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Refinement of hydrogen positions in natural chondrodite by powder neutron diffraction: implications for the stability of humite minerals

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ABSTRACT

The structure of a natural sample of chondrodite ($Mg_{4.89}Fe_{0.07}Si_{2.04}O_8F_{1.54}(OH)_{0.46}$) was refined using powder neutron diffraction data and the Rietveld technique ($P2_1/b$; $Z = 2$; $a = 4.7204(1)$ Å; $b = 10.2360(3)$ Å; $c = 7.8252(2)$ Å; $\alpha = 109.11(1)°$; $V = 357.26(2)$ Å^3). Hydrogen was found to occupy the H1 site. The significance of hydrogen at this site is discussed in terms of hydrogen-bond stabilization of humite structures containing varying amounts of OH, F and Ti. Arguments are proposed as to why the F and Ti contents of natural humites usually result in only one H per formula unit when there is no crystal-chemical reason why fully hydrated samples should not be favoured.

KEYWORDS: powder neutron diffraction, chondrodite, Rietveld refinement, humite minerals.

Introduction

THE humite group minerals have the general formula $n\mathrm{Mg_2SiO_4.Mg_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}}$ where n = 1 (norbergite), 2 (chondrodite), 3 (humite) or 4 (clinohumite) (Jones *et al.*, 1969). The structures of the whole series are, in general, well known and that of chondrodite has been determined previously by both single-crystal X-ray and neutron diffraction (Gibbs *et al.*, 1970; Yamamoto, 1977; Friedrich *et al.*, 2001). The simplistic $n\mathrm{Mg_2SiO_4.Mg(F,OH)_2}$ representation conveniently conveys the compositional variation but is misleading in relation to the structure (Ribbe *et al.*, 1968). The hydrated layer is better described as Mg(F,OH)O, where Mg corresponds to *M*3, leading to an expression of the chondrodite formula as $\mathrm{Mg_3Si_2O_6.2Mg(F,OH)O}$. Substitutions of F and TiO_2 can then be written in the form $\mathrm{Mg_3Si_2O_6.Mg_2F_x(OH)_{1-x}O_2}$ and $\mathrm{Mg_3Si_2O_6.Mg_{2-x}Ti_x(OH)_{2-2x}O_{2+2x}}$.

Humite minerals usually occur in metamorphosed limestones and dolomites. However, titanian clinohumite occurs in metamorphosed mantle rocks (Trommsdorff and Evans, 1980) and both titanian clinohumite and titanian chondrodite have been found in kimberlites (McGetchin *et al.*, 1970; Aoki *et al.*, 1976). Experimental studies indicate that end-member Ti-, OH- and F-bearing clinohumite (together with OH-chondrodite) would all be stable at the pressure (*P*) and temperature (*T*) of the upper mantle and may be of some importance for water storage in this region (Yamamoto and Akimoto, 1977; Burnley and Navrotsky, 1996; Wunder, 1998; Ulmer and Trommsdorff, 1999; Pawley, 2000). Also important is the way in which water is incorporated in the structure (as a hydrated, Si-deficient layer within an olivine-like unit) which may provide a model for the water defect in nominally anhydrous olivine (Kitamura *et al.*, 1987).

The initial humite structure determinations identified a centrosymmetric pair of hydrogen positions arising from a single hydrogen site (H1) (Fujino and Takéuchi, 1978). These positions are separated by only ~1 Å and, if fully occupied, this

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short H...H distance would destabilize the structure (Fig 1*a*). Seemingly to avoid this interaction, natural samples are characterized by the substitution of F for OH and TiO_2 for $Mg(OH)_2$ (Fig. 1*b,c*) at levels which usually (but not always) reduce the amount of H to <1 per formula unit (p.f.u.) and the occupancy of this H site to <0.5 (Jones *et al.*, 1969). The synthesis of OH-clinohumite and OH-chondrodite (hereafter, synthetic materials are referred to by the prefix "OH-") were explained by the need for high pressures to overcome the H...H repulsions (Ribbe, 1979; Cámara, 1997). In reality there are two possible H sites with the OH vector pointing in approximately opposite directions; H1 located near a centre of symmetry within the Mg(OH)O layer and H2 in a cavity of the olivine-like block (Fig. 1*a*) (Berry and James, 2001). This means that OH-rich humites can occur without a destabilizing H...H interaction due to occupancy of both H1 and H2. These two positions were first identified in X-ray Fourier difference maps of OH-chondrodite by Yamamoto (1977) and later confirmed for hydroxylclinohumite by Ferraris *et al.* (2000). They have also been suggested for a range of humite minerals by *ab initio* calculations which indicated that H2 was in fact the favoured site (Abbott *et al.*, 1989). Despite these results, the significance of the two-site model has been ignored and the misconception about the H...H repulsion persisted (Fujino and Takéuchi, 1978; Williams, 1992; Cámara, 1997; Lin *et al.*, 1999, 2000). Only recently have neutron diffraction data been used to unambiguously determine the H positions in OH-clinohumite and OH-chondrodite and establish that there is no crystal-chemical reason why these structures should not occur in nature (Berry and James, 2001; Lager *et al.*, 2001). This coincides with the discovery of natural hydroxylclinohumite (Ferraris *et al.*, 2000).

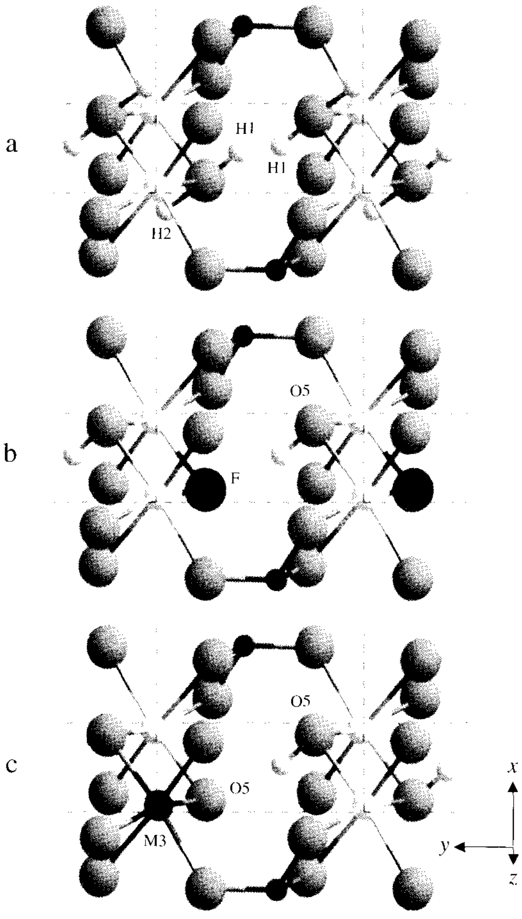

FIG. 1. Substitutions in the hydrated layer of the humite minerals. (*a*) OH end-member showing H1 and H2 positions; only half of the H sites are occupied to prevent a short H...H distance arising from occupancy of the adjacent H1 sites shown; (*b*) substitution of F for O5-H and occupancy of the H1 site; and (*c*) substitution of $TiO5_2$ for $Mg(OH)_2$; Ti on 1/4 of the *M*3 sites removes completely the need for both H1 and H2 sites.

Without a structural impediment to the natural occurrence of OH-rich humites it is now not clear why the substitutions in natural samples are to such an extent as to give the deceptive appearance of occurring so as to stabilize the structure. The critical factors are the favourable site in the humites for Ti and F relative to other phases, and the potential role of hydrogen bonding. In the original structure determinations of the substituted humites, the hydrogen positions were either not identified or only approximately located by X-ray difference maps (Gibbs *et al.*, 1970; Yamamoto, 1977; Fujino and Takéuchi, 1978; Cámara, 1997). Due to the possibility of both H1 and H2 sites, it is unclear which site is occupied when F or Ti substitution results in less than one H p.f.u. Although these maps indicate the presence of H1 it is possible that the region corresponding to H2 was not closely examined. A recent single-crystal neutron study of F-bearing chondrodite, F-bearing titanian clinohumite, and F-free titanian hydroxylclinohumite, each containing <1 H p.f.u. found that in all cases H occupies the H1 site (Friedrich *et al.*, 2001). Here we report the structure of a further sample of F-bearing chondrodite. Based on these results we then discuss the compositions of natural humite minerals.

Experimental

Chondrodite from Orange County, New York, USA (Australian Museum D3142) was hand-picked after dissolution of a calcite matrix in HCl. The chemical composition of the sample was determined using a CAMECA Camebax electron microprobe. Approximately 5 g of powdered material were loaded into a vanadium sample can with a 5 mm diameter. Powder neutron diffraction measurements were made on the High Resolution Powder Diffractometer (HRPD) using thermal neutrons ($\lambda = 1.8842$ Å) from the HIFAR nuclear reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). Data were collected using a bank of 24 ^{3}He detectors over the range $0 < 2\theta < 153°$ steps, in 0.05°. Structural refinements were carried out by the Rietveld method (Rietveld, 1969) using the LHPM program (Howard and Hunter, 1997), with Voigt peak shapes and refined backgrounds.

Results

The chemical composition was calculated on the basis of seven cations as $Mg_{4.89}Fe_{0.07}Si_{2.04}O_8F_{1.54}(OH)_{0.46}$ or $Mg_{2.89}Fe_{0.07}Si_{2.04}O_6.Mg_2F_{1.54}(OH)_{0.46}O_2$. The sample is effectively Ti free with a contribution of only $Ti_{0.007}$ to the chemical formula.

The initial parameters used in the refinement were those determined by Gibbs *et al.* (1970) for $Mg_{2.95}Fe_{0.05}Si_2O_6.Mg_2F_{1.3}(OH)_{0.7}O_2$. Iron was fixed on the *M*1 site in accordance with the findings of Gibbs *et al.* (1970) and Friedrich *et al.* (2001). The H positions were added after an initial refinement of the structure according to the model of Yamamoto (1977). H1 and H2 positions with a maximum occupancy of 0.5 were tried both individually and together for a range of starting coordinates. All refinements involving the H2 position were unstable while those involving H1 invariably converged to a constant and physically reasonable H site. The crystallographic data obtained from the full refinement are given in Table 1, while the atomic coordinates and isotropic thermal parameters are given in Table 2. Selected bond-lengths are given in Table 3 and distances and angles associated with the H1 site are given in Table 4. The results are reported in the unconventional space group $P2_1/b$ (unique axis *a*) to maintain consistency with previous studies which have used this form to emphasize the structural relationship with forsterite (*Pbnm*). The standard space groups $P2_1/c$ (for chondrodite and clinohumite) and *Pmcn* (for both forsterite and the orthorhombic humites) similarly assign the same lattice parameter label to structurally related crystallographic directions. The observed, calculated and difference neutron diffraction profiles are shown

TABLE 1. Crystallographic data for chondrodite.

Formula	$Mg_{4.89}Fe_{0.07}Si_{2.04}O_8F_{1.54}(OH)_{0.46}$
Formula weight	345.13
Colour	white-pale yellow
Space group	$P2_1/b$ (No. 14)
Z	2
a (Å)	4.7204(1)
b (Å)	10.2360(3)
c (Å)	7.8252(2)
α (°)	109.11(1)
V (Å^3)	357.26(2)
D_c (g cm^{-3})	3.184
2θ range (°)	20.0–145.0
Number of reflections	412
R_P/R_B (%)	4.7/8.6

$R_P = \Sigma|y_i(\text{obs}) - y_i(\text{calc})|/\Sigma y_i(\text{obs})$, where y_i is the (gross) intensity at the *i*th step of the profile.
$R_B = \Sigma|I_K(\text{obs}) - I_K(\text{calc})|/\Sigma I_K(\text{obs})$, where I_K is the intensity assigned to the *K*th Bragg reflection.

TABLE 2. Fractional atomic coordinates and isotropic thermal parameters (B_{iso}) (Å^2 × 100) for chondrodite with esd's in parentheses. Mg1 atoms occupy the special 2*d* (1/2,0,1/2) site, while all the other atoms occupy general 4*e* (*x*,*y*,*z*) sites.

Atom	*x*	*y*	*z*	B_{iso}
Mg1/Fe[a]	0.5	0	0.5	0.7(1)
Mg2	0.0125(12)	0.1711(4)	0.3052(7)	0.7(1)
Mg3	0.4979(11)	0.8845(5)	0.0781(7)	0.6(1)
Si	0.0784(11)	0.1459(6)	0.7027(9)	1.0(1)
O1	0.7805(10)	-0.0001(5)	0.2926(10)	1.1(1)
O2	0.7254(10)	0.2417(8)	0.1263(8)	0.7(1)
O3	0.2286(11)	0.1692(8)	0.5263(9)	1.2(1)
O4	0.2657(9)	0.8527(6)	0.2920(11)	0.8(1)
O5/F[b]	0.2726(11)	0.0561(8)	0.1007(10)	0.9(1)
H1[c]	0.082(4)	0.023(2)	0.028(3)	3.0

[a] Occupancy fixed at analytically determined values: Mg1 = 0.93, Fe = 0.07.
[b] Occupancy fixed at analytically determined values: F = 0.77, O5 = 0.23.
[c] Hydrogen occupancy constrained to equal that of O5.

in Fig. 2 and a representation of the structure given in Fig. 3.

Discussion

Hydrogen was found to occupy the H1 site and two centrosymmetric H1 positions occur within 1 Å (H1...H1 0.94(2) Å). The potential for a destabilizing H1...H1 interaction is avoided by the substitution of F for OH. For a given H1 position, the nearest neighbour H1 site must be unoccupied and the associated O5 position occupied by F (Fig. 1*b*). The maximum H1 occupancy is 0.5 which corresponds to 1 OH and 1 F p.f.u. For higher levels of H the H2 site is occupied (Berry and James, 2001; Lager *et al.* 2001). The H1 environment is consistent with that determined by Friedrich *et al.* (2001) for a more OH-rich chondrodite ($Mg_{2.7}Fe_{0.3}Si_2O_6.Mg_2F_{1.02}(OH)_{0.97}O_2$). The O5/F–O5/F distance of 2.939 Å in this compound is shorter than that of 3.040 Å found here, in accordance with the assertion that vacant H positions result in anion-anion repulsion which increases this distance.

TABLE 3. Selected bond-lengths and hydrogen bond distances (Å) with esd's in parentheses.

Atom1–Atom2	Bond-length (Å)
Mg1/Fe–O1 ×2	2.094(6)
Mg1/Fe–O3 ×2	2.110(6)
Mg1/Fe–O4 ×2	2.131(8)
Mg2–O1	2.041(7)
Mg2–O2	2.231(8)
Mg2–O3	2.014(7)
Mg2–O3	2.190(8)
Mg2–O4	2.165(7)
Mg2–O5/F	2.054(8)
Mg3–O1	2.166(8)
Mg3–O2	1.996(8)
Mg3–O2	2.085(8)
Mg3–O4	2.113(9)
Mg3–O5/F	2.011(8)
Mg3–O5/F	2.015(9)
Si–O1	1.646(8)
Si–O2	1.609(9)
Si–O3	1.637(9)
Si–O4	1.625(7)

TABLE 4. Selected bond distances (Å) and angles (°) for the H1 cavity with esd's in parentheses.

O5–H1	1.06(2)
H1...F	1.98(2)
O5–H1...F	174(1)
H1...O1	2.53(2)/2.58(2)
O5–H1...O1	103(1)/98(1)
H1...O2	2.71(2)/2.73(2)
O5–H1...O2	107(1)/93(1)
O5/F...O5/F	3.040(11)
O5/F...O1	2.923(8)/2.951(11)
O5/F...O2	2.984(9)/3.174(9)
O5/F...O4	2.936(10)

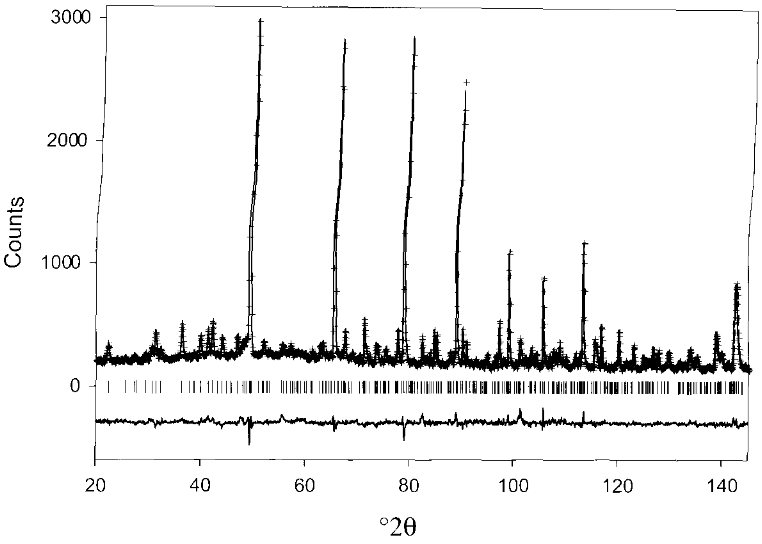

FIG. 2. The observed (+), calculated and difference (solid lines) powder neutron diffraction profiles for chondrodite.

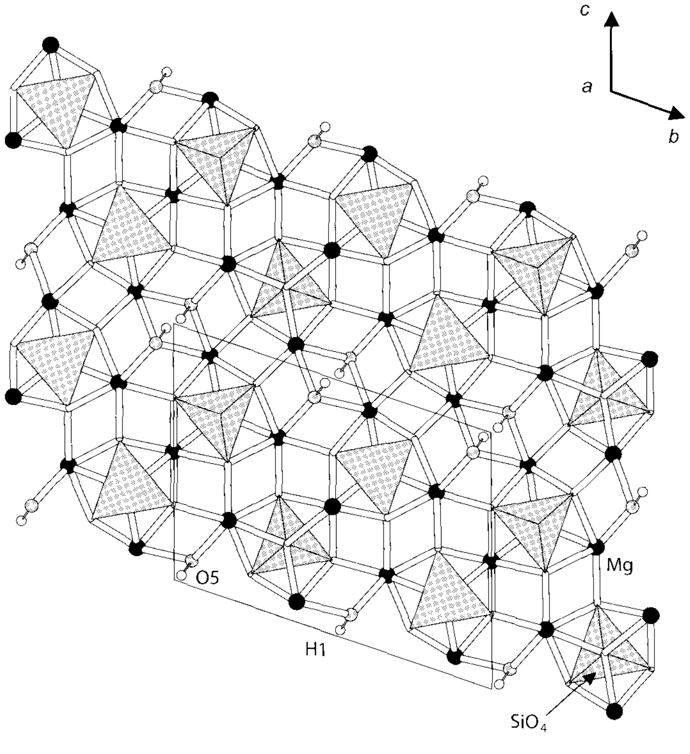

FIG. 3. The structure of chondrodite showing the Mg-O framework and SiO_4 tetrahedra. Fluorine is disordered on the O5 site. All H1 positions generated by symmetry are shown although from the chemical composition only around 1/4 are occupied. Two adjacent H1 positions are never occupied simultaneously. For a given H1 position (which points either up or down) the O5 site associated with the adjacent H1 (directly above or below the proximal H1 in the figure) is occupied by F.

The determination of the H site in substituted humites is important for understanding the stability, composition and extent of F/Ti substitution. The H2 site is located within a forsterite like block and no real stabilization of the structure is possible from hydrogen bonding. In contrast, the H1 site allows hydrogen bonding across the cleavage plane and stabilizes the substitution of F and TiO_2. Cleavage in the humites occurs along the substituted layer and reflects the structural integrity (or intrinsic stability) of the layer binding the forsterite-like units together. Maximum strength will be achieved when a hydrogen bond occurs between every O5–O5/F pair (for chondrodite). This is the case for the OH end-members and F substitution at up to half the O5 sites. Indeed the strongest interlayer bonding might be expected for a F/(F+OH) ratio of 0.5 since F is a stronger H bond acceptor than O. The structure is weakened by F/(F+OH) values greater than 0.5 due to anion-anion repulsion, and the substitution of Ti which is associated with a charge imbalance (discussed below).

F and/or Ti partition preferentially into the humites (Rice, 1980*a*). F appears to be favoured over Ti and it has been suggested that the amount of F controls the level of Ti that can enter the structure (Jones *et al.*, 1969). Indeed such is the favourability of clinohumite for accommodating F that this phase may be much more important as a reservoir of mantle F than of H_2O (Engi and Lindsley, 1980). In the absence of F and Ti, the pure OH end-member humites can be formed within the appropriate stability field. Hydroxylclinohumite has been found in nature (Ferraris *et al.*, 2000) while OH-clinohumite, OH-humite and OH-chondrodite have all been synthesized (Pawley, 2000; Wunder, 1998; Wunder *et al.*, 1995; Burnley and Navrotsky, 1996; Yamamoto and Akimoto, 1977). OH-norbergite is currently unknown.

The importance of hydrogen bonding from the H1 site is apparent from the extent of F substitution. Despite the ability of clinohumite to readily accommodate F, the F/(F+OH) ratio in natural samples is nearly always ~0.5 (from ~0.45 to ~0.6; Jones *et al.*, 1969). This is intrinsically the most stable F content and also a lower limit, since at the P, T and X_{CO_2} at which these minerals form in skarns, the hydroxyl end-member is unstable, or metastable, relative to other phases (Rice, 1980*a,b*; Wunder, 1998). If more F is available, additional layers are formed rather than fully substituting the existing layers. This maintains hydrogen bonding across the layer and stabilizes the structure. The most F-rich clinohumite reported, has F/(F+OH) equal to 0.71 (Satish-Kumar and Niimi, 1998). The F content at which one humite converts to another is a balance between the destabilization caused by increasing the F/(F+OH) ratio of a single layer and the potential instability of F-poor additional layers. For example, if the F/(F+OH) ratio is 0.6 and the number of layers was doubled without the addition of further F, the resultant F/(F+OH) ratio would be 0.3 and the stability of the material restricted to a limited P, T and X_{CO_2} range due to the instability of the OH component (Rice, 1980*a,b*). Fluorine stabilizes the clinohumite + calcite stability field to more CO_2-rich fluids. High clinohumite F contents can also be avoided by a discontinuous reaction forming chondrodite and forsterite (Rice, 1980*b*). The effect of balancing the extent of fluorination in humite transformations is that the amount of F relative to OH increases from clinohumite to norbergite (Jones *et al.*, 1969). Natural chondrodites have F/(F+OH) ratios of up to ~0.8 while for higher F activities norbergite is formed, all known samples of which have ratios >0.8.

For a given geological environment, the stable humite mineral and its F content represents a balance between the intrinsic stability of the structure and the relative stability referenced to the mineral assemblage and fluid composition. This is also apparent from the temperature of the clinohumite breakdown reaction, which for a given pressure increases in the order OH < Ti-bearing < Ti-saturated < Ti, F-bearing < F (Ulmer and Trommsdorff, 1999; Pawley, 2000; Wunder, 1998). This does not reflect the intrinsic stability of each structure but rather the favourable site available for F and Ti in the humites relative to other phases in the $Mg(Fe)O$-SiO_2-TiO_2-H_2O-MgF_2 system (and hence the preferential partitioning). The F site in the humites stabilizes the F end-member relative to the other analogues, even without any hydrogen bonding contribution, due to the high energy of both F substitution into other lattices and of the breakdown product MgF_2/HF. Indeed the stability of the substituted humites correlates negatively with the stability of the breakdown phases, $Mg(OH)_2$/H_2O, TiO_2 and MgF_2/HF.

In Ti-substituted chondrodite, Ti is ordered onto the *M*3 site (Fujino and Takéuchi, 1978) with a maximum occupancy of 0.25. This level results in only 1 H p.f.u. (Fig. 1*c*). Theoretically an occupancy of 0.5 is possible but the substitution is associated with a local charge imbalance which will destabilize the structure (Ribbe, 1979). The sharp limit at 0.25 may be explained by the stabilizing effect of H bonding which can only occur for occupation of the H1 site. This bond is particularly strong since the receptor O5 coordinated to Ti is highly underbonded carrying enhanced negative charge density (Ribbe, 1979). The strength of this bond is reflected in the short O5–O5 distance and straight O5–H1...O5 angle reported by Friedrich *et al.* (2001). At occupancies up to 0.25, every O5 with a charge imbalance can be stabilized by a hydrogen bond. Above 0.25 this does not occur and the structure is unstable. Accordingly we would not expect a composition saturated with Ti to contain any F since stabilization would not be possible. Indeed a negative correlation exists between Ti and F in the humites (Jones *et al.*, 1969; Evans and Trommsdorff, 1983; Dymek *et al.*, 1988) with the maximum amount of F p.f.u. for a given Ti p.f.u., x, being $1-2x$. For any mixed substituted compound the amount of OH p.f.u. must be at least double that of Ti. This relationship is consistent with all known natural samples (see for example Gaspar, 1992). Fully fluorinated compounds are of course possible since hydrogen bonding is not necessary for stabilizing the substitution.

Finally, it is interesting to note the relative ease with which OH-clinohumite and OH-chondrodite (Pawley, 2000; Wunder, 1998; Burnley and Navrotsky, 1996; Yamamoto and Akimoto, 1977) can be synthesized and the rarity of OH-humite (Wunder *et al.*, 1995), despite the overlapping stability fields. The reaction products are dependent upon the stoichiometry of the starting oxides, the water activity, the effect of silica solubility in the fluid, and the reaction conditions. A TEM study of products from the attempted synthesis of OH-clinohumite (Weiss, 1997) found intergrowths of forsterite, clinohumite and chondrodite. Isolated hydrous layers were also observed and olivine blocks of the form $(Mg_2SiO_4)_n.Mg(OH)_2$ within a humite layer always have even n. The rarity of humite may be explained if clinohumite first forms with subsequent layers being inserted between the clinohumite $n = 4$ units to give $n = 2$ chondrodite. Transformation from an $n = 4$ to $n = 3$ structure would involve a rearrangement of the existing network.

Conclusions

There is no crystal chemical reason why humites with >1 H p.f.u. should be unstable since occupation of an H2 site, of similar energy to H1, prevents the occurrence of a short H1...H1 distance that was thought to destabilize the structure. Accordingly, hydroxylclinohumite and other OH-rich humites have been found in nature. In general, however, the amount of H is $\leqslant 1$ p.f.u. due to the presence of F and Ti in the structure. The humites act as a sink for these elements and the substitutions are stabilized by hydrogen bonding from the H1 site. In the case of F, the extent of substitution tends to reduce H to $\leqslant 1$ p.f.u. due to the instability of the OH end-member at the conditions typical of the skarns where most of these compounds form. There is also a tendency not to fully fluorinate layers due to F...F repulsion and the involvement of H1 in a strong O–H...F hydrogen bond. For Ti the substitution is associated with a charge imbalance that is stabilized by hydrogen bonding. The maximum Ti content for which this stabilization can still occur is that which reduces H to 1 p.f.u. The extent of these substitutions is thus a balance between accommodating as much F and Ti as possible while still maintaining the integrity of the structure through hydrogen bonding from the H1 position. Confirmation that H occupies H1 rather than H2 in substituted humites is thus fundamental to our understanding of the chemistry of these minerals.

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