CRYSTAL CHEMISTRY OF THE HUMITE MINERALS

by

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INTRODUCTION

The minerals of the humite group (norbergite [$Mg_2SiO_4 \cdot Mg(OH,F)_2$], chondrodite [$2Mg_2SiO_4 \cdot Mg(OH,F)_2$], humite [$3Mg_2SiO_4 \cdot Mg(OH,F)_2$], and clinohumite [$4Mg_2SiO_4 \cdot Mg(OH,F)_2$] typically occur as pale yellow to russet brown or black, complex, small crystals or granular aggregates, in contact metamorphosed calcareous rocks adjacent to granitic masses. Clinohumite has also been reported in altered peridotite (Lindberg, 1947; Heinrich, 1963), in a kimberlitic tuff plug (Sun, 1954), in a gabbro-granophyre contact zone (Huang, 1957), in kimberlite (Voskresenskays _et_ _al_., 1965), and in a kimberlite breccia (McGetchin and Silver, 1968). The humite minerals are relatively rare; chondrodite is the most common and norbergite the rarest member of the group.

Penfield and Howe (1894) were the first to establish the chemical compositions of chondrodite, humite, and clinohumite satisfactorily. The formulae they proposed, however, although now universally accepted, did not go unchallenged (_e_._g_., Cesaro, 1926). They also predicted the existence of norbergite, its chemical composition, axial ratios, and axial angles. Norbergite was discovered by Geijer (1926). Sjögren (1893) had previously assigned the name "prolectite" to a monoclinic mineral which he said had the composition of norbergite. Geijer (1926), however, showed that "prolectite" was actually chondrodite and the name has been dropped. The term "titanolivine" was first applied to Ti-rich clinohumite by Damour (1855), but the name has not been used in recent years.

A survey of the published chemical analyses (Appendix A) indicates that substitution for Mg in the humite minerals is rather limited. Iron ranges from 0.4 to 7.3 weight percent; Mn from zero to 1.05 weight percent; and Ti from zero to 3.24 weight percent. Hydroxyl is always present in naturally occurring humite minerals, although norbergite may contain only small amounts. Fluorine may be absent in clinohumite, especially if significant amounts of Ti are present. Pure F end-members of each of the humite minerals have been synthesized (Rankama, 1947; Karyakin and Gul'ko, 1954; Fujii and Eitel, 1957; Van Valkenburg, 1955, 1961; Hinz and Kunth, 1960; McCormick, 1966), but Van Valkenburg (1961) was unable to synthesize pure OH end-members. McCormick (1966) and S. R. Lyon (personal communication, 1968) have synthesized Ge analogues of the F end-members.

Although there does not appear to be complete solid solution between Mg and Fe, Mg and Mn, or Mg and Ca humite minerals, Mn analogues of some of the members of the group do occur naturally, and a Ca analogue of chondrodite [$2Ca_2SiO_4 \cdot Ca(OH)_2$] has been prepared synthetically (Buckle and Taylor, 1958). Moore (1967) has found four polytypes of leucophoenicite [$3Mn_2SiO_4 \cdot Mn(OH)_2$]; one of these has the humite structure. Alleghanyite [$2Mn_2SiO_4 \cdot Mn(OH,F)_2$] is structurally analogous to chondrodite and sonolite [$4Mn_2SiO_4 \cdot Mn(OH)_2$] is structurally analogous to clinohumite (Moore, 1967).

Recent chemical studies, especially by Sahama (1953) and Bradshaw and Leake (1964), have indicated that the humite minerals may be non-stoichiometric. Sahama considered the ratio Si:(OH + F + O_{Ti}), where

O_{Ti} is equal to twice the Ti content (on the assumption that Ti is ordered in the (OH,F) region of the structure), and found considerable deviation from the expected values. He concluded that the deviations were primarily due to inaccuracy of the chemical analyses. Bradshaw and Leake, however, felt that the non-stoichiometry was real and could be explained on a structural basis, because the structures of the humite minerals lend themselves to epitaxial intergrowths.

The main purpose of this study is to delineate the extent of chemical substitution in the natural humites by electron microprobe analyses of a number of samples, and to explain the apparent non-stoichiometry indicated by the bulk chemical analyses. In conjunction with this, a single-crystal study was undertaken to examine the effect of chemical substitution on the unit cell parameters and to search for polytypism in the humite minerals as described by Moore (1967) for structurally similar leucophoenicite. This is a part of a larger study which includes crystal structure refinements of each of the humite minerals by Gibbs and Ribbe (e.g., Gibbs and Ribbe, 1968) to determine precise bond lengths and bond angles, and to determine whether Fe and Ti are ordered within the structure.

CRYSTAL STRUCTURES OF THE HUMITES

General

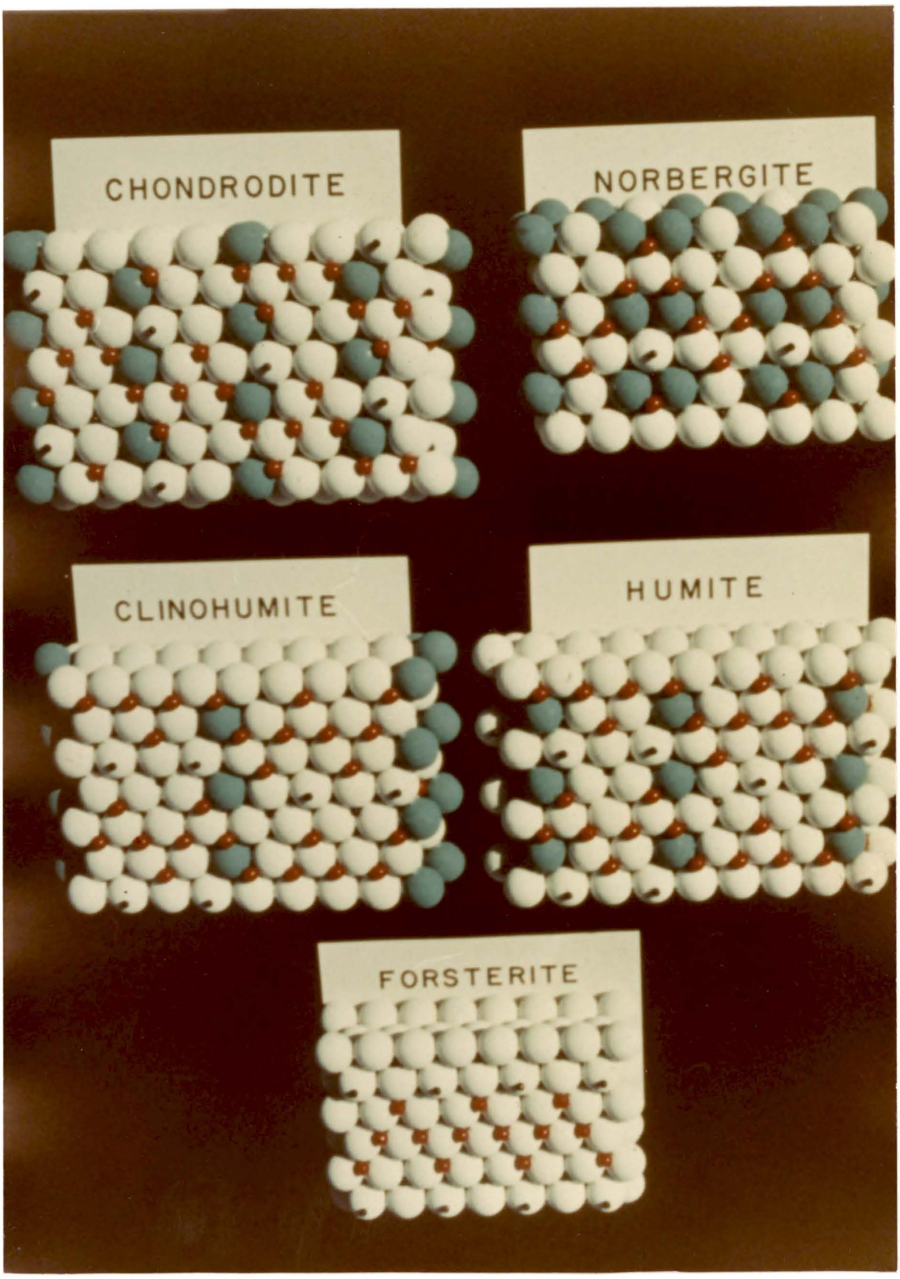
The crystal structures of the humite minerals were determined by Taylor and West (1928, 1929) using the rotating crystal method and selected intensity measurements made with an ionization spectrometer. They found that the x-ray diffraction patterns of the humite minerals are very similar to those of olivine which has a structure based on a slightly distorted hexagonal close-packed array of oxygen anions (Bragg and Brown, 1926). Taylor and West, therefore, proposed structures for norbergite, chondrodite, humite, and clinohumite based on a hexagonal close-packed array of anions (O,OH,F). The ionic radii of OH^{-1} and F^{-1} are similar to that of O^{-2} (Goldschmidt, 1926) so that these anions may easily be incorporated into the close-packed assemblage of anions. Magnesium occupies octahedral sites and Si tetrahedral sites in the close-packed array. Taylor and West assumed, from charge balance considerations, that (OH,F) anions are bonded to three Mg, whereas O, as in olivine, is bonded to one Si and three Mg cations. This requires ordering of (OH,F) anions within the structure. The structures of the humites are summarized in Table I and illustrated in Figure 1. The olivine structure is shown for comparison.

Taylor and West (1929) described the humites in terms of "unit blocks" of $Mg(OH,F)_2$ and Mg_2SiO_4 composition. The different members of the group result from different stacking sequences of these blocks. Thus, norbergite is described as the stacking sequence of one block

TABLE I. Crystal-chemical data for the humite minerals and forsterite. Cell dimensions (in Ångströms) and space groups after Taylor and West (1929).

Mineral	a	b	c	α	d_{001}	Formulas per unit cell	Space Group	Percent tet. sites filled
Norbergite $Mg_2SiO_4 \cdot Mg(OH,F)_2$	4.70	10.2	8.72	90°	6x1.453	4	Pbnm	8.3
Chondrodite $2Mg_2SiO_4 \cdot Mg(OH,F)_2$	4.733	10.27	7.87	109°2'	5x1.488	2	$P2_1/b$	10.0
Humite $3Mg_2SiO_4 \cdot Mg(OH,F)_2$	4.738	10.23	20.9	90°	14x1.490	4	Pbnm	10.7
Clinohumite $4Mg_2SiO_4 \cdot Mg(OH,F)_2$	4.745	10.27	13.7	100°50'	9x1.492	2	$P2_1/b$	11.1
Forsterite Mg_2SiO_4	4.755	10.21	5.98	90°	4x1.495	4	Pbnm	12.5

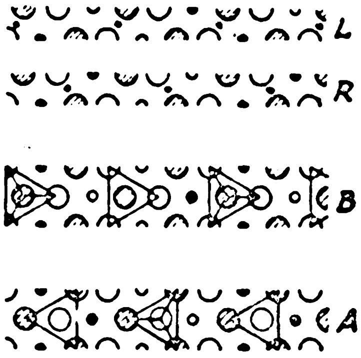
Figure 1. Models of norbergite, chondrodite, humite, clinohumite, and forsterite showing the closest-packed layer of anions (white, oxygen; turquoise, F or OH), chains of octahedrally-coordinated cations (red), and tetrahedrally-coordinated Si (black).


CHONDRODITE
NORBERGITE
CLINOHUMITE
HUMITE
FORSTERITE

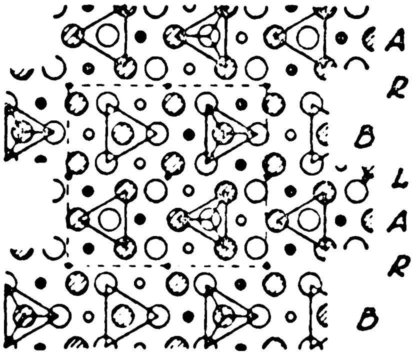
of Mg_2SiO_4 and one block of $Mg(OH,F)_2$, chondrodite as two blocks of Mg_2SiO_4 and one block of $Mg(OH,F)_2$, humite as three blocks of Mg_2SiO_4 and one block of $Mg(OH,F)_2$, and clinohumite as four blocks of Mg_2SiO_4 and one block of $Mg(OH,F)_2$. This interpretation, however, is incorrect and misleading because the "unit blocks" delineated in their drawing (reproduced in Figure 2) do not have these compositions; the compositions are in fact $Mg_2SiO_3(OH,F)$ and $Mg(OH,F)O$.

These statements by Taylor and West have misled several authors into assigning a structural significance to the "$Mg(OH,F)_2$" block. For example, Rankama (1947, p.147) says: "As the construction of the idealized structures of the humite minerals can be carried out merely by stacking together unit blocks of Mg_2SiO_4 and $Mg(OH)_2$, it was thought to be worthwhile to try to carry out the synthesis of the minerals proper by direct coupling of the lattice units" and "...attention must be paid to the fact that the $Mg(OH)_2$ has a lattice of the cadmium iodide type, while MgF_2 has the symmetrically coordinated rutile structure." Borneman-Starynkevitch and Myasnikov (1950) analyzed six Ti-rich clinohumites and suggested that titania is present in the $Mg(OH,F)_2$ blocks in clinohumites. They noted that an increase in the amount of Ti is coupled with a decrease in the amount of F and concluded that this is a reflection of the structural similarity between TiO_2 (rutile) and MgF_2 (sellaite) and the dissimilarity of TiO_2 and $Mg(OH)_2$ (brucite). Sahama (1953) recognized that $Mg(OH)_2$ is not present in the humites with the atomic arrangement of brucite, but referred to the blocks as "sellaite slabs," implying that they have the rutile structure. Deer,

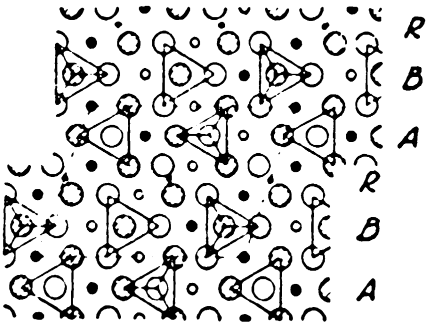
Figure 2. Reproduction of Figure 4, "Structural Scheme of Chondrodite Series" from Taylor and West, 1929. The "unit blocks" do not have the compositions Mg_2SiO_4 and $Mg(OH)_2$, as indicated; the compositions are actually $Mg_2SiO_3(OH,F)$ and $Mg(OH,F)O$.



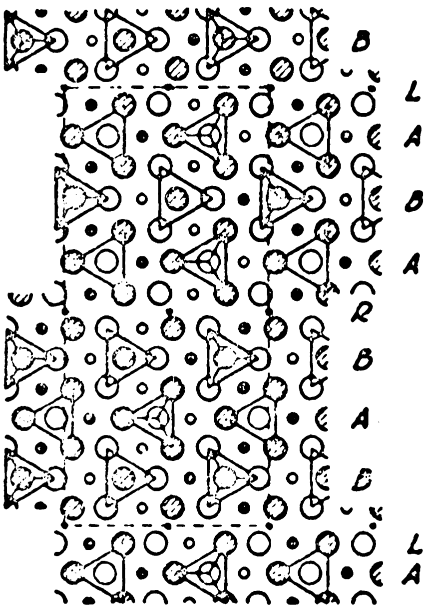
(a) Unit blocks of Mg_2SiO_4 and $Mg(OH)_2$



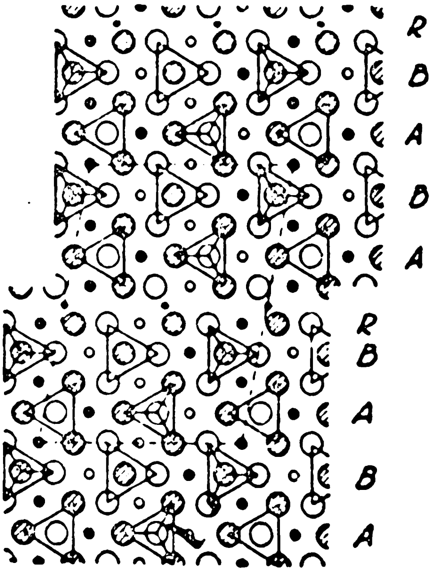
(b) Norbergite



(c) Chondrodite



(d) Humite



(e) Clinohumite

Howie, and Zussman (1962) perpetuated the misconception in their description of the structures (p.50): "The structures consist of layers having an atomic arrangement as in olivine together with layers $Mg(OH,F)_2$ in composition; both the olivine and the brucite-sellaite layers are parallel to the (100) plane." More recently, Christie (1965) has concluded that: "The presence of sellaite layers in humite type minerals stabilizes the olivine structure of the interlayered slabs..." All of these interpretations are incorrect because in none of the humite minerals are the (OH,F) anions suitably arranged to form structural units of brucite or sellaite. R. V. Dietrich (personal communication, 1968) has pointed out that petrologists, noting the similarity of alteration products of olivine and chondrodite, have long suspected that the structures were also possibly similar.

Comparison of the Humite Minerals and Olivine

Much of the following discussion is excerpted from Ribbe, Gibbs, and Jones (1968).

Both olivine and the humite structures are based on a slightly distorted hexagonal close-packed array of anions in which half of the available octahedral sites are filled by divalent cations. It is presumed that the (OH,F) anions in the humites are ordered within the close-packed assembly to maintain local charge balance. If each (OH,F) is coordinated by three divalent cations and if Pauling's (1929) electrostatic valence rule is satisfied, then no Si cations can be bonded to (OH,F) anions (Taylor and West, 1928; confirmed by Gibbs and Ribbe, 1968; see Figure 1). Consequently, none of the available tetrahedral sites coordinated by one or more (OH,F) anions in the close-packed assembly is occupied by Si. This indicates that the humites are structurally analogous to olivine wherein the replacement of four O by four (OH,F) in the close-packed array is balanced by the replacement of one tetrahedrally-coordinated Si by a tetrahedral void. This is exemplified by considering the general formula $Mg_{2x}Si_{x-m}O_{4[x-m]}(OH,F)_{4m}$. When *m* = 0, the formula gives the chemistry of forsterite, and when *m* = 1 and x takes on the values 3, 5, 7, and 9, it gives the humite compositions, as illustrated below:

x	*m* = 0	*m* = 1	
3	$Mg_6Si_3O_{12}$	$Mg_6Si_2O_8(OH,F)_4$	[norbergite]
5	$Mg_{10}Si_5O_{20}$	$Mg_{10}Si_4O_{16}(OH,F)_4$	[chondrodite]
7	$Mg_{14}Si_7O_{28}$	$Mg_{14}Si_6O_{24}(OH,F)_4$	[humite]
9	$Mg_{18}Si_9O_{36}$	$Mg_{18}Si_8O_{32}(OH,F)_4$	[clinohumite]

Notice that when four (OH,F) replace four O of the forsterite, one Si is omitted to maintain electrostatic charge balance in the final unit.

Recent structure analyses of olivine (Birle *et al.*, 1968) indicate "...that the key structural unit is the serrated chain of octahedra lying parallel to the *c*-axis." It was found that the steric details of the olivine structure are dictated to a first approximation by a balance between repulsive and attractive electrostatic forces and that they are essentially independent of (Mg, Fe) substitution. However, the sizes of the octahedra and cell parameters were found to increase with increased substitution of Mg for Fe, the ionic radii of which are 0.66Å and 0.74Å, respectively (Ahrens, 1952).

These principles can be applied to other olivine structures and plots of the mean M-O distance as a measure of the mean size of the octahedra show a linear relationship with the average radius of the octahedral cations and with the volume of the unit cell (Figure 3). It is clear that a linear relationship must also exist between the mean cation radius and the cell volume.

If the key structural unit in olivine is the zigzag chain of edge-sharing octahedra, and if (as previously indicated) the humite structures are indeed analogous to olivine, then it follows that the key structural units in humites are also zigzag chains of octahedra. The nature of the chains in the humite minerals may be compared with that in olivine in Figure 4. Evidence that the octahedral chains control the structural features of the humites in the same way as those of the olivines is found in the close similarity of the $\underline{a}$, $\underline{b}$, d_{001}/n and V' parameters of forsterite and the four Mg-humites (Table II). Notice also the marked similarity of the Ca-members, γ-Ca_2SiO_4 and calcio-chondrodite, and the Mn-members, tephroite and alleghanyite. It is apparent that the effects of specific cation substitutions are the same in both olivine structures and in chemically analogous humites.

It is shown in Figure 3 that a linear relationship exists between the mean cation radius and the cell volume in olivines. If the humites are in fact structurally analogous to olivine, then the same relationship is to be expected to hold for them as well. Figure 5, a composite plot of the cell volume (normalized to half the mean anion-anion distance along the normal to (001)) versus the mean radius

Figure 3. The relationship of the average cation-oxygen (M-O) distance to the average radius of the cation in the M-site and to the unit cell volume in olivine structures. The first four data points are from Birle *et al.* (1968), the fifth from Onken (1965), and the sixth (at *r* = 0.99Å) from Smith, Majumdar, and Ordway (1965).

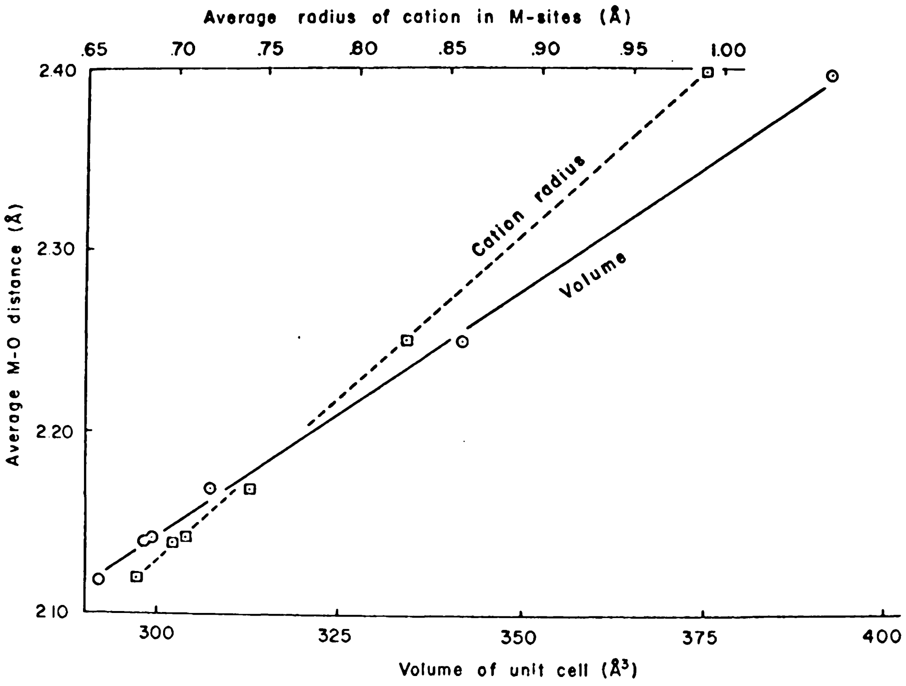

Average radius of cation in M-sites (Å)
.65
.70
.75
.80
.85
.90
.95
1.00
2.40
2.30
2.20
2.10
Average M-O distance (Å)
Cation radius
Volume
300
325
350
375
400
Volume of unit cell (Å³)

Figure 4. Schematic representations of the serrated octahedral chains in forsterite, clinohumite, humite, chondrodite, and norbergite (cf. Figure 1). The circles are octahedral cations in the (100) plane which is the plane of the hexagonal close-packed anion layer.

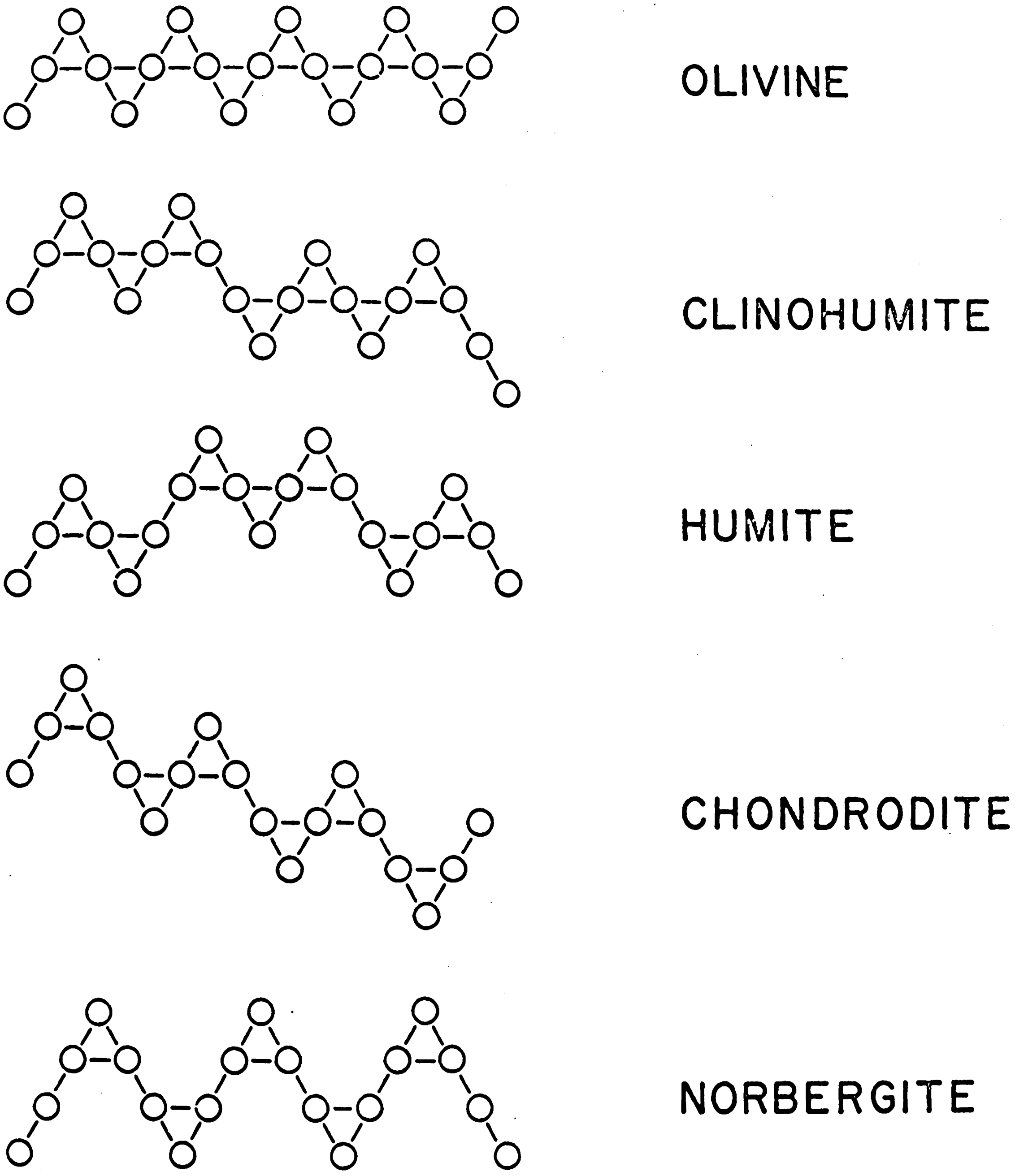

OLIVINE
CLINOHUMITE
HUMITE
CHONDRODITE
NORBERGITE

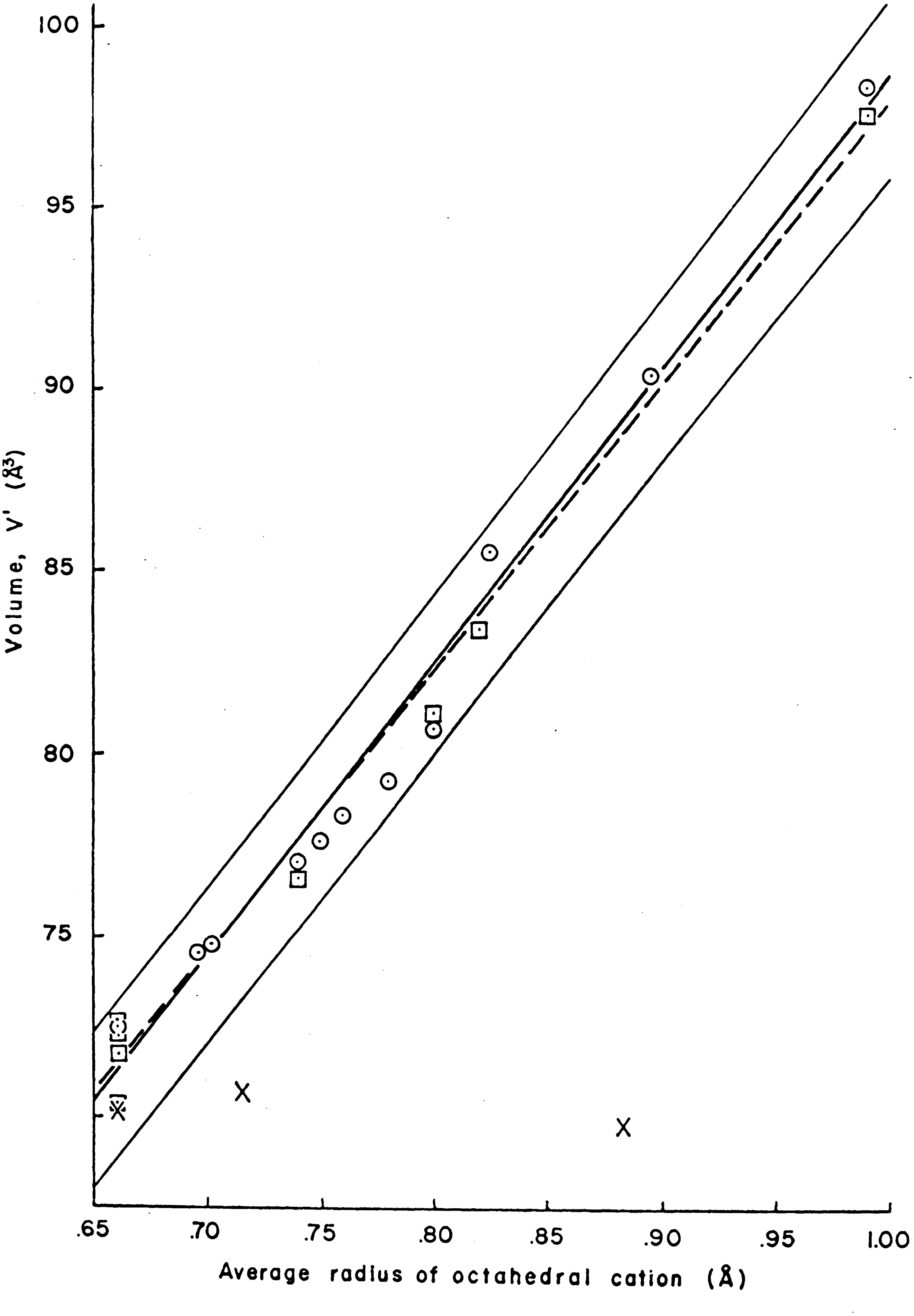
TABLE II. Cell parameters and average ionic radii of octahedrally coordinated cations of selected minerals with olivine- and humite- type structures

MINERAL	FORMULA	_a_(Å)	_b_(Å)	_c_(Å)	$\underline{d}_{001}$(Å)	V' (Å)^3	AVERAGE CATION RADIUS*	REFERENCE
Forsterite	Mg_2SiO_4	4.756	10.195	5.981	4 x 1.495	72.49	0.66	Yoder & Sahama (1957)
Clinohumite	$Mg_9Si_4O_{16}(OH,F)_2$	4.745	10.27	13.68	9 x 1.492	72.71	0.66	Taylor & West (1929)
Humite	$Mg_7Si_3O_{12}F_2$	4.735	10.243	20.72	14 x 1.480	71.78	0.66	Van Valkenburg (1961)
Chondrodite	$Mg_5Si_2O_8(OH,F)_2$	4.733	10.27	7.87	5 x 1.488	72.33	0.66	Taylor & West (1929)
Norbergite	$Mg_3SiO_4F_2$	4.709	10.271	8.727	6 x 1.455	70.37	0.66	Van Valkenburg (1961)
Hyalosiderite	$(Mg_{.535}Fe_{.456}Mn_{.006}Ca_{.002})_2SiO_4$	4.785	10.325	6.038	4 x 1.510	74.58	0.696	Birle, _et al._ (in press)
Hortonolite	$(Mg_{.49}Fe_{.49}Mn_{.01}Ca_{.01})_2SiO_4$	4.787	10.341	6.044	4 x 1.511	74.80	0.704	Birle, _et al._ (in press)
Fayalite	Fe_2SiO_4	4.817	10.477	6.105	4 x 1.526	77.01	0.74	Yoder & Sahama (1957)
Leucophoenicite	$(Mn_{.63}Mg_{.37})_7Si_3O_{12}(OH)_2$	4.82	10.42	21.37	14 x 1.526	76.67	0.74	Moore (personal communication, 1968)
Knebelite	$(Fe_{.826}Mn_{.145}Mg_{.029})_2SiO_4$	4.834	10.518	6.11	4 x 1.528	77.69	0.75	Henriques (1946)
Knebelite	$(Fe_{.575}Mn_{.354}Mg_{.071})_2SiO_4$	4.843	10.556	6.133	4 x 1.533	78.37	0.76	Henriques (1946)
Knebelite	$(Fe_{.453}Mn_{.510}Mg_{.037})_2SiO_4$	4.854	10.602	6.162	4 x 1.541	79.30	0.78	Henriques (1946)
Tephroite	Mn_2SiO_4	4.871	10.636	6.232	4 x 1.558	80.72	0.80	Hurlbut (1961)
Alleghanyite	$Mn_5Si_2O_8(OH,F)_2$	4.94	10.55	8.24	5 x 1.557	81.15	0.80	Lee (1955)
_m_-leucophoenicite	$(Mn_{.9}Ca_{.1})_7Si_3O_{12}(OH)_2$	4.845	10.78	45.18	28 x 1.614	84.30	0.82	Moore (personal communication, 1968)
Monticellite	$CaMgSiO_4$	4.822	11.108	6.382	4 x 1.596	85.49	0.825	Onken (1965)
Glaucochroite	$CaMnSiO_4$	4.944	11.19	6.529	4 x 1.632	90.29	0.895	Caron _et al._ (1965)
γ-Ca_2SiO_4	Ca_2SiO_4	5.091	11.371	6.782	4 x 1.695	98.15	0.99	Smith _et al._ (1965)
Calcio-chondrodite	$Ca_5Si_2O_8(OH)_2$	5.05	11.42	8.94	5 x 1.688	97.35	0.99	Buckles & Taylor (1958)

V' = a x b x d_{001}/n where n = 4 for olivines, 9 for clinohumites, 14 for humites, 5 for chondrodites, 6 for norbergites, and 28 for _m_-leucophoenicite.

*Ahrens' (1952) ionic radii in Ångströms

Figure 5. The relationship of the average radius of the octahedral cation to the normalized cell volume V' for both humites (squares) and olivines (circles) (see Table II). Linear regression analyses produced the heavy solid line-of-best-fit for olivines and the dashed line for humites. The curved lines bracket the 95 percent confidence interval for both sets of data taken together. Crosses represent V' calculated from Christie's (1965) cell parameters for the compounds $Mg_2SiO_4 \cdot MgF_2$, $Zn_2SiO_4 \cdot MgF_2$, and $Ca_2SiO_4 \cdot MgF_2$.


Volume, V' (Å³)
100
95
90
85
80
75
.65
.70
.75
.80
.85
.90
.95
1.00
Average radius of octahedral cation (Å)

of the octahedral cations of olivine and humites of various chemical compositions, shows that this is indeed a valid conclusion. That the separate regression lines calculated for the olivines and for the humites are not significantly different is evinced by the fact that both sets of data fall well within the 95 percent confidence band calculated for all data, excluding those of Christie (1965) which are indicated by X's. It is apparent from this treatment of the data that the structural principles governing olivine and humite structures are likely one and the same; to a first approximation only the size of the octahedral cation is important in determining unit cell parameters. The fact that the cell parameters for the compounds $Mg_2SiO_4 \cdot MgF_2$, $Zn_2SiO_4 \cdot MgF_2$ and $Ca_2SiO_4 \cdot MgF_2$ (X's in Figure 5), which Christie (1965) allegedly synthesized, are the same as the norbergite cell parameters presents an unexplained inconsistency with the proved relationship between mean radius of the octahedral cation and the normalized volume. These data clearly require further investigation.

Morphotropy

Penfield and Howe (1894) recognized that the a and b unit cell dimensions are essentially the same for all of the humites, whereas the c dimensions show a marked and irregular variation from one member to another. Taylor and West (1928), however, noted that the d_{001}-spacing (normalized to half the mean anion-anion distance along the normal to (001)) does show a regular progression from norbergite through clinohumite. This progressive change in crystal structure brought about by systematic chemical substitution illustrates the phenomenon of morphotropy.

Epitaxial Intergrowths and Twinning

Megascopic mutually oriented intergrowths of forsterite, chondrodite, humite, clinohumite, and monticellite have been described by Tilley (1951), and of forsterite, clinohumite, and chondrodite by Trommsdorff (1967). The possibility of fine-scale epitaxial intergrowths between the humite minerals has been suggested by Bradshaw and Leake (1964) and by Gibbs and Ribbe (proposal for N.S.F. Grant G.A.-1133, 1967) to explain the apparent non-stoichiometry indicated by bulk chemical analyses. Although deviations from stoichiometry were not confirmed in the present study, it is worthwhile to discuss the concept of epitaxial intergrowths in the humite minerals.

The most likely direction along which epitaxial intergrowths would occur in the humite minerals appears to be the zone [001]. This is the same direction along which the most common twinning (with an (001) twin plane) occurs in the monoclinic members of the group. This is not surprising, because the two phenomena are based on the same type of "interlocking" between adjacent structural blocks. Epitaxial intergrowths, however, involve the joining of two minerals of different structure and composition, whereas twinning involves the joining of two blocks of the same structure and composition.

Possible epitaxial intergrowths are illustrated in Figures 6 and 7. Although only two are shown, any combination of these minerals is theoretically conceivable. Note that the chains of filled octahedra continue from one structure into the other along the zone [001]. It seems reasonable that such intergrowths could comprise a large enough

Figure 6. Theoretical model of an epitaxial intergrowth between norbergite and chondrodite. Note that the chains of filled octahedra continue from one structure into the other along the zone [001]. Color code as in Figure 1.

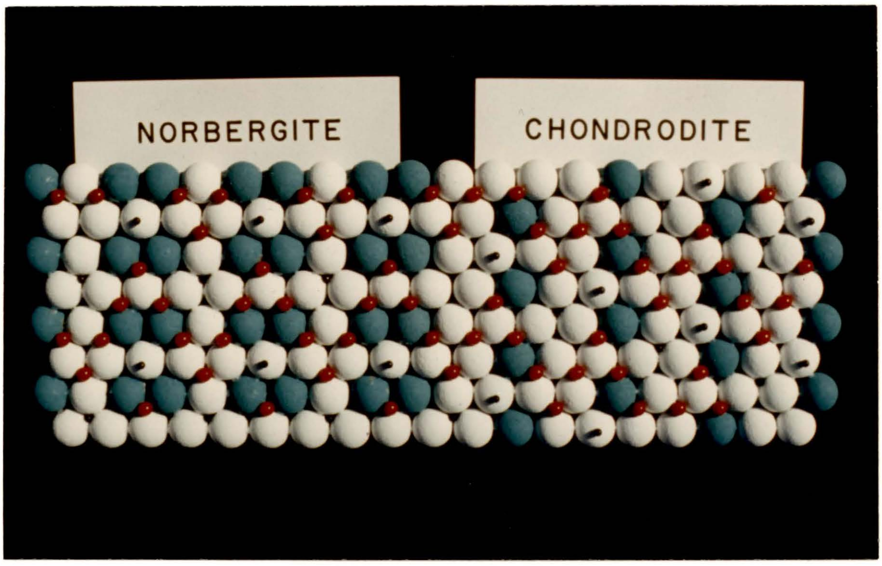
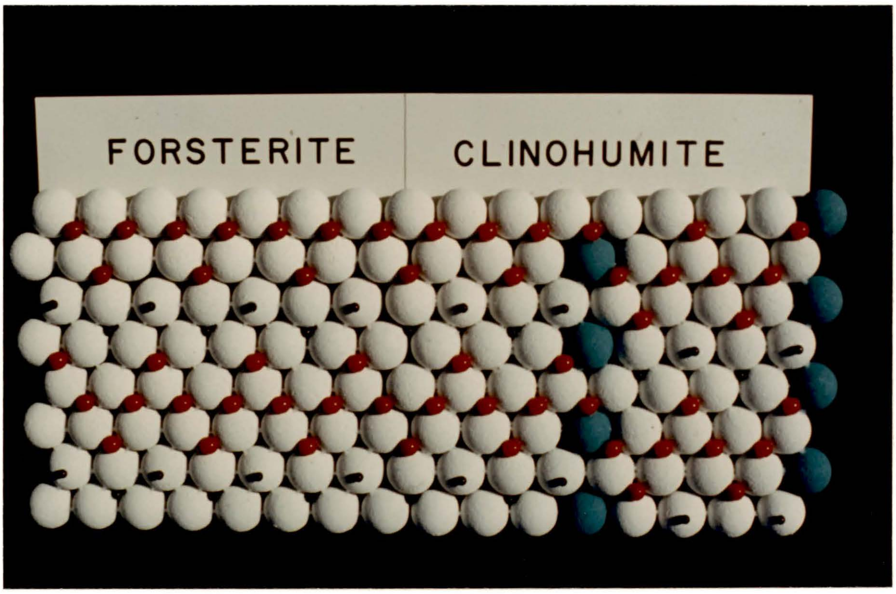

NORBERGITE
CHONDRODITE

Figure 7. Theoretical model of an epitaxial intergrowth between forsterite and clinohumite. Color code as in Figure 1.


FORSTERITE
CLINOHUMITE

volume so that they would affect a bulk chemical analysis, yet individual layers could be small enough so that they would not be detected by x-ray powder methods.

The most common twin plane in the humite minerals is the (001), but twinning may also occur on (015) and $(0\bar{3}5)$ in chondrodite and $(0\bar{1}3)$ in clinohumite (Tilley, 1951). Twinning on (001) was encountered during single crystal x-ray studies of chondrodite and provides an example of pseudo-symmetry. When parallel twinning of this type occurs, the vector $[0\bar{2}1]^*$ of one twin lamella almost exactly coincides in magnitude and direction with the vector $[020]^*$ of the other lamella (Figure 8). Since space group extinctions from each lamella allow diffraction from planes $0k\ell$ only if $k = 2n$, diffraction spots from one twin are superposed on those from the other. $0k\ell$ x-ray photographs thus show intensities and distribution of spots consistent with a pseudo-orthorhombic cell with a halved c^*-axis and a quadrupled b^*-axis (outlined in Figure 8). In upper level photographs, 2*mm* symmetry is present but systematic extinctions do not correspond to any space group extinction rules. When either (015) or $(0\bar{3}5)$ are twin planes such a phenomenon does not occur and diffraction spots from each lamella should be distinct. Such twinning was not observed in the present study.

Choice of Space Group and Crystallographic Axes

Considerable confusion exists in the literature regarding the choice of crystallographic axes and the space groups of the humite minerals. The choices which have been made are shown in Table III. Certain of the space groups adopted by Sahama (1953; after Strunz,

Figure 8. Parallel twinning on (001) in chondrodite as seen on the $\underline{b}^*\underline{c}^*$ reciprocal lattice plane. The vector $[02\bar{1}]^*$ of one twin lamella coincides in magnitude and direction with the vector $\underline{b}^*$ of the other twin lamella and space group symmetry requires that for diffractions of the form $0\underline{k\ell}$, $\underline{k} = 2\underline{n}$ (circled). This results in the superposition of spots from both twin lamellae and a pseudo-orthorhombic cell (in blue) with $\underline{b}_{\text{ortho}}$ parallel to $[04\bar{1}]^*_{\text{mono}}$.

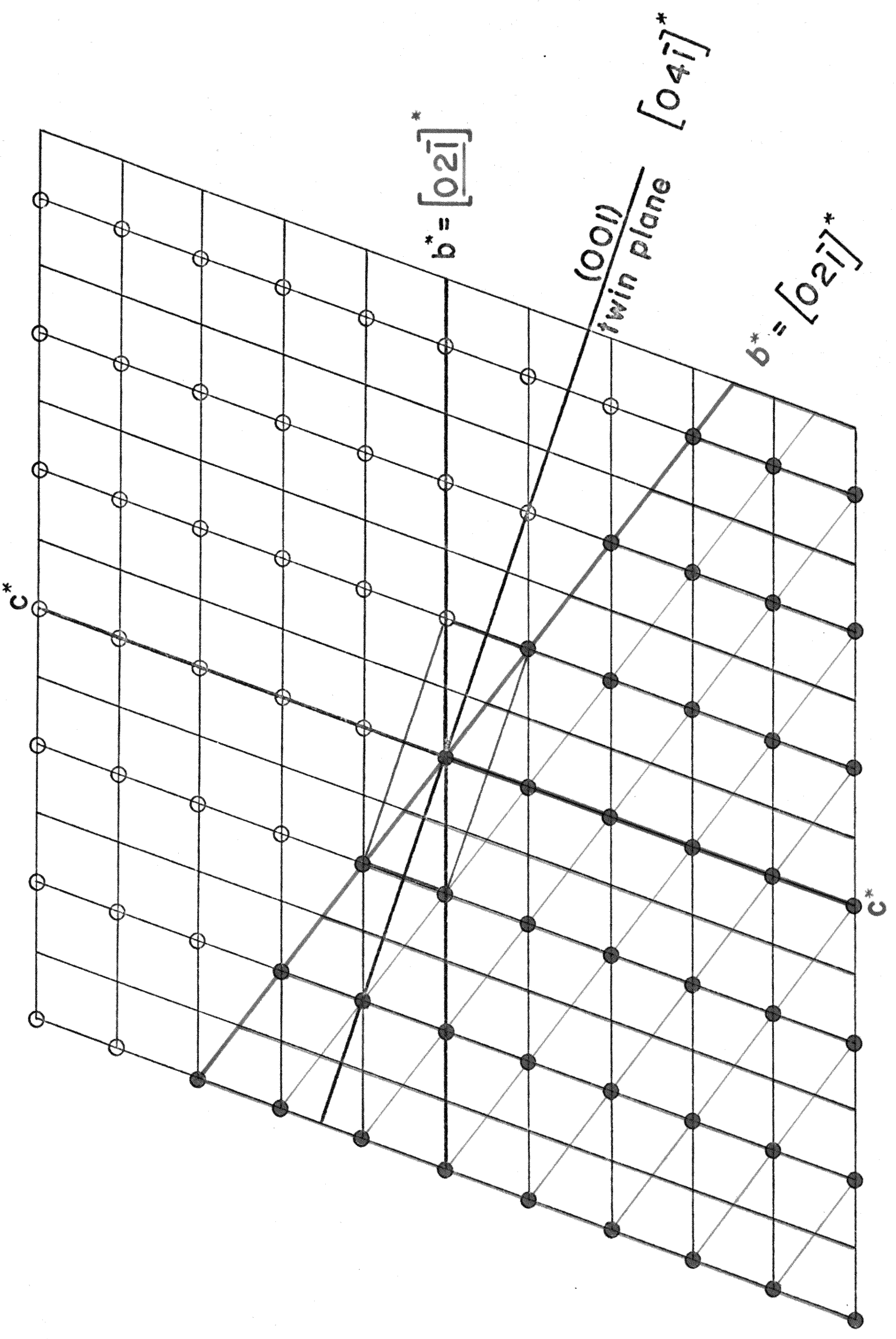

$b^* = [0\bar{2}\bar{1}]^*$
(001) twin plane
$[04\bar{1}]^*$
$b^* = [02\bar{1}]^*$
c^*
c^*

TABLE III. Axial labels and space groups assigned to the humite minerals by various authors. Taylor and West's (1929) convention preferred.

Mineral	Approximate Axial Length (Å)	Axial Labels and Space Groups				
		Taylor and West (1929) Bragg and Claringbull (1965)	Strunz (1949) Sahama (1953) Deer, Howie, Zussman (1962)	A.S.T.M.	Winchell and Winchell (1951)	Strunz (1957)
Norbergite	4.7	a	b	c	a	b
	10.2	b	c	a	b	c
	8.7	c	a	b	c	a
	Space Group	Pbnm	Pbnm (1)	Pnma	Pbnm	Pmcn
Chondrodite	4.7	a	b	b	b	b
	10.3	b	c	a	a	c
	7.9	c	a	c	c	a
	Space Group	$P2_1/b$	$P2_1/c$	$P2_1/a$	$P2_1/c$ (2)	$P2_1/c$
Humite	4.7	a	b	c	a	b
	10.2	b	c	a	b	c
	20.9	c	a	b	c	a
	Space Group	Pbnm	Pbnm (1)	Pnma	Pbnm	Pmcn
Clinohumite	4.7	a	b	b	b	b
	10.3	b	c	c	a	c
	13.7	c	a	a	c	a
	Space Group	$P2_1/b$	$P2_1/c$	$P2_1/c$	$P2_1/c$ (2)	$P2_1/c$
Forsterite	4.755	a	b		a	b
	10.21	b	c		b	c
	5.98	c	a		c	a
	Space Group	Pbnm	Pbnm (1)(3)		Pbnm	Pmcn

---

(1) should be Pmcn.
(2) should be $P2_1/a$.
(3) Deer, Howie, and Zussman are consistent with Taylor and West.

1949), by Deer, Howie, and Zussman (1962), and by Winchell and Winchell (1951) are incorrect because of their choice of axes. It is proposed that Taylor and West's (1929) choices of axes and space groups be accepted because they retain the analogy with olivine (cf. Bragg and Claringbull, 1965, p.175).

The numerous axial labels (Table III) have apparently led to the confusing descriptions of twinning. For example, Deer, Howie, and Zussman (1962) describe simple and multiple twinning on (001); this is correct if Taylor and West's (1928, 1929) axial notation is used, but is not consistent with the axial notation adopted by Deer, Howie, and Zussman. They also report twinning on the (105) and ($\bar{3}05$) for chondrodite and on the ($\bar{1}03$) for clinohumite. These are consistent with the notation adopted by the A.S.T.M. for chondrodite, by Winchell and Winchell (1961) (see Table III), and by Tilley (1951), but not with their own choice of axes. Heinrich (1965) is equally confusing. He apparently adopts Sahama's choice of axes, yet he describes twinning on (001), (105), and ($\bar{3}05$) for chondrodite although with Sahama's choice of axes it should be (100), (501), and (503).

Kerr (1959) apparently adopts the same axial choices as Winchell and Winchell (1961) for chondrodite, but he lists the interaxial angle β as 90° and states (p.351): "Although the mineral is monoclinic, the [angle] β between the a- and c-axes is 90° (orthorhombic syngony)." His Fig. 15-7 indicates that all interaxial angles are 90°, which is incorrect for chondrodite.

CHEMISTRY OF THE HUMITE MINERALS

Composition

The formulae of most naturally occurring humite minerals closely approximate the end-member compositions given in Table I. However, examination of bulk chemical analyses (Appendix A) and microprobe analyses (Table VI, VII) indicate that the following may also be present: Fe^{+2}, Fe^{+3}, Mn, Ti, Al, Ca, Zn, B, P, Na, K, Pb, Cr, Ni, Ba (however, see note (6) in Appendix A, Table XII), Cl, and CO_2. In addition, Schäfer (1896) has described two clinohumites with 1.68 and 1.04 weight percent BeO (analyses unavailable), and Fleischer and Cameron (1955) and Ross (1964) have suggested that Be may be a relatively important constituent of the humite minerals. Unfortunately, Be cannot be detected with the electron microprobe without elaborate instrumentation. The most important of the minor elements mentioned appear to be Fe, Ti, Mn, Al, and Ca; the presence of Al, however, is probably due to impurities as discussed later.

Borneman-Starynkevitch and Myasnikov (1950) analyzed six clinohumites from the southern Urals which showed a range of 0.87 to 2.98 weight percent Fe and 0.41 to 3.24 weight percent Ti. They concluded from stoichiometric calculations that Fe^{+2} replaces Mg only in the "Mg_2SiO_4" part of the structure. Sahama (1953), however, pointed out that this would require ordering of Mg and Fe, which have similar ionic radii and the same charge, and is thermodynamically improbable, implying that Mg and Fe are disordered in the humite minerals. Recent crystal structure analyses of hortonolite from a hypabyssal dike and of hyalosiderite from a plutonic environment (Birle _et al._, 1968) show no evidence of long-range ordering of Mg and Fe; this was confirmed by Mössbauer spectroscopy (Bancroft and Burns, 1966). Since, as shown in a previous section, the humites are structurally analogous to olivine, ordering of Fe and Mg is not expected, although positive confirmation awaits crystal structure refinements. It is presumed that Mn is also disordered in the structure.

Ferric iron is included in nearly all of the bulk chemical analyses given in Appendix A. Its presence is neither confirmed nor denied in this study, but some comment is appropriate. Borneman-Starynkevitch and Myasnikov (1950) found that Fe^{+2} is largely oxidized on mechanical crushing, thereby implying that Fe^{+3} values may be lower than reported. Sahama (1953, p.20), however, says that "...it is a well known fact that natural and artificial fayalite is never entirely free of ferric iron..." and "Therefore, it seems evident that natural humite minerals primarily contain some ferric iron." It is interesting to note that to maintain local charge balance, Fe^{+3} would probably replace Mg in the Mg(OH,F)O region of the structure. The replacement would then be of the form $Fe^{+3} + O = Mg + (OH,F)$ and each Fe^{+3} would be surrounded by five O and one (OH,F).

Calcium occurs in the humites in only minor amounts, as would be expected by analogy with forsterite (see analyses by Smith, 1966). It is noteworthy, however, that in the Mn analogue of humite, _o_-leucophoenicite, Moore (1967, and personal communication, 1968) found that the replacement of 10 percent Mn by Ca resulted in a doubling of the _c_-axis.

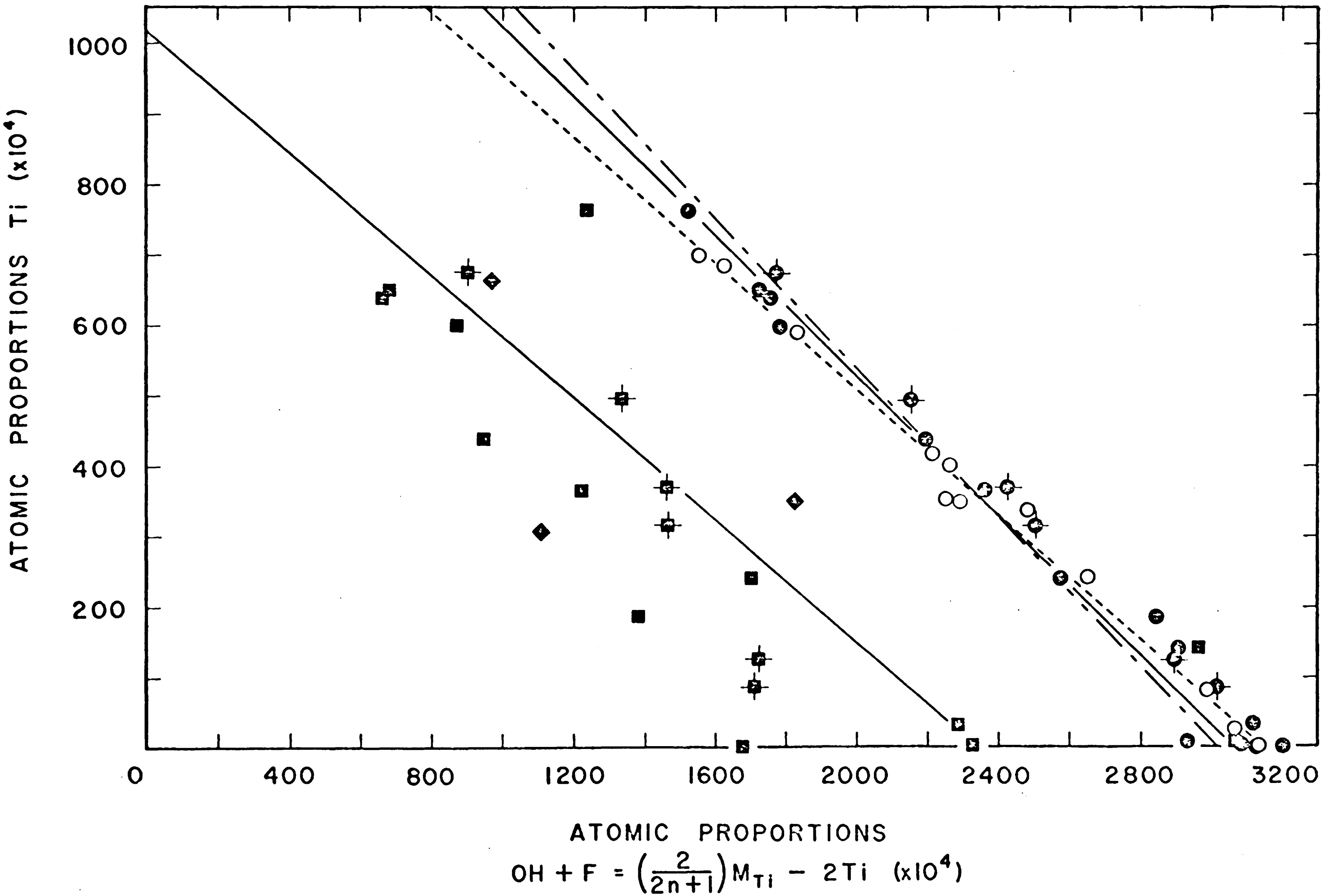
He interprets this as a result of ordering of the Ca. By analogy with the olivine-group minerals, glaucochroite and monticellite, ordering of Ca in the larger octahedral sites in humite minerals is expected. The minor amounts of Ca in the Mg-humites prevents proof of this speculation.

Titanium apparently plays a special role in the humite minerals. The Ti content of olivines is generally quite low; the maximum amount found by Smith (1966) was 0.13 weight percent. However, in the humites, especially clinohumite, relatively significant amounts may occur. Borneman-Starynkevitch and Myasnikov (1950) suggested that Ti occupies only the octahedral sites in the (OH,F) region of the clinohumite structure. Sahama (1953) pointed out that analytical results for all of the humite minerals are in better agreement with the idealized formulae if it is assumed that Ti does not replace Mg in the "silicate" portion of the structure. The most Ti-rich clinohumite specimen described by Borneman-Starynkevitch and Myasnikov has the formula

$$(Mg,Fe)_{8.6}Ti_{0.4}(SiO_4)_4OH_{1.1}F_{0.02}O_{0.87}$$

This implies a coupled substitution of the form $Ti + 2(O) = (Mg,Fe) + 2(OH,F)$. This is further substantiated in Figure 9 which compares atomic proportions Ti with atomic proportions of the quantities (OH + F) and $(2/[2\underline{n} + 1])M_{Ti} - 2Ti$. As shown in Appendix B, the latter two quantities should be equal. If the substitution is of the form suggested, the equation describing it would be $OH + F = (2/[2\underline{n} + 1])M_{Ti} - 2Ti = -2Ti + 3200$. The equations obtained from the data in Tables VI and VII and Appendix A are as follows (the standard errors are given in

Figure 9. Graphical representation of the coupled substitution Ti + 2(O) = M + 2(OH,F). Linear regression curves for microprobe data (open circles, dot-dash line), chemical cation data (solid circles, dashed line), and combined microprobe and chemical cation data (solid line through circles) essentially substantiate the coupled substitution. Chemical anion data (squares, solid line) probably reflect inaccurate H_2O and/or F analyses. Data points with crosses are from Borneman-Starynkevitch and Myasnikov (1950); tilted squares are partial analyses.


ATOMIC PROPORTIONS Ti (x10^4)
1000
800
600
400
200
0
400
800
1200
1600
2000
2400
2800
3200
ATOMIC PROPORTIONS
OH + F = $\left(\frac{2}{2n+1}\right)M_{Ti}$ − 2Ti (x10^4)

brackets):

Probe data:

$$(2/[2\underline{n} + 1])M_{Ti} - 2Ti = -2.25[.07]Ti + 3149[29]$$

Coefficient of correlation = -0.995

Chemical cation data:

$$(2/[2\underline{n} + 1])M_{Ti} - 2Ti = -1.89[.26]Ti + 3020[97]$$

Coefficient of correlation = -0.862

Combined probe and chemical cation data:

$$(2/[2\underline{n} + 1])M_{Ti} - 2Ti = -2.00[.17]Ti + 3057[66]$$

Coefficient of correlation = -0.908

Chemical anion data:

$$OH + F = -2.3[.4]Ti + 2344[157]$$

Coefficient of correlation = -0.794

The equations relating cations to Ti are in fair agreement with the theoretical relation and essentially substantiate the proposed substitution. The equation relating (OH + F) to Ti, however, is in poor agreement with the theoretical relation. This is a reflection of the relative inaccuracy of H_2O and/or F analyses as discussed later. Thus, for every Ti ion introduced, 2(O) replace 2(OH,F) to maintain electrostatic neutrality and the hexagonal closest-packing of the anions. Since the replaced (OH,F) anions were not bonded to Si, it follows that the replacing O is not bonded to Si. This assumption is consistent with Pauling's (1929) rules and further suggests that Ti is ordered in octahedral sites in the Mg(OH,F)O region of the structure as suggested by Borneman-Starynkevitch and Myasnikov (1950).

Based on the preceding discussion, a general formula can be written for the humite group as follows:

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

where M includes the octahedrally coordinated cations Mg, Fe, Mn, Ca, Zn, etc., and $\underline{x}$ is less than or equal to one. The members of the group are distinguished by the value of $\underline{n}$ in the formula: thus $\underline{n} = 1$ describes norbergite; $\underline{n} = 2$, chondrodite, $\underline{n} = 3$, humite; and $\underline{n} = 4$, clinohumite.

Compositional Variation

Complete replacement of Mg by Fe or Mn, or of Mg by Ti in the Mg(OH,F)O region of the structure, apparently does not occur in the humite minerals. The substitutional range of these elements found in this study is illustrated in Figure 10. The amount of substitution for Mg appears to increase from norbergite to clinohumite; this is particularly noticeable for Ti.

Borneman-Starynkevitch and Myasnikov (1950) and later Bradshaw and Leake (1964) noted that Ti-rich clinohumites are F-poor. This is illustrated in Figure 11 for chemically analyzed and microprobe analyzed clinohumites. Bradshaw and Leake suggested that the availability of F determines the amount of Ti which may enter the humite structures. They stated (p.1075): "The formation of norbergite, chondrodite, humite, and clinohumite is progressively more favoured with diminution of available F. Should there be inadequate F even to form clinohumite, then Ti may replace Mg, allowing 2 F^- to be replaced by 2 O^{2-}." It is interesting to note that below about 1.9 weight percent Ti (0.04

Figure 10. Enlargement of hachured area in Mg - Ti - (Fe + Mn) triangular diagram (inset) showing substitution for Mg in the humite minerals; based on ratios of atomic proportions of Mg, Ti, and (Fe + Mn). Solid circles, norbergite; open circles, chondrodite, solid triangles, humite; open triangles, clinohumite.

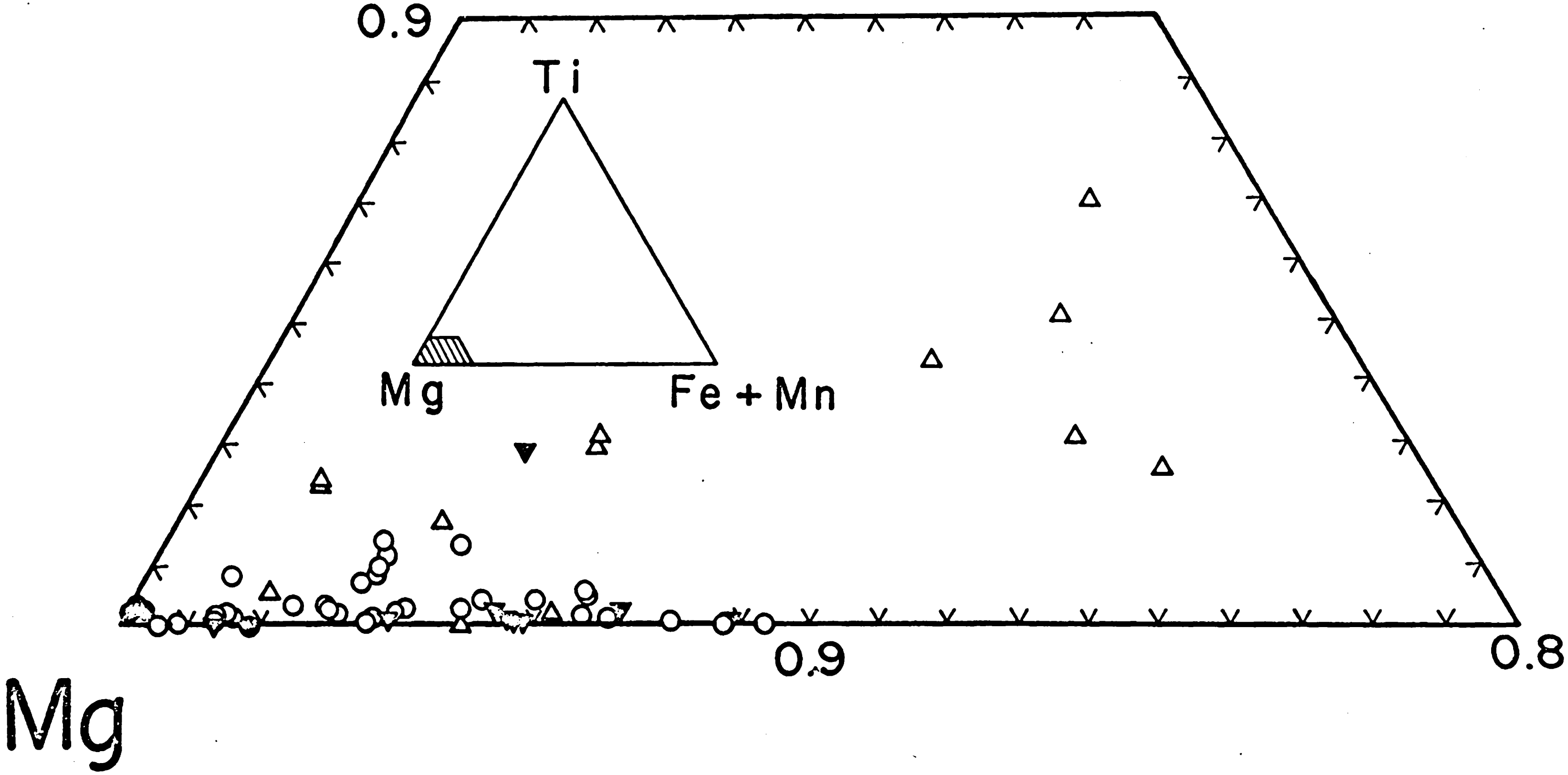
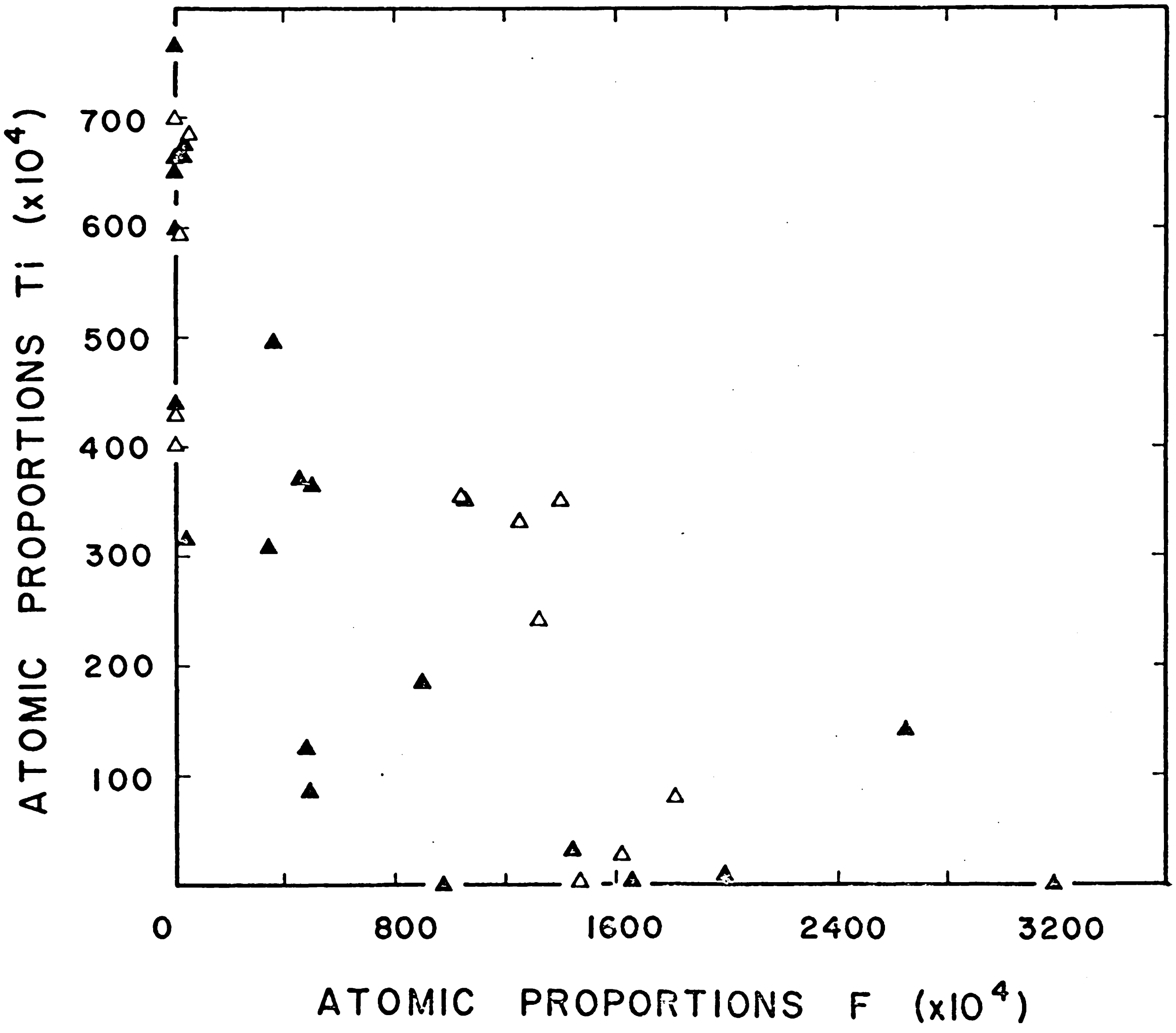

0.9
Ti
Mg
Fe + Mn
0.9
0.8
Mg

Figure 11. The relationship between Ti and F in clinohumite. Below approximately 0.04 atomic proportions Ti (1.9 weight percent) F and OH decrease in roughly equal amounts with increase in Ti. Above 0.04 atomic proportions Ti (which corresponds to the replacement of one-fourth of the Mg in the Mg(OH,F)O portion of the structure) little or no F is present (the single exception is a Ti-clinohumite analyzed by Borneman-Starynkevitch and Myasnikov (1950)). Solid triangles are chemical analyses, open triangles are microprobe analyses.


ATOMIC PROPORTIONS Ti $(\times 10^4)$
700
600
500
400
300
200
100
0
800
1600
2400
3200
ATOMIC PROPORTIONS F $(\times 10^4)$

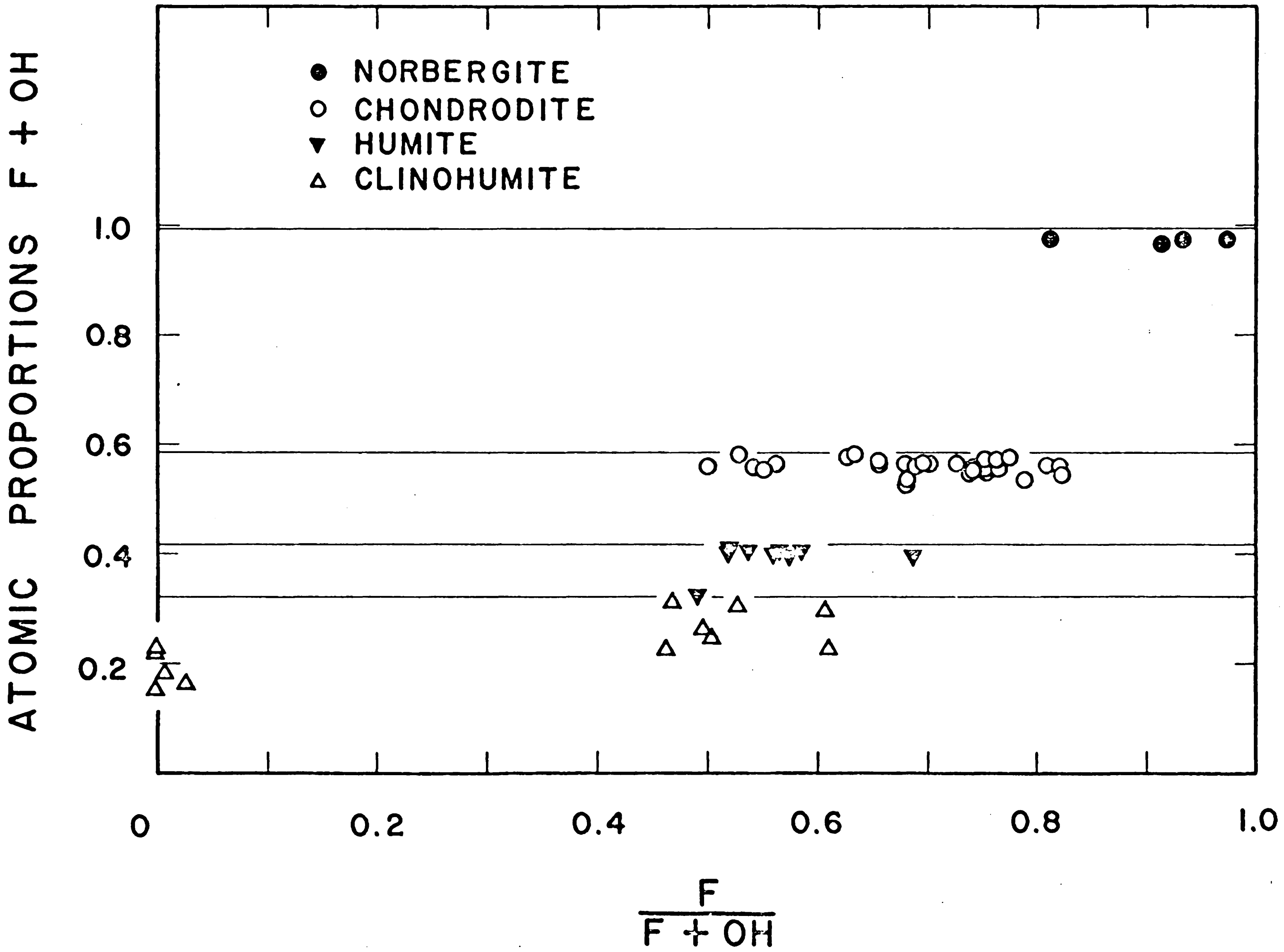
atomic proportions) a relationship between F and Ti is not evident (aside from the decrease brought about from substitution of O for both OH and F as Ti enters the structure). When Ti exceeds about 1.9 weight percent, however, little or no F is present (with but one exception). The value 1.9 weight percent corresponds to a replacement of about one-quarter of the Mg and (OH,F) ions in the Mg(OH,F)O portion of the structure by Ti and 2(O); thus, there may be some structural reason for the absence of F at high Ti levels. Perhaps F is excluded at this level of replacement because it would be more strongly repulsed by the additional O in the Mg(OH,F)O portion of the structure than would proton-bearing OH.

Not only does the amount of (OH + F) decrease through the humite series from norbergite to clinohumite, but the amount of F relative to OH also decreases, as illustrated by the microprobe analyses in Figure 12. It is not clear whether the amount of F contained by each of the members of the group is a function of the availability of F at the time of formation, of the crystal chemistry, or both. Thus, although the chondrodites fall within a range of 0.5 to 0.8 F/[F + OH], many of those from the Franklin, New Jersey area have very similar values (about 0.72). Gibbs and Ribbe (1968) suggest that no more than 50 percent of the F in norbergite could be replaced by OH because of the proton-proton interaction which would result. This may explain why OH-norbergite has not been synthesized.

Stoichiometric Considerations

Sahama (1953) examined the chemical analyses of 46 humite mineral

Figure 12. Illustration of the decrease in (F/[F + OH]) with decrease in (F + OH) in the humite minerals. Horizontal lines represent stoichiometric $\underline{n}Mg_2SiO_4 \cdot MgOHF$.


● NORBERGITE
○ CHONDRODITE
▼ HUMITE
△ CLINOHUMITE
ATOMIC PROPORTIONS F + OH
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
$\frac{F}{F + OH}$

specimens, including 14 of his own, in terms of the ratio of atomic proportions Si to atomic proportions (OH + F + O_{Ti}). O_{Ti} is given by 2(Ti) on the assumption that Ti is ordered in the Mg(OH,F)O region of the structure and that the substitution is of the form Ti + 2(O) = (Mg,Fe) + 2(OH,F). Sahama's results are given in Table IV. He summarizes them as follows (p.16): "The average Si:(O + OH + F) ratios given in the fourth column of Table [IV] agree comparatively well with the corresponding theoretical figures. This fact, however, only proves that the conception of the chemical composition of humite minerals is correct. The ranges of variation of this ratio given in the third column of the same table indicates a considerable deviation of the result of an individual analysis from the ideal composition." The chemical analyses given in Appendix A are summarized in Figures 13b and c in terms of the ratio Si:(OH + F + O_{Ti}) or the ratio Si:(2/[2$\underline{n}$ + 1])M_{T}: the two should be equivalent as shown in Appendix B.

The deviations from ideal composition can be explained by admixtures of two or more humite minerals, by structural defects, by analytical errors, by very fine scale epitaxial intergrowths of more than one humite mineral, or by admixtures of other mineral impurities. Sahama (1953) dismissed the possibility of admixtures of other humite minerals after showing that a mixture of 10 percent humite and 90 percent chondrodite would cause only a small deviation in the ratio Si:(OH + F + O_{Ti}). Schottky or interstitial point defects could produce non-stoichiometry, but it is doubtful that they could account for the large variations reported for the humites.

Chemical analysis of the humite minerals using the normal wet

TABLE IV. Summary of Sahama's (1953) Findings

Mineral	Number of Chemical Analyses	Si : (O + OH + F)		
		Theoretical	Range	Average
Norbergite	3	4 : 8	4 : 7.14-8.78	4 : 8.23
Chondrodite	20	4 : 4	4 : 3.37-4.80	4 : 3.93
Humite	10	12 : 8	12 : 5.98-9.19	12 : 8.07
Clinohumite	13	8 : 4	8 : 2.90-5.30	8 : 4.25

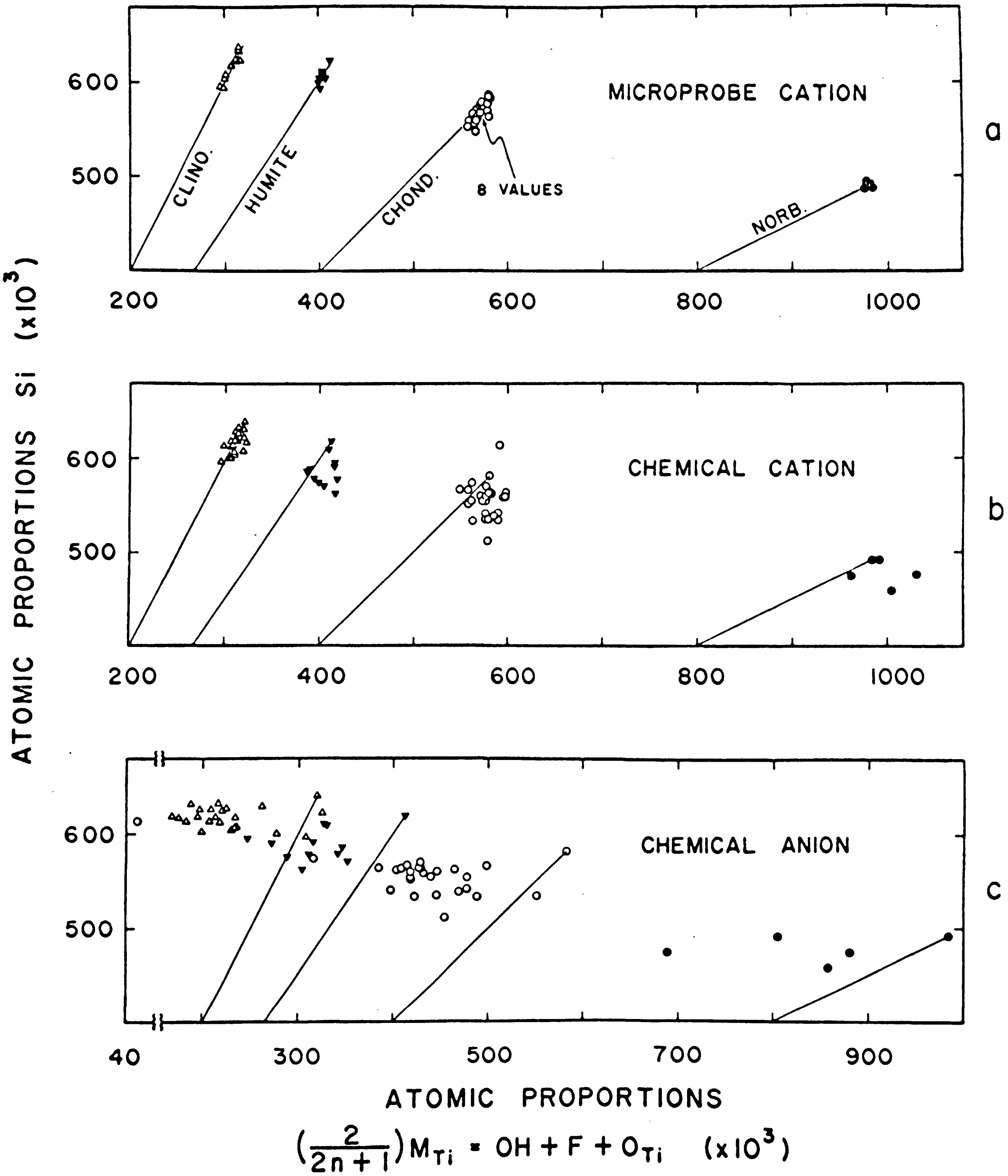
Figure 13. Summary of stoichiometry in the humite minerals. Straight lines represent lines along which analyses should fall for stoichiometric clinohumite (open triangles), humite (solid triangles), chondrodite (open circles), and norbergite (solid circles).

a. Si *vs*. $(2/[2n + 1])M_{Ti}$ for microprobe analyses.

b. Si *vs*. $(2/[2n + 1])M_{Ti}$ for bulk chemical analyses.

c. Si *vs*. $(OH + F + O_{Ti})$ for bulk chemical analyses.

The lack of agreement between b and c implies a charge imbalance.


ATOMIC PROPORTIONS Si (x10^3)
600
500
200
400
600
800
1000
CLINO.
HUMITE
CHOND.
NORB.
8 VALUES
MICROPROBE CATION
a
CHEMICAL CATION
b
CHEMICAL ANION
c
40
300
500
700
900
ATOMIC PROPORTIONS
$\left(\frac{2}{2n+1}\right)M_{Ti} = OH + F + O_{Ti}$ (x10^3)

chemical methods has long been recognized as a difficult task. Penfield and Howe (1894, p.189) stated: "The chemical relations of the minerals have never been satisfactorily determined. This is owing partly to the fact that it has been difficult to obtain pure material in sufficient quantity for analysis, while the analytical difficulties in the accurate determination of silica and fluorine have not always been overcome. Water in the form of hydroxyl, which is an unfailing constituent of the minerals, has either been overlooked or incorrectly determined." Sahama (1953) concluded that the deviations from the ideal composition were mainly due to analytical errors. He stated (p.18): "The general errors in silicate analyses found by Fairbairn and others (1951) cannot be applied to the humite mineral analyses because the materials are different. The high content of fluorine and, in addition, the content of water apparently are the sources of analytical difficulties well known to every analyst who has been working with humite minerals. As has been pointed out by many previous authors, water is held very firmly in the humite mineral structure and will be difficultly expelled."

Bradshaw and Leake (1964, p.1076), on the other hand, concluded that analytical errors are not enough to account for departures from stoichiometry. They suggested "...that sometimes humite minerals are found that contain irregular numbers of $Mg(OH,F)_2$ - TiO_2 layers for a given number of Mg_2SiO_4 layers." As pointed out earlier, epitaxial intergrowths between the various humite minerals or between forsterite and the humites appear to be structurally reasonable. However, it should be noted that whereas most of the deviations of the ratio Si:(OH + F + O_{Ti}) shown in Table IV can be explained by fine scale epitaxial intergrowths, one cannot. Thus, an intergrowth between norbergite and olivine or any of the other members of the humite group produces a ratio of 4:<8. Yet Sahama shows that the range, and indeed the average (albeit based on only three analyses) is 4:>8. This would require intergrowths between norbergite and a more (OH,F)-rich compound of the same structure. Such a compound has not been found in nature, nor could Van Valkenburg (1961) synthesize one of composition $0.5Mg_2SiO_4 \cdot MgF_2$.

Although many of the analysts, particularly Sahama, have taken special precautions to obtain pure material, the possibility of admixed impurities of other minerals should not be dismissed. During the course of the microprobe analyses undertaken for this study, impurities of other minerals were detected. In many instances they were quite small and could probably be separated only with great difficulty, if at all. Spinel, in particular, has apparently not been entirely extracted from samples analyzed by wet chemical means. This point is discussed further in the next section.

Electron Microprobe Analyses

Fifty-five humite group mineral samples were analyzed with an Applied Research Laboratories EMX electron microprobe for Si, Mg, Fe, Mn, Ti, F, Ca, and Zn. In addition, approximately half of the samples were analyzed for P, Cl, Pb, Ni, and Al and checked for Cu, Co, and Cr. Selected samples were scanned throughout the wavelength range of the instrument (which covers elements B - U). A description of the analytical procedures is given in Appendix C and the analytical results are presented in Table VI and VII. Original numbers, localities, and donors of the analyzed samples are listed in Table V. The average oxide sum of these analyses is 99.66 weight percent and the range is from 98.61 to 100.46 weight percent. These sums compare favorably with those given by Smith (1966) who reported ranges between 97.7 and 100.8 weight percent and an average of 99.7 weight percent for the structurally similar olivines. A histogram showing the frequency of oxide totals is given in Figure 14.

It was necessary to calculate O and OH because results on O were erratic and H cannot be determined with the microprobe. The only assumption inherent in these calculations is that there is electrostatic charge balance between cation and anion. The details of these calculations are given in Appendix B. An indication of the accuracy or the deviation from stoichiometry can be obtained by considering the ratio $2(Si):(2\underline{n}/[2\underline{n}+1])M_{Ti}$ which is independent of the anion calculations. M_{Ti} represents the sum of the atomic proportions of all of the octahedral cations, including Ti, and $\underline{n}$ is the integer distinguishing the various members of the group. This ratio is equal to unity for a stoichiometric humite mineral. Its value for each of the minerals analyzed is given with the analyses.

Samples which were analyzed by Sahama and with the microprobe in this study are compared on an individual element basis in Figure 15. Agreement between the two methods is quite good for Fe and F, and fair for Ti and Mn. However, Si is consistently lower and Mg higher

TABLE V-a. Original Numbers, Localities, and Donors of Norbergite Samples in Table VI.

New No.	Original No.	Locality	Donor
1	R12213	Nicol Quarry, Franklin, N. J.	Smithsonian Inst.
2	C6298	Quarry east of filter, Franklin, N. J.	Smithsonian Inst.
3	115542	Sterling Hill, Ogdensburg, N. J.	Smithsonian Inst.
4	1	Norberg, Sweden	Th. G. Sahama

TABLE V-b. Original Numbers, Localities, and Donors of Humite Samples in Table VI.

New No.	Original No.	Locality	Donor
1	47071	Monte Somma, Vesuvius, Italy	Smithsonian Inst.
2	85697	Monte Somma, Vesuvius, Italy	Smithsonian Inst.
3	2	Hermala, Lohja, Finland	Th. G. Sahama
4		Tor Avaly	S. G. Fleet
5		Vesuvius, Italy	S. G. Fleet
6	1	Monte Somma, Vesuvius, Italy	Th. G. Sahama
7	3	Sillböle, Finland	Th. G. Sahama
8	95147	Monte Somma, Vesuvius, Italy	Smithsonian Inst.
9		Monte Somma, Vesuvius, Italy	S. G. Fleet

TABLE V-c. Original Numbers, Localities, and Donors of Clinohumite Samples in Table VI.

New No.	Original No.	Locality	Donor
1	103786	Aker, Sweden	Smithsonian Inst.
2		Santa Lucia Mtns., Monterrey Co., Calif.	W. S. Wise
3	2	Ojamo, Lohja, Finland	Th. G. Sahama
4	134	Unknown	S. G. Fleet
5	C5176	Baline, Ala Valley, Piedmont, Italy	Smithsonian Inst.
6	C5176	Baline, Ala Valley, Piedmont, Italy	Smithsonian Inst.
7	1	Hämeenkylä, Finland	Th. G. Sahama
8	107384	Buell Park, Ariz.	Smithsonian Inst.
9	107384	Buell Park, Ariz.	Smithsonian Inst.
10	94997	Franscia, Val Malenco, Italy	Smithsonian Inst.
11	115658	Dillon, Mont.	Smithsonian Inst.
12	9891	Dillon, Mont.	U. of Minnesota

TABLE V-d. Original Numbers, Localities, and Donors of Chondrodite Samples in Table VII.

New No.	Original No.	Locality	Donor
1	2	Kafveltorp, Sweden	Th. G. Sahama
2	1	Hangleby, Sibbo, Finland	Th. G. Sahama
3		Limecrest Quarry, Sparta, N. J.	Larry Highton
4		New Jersey	S. G. Fleet
5		Limecrest Quarry, Sparta, N. J.	Larry Highton
6	3	Sparta, N. J.	Th. G. Sahama
7	103784	Sparta, N. J.	Smithsonian Inst.
8	95039	Franklin Furnace, N. J.	Smithsonian Inst.
9	R14660	Franklin, N. J.	Smithsonian Inst.
10	36081	Amity, N. Y.	Smithsonian Inst.
11		Limecrest Quarry, Sparta, N. J.	Larry Highton
12		Limecrest Quarry, Sparta, N. J.	Larry Highton
13	13274	Orange Co., N. Y.	Smithsonian Inst.
14	4	Edenville, Orange Co., N. Y.	Th. G. Sahama
15		Franklin, N. J.	S. G. Fleet
16	78560	Edenville, Orange Co., N. Y.	S. G. Fleet
17	105488	Amity, N. Y.	Smithsonian Inst.
18	103287	Taberg, Wermland, Sweden	Smithsonian Inst.
19	R7070	Amity, N. Y.	Smithsonian Inst.
20	103784	Sparta, N. J.	Smithsonian Inst
21	T.W. 2528	Tilley Foster Mine, Brewster, N. Y.	S. G. Fleet
22	7	Tilley Foster Mine, Brewster, N. Y.	Th. G. Sahama
23		Unknown	S. G. Fleet
24		Tilley Foster Mine, Brewster, N. Y.	S. G. Fleet
25		Limecrest Quarry, Sparta, N. J.	Larry Highton
26	3199	Tilley Foster Mine, Brewster, N. Y.	Smithsonian Inst.
27	R78568	Nya-Kopparberg, Sweden	Smithsonian Inst.
28	R3874	Kafveltorp, Sweden	Smithsonian Inst.
29	14327	Brewster, N. Y.	Smithsonian Inst.
30	8	Kafveltorp, Sweden	Th. G. Sahama

TABLE VI. Microprobe analyses of chondrodite, $2M_2SiO_4 \cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$

(in order of increasing Fe)

	Weight Percent Oxide										Atomic Proportions ($\times 10^4$)											
New No.	SiO_2	FeO	MnO	MgO	TiO_2	CaO	ZnO	F	OH calc	Total (1)	Si	Fe	Mn	Mg	Ti	Ca	Zn	F	OH	Stoic. (2)	Formula "x"	New No.
1	35.04	0.55	0.05	58.33	0.00	0.00	0.00	5.80	4.71	99.82	5832	77	7	14470	0	0	0	3053	2769	1.002	0.000	1
2	35.17	0.71	0.17	57.92	0.03	0.01	0.05	6.97	3.61	100.01	5853	98	24	14367	4	2	6	3669	2124	1.009	0.001	2
3	33.87	1.16	0.10	57.24	0.97	0.01	0.10	7.98	2.32	99.30	5636	161	15	14199	121	2	12	4200	1362	0.971	0.042	3
4	34.68	1.27	0.12	57.54	0.12	0.03	0.05	8.49	2.21	99.89	5772	177	16	14273	15	5	6	4469	1299	0.996	0.005	4
5	33.80	1.31	0.06	57.19	0.22	0.03	0.10	8.18	2.40	98.72	5626	183	9	14186	27	5	12	4306	1409	0.975	0.009	5
6	35.26	1.33	0.17	57.44	0.23	0.03	0.06	6.84	3.64	100.41	5868	184	24	14248	29	5	8	3600	2141	1.012	0.010	6
7	34.79	1.42	0.18	56.69	0.18	0.04	0.07	7.53	2.93	99.28	5789	197	25	14063	23	7	9	3963	1721	1.010	0.008	7
8	34.21	2.28	0.13	55.86	0.37	0.03	0.01	8.63	1.81	98.85	5693	317	18	13857	46	5	2	4542	1064	0.999	0.016	8
9	32.41	2.84	0.10	56.71	0.37	0.03	0.01	10.27	(3)		5394	396	15	14067	46	5	2	5406	(3)		0.016	9
10	32.88	2.86	0.12	55.98	0.32	0.04	0.00	9.30	(3)		5472	398	16	13886	40	7	0	4895	(3)		0.014	10
11	34.16	2.88	0.26	55.65	0.23	0.01	0.00	7.80	2.63	99.10	5686	401	36	13804	29	2	0	4106	1545	0.996	0.010	11
12	33.99	2.97	0.26	55.31	0.80	0.03	0.01	7.75	2.44	99.15	5658	414	36	13722	100	5	2	4079	1432	0.991	0.035	12
13	34.46	3.15	0.21	55.13	1.10	0.03	0.01	8.50	1.64	99.88	5736	439	29	13676	138	5	2	4474	966	1.004	0.048	13
14	34.25	3.16	0.14	55.65	1.63	0.01	0.01	6.98	2.90	100.43	5700	440	20	13804	205	2	2	3674	1706	0.985	0.071	14
15	34.04	3.20	0.21	55.45	1.00	0.01	0.00	7.87	2.30	99.69	5665	446	29	13755	125	2	0	4142	1350	0.986	0.044	15
16	34.01	3.27	0.12	54.77	1.33	0.03	0.07	8.03	1.93	99.27	5661	455	16	13586	167	5	9	4227	1134	0.994	0.059	16
17	34.66	3.51	0.10	55.55	0.08	0.04	0.00	7.09	3.35	99.81	5768	489	15	13779	10	7	0	3732	1967	1.008	0.004	17
18	34.23	3.76	0.18	54.78	0.28	0.07	0.06	8.74	1.71	99.33	5697	523	25	13590	35	12	8	4600	1007	1.003	0.013	18
19	34.40	3.81	0.27	54.98	0.33	0.01	0.00	7.48	2.86	99.64	5725	530	38	13639	42	2	0	3937	1680	1.004	0.015	19
20	33.67	4.12	0.23	53.76	1.50	0.04	0.01	6.83	2.86	98.79	5604	573	33	13335	188	7	2	3595	1684	0.991	0.066	20
21	34.16	4.68	0.26	54.45	0.32	0.00	0.02	6.01	4.17	99.58	5686	652	36	13508	40	0	3	3163	2454	0.998	0.014	21
22	34.27	4.88	0.30	54.57	0.30	0.00	0.02	5.32	4.76	100.16	5704	679	42	13537	65	0	3	2800	2801	0.995	0.023	22
23	33.78	5.08	1.61	53.14	0.20	0.07	0.19	7.01	3.28	99.87	5622	707	228	13183	25	12	23	3690	1931	0.991	0.009	23
24	34.16	5.65	0.30	53.81	0.47	0.00	0.02	5.74	4.35	100.03	5686	786	42	13347	58	0	3	3021	2557	0.998	0.021	24
25	32.90	6.33	0.27	53.04	0.62	0.06	0.07	7.78	2.42	99.07	5476	881	38	13158	77	10	9	4095	1421	0.966	0.027	25
26	33.63	6.38	0.25	53.08	0.55	0.00	0.02	5.79	4.21	99.49	5579	888	35	13166	69	0	3	3048	2478	0.988	0.024	26
27	33.59	6.41	1.55	51.65	0.10	0.06	0.19	7.84	2.44	99.38	5590	892	218	12813	13	10	23	4127	1435	1.001	0.004	27
28	33.22	6.60	2.67	50.80	0.03	0.11	0.21	8.10	2.22	99.51	5529	919	378	12603	4	20	26	4264	1307	0.991	0.001	28
29	34.04	6.96	0.14	52.73	0.12	0.00	0.00	7.34	2.96	99.81	5665	969	20	13080	15	0	0	3863	1741	1.006	0.005	29
30	33.46	7.06	1.77	51.78	0.02	0.08	0.22	7.30	3.07	100.25	5569	983	249	12846	2	15	28	3842	1803	0.986	0.001	30

(1) Total less O for F and OH.

(2) Stoic. = $2Si/(2\underline{n}/[2\underline{n} + 1])M_{Ti}$

(3) Single crystal studies of chondrodite No. 10 show a chondrodite diffraction pattern and Nos. 9 and 10 are both Si-deficient, indicating the possibility of another cation in tetrahedral coordination. Therefore, these values were not calculated.

TABLE VII. Microprobe analyses of norbergite, humite, and clinohumite

(in order of increasing Fe)

	Weight Percent Oxide										Atomic Proportions ($\times 10^4$)											
New No.	SiO_2	FeO	MnO	MgO	TiO_2	CaO	ZnO	F	OH calc	Total (1)	Si	Fe	Mn	Mg	Ti	Ca	Zn	F	OH	Stoic. (2)	Formula "x"	New No.
Norbergite $M_2SiO_4\cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$																						
1	29.74	0.06	0.01	58.73	0.42	0.15	0.05	16.77	1.44	99.63	4949	9	2	14569	52	27	6	8827	847	1.012	0.011	1
2	29.59	0.06	0.01	59.01	0.30	0.13	0.05	17.25	1.12	99.73	4924	9	2	14639	38	22	6	9080	656	1.004	0.008	2
3	29.39	0.15	0.04	59.04	0.27	0.11	0.02	18.03	0.45	99.70	4892	21	5	14647	33	20	3	9490	263	0.996	0.007	3
4	29.31	1.84	0.13	57.85	0.00	0.04	0.00	15.08	3.09	99.54	4878	256	18	14351	0	7	0	7938	1818	1.000	0.000	4
Humite $3M_2SiO_4\cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$																						
1	37.46	1.22	0.17	57.27	0.12	0.01	0.01	4.00	3.38	100.37	6234	170	24	14207	15	2	2	2105	1986	1.009	0.007	1
2	36.30	3.06	0.83	55.16	0.13	0.11	0.09	4.50	2.85	99.80	6042	426	116	13685	17	20	11	2369	1676	0.988	0.008	2
3	36.45	3.24	1.28	52.89	3.25	0.01	0.00	3.02	2.79	100.35	6067	451	180	13121	407	2	0	1590	1642	1.000	0.201	3
4	36.60	4.19	1.59	53.67	0.10	0.10	0.01	4.31	2.98	100.34	6092	584	224	13314	13	17	2	2269	1750	1.004	0.006	4
5	36.75	4.25	1.59	53.62	0.10	0.08	0.00	3.96	3.29	100.42	6117	591	224	13302	13	15	0	2084	1932	1.009	0.006	5
6	35.66	4.39	0.99	53.41	0.23	0.10	0.09	5.17	2.10	98.97	5935	611	140	13249	29	17	11	2721	1237	0.985	0.014	6
7	36.43	5.03	0.65	53.84	0.10	0.01	0.00	4.07	3.20	100.11	6064	700	91	13356	13	2	0	2142	1879	0.990	0.006	7
8	36.35	6.19	0.98	52.26	0.27	0.07	0.06	4.30	2.85	100.18	6049	861	138	12965	33	12	8	2263	1675	1.007	0.017	8
9	35.66	6.84	1.96	51.30	0.03	0.21	0.01	4.24	2.99	100.04	5935	953	277	12726	4	37	2	2232	1760	0.989	0.002	9
Clinohumite $4M_2SiO_4\cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$																						
1	38.36	1.76	0.13	55.80	0.65	0.01	0.00	3.45	2.00	99.77	6384	245	18	13841	81	2	0	1816	1174	1.012	0.052	1
2	37.95	1.78	0.01	54.92	2.65	0.01	0.00	2.37	2.12	99.81	6316	247	2	13623	332	2	0	1247	1246	1.000	0.210	2
3	38.08	3.64	0.25	53.89	1.93	0.01	0.00	2.51	2.28	100.46	6338	507	35	13368	242	2	0	1321	1340	1.007	0.154	3
4	37.50	3.90	1.08	54.04	0.02	0.04	0.00	2.79	2.83	99.70	6242	543	153	13405	2	7	0	1469	1662	0.995	0.001	4
5	37.18	4.73	0.66	50.99	3.42	0.00	0.00	0.00	3.77	98.98	6188	659	93	12648	428	0	0	0	2217	1.007	0.279	5
6	37.52	4.79	0.65	50.97	3.20	0.01	0.00	0.00	3.85	99.18	6245	666	91	12644	401	2	0	0	2265	1.018	0.261	6
7	37.54	5.58	0.62	53.03	0.22	0.01	0.00	3.08	2.46	100.08	6249	777	87	13154	27	2	0	1621	1446	1.001	0.017	7
8	36.58	9.19	0.14	47.07	4.72	0.00	0.00	0.03	3.09	99.36	6088	1278	20	11677	591	0	0	16	1818	1.010	0.392	8
9	36.30	10.55	0.21	45.60	5.47	0.00	0.00	0.09	2.69	99.60	6042	1468	29	11311	685	0	0	47	1581	1.008	0.457	9
10	35.90	11.21	0.50	44.16	5.59	0.01	0.00	0.00	2.64	98.77	5975	1560	71	10953	699	2	0	0	1553	1.012	0.474	10
11	35.77	12.18	0.14	45.90	2.79	0.00	0.00	2.66	1.52	99.12	5953	1696	20	11385	349	0	0	1400	892	0.996	0.233	11
12	35.56	12.94	0.14	44.90	2.82	0.01	0.00	1.98	2.06	98.61	5918	1801	20	11139	353	2	0	1042	1211	1.000	0.236	12

(1) Total less O for F and OH

(2) Stoic. = $2Si/(2\underline{n}/[2\underline{n} + 1])M_{Ti}$

Figure 14. Histogram of the frequency of total weight percent oxide for microprobe analyses of the humite minerals.

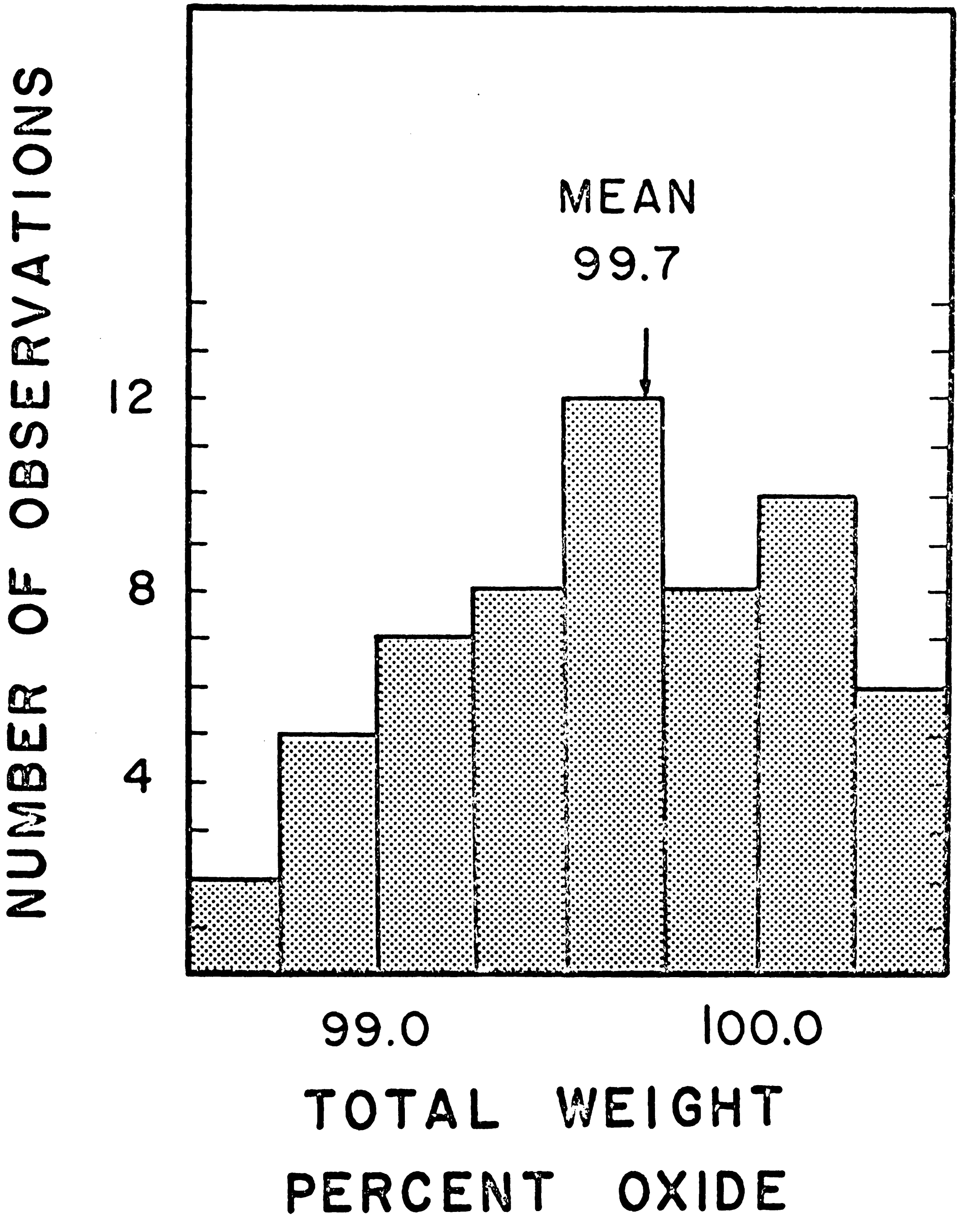
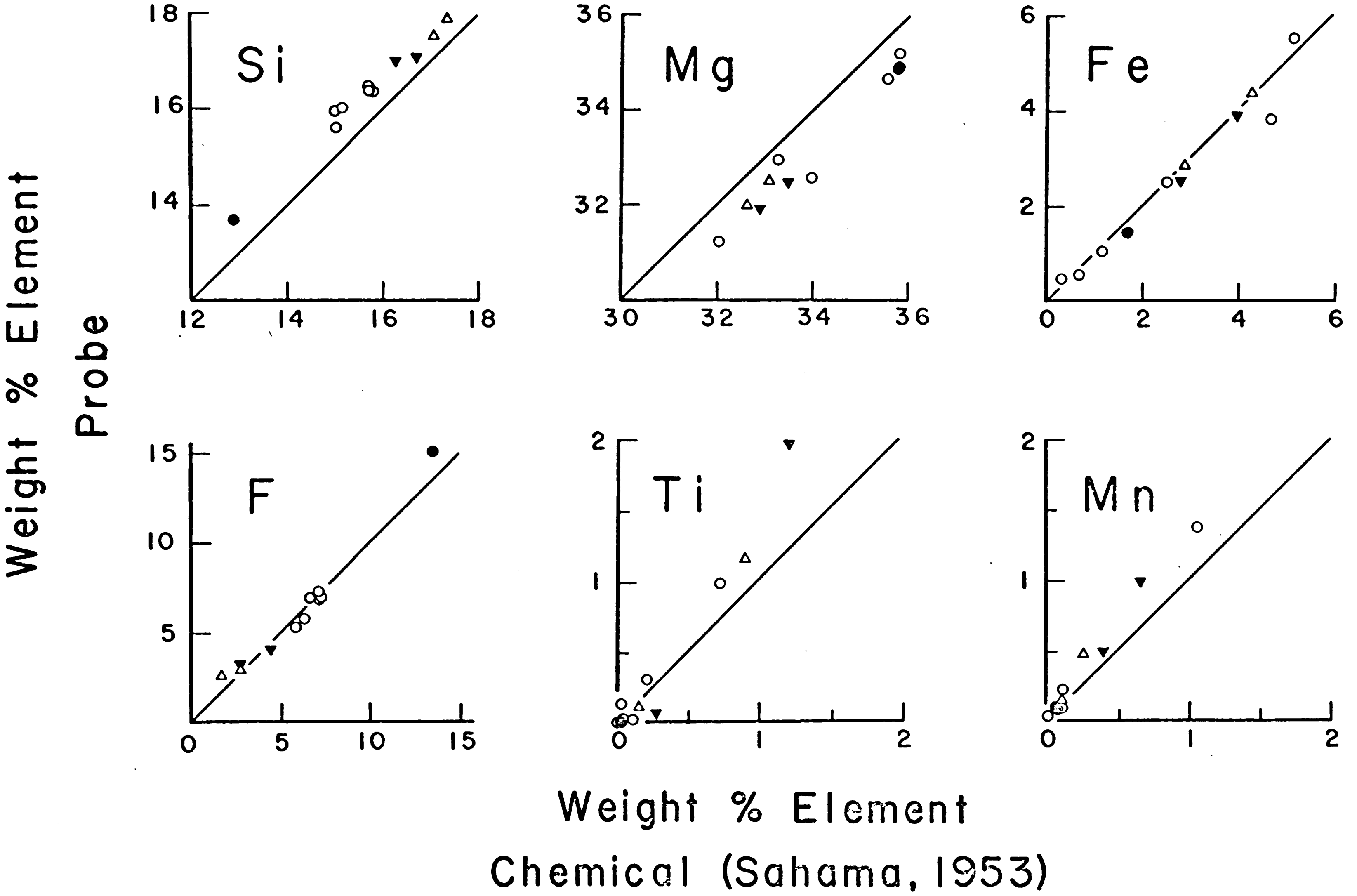

NUMBER OF OBSERVATIONS
4
8
12
MEAN
99.7
99.0
100.0
TOTAL WEIGHT
PERCENT OXIDE

Figure 15. Relation between microprobe (this paper) and bulk chemical (Sahama, 1953) analyses of Si, Mg, Fe, F, Ti, and Mn in norbergite (solid circles), chondrodite (open circles), humite (solid triangles), and clinohumite (open triangles).


Si
Mg
Fe
F
Ti
Mn
18
16
14
12
14
16
18
36
34
32
30
32
34
36
6
4
2
0
2
4
6
15
10
5
0
5
10
15
2
1
0
1
2
2
1
0
1
2
Weight % Element
Probe
Weight % Element
Chemical (Sahama, 1953)

in the chemical analyses when compared to the microprobe analyses. In addition, chemically determined OH is much lower than the values calculated for the microprobe analyses assuming charge balance.

Nearly all of the chemical analyses, including Sahama's, report the presence of Al (see Appendix A). A careful check with the microprobe, however, indicates that Al does not occur in the portions of the humite grains which are free from cracks and inclusions. It is concluded, therefore, that Al does not occur in the humite mineral structure (just as it does not occur in the olivines) and that its presence in the chemical analyses reflects Al-rich inclusions such as spinel (which was observed and which is commonly associated with the humite minerals).

The degree of stoichiometry of the humite minerals as indicated by the microprobe analyses is illustrated in Figure 13a which is a plot of atomic proportions Si versus atomic proportions $(2/[2\underline{n} + 1])M_{Ti}$ (which is equal to the sum $(OH + F + O_{Ti})$; see Appendix B). It can be seen that the microprobe analyses fall, within analytical error, along the lines which represent stoichiometric proportions whereas the chemical analyses (Figures 13b, c) show a much greater spread. Furthermore, $(OH + F + O_{Ti})$ does not equal $(2/[2\underline{n} + 1])M_{Ti}$ for the chemical analyses (with the exception of Van Valkenburg's synthetics). Thus the chemical analyses imply a slight cation excess in the $Mg(OH,F)_2$ part of the formula and a marked anion deficiency resulting in a charge imbalance (Figures 13b, c). This, coupled with the Ti vs. (OH + F) data presented in Figure 9 leads to the conclusion that the chemical analyses are inaccurate with respect to OH and/or F. The close agreement between microprobe and chemical analyses for F shown in Figure 15 implies that chemically determined OH, rather than F, is inaccurate.

The analyses of chondrodites 9 and 10 (Table VII) require special comment. Both are Si-deficient and F-rich, yet single crystal x-ray diffraction studies of 9 indicate that it is chondrodite. The normalized cell volume of 9, however, is somewhat smaller than the cell volumes of the other chondrodites studied (Table VIII). This implies the presence of another tetrahedrally-coordinated cation (such as Be) which has a smaller ionic radius than Si. Unfortunately, Be cannot be detected with the microprobe without elaborate instrumentation. A chemical analyses is clearly desirable.

RELATIONSHIP BETWEEN COMPOSITION AND CELL PARAMETERS

Single crystals of eight humite minerals were studied to determine the effect of chemical substitutions on the unit cell parameters, and to search for polytypism of the type described by Moore (1967) for structurally similar leucophoenicite. Unit cell dimensions (Table VIII) were determined from data obtained on a precision back-reflection Weissenberg x-ray camera and refined on an I.B.M. 7040 computer using the least-squares refinement program described by Burnham (1962).

All samples selected for study were chosen on the basis of composition. Two were chosen to show the effect on the cell parameters of substitution of (Fe + Mn) for Mg, two to show the effect of Ti + 2(O) for Mg + 2(OH,F), and three to show the effect of (OH,F) for O. In addition, the cell dimensions of a norbergite (also used in the crystal structure analysis described by Gibbs and Ribbe, 1968), a Si-deficient chondrodite, and a Ti-clinohumite were determined.

No polytypism was encountered in this study.

(Fe + Mn) for Mg

The cell parameters of two chondrodites (Nos. 2 and 24) were determined in order to elucidate the effect of the substitution of (Fe + Mn) for Mg. A graphical comparison between the two chondrodites and two forsterites with similar (Fe + Mn)/(Fe + Mn + Mg) ratios is shown in Figure 16. Both show similar increases in unit cell volume (normalized to one-half the mean anion-anion distance along c*) as expected.

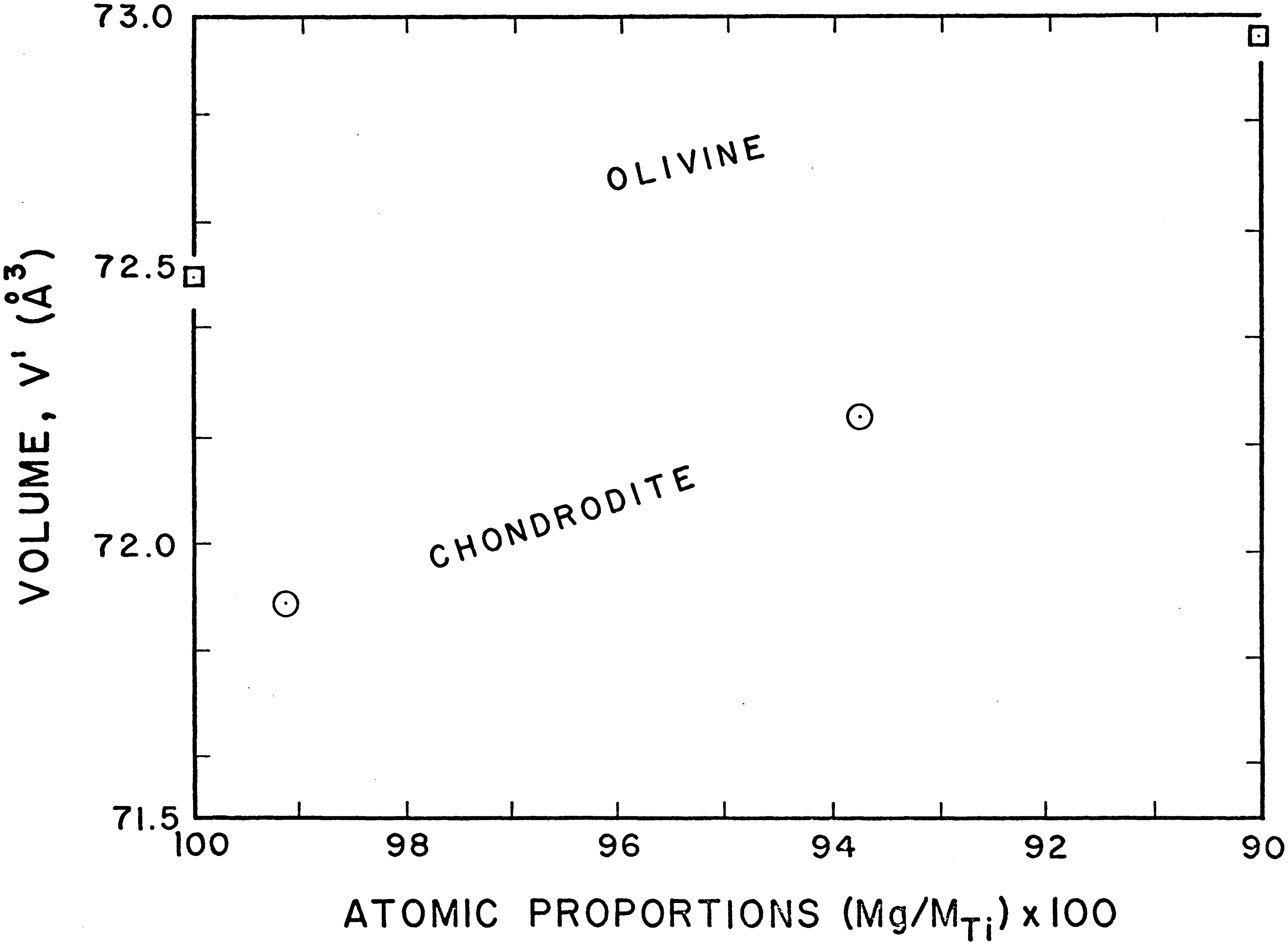
TABLE VIII. Unit cell parameters of selected humite minerals (Å) [1].

Mineral and New Number	a	b	c	α	d_{001}	V'	No. of Obs.
Natural Humites (this study):							
Norbergite 1	4.7104 (1)	10.2718 (3)	8.7476 (4)	90°	6x1.4579	70.540	68
Chondrodite 2	4.7284 (3)	10.2539 (3)	7.8404 (2)	109.059 (2)	5x1.4821	71.859	91
Chondrodite 24	4.7332 (2)	10.2552 (?)	7.8765 (?)	109.128 (?)	5x1.4883	72.242	62
Chondrodite 9	4.7190 (5)	10.2616 (5)	7.8154 (4)	109.147 (3)	5x1.4766	71.504	114
Humite 3	4.7386 (1)	10.2626 (3)	20.8418 (3)	90°	14x1.4887	72.396	112
Humite 7	4.74077 (8)	10.2580 (2)	20.8526 (4)	90°	14x1.4895	72.436	100
Clinohumite 7	4.7441 (2)	10.2501 (5)	13.6635 (3)	100.786 (2)	9x1.4913	72.517	181
Clinohumite 10	4.7451 (8)	10.288 (2)	13.691 (1)	100.657 (8)	9x1.495	72.98	150
Synthetic Humites (Van Valkenburg, 1961):							
Norbergite	4.709	10.271	8.727	90°	6x1.455	70.37	
Humite	4.735	10.243	20.72	90°	14x1.480	71.78	

---

[1] Standard errors in parentheses refer to the last decimal place.

Figure 16. The effect of substitution of (Fe + Mn) for Mg on the normalized cell volume, V', in chondrodite and forsterite with similar Fe-content. Values for Fo_{100} from Yoder and Smith (1957) and for Fo_{90} from Birle *et al*. (1968).


73.0
72.5
72.0
71.5
VOLUME, V' ($\mathring{A}^3$)
OLIVINE
CHONDRODITE
100
98
96
94
92
90
ATOMIC PROPORTIONS (Mg/M_{Ti}) x 100

Ti for Mg

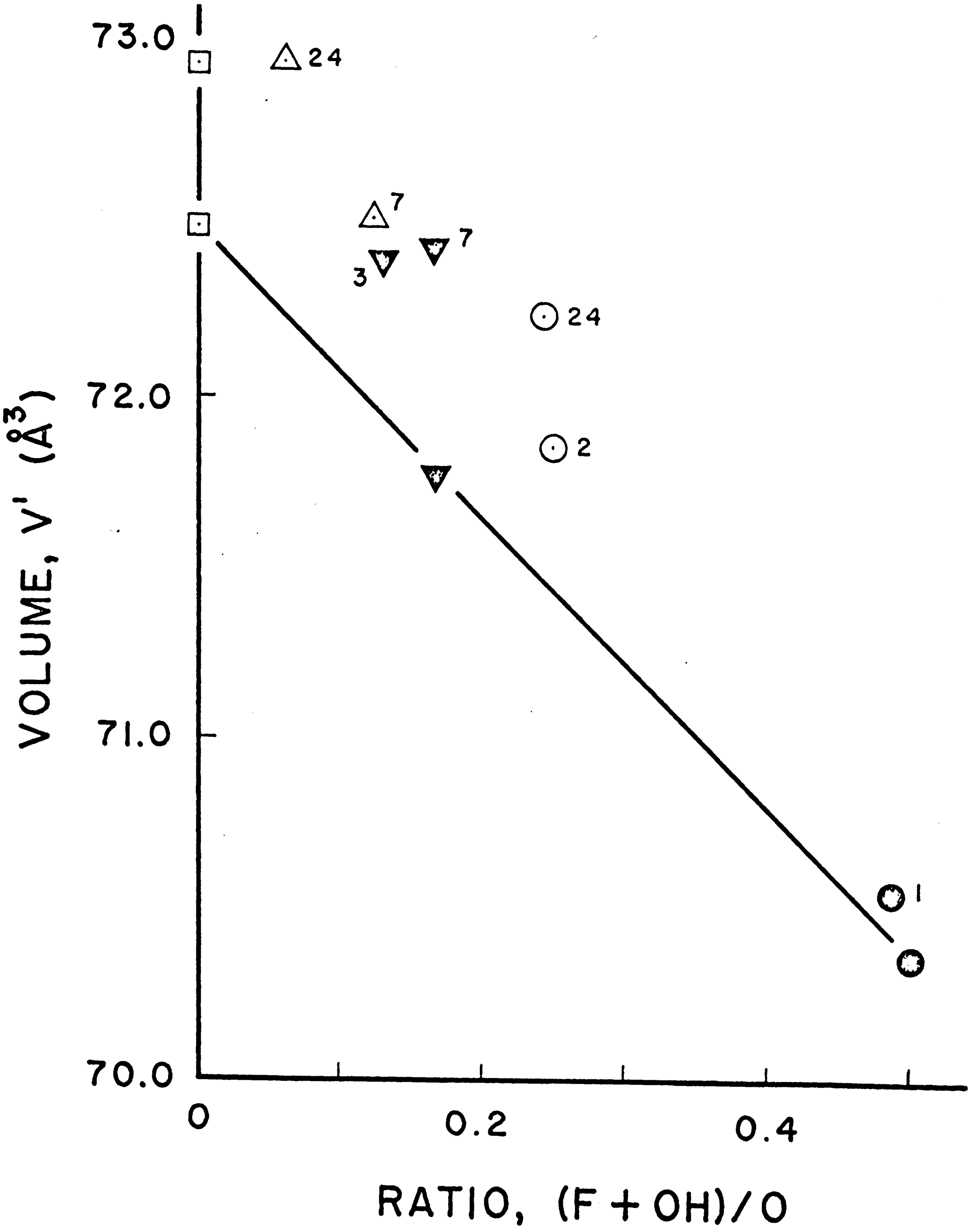
The substitution of Ti for Mg (ionic radii 0.68Å and 0.66Å, respectively, Ahrens, 1952) and concomittant substitution of 2(O) for 2(OH,F) apparently has little effect on the cell parameters as illustrated by two humites (Table VIII, Nos. 3 and 7). There does appear, however, to be a very slight decrease in unit cell volume with increase in Ti content. This may be related to the charge difference between Mg^{+2} and Ti^{+4}. The mean Ti-O distance in rutile is 1.957Å (Cromer and Harrington, 1955) whereas the mean Mg-4(O),2(F) distance in norbergite is 2.086Å (Gibbs and Ribbe, 1968). A shortening of the mean octahedral bond in the M(OH,F)O region of the structure may result in a smaller unit cell volume.

(OH,F) for O

The substitution of (OH,F) for O and concomittant vacancies for Si results in a decrease in normalized cell volume. Figure 17 shows that for synthetic forsterite, F-humite, and F-norbergite (data from Van Valkenburg, 1961) the change is linear. The natural humite minerals and natural forsterite (Fo_{90}) show the same trend; the scatter in the data points is primarily due to the presence of other octahedral cations (Fe,Ti) in addition to Mg.

Chondrodite 24, humite 7, and clinohumite 7 were selected to determine the effect of substitution of (OH,F) for O in natural humite minerals. The amount of substitution for Mg and the ratio F/(OH + F) is essentially the same in each of these samples. As shown in Figure 17, the change in V' with (OH + F)/O appears to be less than the

Figure 17. The relation between the normalized cell volume (a x b x (d_{001}/n)) and (OH + F)/O in norbergite (solid circles), chondrodite (open circles), humite (solid triangles), clinohumite (open triangles), and forsterite (squares). Numbers next to humite mineral data points correspond to those in Tables VI and VII. Solid line connects synthetic Mg_2SiO_4, $3Mg_2SiO_4 \cdot MgF_2$, and $Mg_2SiO_4 \cdot MgF_2$ described in Table II. Fo_{90} data from Birle et al. (1968).


73.0
72.0
71.0
70.0
VOLUME, V' ($\AA^3$)
0
0.2
0.4
RATIO, (F + OH)/O
24
7
7
3
24
2
1

corresponding change in the pure synthetic F-humite minerals. It is not clear whether this effect is real or whether the cell volume is actually affected by the replacement of OH for F. It is possible that the proton associated with the OH may require that the M-OH bond be longer than the M-F bond; presumably this would result in a larger cell volume.

SUMMARY AND CONCLUSIONS

Although a number of authors have described the humite minerals in terms of slabs of forsterite and sellaite and/or brucite composition, this concept is incorrect and misleading. No slabs with either forsterite or brucite-sellaite composition or with brucite or sellaite structures exist in the humite minerals. The humite structures are analogous to the olivine structure in that they consist of a hexagonal close-packed array of anions (O,OH,F). They differ in that none of the available tetrahedral sites coordinated by one or more (OH,F) anions is occupied by Si; this results in a stagger of the chains of edge-sharing octahedra. Substitution of other cations for Mg in both the humite minerals and forsterite results in cell volume changes of similar magnitude. In addition, the substitution of (OH,F) for O and concomittant vacancies for Si results in a regular decrease in normalized cell volume from forsterite to clinohumite to humite to chondrodite to norbergite.

Over the years, the crystallographic axes have been labeled in a number of ways; this has resulted in considerable confusion in the description of cleavage and twinning, and even in the choice of space groups. It is suggested that the axial choices of Taylor and West (1928, 1929) be used. Although their convention corresponds with neither the first nor second setting for the monoclinic members, it is consistent with the olivine notation and, therefore, permits direct comparisons between olivines and the humite minerals.

The chemical study of the humite minerals by Sahama (1953) and a survey of other chemical analyses imply that the humite minerals are non-stoichiometric with anion deficiencies and cation excesses. The microprobe analyses undertaken in this study do not support this implication. Evidence has been presented which indicates that most of the bulk chemical analyses suffer from inaccurate H_2O determination and, perhaps, impure starting material.

The rather restricted occurrence of the humite minerals implies that special physico-chemical conditions are required for their formation. The available evidence indicates that each member of the group is characterized by a rather narrow range of $F/(OH + F)$ and that samples from a given locality cluster around the same value of this ratio. Although this is undoubtedly related in part to the crystal structure of the individual members of the group, it must also be a function of the conditions of formation such as temperature, pressure, and the availability of F and H_2O. Most occurrences of Ti-clinohumite are in ultrabasic rocks. This has led McGetchin and Silver (1968) to suggest that Ti-clinohumite should be considered as a possible site for volatiles in the upper mantle. Further petrologic studies may show that the humite minerals are useful petrogenetic indicators in that they might be useful for determining the fugacity of F during the formation of the rock in which they occur.

APPENDIX A

TABLE IX. Chemical analyses of norbergite

	1	2	3	4	5
SiO_2	29.59	28.63	28.54	29.60	27.56
Al_2O_3		3.12	0.09	0.53	0.11
Fe_2O_3			0.69	0.60	0.28
FeO		0.73	0.82	0.96	1.91
MnO		0.04	0.18	tr.	0.12
MgO	59.58	59.42	56.45	58.70	59.35
TiO_2				n.d.	0.01
CaO			1.01	n.d.	0.00
H_2O^+		0.32	2.90	1.50	2.68
F	18.71	12.78	13.70	13.55	13.49
H_2O^-				0.00	0.00
Total	107.88	105.04	105.59 (1)	105.44	105.51
Less O for F	7.88	5.38	5.77	5.71	5.68
Total	100.00	99.66	99.82	99.73	99.83
$Si/(OH+F+O_{Ti})$	0.500	0.690	0.538	0.619	0.534
$Si/(2/[2n+1])M_{Ti}$	0.500	0.462	0.494	0.497	0.457
$2Si/(2n/[2n+1])M_{Ti}$	1.000	0.924	0.988	0.994	0.913
α	1.548	1.565	1.563	1.563	1.567
β	1.552	1.570	1.567	1.567	1.579
γ	1.570	1.591	1.590	1.590	1.593
2V	33°	49°	49°30'	44°	50°
Sp. Gr.		3.20	(3.13-3.15)	3.181	3.153
Reference	Van Valkenburg (1961) (synthetic)	Larsen, *et al.* (1928), No. 1 Franklin, New Jersey	Larsen, *et al.* (1928), No. 3 Norberg, Sweden (Sp. gr. from Geijer (1926)	Rankama (1938) No. 1, Piukkla, Finland	Sahama (1953) No. 1, Norberg, Sweden

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(1) includes 1.21 CO_2

TABLE X. Chemical analyses of chondrodite.

	1	2	3	4	5
SiO_2	34.96	33.89	33.60	30.79	33.56
Al_2O_3		0.38	0.24	0.69	0.12
Fe_2O_3		0.46	0.05		0.27
FeO		0.43	0.86	1.08	1.26
MnO		0.03	0.16		0.10
MgO	58.65	59.33	59.30	57.04	58.95
TiO_2		0.00	0.06	0.10	0.04
CaO		0.08	0.00	tr.	0.00
H_2O^+		1.38	1.46	3.57	1.23
F	11.05	6.31	6.61	4.82	7.14
H_2O^-		0.00	0.00		0.00
Total	104.65	102.29	102.34	98.09	102.67
Less O for F	4.65	2.66	2.78	2.03	3.00
Total	100.00	99.63	99.56	96.06	99.67
$Si/(OH+F+O_{Ti})$	1.000	1.379	1.298	1.127	1.256
$Si/(2/[2n+1])M_{Ti}$	1.000	0.944	0.937	0.887	0.939
$2Si/(2n/[2n+1])M_{Ti}$	1.000	0.944	0.937	0.887	0.939
α	1.582	1.604	1.600	1.602	1.602
β	1.594	1.613	1.609	1.616	1.611
γ	1.612	1.633	1.628	1.640	1.630
2V	50°	72°	72°	75-79°	72°
Extinction		22°	26°	34-36°	26°
Sp. Gr.		3.161	3.177		3.191
Reference	Van Valkenburg (1961) (synthetic)	Sahama (1953) No. 2 Kafveltorp, Sweden	Sahama (1953) No. 1 Hangelby, Sibbo, Finland	Nozawa (1954) Kamioka, Hida, Japan	Sahama (1953) No. 3 Sparta, New Jersey

TABLE X. Chemical analyses of chondrodite. (Continued)

	6	7	8	9	10
SiO_2	33.80	34.03	36.90	32.41	33.87
Al_2O_3	1.83	0.43	4.22	0.98	
Fe_2O_3		0.12	0.11	0.08	
FeO	2.64	2.81	2.87	3.17	3.66
MnO		0.03	0.29	0.10	
MgO	55.70	53.69	54.11	56.34	56.46
TiO_2		0.12	0.62	1.20	
CaO		0.65		0.00	
H_2O^+	1.46	1.41	0.48	1.04	2.82
F	7.30	7.93	0.20	7.26	5.15
H_2O^-			0.34	0.00	
Total	102.73	101.36 (1)	100.25 (2)	102.58	101.96
Less O for F	3.07	3.34	0.08	3.06	2.16
Total	99.66	98.02	100.17	99.52	99.80
$Si/[OH+F+O_{Ti})$	1.209	1.136	11.699	1.148	1.318
$Si/(2/[2n+1])M_{Ti}$	0.967	1.016	1.039	0.922	0.971
$2Si/(2n/[2n+1])M_{Ti}$	0.967	1.016	1.039	0.922	0.971
α	1.605	1.593	1.643	1.612	1.609
β	1.616	1.603		1.619	1.619
γ	1.636	1.623	1.666	1.641	1.641
2V	73°	71°		73°	
Extinction				26°	
Sp. Gr.	3.168-3.235	3.179		3.224	3.194-3.215
Reference	Penfield and Howe (1894) and Larsen (1928) Warwick, New York	Rankama (1938) No. 4 Ersby, Finland	Serdyuchenko and Glekov (1960) Aldan, S.E., U.S.S.R.	Sahama (1953) No. 4 Eden, New York	Penfield and Howe (1894) and Larsen (1928) Monte Somma, Italy

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(1) includes 0.08 Na_2O and 0.06 K_2O

(2) includes 0.09 B_2O_3 and 0.02 P_2O_5

TABLE X. Chemical analyses of chondrodite. (Continued)

	11	12	13	14	15
SiO_2	33.71	32.07	33.86	33.67	32.57
Al_2O_3	1.23	1.13	0.89	0.81	0.10
Fe_2O_3		0.35	0.56	0.54	0.50
FeO	3.67	3.50	3.46	3.85	3.88
MnO		0.08	0.57	0.23	0.16
MgO	55.02	53.26	54.59	53.97	56.77
TiO_2		0.23	0.45	1.27	0.00
CaO		0.24	0.37	0.28	0.00
H_2O^+	2.90	2.74	2.94	2.04	1.97
F	4.50	6.28	4.01	5.74	7.00
H_2O^-		0.28	0.21		0.00
Total	101.43	100.26	101.74	102.40	102.95
Less O for F	1.42	2.68	1.69	2.42	2.95
Total	100.01	97.58	100.26	99.98	100.00
$Si/(OH+F+O_{Ti})$	1.410	1.093	1.462	1.253	1.134
$Si/(2/[2n+1])M_{Ti}$	0.974	0.950	0.974	0.973	0.920
$2Si/(2n/[2n+1])M_{Ti}$	0.974	0.950	0.974	0.973	0.920
α	1.607	1.601	1.610	1.609	1.608
β	1.620			1.619	1.619
γ	1.643	1.637	1.640	1.641	1.640
2V	72°14'	85–90°		68°	77°
Extinction	26°25'	27.2			27°
Sp. Gr.		3.227	3.185	3.194	3.217
Reference	Von Eckermann (1922) and Larsen (1928) Mansjö Mtn., Sweden	Barth (1924) and Larsen (1928) Christiansand, Norway	Thiele (1940) No. 3a-1 Pyrenees	Thiele (1940) No. 3a-2 Monte Somma, Italy	Sahama (1953) No. 5B Hermala, Lohja, Finland

TABLE X. Chemical analyses of chondrodite. (Continued)

	16	17	18	19	20
SiO_2	34.27	33.30	32.20	33.60	33.28
Al_2O_3	0.22	1.42	0.49	0.18	0.49
Fe_2O_3	0.36	0.69	0.80	1.86	0.63
FeO	4.36	4.24	5.04	4.16	5.34
MnO	0.003	0.08	0.13	0.66	0.61
MgO	55.01	52.65	53.85	53.70	52.96
TiO_2	0.36	n.d.	0.69	n.d.	0.15
CaO	0.04	n.d.	0.00	n.d.	0.83
H_2O^+	0.94	1.00	1.56	1.86	2.71
F	6.99	8.03	8.51	5.99	5.01
H_2O^-			0.00		0.19
Total	102.75 (3)	102.69 (4)	103.27	102.01	101.93
Less O for F	2.94	3.38	3.58	2.52	2.11
Total	99.81	99.31	99.69	99.49	99.82
$Si/(OH+F+O_{Ti})$	1.329	1.159	0.971	1.337	1.326
$Si/(2/[2n+1])M_{Ti}$	0.990	0.988	0.932	0.980	0.968
$2Si/(2n/[2n+1])M_{Ti}$	0.990	0.988	0.932	0.980	0.968
α	1.602	1.599	1.607	1.613	1.618
β	1.612	1.610	1.617	1.623	1.628
γ	1.633	1.630	1.639	1.643	1.651
2V	71°	74°	80°	70°	
Extinction			28°		
Sp. Gr.	3.221	3.201	3.260	3.201	3.224
Reference	Rankama (1938) No. 7 Ersby, Finland	Rankama (1938) No. 5 Parainen, Finland	Sahama (1953) No. 6 Franklin, New Jersey	Rankama (1938) No. 9 Hermala, Finland	Thiele (1940) No. 3a-3 Tilley Foster Mine, Brewster, New York

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(3) includes 0.13 Na_2O and 0.07 K_2O
(4) includes 0.98 Na_2O

TABLE X. Chemical analyses of chondrodite. (Continued)

	21	22	23	24	25
SiO_2	33.75	33.67	32.13	32.16	33.33
Al_2O_3			0.67	0.73	
Fe_2O_3			0.64	0.60	
FeO	5.91	5.94	5.47	6.08	6.62
MnO			0.16	1.35	
MgO	54.88	54.79	55.20	53.21	54.30
TiO_2			0.35	0.20	
CaO			0.00	0.00	
H_2O^+	2.30	2.55	1.96	1.20	1.67
F	5.21	5.30	5.81	7.11	6.60
H_2O^-			0.00	0.00	
Total	102.36	102.25	102.39	102.64	102.52
Less O for F	2.21	2.23	2.45	2.99	2.76
Total	100.15	100.02	99.94	99.65	99.76
$Si/(OH+F+O_{Ti})$	1.398	1.333	1.262	1.200	1.260
$Si/(2/[2n+1])M_{Ti}$	0.973	0.972	0.907	0.924	0.964
$2Si/(2n/[2n+1])M_{Ti}$	0.973	0.972	0.907	0.924	0.964
α	1.619		1.615	1.609	1.608
β	1.626		1.627	1.622	1.620
γ	1.648		1.646	1.643	1.642
2V	74°		75°	79°	74°
Extinction			24°	31°	
Sp. Gr.	3.229	3.204-3.231	3.228	3.241	3.252-3.265
Reference	Thiele (1940) No. 3c-14 Brewster, New York	Penfield and Howe (1894) and Larsen (1928) Brewster, New York	Sahama (1953) No. 7 Tilley Foster Mine, Brewster, New York	Sahama (1953) No. 8 Kafveltorp, Sweden	Penfield and Howe (1894) and Larsen (1928) Kafveltorp, Sweden

TABLE X. Chemical analyses of chondrodite. (Continued)

	26	27	28
SiO_2	34.50	33.20	33.89
Al_2O_3	0.16	0.19	0.30
Fe_2O_3	0.63	0.30	0.14
FeO	6.59	8.70	8.99
MnO	1.50	0.42	0.21
MgO	51.39	50.47	50.75
TiO_2		0.41	
CaO	0.26	0.06	tr.
H_2O^+	1.18	1.15	1.99
F	4.76	6.55	6.03
H_2O^-			0.25
Total	102.03 (5)	101.61 (6)	102.66
Less O for F	2.00	2.76	2.54
Total	100.03	98.85	100.12
$Si/(OH+F+O_{Ti})$	1.817	1.319	1.318
$Si/(2/[2n+1])M_{Ti}$	1.023	0.992	1.011
$2Si/(2n/[2n+1])M_{Ti}$	1.023	0.992	1.011
α		1.613	1.620
β		1.625	
γ		1.646	1.649
2V		78°	
Extinction			
Sp. Gr.	3.24	3.264	3.256
Reference	Sjögren (1882) and Larsen (1928) Kafveltorp, Sweden	Rankama (1938) No. 14 Ristiniemi, Finland	Thiele (1940) No. 3a-4 Kafveltorp, Sweden

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(5) includes 0.16 K_2O and 0.90 Na_2O
(6) includes 0.10 Na_2O and 0.06 K_2O

TABLE XI. Chemical analyses of humite.

	1	2	3	4	5	6
SiO_2	37.20	36.74	36.63	35.55	35.79	33.80
Al_2O_3				0.25	0.79	2.94
Fe_2O_3				1.12	0.33	0.63
FeO		2.22	2.35	2.10	3.31	4.29
MnO				0.71	0.84	0.29
MgO	58.27	56.31	56.45	56.06	54.51	53.50
TiO_2				0.18	2.00	n.d.
CaO				0.00	0.00	n.d.
H_2O^+		2.13	2.45	1.41	0.91	1.49
F	7.84	3.96	3.08 (1)	4.42	2.77	4.21
H_2O^-				0.07	0.00	
Total	103.31	101.36	100.96	101.87	101.25	101.15
Less O for F	3.30	1.66	1.26	1.86	1.17	1.77
Total	100.01	99.70	99.70	100.01	100.08	99.38
$Si/(OH+F+O_{Ti})$	1.500	1.872	2.045	1.874	2.42	1.849
$Si/(2/[2n+1])M_{Ti}$	1.500	1.499	1.489	1.426	1.191	1.352
$2Si/(2n/[2n+1])M_{Ti}$	1.000	0.999	0.992	0.951	0.955	0.901
α	1.598	1.625	1.621	1.621	1.641	1.607
β	1.606	1.635	1.627	1.629	1.649	1.619
γ	1.630	1.656	1.649	1.652	1.672	1.639
2V	59°	70°		65°	75°	77°
Sp. Gr.		3.183-3.225	3.194-3.201	3.214	3.243	3.202
Reference	Van Valkenburg (1961) (synthetic)	Penfield and Howe (1894) and Larsen (1928) Monte Somma, Italy	Penfield and Howe (1894) and Larsen (1928) Monte Somma, Italy	Sahama (1953) No. 1 Monte Somma, Italy	Sahama (1953) No. 2 Hermala, Lohja, Finland	Rankama (1938) No. 11 Hermala, Lohja, Finland

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(1) the value of 3.68 reported by Larsen is apparently a typographical error.

TABLE XI. Chemical analyses of humite. (Continued)

	7	8	9	10	11	12
SiO_2	34.73	34.32	34.81	35.21	34.56	35.44
Al_2O_3	0.00	0.59	0.17	0.07	1.46	0.19
Fe_2O_3	0.40	0.48	1.01	1.06	2.66	0.68
FeO	4.75	5.40	7.93	7.93	7.77	10.96
MnO	0.52	0.01	1.69	1.69	0.66	1.47
MgO	55.51	53.17	48.98	48.33	48.93	47.22
TiO_2	0.46	0.25	0.13	0.07		0.07
CaO	tr.	tr.	0.46	0.11		0.17
H_2O^+	1.25	1.07	1.31	1.85	1.70	1.28
F	4.37	5.43	5.03	4.59	3.68	3.79
H_2O^-	0.00					
Total	101.99	100.72	102.16 (2)	101.45	101.42	101.73
Less O for F	1.84	2.29	2.13	1.93	1.55	1.60
Total	100.15	98.43	100.03	99.52	99.87	100.13
$Si/(OH+F+O_{Ti})$	1.858	1.625	1.698	1.694	1.996	2.168
$Si/(2/[2n+1])M_{Ti}$	1.384	1.413	1.474	1.519	1.445	1.517
$2Si/(2n/[2n+1])M_{Ti}$	0.923	0.942	0.983	1.013	0.963	1.012
α	1.624	1.607	1.628		1.643	1.632
β	1.633	1.623	1.638		1.655	1.643
γ	1.653	1.643	1.655		1.675	
2V	66°	81°	76°		68°	
Sp. Gr.	3.245	3.236	3.275	3.24	3.273	3.32
Reference	Sahama (1953) No. 3 Sillböle, Finland	Rankama (1938) No. 16 Pitkäjärvi, Pernio, Finland	Thiele (1940) No. 3d-6 Nordmark, Sweden	Sjögren (1894) and Larsen (1928) Nordmark, Sweden	Rankama (1938) No. 12 Hermala, Lohja, Finland	Sjögren (1894) and Larsen (1928) Nordmark, Sweden

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(2) includes 0.35 Na_2O and 0.29 K_2O

TABLE XII. Chemical analyses of clinohumite.

	1	2	3	4	5
SiO_2	38.45	37.97	37.65	37.53	37.42
Al_2O_3					
Fe_2O_3					0.46
FeO		1.12	1.29	1.57	1.27
MnO			0.44	1.39	0.10
MgO	58.04	56.60	55.00	53.76	56.32
TiO_2		0.68	1.00	2.96	1.14
CaO		0.30	0.85	0.76	
H_2O^+		2.20	2.25	1.82	0.56
F	6.07	0.93	0.90	0.86	5.04
H_2O^-					
Total	102.56	100.00 (1)	100.04 (2)	100.71	102.31
Less O for F	2.56	0.43	0.38	0.36	2.12
Total	100.00	99.57	99.66	100.35	100.19
$Si/(OH+F+O_{Ti})$	2.000	3.356	3.176	2.835	1.917
$Si/(2/[2n+1])M_{Ti}$	2.000	1.984	1.991	1.971	1.951
$2Si/(2n/[2n+1])M_{Ti}$	1.000	0.992	0.996	0.986	0.975
α	1.608				1.628
β	1.618				1.642
γ	1.636				
2V	76°				
Extinction					
Sp. Gr.		3.157	3.162	3.216	3.17
Reference	Van Valkenburg (1961) (synthetic)	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals	Walker and Parsons (1927) and Larsen (1928) Chaffey's Lake, Ontario

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(1) includes 0.20 CO_2.

(2) includes 0.66 CO_2.

TABLE XII. Chemical analyses of clinohumite. (Continued)

	6	7	8	9	10
SiO_2	37.70	37.18	37.65	37.12	37.50
Al_2O_3				0.77	
Fe_2O_3		0.49		0.32	
FeO	2.51	2.24	3.41	3.44	3.84
MnO	0.03	0.04	0.50	0.15	0.23
MgO	54.10	55.09	51.74	54.85	52.55
TiO_2	2.52	2.92	5.40	1.48	3.96
CaO	0.13		0.10	0.00	
H_2O^+	2.56	1.30	1.57	0.88	1.76
F	0.08	0.95	0.06	1.70	0.68
H_2O^-				0.00	
Total	99.85 (3)	100.46	100.63 (4)	100.71	100.72 (4)
Less O for F	0.07	0.40	0.08	0.72	0.33
Total	99.78	100.06	100.55	99.99	100.39
$Si/(OH+F+O_{Ti})$	2.998	3.170	2.779	3.520	2.685
$Si/(2/[2n+1])M_{Ti}$	2.001	2.001	2.004	1.920	1.985
$2Si/(2n/[2n+1])M_{Ti}$	1.000	1.000	1.002	0.960	0.993
α		1.638		1.633	
β		1.650		1.643	
γ		1.670		1.674	
2V		76°		73°	
Extinction		9°		9°	
Sp. Gr.	3.181	3.23		3.215	3.231
Reference	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals	Muthuswami (1958) Bhandara district, India	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals	Sahama (1953) No. 2 Ojamo, Lohja, Finland	Borneman-Starynkevitch and Myasnikov (1950) Southern Urals

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(3) includes 0.16 Cl.
(4) includes 0.20 Cl.

TABLE XII. Chemical analyses of clinohumite. (Continued)

	11	12a	12b	13	14	15
SiO_2	37.18	37.15	38.03	36.83	36.53	37.78
Al_2O_3	0.26			0.07	0.22	
Fe_2O_3				0.42	0.56	
FeO	4.31	4.72	4.83	4.90	5.04	5.64
MnO	0.23			0.28	0.34	
MgO	53.30	52.74	54.00	51.53	54.16	53.05
TiO_2				1.92	0.26	
CaO	0.84				0.00	
H_2O^+	1.26	1.94	1.94	3.04	1.52	1.33
F	1.86	2.01	2.06	0.03	2.74	3.58
H_2O^-	0.21			0.12	0.04	
Total	100.61 (5)	98.56	100.86	100.80 (6)	101.41	101.38
Less O for F	0.82	0.84	0.86	0.01	1.15	1.50
Total	99.79	97.72	100.00	100.79	100.26	99.88
$Si/(OH+F+O_{Ti})$	3.688	2.897	2.390	2.809	2.585	2.398
$Si/(2/[2n+1])M_{Ti}$	1.981	2.025	2.025	2.005	1.909	2.030
$2Si/(2n/[2n+1])M_{Ti}$	0.990	1.013	1.013	1.002	0.955	1.015
α	1.628		1.625	1.664	1.629	1.632
β			1.638	1.673	1.641	1.644
γ	1.650		1.653	1.698	1.662	1.664
2V			<u>ca</u>.90°	62°	73°	74°
Sp. Gr.				70°29'	11°	
Extinction			3.184-3.222		3.260	3.219-3.258
Reference	Serdyuchenko and Glebov (1961) Aldan, S.E. USSR	Penfield and Howe (1894) 1a Monte Somma, Italy	Penfield and Howe (1894) 1b and Larsen (1928) Monte Somma, Italy	Zanbonini (1919) and Larsen (1928) and Kunitz (1936) Piedmont, Italy	Sahama (1953) No. 1 Hämeenkylä, Finland	Penfield and Howe (1894) and Larsen (1928) Monte Somma, Italy

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(5) includes 0.81 B_2O_3, 0.10 K_2O, 0.02 P_2O_5 and 0.23 Cl.

(6) includes 0.14 PbO, 0.03 Cr_2O_3, 0.07 NiO, 0.12 K_2O and either 1.30 BaO (according to Larsen (1928))

TABLE XII. Chemical analyses of clinohumite. (Continued)

	16	17	18	19	20
SiO_2	36.30	36.87	37.08	36.14	36.24
Al_2O_3					0.37
Fe_2O_3					4.69
FeO	6.00	6.21	6.63	6.89	6.20
MnO	0.60	0.60	1.65	0.19	0.30
MgO	49.65	50.14	51.44	48.31	46.05
TiO_2	5.30	3.51	0.04	6.10	5.20
CaO					
H_2O^+	1.75	1.71	1.21	2.23	1.23
F			3.15		
H_2O^-					
Total	99.60	99.04	101.20	99.86	100.28
Less O for F			1.34		
Total	99.60	99.04	99.86	99.86	100.28
$Si/(OH+F+O_{Ti})$	2.628	3.362	2.639	2.174	3.038
$Si/(2/[2n+1])M_{Ti}$	1.957	1.997	1.995	1.971	1.990
$2Si/(2n/[2n+1])M_{Ti}$	0.978	0.999	0.997	0.985	0.995
α		1.669	1.6317		1.691
β		1.678	1.6430		1.700
γ		1.702	1.6641		1.724
2V		62°	74°12'		58°
Extinction					
Sp. Gr.		3.27	3.28		
Reference	Damour (1879) and Machatschki (1940) Pfunders	Damour (1879) and LaCroix (1890) and Kunitz (1936) and Machatschki (1940) Pfunders	Wickman (1948) Kafveltorp, Sweden	Damour (1879) and Machatschki (1940) Findelengletscher, Switzerland	de Quervain (1941) Alpe Canciano

<u>TABLE XII</u>. Chemical analyses of clinohumite. (Continued)

	21	22	23	24	25
SiO_2	36.86	35.86	37.00		
Al_2O_3			0.26		
Fe_2O_3	1.08	0.22	8.7	1.23	1.20
FeO	10.05	14.25		10.20	11.25
MnO	tr.	1.19	1.8		
MgO	45.50	44.66	major		
TiO_2	4.78	0.06	2.8	5.11	2.45
CaO		tr.	0.32		
H_2O^+	1.57	1.58	1.40	1.14	1.05
F		4.16	2.0	0.06	1.02
H_2O^-					
Total	99.84	102.42 (7)			
Less O for F		1.75			
Total	99.84	100.67			
$Si/(OH+F+O_{Ti})$	2.965	1.935	2.432		
$Si/(2/[2n+1])M_{Ti}$	2.057	2.025			
$2Si/(2n/[2n+1])M_{Ti}$	1.029	1.012			
α	>1.662	1.652		1.707	1.702
β	>1.680	1.663		1.714	1.709
γ				1.734	1.728
2V	58°	76°27'		56°	52-57°
Extinction		12-15°			
Sp. Gr.	3.23	3.35		3.364	
Reference	Brugnattelli (1904) and Kunitz (1936) and Machatschki (1940) Val Malenco, Italy	Sjögren (1894) and Larsen (1928) Nordmark, Sweden	Salotti (1965) Cotopaxi, Colo.	Sun (1954) Buell Park, Ariz.	Huang (1957) Wichita Mtns., Oklahoma

APPENDIX B

Calculations of OH, O, and Stoichiometric Ratios

Calculation of OH and O

Oxygen and OH could not be analytically determined with the microprobe, so it was necessary to calculate these values. The calculations are based on the assumption that Ti is ordered in the Mg(OH,F)O region of the structure, whereas Mg, Fe, Mn, Ca, and Zn are disordered in the structure.

If M_{Ti} represents the sum of the atomic proportions of all of the octahedral cations (including Ti), then from the general formula $\underline{n}[M_2SiO_4]\cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$ it can be deduced that $(2\underline{n}/[2\underline{n}+1])M_{Ti}$ represents the atomic proportions of octahedral cations in the M_2SiO_4 part of the formula. Similarly, $(1-(2\underline{n}/[2\underline{n}+1]))M_{Ti} = (1/[2\underline{n}+1])M_{Ti}$ represents the atomic proportions of octahedral cations in the $M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$ part of the formula. Each divalent M-cation in the M_2SiO_4 part of the formula is balanced by one O, each Si by two O, and each Ti by two O. Thus, the atomic proportions of O are given by:

$$O = (2\underline{n}/[2\underline{n}+1])M_{Ti} + 2Si + 2Ti.$$

Each M-cation in the $M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$ part of the formula is balanced by 2(OH,F) anions. If no Ti were present the atomic proportions of (OH + F) would be given by $2(1/[2\underline{n}+1])M_{Ti}$. When Ti is present, however, 2(OH,F) are replaced by 2(O) for each Ti. Thus, $OH + F = 2(1/[2\underline{n}+1])M_{Ti} - 2Ti$, or

$$OH = (2/[2\underline{n}+1])M_{Ti} - 2Ti - F.$$

The relationship for each of the humite minerals are given in the following table:

	n	$O =$	$OH =$
Norbergite	1	$2/3M_{Ti} + 2Si + 2Ti$	$2/3M_{Ti} - 2Ti - F$
Chondrodite	2	$4/5M_{Ti} + 2Si + 2Ti$	$2/5M_{Ti} - 2Ti - F$
Humite	3	$6/7M_{Ti} + 2Si + 2Ti$	$2/7M_{Ti} - 2Ti - F$
Clinohumite	4	$8/9M_{Ti} + 2Si + 2Ti$	$2/9M_{Ti} - 2Ti - F$

Stoichiometric Calculations

If Ti is ordered in the structure and the substitution is of the form Ti + 2(O) = M + 2(OH,F), then there must be two oxygen anions for each Ti (*i.e.*, $O_{Ti} = 2Ti$). If O_{Ti} is substituted for 2Ti in the expression given for OH and the equation is solved for $(2/[2\underline{n} + 1])M_{Ti}$, the following relation is obtained:

$$(2/[2\underline{n} + 1])M_{Ti} = O_{Ti} + OH + F.$$

For each of the humite minerals this becomes:

Norbergite	$2/3M_{Ti} = O_{Ti} + OH + F$
Chondrodite	$2/5M_{Ti} = O_{Ti} + OH + F$
Humite	$2/7M_{Ti} = O_{Ti} + OH + F$
Clinohumite	$2/9M_{Ti} = O_{Ti} + OH + F$

It is obvious that $Si/(O_{Ti} + OH + F) = Si/(2/[2\underline{n} + 1])M_{Ti}$. If stoichiometry is obtained, the Si/anion = Si/cation ratios should have the values tabulated below for each of the humite minerals.

Norbergite	1/2
Chondrodite	1/1
Humite	3/2
Clinohumite	2/1

APPENDIX C

Microprobe Techniques

Operating Conditions

Humite mineral grains with maximum dimensions of 0.5 to 1.5 mm were hand picked from crushed samples and mounted in epoxy cement in holes in brass disks. They were polished on a 320 micron silicon carbide lap long enough to expose the grains, then polished overnight in a 0.3 micron alumina slurry on a Syntron vibrating polisher. The samples and the olivine standard were sputtered simultaneously with a thin layer of carbon to make them conducting.

An Applied Research Laboratories Electron Microprobe X-ray Analyzer (model EMX) in the Molecular Structures Laboratory of the Virginia Polytechnic Institute was used for this investigation. The analyzing crystals available with this instrument are LiF, ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KAP), and lead stearate decanoate (LSD). These crystals allow analytical determination of elements boron through uranium. Fe, Mn, Zn, and Ni were run on a LiF spectrometer using an "Exatron" sealed argon proportional counter with a Be window; Si, Ca, Pb, Al, and P were run on an ADP spectrometer and Ti on a LiF spectrometer using the same counter; F and Mg were run on a KAP spectrometer using a flow proportional counter with an ultra-thin nitrocellulose window and P10 gas, and Al was re-run on the same spectrometer.

Beam current was monitored during all of the analyses and maintained at a constant value. Reference standards were run at least once every hour to allow for correction for drift. If drift exceeded approximately three percent on elements present in amounts greater than one percent, the analyses were re-run. Analyzing conditions are summarized in Table XIII.

In addition to fixed time analyses for elements thought to be present on the basis of previous chemical analyses, selected specimens were scanned using LiF, ADP, and KAP spectrometers. Elements Na through U present in amounts greater than about 0.05 weight percent could be detected in these scans.

Data Corrections

The data obtained directly from the microprobe must be corrected for effects related to the microprobe and to the sample investigated. In order to obtain a weight percentage value for the element of interest, it is necessary to compare the sample data with data obtained under the same conditions from a reference standard with a known composition. The best standard is one with a composition as close as possible to that of the material being analyzed. This is particularly important in the case of the major elements because the correction factors used are approximations and any errors will have a larger effect on major elements than on minor ones. The compositions of the reference standards used in this study are given in Table XIV.

Corrections for drift, dead time, background, mass absorption, and atomic number were made in this study. Corrections for secondary fluorescence must be made with certain chemical systems, but were found to be unnecessary here. A discussion of the general correction

TABLE XIII. Summary of microprobe analyzing conditions.

Elements	X-ray Emission Line	Operating Voltage (kV)	Beam Current (μ amps)	Approx. Beam Spot Size (μ)	Counting Interval (seconds)	Ave. No. Pts. Anal./Spec.	Reference Standard
Si	$K\alpha_{1,2}$	15	0.25	1-2	20	10	Marjalahti olivine
Mg	$K\alpha_{1,2}$	15	0.25	1-2	20	10	Marjalahti olivine
Fe	$K\alpha_{1,2}$	15	0.25	1-2	20	10	Marjalahti olivine
Mn	$K\alpha_{1,2}$	15	0.8	1-2	40	7	Mn metal
Ti	$K\alpha_{1,2}$	15	0.8	1-2	40	7	Ti metal
F	$K\alpha_{1,2}$	5	1.0,1.5	2-4	40	5	Fluorite
Al (ADP)	$K\alpha_{1,2}$	5	1.5	2-4	40	5	Synthetic cordierite
Al (KAP)	$K\alpha_{1,2}$	15	0.8	1-2	40	7	Anorthite
Ca	$K\alpha_{1,2}$	15	1.0	1-2	40	5	Synthetic diopside
Zn	$K\alpha_{1,2}$	20	1.0	1-2	40	5	Sphalerite
Ni	$K\alpha_{1,2}$	20	1.0	1	40	5	Ni metal
P	$K\alpha_{1,2}$	5	1.0	1-2	40	5	Cruft apatite
Pb	$M\alpha_1$	20	1.0	1	40	5	Galena

TABLE XIV. Chemical compositions of reference standards.
(in weight percent element)

Olivine from Marjalahti meteorite		Synthetic Diopside (1)		Fluorite, Yuma, Ariz. (1)		Sphalerite (1)		Ti metal (1)		Mn metal (1)	
Si	18.88	Si	25.94	Ca	51.33	Zn	67.10	Ti	100.00	Mn	100.00
Ti	0.00	Mg	11.23	F	48.67	S	32.90				
Cr	0.07	Ca	18.51	Total	100.00	Total	100.00				
Fe	8.97	O	44.22								
Mn	0.22	Total	100.00								
Ni	0.01										
Mg	28.70										
Zn	0.01										
Cu	0.01										
Ca	0.01										
O	43.07										
Total	99.95										

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(1) assumed stoichiometric and pure.

procedures is given by Keil (1967), but because some of the methods used in the present study are slightly different (especially those for mass absorption and atomic number) they are also discussed here.

Drift

Drift, due mainly to filament warping, can be detected by analyzing the reference standard several times during the analyzing period. Accuracy requirements and stability of the instrument used will determine how often the standard should be run, but in general, once an hour is minimal (Keil, 1967). Before a set of data is internally comparable it must be corrected for drift. This is accomplished most easily by plotting the points representing the reference standard on a graph of time vs. (counts at t_1/counts at t_x), where t_1 represents the first standardization and t_x represents the x'th standardization. The intermediate samples can then be corrected by linear interpolation between standards and multiplication by appropriate factors.

Dead Time

According to Keil (1967, p.27) the following relation holds for a dead time not larger than 10 microseconds:

$$N = \frac{N'}{1 - N'\tau}$$

where N is the true number of counts per second, N' is the observed number of counts per second, and τ is the dead time in seconds. For counting intervals other than one second this expression becomes:

$$N = \frac{N'}{1 - N'(\tau/t)}$$

where t is the counting interval. Repeated dead time determinations by M. R. Hall for different elements on the instrument used in this study have led to the use of a general value of 7 microseconds dead time.

Background

A certain amount of background x-radiation which is not due to excitation of characteristic x-rays is always present. The number of counts due to this background is determined for each sample by measuring the intensity on both sides of the characteristic x-ray peak and interpolating to the peak position. The value thus obtained is then subtracted from the value previously corrected for drift and dead time. In this study the background on one or several of the humite minerals was determined and used for the others. A first approximation of the composition of the sample may be obtained from the relation

$$\frac{I'\text{(sample)}}{I'\text{ (standard)}}\ (\%\text{ element in standard}) = \%\text{ element in sample},$$

where I' represents counts of emitted x-rays per given time interval corrected for drift, dead time, and background. This first approximation is used in making the mass absorption and atomic number corrections.

Mass Absorption

X-rays generated in the sample are partially absorbed before they leave the sample. The amount of absorption depends on the chemistry and, to a minor extent, the structure of the material. If the reference standard and the sample have different compositions, differential absorption must be taken into account. The absorption correction factor used in this study is Smith's (1965) modification of Philibert's (1963) correction factor which is:

$$f(\chi) = \frac{1 + \underline{h}}{(1 + \chi/\sigma)(1 + \underline{h}(1 + \chi/\sigma)} ,$$

where $\underline{h} = 1.2A/Z^2$ (A = atomic weight, Z = atomic number); $\chi = \langle\mu/\rho\rangle \text{cosec.}\theta$ ($\langle\mu/\rho\rangle$ is the average mass absorption coefficient, θ is the x-ray takeoff angle = 52.5° in the ARL microprobe); and σ is an empirical quantity dependent on the operating voltage. Smith empirically determined a set of $\underline{h}$-values for silicates at 15kV operating voltage which he denotes as $\underline{i}$-values. For all runs at 15kV his $\underline{i}$-values were used for calculating $f(\chi)$.

The absorption correction is performed by dividing I' by $f(\chi)$.

Atomic Number

Because the depth of electron penetration decreases with increasing atomic number and the number of back scattered electrons increases with atomic number, the number of x-rays reaching the detector depends on the average atomic number of the specimen. The data must be corrected to account for the difference in average atomic number between the sample and the standard. In this study the factor developed by Long and Reed and published by Smith (1965, p.838) was used. The factor,

$$\frac{[4.7 + 0.9\ln(V_o - V_k) - \ln \langle Z\rangle][\langle Z/A\rangle]}{R}$$

where V_o is the operating voltage in kilovolts, V_k is the critical excitation voltage in kilovolts, $\langle Z \rangle$ is the average atomic number, $\langle Z/A \rangle$ is the average ratio of atomic number to atomic weight, and R is Green's (1963) backscatter coefficient, is multiplied by the number of counts corrected for drift, dead time, background, and absorption.

Elemental Concentration

A second approximation of the elemental concentration is determined using the intensities corrected according to the procedure outlined in the preceding paragraphs in the following relation:

$$\frac{I\ (\text{sample})}{I\ (\text{standard})}\ (\%\ \text{element in standard}) = \%\ \text{element in sample}$$

A better approximation may be obtained by re-calculating mass absorption and atomic number corrections using the new values of weight percent element. These new correction factors are then applied to the first approximation values. Three applications of mass absorption and atomic number corrections were found to be sufficient in reducing the data presented here.

Accuracy of Microprobe Analyses

It is difficult to evaluate errors in microprobe analysis because there are numerous sources and they are hard to interrelate. Statistical errors are inherent in the x-ray counts obtained directly from the microprobe, and slight inhomogeniety of the sample gives rise to variations which are difficult to separate from the statistical errors. Drift is assumed to be linear between standardizations, but most likely it is not. Finally, absorption and atomic number corrections involve approximations and the error associated with these corrections is not well known. Keil (1967) states that when correction procedures such as applied in this study are used it is possible to get within ±5 percent of the true values. No attempt at a complete error evaluation was made in this study. However, in order to get a feeling for the magnitude of the error, the range in composition as implied by the range in counts/second for a given element in a given sample was examined, and the following average values were obtained: Si and Mg, ±1.5% of the amount present; Fe, ±1.5% in most samples, but about ±40% in chondrodite #20; Ti, ±5% in most, but several samples showed wide variation (i.e., clinohumite #2 and 3, chondrodite #15); Mn, ±2.5%, but up to ±15% in humite; and Ca, ±5%, but up to ±30% in norbergite #1. The wide variations mentioned are for minor elements and certainly reflect compositional, in addition to statistical, variation.

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CRYSTAL CHEMISTRY OF THE HUMITE MINERALS

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Abstract

The minerals of the humite group have the formula $\underline{n}M_2SiO_4 \cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$ where M is Mg, Fe, Mn, Ca, Zn in decreasing order of abundance, $x \leq 1$, and $\underline{n} = 1$ for norbergite, $\underline{n} = 2$ for chondrodite, $\underline{n} = 3$ for humite, and $\underline{n} = 4$ for clinohumite.

Description of the humites as alternating layers of forsterite (Mg_2SiO_4) and sellaite and/or brucite (MgF_2 and $Mg(OH)_2$) composition is incorrect because no layers with these compositions are present in the structure. The humites are structurally analogous to olivine in that both consist of a hexagonal close-packed array of anions (O, OH,F), zigzag chains of edge-sharing, M-filled octahedra and isolated SiO_4 tetrahedra. They differ from olivine in that none of the available tetrahedral sites coordinated by one or more OH or F anions is occupied by Si; this results in a stagger of the chains of octahedra. Substitution of Fe, Mn, and Ca for Mg has the same effect on the unit cell volume (normalized to half the mean anion-anion distance along the normal to (001)) in minerals with the humite structure as it does in minerals with the olivine structure.

Fifty-five humite mineral samples have been analyzed by microprobe x-ray emission methods for F, Mg, Si, Ca, Ti, Mn, Fe, and Zn. Al, P, Cl, Cr, Co, Ni, Cu, and Pb were not detected by analysis or wavelength scanning at the less than 0.03 weight percent level. The OH^{-1} concentrations were calculated using atomic proportions and assuming electro-

static charge balance in the $M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$ part of the formulae.

Epitaxial intergrowths between members of the humite group have been predicted on the basis of their similar structures and wet chemical analyses. Most chemical analyses of humite minerals show substantial anion deficiencies which lead to non-stoichiometric Si:(OH + F + O_{Ti}) ratios; many also indicate non-stoichiometry in the olivine-equivalent portion of the formula. In contrast, the microprobe analyses indicate that the humite minerals are stoichiometric. They also suggest that most bulk chemical analyses are deficient in H_2O and were made with material which contained minor amounts of other mineral impurities.

Single crystal x-ray diffraction studies were made on nine microprobe analyzed humites to determine the effects of minor chemical substitution on the unit cell parameters. These studies show that the substitution of (Fe + Mn) for Mg increases the normalized cell volume; that Ti + 2(O) for Mg + 2(OH,F) has little effect on the cell volume; and that (OH,F) + tetrahedral vacancies for O + Si results in a decrease in cell volume.