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A SHORT-RANGE O–H POTENTIAL FOR AMPHIBOLES BASED ON OH-STRETCHING FREQUENCIES

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ABSTRACT

A short-range potential for OH in tremolite was determined empirically on the basis of the observed hydrogen position and observed fundamental OH-stretching frequency. The short-range repulsion between oxygen and hydrogen was formulated as $W_r = \lambda_{OH} \exp(-r_{OH}/\rho_{OH})$, using the Born approximation. For tremolite, the best values for the short-range coefficients were found to be λ_{OH} = 30500 kJ and ρ_{OH} = 0.2560 Å. In order to assess the transferability of the short-range coefficients, energy calculations were done on cummingtonite, grunerite, glaucophane, pargasite, and tschermakitic hornblende. Conclusions: (1) For tremolite, short-range OH repulsion coefficients can be determined empirically from two observations, a reliable hydrogen position, and the fundamental OH-stretching frequency. (2) The short-range OH coefficients for tremolite can be transferred reasonably well to other simple amphiboles (cummingtonite, grunerite). Values for λ_{OH} and ρ_{OH} based on tremolite lead to somewhat low calculated stretching frequencies for glaucophane. (3) Values for λ_{OH} and ρ_{OH} based on tremolite can be applied, cautiously, to some local structural environments in more complex amphiboles (*i.e.*, with $Al_{T(1)}$, $Al_{M(2)}$, Na_A, and $\square_A$). Calculated frequencies for pargasite and tschermakitic hornblende are somewhat too high or distinctly too low depending on the local distribution of $Al_{M(2)}$, $Al_{T(1)}$, Na_A, and $\square_A$.

Keywords: amphiboles, OH-stretching, anharmonic oscillator model, infrared absorption.

SOMMAIRE

Le potentiel d'énergie localisé d'un groupement OH dans la trémolite a été déterminé de façon empirique en utilisant les positions mesurées des atomes d'hydrogène et la fréquence de l'étirement fondamental dans la liaison O–H. La répulsion locale W_r entre atomes d'oxygène et d'hydrogène est exprimée par $\lambda_{OH}\exp(-r_{OH}/\rho_{OH})$, qui utilise l'approximation de Born. Pour la trémolite, les meilleures valeurs des coefficients λ_{OH} et ρ_{OH} à courte échelle seraient 30500 kJ et 0.2560 Å, respectivement. Des calculs de l'énergie de la cummingtonite, grunerite, glaucophane, pargasite et hornblende tschermakitique ont été faits afin d'évaluer l'applicabilité de ces coefficients à d'autres amphiboles. Pour la trémolite, les coefficients de répulsion O–H à courte échelle découlent de la détermination de la position précise des atomes d'hydrogène et de la fréquence de l'étirement fondamental O–H. On peut appliquer assez bien les coefficients de la trémolite aux autres amphiboles simples (*e.g.*, cummingtonite, grunerite). Dans le cas de la glaucophane, les valeurs de λ_{OH} et ρ_{OH} de la trémolite mènent à des valeurs trop basses de la fréquence de l'étirement. Il est possible d'appliquer les valeurs de λ_{OH} et ρ_{OH} à certains environnements locaux des amphiboles plus complexes (*i.e.*, pour $Al_{T(1)}$, $Al_{M(2)}$, Na_A et $\square_A$). Les fréquences calculées pour la pargasite et la hornblende tschermakitique sont soit trop élevées, soit trop faibles, selon la distribution locale de $Al_{T(1)}$, $Al_{M(2)}$, Na_A *et* $\square_A$.

(Traduit par la Rédaction)

Mots-clés: amphiboles, étirement O–H, modèle de l'oscillateur anharmonique, absorption infra-rouge.

INTRODUCTION

For the purpose of modeling hydroxyl-bearing mineral structures, Abbott *et al.* (1989a,b) used a simple Born–Huang (1954) formulation for the short-range repulsion between oxygen and hydrogen,

$$W_r = \lambda \exp(-r/\rho), \qquad (1)$$

where λ and ρ are constants, and r is, the O–H separation. Values for λ and ρ were determined empirically in such a way that they would be compatible with formal ionic charges on O (–2) and H (+1) in the Coulombic contribution to the energy of the OH pair. Values for λ and ρ of 30000 kJ and 0.25 Å, respectively, were found to work well in a wide range of structures (Abbott *et al.* 1989a,b, Abbott 1990). It was known at the time that the value for λ depends on the value for ρ, and that a unique value for ρ is not available on purely theoretical grounds. For instance, short-range OH potentials cannot be calculated using Modified Electron Gas (MEG) theory (Muhlhausen & Gordon 1981a,b). A value of ρ of 0.25 Å was chosen for two reasons (Abbott *et al.* 1989b): (1) for other cation–anion (i–j) pairs, ρ_{ij} depends mainly on the anion; (2) values for ρ_{iO} (based on MEG theory) are close to 0.25 Å for most cation–oxygen pairs (Post & Burnham 1986, Abbott *et al.* 1989b). A λ_{OH} value consistent with the observed locations of hydrogen atoms in various structures was then derived empirically.

By analogy with other cation–oxygen pairs (Post & Burnham 1986), the short-range OH coefficients λ_{OH} and ρ_{OH} should vary from one structural environment to another, but no details are available (Abbott *et al.* 1989b). With no apology for the small number of significant digits, the values for λ_{OH} and ρ_{OH} noted above are at least consistent with the uncertainty in the observed positions for the hydrogen atoms. However, for a different starting value of ρ_{OH} (*e.g.*, 0.27 Å or 0.23 Å), it is generally possible to determine a value for λ_{OH} that is consistent with a given observed position of hydrogen. The position of a hydrogen atom alone is not sufficient to define unique values for λ_{OH} and ρ_{OH}.

The purpose of this paper is to develop a method to obtain improved short-range coefficients for OH using observed OH-stretching frequencies in addition to the positional information. Amphiboles were chosen for this work because of the wide range of compositions, large number of structure determinations, and availability of relevant infrared (IR) absorption data. The objectives are as follows:

1. For the simple, well-documented environment of hydroxyl in tremolite (#56, Hawthorne 1983), determine λ_{OH} and ρ_{OH} values that best satisfy both the fundamental OH-stretching frequency of 3674 cm^{-1} (Sheu & McMillan 1988, Hawthorne 1981, 1983) and the observed location of the hydrogen atom (Hawthorne 1983).
2. Test for transferability of the OH short-range potential to other, simple amphiboles, specifically cummingtonite, grunerite, and glaucophane. The test consists of a comparison of calculated and observed frequencies of OH-stretching.
3. Using a pargasite and a tschermakitic hornblende (hereafter referred to as Ts-hornblende), explore the effects on the hydrogen environment of complex exchanges, such as $NaAl_3\square_{-1}Mg_{-1}Si_{-2}$ and $Al_2Mg_{-1}Si_{-1}$.

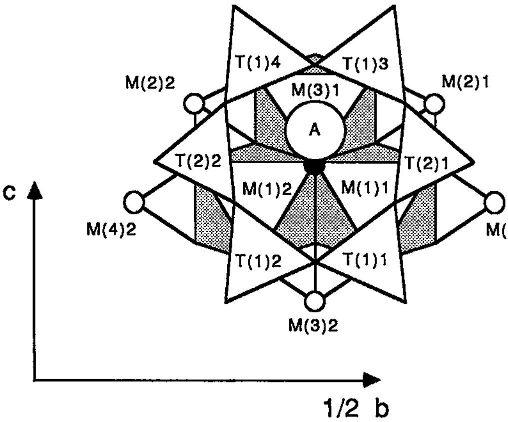

FIG. 1. Local OH structural environment in an amphibole. Sites are labeled according to the usage in the paper: Tetrahedra: *T*(1) and *T*(2), represented by triangular bases of the tetrahedra. Octahedra: *M*(1) and *M*(3). Small stippled circles: *M*(2) and *M*(4) sites; small filled circle: H. Large open circle: Na (*A* site). *T*(1)*n* (*n* = 1, 2, 3, 4) sites are symmetrically equivalent, *T*(2)*n* (*n* = 1, 2) are symmetrically equivalent, *M*(1)1 = *M*(1)2, *M*(2)1 = *M*(2)2, *M*(3)1 = *M*(3)2, *M*(4)1 = *M*(4)2.

TEST STRUCTURES

Except for the Ts-hornblende, all calculations were done on structure determinations reported in Hawthorne (1983). Calculations on Ts-hornblende were done on the H-1 structure determination of Phillips *et al.* (1989). Only *C*2/*m* clinoamphiboles were considered.

Except for the tremolite, all of the amphiboles used in this study have appreciable amounts of Fe^{2+} and Mg. Under these circumstances, there are typically four fundamental OH-stretching frequencies (Strens 1974, Hawthorne 1981, 1983), corresponding to different combinations of Fe^{2+} and Mg at the

TABLE 1. RESULTS OF CALCULATIONS ON TREMOLITE

QUICKSIT		
Short-range coefficients: λ_{OH} = 30500 kJ, ρ_{OH} = 0.2560 Å		
Hydrogen position:		
	observed	calculated
x	0.2088(6) (note 1)	0.2080
y	0.0	0.0
z	0.7628(14)	0.7911
H-O (Å)	0.960(6)	0.961
STRETCH		
Constants in anharmonic oscillator function, U_{OH}:		
k_1 (kJ/Å^2)		4850 (+/- 5)
k_2 (kJ/Å^3)		-23730 (+/- 30)
k_3 (kJ/Å^4)		58680 (+/- 120)
r_o (Å)		0.951
R_{wp} = 0.0041, R_{ex} = 0.0205 (N = 43), GoF = 0.0396 (note 2)		
Constants in vibrational energy functions, $[E(v)-U_{OH,minimum}]$ /h/c and $V(v_2,v_1)$		
v_e (cm^{-1})	3840	3797.6
x_ev_e (cm^{-1})	83 (note 3)	61.8
Y_{00}/c (cm^{-1})	--	-3.6
Absorption frequencies:		
V(1,0) (cm^{-1})	3674 (note 4)	3674 (fundamental)
V(2,0) (cm^{-1})	7180 (note 5)	7224 (1st overtone)

1. x, y, z, and H-O from Hawthorne (1983), ( ) = uncertainty in last digit(s).
2. $R_{wp} = [\Sigma_i[W_{OH}(r_i)-U_{OH}(r_i)]^2/\Sigma_i[W_{OH}(r_i)]^2]^{0.5}$,
   $R_{ex} = [(N-P)/\Sigma_i [W_{OH}(r_i)]^2]^{0.5}$, N = number of data points (samples of W_{OH})
   P = number of parameters refined = 4
   $GoF = (R_{wp}/R_{ex})^2$.
3. Burns & Strens (1966).
4. Sheu & McMillan (1988).
5. Burns (1970).

$M(3)$ and two $M(1)$ sites adjacent to each hydroxyl group. The four absorption bands, designated A, B, C, and D, have been correlated, respectively, with the following combinations of OH ligands: Mg_3, Mg_2Fe^{2+}, $MgFe^{2+}{}_2$, and $Fe^{2+}{}_3$. In the present calculations, the four bands (A, B, C, D) cannot be separated for two reasons. First, Mg and Fe are both treated as having +2 point charges. Thus, with regard to Coulombic interactions, the calculations make no distinction between Mg and Fe^{2+}, other than distinctions in the local geometry (*e.g.*, distinctions in M–O distance). Second, regardless of the ratio of Fe^{2+}/Mg in each amphibole, the mean M–O distances are nearly the same for the $M(1)$ and $M(3)$ sites, indicating that Fe^{2+} and Mg are disordered over those sites. In calculating stretching frequencies, this means that the distinctions among A, B, C, and D bands cannot be modeled because the $M(1)$ and $M(3)$ octahedra in each of the structure determinations have average geometries consistent with a single Fe^{2+}/Mg ratio. Using Distance–Least–Squares (DLS) analysis (Meier & Villiger 1969, Baur 1977), it may be possible in future work to develop model structures with appropriate $M(1)$ and $M(3)$ octahedral geometries so as to remove this degeneracy. For now, it is not entirely clear how the frequency of a calculated "ABCD-hybrid" band should be related to observed frequencies of the A, B, C, and D bands.

Tremolite

Hawthorne's (1983) near-end-member tremolite #56 was selected for three reasons: (1) the composition is simple; (2) a presumably accurate position for hydrogen is available from neutron-diffraction experiments; (3) the IR absorption spectrum is simple. The $M(1)$, $M(2)$, and $M(3)$ sites (Fig. 1) are occupied by Mg, $M(4)$ sites are occupied by Ca, and all tetrahedrally coordinated sites are occupied by Si. The hydrogen coordinates (Table 1) are such that the OH dipole is oriented nearly perpendicular to (1 0 0), with an O–H separation of 0.96 Å. The fundamental OH-stretching frequency for tremolite is represented by a single, sharp A band at 3674 cm^{-1} (Sheu & McMillan 1988). According to Burns (1970), the first-overtone frequency of the A band is 7180 cm^{-1} for an actinolite (near tremolite) with $Mg/(Fe+Mg) = 0.9$.

Cummingtonite

Hawthorne's (1983) structure determination #21 was used for cummingtonite. The material has a modest amount of Fe^{2+} [$Fe^{2+}/(Mg + Fe^{2+}) = 0.38$], but only traces of ^{VI}Al, Mn and Ca. IR absorption data are not available for this particular cummingtonite, but the spectrum for a cummingtonite of similar composition is illustrated in Hawthorne (1983). Four fundamental bands are present, A, B, C, and D, between 3670 and 3600 cm^{-1} (Hawthorne 1983). For a different cummingtonite, Burns (1970) reported 7172, 7143, 7112 and 7068 cm^{-1} for the first-overtone frequencies of the A, B, C, and D bands, respectively.

Grunerite

Hawthorne's (1983) structure determination #22 was used. Chemical analyses show a small amount of Mg [$Fe^{2+}/(Mg + Fe^{2+}) = 0.89$], only traces of Mn and Ca, and no Al. All of the iron was reported as Fe^{2+}, and the stoichiometry permits only minor amounts of Fe^{3+}. The IR spectrum is dominated by C and D absorption bands between approximately 3610 and 3625 cm^{-1} (Hawthorne 1983). First-overtone frequencies of the C and D bands are the same as for the corresponding bands of cummingtonite (*i.e.*, 7112 and 7068 cm^{-1}, respectively: Burns 1970).

Glaucophane

Hawthorne's (1983) amphibole #26 was used. Chemical analyses show significant departures from the end-member composition, $Na_2Al_2Mg_3Si_8O_{22}(OH)_2$, but only involving Fe^{3+}, Fe^{2+}, and Ca. The composition of glaucophane can be related to the composition of cummingtonite by the exchange operation $NaAlMg_{-2}$, where the Na occupies the $M(4)$ site, and the smaller Al occupies the neighboring $M(2)$ site. The $M(1)$ and $M(3)$ sites are occupied primarily by Mg and Fe^{2+}. Mean M–O distances for the $M(1)$ and $M(3)$ octahedra are nearly the same, indicating that the Fe and Mg are disordered over the two sites. Thus, natural glaucophane typically shows the four Fe^{2+}–Mg bands (A, B, C, D: Strens 1974), with relative intensities depending on the ratio of Fe^{2+} to Mg. For glaucophane, Ernst & Wai (1970) reported 3660, 3644, 3630 and 3614 cm^{-1} for the fundamental frequencies of the A, B, C and D bands, respectively; Burns (1970) reported 7164, 7138, 7108 and 7073 cm^{-1} for the corresponding first-overtone frequencies.

Pargasite

Like other natural examples of pargasite, the composition of Hawthorne's (1983) amphibole #71 is complicated. For the purposes of calculating OH-stretching frequencies, the composition was treated as a simple departure from tremolite according to the exchange operation $NaAl_3\square_{-1}Mg_{-1}Si_{-2}$, which is the sum of the familiar Tschermaks exchange $Al_2Mg_{-1}Si_{-1}$ and the exchange $NaAl\square_{-1}Si_{-1}$. Na occupies the A site, one-third of the Al occupies octa-

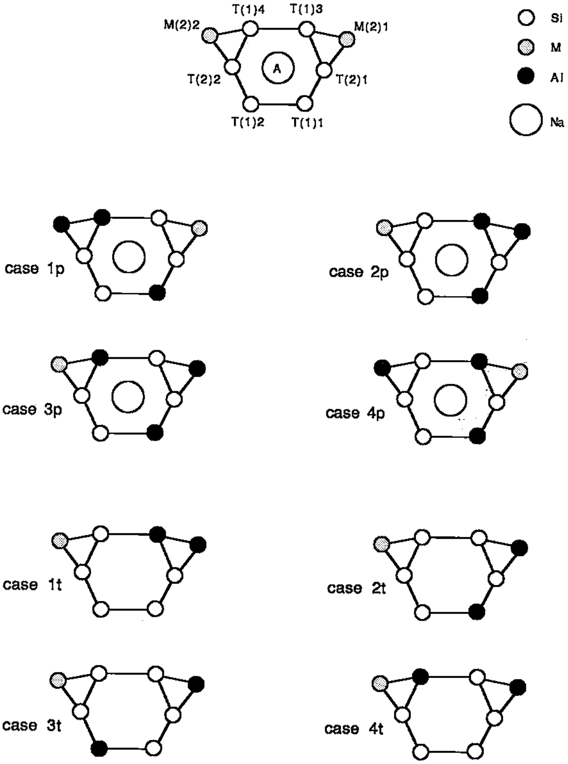

FIG. 2. Different local orderings of Al, Si, M^{2+}, Na, and $\square$ (vacancy), at T(1), M(2) and A sites. Atoms at adjacent cation-sites are connected by line segments.

hedrally coordinated sites, and two-thirds occupy tetrahedrally coordinated sites. Several structure determinations of natural pargasite and hornblende (Hawthorne 1983, Phillips *et al.* 1989, Makino & Tomita 1989) show ^{VI}Al strongly ordered at M(2), and ^{IV}Al equally strongly ordered at T(1). Four local orderings of ^{IV}Al, ^{VI}Al, Mg, Si and Na in the structural environment of Figure 1 are stoichiometrically consistent with the $NaAl_3\square_{-1}Mg_{-1}Si_{-2}$ exchange. Individual sites are identified according to the scheme of labeling shown in Figure 1. The four local orderings (Fig. 2) are: case 1p: Na on site A, Al at sites T(1)1, T(1)4, and M(2)2; case 2p: Na at A, Al at T(1)1, T(1)3, and M(2)1; case 3p: Na at A, Al at T(1)1, T(1)4 and M(2)1, and case 4p: Na at A, Al at T(1)1, T(1)3, and M(2)2. In local orderings 1p and 2p, the two Al of the "Tschermaks" part of the exchange ($Al_2Mg_{-1}Si_{-1}$) occupy adjacent tetrahedral and octahedral sites (*i.e.*, case 1p, Al at T(1)4 and M(2)2; case 2p, Al at T(1)3 and M(2)1). These arrangements give the best distributions of local charges, with the sum of Pauling bond-strengths equal to 1.91 v.u. (= valence units) at the oxygen shared by ^{IV}Al and ^{VI}Al. Local orderings 3p and 4p each involve oxygen atoms in two kinds of M–O–T environments: ^{VI}Al–O–Si, for which the sum of Pauling bond-strengths at the oxygen is 2.17 v.u.; and Mg–O–^{IV}Al, for which the sum of Pauling bond-strengths at the oxygen is 1.75 v.u. Thus, it is surmised that the local orderings 1p and 2p should be more important than the local orderings of cases 3p and 4p in any amphibole. Other, non-stoichiometric arrangements of cations, which may be important locally, will not be considered.

Except for the relative intensities of the major bands, absorption spectra of reduced synthetic hastingsite and pargasite are similar to the absorption spectra of natural magnesio-hastingsite (Semet 1973). Spectra typically consist of two broad OH-stretching bands, with maximum absorbances near 3705 and 3675 cm^{-1}. The higher frequency has been assigned to an A band, and the lower frequency, to a B band (Semet 1973). For magnesio-hastingsite synthesized under more oxidizing conditions, the B band near 3675 cm^{-1} all but disappears, and a new, lower-frequency band appears at 3660 cm^{-1}. This behavior is consistent with the conversion (by oxidation) of the local environment responsible for the B band (HO-Mg_2Fe^{2+}) to the local environment responsible for an E band (HO-Mg_2Fe^{3+}: Hawthorne 1983). Oxidation experiments had no effect on the high-frequency band at 3705 cm^{-1}. Thus for magnesio-hastingsite (Semet 1973), and by extension for at least some compositions of pargasite and hornblende, the experiments leave little doubt regarding the band assignment.

The synthetic pargasites studied by Raudsepp *et al.* (1987) contain no Fe. Hence B, C, and D bands are not possible. The IR spectrum of synthetic pargasite (M^{3+} = Al) shows two major absorption bands near 3709 and 3676 cm^{-1}, assigned respectively to A and K bands (Raudsepp *et al.* 1987). A K band corresponds to a hydroxyl group with the ligand combination Mg_2Al (Hawthorne 1983). Presumably, the K band should not be important in natural amphiboles (Semet 1973), inasmuch as structure determinations (Hawthorne 1983, Makino & Tomita 1989) show that trivalent octahedral cations (Al, Fe^{3+}) are strongly ordered onto M(2) sites, and not onto M(1) or M(3) sites. Like natural magnesio-hastingsite, the A band is shifted significantly to higher frequencies (> +30 cm^{-1}) relative to the same bands in tremolite or cummingtonite. Obviously, the high frequency of the A band cannot have anything to do with +3 cations at M(1) or M(3) sites, but must instead be due to the combined effects of Na at the A site, Al at T(1), and Fe^{3+} or Al at M(2). Unfortunately, individual effects are difficult to isolate. It has been indicated (Hawthorne 1981, 1983) that Na_A causes a +24 cm^{-1} shift in the frequency of the A band, whereas ^{IV}Al causes a –75 cm^{-1} shift. For a local environment involving one

Na_A and two $Al_{T(1)}$, as in pargasite, the net shift would be $+24 + 2(-75)$ cm^{-1}, or -126 cm^{-1}. Yet the observed shift in the frequency of the A band for hastingsite or pargasite is approximately $+30$ cm^{-1} relative to the frequency of the *A* band for tremolite or cummingtonite.

Ts-hornblende

Calculations were done on results of the H-1 structure determination of Phillips *et al.* (1989). For the purpose of calculating OH-stretching frequencies, the composition was simplified to $Na_{0.5}Ca_2Mg_4Al[Si_{6.5}Al_{1.5}]O_{22}(OH)_2$, which is related to the composition of tremolite $[Ca_2Mg_5Si_8O_{22}(OH)_2]$ by adding ½ of the "pargasite" exchange (*i.e.*, ½ $NaAl_3\square_{-1}Mg_{-1}Si_{-2}$), and ½ of the Tschermak exchange (*i.e.*, ½ $Al_2Mg_{-1}Si_{-1}$). Presumably, half of the local environments (Fig. 1) would have cation arrangements like those already described for pargasite, and half of the local environments would have cation arrangements involving one ^{IV}Al and one ^{VI}Al, but no Na at the *A* sites. For the latter, there are four distinct possibilities: case 1t: Al at *T*(1)3 and *M*(2)1; case 2t: Al at *T*(1)1 and *M*(2)1; case 3t: Al at *T*(1)2 and *M*(2)1, and case 4t: Al at *T*(1)4 and *M*(2)1. Only one case (1t) involves the ^{IV}Al–O–^{VI}Al configuration, which comes closest to satisfying the Pauling bond-strength rule. Each of the other cases (2t, 3t, 4t) involves two oxygen atoms that are respectively undersaturated and oversaturated with respect to Pauling bond-strength sums. Presumably, local Tschermak ordering 1t should be the most important in real amphiboles.

The IR absorption spectrum for Ts-hornblende has been interpreted as a complicated pattern of many overlapping fundamental OH-stretching bands (Phillips *et al.* 1989). High absorbance occurs continuously over a range of frequencies from approximately 3600 cm^{-1} to approximately 3700 cm^{-1}. The maximum absorbance occurs near 3615 cm^{-1}, consistent with a D band, but the modest fraction of Fe [Fe/(Mg + Fe) = 0.47] suggests that factors other than local ordering of Fe and Mg on *M*(1) and *M*(3) also must be involved. According to their best assessment of the complicated absorption spectrum, Phillips *et al.* (1989) suggested 3672, 3657, 3641 and 3621 cm^{-1} for the frequencies of the A, B, C and D bands, respectively. The frequencies do not differ much from the frequencies of corresponding bands for cummingtonite, grunerite or glaucophane. Higher frequencies, up to 3691 cm^{-1}, are ascribed to the influence of *A*-site cations (mainly Na).

METHODS

All calculations were done in two steps with the programs QUICKSIT and STRETCH. Both programs (available from the author) are written in PASCAL for either a MacIntosh or an IBM-compatible PC.

QUICKSIT

This program uses a modified simplex method (Cooper 1981) to search for the minimum-energy position of an atom in a local environment of a finite number of neighboring atoms. For the amphiboles used in this study, the search was done for the position of lowest energy for a hydrogen atom in the cluster of atoms shown in Figure 1. Depending on whether or not the *A* site is occupied, the local environment consists of 39 or 40 neighboring atoms, which include 25 oxygen atoms, 6 tetrahedral cations (*T* sites), 8 octahedral cations [2 each of *M*(1), *M*(2), *M*(3), and *M*(4)] and, where relevant, 1 *A*-site cation.

In QUICKSIT, the energy of the hydrogen atom is calculated as

$$W_H = \Sigma_i[q_i q_H / r_{iH}] + \Sigma_i[\lambda_{iH} \exp(-r_{iH}/\rho_{iH})], \qquad (2)$$

where q_H and q_i are the formal ionic charges on H (+1) and atom *i*, respectively, and r_{iH} is the interatomic distance between *i* and H; λ_{iH} and ρ_{iH} are short-range repulsion coefficients for the *i*–H pair of atoms. Thus the first summation is the Coulombic contribution to the energy, and the second summation is the contribution due to short-range repulsions. Abbot *et al.* (1989a,b) determined that values of λ_{OH} = 30000 kJ and ρ_{OH} = 0.25 Å are generally consistent with observed positions of hydrogen atoms in tremolite, various phyllosilicates, and the humite minerals. For observed H–*i* distances (where *i* is a cation), the corresponding short-range contributions are negligible (Abbott *et al.* 1989a,b). In order to simplify the calculations, all short-range terms involving *M*(1), *M*(2), *M*(3), *M*(4), *A*, and *T* cations were omitted from the summation by setting the corresponding λ_{iH} coefficients to zero.

The choice of an appropriate cluster was based on three criteria (see also Abbott 1990). (1) For the tremolite (#56: Hawthorne 1983), there must exist values for λ_{OH} and ρ_{OH} such that the calculated position of the hydrogen is close to the observed position. (2) Obviously, there must be sufficient *M*(1), *M*(2), *M*(3), *M*(4), *A*, and *T* sites to adequately simulate effects related to different distributions of charges on these kinds of sites. (3) For reasons related to the second criterion, the distribution of sites in the cluster must be consistent with the observed point-symmetry of the hydroxyl oxygen. Thus the sites of the cluster must be related by an (0 1 0) mirror passing through the hydroxyl oxygen. Beyond these constraints, the precise number of atoms in the cluster, the net charge on the cluster (–10), and any net dipole moment are not critical. For the present purposes, it is only important that the 40-site cluster has a similar geometry for each of the amphiboles, and the net charge on the cluster is the same. Because the sites are arranged relatively symmetrically with respect to the hydrogen atom (*i.e.*, the sites are all within a radius of approximately 5.25 Å from the hydrogen atom), the net dipole moment would presumably be small, and more or less the same for each of the amphiboles. The limited number of atoms in the cluster would be a matter of some concern if the approach were not empirical. The effects of using a limited number of atoms in the cluster were evaluated by adding or subtracting sites from the cluster, with the result that the calculated position of the hydrogen and corresponding energy (W_H) at the minimum do change, but changes in the hydrogen position were not significant.

Alternative methods involving the total cohesive energy (Post & Burnham 1986) of an extended structure give nearly the same hydrogen position in cummingtonite (using λ_{OH} = 30000 kJ, ρ_{OH} = 0.25 Å, Abbott & Burnham, in prep.) as with the simpler cluster. However, most procedures used to calculate the total cohesive energy use some variant of the Ewald–Bertaut–Williams method (Busing 1981), which applies only to perfectly ordered structures. Problems associated with short-range ordering, such as those involving different local distributions of ^{IV}Al, ^{VI}Al, Mg, Si, and Na in amphiboles, cannot be treated entirely satisfactorily.

STRETCH

This program was used to determine stretching-mode frequencies for a pair of atoms, in this case O and H, in a local environment involving a finite number of neighboring sites. In each round of calculations, the local environment was the same as that used in the corresponding QUICKSIT calculations. STRETCH calculations proceed in two stages: (1) determination of OH pair-energies for different interatomic distances; (2) calculation of an anharmonic oscillator to model the calculated energies.

For the O–H pair in the local environment of an amphibole, the energy is given by

$$W_{OH} = W_H + W_O, \qquad (3)$$

where W_H is the energy of the hydrogen atom (equation 2), the same as for QUICKSIT, and W_O is the energy of the hydroxyl oxygen, less the contribution due the O–H pair, which is already included in W_H. The contribution due to the hydroxyl oxygen is therefore given by

$$W_O = \Sigma_{i\neq H}[q_O q_i/r_{iO}] + \Sigma_{i\neq H}[\lambda_{iO}\exp(-r_{iO}/\rho_{iO})]. \qquad (4)$$

Values for λ_{iO} and ρ_{iO} (where i = Mg, Al, Si, O) were taken from Post & Burnham (1986). Note that the neighboring atoms i include oxygen atoms other than the hydroxyl oxygen, and hence it is necessary to include Coulombic and short-range contributions from O–O pairs. All λ_{iO} and ρ_{iO} values were referred to an oxygen shell-radius (Post & Burnham 1986) of 1.01 Å. More precise values for λ_{iO} and ρ_{iO}, that would otherwise take into account different shell-radii for different oxygen atoms, are not critical in the present calculations because W_O, as formulated above, does not vary significantly as a function of O–H distance. That W_O should vary at all becomes apparent only when the frame of reference is specified for variations in the O–H distance. In calculating the energy of the pair, W_{OH}, for different O–H distances, both O and H were displaced relative to the center of gravity of the pair. Thus the contribution of the Oi pairs, W_O, does vary. However, for a given change in the O–H distance, the change in W_O is small by comparison with the change in W_H, simply because the displacement of the oxygen atom (being 16 times more massive than the hydrogen atom) is small in comparison with the displacement of the hydrogen atom.

The energy of the OH, W_{OH}, was calculated for O–H distances differing by increments of 0.01 Å, such that the positions for O and H were always on the line defined by the observed position for O and a previously calculated (QUICKSIT) minimum-energy position for H. Accordingly, the OH pair-energy function, W_{OH}, was "sampled" for regular increments of the O–H distance. Values for W_{OH} were calculated for O–H distances both longer and shorter than the minimum energy O–H distance, but only for energies less than 100 kJ above the minimum energy, *i.e.*, the O–H energy "well" was sampled only up to a "water level" of 100 kJ. A typical "sampling" involved from 40 to 50 O–H distances and corresponding pair-energies, providing adequate information regarding the relevant part of the OH pair-energy function. The second stage of a STRETCH calculation shows that observed fundamental OH-stretching frequencies in minerals (3000 to 4000 cm^{-1}) typically involve OH pair-energies up to approximately 60 kJ higher than the minimum energy. [Note: this paper maintains the long-standing, albeit confusing, tradition of referring to a frequency by its corresponding wavenumber through the relationship $f = c\nu$, where f = frequency (s^{-1}), c = velocity of light (cm/s), and ν = wavenumber (cm^{-1}) = $1/\lambda$, where λ = wavelength (cm).].

In the second stage of a STRETCH calculation, an anharmonic oscillator model is fitted by least squares to the sampled points on the OH pair-energy function. The potential for an anharmonic oscillator was represented by a Taylor expansion truncated at the fourth-order term (Levine 1970), for OH:

$$U_{OH} - U_{OH,\ minimum} = 1/2\ k_1(r_{OH}-r_o)^2 + 1/6\ k_2(r_{OH}-r_o)^3 + 1/24\ k_3(r_{OH}-r_o)^4 \qquad (5)$$

where k_1, k_2, k_3, and r_o are constants evaluated in the least-squares procedure. The O-H distance r_o corresponds to the minimum value for U_{OH}. Values calculated for r_o were found to be typically the same as the O-H distance for the minimum energy on the W_{OH} function. For an ideal harmonic oscillator, $k_2 = k_3 = 0$. Values for k_1, k_2, and k_3 were determined to tolerances of ± 5 kJ/Å^2, ± 30 kJ/Å^3, and ± 120 kJ/Å^4, respectively. The tolerance on r_o, ± 0.01 Å, is equal to the sampling increment in r_{OH} for the OH pair-energy W_{OH}. The closeness of the fit was measured by standard statistical parameters, R_{wp}, R_{ex}, and GoF (see footnote to Table 1; *e.g.*, Post & Bish 1989). All samples of the W_{OH} function were weighted equally in the least-squares procedure. A perfect fit would give R_{wp} = GoF = 0. For practical purposes, a GoF = R_{wp}/R_{ex} less than or equal to one indicates an exceptionally close fit. Typical values for R_{wp} were close to 0.02, with goodness-of-fit values, GoF, substantially less than 0.5. Thus the OH pair-energy function, W_{OH}, can be very accurately described by the anharmonic potential function U_{OH}.

For the anharmonic potential function, U_{OH}, Levine (1970) gave the following quantum mechanical solution for the vibrational energy:

$$[E(v)-U_{OH,minimum}]/h/c = \nu_e(0.5+v) - x_e\nu_e(0.5+v)^2 + Y_{00}/c \qquad (6)$$

where v is the quantum number (0, 1, 2, ...), c is the speed of light, and h is Planck's constant. The terms ν_e, $x_e\nu_e$, and Y_{00} are complex functions of k_1, k_2, k_3, and r_o. The expression gives the energy in wavenumbers (cm^{-1}) for different vibrational states (v = 0, 1, 2,...) relative to the minimum energy ($U_{OH,minimum}$). For an ideal harmonic oscillator, $x_e\nu_e = Y_{00} = 0$, hence the magnitudes of these constants can be used as measures of departure from an ideal harmonic oscillator. The $x_e\nu_e$ parameter is commonly referred to as the "anharmonicity" constant. The absorption frequency (in cm^{-1}) corresponding to a change from state v = v_1 to v = v_2 is given by

$$V_2(v_2,v_1) = [E(v_2) - E(v_1)]/c/h = \nu_e(v_2-v_1) - x_e\text{-}\nu_e[(0.5+v_2)^2 - (0.5+v_1)^2] \qquad (7)$$

Thus V(1,0) is the frequency for the fundamental stretching mode, and V(2,0) is the frequency for the first overtone. For an ideal harmonic oscillator, V(2,0) is equal to 2V(1,0). For hydroxyl groups in

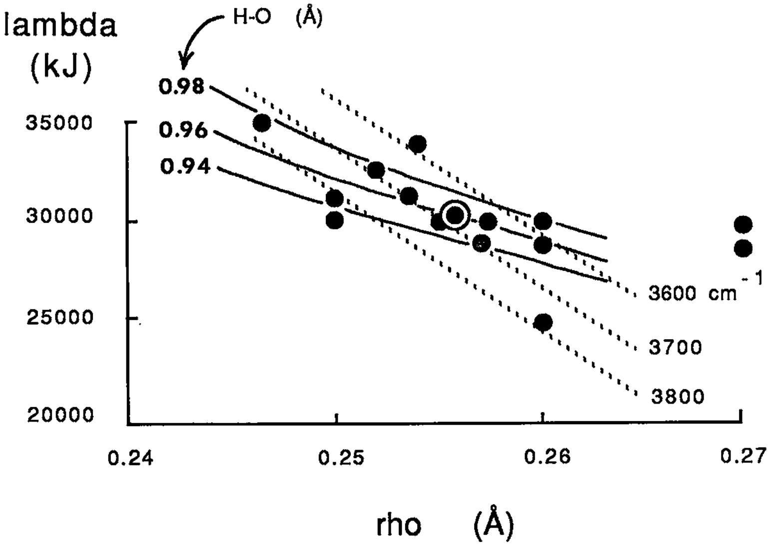

FIG. 3. Results of QUICKSIT and STRETCH calculations on tremolite. Small dots mark λ_{OH} - ρ_{OH} combinations for which calculations were performed. Solid contours are for calculated O-H distances (in Å); dashed contours are for the OH-stretching frequency (in cm^{-1}). The circled dot marks the best λ_{OH} - ρ_{OH} combination for the closest agreement with the observed O-H distance and observed OH-stretching frequency.

minerals, V(2,0) is less than 2V(1,0), hence the OH group vibrates anharmonically such that $x_e\nu_e$ exceeds 0. This is also the usual relationship for isolated diatomic molecules involving other atoms (H_2, HF, N_2, CO, O_2, and I_2: Levine 1970).

RESULTS AND DISCUSSION

An improved O-H short-range potential for tremolite

Minimum-energy positions for hydrogen in tremolite were determined for different combinations of values for the short-range coefficients λ_{OH} and ρ_{OH}. Figure 3 shows the variation in the O–H distance (solid contours) as a function of λ_{OH} and ρ_{OH}. The solid dots correspond to the individual λ_{OH}–ρ_{OH} combinations on which the calculations were done. For a given O–H distance, λ_{OH} varies inversely with respect to ρ_{OH}. Thus for the observed O–H distance in tremolite (0.960 Å: Hawthorne 1983), values for λ_{OH} and ρ_{OH} are not defined uniquely.

Using STRETCH, fundamental OH-stretching frequencies were then calculated for each of the different λ_{OH}–ρ_{OH} combinations. Figure 3 also shows the variation in the calculated stretching frequency (dashed contours) as a function of λ_{OH} and ρ_{OH}. The observed fundamental OH-stretching frequency for tremolite is 3674 cm^{-1} (Sheu & McMillan 1988). The λ_{OH}–ρ_{OH} combination marked by the circled dot in Figure 3 gave the best agreement between observed and calculated relationships (Table 1). Accordingly, the best values for λ_{OH} and ρ_{OH} are 30500 kJ and 0.2560 Å, respectively. Further refinement of λ_{OH} and ρ_{OH} is possible, but hardly warranted, given the uncertainty in the observed position for the hydrogen atom. The new values for λ_{OH} and ρ_{OH} do not differ greatly from values determined on the basis of admittedly less stringent criteria (λ_{OH} = 30000 kJ, ρ_{OH} = 0.25 : Abbott *et al.* 1989b). For the simple purpose of calculating realistic positions for the hydrogen, precise values for λ_{OH} and ρ_{OH} are not so critical. In the case of tremolite, if the O–H distance were not known, Figure 3 would give the impression that generally reasonable O-H distances (*e.g.*, 0.92 to 0.98 Å) could be accommodated by a relatively wide range of values for λ_{OH} and ρ_{OH}, but not all λ_{OH} – ρ_{OH} combinations would give reasonable OH-stretching frequencies. A reasonable OH-stretching frequency (*e.g.*, 3674 cm^{-1} for tremolite) can only be accommodated by a rather more restricted range of λ_{OH} and ρ_{OH} values. Thus, with respect to small changes in λ_{OH} and ρ_{OH}, the OH-stretching frequency is very much more sensitive than the O–H distance.

In addition to improved values for λ_{OH} and ρ_{OH}, the STRETCH calculations also provide important information on the departure from ideal harmonic behavior. Relevant constants corresponding to the best values for λ_{OH} and ρ_{OH} are presented in Table 2. The relative magnitude of the anharmonic potential constants k_1, k_2, and k_3 are consistent with values calculated for diatomic molecules (Levine 1970). The O–H distance r_o for the minimum energy on the anharmonic potential function, U_{OH}, is slightly less (0.01 Å less) than the O–H distance for the minimum energy on the OH pair-energy function, W_{OH}, and similarly less than the observed O–H distance. However, the reader should note that the observed O–H distance for an anharmonic oscillator should not be the same as the O–H distance for the minimum energy on the anharmonic potential function. This is because of the asymmetry of the U_{OH} function and the fact that the zero-state (v = 0) vibrational energy is not the same as the minimum on the U_{OH} function (when v = 0, $[E(0)-U_{OH,minimum}]/h/c = \frac{1}{2}\,\nu_e - \frac{1}{4}\,x_e\nu_e + Y_{00}/c$). By analogy with other diatomic systems (Levine 1970), the observed O–H distance should be slightly longer than the O–H distance, r_o, corresponding to the minimum on the anharmonic potential function, $U_{OH,minimum}$.

The calculated constants of vibrational energy, ν_e, $x_e\nu_e$, and Y_{00} (Table 1), are reasonable for a diatomic molecule (Levine 1970). The harmonic constant, ν_e, is very much larger than either the anharmonic constant, $x_e\nu_e$, or the Y_{00} constant, which indicates that the departure from an ideal harmonic oscillator is not extreme. This is perhaps easier to appreciate from the calculated frequency for the first overtone, V(2,0) = 7224 cm^{-1}, which is not much less than twice the fundamental frequency, 2V(1,0) = 7348 cm^{-1}. The departure from ideal harmonic behavior, as reflected by the calculated stretching frequencies, is generally consistent with observed IR OH-absorption data for other minerals (Rossman 1984, 1988, Hawthorne 1981). The calculated first-overtone frequency (7224 cm^{-1}), which in the present case corresponds to a "pure" *A* band, agrees well with an observed first-overtone frequency of 7180 cm^{-1} (Burns 1970) for the *A* bands of two samples of actinolite.

The calculated anharmonicity constant $x_e\nu_e$ = 62 cm^{-1} (Table 1) is reasonably close to the experimental value of 83 cm^{-1} (Burns & Strens 1966) and represents a decided improvement over a value of 37 cm^{-1} calculated from molecular orbital theory (Sheu & McMillan 1988). The latter method (Sheu & McMillan 1988) consistently predicts fundamental OH-stretching frequencies more than 150 cm^{-1} higher than the observed frequency, and consistently gives longer minimum-energy O–H distances than the observed distance. Problems with the molecular orbital approach presumably stem from oversimplification of the local structural environment of the hydroxyl oxygen.

Transferability of OH short-range potential to other structures

The short-range coefficients λ_{OH} and ρ_{OH} determined for tremolite were applied to three other amphiboles: cummingtonite, grunerite, and glaucophane. These amphiboles were chosen because they are well ordered, except with regard to $FeMg_{-1}$ exchange. In each case, no experimentally determined position for hydrogen was available for comparison with a position calculated by QUICKSIT. However, for each of the amphiboles, there are good IR absorption data for comparison with the calculated OH-stretching frequencies. The results of QUICKSIT and STRETCH calculations are reported in Table 2.

With regard to OH-absorption, the important structural differences between cummingtonite and grunerite involve the proportion of Fe^{2+} and Mg at the various *M* sites. As discussed earlier, the absorption patterns for both minerals show A, B, C, and D bands, but the relative absorbances are different. However, in the present calculations, because the structure determinations are averages consistent with *C2/m* symmetry, all local OH environments are symmetrically equivalent. This means that only one "ABCD-hybrid" stretching frequency can be calculated for each structure. Calculated frequencies for cummingtonite and grunerite are in the range of observed frequencies for A, B, C, and D bands (3700 to 3600 cm^{-1}: Hawthorne 1983), and within 11 cm^{-1} of the observed frequency of the *A* band for tremolite (3674 cm^{-1}: Sheu & McMillan 1988). Calculated first-overtone frequencies are somewhat greater than, but reasonably consistent with, the observed first-overtone frequency of the *A* band for cummingtonite (7172 cm^{-1}: Burns 1970).

The various constants, k_1, k_2, k_3, r_o, ν_e, $x_e\nu_e$, and Y_{00} for cummingtonite do not differ greatly from the corresponding constants for grunerite. The calculated O–H distances and the hydrogen coordinates themselves are remarkably similar. One wonders then just how significant is the difference between the calculated OH-stretching frequencies. Bearing in mind that the average local environment (on which the calculations were done) cannot correspond to any one local environment in an actual mineral, an assessment of the significance of the calculated OH-stretching frequencies becomes somewhat of a problem. As a point of departure, it might be assumed that the difference between the calculated frequencies for the two minerals might be proportional to the difference between the fractions $X_{Fe} = Fe^{2+}/(Mg + Fe^{2+})$ at the *M*(1) and *M*(3) sites for the two minerals relative to the observed difference in the frequencies for A and D bands. According to Strens (1974), the frequency of the D band differs from that of the *A* band by approximately –47 cm^{-1}. If so, then

$$[V(1,0)_{gru} - V(1,0)_{cum}] = (-47\ cm^{-1})[X_{Fe,gru} - X_{Fe,cum}] \quad (8)$$

Values for $X_{Fe,gru}$ and $X_{Fe,cum}$ are 0.861 and 0.290, respectively (Hawthorne 1983), which gives a difference in frequency of approximately –27 cm^{-1}; this value can be compared directly with the results of QUICKSIT–STRETCH calculations (Table 2), which give a difference of –18 cm^{-1}. The sense of the shift is correct, and the magnitudes are similar. Thus, once the average nature of *C2/m* structure is taken into account, albeit crudely, it seems that the difference in the calculated frequencies (Table 2) is reasonably consistent with observed differences in the frequencies for the *A* and *D* bands.

The important distinction between glaucophane and tremolite or cummingtonite has to do with the atoms occupying the *M*(2) and *M*(4) sites. The occupancies of the *M*(1) and *M*(3) sites are more or less the same in cummingtonite #21 (Hawthorne 1983) and glaucophane #26 (Hawthorne 1983). Therefore, the low calculated OH-stretching frequency of 3610 cm^{-1} for glaucophane (Table 2) must necessarily be due to the Na at the *M*(4) sites

TABLE 2. RESULTS OF CALCULATIONS ON CUMMINGTONITE, GRUNERITE, AND GLAUCOPHANE

	Cummingtonite	Grunerite	Glaucophane
QUICKSIT			
Short-range coefficients: $\lambda_{OH} = 30500$ kJ, $\rho_{OH} = 0.2560$ Å			
Hydrogen positions:			
x	0.2149	0.2157	0.2154
y	0.0	0.0	0.0
z	0.7711	0.7763	0.7241
H-O dist. (Å)	0.957	0.947	0.965
STRETCH			
Constants in anharmonic oscillator function, U_{OH}:			
k_1 (kJ/Å^2)	4880	4850	4710
k_2 (kJ/Å^3)	-26220	-27060	-24930
k_3 (kJ/Å^4)	98640	109200	80640
r_0 (Å)	0.946	0.947	0.955
$^1R_{wp}$	0.0056	0.0089	0.0060
$^1R_{ex}$	0.0211 (N = 42)	0.0204 (N = 43)	0.0211 (N = 43)
^1GoF	0.0692	0.1907	0.0805
Constants in vibrational energy functions, $[E(v)-U_{OH,minimum}]/h/c$ and $V(v_2,v_1)$			
v_e (cm^{-1})	3809.3	3797.6	3742.4
x_ev_e (cm^{-1})	62.0	65.3	65.7
Y_{00}/c (cm^{-1})	-1.2	-0.9	-2.6
Calculated absorption frequencies:			
V(1,0) (cm^{-1})	3685	3667	3610
V(2,0) (cm^{-1})	7247	7204	7090

1. See footnote in Table 1.

and Al at the *M*(2) sites. Additional calculations were done on tremolite, but with the charge distribution changed to that in glaucophane (*i.e.*, consistent with the exchange $2NaAlCa_{-1}Mg_{-1}$). The calculated OH-stretching frequency for this modified tremolite was found to be 3580 cm^{-1}, which supports the contention that the site occupancies of the *M*(4) and *M*(2) sites are directly responsible for the low, calculated OH-stretching frequency. Observed frequencies for A, B, C, and D bands in glaucophane (3660, 3644, 3630, 3614 cm^{-1} respectively: Ernst & Wai 1970) are all higher than the calculated frequencies. Quite clearly, λ_{OH} and ρ_{OH} values based on tremolite are not strictly transferable to glaucophane because of the Na at *M*(4) and Al at *M*(2). This means that cation substitutions at the relatively distant *M*(2) and *M*(4) sites can have an important effect on λ_{OH} and ρ_{OH}, and hence an important effect on the short-range OH repulsion.

Application to chemically complex amphiboles

Both pargasite (#71: Hawthorne 1983) and Ts-hornblende (Phillips *et al.* 1989) have Al at tetrahedral and octahedral sites, and Na at some or all of the *A* sites. The results of QUICKSIT–STRETCH calculations are reported in Table 3 for some probable local orderings of the cations.

TABLE 3. RESULTS OF CALCULATIONS ON PARGASITE AND TS-HORNBLENDE

			QUICKSIT		
Short-range coefficients: λ_{OH} = 30500 kJ, ρ_{OH} = 0.2560 Å					
	PARGASITE		TS-HORNBLENDE		
[1]Ordering	1p	2p	1p	2p	1t
H-positions:					
x	0.1937	0.2003	0.1925	0.1995	0.2049
y	0.0189	0.0161	0.0197	0.0170	0.0028
z	0.6859	0.7116	0.6716	0.6937	0.8314
H-O dist. (Å)	0.950	0.950	0.950	0.950	0.979
			STRETCH		
Constants in anharmonic oscillator function, U_{OH}:					
k_1 (kJ/Å^2)	5030	5070	4990	5040	4380
k_2 (kJ/Å^3)	-30270	-27870	-31680	-28530	-24030
k_3 (kJ/Å^4)	147000	109320	169440	120000	82330
r_o (Å)	0.940	0.940	0.940	0.940	0.969
[2]R_{wp}	0.0156	0.0100	0.0199	0.0120	0.0067
[2]R_{ex} (N)	0.0214 (41)	0.0203 (42)	0.0216 (41)	0.0204 (42)	0.0202 (46)
[2]GoF	0.5305	0.2348	0.8541	0.3501	0.1090
Constants in vibrational energy functions, $[E(v)-U_{OH,minimum}]/h/c$ and $V(v_2,v_1)$					
v_e (cm^{-1})	3867.4	3882.8	3852.0	3871.3	3608.9
$x_e v_e$ (cm^{-1})	69.2	64.0	73.8	65.8	69.7
Y_{00}/c (cm^{-1})	0.6	-1.1	1.8	-0.6	-2.7
Calculated absorption frequencies:					
V(1,0) (cm^{-1})	3729	3755	3704	3740	3469
V(2,0) (cm^{-1})	7320	7381	7261	7348	6799

1. Case 1p = Na on A, Al on T11, T14, M22 (Fig. 2).
   Case 2p = Na on A, Al on T11, T13, M21.
   Case 1t = [ ] on A, Al on T13, M21.
2. See footnote in Table 1.

Two frequencies of OH-stretching were calculated for pargasite, 3729 cm^{-1} (ordering 1p) and 3746 cm^{-1} (ordering 2p), both of which are somewhat higher than the highest observed frequency for pargasite and hastingsite (*A* band at 3705 cm^{-1}: Semet 1973, Raudsepp *et al.* 1987). Calculated stretching frequencies for the less probable local orderings 3p and 4p (Fig. 2) were 3326 and 3322 , respectively, both of which are approximately 300 cm^{-1} lower than the lowest observed frequency of OH-absorption. Further calculations, done on tremolite (#56), but using charge distributions consistent with orderings 1p and 2p (Fig. 2), gave absorption frequencies of 3682 cm^{-1} and 3705 cm^{-1}, respectively, which quite by accident agree surprisingly well with the observed frequencies of the A and B bands for natural hastingsite (3675 and 3705 cm^{-1} respectively: Semet 1973). This result serves only to emphasize that the local 1p and 2 p orderings of $Al_{M(2)}$, $Al_{T(1)}$, and Na_A are probably important in both A and B bands and, by extension C and D bands also.

The Ts-hornblende must involve both of the important "pargasite" local orderings (1_p and 2_p), in which the *A* site is occupied by Na, and also the local ^{IV}Al–^{VI}Al ordering 1t, in which the *A* site is vacant. Results of QUICKSIT–STRETCH calculations are reported in Table 3. Calculated frequencies for local orderings 1p and 2p (3704 and 3740 cm^{-1}, respectively) are both higher than the highest observed frequency, but similar to frequencies calculated for the same local orderings in pargasite (Table 3). The calculated frequency for local ordering 1t (3469 cm^{-1}) is unusually low and does not correspond with any known frequency of absorption. Calculations also were done on tremolite, but with local ordering 1t. The resulting frequency (3443 cm^{-1}) for the modified tremolite was found to be comparable to the frequency for the same local ordering in Ts-hornblende. Clearly, the low calculated frequency associated with local ordering 1t is due to the combined effects of a vacant *A* site, and Al on adjacent *T*(1) and *M*(2) sites.

The calculations show that λ_{OH} and ρ_{OH} values based on tremolite can be transferred reasonably well to local orderings 1p and 2p in pargasite and Ts-hornblende, but cannot be transferred successfully to local ordering 1t. With regard to local ordering 1p, the calculated shift in the frequency (> +30 cm^{-1}), relative to the frequency of the A band for tremolite or cummingtonite, is consistent with observed relationships. Thus the high frequency of the A band in natural and synthetic hastingsite and pargasite probably results from the combined effects of Na_A, $Al_{T(1)}$ and $2Al_{M(2)}$, where $Al_{T(1)}$ and one of the $Al_{M(2)}$ share an oxygen.

CONCLUSIONS

1. For OH-bearing minerals in general, and amphiboles in particular, improved short-range OH repulsion coefficients can be determined empirically from two observations, a reliable position of the hydrogen (preferably determined on the basis of neutron-diffraction experiments), and an OH-stretching frequency that can be correlated unambiguously with the local structural environment of the hydrogen. For tremolite #56 (Hawthorne 1983), calculated short-range OH coefficients are λ_{OH} = 30500 kJ and ρ_{OH} = 0.2560 Å, which do not differ much from values determined previously by Abbott *et al.* (1989b) on the basis of "less stringent" criteria.
2. The short-range parameters can be transferred reasonably well to other well-ordered amphiboles for the purpose of calculating hydrogen positions and OH-stretching frequencies. Calculations were done on Fe-bearing cummingtonite, Mg-bearing grunerite, and Fe-bearing glaucophane. For each of these minerals, the structure is an average, consistent with *C2/m* symmetry, such that the observed local structural environment cannot correspond to an actual local structural environment in the mineral. Hence in each case, only an average hydrogen position and an average OH-stretching frequency can be calculated. If due allowance is made for this averaging, specifically with regard to the mole fraction $Fe^{2+}/(Mg+Fe^{2+})$ at the *M*(1) and *M*(3) sites, the calculated, "average" frequencies of OH-stretching for cummingtonite and grunerite are reasonably consistent with observed relationships for well-documented A and D absorption bands. The calculated stretching frequency for glaucophane is too low, indicating that values for λ_{OH} and ρ_{OH} based on tremolite are not appropriate. The problem has to do with the presence of $Na_{M(4)}$ and $Al_{M(2)}$ in the glaucophane.
3. Coefficients of short-range OH repulsion based on tremolite transfer reasonably well to certain local structural environments in more complex amphiboles. Values for λ_{OH} and ρ_{OH} based on tremolite seem to transfer reasonably well to local structural environments involving Na_A, $Al_{T(1)}$ and $2Al_{M(2)}$. The high observed and calculated frequencies agree reasonably well. Values for λ_{OH} and ρ_{OH} based on tremolite do not transfer successfully to local structural environments involving $\square_A$, $Al_{T(1)}$ and $Al_{M(2)}$ (*e.g.*, local ordering 1t). Low calculated frequencies related to local environments involving Al at *T*(1) and *M*(2), but with no Na at *A*, do not correspond to any observed absorption bands.

The success of the approach seems to depend very much on how realistic is the local structural environment of the OH. In the present study, the positions of the atoms making up the local environment were in all cases, except tremolite, necessarily but unrealistically constrained by the observed *C2/m* symmetry. Hopefully, in the future, this limitation can be overcome by using DLS analysis (Baur 1977) to generate more realistic local structural environments.

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