

## The Crystal Structures of the Humite Minerals. IV. Clinohumite and Titanoclinohumite

KEITH ROBINSON<sup>1</sup>, G. V. GIBBS AND PAUL H. RIBBE

Department of Geological Sciences  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061

### Abstract

The crystal structures of clinohumite [ $\text{Mg}_{8.42}\text{Fe}_{0.50}\text{Mn}_{0.06}\text{Ti}_{0.02}\text{Ca}_{0.001}(\text{SiO}_4)_4\text{F}_{1.04}\text{H}_{0.93}\text{O}_{0.03}$ ;  $a = 4.7441(2)$ ;  $b = 10.2501(5)$ ;  $c = 13.6635(3)\text{\AA}$ ;  $\alpha = 100.786(2)^\circ$ ;  $P2_1/b$ ] and titanoclinohumite [ $\text{Mg}_{7.33}\text{Fe}_{1.04}\text{Mn}_{0.05}\text{Ti}_{0.47}\text{Ca}_{0.001}(\text{SiO}_4)_4\text{OH}_{1.04}\text{O}_{0.96}$ ;  $a = 4.7451(8)$ ;  $b = 10.288(2)$ ;  $c = 13.709(3)\text{\AA}$ ;  $\alpha = 101.00(2)^\circ$ ;  $P2_1/b$ ] have been refined by three-dimensional least-squares methods to  $R = 0.051$  and  $R = 0.042$ , respectively.

Their structures are based on a hexagonal close-packed array of anions and are similar to those of other minerals in the humite series and to the olivines. The serrated chain of edge-sharing octahedra in clinohumite consists of five unique octahedra; of these,  $M(1)_C$  and  $M(2)_6$  are like those in the olivines;  $M(1)_N$ ,  $M(2)_6$  and  $M(3)$  are like those in humite. One-half the octahedral sites and one-ninth the tetrahedral sites are filled.

The distribution of transition metal ions in clinohumite is consistent with that in humite and chondrodite,  $\text{Fe}^{2+}$  being ordered into the more distorted  $\text{MO}_6$  "olivine-like portion" of the structure. However, the distribution in titanoclinohumite is not consistent with any of the humite minerals previously studied. The distribution of Ti appears to be random and the  $M(3)$  site, with one (OH) ligand, appears to be slightly enriched in Fe, the balance of the Fe being randomly distributed amongst the octahedral sites.

### Introduction

The humite series of minerals have the general formula  $nM_2\text{SiO}_4 \cdot M_{1-x}(\text{OH},\text{F})_{2-2x}\text{Ti}_x\text{O}_{2x}$  where  $x \leq 1$ , and where  $n = 1$  for norbergite,  $n = 2$  for chondrodite,  $n = 3$  for humite,  $n = 4$  for clinohumite; and  $M$  represents Mg, Fe, Mn, Ca, and Zn in decreasing order of abundance (Jones, Ribbe, and Gibbs, 1969). The structure is based on a hexagonal close-packed array of anions similar to that of forsterite (Bragg and West, 1927; Taylor and West, 1928; Taylor, 1929). Recently Ribbe, Gibbs and Jones (1968) recognized that the key structural unit in the humites is a serrated chain of edge-sharing octahedra similar to that in olivines (Birle, Gibbs, Moore, and Smith, 1968). Structure refinements of norbergite (Paper I, Gibbs and Ribbe, 1969), chondrodite (Paper II, Gibbs, Ribbe and Anderson, 1970) and humite (Paper III, Ribbe and Gibbs, 1971) show that the distortion of the *hcp* anion array in these structures can be attributed to cation-cation repulsion across shared polyhedral

edges. Site refinements of humite and chondrodite produced evidence of  $\text{Mg}/\text{Fe}^{2+}$  ordering in the octahedral chain. Borneman-Starynkevich and Myasnikov (1950) suggested that the replacement of Mg by Fe takes place in the "olivine portion" ( $M_2\text{SiO}_4$ ) of the humite structure and not in the  $M_{1-x}(\text{OH},\text{F})_{2-2x}\text{Ti}_x\text{O}_{2x}$  portion. Accordingly, Robinson (1971) refined the structures of clinohumite and titanoclinohumite to establish cation distribution in the  $M$  sites.

### Experimental

The clinohumite crystals used in this study are from Hämeenkylä, Finland, and Franscia, Val Malenco, Italy. The Hämeenkylä specimen, from a "limestone," was originally analyzed by Sahama (1953, his specimen No. 1) and later by Jones *et al.* (1969, their specimen No. 7). The Val Malenco specimen, from a "dynamically metamorphosed peridotite" (Brugnatelli, 1904) was obtained from Dr. Joel Arem and Dr. John White, Jr. of the U. S. National Museum (specimen No. 94997) and analyzed by Jones *et al.* (1969, their specimen No. 10). The compositions, unit cell parameters and physical properties of clinohumite and titanoclinohumite are listed in Table 1. Space group  $P2_1/b$  ( $\alpha$  obtuse) is consistent with that determined by Taylor and West (1928) and is preferred over other settings be-

<sup>1</sup>Now at U. S. Geological Survey, Federal Center, Denver, Colorado.

TABLE 1. MICROPROBE ANALYSIS AND PHYSICAL PROPERTIES OF CLINOHUMITE FROM HÄMEENKYLA, FINLAND AND TI-CLINOHUMITE FROM FRANSCIA, VAL MALENCO, ITALY

	Clinohumite	Ti-Clinohumite
Microprobe analyses (Jones <i>et al.</i> , 1969)		
SiO <sub>2</sub>	37.54 wt.%	35.90 wt.%
FeO	5.58	11.21
MnO	0.62	0.50
MgO	53.03	44.16
TiO <sub>2</sub>	0.22	5.59
CaO	0.01	0.01
ZnO	0.00	0.00
F	3.08	0.00
OH(calc)	2.46	2.64
Total, corr. for F,OH:	100.08 wt.%	98.77 wt.%
Unit cell parameters (Jones <i>et al.</i> , 1969)*		
a	4.7441(2)	4.7451(8)
b	10.2501(5)	10.288(2)
c	13.6635(3)	13.709(3)
α	100.786(2)	101.00(2)
V	652.69Å <sup>3</sup>	660.81Å <sup>3</sup>
Space group	P2 <sub>1</sub> /b	P2 <sub>1</sub> /b
Z	2	2
Refractive indices and density**		
α	1.629	1.662
β	1.641	1.680
γ	1.662	
2V	73°	58°
ρ	3.260 gm/cc	3.23 gm/cc
Chemical formula, normalized to four Si:		
Clinohumite		
Mg <sub>7.437</sub> Fe <sub>0.497</sub> Mn <sub>0.056</sub> Ca <sub>0.001</sub> (SiO <sub>4</sub> ) <sub>4</sub> ·Mg <sub>0.983</sub> Ti <sub>0.017</sub> F <sub>1.038</sub> OH <sub>0.926</sub> O <sub>0.034</sub>		
Ti-Clinohumite		
Mg <sub>6.800</sub> Fe <sub>1.044</sub> Mn <sub>0.048</sub> Ca <sub>0.001</sub> (SiO <sub>4</sub> ) <sub>4</sub> ·Mg <sub>0.532</sub> Ti <sub>0.468</sub> OH <sub>1.040</sub> O <sub>0.960</sub>		
* Estimated standard deviations for unit cell parameters are enclosed in parentheses and refer to the last decimal place cited. Thus, 4.7441(2) represents an <i>esd</i> of 0.0002.		
** Clinohumite data from Sahara (1933); Ti-Clinohumite data from Brugnattelli (1904), Kunitz (1936) and Machatschki (1930).		

cause it permits direct comparison with the olivines and other humites (Jones, 1969).

Intensity data were collected in the range  $0.1 < \sin \theta/\lambda < 0.63$  for clinohumite and  $0.1 < \sin \theta/\lambda < 0.43$  for titanoclinohumite on an automated Picker system using Nb filtered Mo radiation. More than 1600 intensities for clinohumite and 1340 for titanoclinohumite were reduced to  $|F_o|$ 's using Prewitt's unpublished data reduction program, correcting for background and Lp effects. No corrections were made for absorption effects because of the small  $\mu$  and crystal size ( $< 0.1$  mm).

The positional parameters of Taylor and West (1928) were taken to initiate the least-squares refinements of both structures, using Busing, Martin and Levy's (1962) ORFLS program. Throughout the calculation neutral atom, relativistic scattering factors (Doyle and Turner, 1968) were used uncorrected for anomalous dispersion. Following convergence of the refinements using unit weights, the  $|F_o|$ 's were weighted according to a method proposed by Hanson (1965) and outlined in Paper II, p. 1184. The weighting parameters and other details of the refinement are given by Robinson (1971).

Two types of octahedral site refinements were carried out on both clinohumites using Finger's (1969) RFINE program. In one the positional parameters were fixed and site occupancy, isotropic thermal parameters, and scale factor were varied. In the other both positional and thermal parameters were fixed, varying only site occupancy and scale factor. In both cases, the octahedral site chemistries were constrained to agree with the chemical analyses. In clinohumite, only Mg and Fe' distributions were refined, where Fe' = (Fe + Ti + Mn); Mg was designated the independent variable and Fe' the dependent variable. In titanoclinohumite, the distributions of Mg, Fe and Ti were

TABLE 2. OCTAHEDRAL SITE OCCUPANCY AND ISOTROPIC TEMPERATURE FACTORS FOR TWO MODES OF SITE REFINEMENT

CLINOHUMITE									
Site	Anion chemistry of octahedron	Refine			B(Constr.)	Refine			
		Mg <sup>a</sup>	Fe'	B		Mg	Fe'	B	
M(1) <sub>C</sub>	O <sub>6</sub>	.90	.10*	[.42]	.94	.06	[.30]		
M(1) <sub>N</sub>	O <sub>6</sub>	.91	.09	[.42]	.91	.09	[.44]		
M(2) <sub>5</sub>	O <sub>5</sub> (F,OH)	.97	.03	[.42]	.94	.06	[.64]		
M(2) <sub>6</sub>	O <sub>6</sub>	.88	.12	[.42]	.92	.08	[.20]		
M(3)	O <sub>4</sub> (F,OH) <sub>2</sub>	1.00	.00	[.42]	.97	.03	[.58]		
TI-CLINOHUMITE									
Site	Anion chemistry of octahedron	Refine			B(Constr.)	Refine			
		Mg <sup>b</sup>	(Fe+Mn)	Ti		Mg	(Fe+Mn)	Ti	B
M(1) <sub>C</sub>	O <sub>6</sub>	.86	.09	.05	[.48]	.85	.10	.05	[.62]
M(1) <sub>N</sub>	O <sub>6</sub>	.84	.10	.06	[.48]	.86	.08	.06	[.37]
M(2) <sub>5</sub>	O <sub>5.5</sub> (OH) <sub>0.5</sub>	.85	.10	.05	[.48]	.84	.11	.05	[.60]
M(2) <sub>6</sub>	O <sub>6</sub>	.85	.10	.05	[.48]	.87	.09	.04	[.34]
M(3)	O <sub>5</sub> (OH)	.75	.20	.05	[.48]	.74	.21	.05	[.58]

\* Estimated standard errors in site occupancy range between 0.005 and 0.02.

<sup>a</sup> Total site occupancy set at Mg + Fe' = 1.0, refining occupancy of independent variable Mg where dependent Fe' = (1.0-Mg), where Fe' = (Fe + Ti + Mn).

<sup>b</sup> Total site occupancy set at Mg + (Fe+Mn) + Ti = 1.0, initially refined occupancy of independent variable Mg, where dependent (Fe+Mn+Ti) = (1.0-Mg). Next refined occupancy of independent variable (Fe+Mn), where Ti = [1.0-Mg-(Fe+Mn)] with Mg constant.

TABLE 3. CLINOHUMITE AND TI-CLINOHUMITE POSITIONAL PARAMETERS, ISOTROPIC TEMPERATURE FACTORS, AND r.m.s. EQUIVALENTS

	Clinohumite	Ti-Clinohumite		Clinohumite	Ti-Clinohumite	
M(1) <sub>C</sub>	x	0.5	0(1,2)	x	0.2832(13)	
	y	0.0		y	0.4211(6)	
	z	0.5		z	0.3877(4)	
	$\langle\mu\rangle^a$	0.41(5)	0.50(4)	B	0.58(10)	
M(1) <sub>N</sub>	x	0.072		$\langle\mu\rangle$	0.086	
	y	0.4977(7)	0.4961(5)	0(1,3)	x	0.2192(14)
	z	0.9463(2)	0.9461(2)		y	0.1130(6)
	$\langle\mu\rangle^a$	0.2738(2)	0.2744(1)		z	0.2936(4)
M(2) <sub>5</sub>	x	0.41(2)	0.47(2)		B	0.42(10)
	y	0.0101(6)	0.0143(4)	0(1,4)	x	0.2188(14)
	z	0.1398(2)	0.1403(1)		y	0.1586(6)
	$\langle\mu\rangle^a$	0.1703(1)	0.1699(1)		z	0.4853(4)
M(2) <sub>6</sub>	x	0.41(3)	0.49(3)		B	0.52(10)
	y	0.5101(6)	0.5106(4)	0(2,1)	x	0.2353(16)
	z	0.2503(2)	0.2508(1)		y	0.3218(6)
	$\langle\mu\rangle^a$	0.3888(1)	0.3878(1)		z	0.1610(5)
M(3)	x	0.42(4)	0.45(3)		B	0.54(13)
	y	0.4939(6)	0.4956(3)	0(2,2)	x	0.7802(13)
	z	0.8780(2)	0.8837(1)		y	0.9483(6)
	$\langle\mu\rangle^a$	0.0428(2)	0.0409(1)		z	0.1619(4)
Si(1)	x	0.0715(5)	0.0727(3)	0(2,3)	x	0.7255(15)
	y	0.0663(2)	0.0667(1)		y	0.2803(6)
	z	0.3891(1)	0.3900(1)		z	0.2625(6)
	$\langle\mu\rangle^a$	0.18(3)	0.26(3)		B	0.30(10)
Si(2)	x	0.048	0.057		$\langle\mu\rangle$	0.062
	y	0.0759(5)	0.0762(3)	0(2,4)	x	0.7296(13)
	z	0.1771(2)	0.1764(1)		y	0.2262(6)
	$\langle\mu\rangle^a$	0.8354(1)	0.8351(1)		z	0.0699(4)
O(1,1)	x	0.21(3)	0.25(3)		B	0.29(9)
	y	0.052	0.056		$\langle\mu\rangle$	0.061
	z	0.7315(17)	0.7315(11)	(F,OH,O)	x	0.2629(14)
	$\langle\mu\rangle^a$	0.0633(7)	0.0650(4)		y	0.0453(6)
	x	0.3871(5)	0.3876(4)		z	0.0558(5)
	y	0.37(12)	0.72(9)		B	0.71(10)
	z	0.068	0.095		$\langle\mu\rangle$	0.095
	$\langle\mu\rangle^a$					

<sup>a</sup> Root-mean-square displacements  $\langle\mu\rangle$  calculated using the expression  $\langle\mu\rangle = [8/3\pi^2]^{1/2}$ . Estimated standard errors in parentheses refer to the last decimal place.

refined, the minor amount of Mn being included with Fe; Mg was designated the independent variable and refined against total transition metals, Fe'. The Mg content was then held constant and (Fe + Mn) designated the independent variable, being refined against dependent Ti. Site occupancy constraints and results are given in Table 2.

The ORFLS and RFINE programs were alternated, using the site populations obtained in RFINE to calculate revised scattering curves for ORFLS, and the new positional parameters obtained in ORFLS as the fixed parameters in RFINE, until no further significant changes in either site chemistry, positional parameters or R-factor resulted.

Attempts to locate the hydrogen atom in clinohumite and titanoclinohumite were unsuccessful, and no attempt was made to refine anisotropic temperature factors. The weighted and unweighted R-factors for clinohumite are 0.051 and 0.034, and for titanoclinohumite are 0.042 and 0.028. Final positional and isotropic thermal parameters, together with calculated rms equivalents are listed in Table 3. Interatomic distances, angles and estimated standard errors were calculated using Busing, Martin and Levy's (1964) ORFFE program. The results are given in Table 4.

## Discussion

The crystal structures of the clinohumites are similar to other members of the humite group of minerals, norbergite, chondrodite and humite, and to that of the olivines (Fig. 1). The structure is based on a slightly distorted hexagonal close-packed array of divalent oxygen and monovalent (F,OH)

anions with one-half of the octahedral and one-ninth the tetrahedral sites filled. In this respect clinohumites, with a greater fraction of the tetrahedral sites filled than any of the other humite minerals, are more closely related to the olivines, where one-eighth of the tetrahedral sites are occupied.

There are five distinct octahedral sites in clinohumites.  $M(1)_C$  and  $M(2)_6$  are similar to  $M(1)$  and  $M(2)$  in the olivines, and  $M(1)_N$ ,  $M(2)_5$  and  $M(3)$  are like those in humite (Paper III). There are two distinct tetrahedra similar to those in humite, Si(1) and Si(2), which cross-link the edge-sharing octahedral chains (Fig. 1; see also Ribbe *et al.*, 1968, Fig. 3). In general all the oxygens in clinohumites are coordinated to one Si and three M-cations, as in olivine and the other humites. However, when oxygen replaces some of the monovalent anions, as in titanoclinohumite, this oxygen is coordinated to only three M-cations. The monovalent anions are ideally coordinated to three M-cations in a nearly planar array (see Paper I, Fig. 5a).

## Anion Coordination

The monovalent anion site in clinohumite is occupied by ~0.5 fluorine and 0.5 hydroxyl. Titanoclinohumite contains no F and the monovalent site is occupied by ~0.5 hydroxyl and 0.5 oxygen, assuming electrostatic charge balance (Jones *et al.*, 1969). Thus in titanoclinohumite only one-half the usual number of monovalent anions are present. This is an important distinction between clinohumite and titanoclinohumite: not only does the presence of oxygen and the absence of fluorine in the monovalent anion site of titanoclinohumite allow for a significant increase in the more highly charged cations (Ti<sup>4+</sup> and possibly Fe<sup>3+</sup>; Jones, 1968), but it makes the titanoclinohumite structure more closely related to olivine in which no monovalent anions are present.

There are eight unique oxygen atoms in the clinohumites compared to three in norbergite, four in chondrodite and seven in humite. However, in all these structures there are essentially two topologically unique oxygen coordination polyhedra (*cf.* Ribbe and Gibbs, 1971, Figs. 2 and 3). One coordination polyhedron has an apical octahedral M-cation, two basal M-cations and a basal Si, while the other type of polyhedron has an apical Si and three basal M-cations. As in the other humite minerals, the  $M_A$ -O and  $Si_A$ -O bonds (see Tables IV-5 and -6 in Robinson, 1971) are shorter than the respective

TABLE 4. CLINOHUMITE AND TI-CLINOHUMITE INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES)\*

CLINOHUMITE		TI-CLINOHUMITE	
<b>Si(1) Tetrahedron</b>			
	<u>Distance</u>		<u>Distance</u>
Si(1)-O(1,1)	1.626(9)	1.620(6)	
-O(1,2)	1.632(7)	1.648(4)	
-O(1,3)	1.625(6)	1.646(4)	
-O(1,4)	1.622(7)	1.625(5)	
mean	1.626	1.635	
	<u>O-Si-O angle</u>		<u>O-Si-O angle</u>
O(1,1)-O(1,2)	2.725(10)	2.747(6)	114.6(2)
-O(1,3)	2.737(10)	2.746(7)	114.5(3)
-O(1,4)	2.758(11)	2.758(7)	116.5(2)
O(1,2)-O(1,3)	2.544(9) <sup>‡</sup>	2.553(6) <sup>‡</sup>	101.6(2)
-O(1,4)	2.547(9) <sup>‡</sup>	2.569(6) <sup>‡</sup>	103.4(2)
O(1,3)-O(1,4)	2.574(8) <sup>‡</sup>	2.588(5) <sup>‡</sup>	104.6(2)
mean	2.643	2.660	109.2
<b>Si(2) Tetrahedron</b>			
	<u>Distance</u>		<u>Distance</u>
Si(2)-O(2,1)	1.617(8)	1.615(5)	
-O(2,2)	1.646(6)	1.643(4)	
-O(2,3)	1.645(6)	1.632(5)	
-O(2,4)	1.645(6)	1.646(5)	
mean	1.638	1.634	
O(2,1)-O(2,2)	2.745(10)	2.745(6)	114.8(2)
-O(2,3)	2.781(12)	2.756(7)	116.2(3)
-O(2,4)	2.748(10)	2.743(6)	114.5(3)
O(2,2)-O(2,3)	2.569(8) <sup>‡</sup>	2.563(5) <sup>‡</sup>	103.0(2)
-O(2,4)	2.564(9) <sup>‡</sup>	2.550(6) <sup>‡</sup>	101.7(2)
O(2,3)-O(2,4)	2.586(8) <sup>‡</sup>	2.598(6) <sup>‡</sup>	104.9(2)
mean	2.666	2.659	109.2
<b>M(1)<sub>C</sub> Octahedron</b>			
	<u>Distance</u>		<u>Distance</u>
M(1) <sub>C</sub> -O(1,1) [2]	2.093(8)	2.103(5)	
-O(1,2) [2]	2.086(6)	2.089(4)	
-O(1,4) [2]	2.141(6)	2.151(4)	
mean	2.107	2.114	
	<u>O-M-O angle</u>		<u>O-M-O angle</u>
O(1,2)-O(1,4) [2]	2.547(9) <sup>‡</sup>	2.569(6) <sup>‡</sup>	74.6(2)
O(1,1)-O(1,2) [2]	2.845(10) <sup>‡</sup>	2.849(6) <sup>‡</sup>	85.6(2)
O(1,4)-O(1,1) [2]	2.860(12) <sup>‡</sup>	2.859(8) <sup>‡</sup>	84.5(2)
O(1,2)-O(1,1) [2]	3.061(9)	3.075(6)	94.4(2)
O(1,1)-O(1,4) [2]	3.122(8)	3.150(6)	95.5(2)
O(1,2)-O(1,4) [2]	3.373(9)	3.374(6)	105.4(2)
mean	2.968	2.979	90.0
<b>M(1)<sub>N</sub> Octahedron</b>			
	<u>Distance</u>		<u>Distance</u>
M(1) <sub>N</sub> -O(1,1)	2.090(8)	2.103(5)	
-O(1,2)	2.101(7)	2.084(5)	
-O(1,3)	2.137(7)	2.134(5)	
-O(2,1)	2.119(7)	2.101(4)	
-O(2,2)	2.077(6)	2.075(5)	
-O(2,3)	2.132(7)	2.149(5)	
mean	2.109	2.108	
O(2,2)-O(2,3)	2.569(8) <sup>‡</sup>	2.563(5) <sup>‡</sup>	74.7(2)
O(1,2)-O(1,3)	2.544(9) <sup>‡</sup>	2.553(6) <sup>‡</sup>	74.5(2)
O(1,1)-O(1,3)	2.836(10) <sup>‡</sup>	2.831(7) <sup>‡</sup>	83.8(2)
O(1,2)-O(1,1)	2.845(10) <sup>‡</sup>	2.849(6) <sup>‡</sup>	85.8(2)
O(2,1)-O(2,2)	2.869(10) <sup>‡</sup>	2.861(7) <sup>‡</sup>	86.5(2)
O(2,1)-O(2,3)	2.859(12) <sup>‡</sup>	2.854(7) <sup>‡</sup>	84.4(2)
O(2,3)-O(1,1)	3.083(8)	3.122(5)	94.5(2)
O(1,1)-O(2,2)	3.058(9)	3.059(6)	94.1(2)
O(2,1)-O(1,2)	3.082(9)	3.051(6)	93.6(2)
O(1,3)-O(2,1)	3.196(8)	3.179(5)	97.3(2)
O(2,3)-O(1,2)	3.329(9)	3.338(6)	104.1(2)
O(1,3)-O(2,2)	3.394(7)	3.378(5)	106.7(2)
mean	2.972	2.970	90.0
<b>M(2)<sub>6</sub> Octahedron</b>			
	<u>Distance</u>		<u>Distance</u>
M(2) <sub>6</sub> -O(1,2)	2.057(6)	2.062(4)	
-O(2,3)	2.076(6)	2.080(5)	
-O(1,1)	2.183(7)	2.179(5)	
-O(1,3)	2.212(7)	2.207(4)	
-O(1,4)	2.052(7)	2.053(5)	
-O(1,4)'	2.236(7)	2.256(5)	
mean	2.136	2.140	

TABLE 4, continued

CLINOHUMITE		TI-CLINOHUMITE	
<b>M(2)<sub>6</sub> Octahedron</b>			
	<u>Distance</u>	<u>O-M-O angle</u>	<u>Distance</u>
O(1,3)-O(1,4)'	2.574(8) <sup>‡</sup>	70.7(2)	2.588(5) <sup>‡</sup>
O(1,3)-O(1,1)	2.836(10) <sup>‡</sup>	80.4(3)	2.831(7) <sup>‡</sup>
O(1,1)-O(1,4)'	2.860(12) <sup>‡</sup>	80.7(3)	2.859(8) <sup>‡</sup>
O(1,1)-O(1,4)	3.051(8)	92.1(3)	3.029(6)
O(1,4)-O(2,3)	3.384(9)	110.1(3)	3.407(6)
O(2,3)-O(1,1)	3.044(7)	91.2(3)	3.056(5)
O(1,4)'-O(1,2)	3.234(8)	97.7(3)	3.247(5)
O(1,2)-O(1,3)	3.193(9)	96.8(2)	3.193(5)
O(1,4)'-O(1,4)	3.003(8)	88.8(2)	2.997(5)
O(1,4)-O(1,2)	2.912(10)	90.2(3)	2.929(7)
O(1,2)-O(2,3)	2.913(8)	89.6(2)	2.924(6)
O(2,3)-O(1,3)	3.026(10)	89.7(3)	3.018(7)
mean	3.003	89.8	3.007
<b>M(2)<sub>5</sub> Octahedron</b>			
	<u>Distance</u>		<u>Distance</u>
M(2) <sub>5</sub> -O(1,3)	2.017(6)		2.024(5)
-O(2,2)	2.053(6)		2.082(4)
-O(2,3)	2.192(6)		2.197(5)
-O(2,4)	2.212(6)		2.275(5)
-O(2,1)	2.174(7)		2.172(5)
-F,OH	2.064(7)		2.056(5)
mean	2.119		2.134
O(2,3)-O(2,4)	2.586(8) <sup>‡</sup>	71.9(2)	2.598(6) <sup>‡</sup>
O(2,4)-O(2,1)	2.794(10) <sup>‡</sup>	79.1(3)	2.834(7) <sup>‡</sup>
O(2,3)-O(2,1)	2.859(12) <sup>‡</sup>	81.8(3)	2.854(7) <sup>‡</sup>
O(1,3)-O(2,1)	3.052(7)	93.4(3)	3.060(5)
O(2,4)-O(2,2)	3.141(8)	94.8(3)	3.215(5)
O(2,2)-O(2,3)	3.246(8)	99.7(2)	3.238(5)
O(2,2)-O(1,3)	2.963(7)	93.4(2)	2.970(5)
O(1,3)-O(2,3)	2.979(10)	90.0(3)	2.999(7)
F,OH-O(2,2)	2.898(10)	89.5(3)	2.904(6)
F,OH-O(2,1)	2.932(7)	87.5(2)	2.974(5)
F,OH-O(1,3)	3.199(8)	103.3(3)	3.230(6)
F,OH-O(2,4)	3.122(9)	93.7(2)	3.148(6)
mean	2.981	89.8	3.002
<b>M(3) Octahedron</b>			
	<u>Distance</u>		<u>Distance</u>
M(3)-O(2,4)'	2.005(6)		2.002(4)
-O(2,4)	2.120(6)		2.155(4)
-O(2,2)	2.188(6)		2.191(4)
-O(2,1)	2.115(7)		2.190(4)
-F,OH'	2.040(7)		2.000(5)
-F,OH	2.015(7)		1.981(4)
mean	2.081		2.087
O(2,4)-O(2,2)	2.564(9) <sup>‡</sup>	73.0(3)	2.550(6) <sup>‡</sup>
O(2,4)-O(2,1)	2.794(10) <sup>‡</sup>	82.6(3)	2.834(7) <sup>‡</sup>
O(2,1)-O(2,2)	2.869(10) <sup>‡</sup>	83.6(3)	2.861(7) <sup>‡</sup>
F,OH'-F,OH	2.778(13) <sup>‡</sup>	86.5(3)	2.799(9) <sup>‡</sup>
-O(2,2)	2.959(8)	88.7(3)	2.958(6)
-O(2,4)	3.157(7)	98.7(3)	3.121(5)
-O(2,4)'	2.872(9)	90.5(3)	2.911(6)
F,OH-O(2,4)'	2.985(7)	95.9(3)	2.986(5)
-O(2,2)	3.029(8)	92.1(2)	3.070(6)
-O(2,1)	2.924(6)	90.1(3)	2.949(5)
O(2,4)-O(2,1)	3.102(8)	97.6(3)	3.108(6)
-O(2,4)	3.141(7)	99.2(2)	3.095(5)
mean	2.931	89.9	2.937

$M_B$ -O and  $Si_B$ -O bonds, where the subscripts A and B indicate apical and basal positions, respectively, in the oxygen coordination polyhedron.

### Cation Coordination

Steric details of the two  $SiO_4$  tetrahedra and five  $M$  octahedra in clinohumite and titanoclinohumite are given in Table 4 and illustrated in Figures 2a and 2b, respectively.

**Silicate tetrahedra.** The clinohumites contain two crystallographically distinct  $SiO_4$  tetrahedra as in humite. However, because of the additional oxygen atom in clinohumites, both tetrahedra have sym-

\* Estimated standard errors are given in parentheses and refer to last decimal place.

<sup>‡</sup> Edge shared between tetrahedron and octahedron

<sup>‡</sup> Edge shared between two octahedra

\*\* Multiplicity factors in square brackets



$M(1)$  in the olivines and  $M(1)_N$  is similar to the  $M(1)$  octahedron of humite.

The  $M(2)_5$  octahedron shares two edges with octahedra,  $M(1)_N$ ,  $M(3)$ , and one edge with a tetrahedron,  $Si(2)$ . Thus it is similar to the  $M(2)_5$  in humite. In clinohumite there are two monovalent anions in the formula unit, and the coordination polyhedron has ligancy  $O_5(F,OH)$ . However, in titanoclinohumite, where only half the monovalent anions are present, the ligancy becomes  $\sim O_{5.5}(OH)_{0.5}$  on the average. This is reflected in the mean metal-anion bond lengths for  $M(2)_5$  (cf. Table IV-7, Robinson, 1971), where the mean  $M(2)-(OH,O)$  bond in titanoclinohumite is 0.012–0.018Å longer than in clinohumite, humite and chondrodite. Thus the  $M(2)_{5.5}$  octahedron in titanoclinohumite more closely approaches the ligancy, environment and mean bond lengths of the  $M(2)_6$  in humites and the olivines, except that it does not share edges with only  $MO_6$  octahedra.

The  $M(2)_6$  octahedron in clinohumites shares two edges with other octahedra,  $M(1)_C$ ,  $M(1)_N$ , and one edge with a tetrahedron,  $Si(1)$ . Thus it is similar to the  $M(2)_6$  octahedron in humite and olivine. It has six oxygen ligands and like the  $M(2)_5$  in clinohumite and titanoclinohumite, all three shared edges are at one end of the octahedron. This results in the cation being repelled toward the unshared edges at the opposite end.

The  $M(3)$  octahedron in clinohumites shares three edges with other octahedra,  $M(1)_N$ ,  $M(2)_5$ ,  $M(3)$ , and one edge with a tetrahedron,  $Si(2)$ . Thus it is similar to the  $M(3)$  octahedron in humite, chondrodite and norbergite. The  $(F,OH)-(F,OH)$  edge is shared with an adjacent  $M(3)$  octahedron and is at the opposite end of the octahedron from the other three shared edges. Bonds to oxygens involved in shared edges are comparable with those in humite and chondrodite and are longer ( $\sim 0.01$ – $0.21$ Å) than bonds to  $(F,OH)$  ions involved in a shared edge. In the clinohumite the bonds to  $(F,OH)$  ions are longer (0.01–0.035Å) than that to the oxygen,  $O(2,4)'$ , which is not involved in edge sharing. However, in titanoclinohumite the  $M(3)-O(2,4)'$  is 0.002–0.021Å longer than the  $M(3)-(OH,O)$  bonds. The mean metal-anion distances are statistically identical in the  $M(3)$  of clinohumite, titanoclinohumite, and humite. In clinohumite, with two monovalent anions in the formula unit, the coordination polyhedron has ligancy  $O_4(F,OH)_2$ ; however, in titanoclinohumite with only

one monovalent anion present, the coordination polyhedron has ligancy  $O_5(OH)$ . Thus  $M(3)$  ligancy in titanoclinohumite more closely approaches that of  $M(2)_5$  than any humite previously studied.

#### *Mg,Fe,Ti Distribution in Clinohumites*

The results of the octahedral site refinements are given in Table 2. The Mg and Fe distribution observed in clinohumite is almost identical with that in humite (Paper III). The more distorted  $M(1)_C$ ,  $M(1)_N$  and  $M(2)_6$  octahedra (see Table IV-8 in Robinson, 1971) have six oxygen ligands and contain approximately 90 percent of the Fe. The Fe/Mg distribution in clinohumite is consistent with the minerals in the humite series previously examined (Paper III, Fig. 9).

The observed distribution of Mg, Fe and Ti in titanoclinohumite does not conform with the distribution observed in clinohumite or any of the humite minerals previously examined. Ti appears to be randomly distributed in the octahedral sites and  $M(3)$  appears to be relatively enriched in Fe, all the other  $M$  sites having essentially equal cation contents, *i.e.*  $\sim 0.1$  Fe,  $\sim 0.05$  Ti,  $\sim 0.85$  Mg. Thus  $M(3)$ , the smallest and least distorted octahedron (Table IV-8, Robinson, 1971) has  $O_5(OH)$  ligancy and is enriched in Fe. This is in contrast to clinohumite and humite where Fe is enriched in the more distorted octahedral  $M$  sites with six oxygen ligands.

There is no obvious explanation for the transition metal distribution calculated with the site refinement program either in terms of previous studies of humite minerals or the sizes of the octahedra. This problem may eventually be resolved by examining an Fe-poor, Ti-rich clinohumite, because the Ti-poor clinohumite refined in this study gave results consistent with previous refinements of humite, chondrodite and norbergite (Papers I, II, and especially III).

#### **Acknowledgments**

This study was supported in part by N.S.F. grants GA-1647 and GA-12702 and by generous computing funds from the Research Division of Virginia Polytechnic and State University. The senior author is grateful for a National Defense Education Act Fellowship.

#### **References**

- BIRLE, J. D., G. V. GIBBS, P. B. MOORE, AND J. V. SMITH (1968) Crystal structures of natural olivines. *Amer. Mineral.* 53, 807–824.

- BORNEMAN-STARYNKEVITCH, I. D. AND V. S. MYASNIKOV (1950) On isomorphous replacements in clinohumite. *Dokl. Akad. Sci. USSR* **71**, 137-144 [in Russian].
- BRAGG, W. L., AND J. WEST (1927) The structure of certain silicates. *Proc. Roy. Soc. (London)* **114**, 450-473.
- BRUGNATELLI, L. (1904) Über Titanolivin der Umgebung von Chiesa, Val Malenco: Beitr. Z. Kenntn. d. Titanolivin. *Z. Kristallogr.* **39**, 209-219.
- BUSING, W. R., K. O. MARTIN AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Nat. Tech. Inform. Serv.* **ORNL-TM-305**.
- , ——— and ——— (1964) ORFFE, a Fortran crystallographic function and error program. *U.S. Nat. Tech. Inform. Serv.* **ORNL-TM-306**.
- DOYLE, R. A., AND P. S. TURNER (1968) Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Crystallogr.* **24A**, 390-397.
- FINGER, L. W. (1969) Determination of cation distributions by least-squares refinement of single-crystal X-ray data. *Carnegie Inst. Washington Year Book* **67**, 216-217.
- GIBBS, G. V., AND P. H. RIBBE (1969) The crystal structures of the humite minerals: I. Norbergite. *Amer. Mineral.* **54**, 376-390.
- , ———, AND C. P. ANDERSON (1970) The crystal structures of the humite minerals: II. Chondrodite. *Amer. Mineral.* **55**, 1182-1194.
- HANSON, A. W. (1965) The crystal structure of the azulene S-trinitrobenzene complex. *Acta Crystallogr.* **19**, 19-26.
- JONES, N. W. (1968) *Crystal Chemistry of the Humite Minerals*. Ph.D. thesis, Virginia Polytechnic Institute, Blacksburg, Virginia.
- (1969) Crystallographic nomenclature and twinning in the humite minerals. *Amer. Mineral.* **54**, 309-313.
- , P. H. RIBBE, AND G. V. GIBBS (1969) Crystal chemistry of the humite minerals. *Amer. Mineral.* **54**, 391-411.
- KUNITZ, W. (1936) Die Rolle des Titans und Zirkoniums in den gesteinsbildenden Silikaten. *N. Jahrb. Mineral.* **70**, Abt. A, 385-466.
- MACHATSCHKI, F. (1930) Über "Titanolivin." Ein Beitrag zur Frage der Rolle des Titans in Silikaten. *Zentralbl. Min., Geol., Paleon., Abt. A*, 191-200.
- RIBBE, P. H., G. V. GIBBS, AND N. W. JONES (1968) Cation and anion substitutions in the humite minerals. *Mineral. Mag.* **37**, 966-975.
- , AND ——— (1971) Crystal structures of the humite minerals. III. Mg/Fe ordering in humite and its relation to other ferromagnesian silicates. *Amer. Mineral.* **56**, 1155-1173.
- ROBINSON, KEITH (1971) *The crystal structures of zircon, clinohumite, and the hornblendes: A determination of polyhedral distortion and order-disorder*. Ph.D. dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.
- SAHAMA, TH. G. (1953) Mineralogy of the humite group. *Ann. Acad. Sci. Fennicae, III. Geol. Geogr.* **31**, 1-50.
- TAYLOR, W. H. (1929) The structure of norbergite. *Z. Kristallogr.* **70**, 461-474.
- , AND J. WEST (1928) The crystal structure of the chondrodite series. *Proc. Roy. Soc. (London)* **117**, 517-532.

*Manuscript received, September 15, 1972; accepted for publication, October 13, 1972.*