Cation and anion substitutions in the humite minerals

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Summary. The humites are structurally analogous to olivine wherein the replacement of four oxygen by four (F,OH) anions in the slightly distorted, hexagonal close-packed array is balanced by the replacement of one tetrahedrally coordinated Si by a tetrahedral void, according to the general formula $Mg_{2x}Si_{x-1}O_{4x-4}(F,OH)_4$ where $x = 3, 5, 7, 9$. In humites the key structural units are not 'olivine and sellaite (or brucite) layers', as previously assumed, but are zigzag chains of edge-sharing octahedra, just as in olivines. It is shown that for humites and olivines alike the unit cell parameters a, b, and d_{001}/n and the cell volume (normalized to one-half the mean anion–anion distance along the normal to (001)) vary linearly with the average radius of the octahedrally coordinated cation in the chain.

Substitutions of (F,OH) for O and vacancies for Si have second-order effects on the unit cell parameters, causing a linear decrease of the normalized cell volume with increase in F/O ratio in the synthetic series forsterite–humite–norbergite. Comparison of the crystal structures of forsterite and norbergite shows that the polyhedral distortions in norbergite are smaller than in forsterite in accord with the decreased number of shared edges: the fluorines in norbergite are bonded to three Mg atoms whereas all anions in forsterite are bonded to three Mg and one Si atom.

TAYLOR and West (1928, 1929), recognizing similarities in the X-ray diffraction patterns of the humites and olivine, proposed structures for norbergite, chondrodite, humite, and clinohumite based on a hexagonal close-packed array of anions (O,F,OH) within which Mg is in octahedral and Si in tetrahedral coordination. From charge balance considerations it was assumed that the (F,OH) anions are bonded to three Mg, whereas O, as in olivine, is bonded to one Si and three Mg cations. They interpreted the compositional and crystallographic relationships of the humites in terms of different stacking sequences of layers of $Mg(F,OH)_2$ and Mg_2SiO_4 composition. For example: norbergite was described as the stacking sequence one layer

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Mg_2SiO_4 and one layer $Mg(F,OH)_2$, chondrodite as two layers Mg_2SiO_4 and one layer $Mg(F,OH)_2$, etc.

A recent structure analysis of norbergite (Gibbs and Ribbe, 1968) has confirmed that Taylor and West's idealized drawings of the humite structures are correct. However, their description of the structures as alternating layers of $Mg(F,OH)_2$ and Mg_2SiO_4 composition is misleading, because the 'unit blocks' delineated in their drawings (cf. Fig. 122, Bragg and Claringbull, 1965) do not have these compositions; the compositions are in fact $Mg(F,OH)O$ and $Mg_2SiO_3(F,OH)$.

Taylor and West's incorrect statement of the composition of the '$Mg(F,OH)_2$ layer' has led several workers to attach a *structural* significance to the layer based on its composition; e.g. Rankama (1947) states that 'In case of humite minerals . . . 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-Starynkevich and Myasnikov (1950) analysed fluorine-deficient clinohumites, and assumed the layer to be $Mg(OH)_2$, which they said possessed the brucite structure. Sahama (1953) recognized the error in their statement, yet in referring to the layer as 'sellaite' (MgF_2), he implies that the layer has the rutile structure. More recently the humite minerals were described by Deer *et al.* (1962) as alternating layers of forsterite and brucite–sellaite composition and by Bradshaw and Leake (1964) as layers of Mg_2SiO_4 and $Mg(OH,F)_2$–TiO_2. None of these interpretations is correct, because in none of the humite minerals are the (F,OH) anions suitably arranged to form contiguous structural units of brucite *or* sellaite (see fig. 1). Therefore, Christie's (1965) statement '. . . that norbergite is constructed of a rigid oxygen–sellaite framework' is likewise incorrect.

Structural comparison of olivine and the humites

Both forsterite and the humite structures are based on a hexagonal close-packed array of anions with one-half the available octahedral sites filled. It is presumed that the (F,OH) atoms in the humites are ordered within the close-packed assembly to maintain local charge balance. If each (F,OH) is coordinated by three divalent cations and if Pauling's (1929) electrostatic valence rule is satisfied, then no Si atoms can be bonded to (F,OH) (Taylor and West, 1928; confirmed by Gibbs and Ribbe, 1968; see fig. 1). Consequently none of the available tetrahedral sites coordinated by one or more (F,OH) anions in the close-packed assembly is occupied by an Si atom. This indicates that the humites are structurally analogous to olivine wherein the replacement of four O by four (F,OH) in the close-packed array is balanced by the replacement of one tetrahedrally coordinated Si by a tetrahedral void, according to the general formula $Mg_{2x}Si_{x-1}O_{4x-4}(F,OH)_4$ where $x = 3, 5, 7$, and 9 for norbergite, chondrodite, humite, and clinohumite, respectively. Recent structure analyses of olivine (Birle *et al.*, 1968) indicated '. . . 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 ($r = 0{\cdot}66$ Å) by Fe ($r = 0{\cdot}74$ Å).

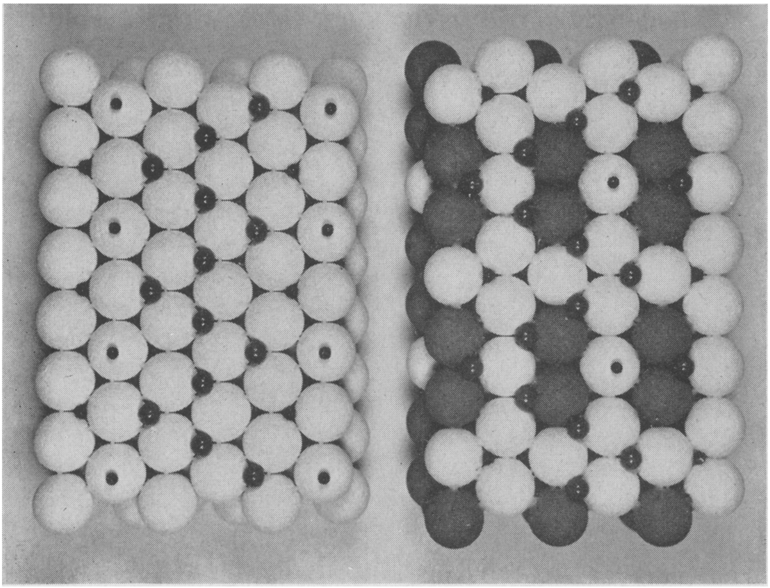

FIG. 1. Models of forsterite (left) and norbergite (right) showing the close-packed anion layer (large spheres—white, oxygen; grey, F or OH), chains of octahedrally coordinated cations (medium-sized spheres) and the location of tetrahedrally coordinated Si (small spheres).

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 (fig. 2). 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 indicated above) the humite structures are indeed analogous to olivine, then it follows that the key structural units in humites are also zigzag octahedral chains. Fig. 3 compares the nature of the chains in olivine with those in clinohumite, humite, chondrodite, and norbergite (see also fig. 1). 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 a, b, d_{001}/n, and V' parameters of forsterite and the four Mg-humites (table I). Notice also the marked similarity of the Ca-members, γ-Ca_2SiO_4 and calcio-chrondrodite, and the Mn-members, tephroite and alleghanyite. It is apparent, then, that the effects of specific cation substitutions are the same in both olivine structures and in chemically analogous humites.

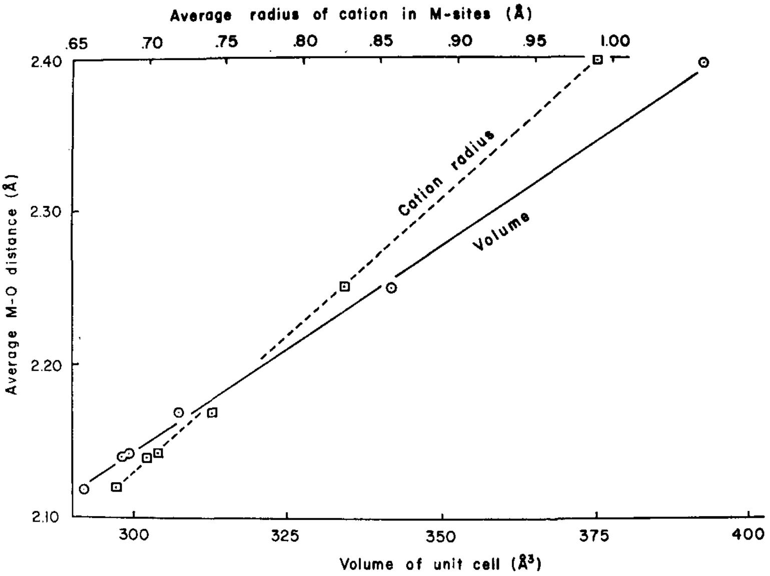

FIG. 2. The relationship of the average cation–oxygen (M–O) distance to the average radius of the cation in the M-site and to the unit cell volume in olivine structures. The first four data points are from Birle *et al.* (1968), the fifth from Onken (1965), and the sixth (at $r = 0{\cdot}99$ Å) from Smith *et al.* (1965).

It was demonstrated in fig. 2 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 expected to hold for them as well. Fig. 4, a composite plot of the unit cell volume (normalized to one-half the mean anion–anion distance along the normal to (001)) versus mean radius of the octahedral cations of olivines 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 % confidence band calculated for *all* data, excluding those of Christie (1965) which are indicated by × s. It is apparent from this treatment of the data that the structural principles governing olivine

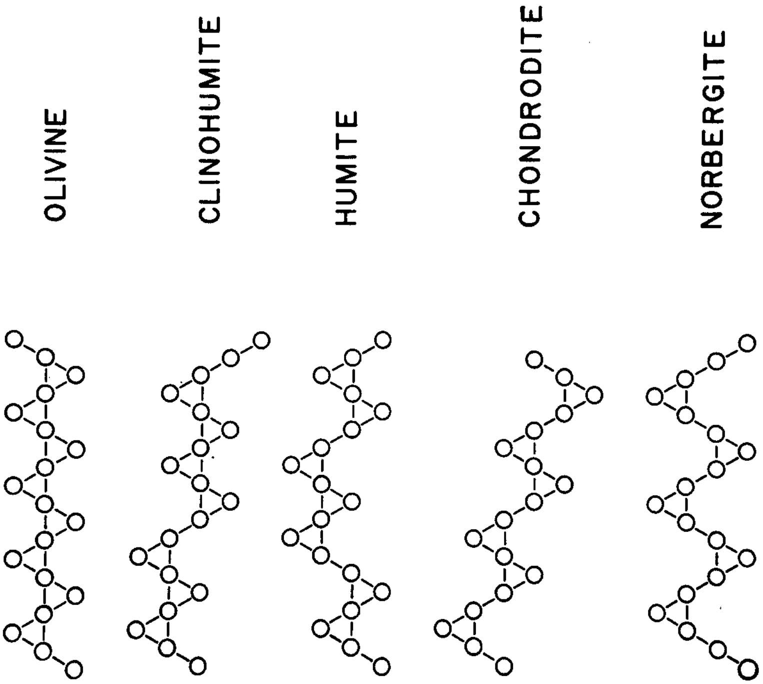

Fig. 3. Schematic representations of the serrated octahedral chains in olivine, clinohumite, humite, chondrondite, and norbergite (cf. fig. 1). The circles are octahedral cations in the (001) plane, which is the plane of the hexagonal close-packed anion layer.

TABLE I

Formula, mineral name, (reference)	a(Å)	b(Å)	c(Å)	d_{001}(Å)	V'(Å^3)	*Average cation radius**
Mg_2SiO_4 forsterite (1)	4·756	10·195	5·981	4×1·495	72·49	0·66
$Mg_9Si_4O_{16}(OH, F)_2$ clinohumite (2)	4·745	10·27	13·68	9×1·492	72·71	0·66
$Mg_7Si_3O_{12}F_2$ humite (3)	4·735	10·243	20·72	14×1·480	71·78	0·66
$Mg_5Si_2O_8(OH, F)_2$ chondrodite (2)	4·733	10·27	7·87	5×1·488	72·33	0·66
$Mg_3SiO_4F_2$ norbergite (3)	4·709	10·271	8·727	6×1·455	70·37	0·66
$(Mg_{0\cdot535}Fe_{0\cdot456}Mn_{0\cdot006}Ca_{0\cdot002})_2SiO_4$ hyalosiderite (4)	4·785	10·325	6·038	4×1·510	74·58	0·696
$(Mg_{0\cdot49}Fe_{0\cdot49}Mn_{0\cdot01}Ca_{0\cdot01})_2SiO_4$ hortonolite (4)	4·787	10·341	6·044	4×1·511	74·80	0·704
Fe_2SiO_4 fayalite (1)	4·817	10·477	6·105	4×1·526	77·01	0·74
$(Mn_{0\cdot63}Mg_{0\cdot37})_7Si_3O_{12}(OH)_2$ leucophoenicite (5)	4·82	10·42	21·37	14×1·526	76·64	0·74
$(Fe_{0\cdot826}Mn_{0\cdot145}Mg_{0\cdot029})_2SiO_4$ knebelite (6)	4·834	10·518	6·11	4×1·528	77·69	0·75
$(Fe_{0\cdot575}Mn_{0\cdot354}Mg_{0\cdot071})_2SiO_4$ knebelite (6)	4·843	10·556	6·133	4×1·533	78·37	0·76
$(Fe_{0\cdot453}Mn_{0\cdot510}Mg_{0\cdot037})_2SiO_4$ knebelite (6)	4·854	10·602	6·162	4×1·541	79·30	0·78
Mn_2SiO_4 tephroite (7)	4·871	10·636	6·232	4×1·558	80·72	0·80
$Mn_5Si_2O_8(OH, F)_2$ alleghanyite (8)	4·94	10·55	8·24	5×1·557	81·15	0·80
$(Mn_{0\cdot9}Ca_{0\cdot1})_7Si_3O_{12}(OH)_2$ *m*–leucophoenicite (5)	4·845	10·78	45·18	28×1·614	84·30	0·82
$CaMgSiO_4$ monticellite (9)	4·822	11·108	6·382	4×1·596	85·49	0·825
$CaMnSiO_4$ glaucochroite (10)	4·944	11·19	6·529	4×1·632	90·29	0·895
Ca_2SiO_4 γ–Ca_2SiO_4 (11)	5·091	11·371	6·782	4×1·695	98·15	0·99
$Ca_5Si_2O_8(OH)_2$ calcio-chondrodite (12)	5·05	11·42	8·94	5×1·688	97·35	0·99

$V' = a \times b \times d_{001}/n$ 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.

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2. Taylor and West (1929).
3. Van Valkenburg (1961).
4. Birle *et al.* (1968).
5. Moore (1967 and priv. comm.).
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12. Buckle and Taylor (1958).

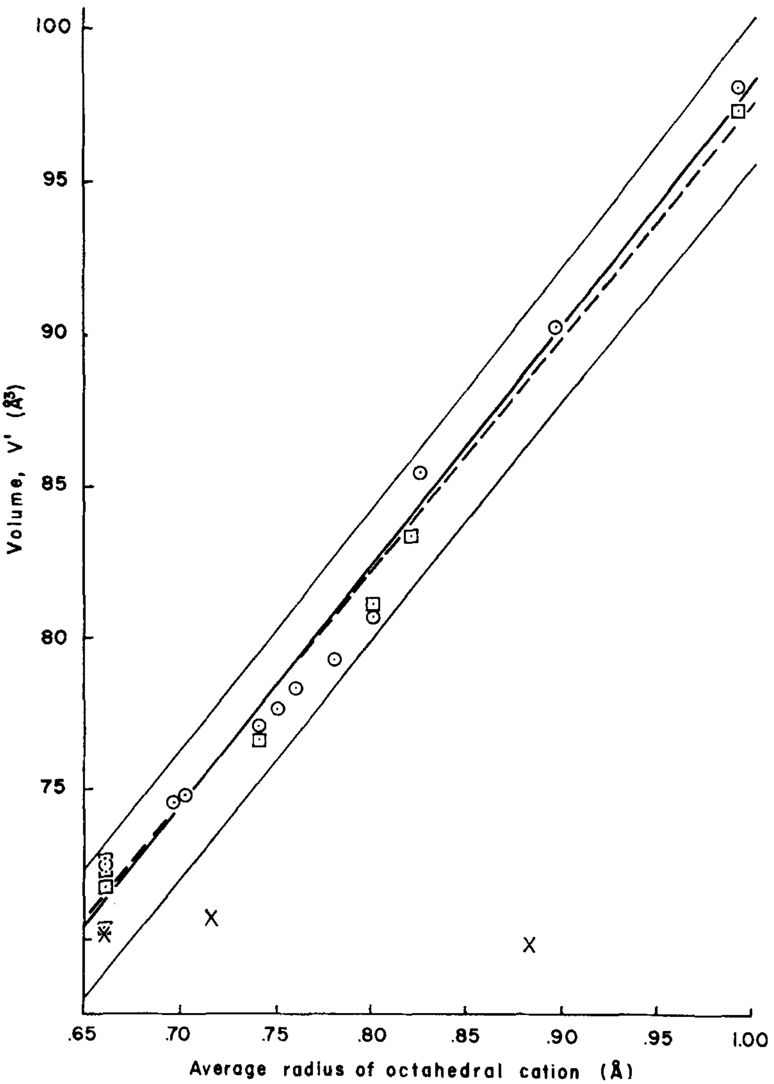

FIG. 4. The relationship of the average radius of the octahedral cation to the normalized cell volume V' for both humites (squares) and olivines (circles) (see table I). Linear regression analyses produced the heavy solid line-of-best-fit for olivines and the dashed line for humites. The curved lines bracket the 95 % confidence interval for both sets of data taken together. Crosses represent V' calculated from Christie's (1965) cell parameters for the compounds $Mg_2SiO_4.MgF_2$, $Zn_2SiO_4.MgF_2$ and $Ca_2SiO_4.MgF_2$.

and humite structures must be 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 $Mg_2SiO_4.MgF_2$, $Zn_2SiO_4.MgF_2$ and $Ca_2SiO_4.MgF_2$ (×s in fig. 4) which Christie (1965) claims to have synthesized, are the same as the norbergite cell parameters presents an unexplained inconsistency with the proven relationship between mean radius of the octahedral cation and the normalized volume. These data clearly require further investigation.

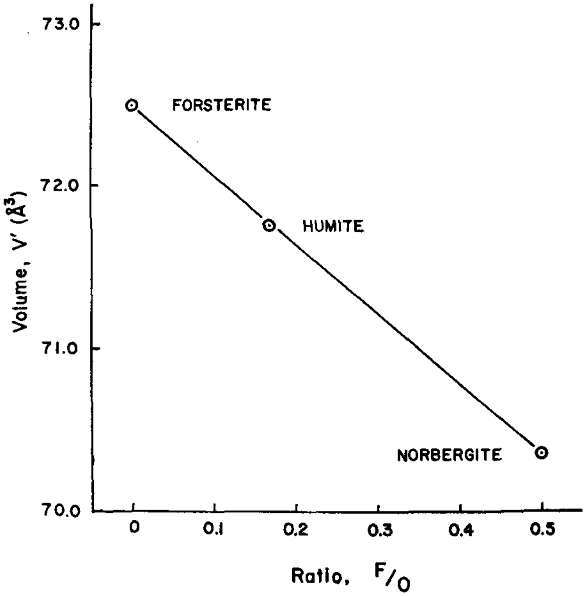

FIG. 5. The normalized cell volume V' for synthetic Mg_2SiO_4, $Mg_7Si_3O_{12}F_2$ and $Mg_3SiO_4F_2$ plotted as a function of the F/O ratio (≡ tetrahedral-void/Si ratio).

The substitutions of (F,OH) for O and vacancies for Si have second-order effects on the cell parameters. Fig. 5 shows that for synthetic forsterite, humite, and norbergite, the normalized volume decreases linearly with increased F/O ratio (≡ tetrahedral-void/Si ratio). This is primarily due to the substitution of smaller F for O. A secondary effect on the volume is the decrease in polyhedral distortions due to the increased substitution of tetrahedral voids for tetrahedrally coordinated Si and the concomitant decrease in the number of shared polyhedral edges. Presumably the decreases in the distortions of octahedra and tetrahedra permit a more efficient packing of anions, thereby decreasing the normalized volume from forsterite to humite to norbergite. These conclusions are based on data from a refinement of the structure of norbergite by Gibbs and Ribbe (1968).

Further study

Of particular interest for further study are humites that show substantial replacements Mg $\rightleftarrows$ Fe and Ti+2(O) $\rightleftarrows$ Mg+2(F,OH). On the basis of stoichiometric calculations Borneman-Starynkevich and Myasnikov (1950) concluded that the replacement of Mg by Fe takes place in the 'olivine portion' of the structure and not in the '(F,OH) portion'. Sahama (1953) doubts the validity of this conclusion from thermodynamic considerations and implies that Mg and Fe are probably disordered because of their similar size and charge. In this connexion it is of interest that crystal-structure analyses of hortonolite from a hypabyssal dike and of hyalosiderite from a plutonic environment show no evidence of long-range order of Mg and Fe (Birle *et al.*, 1968); this has been confirmed by Mössbauer spectroscopy (Bancroft and Burns, 1968). Since, as shown above, the humite structures are analogous to olivine, Mg, Fe ordering in humites is not anticipated.

The substitution Ti+2(O) $\rightleftarrows$ Mg+2(F,OH) was found by Borneman-Starynkevich and Myasnikov (1950) in several clinohumites from Achmatovsk, Russia (cf. Jones *et al.*, 1967). Their most Ti-rich specimen has the formula $(Mg,Fe)_{8\cdot6}Ti_{0\cdot4}(SiO_4)_4OH_{1\cdot11}F_{0\cdot02}O_{0\cdot87}$. Notice that the coupled substitution is of the form $(Mg,Fe)_{9-y}Ti_y(SiO_4)_4(OH,F)_{2-2y}O_{2y}$, where $y < 1$. This implies that the substitution is *not* of the form Ti+vacancy $\rightleftarrows$ 2Mg. For every Ti introduced there are two oxygens replacing two fluorine atoms to maintain electrostatic neutrality and hexagonal close-packing of the anions. Since the replaced fluorines were not bonded to Si, it follows that the replacing oxygens will not be bonded to Si. This assumption is consistent with Pauling's rules (1929) and further suggests that Ti is ordered in the Mg(OH,F)O region of the structure. A structure analysis of a Ti-rich clinohumite will establish whether Ti is ordered in the Mg(OH)O region of the structure and perhaps explain why there is almost no F in any of the humite minerals with 0·5 Ti atoms per formula unit and why these specimens invariably adopt the clinohumite structure. The effect of Ti+2(O) $\rightleftarrows$ Mg+2(F,OH) on the cell parameters is currently being investigated (Jones, 1968, Ph.D. thesis).

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