated with the (OH,F)$^-$ part of the structure, in which case the $M(3)$ site, with two (OH,F) in the co-ordination polyhedron, would

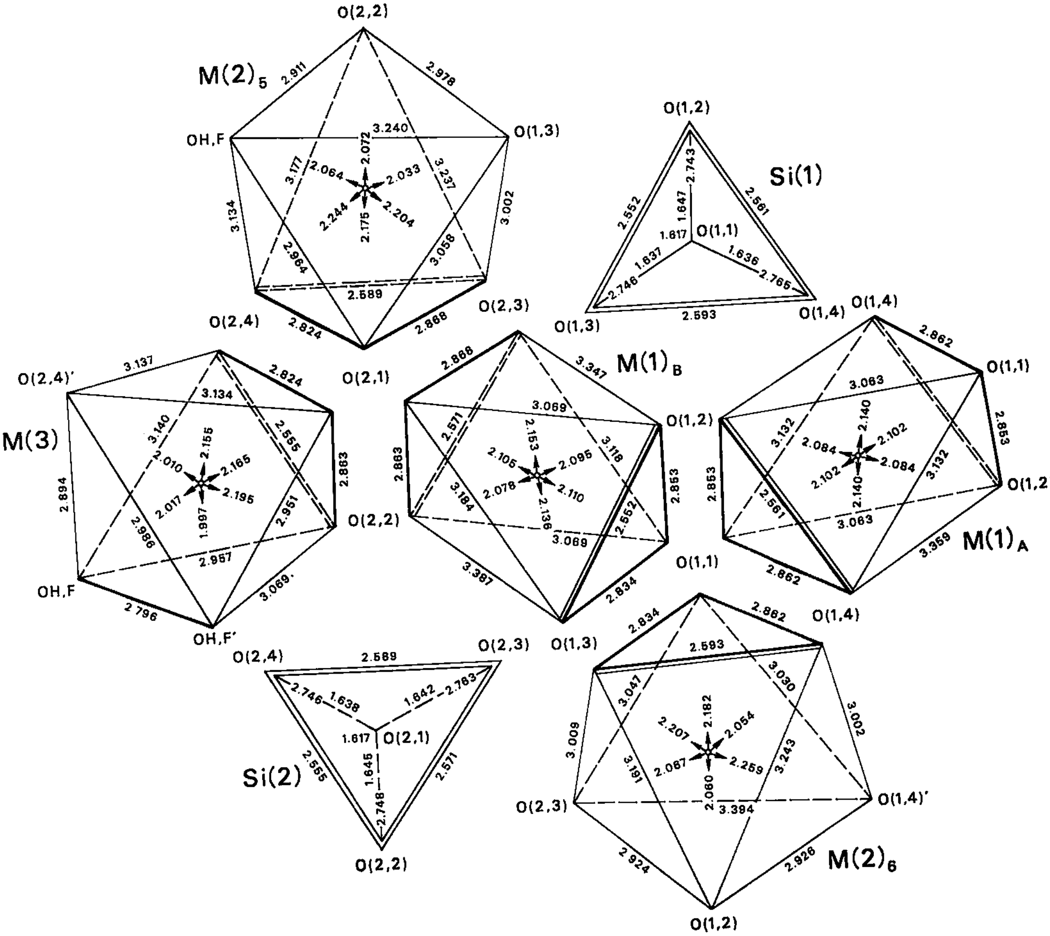

FIG. 1. Exploded (100) projection of the steric features of the cation co-ordination polyhedra in clinohumite. Heavy lines indicate polyhedral edges shared between two octahedra; double lines are edges shared between an octahedron and a tetrahedron.

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* Table 6 has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to : Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

be preferred. At 2.089*Å*, $M(3)O_4(OH,F)_2$ has the shortest mean $M(3)$-(OH,F,O) bond length of all the five octahedra, and this is consistent with the substitution of Ti^{4+} ($r = 0.68$Å) for Fe^{2+} ($r = 0.76$Å). $M(3)O_4(OH,F)_2$ is the smallest octahedron because two of its anions $(OH,F)^-$ are in planar 3-fold co-ordination, instead of tetrahedral co-ordination as are the rest of the O^{2-}. Hence we may expect some of the ligands to be drawn more closely to the $M(3)$ ion, particularly since the contribution of Ti^{4+} will be to increase its attraction. However, if we look at the mean $M(3)$-(O,OH,F) bond length in the $M(3)O_4(OH,F)_2$ octahedra in each of the humite minerals, we find increasing values from norbergite to clinohumite thus, 2.068Å in norbergite, 2.078Å in chondrodite, 2.087Å in humite, and 2.090Å in clinohumite.

In the TiO_2 minerals (rutile, anatase, brookite) the mean Ti-O bond length in the TiO_6 octahedra is 1.96Å (Baur 1961), which is smaller than any of the $M(3)$-(O,OH,F) bonds listed above. It is perhaps surprising therefore that of all the humite minerals it is the one with the largest $M(3)$ octahedron, clinohumite, which most commonly contains significant amounts of Ti. Norbergite and chondrodite rarely contain as much as 0.5% TiO_2, but these minerals always contain large amounts of F (5-16%, Jones *et al.* 1969) in contrast to humite and clinohumite. Clinohumite in particular contains very little F, especially in the high Ti varieties. There appears to be no structural reason why Ti is restricted to the clinohumite species, but high Ti concentrations (~3-4% TiO_2) seem to be incompatible with high F (3-4%). The element F is essential for the formation of norbergite and chondrodite, and so Ti necessarily becomes associated only with the low F bearing varieties of humite and clinohumite, particularly the latter.

A remarkable similarity in interatomic distances and angles exists between this determination of clinohumite and the other humite minerals, in particular humite (Ribbe & Gibbs 1971). A small but consistent difference seems to lie in the slightly larger dimensions of the coordination polyhedra in clinohumite over humite, the average cation-anion bond being about 0.3% longer. This increase may be ascribed to the high concentration of Fe (14.6% FeO) in the present sample contrasted with previously determined humite minerals where the highest concentration is 5.03% FeO. This degree of expansion of coordination polyhedra is exactly what would be expected using the dependence of Fe of olivine cell parameters as a guide. The mean increase of olivine cell edges is 0.31% per 10% FeO.

It is not possible to determine unambiguously the cation distribution among different sites when more than two species of atom are present. The Finger program will adjust the proportions of two species, *e.g.* Fe and Mg, to give a concentration of composite scattering matter at each position (*f*, Table 5), and the contribution of each species can be deduced. Where more than two elements are present (in this case Ti is significant) the best that can be done is to distribute

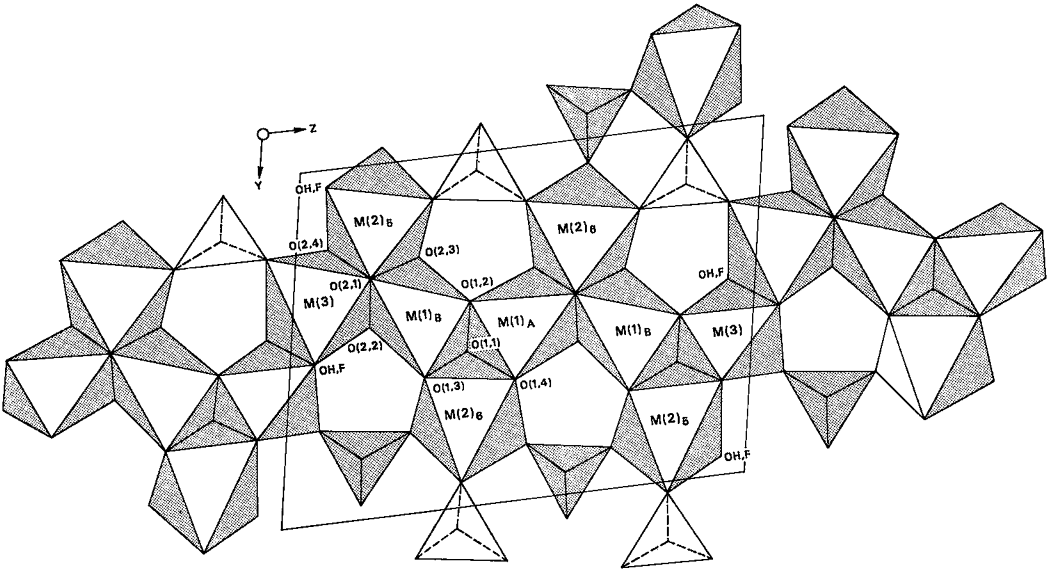

FIG. 2. Projection along [100] diad axis showing the chain of *M*-octahedra, and the SiO_4-tetrahedra, relative to the *y* and *z* axes in one-half of the unit cell.

the different atoms in each site such that the *f* values are unchanged when the contribution of the proportion of each cation species is considered. The assignment of Ti was thus made on the basis of crystal chemical arguments and the indication from the chemical formula that Ti occupies a distinct position.

The Finger refinement indicated relatively low Fe concentration in the $M(3)$ position and high in $M(2)_6$. This is the same distribution which has been observed previously in the humites, and Ribbe and Gibbs have shown that Fe definitely tends to avoid the $M(3)$ position. If this is the case we may confidently assign Ti to this site, and if all the Ti is confined exclusively to the $M(3)$ site then 0.81 atom Mg and only 0.06 atom Fe are required to fill it. It is possible, of course, that Ti may also enter the $M(2)_5$ site because (OH,F) is also contained in its co-ordination polyhedron and *f* for $M(2)_5$ is relatively low (see Table 5), but the assignment would be arbitrary. The Fe-Ti-Mg distributions shown in Table 5 indicate our conclusions.

The quadratic elongation parameter described by Robinson, Gibbs & Ribbe (1971) is a useful measure of the distortion of co-ordination polyhedra. This parameter has been calculated for the Si and *M* polyhedra in clinohumite, and values are listed in Tables 4 and 5. The values are very similar to those of the corresponding sites in humite; the highest values correspond to the highest Fe occupancies and *vice versa.* This is a further confirmation that it is the distortion of the octahedron rather than its size which is most closely correlated with the Fe distribution. The least distorted site is $M(3)$ to which Ti has been assigned. This is in accordance with the suggestion of Burns (1970) that both Ti^{4+} and Mg^{2+} possess no *d* electron orbitals; all bonding forces will be along cartesian axes and distortion from a regular octahedron will be minimized.

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TABLE 5. OCCUPANCY AND SITE DISTORTION FOR CLINOHUMITE AND HUMITE

	Ti-clinohumite (this study)						Humite (Ribbe & Gibbs 1971)	
Site	Multiplicity	*f*	Fe	Ti	Mg	Q.E.*	Fe	Q.E.*
$M(1)_A$	1	14.71	0.194	----	0.806	1.0286	--	-----
$M(1)_B$	2	14.75	0.197	----	0.803	1.0296	0.09	1.0293
$M(2)_5$	2	14.23	0.160	----	0.840	1.0235	0.03	1.0223
$M(2)_6$	2	15.36	0.241	----	0.759	1.0300	0.12	1.0291
$M(3)$	2	14.15	0.060	0.13	0.810	1.0198	0.01	1.0190
Total number of atoms in all sites with allowance for multiplicity.								
	Total:		1.51	0.26	7.23			
	Probe analysis:		1.45**	0.26	7.34			

f corresponds to a value for the scattering factor at $(\sin\theta)/\lambda=0$ as given by the Finger refinement.

*Q.E.=quadratic elongation **includes 0.08 atom Mn

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