

Hydrogen in humite-group minerals: Structure-energy calculations

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ABSTRACT

Energy calculations were used to locate H⁺ in selected humite minerals: norbergite, OH-end-member chondrodite, magnesian alleghanyite, titanian chondrodite, and titanian clinohumite. The calculations involved a search for the position of lowest energy for H⁺ in a cluster of up to 27 neighboring atoms. The influence on the H⁺ position of the exchanges F(OH)₋₁ and TiO₂M₋₁(OH)₋₂ was explored by performing calculations on models with different local distributions of Ti⁴⁺, M²⁺, O²⁻, F⁻, and neighboring H⁺.

In all but one of 18 models, two energy minima were found near the hydroxyl oxygen. The calculated minima, 35 in all, are located in two clusters, corresponding to two kinds of observed H positions, H1 sites (Yamamoto, 1977; Fujino and Takéuchi, 1978) and H2 sites (Yamamoto, 1977). Calculated O-H distances are consistent with, or more realistic than, observed distances in OH-end-member chondrodite (Yamamoto, 1977) and titanian clinohumite (Fujino and Takéuchi, 1978).

Several conclusions may be drawn: (1) Energy calculations give realistic H positions for humite minerals. (2) Primary H1-type energy minima were found only for models with hydroxyls on adjacent anion sites (i.e., neither Ti nor F in the local structural environment). Furthermore, when hydroxyl oxygens are on adjacent anion sites, one H is at an H2 site, and the other is at an H1 site. (3) Ti substitution favors H2 sites for hydrogens of nearby hydroxyls. (4) F substitution also favors H2 sites for hydrogens of nearby hydroxyls. (5) Structural distortions due to Mn substitution in chondrodite (e.g., magnesian alleghanyite) seem to have little or no special influence on the H positions.

INTRODUCTION

Certain problems having to do with positional disorder of one or more atoms in a mineral cannot be solved by conventional diffraction methods because such methods give only average atomic positions within the constraints of an observed or assumed space group. It is not always clear whether the position reflects an average of the range of thermal vibrations relative to a single minimum-energy position, or an average of a number of discrete minimum-energy positions. In either case the position of an atom depends fundamentally on local structural details—details that are commonly missing in the average structure. In this paper we address the problem of disordering of H in humite minerals. The important local details involve the distribution of F and Ti atoms. The motivations for this study were to further test our method of using energy calculations to determine H positions (Abbott et al., 1988, 1989) and to illustrate an application of the method to problems of positional disordering related to cation and anion substitutions. Abbott et al. (1989) and Giese (1984) have given historical perspectives on

the use of energy calculations to predict H positions in other minerals, mainly phyllosilicates.

Humite minerals are important because of their structural relationship to olivine (Ribbe and Gibbs, 1971; Ribbe, 1982; Deer et al., 1982) and because they may afford a mineralogical site for H in the upper mantle (McGetchin et al., 1970; Horiuchi et al., 1970; Papike and Cameron, 1976; Yamamoto, 1977; Fujino and Takéuchi, 1978). Even if humite minerals are not very abundant in the mantle, the local structural environment of the H in these minerals serves as a valuable model for the way in which H could be accommodated as defects in olivine. Like olivine, the structures of the humite minerals are based on hexagonal close-packed anions. Si occupies tetrahedral sites in essentially the same local structural environment as the Si in olivine. In nontitaniferous humites, divalent cations (e.g., Mg, Fe, Mn) occupy octahedral sites, and a proportion of the anions are monovalent, F⁻ or OH⁻. Ti⁴⁺ substitutes for divalent cations according to the exchange TiO₂M₋₁(OH,F)₋₂, where M is a divalent cation (Jones et al., 1969; Kocman and

Rucklidge, 1973; Fujino and Takéuchi, 1978; Ribbe, 1979, 1982).

All members of the homologous humite series have in common the local structural environment shown in Figure 1. Twelve anions form the corners of a distorted 14-sided polyhedron and are more or less equidistant from a thirteenth anion at the centrally located O5₁ site. Cations inside the anion polyhedron include one or two H atoms and one octahedral cation (marked by an "x" in Fig. 1), which is practically on the surface of the polyhedron. All other cations shown in Figure 1 are outside the polyhedron. Selected sites are labeled according to the scheme used by Yamamoto (1977) for OH-end-member chondrodite, but with subscripts to distinguish between symmetrically equivalent sites. The octahedral M3 sites occur in pairs, such that the two M3 octahedra of each pair are related by a center of symmetry at the midpoint of a shared octahedral edge. The shared edge is formed by two O5 anions. In Figure 1, cation sites M3₁ and M3₄ are related by a center of symmetry at the midpoint of the O5₁-O5₃ shared-edge. In nontitaniferous humites monovalent anions, F⁻ or OH⁻, occupy all of the O5 sites. Ti substitutes in appreciable amounts only on the M3 sites (Kocman and Rucklidge, 1973; Fujino and Takéuchi, 1978; Ribbe, 1979, 1982). The theoretical limit for the Ti exchange is reached when all of the monovalent O5 anions are replaced by divalent anions (O²⁻). This would happen when 50% of the M3 sites are occupied by Ti⁴⁺. Only one M3 site of a pair (e.g., M3₁ or M3₄ in Fig. 1) can be occupied by Ti. In real humites, Ti does not occupy more than approximately 25% of the M3 sites (Jones et al., 1969; Ribbe, 1979, 1982).

Pauling bond-strength arguments show that monovalent anions, OH⁻ and F⁻, are on O5 sites. For hydroxyl-bearing humites the position of the H atom has been determined in only two cases—in both cases on the basis of Fourier-difference maps. Yamamoto (1977) identified two kinds of hydrogen sites (H1 and H2 in Table 1, labeled H1₁ and H2₁ in Fig. 1). Site-occupancy refinement showed that approximately half of the H atoms were on H1 sites, and approximately half were on the H2 sites. He proposed a parity rule for the H atoms of adjacent O5 oxygens that *do not* form a shared M3 octahedral edge (e.g., O5₁ and O5₂ in Fig. 1). The rule simply states that neighboring hydrogens occupy different kinds of sites. For example in Figure 1, if the H associated with O5₂ is at an H1 site (H1₂ in Fig. 1), the H of the adjacent O5₁ will be at an H2 site (H2₁ in Fig. 1). And, if the H associated with O5₂ is at an H2 site (H2₂ in Fig. 1), the H of the adjacent O5₁ will be at an H1 site (H1₁ in Fig. 1). In their structure determination of titanian clinohumite, Fujino and Takéuchi (1978) used Fourier-difference maps to locate a H position like the H1 position in OH-end-member chondrodite.

The purposes of this research were (1) to test the transferability of short-range O-H potentials (Abbott et al., 1988, 1989) to members of the humite series, (2) to test Yamamoto's (1977) parity rule, (3) to determine the in-

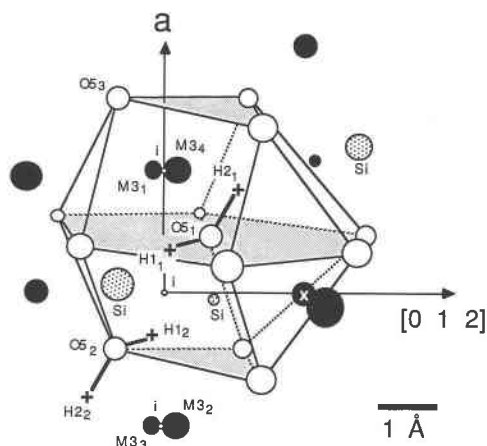


Fig. 1. Projection onto (021) part of the structure of OH-end-member chondrodite, based on the structure determination by Yamamoto (1977). Coordinates for H1₁ and H2₁ are given in Table 1. Twelve anion sites (open circles) form a distorted 14-sided polyhedron centered on a thirteenth anion site, labeled O5₁. Stippled circles are Si sites; black circles are Mg sites. Bold crosses labeled H1₁ and H2₁ are possible H sites near the O5₁ anion, as determined by Yamamoto (1977). Specific M3 sites and O5 sites are distinguished by subscripts. The M3 sites are related to each other by centers of symmetry (*i*), as are the O5 sites. The O5 sites correspond to the O9 sites of Fujino and Takéuchi (1978) in titanian clinohumite and to the F sites of Gibbs and Ribbe (1969) in norbergite.

fluence of Ti substitution on the location of a nearby H atom, (4) to determine the influence of F substitution on the location of a nearby H atom, and (5) to determine how the location of a H atom is influenced by structural distortions due to Mn substitution.

STRUCTURES USED IN CALCULATIONS

Norbergite

Calculations on norbergite were based on the structure determination by Gibbs and Ribbe (1969). The composition is approximately Mg₂SiO₄·MgF_{1.8}(OH)_{0.2}; most of the monovalent-anion sites (O5 sites in Fig. 1) are occupied by F. The structure refinement did not give a position for H. Assuming the hydroxyls are evenly distributed over the structure, H-H repulsions would not be very important, and the hydroxyls can be treated like isolated point defects.

TABLE 1. H position in OH-end-member chondrodite and titanian clinohumite

| | H coordinates | | | H-O5 (Å) | a-O5-H (°) |
|---|---------------|-------|-------|-------------|---------------|
| | x | y | z | | |
| OH-end-member chondrodite (Yamamoto, 1977) | | | | | |
| H1 | 0.15 | 0.03 | 0.06 | 0.68 | -144.0 |
| H2 | 0.42 | 0.10 | 0.20 | 1.03 | 44.5 |
| Titanian clinohumite (Fujino and Takéuchi, 1978) | | | | | |
| H1 | 0.06 | 0.022 | 0.027 | 1.02 | -157.2 |

OH-end-member chondrodite

Yamamoto (1977) synthesized this pure OH-end-member chondrodite $2\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH})_2$ in high-pressure experiments and determined its structure. The structure is nearly the same as the structure determined by Gibbs et al. (1970) for a different chondrodite. The phase is special because it contains no F. H atoms are necessarily fairly close to each other. It has been suggested (Fujino and Takéuchi, 1978; Ribbe, 1982) that natural OH-end-member humites are unknown because of the destabilizing influence of H-H repulsions. However, the important exchange mechanisms, $\text{F}(\text{OH})_{-1}$ and $\text{Ti-O}_2\text{M}_{-1}(\text{OH})_{-2}$, serve to minimize or eliminate altogether the number of such H-H interactions. This interpretation is consistent with Ribbe's (1982) observation that the only natural F-free humites are titanian chondrodites and titanian clinohumites (Fujino and Takéuchi, 1978; see below).

As described in the Introduction, the structure determination of OH-end-member chondrodite gave two kinds of H sites (Table 1). The reported O-H distances were $\text{H1-O5} = 0.68 \text{ \AA}$ and $\text{H2-O5} = 1.03 \text{ \AA}$.

Magnesian alleghanyite

Alleghanyite is the Mn analogue of chondrodite. The energy calculations were based on the structure determination by Francis (1985) of natural material having the composition $2(\text{Mn}_{0.71}\text{Mg}_{0.24}\text{Zn}_{0.05})_2\text{SiO}_4 \cdot \text{MgF}_{0.94}(\text{OH})_{1.06}$. Problematic H-H repulsions cannot be avoided altogether because there is more OH than F. The Mg occupies the smaller M3 sites; Mn occupies M1 and M2 sites.

Titanian chondrodite

The structure of this mineral and the structure of coexisting titanian clinohumite were determined by Fujino and Takéuchi (1978). The chondrodite is approximately $2\text{M}_2\text{SiO}_4 \cdot \text{M}_{0.58}\text{Ti}_{0.42}\text{O}_{0.84}(\text{OH})_{1.16}$. The M cations included (in order of decreasing abundance) Mg, Fe, Mn, Ni, and Cr. The mineral contained no F detectable by analytical electron microprobe. H-H repulsions are minimized by substitution of O for OH on approximately 42% of the O5 sites, in conjunction with the Ti exchange. Even though the local environment (Fig. 1) is essentially the same as in the coexisting titanian clinohumite, Fujino and Takéuchi (1978) were unable to determine a position for the H atoms as they did for titanian clinohumite.

Titanian clinohumite

Fujino and Takéuchi (1978) determined the structure of natural material having approximately the composition $4\text{M}_2\text{SiO}_4 \cdot \text{M}_{0.57}\text{Ti}_{0.43}\text{O}_{0.86}(\text{OH})_{1.14}$. The M cations included Mg, Fe, Mn, Ni, and Cr in nearly the same proportions as in the coexisting titanian chondrodite. Like the titanian chondrodite, the titanian clinohumite contained no F detectable by analytical electron microprobe. Furthermore, the ratio of (OH)/O on O5-type sites was nearly the same in both minerals: (OH)/O = 1.331 for

the clinohumite versus (OH)/O = 1.358 for the chondrodite. Fourier-difference maps suggested a single kind of H position (Table 1) similar to the H1 site in OH-end-member chondrodite (Yamamoto, 1977). If fully occupied by H, the shortest H-H distance would be 0.87 Å. The ratio of (OH)/O on the O5-type sites in this clinohumite (O9 of Fujino and Takéuchi, 1978) and the ratio of (OH)/O on O5 sites in the coexisting chondrodite are nearly the same. Because the ratio is greater than one, short H-H distances cannot be avoided without a second kind of H site, perhaps like the H2 site in OH-end-member chondrodite. A second site of this kind, occupied by the smaller proportion of the H might be overlooked easily in Fourier-difference maps.

CALCULATIONS

H positions were calculated using the method detailed by Abbott et al. (1988, 1989). Perhaps the most important contribution of this earlier work was a new formulation for the short-range repulsion between H^+ and O^{2-} — a formulation that could be used in modified electron gas (MEG) theoretical calculations (Post and Burnham, 1986; Muhlhausen and Gordon, 1981a, 1981b). MEG theory is predicated on formal ionic charges, but only accommodates ions with closed electron shells. Short-range repulsions between H^+ and O^{2-} cannot be predicted because H^+ has no electrons in the theory. Abbott et al. (1988, 1989) therefore used empirical methods to formulate a description of the short-range H-O repulsion. The resulting description, which works well in a remarkably wide range of structural situations (Abbott et al., 1988, 1989), was cast in the simple Born exponential form (Born and Huang, 1954) such that the energy of an O-H pair has two contributions, a Coulombic term and the short-range term,

$$W_{\text{OH}} = q_{\text{O}}q_{\text{H}}/r_{\text{OH}} + \lambda_{\text{OH}}\exp(-r_{\text{OH}}/\rho_{\text{OH}}).$$

The ionic charges q are -2 for oxygen and $+1$ for H; r_{OH} is the interatomic distance. The coefficients λ_{OH} and ρ_{OH} in the second term describe the short-range OH repulsion. We stress that for compatibility with MEG theoretical calculations the values for λ_{OH} and ρ_{OH} must be consistent with formal ionic charges in the Coulombic term. Provided that the electrostatic potential of the oxygen of the O-H pair is close to $2 \text{ e}/\text{\AA}$, Abbott et al. (1988, 1989) found that the best values for the coefficients are $\lambda_{\text{OH}} = 30000 \text{ kJ}$ and $\rho_{\text{OH}} = 0.25 \text{ \AA}$.

For determining H positions in the humite minerals the calculations were performed on a discrete cluster of the structure. This strategy was adopted because the H atoms are not distributed periodically over the lattice. Depending on the specific model, the cluster consisted of 26 or 27 atoms, the relative positions of which are shown for OH-end-member chondrodite in Figure 1. In all of the models the target H position was the one associated with an oxygen at the O5₁ site (i.e., H near H1₁ or H2₁). The neighboring cation sites included the M3, M2, M1, and Si sites within a 4-Å radius of the O5₁ site. Also

TABLE 2. Calculated H positions in various humite minerals

| Model code | Charge distribution | | | | | | H coordinates | | | H-O ₅ (Å) | a-O ₅ -H (°) | W _H * (kJ) |
|---|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------|---------|---------|-------------------------|----------------------------|--------------------------|
| | O ₅ ₂ | O ₅ ₃ | M ₃ ₂ | M ₃ ₃ | H ₁ ₂ | H ₂ ₂ | x | y | z | | | |
| Norbergite (after Gibbs and Ribbe, 1969): a = 4.7104, b = 10.274, c = 8.746 Å; α = β = γ = 90° | | | | | | | | | | | | |
| N.1 | -1 | -1 | +2 | +2 | — | — | 0.2153 | -0.0409 | -0.0109 | 1.014 | -104.9 | 1731 |
| | -1 | -1 | +2 | +2 | — | — | 0.4643 | 0.0182 | -0.1538 | 1.110 | 35.8 | 1669 |
| N.2 | -2 | -1 | +2 | +2 | — | +1 | 0.1886 | -0.0386 | -0.0139 | 1.021 | -112.3 | 1548 |
| | -2 | -1 | +2 | +2 | — | +1 | 0.4574 | 0.0174 | -0.1534 | 1.083 | 35.8 | 1597 |
| N.3 | -2 | -1 | +2 | +2 | +1 | — | 0.2323 | -0.0470 | -0.0030 | 1.087 | -99.6 | 1820 |
| | -2 | -1 | +2 | +2 | +1 | — | 0.4753 | 0.0173 | -0.1549 | 1.159 | 33.8 | 1733 |
| OH-end-member chondrodite (after Yamamoto, 1977): a = 4.752, b = 10.350, c = 7.914 Å; α = 108.71°, β = γ = 90° | | | | | | | | | | | | |
| OH-Ch.2 | -2 | -2 | +2 | +2 | — | +1 | 0.1927 | -0.0183 | 0.0126 | 0.970 | -110.8 | 715 |
| | -2 | -2 | +2 | +2 | — | +1 | 0.4463 | 0.0562 | 0.1672 | 0.994 | 29.2 | 756 |
| OH-Ch.3 | -2 | -2 | +2 | +2 | +1 | — | 0.2815 | -0.0223 | -0.0065 | 1.021 | -85.6 | 980 |
| | -2 | -2 | +2 | +2 | +1 | — | 0.4597 | 0.0561 | 0.1602 | 1.025 | 25.5 | 895 |
| Alleghanyite (after Francis, 1985): a = 4.815, b = 10.574, c = 8.083 Å; α = 108.74°, β = γ = 90° | | | | | | | | | | | | |
| Al.1 | -1 | -1 | +2 | +2 | — | — | 0.1510 | -0.0212 | 0.0348 | 0.935 | -124.7 | 1236 |
| | -1 | -1 | +2 | +2 | — | — | 0.3768 | 0.0589 | 0.1968 | 0.999 | 56.2 | 1167 |
| Al.2 | -2 | -1 | +2 | +2 | — | +1 | 0.1106 | -0.0040 | 0.0392 | 0.951 | -139.8 | 1069 |
| | -2 | -1 | +2 | +2 | — | +1 | 0.3709 | 0.0581 | 0.1974 | 0.988 | 57.8 | 1106 |
| Al.3 | -2 | -1 | +2 | +2 | +1 | — | 0.1990 | -0.0361 | 0.0239 | 0.970 | -108.0 | 1408 |
| | -2 | -1 | +2 | +2 | +1 | — | 0.3844 | 0.0585 | 0.1965 | 1.018 | 54.4 | 1249 |
| Titanian chondrodite (after Fujino and Takéuchi, 1978): a = 4.7271, b = 10.318, c = 7.9073 Å, α = 109.33°, β = γ = 90° | | | | | | | | | | | | |
| Ti-Ch.1 | -1 | -2 | +2 | +2 | — | — | 0.2028 | -0.0321 | 0.0074 | 0.976 | -105.1 | 862 |
| | -1 | -2 | +2 | +2 | — | — | 0.4078 | 0.0644 | 0.1924 | 1.026 | 45.8 | 780 |
| Ti-Ch.2 | -2 | -2 | +2 | +2 | — | +1 | 0.1534 | -0.0233 | 0.0192 | 0.970 | -120.2 | 662 |
| | -2 | -2 | +2 | +2 | — | +1 | 0.4001 | 0.0633 | 0.1938 | 1.011 | 47.9 | 699 |
| Ti-Ch.3 | -2 | -2 | +2 | +2 | +1 | — | 0.2475 | -0.0343 | -0.0040 | 1.000 | -92.5 | 1034 |
| | -2 | -2 | +2 | +2 | +1 | — | 0.4128 | 0.0649 | 0.1926 | 1.043 | 44.9 | 844 |
| Ti-Ch.4 | -2 | -2 | +4 | +2 | — | — | 0.1893 | -0.0351 | 0.0096 | 1.008 | -108.4 | 999 |
| | -2 | -2 | +4 | +2 | — | — | 0.4123 | 0.0619 | 0.1913 | 1.039 | 44.9 | 990 |
| Ti-Ch.5 | -2 | -2 | +2 | +4 | — | — | 0.2057 | -0.0275 | -0.0065 | 0.994 | -104.0 | 1041 |
| | -2 | -2 | +2 | +4 | — | — | 0.4273 | 0.0673 | 0.1815 | 1.033 | 38.7 | 1013 |
| Titanian clinohumite (after Fujino and Takéuchi, 1978): a = 4.745, b = 10.283, c = 13.699 Å, α = 101.00°, β = γ = 90° | | | | | | | | | | | | |
| Ti-Cl.1 | -1 | -2 | +2 | +2 | — | — | 0.2013 | -0.0327 | 0.0047 | 0.975 | -105.8 | 857 |
| | -1 | -2 | +2 | +2 | — | — | 0.4089 | 0.0433 | 0.1063 | 1.024 | 45.2 | 781 |
| Ti-Cl.2 | -2 | -2 | +2 | +2 | — | +1 | 0.1559 | -0.0249 | 0.0103 | 0.966 | -119.8 | 677 |
| | -2 | -2 | +2 | +2 | — | +1 | 0.4028 | 0.0424 | 0.1068 | 1.008 | 46.7 | 708 |
| Ti-Cl.3 | -2 | -2 | +2 | +2 | +1 | — | — | — | — | — | — | — |
| | -2 | -2 | +2 | +2 | +1 | — | 0.4171 | 0.0444 | 0.1072 | 1.056 | 44.0 | 902 |
| Ti-Cl.4 | -2 | -2 | +4 | +2 | — | — | 0.1890 | -0.0359 | 0.0058 | 1.007 | -108.7 | 996 |
| | -2 | -2 | +4 | +2 | — | — | 0.4139 | 0.0410 | 0.1057 | 1.035 | 44.1 | 991 |
| Ti-Cl.5 | -2 | -2 | +2 | +4 | — | — | 0.2048 | -0.0265 | -0.0032 | 0.993 | -104.5 | 1037 |
| | -2 | -2 | +2 | +4 | — | — | 0.4281 | 0.0471 | 0.1003 | 1.031 | 38.1 | 1012 |

* Energy is for 1 mol of H. The values are positive because of the design of the cluster.

included in the set of neighboring atoms, if dictated by the details of the model, was a H atom at either the H₂ site or the H₁ site. Adding more ions to the set of neighbors, out to a distance of 5 Å, did not significantly change the calculated H position.

The calculations involved a search for the position of lowest energy for the H. The energy of the target H, W_H, was figured according to

$$W_H = \sum_i [q_i/r_{i-H} + \lambda_{i-H} \exp(-r_{i-H}/\rho_{i-H})],$$

where *i* refers to the 26 or 27 neighboring atoms. Because *i*-H distances involving neighboring cations (*i* = Mg, Si, H, etc.) are long (>2.5 Å), the corresponding short-range repulsions were ignored. The search was conducted by a modified simplex method (Cooper, 1981) in the program QUICKSITE, prepared by one of us (R.N.A.).

The two important substitutions, F(OH)₋₁ and Ti-O₂M₋₁(OH)₋₂, were treated by changing the charges at the appropriate cation or anion sites. In all, 18 models

were considered, details of which are given in Table 2. The models are identified according to a code consisting of an abbreviation for the mineral (e.g., No. for norbergite, OH-Ch. for OH-end-member chondrodite, etc.) and a number that relates to the charge distribution. With the exception of the charge placed on the O₅ site (-1 in norbergite and alleghanyite, -2 in the other minerals), models with the same code number have the same charge distribution. For models involving a neighboring hydroxyl (number-coded .2 and .3), the oxygen was placed at the O₅ site, and the H was placed at either the H₁ site or the H₂ site (Fig. 1). Except for the titanian clinohumite model Ti-Cl.3, the position of the H₁ site or H₂ site was consistent with corresponding positions reported by Yamamoto (1977) for H in OH-end-member chondrodite (Table 1). In model Ti-Cl.3, the position of the H₁ site was symmetrically equivalent to the position reported by Fujino and Takéuchi (1978) for H in titanian clinohumite (Table 1). In some models a -1 charge (F) was

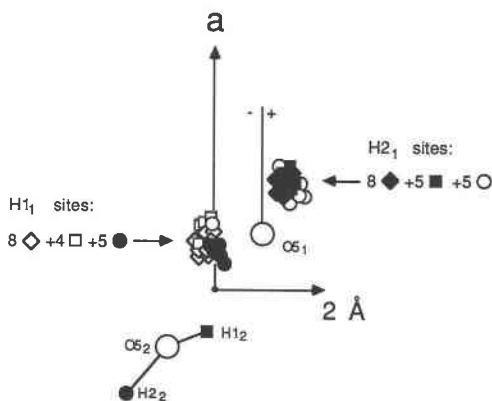


Fig. 2. Composite of all calculated minimum-energy positions (Table 2). For each model, the minimum-energy positions were projected onto the plane defined by the a axis and the $[000]$ - $O5_1$ vector. The plane corresponds to (021) in chondrodite and alleghanyite, (021) in norbergite, and $(0\bar{1}1)$ in titanian clinohumite. Calculated H1-type positions are on the positive side of the vertical line extending upward from the $O5_1$ position (i.e., angles a - $O5_1$ -H $> 0^\circ$); calculated H2-type positions are on the negative side of the vertical line (i.e., angles a - $O5_1$ -H $< 0^\circ$). Symbols indicate primary (●) or secondary (○) minimum with neighboring H at $H2_2$, primary (■) or secondary (□) minimum with neighboring H at $H1_2$, and primary (◆) or secondary (◇) minimum with no neighboring H, but with F at $O5_2$, or Ti at $M3_2$ or $M3_3$.

placed at the $O5_2$ site (models number-coded .1), or a +4 charge (Ti) was placed on either the $M3_2$ site or the $M3_3$ site (models number-coded .4 or .5). In such cases no neighboring H atom (at $H1_2$ or $H2_2$) was included. No models were constructed with Ti at the $M3_1$ site or the $M3_4$ site. In such cases, because of the Ti-exchange mechanism, no H atoms would be associated with either the oxygen at the $O5_1$ site or at the $O5_3$ site.

Because of the low ratio of (OH)/F in norbergite (No), and assuming no special reason for clustering of the hydroxyls, we considered only models with -1 charge at the $O5_3$ site. Presumably model No. 1, which has F on both $O5$ sites adjacent to the hydroxyl oxygen at the $O5_1$ site (no clustering of hydroxyls), would be more important than either model No. 2 or No. 3, both of which have hydroxyl oxygens on adjacent $O5_1$ and $O5_2$ sites (hydroxyls clustered in pairs). For alleghanyite we also considered only models with -1 charge at the $O5_3$ site. But in this case, because the ratio of (OH)/O on $O5$ sites is not so low, a certain amount of hydroxyl clustering must be admitted. Thus it is not so clear that model Al.1 should be any more important than either Al.2 or Al.3. Some of the charge distributions may not be very important in the corresponding real minerals, but were included for the purposes of comparison. In this regard, one model each for titanian chondrodite and titanian clinohumite was constructed with -1 charges (F) at the $O5_2$ sites (models Ti-Ch.1 and Ti-Cl.1) even though no F was detectable by analytical electron microprobe in either mineral. Perhaps

it is worth noting that significant amounts of F, but still below the level of detection by analytical electron microprobe, may figure importantly in explaining observed average H positions.

RESULTS AND DISCUSSION

In each of the models, except model Ti-Cl.3, two local energy minima were found at positions like those given by Yamamoto (1977) for H in OH-end-member chondrodite (Table 1, Fig. 2). The location of the primary minimum (i.e., the local minimum having the lowest energy) depends on the charge distribution over the neighboring atom sites. Models with the same local charge distribution gave remarkably similar results with regard to minimum energies, calculated O-H distances, and OH orientations. For instance in Table 2, compare the results for the OH-end-member chondrodite models (OH-Ch.2 and OH-Ch.3) with the results for the corresponding titanian chondrodite models (Ti-Ch.2 and Ti-Ch.3). Except for the titanian clinohumite model Ti-Cl.3, which used a different position for the $H1_2$ site, the titanian chondrodite models and titanian clinohumite models gave essentially the same energies, O-H distances, and OH orientations. Of course this was expected because of the remarkable similarity of the local structural environments (Fujino and Takéuchi, 1978).

Agreement with observed H positions can be taken, with some caution, as a measure of the reliability of the energy calculations in predicting H positions. In the present context, it is especially important to bear in mind the uncertainty in determining H positions on the basis of the often small and poorly defined residuals in X-ray diffraction Fourier-difference maps. Our calculated H positions for OH-end-member chondrodite (Table 2) compare favorably with the positions (Table 1) offered by Yamamoto (1977). The calculated and observed OH orientations are similar. The calculated H2-O5 distance of 1.025 Å (model OH-Ch.3, primary energy minimum) is practically the same as the observed distance, but the calculated H1-O5 distance of 0.970 Å (model OH-Ch.2, primary energy minimum) is arguably more realistic than Yamamoto's (1977) very short H1-O5 distance of 0.68 Å. For the other test case, titanian clinohumite (Table 2), only one model (Ti-Cl.2) gave a primary energy minimum close to the H position (Table 1) determined by Fujino and Takéuchi (1978). Interestingly, in this particular model there was no Ti^{4+} in the local environment. In the other titanian clinohumite models, only secondary energy minima were consistent with the observed H position. For a H atom at one of these secondary energy minima (models Ti-Cl.1, Ti-Cl.4, and Ti-Cl.5) the calculated H1-O5 distance (0.975 Å to 1.007 Å) would be close to the observed distance (1.02 Å), and the orientation of the OH dipole would be close to the observed orientation.

Figure 2 shows the positions of calculated energy minima for all of the models in Table 2. The positions of the energy minima were projected onto the plane defined by

the a axis and the $[000]$ -O₅ vector. All of the energy minima lie close to this plane. The energy minima form two distinct groups, which correspond to the two kinds of H positions, H1 and H2 (Table 1), offered by Yamamoto (1977) for OH-end-member chondrodite. The two general H positions given by the energy calculations are easily distinguished by the angle between the a axis and the O₅-H₁ vector or the O₅-H₂ vector, whichever applies. All of the a -O₅-H₁ angles in Table 2 are between -80° and -140° , the absolute values of which are slightly less than the angles of 144° and 157° for H1 sites given by Yamamoto (1977) and Fujino and Takéuchi (1978). All of the a -O₅-H₂ angles in Table 2 are between 25° and 60° , which fairly well bracket the 44.5° angle for the H2 site given by Yamamoto (1977). It should be noted that there were only five calculated, primary H₁-type energy minima, and these are generally closer to the observed H1 sites (Yamamoto, 1978; Fujino and Takéuchi, 1978) than the twelve calculated, secondary H₁-type energy minima. H₁-type energy minima are primary only in those models with a neighboring H at the H₂ site near an O₅ oxygen. Conversely, all models with a neighboring H at the H₁ site near an O₅ oxygen gave primary energy minima at an H₂-type position near the O₅ oxygen. Thus the energy calculations corroborate Yamamoto's (1977) parity rule. The energy relationships for the OH-end-member chondrodite models are illustrated in more detail in Figure 3.

Figure 2 shows another feature that might not otherwise be obvious in Table 2. All of the models involving either the TiO₂M₋₁(OH)₋₂ exchange or the F(OH)₋₁ exchange exhibit H₂-type primary energy minima. With regard to the F(OH)₋₁ exchange, this makes sense because of the reduced attraction of a F atom on the O₅ site. With regard to the TiO₂M₋₁(OH)₋₂ exchange, the calculated primary energy minima contradict the observed H position in titanium clinohumite (Table 1), but make some sense because of the repulsion due to a Ti atom on either the M₃ site or the M₃ site. As noted above, the ratio of (OH)/O on O₅ sites is greater than 1 for both the titanian chondrodite and the titanian clinohumite. This means at least some pairs of H atoms must be associated with adjacent O₅ oxygens. Hydrogens so paired would be subject to Yamamoto's (1977) parity rule. Thus while Fourier-difference maps indicate H at H1 sites, some of the H may very well be at H2 sites. Presumably the observed H1 hydrogens would not be near M₃ sites occupied by Ti. Even though the local structural environments are so nearly the same in the titanian chondrodite and titanian clinohumite, Fujino and Takéuchi (1978) found no well-defined H position in Fourier-difference maps of the former. Instead, a number of peaks were present in the map, only one of which was like the H1 position they located in the titanian clinohumite. For similar reasons it may well be that H positions of the H₂ type were simply overlooked in both minerals. Perhaps there were a number of similar H₂ sites (corresponding to various H₂-type energy minima like those in Fig. 2), each having such a low

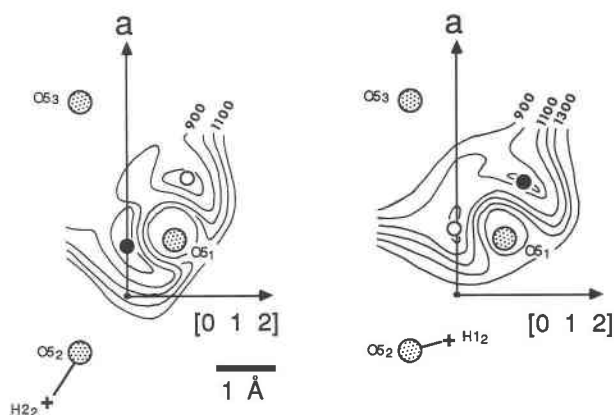


Fig. 3. Contoured maps of the site energy (W_H in kJ) of a H atom at various places in the $(0\bar{2}1)$ plane of OH-end-member chondrodite. The plane is the same as the projection plane used in Figs. 1 and 2. (Left) Model OH-Ch.2 (Table 2). (Right) Model OH-Ch.3 (Table 2). For each model, the stippled circles are O₅ sites; the small, filled circle marks the position of the primary energy minimum; and the small, open circle marks the position of the secondary minimum.

occupation of H atoms, that none registered clearly on the Fourier-difference maps. By all indications the fact that the clinohumite is titaniferous does not mean that the observed H1 position necessarily reflects the influence of the Ti. On the contrary, the energy calculations suggest that the observed H position has little or nothing to do with the Ti.

CONCLUSIONS

1. Energy calculations provide realistic H positions for humite group minerals. Except for the norbergite models, calculated O-H distances fall in the range from 0.94 Å to 1.06 Å. For the norbergite models, some of the calculated energy minima would correspond to somewhat long O-H distances from 1.08 Å to 1.16 Å. The only significant differences between observed and calculated O-H distances involved the questionably short O₅-H₁ distance of 0.68 Å observed by Yamamoto (1977). The calculated H positions are consistent with two general OH orientations, like the two orientations offered by Yamamoto (1977) for OH-end-member chondrodite. The two orientations are distinguished by the angle between the a axis and the O-H vector. Calculated H₂ sites have a -O₅-H₂ angles between 25° and 60° . Calculated H₁ sites have a -O₅-H₁ angles between -80° and -140° .

2. The energy calculations corroborate Yamamoto's (1977) parity rule. In local structural environments without Ti or F, H atoms of adjacent hydroxyls occupy different kinds of sites. If one of the hydrogens is at an H₂ site, the other is at an H₁ site, and vice versa. Primary energy minima consistent with an H₁ site were found only for models with no F or Ti.

3. The calculated primary energy minimum for the H of a hydroxyl near Ti⁴⁺ is of the H₂-type. Thus the ex-

change $\text{TiO}_2\text{M}_{-1}(\text{OH})_{-2}$ favors H2 sites for the hydrogens of nearby hydroxyls. This contradicts the H position determined by Fujino and Takéuchi (1978) for titanian clinohumite. The energy relationships suggest that the observed H position may have little to do with the influence of the Ti. The precise location of the H2 site depends on the distribution of the Ti atoms, such that there may be very many discrete H2-type sites in a given titaniferous humite. In such cases, the average H2 position would be very difficult to detect in Fourier-difference maps.

4. The calculated primary energy minimum for the H of a hydroxyl near F^- is of the H2 type. Thus the exchange $\text{F}(\text{OH})_{-1}$ favors H2 sites for the hydrogens of nearby hydroxyls. The calculations on norbergite and magnesian alleghanyite show that isolated hydroxyls have their hydrogens at H2 sites.

5. The Mn in magnesian alleghanyite distorts the local structural environment of the hydroxyl, relative to the corresponding structural environments in OH-end-member chondrodite (Fig. 1) or titanian chondrodite. The distortions, however, seem to have little influence on calculated O-H distances and OH orientations.

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