

## Titanium, fluorine, and hydroxyl in the humite minerals

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### Abstract

In the humite homologous series,  $nM_2SiO_4 \cdot M_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}$  (where  $n = 1$  for norbergite, 2 for chondrodite, 3 for humite, and 4 for clinohumite,  $M = Mg \gg Fe > Mn > Ca, Zn, Ni$  and  $0 \leq x \leq 1$ ),  $x$  appears never to exceed  $\sim 0.5$  Ti atoms per formula unit, because local electrostatic charge imbalances at the 3-coordinated (F,OH,O) anion and the 4-coordinated oxygen atoms increase very rapidly as  $Ti^{4+}$  substitutes for  $M^{2+}$ , even with the concomitant substitution of 3-coordinated  $O^{2-}$  for  $(F,OH)^{1-}$ . Both electrostatic and geometric arguments suggest that Ti orders into the  $M(F,OH)O$  "layer" of the humite structures, *i.e.*, into the  $M(3)O_4^IV(F,OH,O)_2^{III}$  octahedron, which is the smallest of all octahedra in all the humite minerals (*cf.* Fujino and Takéuchi, 1978).

Refractive indices, density, unit-cell dimensions, and volume are dramatically affected by the substitution of OH for F, and this has been studied as chemistry varies from  $1.0 \leq (F,OH)^{III}/[(F,OH)^{III} + O^{IV}] \leq 0.0$  and  $0.0 \leq Si^{IV}/2(F,OH,O) \leq 1/8$  from sellaite  $Mg(F,OH)_2$  ( $n = 0$ ) through the humites to forsterite ( $n = \infty$ ). The volume per anion increases much more rapidly as OH substitutes for F in these minerals than would be expected on the basis of observed differences in individual  $M-(F,OH)$  distances. As Yamamoto (1977) noted, the effective radius of  $OH^{III}$  would be  $\sim 0.06A$  larger than that of  $F^{III}$  based on individual bond lengths. However, if the grand mean  $M-(F,OH,O)$  distance minus the effective radius of the  $M$  cation is used,  $OH^{III}$  would have to be  $\sim 0.15A$  larger, and if the effective anion radius calculated from the observed volume per anion is used, values  $\sim 0.10A$  larger are expected. Proton-proton repulsions, which increase dramatically both within a given mineral series (say F- to OH-chondrodite) and as  $n$  goes from 4 to 0, expand the unoccupied polyhedra for the hcp anion array very much more than the occupied octahedra; physical parameters are accordingly affected.

### Introduction

The formula for the homologous series of minerals collectively called "humites" is  $nM_2SiO_4 \cdot M_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}$  where  $n = 1$  for norbergite, 2 for chondrodite, 3 for humite, 4 for clinohumite,  $M$  is  $Mg \gg Fe > Mn, Ca, Zn, Ni$ , and  $0 \leq x \leq 1$ . A series of Mn-isotypes for  $n = 2$  (alleghanyite), 3 (manganhumite), and 4 (sonolite) also exists in nature, and these exhibit a substantial range of solid solution with Mg; most are OH-rich.

Titanium-rich clinohumites and chondrodite ( $x > 0.25$ ) have recently attracted attention as possible mineralogical sites for water in the earth's upper mantle (McGetchin *et al.*, 1970; Merrill *et al.*, 1972; Aoki *et al.*, 1976; Mitchell, 1978), and as a result the

crystal structures of no less than three titanian clinohumites (Ti-Cl) and one titanian chondrodite (Ti-Ch) have been examined. Least-squares site refinements have produced somewhat conflicting results, leaving us with two questions regarding titanium: (1) Why does  $x$  appear never to exceed 0.5 Ti atoms per formula unit in natural specimens? (2) Is Ti really ordered into the  $M3$  octahedral site, and if so, why? Fujino and Takéuchi (1978) implied answers to these questions with vague references to Pauling's electrostatic valence rule. One purpose of this paper is to address that matter more specifically.

Another crystal-chemical problem has to do with the nature of the  $OH \rightleftharpoons F$  substitution in all the humites. The recent synthesis of OH-Ch and OH-Cl by Yamamoto and Akimoto (1974, 1977), the determi-

nation of the structure of OH-Ch by Yamamoto (1977), and the synthesis of many F,OH intermediate compounds by Duffy (1977) have provided a data base from which the systematics of the  $\text{OH} \rightleftharpoons \text{F}$  substitution has been deduced.

### Titanium in natural humites

#### Titanium content

Table 1 lists, among others, the compositions of the most Ti-rich humite minerals analyzed to date. Note that  $x$  does not exceed 0.5 Ti atoms per formula unit in any of the humites. Norbergite (No;  $n = 1$ ) is rare in nature and apparently is relatively Ti-free. Clinohumite (Cl;  $n = 4$ ) commonly is Ti-rich (Jones *et al.*, 1969, Fig. 4), but only one titanian chondrodite (Ch;  $n = 2$ ) has ever been reported (Aoki *et al.*, 1976), and it is epitaxially associated with a Ti-Cl which contains the same number of Ti atoms per formula unit as Ti-Ch. Notably absent from this intergrowth is the intermediate phase, humite (Hu;  $n = 3$ ).

#### Titanium distribution

The structures of both Ti-Ch and Ti-Cl have been determined by Fujino and Takéuchi (1978) who found by least-squares site refinement that most, if not all, of the Ti is ordered in the  $M(\text{OH})\text{O}$  layers, *i.e.*, in the  $M3$  octahedral sites. Of course there are problems associated with determining unambiguously the cation distribution among the octahedral sites when three species of atom are present, namely Mg ( $f = 12$ ), Fe + minor Mn, Ni ( $f \sim 26$ ) and Ti ( $f = 22$ ) ( $f$  is the atomic scattering factor at  $\sin\theta/\lambda = 0.0$ ). Some basically unsatisfying assumptions must be made to obtain convergence: in refining site occu-

pancies in Ti-Cl Robinson *et al.* (1973a,b) took different approaches than Fujino and Takéuchi (1978); the former report disordered Ti, the latter ordered. Kocman and Rucklidge (1973)—perhaps most wisely—simply assigned Ti to  $M3$  and refined Mg/Fe distributions within the constraints of their chemical analysis.

Fujino and Takéuchi's (1978) reference to Pauling's electrostatic valence principle holds the key to both the restricted Ti substitution and Ti distribution among the nonequivalent octahedral sites in humites. Let us consider the hypothetical homologues,  $n\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}_{1-x}\text{Ti}_x(\text{F,OH})_{2-2x}\text{O}_{2x}$  with  $0 \leq x \leq 1$ . Note that one half of the octahedral sites are filled with cations in the proportion  $[(x)\text{Ti} + (2n + 1 - x)\text{Mg}]$ .

*Charge imbalance with Ti disordered.* With Ti disordered there are only two types of anions as far as local charge balance is concerned, regardless of mineral species. The average charge on all  $M$  cations is the same:  $\langle z \rangle = 4[x/(2n + 1)] + 2[(2n + 1 - x)/(2n + 1)]$ . The oxygens are 4-coordinated to  $1\text{Si} + 3M$  and are all overbonded by  $[1 + 3\langle z \rangle/6] - 2.00$  esu. The (F,OH,O) anion is bonded to  $3M$  atoms and is always underbonded by an amount  $3\langle z \rangle/6 - (1 + x)$  esu, where  $x = \text{O}_{\text{Ti}}/(\text{F} + \text{OH} + \text{O}_{\text{Ti}})$ . Figure 1a indicates the imbalances as a function of  $x$  for each of the four humites in which Ti is disordered.

*Charge imbalance with Ti ordered.* If all the titanium is ordered into  $M3$ , there are collectively among the humite homologues three types of 4-coordinated oxygens,  $\text{O}_0, \text{O}_1, \text{O}_2$ , the subscripts referring to the number of  $M3$  atoms to which they are bonded, plus one (F,OH,O) anion. From the multiplicities of  $M$  sites in the humites (Table 2) it can be

Table 1. Compositional data for humite minerals whose structures have been refined

$n$	Mineral (space group)	Wt % $\text{TiO}_2$ (max. if $x=1$ )	$x$	Mg	Fe	Mn	Ni	Ca	$\text{SiO}_4$	Ti	F	OH*	$\text{O}_{\text{Ti}}$	
1	Norbergite ( $P\bar{6}2m$ )**	0.42 (36.2)	0.011	1.99	<.01	<.01	--	<.01	1	0.01	1.81	0.17	0.02	Jones <i>et al.</i> (1969)
2	Chondrodite ( $P2_1/b$ )	9.36 (22.1)	0.424	3.99	0.57	0.01	0.01	--	2	0.42	0	1.15	0.85	Fujino & Takéuchi (1978)
		0.03 (22.1)	<.01	4.95	0.03	0.01	--	0.01	2	<.01	1.27	0.73	<.01	Gibbs <i>et al.</i> (1970)
3	Humite ( $P\bar{6}2m$ )	3.25 (15.9)	0.201	6.49	0.22	0.09	--	<.01	3	0.20	0.79	0.81	0.40	Jones <i>et al.</i> (1969)***
		0.10 (15.9)	0.01	6.60	0.35	0.05	--	<.01	3	0.01	1.06	0.93	0.01	Ribbe & Gibbs (1971)
4	Clinohumite ( $P2_1/b$ )	5.59 (12.4)	0.468	7.33	1.04	0.05	--	<.01	4	0.47	0	1.06	0.94	Robinson <i>et al.</i> (1973)
		3.14 (12.4)	0.26	7.34	1.36	0.08	--	4	0.26	0.40	1.08	0.52	Kocman & Rucklidge (1973)	
		5.07 (12.4)	0.429	7.44	1.09	0.02	0.02	--	4	0.43	0	1.14	0.86	Fujino & Takéuchi (1978)
		0.22 (12.4)	0.02	8.42	0.50	0.06	--	<.01	4	0.02	1.04	0.93	0.03	Robinson <i>et al.</i> (1973)

\* Calculated by difference:  $\text{OH} = 2 - (\text{F} + \text{O}_{\text{Ti}})$ , where  $\text{O}_{\text{Ti}} = \text{O}_{2x}$ .

\*\* Space group convention of Jones (1969).

\*\*\* Most Ti-rich humite analysis reported; the structure of this specimen has *not* been refined.

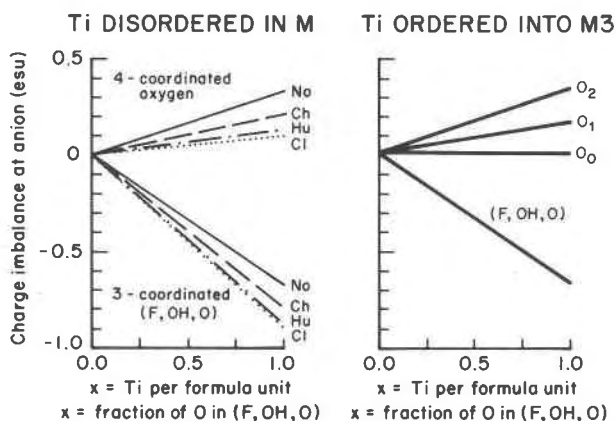


Fig. 1. Plots of  $x$  vs. charge imbalance at the anion for the humite minerals assuming (a) Ti disordered in all the  $M$  octahedra and (b) Ti ordered into  $M3$ . Symbols are explained in the text and Table 2. The charge imbalance was calculated in the following manner for the (F,OH,O) site:  $S - (1 + x)$ , where  $S$  is the sum of the Pauling bond strengths to the anion and  $x$  is the fraction of O in that site. For the oxygens, charge imbalance is simply  $S - 2$ .

seen that if all the Ti is ordered into the  $M3$  sites, the maximum Ti occupancy of  $M3$  is  $x/2$ , because  $x/(2n + 1)$  is the fraction of Ti in the  $(2n + 1)$   $M$  sites and  $2/(2n + 1)$  is the fraction of  $M$  sites which are  $M3$  sites. The  $O_0$  oxygens are charge-balanced because they are not bonded to  $M3$ , the  $O_1$  oxygens are over-bonded by  $x/6$ , the  $O_2$ 's by  $2x/6$ , and the (F,OH,O) anions are always underbonded by  $4x/6$ . Figure 1b shows the imbalances for any of the hypothetical or-

dered humites; the proportions of  $O_0$ ,  $O_1$ ,  $O_2$  and (F,OH,O) anions per formula unit are listed in Table 2 for each of the structure types.

It is clear from Figure 1 that the more Ti, the greater the local charge imbalances, regardless of whether Ti is ordered or disordered in any of the homologues. Quite likely these imbalances place a practical upper limit on Ti substitution. Comparing the two graphs, it is also evident that charge balance is somewhat improved when Ti is ordered into  $M3$ , except for norbergite in which all anions are bonded to two  $M3$  sites. Thus one may argue that Ti prefers  $M3$  for reasons of charge balance, but it should also be observed that  $M3$  is always smaller than the other octahedra (even in the Mn-isotypes), although it has fewer shared edges than  $M1$  (see Table 2). This is in part explained by the fact that  $M3$  is bonded to two monovalent (F,OH) atoms when no Ti is present. Quadrivalent Ti ( $r \sim 0.61\text{\AA}$ ) is smaller than  $Mg^{2+}$  ( $r \sim 0.72\text{\AA}$ ) and the other  $M^{2+}$  cations found in humites, and quite likely prefers the  $M3$  site for that reason as well.

Thus the crystal-chemical arguments all point to an ordered distribution of  $Ti^{4+}$  in  $M3$ , the somewhat questionable least-squares site refinements (Robinson *et al.*, 1973a,b) notwithstanding. Probably the most compelling argument for  $Ti^{4+}$  order is that made by Fujino and Takéuchi (1978, p. 537-539). In addition to least-squares site refinements of Ti-Ch and Ti-Cl, which both converged with relatively

Table 2. Fraction of tetrahedral sites filled, number and types of octahedral sites (per formula unit), and number and types of oxygen atoms and (F,OH,O) sites (per unit cell) for the humite minerals and forsterite. In italics is listed the number of octahedral edges shared with other octahedra ( $o$ ) and with tetrahedra ( $t$ ).

$n$	$Z$	Mineral (symbol)	Fraction of tet'1 sites	Number of octahedral sites of type:*							Number of 4-coord. oxygens of type:			Number of (F,OH,O) III
				$M1_n$	$M1_c$	$M2_6$	$M2_5$	$M2_4$	$M3$	$O_0$	$O_1$	$O_2$		
1	4	Norbergite (No)	1/12					1	2				16	8
2	2	Chondrodite (Ch)	1/10		1		2		2	4	8	4	4	4
3	4	Humite (Hu)	3/28	2		1	2		2	30	12	6	8	8
4	2	Clinohumite (Cl)	1/9	2	1	2	2		2	20	8	4	4	4
$\infty$	4	Forsterite (Fo)	1/8		1	1				16			0	0
Shared oct'1 edges:				<i>4o,2t</i>	<i>4o,2t</i>	<i>2o,1t</i>	<i>2o,1t</i>	<i>2o,1t</i>	<i>3o,1t</i>					

\* Subscripts  $n$  and  $c$  in the  $M(1)O_6$  octahedra signify 1 and  $\bar{1}$  site symmetry, respectively. Subscripts 6, 5 and 4 refer to the number of ligands to the  $M2$  octahedra which are 4-coordinated oxygens, e.g.,  $M2_5 = M(2)O_5^{IV}(F,OH,O)_1^{III}$ . The  $M3$  octahedron has the "formula"  $M(3)O_4^{IV}(F,OH,O)_2^{III}$ .

large estimated standard errors ( $\pm 0.08$  Ti) to indicate all Ti in  $M3$ , they found that in these epitaxially intergrown specimens Ti–Ch had a Ti/Si ratio of 0.212, almost exactly twice as great as that in Ti–Cl (0.107). This is precisely the relationship expected if Ti is preferentially ordered into  $M3$  in both structures: the  $M3$ /Si ratio is 2 in chondrodite, 1 in clinohumite.

Epitaxial intergrowths such as the one reported by Tilley (1951), but more particularly those containing substantial Ti, should be carefully analyzed in the future for additional confirmation of these conclusions regarding the ordering of Ti.

### Fluorine and hydroxyl

Van Valkenburg (1961) synthesized F-end members of the humite series from melts and by solid-state reactions, but OH-end members have been synthesized only at high temperatures and pressures—OH–Ch and OH–Cl were found to be stable between 700–1000°C and 29–77 kbar (Yamamoto and Aki-moto, 1974, 1977). Duffy (1977) synthesized F–No, F–Ch and F–Cl and many intermediate (F,OH)–humites, sellaite ( $MgF_2$ ), and “intermediate sellaite,”  $MgFOH$ ,<sup>1</sup> as part of his investigation of the system  $MgO$ – $MgF_2$ – $SiO_2$ – $H_2O$ . He also calculated least-squares expressions for molar volumes as a function of composition for the phases of variable F–OH content in this system, and found that with the exception of brucite “all the volume functions are linear in composition. For sellaite and humites the difference in volume between the hydroxyl- and fluoro-end members is  $2.95 \pm 0.19 \text{ cm}^3 \text{ mol}^{-1}$  of  $(OH)_2$ ” (p. 6; see his Table VI, p. 51). Duffy also gives equations for variations of interplanar  $d$ -spacings with  $F \rightleftharpoons OH$  for sellaite (Sel), No, Ch, and Cl (his Table V, p. 50). His data and some of those listed in Tables 1 and 3 are used in the following more detailed discussion of the relative effects of  $F \rightleftharpoons OH$  and other substitutions on the unit-cell volumes of sellaite, the humites, and forsterite. In all these structures the octahedral sites in the hexagonal closest-packed anion array are half-filled with Mg, and to all intents and purposes the  $[SiO_4]$  tetrahedra (where present) are the same size (mean Si–O  $\sim 1.63$  Å) and each shares the same three edges with  $M$  octahedra. But the compositional vari-

ation from Sel  $\rightarrow$  No  $\rightarrow$  Ch  $\rightarrow$  Hu  $\rightarrow$  Cl  $\rightarrow$  Fo is more complex than just (F,OH) for O. The charge-balanced substitution is  $\square^{IV} + 4(F,OH)^{III} \rightarrow Si^{IV} + 4O^{IV}$ , where  $\square^{IV}$  is a tetrahedral void. The fraction of tetrahedral sites occupied by Si in the hcp array decreases from 1/8 in Fo to 1/12 in No to zero in Sel (see Fig. 2 and Table 2).

For the sake of comparing these structurally related compounds, Ribbe *et al.* (1968) suggested that it would be convenient to normalize unit-cell volumes to a reduced cell of volume  $V' = [abc \sin \alpha] \div q$ , where  $q$  is 4 for Fo, 6 for No, 5 for Ch, 14 for Hu, 9 for Cl. The parameter  $q$  was chosen to give a third dimension  $d_{(001)} \div q \sim 1.5$  Å, *i.e.*, approximately equal to the radius of an average anion in the hcp array. Another perhaps more physically useful volume term is  $V_A = V'/4$ , the volume per anion, from which may

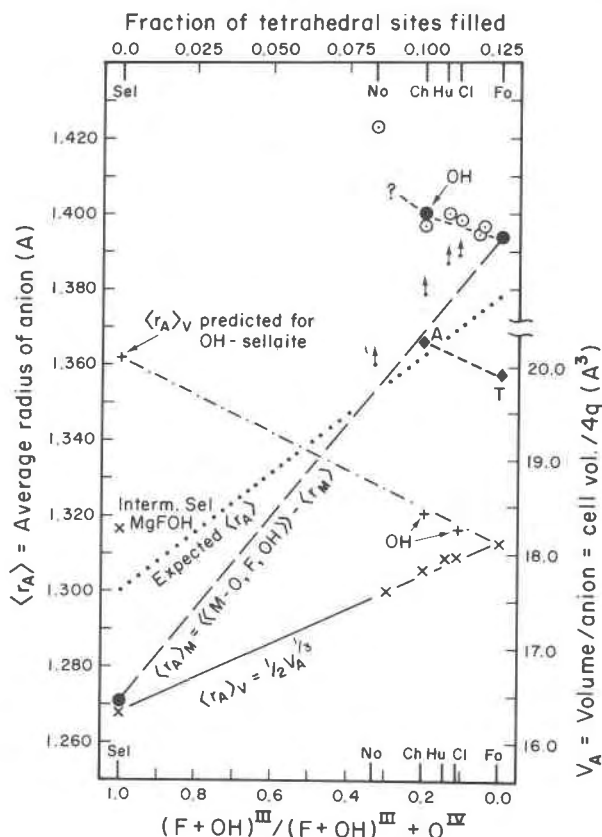


Fig. 2. The average radius of anions ( $r_A$ ) plotted against  $(F + OH)^{III}/[(F + OH)^{III} + O^{IV}]$  and the fraction of tetrahedral sites filled for the series of hcp compounds Sel  $\rightarrow$  No  $\rightarrow$  Ch  $\rightarrow$  Hu  $\rightarrow$  Cl  $\rightarrow$  Fo. A = alleghanyite, T = tephroite. Dots at the tails of arrows represent  $\langle r_A \rangle_M$  for natural Mg-equivalent homologues (Table 3) corrected for effects of  $M$  site substituents; arrows point to open circles which are values of  $\langle r_A \rangle_M$  predicted for OH-end members by simple proportionation.

<sup>1</sup> Tetragonal sellaite,  $MgF_2$ , has the hcp rutile structure (Baur, 1976):  $a = 4.6213$ ,  $c = 3.0519$  Å,  $V' = a^2c$ . “Intermediate sellaite,”  $MgFOH$ , is orthorhombic and is similar in two dimensions and  $c/q$  to the humites and olivine. Its cell parameters (Duffy, 1977) are  $a = 4.686$ ,  $b = 10.123$ ,  $c = 3.078$  Å;  $q = 2$  (see definition of  $q$  below).

be calculated a mean radius for the anion,  $\langle r_A \rangle_V = 0.5V_A^{1/3}$ , assuming  $V_A$  is a cube of dimensions  $2 \langle r_A \rangle_V$ .

#### Effective radii of F and OH

In Figure 2 there are three lines representing anion radii calculated in different ways (see Table 3); all are plotted against the ratio  $(F + OH)^{III}/[(F + OH)^{III} + O^{IV}]$ , which is of course related to the fraction of tetrahedral sites filled with Si (*cf.* upper and lower abscissas). The first is a line labelled "Expected  $\langle r_A \rangle$ ", which joins the 1.300A value for the radius of  $F^{III}$  and the 1.378A value for the radius of  $O^{IV}$  (Shannon and Prewitt, 1969), and assumes that a proportional mix of  $F^{III}$  and  $O^{IV}$  will produce the line  $\langle r_A \rangle = 1.378 - 0.078[F/(F + O)]$ . Of course there are no structures to which such a line may apply, but it serves as reference.

An effective "radius" of  $F^{III}$  in Sel was calculated by subtracting  $r_{Mg} = 0.72A$  from the grand mean Mg-F distance (1.988A; Baur, 1976), and an effective "radius" of  $O^{IV}$  in Fo was determined similarly using  $\langle (Mg-O) \rangle = 2.114A$  (Smyth and Hazen, 1973). Since the  $F^{III}/(F^{III} + O^{IV})$  ratio *decreases* and the fraction of filled tetrahedral sites *increases* linearly from left to right in Figure 2, one might expect that the dashed straight line,  $\langle r_A \rangle_M = 1.394 - 0.123[F/(F + O)]$ , joining Sel and Fo would contain points representing all the F-Mg-humite minerals. Unfortunately no structures of F-Mg-end members have been refined, but if the grand mean M-O,F,OH distances,  $\langle (M-O,F,OH) \rangle$ , minus the mean radii of the M cations,  $\langle r_M \rangle$ , are plotted (dotted tails of arrows) for each of the refined natural specimens, they all fall above the dashed line. This is mainly due to  $OH^{III}$  substituting for  $F^{III}$  in the hcp anion array. On that assumption values of  $\langle r_A \rangle_M$  (shown as centered circles) have been predicted for OH-end members by simple proportionation of the OH/(F + OH) ratios observed (Table 3) and the difference between observed radii and those expected for pure F-end members. This assumption is more fully supported in later discussion, but attention is called here to the fact that the line joining the  $\langle r_A \rangle_M$  values for Fo and OH-Ch is close to the predicted values for OH-end members (the point for No is subject to large errors due to the long extrapolation). Furthermore it becomes obvious that the net effect of OH substitution for F ( $r = 1.300A$ ) is to expand the structure as characterized by  $\langle (M-O,F,OH) \rangle$  rather more than expected based on the value of 1.35<sub>8</sub>A suggested by Yamamoto (1977) for the radius of  $OH^{III}$ , and much more than the 1.34A

value determined by Ribbe and Gibbs (1971, p. 1166). In fact, some simple arithmetic<sup>2</sup> using  $\langle r_A \rangle_M = 1.370A$  predicted for F-Ch and  $\langle r_A \rangle_M = 1.400$  observed for OH-Ch shows that the effective "radius" of  $OH^{III}$  must be 0.150A larger than  $F^{III}$ .

Consider now the third line,  $\langle r_A \rangle_V = 1.316 - 0.048[F/(F + O)]$ , near the bottom of Figure 2. Here the effective anion radius  $\langle r_A \rangle_V$  is calculated from  $V_A$ , the volume per anion:  $\langle r_A \rangle_V = 0.5V_A^{1/3}$ . This "radius" reflects not only changes in mean M-O,F,OH bond lengths but also the effects of  $Si^{IV}$  substituting for  $\square^{IV}$ , which are normally thought to be bypassed in the determination of an anion radius based strictly on M-O,F,OH bond-length considerations. Thus the effective "radius" of  $OH^{III}$  is 0.064, 0.075 and 0.097A larger than  $F^{III}$ , as calculated from  $\langle r_A \rangle_V$  values for the pairs F-Cl|OH-Cl, F-Ch|OH-Ch and F-Sel|FOH-Sel, taking into account the proportion of anions in each structure which are  $O^{IV}$ . The dash-dot line, representing the substitution  $\square^{IV} + 4OH^{III} \rightarrow Si^{IV} + 4O^{IV}$  joins a value of  $\langle r_A \rangle_V$  predicted for a hypothetical OH-Sel with that observed for Fo, passing near the observed values for OH-Ch and OH-Cl and having nearly the same slope (0.048 vs. 0.044) as the line A-T joining  $\langle r_A \rangle_V$  for OH-Mn-Ch (alleganyite) and  $\langle r_A \rangle_V$  for Mn-Fo (tephroite). Although the data base is small, this is certainly no coincidence. Furthermore the slopes of these lines are equal but opposite in sign to that representing the substitution  $\square^{IV} + 4F^{III} \rightarrow Si^{IV} + 4O^{IV}$ .

Just what value should be assigned to the radius of  $OH^{III}$  is something of a puzzle. If the effect of the  $\square \leftrightarrow Si$  substitution could be ignored, we would say the radius of  $OH^{III}$  would have to be as much larger than  $O^{IV}$  as  $F^{III}$  is smaller (*i.e.*,  $r_{OH} - r_F = 2 \times 0.078A$ ), but this is probably not the case, even though the  $\langle r_A \rangle_M$  calculations indicated a difference of  $2 \times 0.075A$ . Yamamoto (1977, p. 1483) noted that even the mean Mg-O distances in OH-Ch were slightly larger than corresponding ones in the F,OH-Ch refined by Gibbs *et al.* (1970), and he said "The replacement of F by OH causes an expansion of the whole anion array." A study of the *unoccupied* polyhedra in the humites would be most enlightening. Surely proton-proton interactions (see Fujino and Takéuchi, 1978, Fig. 3) serve to expand the structures of OH-rich humites considerably more than is indicated by comparing M-O,F,OH bond lengths. Perhaps that ex-

<sup>2</sup> Since 80% of the M-O,F,OH bonds in Ch are to  $O^{VI}$ ,  $0.8r_O + 0.2r_F = 1.370A$  and  $0.8r_O + 0.2r_{OH} = 1.400A$ . Subtracting the two equations gives  $r_{OH} - r_F = 0.030/0.2 = 0.15A$ .

Table 3. Numbers and ratios of three-coordinated anions in synthetic and natural humites, forsterite, sellaite, and brucite together with normalized volumes,  $V'$ , corrections to volume due to transition metal content,  $\Delta V' = [(r_M) - r_{M_0}]V'/r_{M_0}$ , and calculated densities.

Name, $q$ , reference*	Symbols, Fig. 3	No. of F	3-coord. OH	anions $O_{Ti}$	$F+0.5 O_{Ti}$ $F+OH+O_{Ti}$	$(F+OH)^{III}$ $(F+OH)^{III}+O^{IV}$	$V' (A^3)$	$\Delta V' (A^3)$	Calc'd density
Norbergite $q = 6$	1.0 ●	2.00			1.00	0.33	70.25		3.199
	0.9 ●	1.80	0.20		0.90		70.56		
	0.7 ●	1.40	0.60		0.70		71.19		
	V ○	2.00			1.00		70.37		
	1 ○	1.81	0.17	0.02	0.91		70.54	0.00	
Chondrodite $q = 5$	1.0 ⊙	2.00			1.00	0.20	71.23		3.205
	1.0 ⊙	2.00			1.00		71.27		
	0.8 ⊙	1.60	0.40		0.80		71.68		
	0.8 ⊙	1.60	0.40		0.80		71.67		
	0.7 ⊙	1.40	0.60		0.70		71.82		
	0.6 ⊙	1.20	0.80		0.60		72.14		
	2 ⊕	1.27	0.73	0.00	0.63		71.86	-0.03	
	9 ⊕	1.86	0.11	0.03	0.94		71.50	-0.10	
(OH-Ch) (Ti-Ch)	Y ⊕ F&T ⊕	1.06	0.90	0.04	0.54	0.20	72.24	-0.22	
			2.00		0.00		73.74		3.060
		0.00	1.11	0.89	0.22		72.76	+0.17	
Humite $q = 14$	V □	2.00			1.00	0.14	71.78		
	3 □	0.84	0.80	0.36	0.51		72.40	0.00	
	7 □	1.06	0.93	0.01	0.53		72.44	-0.22	
Clinohumite $q = 9$	1.0 ▲	2.00			1.00	0.11	71.83		3.211
	0.5 ▲	1.00	1.00		0.50		72.36		
	0.4 ▲	0.80	1.20		0.40		72.44		
	7 ▲	1.04	0.92	0.04	0.53		72.52	-0.29	
	(OH-Cl) (Ti-Cl)	Y&A ▲ K&R ▲		2.00		0.00	0.11	73.02	
		0.42	1.05	0.53	0.34		73.08	-0.45	
		0.00	1.05	0.95	0.24		72.98	-0.12	
	F&T ▲	0.00	1.10	0.90	0.22		72.89	-0.16	
Forsterite, $Mg_2SiO_4$ (Yoder and Sahama, 1957)						$q = 4$	0.00	72.50	3.222
Sellaite, $MgF_2$ (Duffey, 1977)						$q = 1$	1.00	65.18	3.174
$MgOHF$ (Duffey, 1977)						$q = 2$	1.00	73.10	2.743
$Mg(OH)_2$ hypothetical						$q = 1$	1.00	81.03	2.312
Brucite, $Mg(OH)_2$							1.00	47.22	2.051

\* Specimen numbers with decimals were synthesized by Duffey (1977):  $0.9 \equiv nMg_2SiO_4 \cdot Mg(F, 9OH, 1)_2$ . Those with integral numbers are from Jones *et al.* (1969), V = Van Valkenburg (1961), Y = Yamamoto (1977), F&T = Fujino and Takéuchi (1978), Y&A = Yamamoto and Akimoto (1977), and K&R = Kocman and Rucklidge (1973).

plains why OH-No, which would have an abundance of both shared and unshared OH...OH octahedral edges, has not yet been synthesized and may be unstable except at very high pressures (>150 kbar?). Fujino and Takéuchi (1978, p. 541-542) make a strong argument for H...H repulsion as the cause of structural instability and suggest that "under a F-free condition, OH-Ch and OH-Cl appear to be stabilized through incorporation of Ti in place of Mg." Obviously it is the concomitant substitution of  $O_{Ti}$  for OH that "stabilizes" the structure, because Ti itself "destabilizes" the structure by increasing local electrostatic charge imbalance (Fig. 1).

#### Unit-cell volumes and ionic radii

Using the normalized volumes  $V'$ , corrected by an amount  $\Delta V'$  to account for differences in the mean

octahedral cation radius from one structure to the next, all the humite minerals may be systematized according to the average occupancy of the 3-coordinated (F,OH, $O_{Ti}$ ) site. Pertinent data are compiled in Table 3 and plotted in Figure 3, where curves have been drawn through the points representing synthetic specimens. Because the substitution of Ti into  $M3$  is accompanied by a charge-balancing substitution of  $O_{Ti}^{III}$  for  $(F,OH)^{III}$ ,  $O_{Ti}$  had to be apportioned properly based on its effective ionic radius in order to model the volume relationships established in Figure 3. Since there is a great deal of uncertainty about anion radii in any case, it was guessed that  $O^{III}$  ( $r = 1.357 \pm 0.010A$ ; Shannon and Prewitt, 1969) is somewhere nearly half as much larger than  $F^{III}$  ( $r = 1.300 \pm 0.012A$ ), as  $OH^{III}$  is ( $1.36 < r < 1.45A$ , depending on how it is calculated—see previous para-

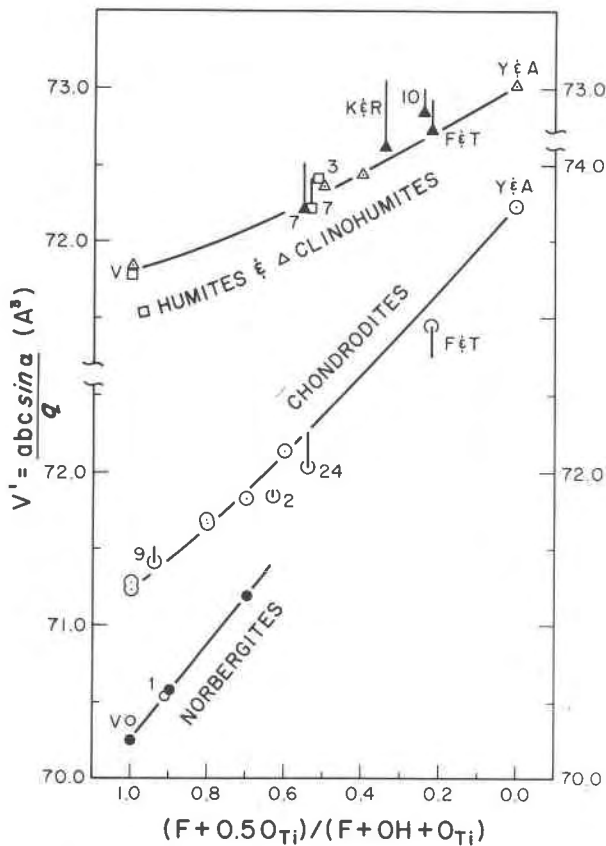


Fig. 3. A plot of normalized cell volumes,  $V' = \text{Vol} + q$  vs.  $(F + 0.5 O_{\text{Ti}})/(F + OH + O_{\text{Ti}})$ . Tails of vertical lines represent data points uncorrected for the deviation of  $\langle r_{\text{M}} \rangle$  from 0.72A, the radius of  $\text{Mg}^{2+}$ . Symbols and labels are listed in Table 3.

graphs). So the abscissa is labelled  $(F + 0.5O_{\text{Ti}})/(F + OH + O_{\text{Ti}})$ , and this scheme is apparently successful. Only five of the 27 humite specimens listed in Table 3 have sufficient Ti to be significantly affected.

Several observations on Figure 3 are pertinent. (1) The humites and clinohumites are apparently indistinguishable in this sort of plot, although there are no synthetic humites other than the F-end member to test this observation. (2) The approximate slopes of the lines vary from  $-3.5$  for No to  $-2.25$  for Ch to  $-1.2$  for Hu-Cl, suggesting that the relative effect of  $\text{OH}^{\text{III}}$  on the normalized volume increases with the proportion of OH in the total  $(F, \text{OH}, \text{O})^{\text{III}}\text{O}^{\text{IV}}$  anion array. This lends further support to the idea that increasing numbers of proton-proton interactions in the "unoccupied" polyhedra decrease the stability of the humite homologues, accounting for the extremely high pressures required to synthesize OH-Ch and OH-Cl and for the fact that OH-No has not yet been made.

## Effects of $F \rightleftharpoons \text{OH}$ on physical properties

### Optical properties

Misplaced emphasis upon the isolated  $[\text{SiO}_4]$  tetrahedron as the key structural unit in orthosilicates has diverted attention from the fact that most orthosilicates have prismatic habits and cleavage and are for the most part optically positive (Ribbe, 1976). The Mg-humites are optically positive because in all of them serrated edge-sharing octahedral chains are in fact the dominant structural units.

Sahama (1953) calculated mean refractive indices,  $\langle \text{R.I.} \rangle = (\alpha\beta\gamma)^{1/3}$  or  $(\omega^2\epsilon)^{1/3}$ , for the F- and OH-members of the humites based on molar refractivity, plotting them against  $1/(n+1)$ , with the end members being Fo ( $n = \infty$ ) and the F- and OH-sellaite ( $n = 0$ ),  $\text{MgF}_2$  and  $\text{Mg}(\text{OH})_2$  (hypothetical). His curves (*cf.* Deer *et al.*, 1962, p. 55, Fig. 18) become essentially straight lines when the data are plotted against  $(F, \text{OH})/[(F, \text{OH}) + \text{O}]$ , as in Figure 4. Refractive indices of the F-series (Van Valkenburg, 1955) and OH-CH and OH-Cl (Yamamoto and Akimoto, 1974, 1977) are represented by +'s in Figure 4, and they fall very close to Sahama's calculated values. The effect of substituting Fe + Mn for Mg is to increase  $\langle \text{R.I.} \rangle$  by  $\sim 0.02$  per mol % Fe + Mn; Ti is expected to have a somewhat greater effect. But of course  $\text{OH} \rightarrow \text{F}$  and  $\text{O}_{\text{Ti}} \rightarrow \text{F}$  also affect  $\langle \text{R.I.} \rangle$  and  $2V$ , leading to the conclusion that, except for norbergite, which is generally very F-rich and Fe- and Ti-poor, naturally occurring members of the homologous series cannot be distinguished on the basis of refractive indices or  $2V$  (Sahama, 1953; Deer *et al.*, 1962).<sup>3</sup>

### Density

Densities of the F- and OH-series Sel  $\rightarrow$  No  $\rightarrow$  Ch  $\rightarrow$  Hu  $\rightarrow$  Cl  $\rightarrow$  Fo (and brucite for comparison) were calculated from Mg-end member chemistries and unit-cell volumes (see Table 3:  $\text{Vol.} = V' \times q$ ). In Figure 4 the F-humites are barely distinguishable, but OH has a profound effect on molar volume, as noted earlier (*cf.* Fig. 2). Counteracting effects of heavier transition metals substituting for Mg and

<sup>3</sup>Sahama (1953) showed that only the extinction angle  $c:\alpha$  on (100) [axial convention as in Jones (1969)] could be used to differentiate between chondrodite ( $22^\circ\text{--}31^\circ$ ) and clinohumite ( $9^\circ\text{--}15^\circ$ ), and thus of course distinguish the monoclinic phases from their orthorhombic homologues. These extinction angles reflect the angle between  $c^*$  and the serrated octahedral chains parallel to  $c$ :  $\sim 19^\circ$  in chondrodite,  $\sim 11^\circ$  in clinohumite.

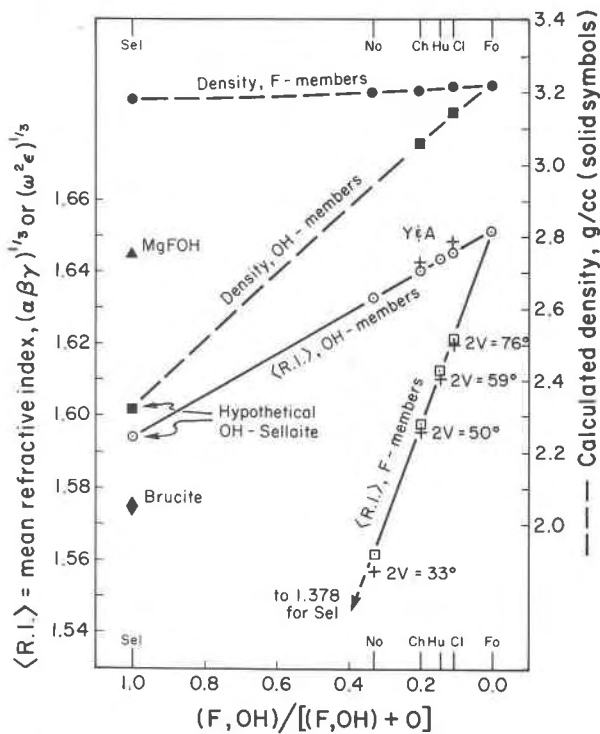


Fig. 4. Calculated densities and mean refractive indices of the F- and OH-series of synthetic compounds, Sel  $\rightarrow$  No  $\rightarrow$  Ch  $\rightarrow$  Hu  $\rightarrow$  Cl  $\rightarrow$  Fo. Volume data used in density calculations are from Table 3; refractive indices from Sahama (1953), and observed values (+) for F-humites from Van Valkenburg (1955) and for OH-Ch and OH-Cl from Yamamoto and Akimoto (1974, 1977).

larger OH (and  $O_{Ti}$ ) substituting for F lead to the conclusion that density, much like refractive indices, is useless as a determinative method. X-ray diffractometry and electron probe microanalysis are obviously the most reliable techniques for identifying and characterizing humite minerals.

### Conclusions

All crystal-chemical arguments and most chemical and X-ray data point to an ordered distribution of Ti into the  $M3$  site in the  $M(F,OH)O$  "layers" of all the humite structures. The limited substitution ( $x < 0.5$ ) of  $Ti + O \rightarrow M^{2+} + (F,OH)$  is explicable on the basis of the fact that local electrostatic charge imbalance increases significantly with increasing  $Ti + O$ .

From  $M-OH$ , F bond lengths,  $OH^{III}$  is found to be  $\sim 0.06\text{\AA}$  larger in its effective radius than  $F^{III}$  (Yamamoto, 1977). But as  $n$  goes from 4 to zero in the OH humite-sellaite series or from (say) F-Ch to OH-Ch, it can only be the increase in proton-proton repulsion in the unoccupied polyhedra in the hcp anion array that explains the large increase in volume per

anion and decrease in density that is observed. This repulsion explains the high pressure stability field for the OH-humites and the fact that OH-norbergite has not yet been synthesized.

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### References

- Aoki, K., K. Fujino and M. Akaogi (1976) Titanochondrodite and titanoclinohumite derived from the upper mantle in the Buell Park kimberlite, Arizona, U.S.A. *Contrib. Mineral. Petrol.*, **56**, 243-253.
- Baur, W. H. (1976) Rutile-type compounds. V. Refinement of  $MnO_2$  and  $MgF_2$ . *Acta Crystallogr.*, **B32**, 2200-2204.
- Deer, W. A., R. A. Howie and J. Zussman (1962) *Rock-forming Minerals, Vol. 1: Ortho and Ring Silicates*. Wiley, New York.
- Duffy, C. J. (1977) *Phase Equilibria in the System  $MgO-MgF_2-SiO_2-H_2O$* . Ph.D. Dissertation, University of British Columbia, Vancouver, B.C., Canada.
- Fujino, K. and Y. Takéuchi (1978) Crystal chemistry of titanian chondrodite and titanian clinohumite of high-pressure origin. *Am. Mineral.*, **63**, 535-543.
- Gibbs, G. V., P. H. Ribbe and C. W. Anderson (1970) The crystal structures of the humite minerals. II. Chondrodite. *Am. Mineral.*, **55**, 1182-1194.
- Jones, N. W. (1969) Crystallographic nomenclature and twinning in the humite minerals. *Am. Mineral.*, **54**, 309-313.
- , P. H. Ribbe and G. V. Gibbs (1969) Crystal chemistry of the humite minerals. *Am. Mineral.*, **54**, 391-411.
- Kocman, V. and J. Rucklidge (1973) The crystal structure of a titaniferous clinohumite. *Can. Mineral.*, **12**, 39-45.
- McGetchin, T. R., L. T. Silver and A. A. Chodos (1970) Titanoclinohumite: a possible mineralogical site for water in the upper mantle. *J. Geophys. Res.*, **75**, 255-259.
- Merrill, R. B., J. K. Robertson and P. J. Wyllie (1972) Dehydration reaction of titanoclinohumite: reconnaissance to 30 kilobars. *Earth Planet. Sci. Lett.*, **14**, 259-262.
- Mitchell, R. H. (1978) Manganoan magnesian ilmenite and titanian clinohumite from the Jacupiranga carbonatite, São Paulo, Brazil. *Am. Mineral.*, **63**, 544-547.
- Ribbe, P. H. (1976) Polyhedral chains in the structures of gem orthosilicates: relationships to physical properties. *25th Int. Geol. Congr. Abstracts*, **2**, 593-594.
- and G. V. Gibbs (1971) Crystal structures of the humite minerals: III. Mg/Fe ordering in humite and its relation to other ferromagnesian silicates. *Am. Mineral.*, **56**, 1155-1173.
- , ——— and N. W. Jones (1968) Cation and anion substitutions in the humite minerals. *Mineral. Mag.*, **37**, 966-975.
- Robinson, K., G. V. Gibbs and P. H. Ribbe (1973a) The crystal structures of the humite minerals. IV. Clinohumite and titanoclinohumite. *Am. Mineral.*, **58**, 43-49.
- , ——— and ——— (1973b) Correction: The crystal struc-



- tures of the humite minerals. IV. Clinohumite and titanoclinohumite. *Am. Mineral.*, 58, 346.
- Sahama, Th.G. (1953) Mineralogy of the humite group. *Ann. Acad. Sci. Fennicae, III. Geol. Geogr.*, 31, 1-50.
- Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, B25, 925-946.
- Smyth, J. R. and R. M. Hazen (1973) The crystal structures of forsterite and hortonolite at several temperatures up to 900°C. *Am. Mineral.*, 58, 588-593.
- Tilley, C. E. (1951) The zoned contact-skarns of the Broadford area, Skye: a study of boron-fluorine metasomatism in dolomites. *Mineral. Mag.*, 29, 621-665.
- Van Valkenburg, A. (1955) Synthesis of the humites (abstr.). *Am. Mineral.*, 40, 339.
- (1961) Synthesis of the humites  $n\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{F},\text{OH})_2$ . *J. Res. Nat. Bur. Stand., A. Phys. Chem.*, 65A, 415-428.
- Yamamoto, K. (1977) Hydroxyl-chondrodite. *Acta Crystallogr.*, B33, 1481-1485.
- and S. Akimoto (1974) High pressure and high temperature investigations in the system  $\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}$ . *J. Solid State Chem.*, 9, 187-195.
- and ——— (1977) The system  $\text{MgO}-\text{H}_2\text{O}-\text{SiO}_2$  at high pressures and temperatures—stability field for hydroxyl-chondrodite, hydroxyl-clinohumite and 10A-phase. *Am. J. Sci.*, 277, 288-312.

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