

CRYSTAL CHEMISTRY OF THE HUMITE MINERALS

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ABSTRACT

The minerals of the humite group have the formula



where M is Mg, Fe, Mn, Ca, Zn in decreasing order of abundance, $x < 1$, and $n=1$ for norbergite, $n=2$ for chondrodite, $n=3$ for humite and $n=4$ for clinohumite. Fifty-five humite minerals were 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 at the 0.05 weight percent level.

Most chemical analyses of humite minerals show substantial anion deficiencies resulting in nonstoichiometric 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 H₂O and were made with material which contained minor amounts of other mineral impurities.

Single crystal X-ray studies of eight microprobe-analyzed humites 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. No polytypism was observed.

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 in contact metamorphic calcareous rocks adjacent to granitic masses. Clinohumite has also been reported in altered periodotite (Lindberg, 1947; Heinrich, 1963), in a kimberlitic tuff plug (Sun, 1954), in a gabbro-granophyre contact zone (Huang, 1957), in kimberlite (Voskresenskaya *et al.*, 1965) and in a kimberlite breccia (McGetchin and Silver, 1968); chondrodite has been reported in a carbonatite (Russell, Hiemstra and Groeneveld, 1954).

The crystal structures of the humite minerals were determined by Taylor and West (1928, 1929). They found that the X-ray diffraction patterns of the humite minerals are similar to that 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

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based on a hexagonal close-packed array of anions (O, F, OH). Zigzag chains of edge-sharing, metal-filled octahedra and isolated SiO_4 tetrahedra are present in the humite minerals, just as they are in olivine. However, in the humites 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. Taylor and West (1928, 1929) chose axial labels for the humite minerals which are consistent with the olivines, but later authors have made other choices. Jones (1969) pointed out descriptive mistakes which have apparently arisen from the numerous choices and suggested that Taylor and West's settings be adopted because of the analogy with olivine.

Ribbe, Gibbs and Jones (1968) showed that substitution of Fe, Mn, Ca for Mg in octahedral coordination has the same effect on the cell volume (normalized to half the mean anion-anion distance along c^*) in minerals with humite structures as it does in minerals with olivine structures. They also pointed out that the common description of the humites as alternating layers of forsterite (Mg_2SiO_4) and sellaite and/or brucite (MgF_2 and $\text{Mg}(\text{OH})_2$) composition is incorrect because no layers with these compositions are present in the structure; instead, the so-called layers have the compositions $\text{Mg}_2\text{SiO}_3(\text{OH},\text{F})$ and $\text{Mg}(\text{OH},\text{F})\text{O}$.

A survey of the published chemical analyses (Jones, 1968) indicates that substitution for Mg in the humite minerals is rather limited. Iron ranges from 0.4 to 7.3 weight percent; Mn from 0.0 to 1.05 weight percent; and Ti from 0.0 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 [$2\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}(\text{OH})_2$] has been prepared synthetically (Buckle and Taylor, 1958). Moore (1967) has found four polytypes of leucophoenicite [$3\text{Mn}_2\text{SiO}_4 \cdot \text{Mn}(\text{OH})_2$]; one of these has the humite structure. Alleghanyite [$2\text{Mn}_2\text{SiO}_4 \cdot \text{Mn}(\text{OH}, \text{F})_2$] is structurally analogous to chondrodite, and sonolite [$4\text{Mn}_2\text{SiO}_4 \cdot \text{Mn}(\text{OH})_2$] 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 $\text{Si}:(\text{OH}+\text{F}+\text{O}_{\text{Ti}})$, 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 errors in the bulk 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 large 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 part of a larger study which includes crystal structure refinements of minerals of the humite and olivine groups to determine the inductive effect of cation and anion replacements on the Si-O bond and to determine cation distributions within the structures.

ELECTRON MICROPROBE ANALYSES

Analytical procedure. Fifty-five humite group mineral samples were analyzed with an Applied Research Laboratories EMX electron microprobe in the Molecular Structures Laboratory of Virginia Polytechnic Institute for Si, Mg, Fe, Ti, Mn, 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 (elements B-U).

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 of instrumental drift. If drift exceeded approximately three percent the analyses were re-run. The reference standard used for Si, Mg, and Fe is an olivine from the Marjalahti meteorite, contributed by Dr. W. R. Van Schmus. Its composition with respect to these elements was carefully checked against eight other olivines previously analyzed by Yoder and Sahama (1957) and Smith (1966) and was found to be as follows: SiO_2 , 40.39; MgO , 47.59; FeO , 11.54 weight percent; minor elements were assumed to be the same as given by Smith (1966) for his YS 24 (also from the Marjalahti meteorite). Other standards used were synthetic $\text{CaMgSi}_2\text{O}_6$ for Ca, Ti metal and synthetic TiO_2 for Ti, Mn metal for Mn, fluorite (CaF_2) for F and sphalerite (ZnS) for Zn.

Corrections for drift, decay time and background were made in the usual manner. Mass absorption corrections were made using Smith's (1965) modification of Philibert's (1963) correction factor and Henke *et al.* (1967) and Heinrich's (1966) mass absorption coefficients. The data were also corrected for atomic number effects using the factor developed by Løng and Reed and published by Smith (1965). Correction for fluorescence effects was found to be unnecessary.

Calculation of OH. It was necessary to calculate OH because H cannot be determined with the microprobe. The calculations are based on the assumption that Ti is ordered in the Mg(OH, F)O region of the structure (discussed later) and that there is electrostatic charge balance between cations and anions.

If M_{Ti} represents the sum of the atomic proportions of all of the octahedral cations (including Ti), then from the general formula for the humite group minerals, $n[M_2SiO_4] \cdot M_{1-x}Ti_x(OH, F)_{2-2x}O_{2x}$ (where $n=1$ for norbergite, $n=2$ for chondrodite, $n=3$ for humite, and $n=4$ for clinohumite; see *General Formula*, below) it can be deduced that $(2n/[2n+1])M_{Ti}$ represents the atomic proportion of octahedral cations in the M_2SiO_4 part of the formula. Similarly, $(1-(2n/[2n+1]))M_{Ti} = (1/[2n+1])M_{Ti}$ 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 M-cation in the latter part of the formula is balanced by 2(OH, F) anions. If no Ti is present the atomic proportion of (OH+F) is given by $2(1/[2n+1])M_{Ti}$. When Ti is present, however, 2(OH, F) are replaced by 2(O) for each Ti. Thus $OH+F = 2(1/[2n+1])M_{Ti} - 2Ti$, or

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

The analytical results and calculated OH values for the humite minerals are given in Table 1 and original numbers, localities, and donors of the analyzed samples are listed in Table 2.¹ The average oxide sum of these analyses is 99.7 weight percent; there is a near normal distribution about the average ranging from 98.6 to 100.5 weight percent.

CRYSTAL CHEMISTRY

Although the formulae of most naturally occurring humite minerals closely approximate the end-member compositions stated in the introduction, bulk chemical and microprobe analyses (Jones, 1968) show that Fe, Mn, Ti, Ca and Zn may replace Mg in limited amounts. Al, B, P, Na, K, Pb, Cr, Ni, Cl and CO₂ have been reported in bulk chemical analyses, but were not detected with the microprobe in 55 natural specimens. Schäfer (1896) has also described two clinohumites with 1.68 and 1.04 weight percent BeO, 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 substitutional range of (Fe+Mn) and Ti for Mg found by microprobe analysis is illustrated in Figure 1. The amount of substitution for Mg appears to increase from norbergite to clinohumite; this is particularly noticeable for Ti.

In addition to microprobe analysis, 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 3) were determined from data obtained on a precision

¹ To obtain copies of Table 1 (with all 55 analyses) and Table 2, order NAPS Document #00345 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting \$1.00 for microfiche or \$3.00 for photocopies, payable to ASIS/NAPS.

TABLE 1. MICROPROBE ANALYSES OF THE NORBERGITE, CHONDRODITE, HUMITE AND CLINOHUMITE SPECIMENS USED FOR X-RAY STUDY (cf. Table 3)^a

Oxide	Weight Percent Oxide							
	Norber- gite	Chondrodite			Humite		Clinohumite	
	1	2	9	24	3	7	7	10
SiO ₂	29.74	35.17	32.41	34.16	36.45	36.43	37.54	35.90
FeO	0.06	0.71	2.84	5.65	3.24	5.03	5.58	11.21
MnO	0.01	0.17	0.10	0.30	1.28	0.65	0.62	0.50
MgO	58.73	57.92	56.71	53.81	52.89	53.84	53.03	44.16
TiO ₂	0.42	0.03	0.37	0.47	3.25	0.10	0.22	5.59
CaO	0.15	0.01	0.03	0.00	0.01	0.01	0.01	0.01
ZnO	0.05	0.05	0.01	0.02	0.00	0.00	0.00	0.00
F	16.77	6.97	10.27	5.74	3.02	4.07	3.08	0.00
OH calc.	1.44	3.61	°	4.35	2.79	3.20	2.46	2.64
Total ^b	99.63	100.01	°	100.03	100.35	100.11	100.08	98.77
Element	Atomic Proportions ($\times 10^4$)							
Si	4,949	5,853	5,394	5,686	6,067	6,064	6,249	5,975
Fe	9	98	396	786	451	700	777	1,560
Mn	2	24	15	42	180	91	87	71
Mg	14,569	14,367	14,067	13,347	13,121	13,356	13,154	10,953
Ti	52	4	46	58	407	13	27	699
Ca	27	2	5	0	2	2	2	2
Zn	6	6	2	3	0	0	0	0
F	8,827	3,669	5,406	3,021	1,590	2,142	1,621	0
OH	847	2,124	°	2,557	1,642	1,879	1,446	1,553
Stoichi- ometry ^d	1.012	1.009	°	0.998	1.000	0.990	1.001	1.012
'x' in formula ^e	0.001	0.001	0.016	0.021	0.201	0.006	0.017	0.474

^a Specimen numbers refer to the complete Tables 1 and 2 which appear in the document file (see footnote in text).

^b Total, less O for F and OH.

^c X-ray studies of chondrodite 9 show chondrodite diffraction patterns. Ch-9 is Si-deficient, indicating the possibility of another cation in tetrahedral coordination; therefore, these values were not calculated.

^d Stoichiometry = $2\text{Si}/2n\text{M}_{\text{Ti}}[2n+1]$. See text.

^e x in the formula $n\text{M}_2\text{SiO}_4\text{M}_{1-x}\text{Ti}_x(\text{OH},\text{F})_{2-2x}\text{O}_{2x}$ where $n=1$ for norbergite, 2 for chondrodite, 3 for humite and 4 for clinohumite.

back-reflection Weissenberg camera and were refined using the least-squares program described by Burnham (1962).

The elements are discussed on the following pages in terms of occurrence in the structures, effect on the cell parameters, and interdependent substitutions.

Silicon. Silicon occupies tetrahedral sites in the humite mineral structures, just as it does in the olivines. It does not, however, occupy those sites coordinated by one or more (OH, F) anions. Although no other elements were identified which would likely be in tetrahedral coordination, two chondrodites (Nos. 9 and 10, Table 1) are Si-deficient (and F-rich).

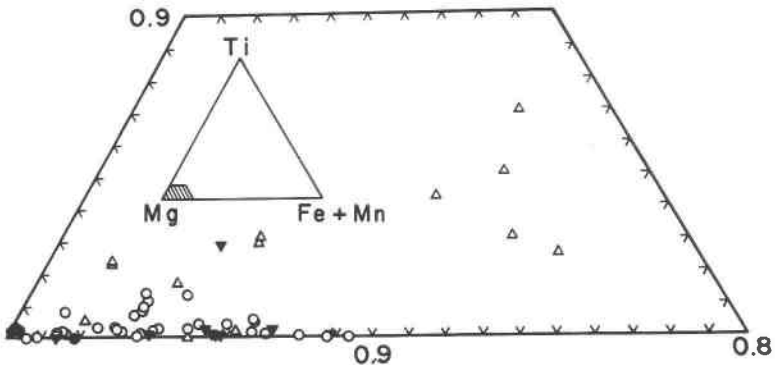


FIG. 1. Enlargement of hachured area in Mg-Ti-(Fe+Mn) triangular diagram (inset) showing substitution for Mg in the humite minerals based on ratios of atomic proportions of Mg, Ti and (Fe+Mn) from Table 1. Solid circles, norbergite; open circles, chondrodite; solid triangles, humite; open triangles, clinohumite.

Single crystal studies of 9 and the x-ray powder pattern of 10 indicate that both are chondrodites. The normalized cell volume of 9, however, is somewhat smaller than the cell volumes of the other chondrodites studied (Table 3). This implies the presence of another tetrahedrally-coordinated cation which is smaller than Si. A chemical analysis of this specimen is clearly desirable.

Aluminum. Nearly all chemical analyses report Al in natural humites. A careful check with the microprobe, however, indicated that Al is not present in portions of humite grains which are free from cracks and inclusions. It is concluded, therefore, that Al does not occur in humite mineral structures (just as it does not occur in the olivines) and that its presence in chemical analyses reflects Al-rich inclusions such as spinel (which was observed and which is commonly associated with the humite minerals).

Magnesium. Magnesium is the major octahedrally-coordinated cation in the humite minerals and also has the smallest ionic radius of those cations presumed to occupy octahedral sites. As such, the most Mg-rich humite minerals have the smallest unit cell volume.

Iron and manganese. Ferrous iron replaces Mg to a greater extent than do other octahedrally-coordinated cations, whereas Mn is generally a very minor constituent of the humite minerals. 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. 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. He stated that this is thermodynamically improbable, and thereby implied 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 by Ribbe *et al.* (1968), the humites are structurally analogous to olivine, ordering of Fe and Mg is not expected, although positive confirmation awaits crystal structure refinements. The small amount of Mn present in these Mg-humites is presumably disordered in the structures.

Ferric iron is reported in nearly all of the bulk chemical analyses. Its presence cannot be confirmed by microprobe analysis, but some comment is appropriate. Borneman-Starynkevitch and Myasnikov (1950) found that Fe^{2+} is oxidized on mechanical crushing, thereby implying that Fe^{3+} values may be lower than reported. The presence of Fe^{3+} in natural and artificial fayalite led Sahama (1953) to conclude that the structurally analogous humites must also contain some Fe^{3+} . In order to maintain local charge balance, Fe^{3+} would probably replace Mg in the $\text{Mg}(\text{OH},\text{F})\text{O}$ region of the structure. Thus the replacement would be of the form $\text{Fe}^{3+} + \text{O} = \text{Mg} + (\text{OH},\text{F})$, and each Fe^{3+} would be surrounded by five O and one (OH, F). It was assumed in the treatment of microprobe data that all of the Fe is Fe^{2+} [*cf.* Smith's (1966) olivine analyses].

The cell parameters of two chondrodites (Nos. 2 and 24) were measured specifically in order to determine the effect of substitution of (Fe+Mn) for Mg. They contain similar amounts of minor cations and have similar OH/F ratios. As expected, the unit cell volume of the more Fe-rich chondrodite (No. 24) is larger than the Fe-poor chondrodite. The change in normalized cell volume (normalized to half the mean anion-anion dis-

tance along c^*) is comparable to the change in normalized cell volume in Mg-Fe olivines with similar $(\text{Fe}+\text{Mn})/(\text{Fe}+\text{Mn}+\text{Mg})$ ratios (Ribbe *et al.*, 1968). The effect of the replacement of Mg by Fe in other samples for which cell parameters were determined can be intimated from Figure 2; points falling above the line passing through synthetic forsterite, humite and norbergite contain other cations in addition to Mg (mainly Fe) and therefore have larger cell volumes than the synthetics.

Calcium. Only minor amounts of Ca are present in the humite minerals, 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; personal communication, 1968) found that the replacement of 10 percent Mn by Ca resulted in a doubling of the *c*-axis. He interpreted 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 the humite minerals is expected. The minor amounts of Ca in the Mg-humites obviate proof of this speculation.

Titanium. 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, significant amounts may occur. Borneman-Starynkevitch and Myasikov (1950) suggested that Ti occupies only the octahedral sites in the (OH, F) region of the clinohumite structure. (There is a possibility that very small amounts of Ti are present as Ti^{3+} rather than Ti^{4+} , but Ti^{4+} is reported in all of the chemical analyses and current microprobe techniques do not permit us to distinguish oxidation states; thus all Ti has been assumed to be Ti^{4+} in the following discussion.) Sahama (1953) pointed out that analytical results for all of the humite minerals are in better agreement with idealized formulae if it is assumed that Ti does not replace Mg in the "silicate" portion of the structures. These studies imply a coupled substitution of the form $\text{Ti}+2(\text{O})=(\text{Mg}, \text{Fe})+2(\text{OH}, \text{F})$. If Ti is ordered in the structure and the substitution is of this form, then there must be two O anions for each Ti (*i.e.*, $\text{O}_{\text{Ti}}=2\text{Ti}$). If O_{Ti} is substituted for 2Ti in the expression given for OH above and the equation is solved for $(2/[2n+1])\text{M}_{\text{Ti}}$, the following relation is obtained:

$$(2/[2n+1])\text{M}_{\text{Ti}} = \text{O}_{\text{Ti}} + \text{OH} + \text{F}.$$

For norbergite ($n=1$) the left hand side of the equation becomes $2/3\text{M}_{\text{Ti}}$; for chondrodite ($n=2$), $2/5\text{M}_{\text{Ti}}$; for humite ($n=3$), $2/7\text{M}_{\text{Ti}}$; and for

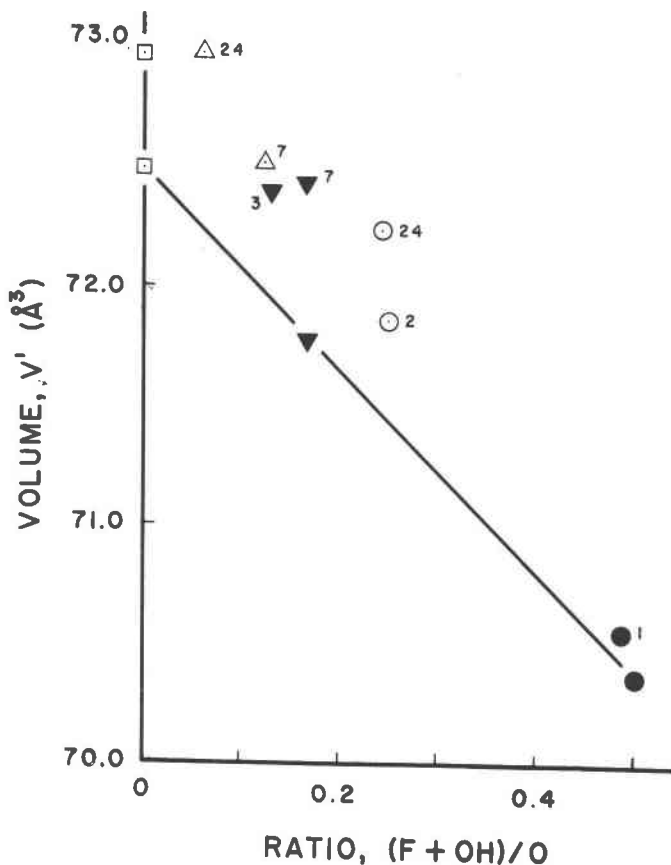


FIG. 2. The relation between the normalized cell volume $a \times b \times (d_{001}/n)$ and $(F+OH)/O$ in norbergite (solid circles), chondrodite (open circles), humite (solid triangles), clinohumite (open triangles) and forsterite (squares). Numbers next to humite mineral data points correspond to those in Table 1. Solid line connects synthetic Mg_2SiO_4 (data from Yoder and Smith, 1957), $3Mg_2SiO_4 \cdot MgF_2$ and $Mg_2SiO_4 \cdot MgF_2$ (data from Van Valkenburg, 1961). Fo_{90} data from Birle *et al.* (1968).

clinohumite ($n=4$), $2/9M_{Ti}$. Figure 3 compares atomic proportions Ti with atomic proportions of the quantities $(OH+F)$ and $2/9M_{Ti}-2Ti$ for clinohumites. If the substitution is of the form suggested, the equation describing it is

$$OH + F = 2/9M_{Ti} - 2Ti \approx -2Ti + 3200.$$

The equations actually obtained from bulk chemical and microprobe data by linear regression methods are as follows (standard errors are given in brackets):

Microprobe data:

$$2/9M_{\text{Ti}} - 2\text{Ti} = -2.25[.07]\text{Ti} + 3149[29]$$

$$\text{Coefficient of correlation} = -0.995$$

Chemical cation data:

$$2/9M_{\text{Ti}} - 2\text{Ti} = -1.89[.26]\text{Ti} + 3020[97]$$

$$\text{Coefficient of correlation} = -0.862$$

Combined microprobe and chemical cation data:

$$2/9M_{\text{Ti}} - 2\text{Ti} = -2.00[.17]\text{Ti} + 3057[66]$$

$$\text{Coefficient of correlation} = -0.908$$

Chemical anion data:

$$\text{OH} + \text{F} = -2.3[.4]\text{Ti} + 2344[157]$$

$$\text{Coefficient of correlation} = -0.794$$

The equations relating cations to Ti are in reasonable agreement with

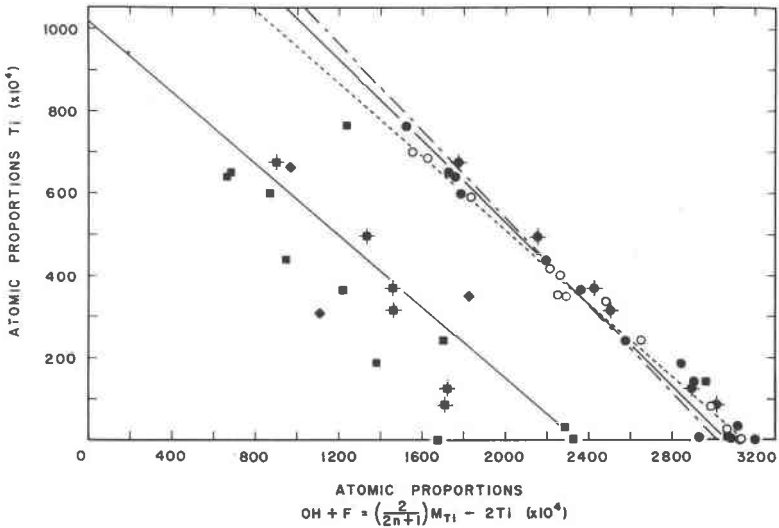


FIG. 3. Graphical representation of the coupled substitution $\text{Ti} + 2(\text{O}) = \text{M} + 2(\text{OH}, \text{F})$. Linear regression curves for microprobe data (open circles, dot-dash line), chemical cation data (solid circles, dashed line) and combined microprobe and chemical cation data (solid 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.

the theoretical relation and essentially substantiate the proposed substitution. The equation relating (OH+F) to Ti (*chemical anion data*), however is in poor agreement with the theoretical relation, presumably reflecting relative inaccuracy of H₂O 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).

TABLE 3. UNIT-CELL PARAMETERS OF SELECTED HUMITE MINERALS (A)^a

Mineral and new number	<i>a</i>	<i>b</i>	<i>c</i>	α	<i>d</i> ₀₀₁	<i>V'</i>	No. of Obs.
Natural humites (this study)							
Norbergite 1	4.7104 (1)	10.2718 (3)	8.7476 (4)	90°	6×1.4579	70.540	68
Chondrodite 2	4.7284 (3)	10.2539 (3)	7.8404 (2)	109.059 (2)	5×1.4821	71.859	91
Chondrodite 24	4.7332 (2)	10.2552 (2)	7.8765 (2)	109.128 (2)	5×1.4883	72.242	62
Chondrodite 9	4.7190 (5)	10.2616 (5)	7.8154 (4)	109.147 (3)	5×1.4766	71.504	114
Humite 3	4.7386 (1)	10.2626 (3)	20.8418 (3)	90°	14×1.4887	72.396	112
Humite 7	4.7408 (1)	10.2580 (2)	20.8526 (4)	90°	14×1.4895	72.436	100
Clinohumite 7	4.7441 (2)	10.2501 (5)	13.6635 (3)	100.786 (2)	9×1.4913	72.517	181
Clinohumite 10	4.7451 (8)	10.288 (2)	13.691 (1)	100.657 (8)	9×1.495	72.98	150
Synthetic humites (Van Valkenburg, 1961)							
Norbergite	4.709	10.271	8.727	90°	6×1.455	70.37	
Humite	4.735	10.243	20.72	90°	14×1.480	71.78	

^a Standard errors in parentheses refer to the last decimal place.

The substitution of Ti for Mg (ionic radii 0.68Å and 0.66Å, respectively; Ahrens, 1952) and concomitant substitution of 2(O) for 2(OH, F) apparently has little effect on the cell parameters as illustrated by two humites (Table 3, Nos. 3, 7). However, there does appear to be a very slight decrease in unit cell volume with increase in Ti content. This may be related to the charge difference between Mg²⁺ and Ti⁴⁺. The mean Ti-O distance in rutile is 1.959Å (Cromer and Harrington, 1955) whereas the mean Mg-anion distance in norbergite is 2.086Å (Gibbs and Ribbe, 1969). A shortening of the mean octahedral bond in the Mg(OH,F)O region of the structure may result in a smaller unit cell volume.

Fluorine and titanium. Borneman-Starynkevitch and Myasnikov (1950) and Bradshaw and Leake (1964) noted that Ti-rich clinohumites are

F-poor. This is illustrated in Figure 4 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 $2F^-$ to be replaced

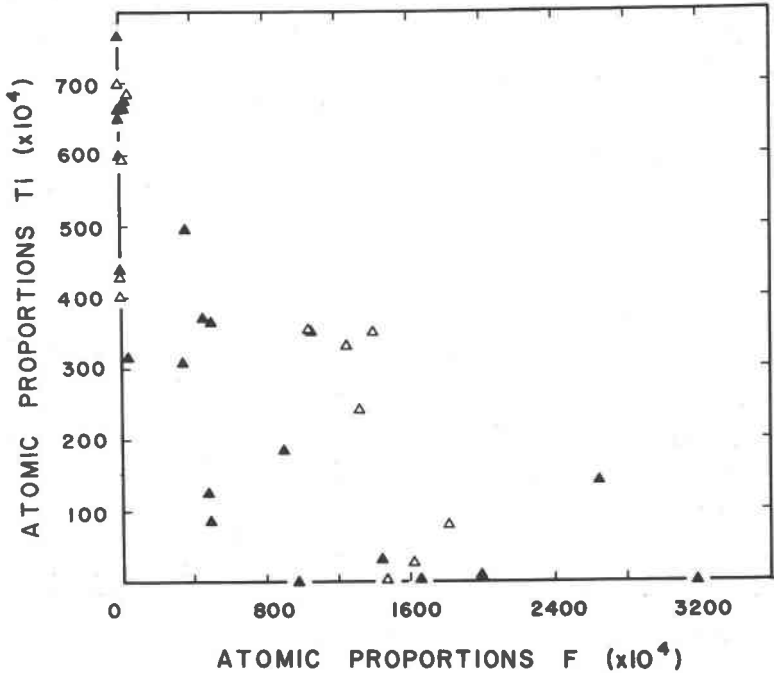


FIG. 4. The relationship between Ti and F in clinohumites. See text for discussion. Solid triangles are chemical analyses, open triangles are microprobe analyses.

by $2O^{2-}$." It may be noted in Figure 4 that below about 1.9 weight percent Ti (0.04 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 $Mg(OH,F)O$ region 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 $Mg(OH,F)O$ region of the structure than would proton-bearing OH.

Fluorine and hydroxyl. Not only does the amount of (OH,F) decrease in 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 5. It is not clear whether the amount of F contained by each of the members of the group is a function of the chemical activity of F

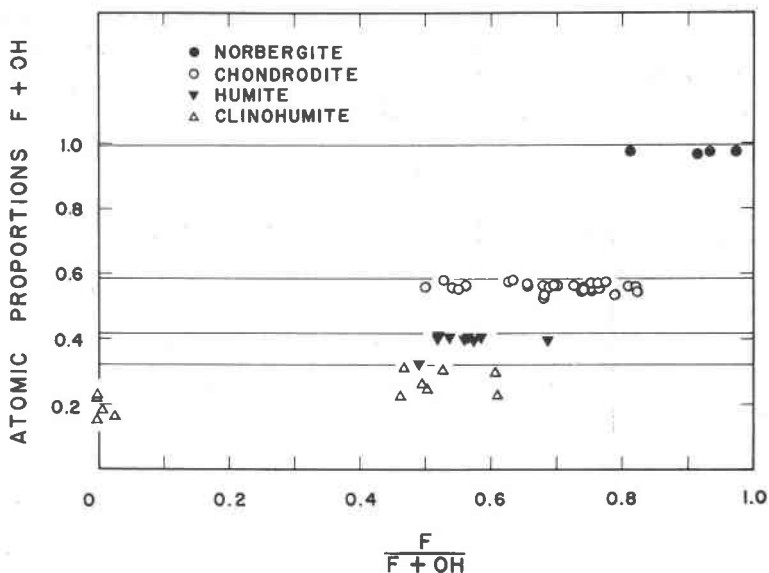


FIG. 5. Illustration of the decrease in $(F/[F+OH])$ with decrease in $(F+OH)$ in the humite minerals. Horizontal lines represent stoichiometric $nMg_2SiO_4 \cdot MgFOH$. Titanium-rich clinohumites cluster near the origin.

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). Also, it may be that no more than 50 percent of the F in norbergite could be replaced by OH because proton-proton interaction would result in strong anion repulsion; this may explain why OH-norbergite has not been synthesized.

The substitutions (OH, F) for O and concomitant vacancies for Si from forsterite to norbergite results in a decrease in normalized cell volume. Figure 2 shows that the change is linear for synthetic forsterite, F-humite and F-norbergite. The natural humite minerals and natural

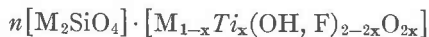
forsterite ($F_{0.90}$) show the same trend; the scatter in the data points is primarily due to the presence of octahedral cations larger than Mg. Chondrodite 24, humite 7 and clinohumite 7 were selected to determine the effect of substitution of (OH, F) for O on the cell parameters of natural humite minerals. The amount of substitution for Mg and the ratio $F/(F+OH)$ is essentially the same in each of these samples. As shown in Figure 2, the change in normalized cell volume (V') with $(F+OH)/O$ appears to be less than the corresponding change in the synthetic F-humite minerals. It is not clear whether the difference is significant or whether the cell volume is actually affected by the replacement of OH for F. The standard errors associated with the cell volumes are smaller than the data points, but the errors associated with the $(F+OH)/O$ ratios are unknown. It is possible that the proton associated with the

TABLE 4. 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

OH may require that the M-OH bond be longer than the M-F bond, resulting in the observed larger cell volume.

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



where M includes the octahedrally coordinated cations Mg, Fe, Mn, Ca, Zn, etc. and $x < 1$. The members of the group are distinguished by the value of n in the formula: thus $n=1$ describes norbergite; $n=2$, chondrodite; $n=3$, humite; and $n=4$, clinohumite.

STOICHIOMETRIC CONSIDERATIONS

Sahama (1953) examined the chemical analyses of 46 humite mineral specimens, including 14 of his own, in terms of the ratio of atomic proportions Si to atomic proportions $(OH+F+O_{Ti})$, where O_{Ti} is given by $2Ti$. Sahama's results are given in Table 4. He summarizes them as follows (p. 16): "The average Si:(O+OH+F) ratios given in the fourth

column of Table [4] 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 deviations from ideal composition could 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 $\text{Si}:(\text{OH} + \text{F} + \text{O}_{\text{Ti}})$. Structural defects or site vacancies could produce non-stoichiometry, but it is doubtful that they would account for the large variations reported for the humites.

Chemical analysis of the humite minerals using the normal wet chemical methods has long been recognized as a difficult task. Penfield and Howe (1894) attributed this to difficulties in obtaining pure material and to analytical problems in determining Si, F and H_2O . Sahama (1953) concluded that the deviations from the ideal composition indicated by chemical analyses were mainly due to analytical errors, particularly for F and H_2O . He stated (p. 18) that ". . . 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 $\text{Mg}(\text{OH}, \text{F})_2 - \text{TiO}_2$ layers for a given number of Mg_2SiO_4 layers." Jones, Ribbe and Gibbs (1967) showed that epitaxial intergrowths between the various humite minerals or between forsterite and the humites appear to be structurally reasonable. It should be noted, however, that whereas most of the deviations of the ratio $\text{Si}:(\text{OH} + \text{F} + \text{O}_{\text{Ti}})$ shown in Table 4 can be explained by fine-scale epitaxial intergrowths, one cannot. Thus, an intergrowth between norbergite and forsterite 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 did Van Valkenburg (1961) succeed in synthesizing one of composition $0.5\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$.

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, and it is probably responsible for Al and some of the excess Mg reported in bulk chemical analyses.

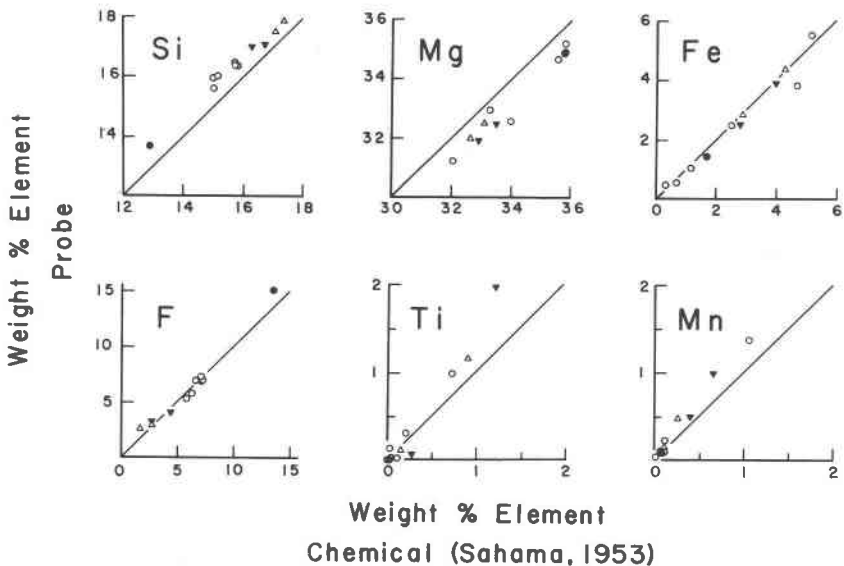


FIG. 6. Relation between microprobe (this paper) and bulk chemical (Sahama, 1953) analyses of Si, Mg, Fe, F, Ti and Mn in norbergite (solid circles), chondroditite (open circles), humite (solid triangles) and clinohumite (open triangles).

DISCUSSION OF ANALYSES

We were very fortunate to obtain the samples which were analyzed by Sahama (1953) and his chemical analyses are compared with the microprobe analyses of these samples in Figure 6. Agreement between the two methods is quite good for Fe and F, and fair for Ti and Mn. Because considerable variation from grain to grain was noted for Ti and Mn concentrations during microprobe analyses of some samples, lack of agreement between microprobe and gravimetric analyses for Ti and Mn was not unexpected. Si is consistently lower and Mg higher in the chemical analyses when compared to the microprobe analyses. Smith and Ribbe

(1966) pointed out that SiO_2 is generally too low in gravimetric analyses of feldspars and Sahama (1953) found that for the humite minerals normal methods of SiO_2 analysis resulted in loss of SiO_2 . In addition to apparent analytical difficulties, the presence of Si-poor, Mg-bearing mineral impurities may perhaps explain the lack of agreement between microprobe and chemical analyses for Si and Mg.

An indication of the accuracy and/or the deviation from stoichiometry implied by the microprobe analyses can be obtained by considering the ratio $2\text{Si}:(2n/[2n+1])M_{\text{Ti}}$ 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 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 along with the analyses in Table 1.

The degree of stoichiometry of the humite minerals as indicated by the microprobe analyses is also illustrated in Figure 7a which is a plot of atomic proportions Si versus atomic proportions $(2/[2n+1])M_{\text{Ti}}$ (equal to the sum $(\text{OH}+\text{F}+\text{O}_{\text{Ti}})$). It can be seen that the microprobe analyses fall, within analytical error, along the lines which represent stoichiometric proportions whereas the chemical analyses (Fig. 7b, c) show a much greater spread. Furthermore, $(\text{OH}+\text{F}+\text{O}_{\text{Ti}})$ does not equal $(2/[2n+1])M_{\text{Ti}}$ for the chemical analyses (with the exception of Van Valkenburg's synthetics). Thus the chemical analyses imply a slight cation excess in the $\text{Mg}(\text{OH},\text{F})_2$ part of the formula and a marked anion deficiency resulting in a charge imbalance (Fig. 7b, c). This, coupled with the Ti *vs* $(\text{OH}+\text{F})$ data presented in Fig. 3 lead 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 6 implies that chemically determined OH, rather than F, is inaccurate. It should also be noted that Figure 7b indicates a deficiency in Si and an excess in octahedral cations (principally Mg), just as does the comparison between microprobe and chemical analyses illustrated in Figure 6.

SUMMARY AND CONCLUSIONS

The chemical study of the humite minerals by Sahama (1953) and a survey of other chemical analyses (Jones, 1968) imply that the humite minerals are nonstoichiometric. Sahama attributed this to inaccuracy of chemical analyses. Bradshaw and Leake (1964) suggested that the humite minerals may sometimes contain irregular numbers of $\text{Mg}(\text{OH},\text{F})_2-\text{TiO}_2$ layers for a given number of Mg_2SiO_4 layers, resulting in non-stoichiometry. Although Ribbe *et al.* (1968) have shown that the "layer" concept

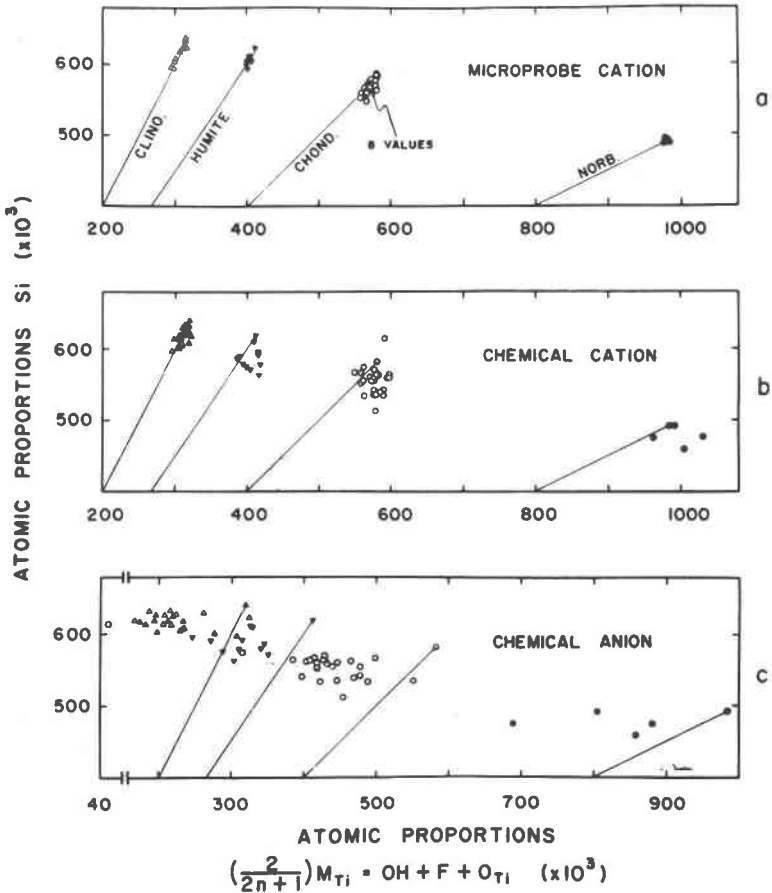


FIG. 7. Summary of stoichiometry in the humite minerals. Straight lines represent lines along which analyses should fall for stoichiometric clinohumite (open triangles), humite (solid triangles), chondrodite (open circles) and norbergite (solid circles). *a.* Si vs. $(2/[2n+1])M_{Ti}$ for microprobe 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 substantial electrostatic charge imbalance.

of the humite minerals is incorrect, Jones *et al.* (1967) showed that epitaxial intergrowths between the humite minerals are theoretically possible and could explain the non-stoichiometry.

Microprobe analyses of a large number of humite mineral samples and single crystal studies were undertaken in an attempt to explain the deviations from the ideal formulae. The microprobe analyses did not, within the limits of analytical error, give any indication of non-stoichiometry,

nor did the single crystal studies give any indication of epitaxial intergrowths or polytypism of the type described by Moore (1967) for the Mn analogue of humite, leucophoenicite. Evidence has been presented which indicates that most of the bulk chemical analyses of humite minerals suffer from inaccurate H₂O determinations and, perhaps, impure starting material.

Both chemical and microprobe analyses show that substitutions for Mg are rather restricted in the humite minerals and that the amount of replacement increases from norbergite to chondrodite to humite to clinohumite. Iron is the major substituent, but Ti may also be significant, especially in clinohumite. Titanium is ordered in the Mg(OH,F)O region of the structure and replaces Mg according to the relation $Ti + 2(O) = Mg + 2(OH,F)$. When more than about one-quarter of the Mg in the Mg(OH,F)O region of the structure has been replaced, little or no F is present. A decrease in F relative to OH is also noted from norbergite to clinohumite.

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 $F/(F+OH)$ 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 conditions of formation such as temperature, pressure and the availability and activity of F and H₂O. 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.

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