Canadian Mineralogist
Vol. 30, pp. 335-342 (1992)

CALCULATED FREQUENCIES OF O–H STRETCHING FOR DIFFERENT LOCAL ORDERINGS OF Fe AND Mg IN SIMPLE CLINOAMPHIBOLES

RICHARD N. ABBOTT, JR.
Department of Geology, Appalachian State University, Boone, North Carolina 28607, U.S.A.

CHARLES W. BURNHAM
Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

ABSTRACT

The short-range repulsion between oxygen and hydrogen can be represented conveniently in an exponential form, $W_r = \lambda\exp(-r/\rho)$, where r is the O–H separation; λ and ρ are constants characteristic of the O–H interaction. Values for λ and ρ can be determined empirically by conducting a search for the values that best satisfy the observed position of hydrogen and the observed frequency of O–H stretching. The procedure, as originally developed, does not adequately account for local structural details (related to nonconvergent disorder of cations) that are not resolved in structure analyses based on diffraction data. In this paper, we use Distance-Least-Squares (DLS) analysis to create more realistic geometries for the *M*(1) and *M*(3) polyhedra in simple clinoamphiboles containing Fe and Mg. Frequencies of O–H stretching are then calculated for structures consistent with the different local arrangements of Fe and Mg at the *M*(3) and *M*(1) sites. The DLS-adjusted local structures are tested by comparing calculated and observed frequencies of O–H stretching. By reproducing reasonable frequencies for the A, B, C and D bands, our goal is to learn more about local deviations from the average structures of simple Fe-clinoamphiboles. Differences in the frequencies of the A, B, C and D bands are specifically related to local variations in the structure, especially with regard to the position of the hydroxyl oxygen, O(3). The most important factor influencing the position of the O(3) oxygen is the ionic radius of the *M*(1) and *M*(3) cations.

Keywords: amphiboles, O–H stretching, local Fe–Mg order, Distance-Least-Squares approach, anharmonic oscillator model.

SOMMAIRE

On peut représenter la répulsion à courte échelle entre l'oxygène et l'hydrogène de façon commode au moyen de l'expression exponentielle, $W_r = \lambda\exp(-r/\rho)$, dans laquelle r représente la séparation O–H; λ et ρ sont des constantes caractéristiques de l'interaction des atomes O et H. On peut déterminer les valeurs de λ et ρ de façon empirique en cherchant les valeurs qui satisfont le mieux aux positions observées de l'hydrogène et à la fréquence de l'étirement O–H. La procédure, telle qu'originalement développée, ne rend pas compte de façon adéquate des détails structuraux locaux (liés au désordre non convergent parmi les cations), non résolus dans les analyses structurales fondées sur les données diffractométriques. Dans ce travail, nous nous servons d'une analyse par moindres carrés des distances pour créer des géométries plus réalistes pour les polyèdres *M*(1) et *M*(3) dans les clinoamphiboles simples à Fe et Mg. Les fréquences de l'étirement O–H sont ensuite calculées pour les structures, conformément aux différents agencements locaux des atomes Fe et Mg aux sites *M*(1) et *M*(3). Les structures locales ainsi ajustées par analyse par moindres carrés des distances sont ensuite évaluées en comparant les fréquences calculées et observées de l'étirement O–H. En reproduisant des fréquences raisonnables des bandes A, B, C et D, nous essayons de comprendre davantage les déviations locales des structures moyennes des clinoamphiboles simples à Fe–Mg. Nous attribuons spécifiquement les différences dans les fréquences des bandes A, B, C et D aux variations structurales locales, surtout par rapport à la position de l'atome d'oxygène [O(3)] faisant partie de l'hydroxyle. Le rayon des cations *M*(1) et *M*(3) exercerait le contrôle le plus important sur la position de l'atome O(3).

(Traduit par la Rédaction)

Mots-clés: amphiboles, étirement O–H, ordre Fe–Mg local, calcul par moindres carrés des distances, modèle d'oscillateur anharmonique.

INTRODUCTION

Abbott (1990) developed and tested a method to determine the short-range potential between the oxygen and hydrogen of hydroxyl groups in amphiboles. The short-range O–H potential was modeled as a simple Born–Huang (1954) exponential,

$$W_r = \lambda \exp(-r/\rho), \tag{1}$$

where λ and ρ are constants, and r is the O–H separation. The method involved a search for the λ and ρ values that best satisfy the observed position of the hydrogen atom and the observed frequency of O–H stretching. For tremolite, λ and ρ were determined to be 30500 kJ/mole of H and 0.2560 Å, respectively. The values for λ and ρ are consistent with formal ionic charges in the Coulombic contribution to the energy. Whereas the short-range potential seems to transfer reasonably well to other clinoamphiboles, Abbott (1990, 1991) acknowledged that the transferability to amphiboles containing both Fe and Mg is less straightforward. The problem arises because observed frequencies of O–H stretching depend on local structural details that are not preserved in the observed *C2/m*-averaged structures. It is quite well understood now that the observed frequencies of O–H stretching for simple clinoamphiboles depend mainly on the specific cations occupying the one *M*(3) site and two *M*(1) sites coordinated by the hydroxyl oxygen. The four possible ligand compositions, HO–Mg_3, HO–Mg_2Fe, HO–$MgFe_2$ and HO–Fe_3, give rise to four frequencies of infrared (IR) absorption, respectively designated as the A, B, C and D bands (Strens 1974, Hawthorne 1981, 1983).

A further complication has to do with different arrangements of the ligands associated with the B and C bands. For each of these bands, there are two possible local structures. For the B band, the Fe atom could be at the *M*(3) site (B′ band, Strens 1974) or at one of the otherwise symmetrically equivalent *M*(1) sites (B″ band). Observation (Strens 1974, Hawthorne 1983, Skogby & Rossman 1991) suggests that different complexions of the same ligand composition give rise to nearly the same frequency of O–H stretching. Similarly for the C band, the Mg atom could be at the *M*(3) (C′ band, Strens 1974) or one of the adjoining *M*(1) sites (C″ band), with practically no detectable difference between the corresponding, observed frequencies of O–H stretching.

Partial to complete disorder of Fe and Mg over the *M*(1) and *M*(3) sites is reflected in the geometries of the coordination polyhedra for these sites (Hawthorne 1983). Only for Mg end-member or Fe end-member amphiboles will observed *M*(1)–O, *M*(3)–O, and relevant O–O distances correspond to actual interatomic distances. Otherwise, where both Fe and Mg are present, observed *M*(1)–O, *M*(3)–O, and O–O distances are averages that reflect the average Fe–Mg population of all *M*(1) and *M*(3) sites. Thus, applying the method of Abbott (1991) directly to a *C2/m* Mg–Fe amphibole can yield only a single, calculated frequency of O–H stretching, based on the averaged HO–M_3 ligand configuration. The calculated frequency will lie between those calculated for pure Fe and Mg end-member structures; the observed frequencies of A, B, C and D bands are inaccessible because the local configurations of cations are averaged in the observed structure.

In this paper, we use Distance-Least-Squares (DLS) analysis to create realistic geometries for the *M*(1) and *M*(3) polyhedra in simple clinoamphiboles containing Fe and Mg. Then using the method of Abbott (1990, 1991), we calculate frequencies of O–H stretching for DLS structures with different local arrangements of Fe and Mg. The DLS-adjusted local structures are tested by comparing calculated and observed frequencies of O–H stretching. By reproducing reasonable frequencies for the A, B, C and D bands, one goal is to learn more about local deviations from the average structures of simple Fe–Mg clinoamphiboles.

STRUCTURES

Calculations were performed on three amphiboles, the structures of which were reported by Hawthorne (1983), tremolite (#56), cummingtonite (#21) and grunerite (#22). The structures were chosen because they are chemically simple, and relevant IR absorption data are available.

Tremolite

The tremolite structure (#56, Hawthorne 1983) was used to evaluate the short-range repulsion parameters λ_{OH} = 30500 kJ/mole of H and ρ_{OH} = 0.2560 Å (Abbott 1991). Of the structures used in this study, this is the only one pertaining to a nearly end-member composition; it is also the only one for which atomic coordinates for hydrogen have been determined (Hawthorne & Grundy 1976). The OH dipole is perpendicular to (100), with an O-H separation of 0.96 Å.

The observed fundamental frequency of O–H stretching in tremolite is 3674 cm^{-1} (Sheu & McMillan 1988). Because the tremolite is an Mg end-member, this frequency necessarily corresponds to the A band. The first overtone frequency is 7180 cm^{-1} (Burns 1970). For actinolite,

TABLE 1. HYDROXYL LIGAND COMBINATIONS

	SITES			BAND	OBSERVED FREQUENCY*
	M(1)1	M(1)2	M(3)2		(cm^{-1})
				TREMOLITE	
1.	Mg	Mg	Mg	A	3674
2.	Mg	Mg	Fe	B'	3660
3.	Fe	Fe	Mg	C'	3643
4.	Fe	Fe	Fe	D	3625
				CUMMINGTONITE	
5.	Mg	Mg	Mg	A	3666
6.	Mg	Mg	Fe	B'	3654
7.	Fe	Fe	Mg	C'	3637
8.	Fe	Fe	Fe	D	3616
				GRUNERITE	
9.	Mg	Mg	Mg	A	?
10.	Mg	Mg	Fe	B'	?
11.	Fe	Fe	Mg	C'	3625
12.	Fe	Fe	Fe	D	3610

* Strens (1974), Hawthorne (1983).

Strens (1974) reported 3675, 3660, 3643 and 3625 cm^{-1} for the A, B, C and D bands, respectively (Table 1).

Cummingtonite

The structure determination (#21, Hawthorne 1983) was carried out with a cummingtonite having $Fe^{2+}/(Mg+Fe^{2+})$ equal to 0.38. Hawthorne (1983) illustrated an IR absorption spectrum for a cummingtonite of similar composition. The spectrum for a ferroan cummingtonite (Table 1) consists of four fundamental frequencies of O–H stretching, 3666, 3654, 3627 and 3616 cm^{-1}, for the A, B, C and D bands, respectively (Strens 1974). Using the short-range O–H potential from tremolite, Abbott (1991) calculated an "average" frequency of 3685 cm^{-1} for O–H stretching, which of course pertains to the average local structural environment. That the calculated frequency is slightly higher than the observed frequency of the A band indicates that the values for the short-range parameters, λ_{OH} and ρ_{OH}, do not transfer precisely from tremolite to cummingtonite, and should be modified slightly. For a different sample of 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

Chemical analyses of the grunerite (#22, Hawthorne 1983) indicate a relatively small departure from the end-member composition, mainly in Mg content: $Fe^{2+}/(Mg+Fe^{2+})$ = 0.89. The IR spectrum contains two main absorption frequencies between 3610 and 3625 cm^{-1}, corresponding to D and C bands (Hawthorne 1983). Burns (1970) reported first-overtone frequencies that are the same as for the corresponding bands of cummingtonite (*i.e.*, 7068 and 7112 cm^{-1}, respectively). Using the short-range O–H potential from tremolite, Abbott (1991) calculated a frequency of 3667 cm^{-1} for O–H stretching in the average local structural environment. Of course, this calculated frequency corresponds to no actual local environment. That the calculated frequency is higher than the observed frequency of the C band (approximately 3625 cm^{-1}) indicates that the values for the short-range parameters, λ_{OH} and ρ_{OH}, again need to be adjusted slightly. Given the Fe-rich composition, it is not surprising that A and B absorption bands corresponding to $HO–Mg_3$ and $HO–Mg_2Fe$ compositions are not observed.

Lacking a structure for pure grunerite, we proceeded to use the relevant *M*–O and O–O distances from this structure to represent those of the Fe end-member. Since these distances are presumably slightly shorter than those of the true end-member, some error will consequently propagate through our DLS analyses.

METHOD

The calculations were performed in three stages: (1) adjust atomic coordinates by DLS analysis, (2) search for the minimum-energy hydrogen position, and (3) calculate the frequency of O–H stretching. Atomic coordinates were adjusted for different arrangements of Fe and Mg at the *M*(3) and *M*(1) sites. Frequencies of O–H stretching were calculated for the DLS structures and then compared with observed frequencies for A, B, C and D bands. The calculations were done using three computer programs, DLS76 (Baerlocher *et al.* 1976, Meier & Villiger 1969), QUICKSIT and STRETCH. The latter two programs were written by one of us (RNA), and are available upon request.

DLS76

In Distance-Least-Squares analysis of a structure, the atomic coordinates and usually unit-cell dimensions are varied to minimize the discrepancy between calculated and prescribed (usually observed) interatomic distances. The procedure has been described in detail by Meier & Villiger (1969). Some applications and limitations of the procedure are described by Burnham (1985). The version of the program (DLS76) used in this study was written in FORTRAN by Baerlocher *et al.* (1976), and compiled with slight modifications by one of us (CWB) for an IBM-compatible PC.

For a particular arrangement of Mg and Fe, the *M*(1) or *M*(3) octahedra were modeled using prescribed distances from tremolite for octahedra occupied by Mg, and prescribed distances from grunerite for octahedra occupied by Fe^{2+}. The DLS

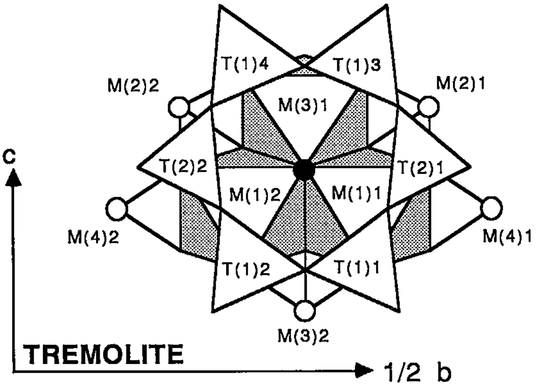

FIG. 1. Structure of tremolite. Cluster of 39 sites used in QUICKSIT and STRETCH calculations. *T*(1)n, *T*(2)n = Si tetrahedra; *M*(1)n, *M*(3)1 = M^{2+} octahedra; *M*(2)n, *M*(3)2, *M*(4)n = M^{2+} sites (n = 1,2,3,4). H projects onto the O(3) site at the small, filled circle.

TABLE 2. EQUATIONS

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

QUICKSIT ⇒ $[x,y,z]_H$

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

STRETCH ⇒ frequency of O-H stretching

3. $W_{OH} = W_H + \Sigma_{i\neq H}[q_i q_O/r_{iO} + \lambda_{iO}\exp(-r_{iO}/\rho_{iO})]$

4. $U_{OH}-U_{OH,min} = 1/2\ k_1(r-r_0)^2 + 1/6\ k_2(r-r_0)^3 + 1/24\ k_3(r-r_0)^4$

5. $[V(v)-U_{OH,min}]/h/c = v_e(v+1/2) - x_e v_e(v+1/2)^2 + Y_{00}/c$

6. $\Delta(v_2,v_1) = [V(v_2) - V(v_1)]/h/c$
$= v_e(v_2-v_1) - x_e v_e[(v_2+1/2)^2 - (v_1+1/2)^2]$

analysis varied all appropriate atomic coordinates; thus the geometries of all coordination polyhedra were optimized to prescribed distances. Cell parameters also were allowed to vary. Different kinds of distances (*e.g.*, Si-O, M^{2+}-O, and O-O distances in octahedra and tetrahedra) were weighted according to the scheme used on olivine by Bish & Burnham, (1984; also see Burnham 1985).

These DLS analyses present some special problems. *M*(3) octahedra share edges with *M*(1) and *M*(2) octahedra (Fig. 1). Because the observed lengths of these O-O distances are averages, it is not possible to determine correct prescribed distances for different local arrangements of Mg and Fe. Thus the DLS calculations were performed without prescribed distances for edges shared between Mg- and Fe-bearing octahedra.

Figure 1 illustrates a portion of the structure of tremolite with the cation sites labeled according to the usage in this paper. Table 1 gives the ligand combinations considered for tremolite, cummingtonite and grunerite, with observed frequencies of O-H stretching.

QUICKSIT and STRETCH

Details of the QUICKSIT and STRETCH calculations, as applied to amphiboles in this study, can be found in Abbott (1991). Table 2 gives the important equations used in the programs.

QUICKSIT was used to calculate the minimum-energy position for a hydrogen atom near the center of a cluster of 39 neighboring atoms (Fig. 1). Justification for performing the calculations on a cluster (as opposed to the extended structure, by some variant of the Ewald-Bertaut-Williams method, *e.g.*, Busing 1980) and justification for the size of the cluster are given in Abbott (1991). Actual clusters were created from the results of the DLS analyses. Equation 2 (Table 2) gives W_H, the site-energy of hydrogen. The first summation in W_H is for Coulombic contributions involving H paired with each of the other atoms, i, in the cluster; q_H and q_i are the formal ionic charges on H and i, respectively; r_{Hi} is the interatomic distance. The second summation in W_H is for the short-range repulsions between H and each of the neighboring atoms. In tremolite, the values for λ_{OH} and ρ_{OH} were previously determined to be 30500 kJ/mole of H and 0.2560 Å, respectively (Abbott 1991). Contributions due to short-range repulsions between H and other cations were omitted from the summation. The search for the minimum-energy position for the hydrogen atom was conducted by the modified Simplex method (Cooper 1981).

The STRETCH program was used to calculate frequencies of O-H stretching for the hydroxyl in the same cluster of atoms used in QUICKSIT. The OH pair-energy, W_{OH} (3, Table 2), includes a contribution from H, W_H (2, Tables 2), and a contribution from the hydroxyl oxygen, W_O. The latter contribution includes Coulombic and short-range terms for atom pairs involving the hydroxyl oxygen and each of the other atoms in the cluster, except H. The OH pair-energy function was sampled by evaluating W_{OH} for regular increments of the O-H separation. In a plot as a function of O-H separation, W_{OH} defines an asymmetrical energy-well. The potential energy, $U_{OH}-U_{OH,minimum}$ (4, Table 2), of an anharmonic oscillator is represented as a Taylor series truncated at the fourth-order term (Levine 1970). The constants, k_1, k_2 and k_3, and O-H separation, r_0, corresponding to the minimum-energy configuration, were evaluated by fitting the potential energy function

(U_{OH}–$U_{OH,minimum}$) to the sampled OH pair-energies (actually W_{OH}–$W_{OH,minimum}$) by least squares. Equation 5 (Table 2) gives the vibrational energies, V(v), of the anharmonic oscillator (Levine 1970). Constants ν_e, $x_e\nu_e$ and Y_{00} are complex functions of k_1, k_2, k_3 and r_0; v = 0, 1, 2, ... is the quantum number. The absorption frequency (in cm^{-1}) corresponding to a change from state $v = v_1$ to $v = v_2$ is given by $\Delta(v_2,v_1)$ (6, Table 2). Thus $\Delta(1,0)$ is the frequency for the fundamental frequency; $\Delta(2,0)$ is the frequency for the first overtone.

During the course of the calculations, it became apparent that fundamental frequencies of O–H stretching calculated for cummingtonite and grunerite were systematically high compared to observed frequencies. Assuming O–H distances close to 0.96 Å, as observed for tremolite (Hawthorne & Grundy 1976), values for λ_{OH} and ρ_{OH} were adjusted slightly according to the method described in detail by Abbott (1991). Values for λ_{OH} and ρ_{OH} of 30067 kJ/mole of H and 0.2586 Å, respectively, were found to be satisfactory for both grunerite and cummingtonite. The differences between λ_{OH} and ρ_{OH} values for tremolite and for grunerite or cummingtonite are apparently related to the effects of differing geometries of *M*(4) polyhedra (Ca *versus* Mg or Fe) on the site potential of the hydroxyl oxygen.

RESULTS AND DISCUSSION

Structural details, generated as the result of DLS analysis, are complicated and not all easily anticipated. Most of the adjustments are subtle and arguably not significant with regard to the objectives of the exercise. As anticipated, Fe-bearing octahedra modeled in tremolite or cummingtonite are larger than corresponding observed octahedra, such that the model Fe-bearing octahedra more nearly approach geometries in grunerite. Similarly, Mg-bearing octahedra modeled in grunerite or cummingtonite are smaller than corresponding observed octahedra, such that the model Mg-bearing octahedra more nearly approach geometries in tremolite. During the course of DLS analysis, the articulation of the Si-bearing tetrahedra changed slightly, but with practically no change in individual tetrahedral geometries (*i.e.*, practically no change in Si–O and O–O distances of tetrahedra).

With regard to the local structural environment of the hydrogen, the most obvious and consistent relationship is between the *x* coordinate of the O(3) oxygen, $x_{O(3)}$, and number of Fe and Mg atoms coordinated to the hydroxyl oxygen. Figure 2 illustrates this relationship in terms of the distance between the DLS-adjusted O(3) site and the (100) plane passing through the octahedrally coordinated *M* cations (at $x = 0$). Successive substitutions of Fe^{2+} for Mg at the three M^{2+} sites coordinated to an OH in tremolite increases $x_{O(3)}$. The same relationship is apparent for the DLS-adjusted structures of cummingtonite and grunerite. In cummingtonite, the DLS-adjusted $x_{O(3)}$ coordinate for the HO–Mg_2Fe ligand composition is nearly the same as the observed $x_{O(3)}$. This is consistent with the fact that the observed, bulk $Fe^{2+}/(Mg+Fe^{2+})$ in cummingtonite is 0.38, only slightly greater than $Fe^{2+}/(Mg+Fe^{2+}) = 0.33$ for the modeled ratio of $Fe/Mg \doteq 1/2$. This in turn tends to support the use of values for λ_{OH} and ρ_{OH} that are slightly different from those determined for tremolite. For the one ligand composition with a lower Fe/Mg ratio, (0/3), $x_{O(3)}$ is lower than the observed $x_{O(3)}$. For ligand compositions with higher Fe/Mg ratios (2/1 or 3/0), the DLS-adjusted $x_{O(3)}$ is proportionately higher. In grunerite, Mg substituting for Fe has the effect of decreasing $x_{O(3)}$.

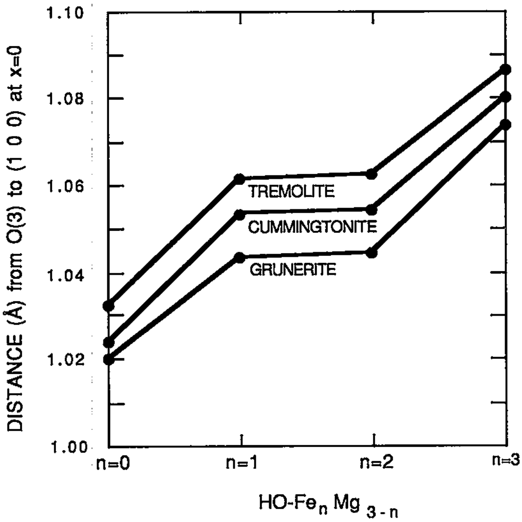

FIG. 2. Distance (Å) between DLS-adjusted O(3) position and (100) plane passing through octahedrally coordinated cations, for different proportions of Fe and Mg in the HO-M_3 ligand composition.

Tables 3, 4 and 5 report the results of the QUICKSIT and STRETCH calculations on the DLS-adjusted structures. The calculated coordinates of hydrogen are such that corresponding O–H distances are consistently close (± 0.01 Å) to 0.96 Å, which is the observed distance in tremolite. Thus the calculated position of the hydrogen atom is strongly correlated with the position of the O(3) oxygen, but in such a way that the calculated O–H distance is relatively insensitive to the position of

TABLE 3. RESULTS OF CALCULATIONS ON TREMOLITE

		QUICKSIT		
Short-range coefficients: λ_{OH} = 30500 kJ, ρ_{OH} = 0.2560 Å				
# (Table 1)	1	2	3	4
OH-ligand composition	Mg_3	Mg_2Fe	$MgFe_2$	Fe_3
H-O (Å)	0.9610	0.9573	0.9587	0.9620
		STRETCH		
Band	A	B'	C'	D
Constants in anharmonic oscillator function, U_{OH}:				
k_1 (kJ/Å^2) (+/- 10)	4840	4790	4760	4750
k_2 (kJ/Å^3) (+/- 30)	-23760	-25230	-25770	-26310
k_3 (kJ/Å^4) (+/- 120)	61440	101520	108960	99120
Least-squares statistics*:				
R_{wp}	0.0034	0.0042	0.0050	0.0086
R_{ex}	0.0205	0.0204	0.0205	0.0209
GoF	0.0272	0.0425	0.0587	0.1695
Constants in vibrational energy functions, $[V(v)-U_{OH,minimum}]$ /h/c and $\Delta(v_2,v_1)$:				
ν_e (cm^{-1})	3793.7	3774.0	3762.2	3758.2
$x_e\nu_e$ (cm^{-1})	61.1	55.7	57.7	67.3
Y_{00}/c (cm^{-1})	-3.4	-0.2	0.1	-1.7
Absorption frequencies:				
$\Delta(1,0)$ (cm^{-1})	3672	3663	3647	3624
$\Delta(2,0)$ (cm^{-1})	7221	7214	7178	7113

* $R_{wp} = [\Sigma_i[W_{OH}(r_i)-U_{OH}(r_i)]^2/\Sigma_i[W_{OH}(r_i)]^2]^{0.5}$,

$R_{ex} = [(N-P)/\Sigma_i[W_{OH}(r_i)]^2]^{0.5}$, N = number of data points (samples of W_{OH})

P = number of parameters refined = 4

GoF = $(R_{wp}/R_{ex})^2$, goodness-of-fit. GoF < 1 indicates very good fit.

the O(3) oxygen. Whereas the orientation of the OH dipole is implicitly controlled by other atoms in the structure, the O–H distance is not so strongly influenced.

From past experiences (Abbott 1990, 1991), we have learned that calculated frequencies for O–H stretching are extremely sensitive to even the slightest changes in a structure, especially with regard to the position of the hydroxyl oxygen, and ligands other than the hydrogen. Although not completely satisfactory, we consider the agreement between calculated and observed frequencies of O–H stretching to be quite encouraging.

TABLE 4. RESULTS OF CALCULATIONS ON CUMMINGTONITE

		QUICKSIT		
Short-range coefficients: λ_{OH} = 30067 kJ, ρ_{OH} = 0.2586 Å				
# (Table 1)	5	6	7	8
OH-ligand composition	Mg_3	Mg_2Fe	$MgFe_2$	Fe_3
H-O (Å)	0.9591	0.9624	0.9637	0.9671
		STRETCH		
Band	A	B'	C'	D
Constants in anharmonic oscillator function, U_{OH}:				
k_1 (kJ/Å^2) (+/- 10)	4820	4800	4770	4680
k_2 (kJ/Å^3) (+/- 30)	-23490	-23760	-25290	-25320
k_3 (kJ/Å^4) (+/- 120)	79680	67200	88560	92280
Least-squares statistics*:				
R_{wp}	0.0042	0.0030	0.0067	0.0081
R_{cx}	0.0211	0.0206	0.0208	0.0212
GoF	0.0395	0.0218	0.1050	0.1465
Constants in vibrational energy functions, $[V(v)-U_{OH,minimum}]$ /h/c and $\Delta(v_2,v_1)$:				
ν_c (cm^{-1})	3785.8	3778.0	3766.1	3730.4
$x_e\nu_e$ (cm^{-1})	51.2	59.7	62.9	64.6
Y_{00}/c (cm^{-1})	-1.1	-2.8	-1.8	-1.7
Absorption frequencies:				
$\Delta(1,0)$ (cm^{-1})	3683	3659	3640	3601
$\Delta(2,0)$ (cm^{-1})	7264	7198	7155	7073

* see Table 3.

TABLE 5. RESULTS OF CALCULATIONS ON GRUNERITE

		QUICKSIT		
Short-range coefficients: λ_{OH} = 30067 kJ, ρ_{OH} = 0.2586 Å				
# (Table 1)	9	10	11	12
OH-ligand Composition	Mg_3	Mg_2Fe	$MgFe_2$	Fe_3
H-O (Å)	0.9571	0.9599	0.9612	0.9660
		STRETCH		
Band	A	B'	C'	D
Constants in anharmonic oscillator function, U_{OH}:				
k_1 (kJ/Å^2) (+/- 10)	4850	4780	4750	4710
k_2 (kJ/Å^3) (+/- 30)	-24840	-24420	-25140	-25800
k_3 (kJ/Å^4) (+/- 120)	100800	96240	105480	98520
Least-squares statistics*:				
R_{wp}	0.0042	0.0036	0.0049	0.0087
R_{cx}	0.0209	0.0213	0.0205	0.0210
GoF	0.0407	0.0292	0.0580	0.1708
Constants in vibrational energy functions, $[V(v)-U_{OH,minimum}]$ /h/c and $\Delta(v_2,v_1)$:				
ν_e (cm^{-1})	3797.6	3770.1	3758.2	3742.4
$x_e\nu_e$ (cm^{-1})	51.0	51.9	54.4	64.7
Y_{00}/c (cm^{-1})	0.2	-0.1	0.2	-1.3
Absorption frequencies:				
$\Delta(1,0)$ (cm^{-1})	3696	3666	3649	3613
$\Delta(2,0)$ (cm^{-1})	7289	7229	7190	7097

* see Table 3.

For tremolite, the agreement between the observed and calculated frequencies for the A band is no coincidence, inasmuch as this frequency and the observed O–H distance were the basis for determining the values for the short-range repulsion parameters, λ_{OH} and ρ_{OH}. The important achievement of the calculations is that the calculated frequencies for the four bands differ from observed frequencies by no more than 4 cm^{-1}.

For cummingtonite, the calculated frequency of the A band is close to the calculated (and observed) frequency of this band for tremolite. Calculated frequencies of the B′ and C′ bands are respectively 5 and 3 cm^{-1} higher than observed, whereas the calculated frequency of the D band is approximately 15 cm^{-1} lower than observed. Despite the discrepancies, the calculations correctly reproduce the order of the frequencies. Disagreement between observed and calculated frequencies may be attributable to a slight exaggeration of otherwise qualitatively correct local structural details, or it may be that values for λ_{OH} and ρ_{OH} should vary slightly as a function the Fe–Mg composition of the HO–M_3 ligands.

Four frequencies of OH-stretching were calculated for grunerite, corresponding to the A, B′ C′ and D bands. The agreement between calculated and observed frequencies is good only for the D band, for which the local HO-M_3 ligand composition corresponds most closely to the actual composition of the grunerite. The other O–H stretching frequencies are too high by as much as 20 cm^{-1}. It is perhaps noteworthy that the calculated frequency of the A band (3696 cm^{-1}) is reasonably close to observed frequencies of this band for magnesio-hastingsite (3705 cm^{-1}, Semet

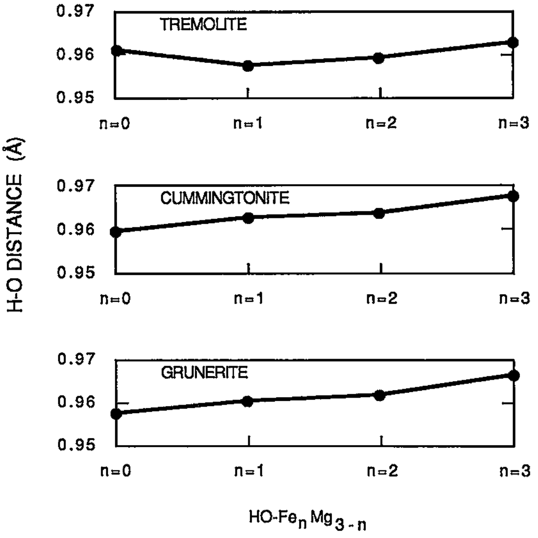

FIG. 3. Calculated O-H distance (Å) for different proportions of Fe and Mg in the HO-M_3 composition.

1983) and synthetic Mg-rich pargasite (3709 cm^{-1}, Raudsepp *et al.* 1987).

In general, the agreement seems to be best where the Fe/Mg ratio in the local HO-M_3 configuration is reasonably close to the observed ratio for the whole structure.

CONCLUSIONS

1. For simple amphiboles, DLS-adjusted structures for different arrangements of Mg and Fe at the *M*(3) and *M*(1) sites yield calculated O-H stretching frequencies that are reasonably consistent with those observed. Problems in the approach have mostly to do with the prescribed distances used in the DLS analysis, and the precise values for the short-range repulsion parameters, λ_{OH} and ρ_{OH}.

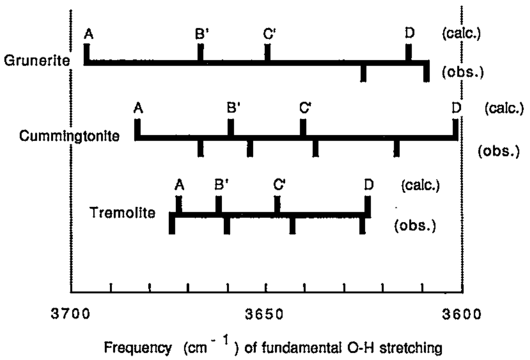

FIG. 4. Calculated (calc.) and observed (obs.) frequencies of O-H stretching.

2. Values for λ_{OH} and ρ_{OH} vary slightly depending on the occupancy of the *M*(4) sites. For tremolite, the best values are λ_{OH} = 30500 kJ/mole of H, and ρ_{OH} = 0.2560 Å. For grunite or cummingonite, the best values are λ_{OH} = 30067 kJ/mole of H, and ρ_{OH} = 0.2586 Å. For a given mineral, values for λ_{OH} and ρ_{OH} may vary slightly as a function of the Fe/Mg ratio in the composition of the HO-M_3 ligands.

By all indications, the differences in the frequencies of the A, B, C and D bands are specifically related to local variations in the structure, especially with regard to the position of the hydroxyl oxygen, O(3). The single most important factor influencing the position of the O(3) oxygen appears to be the ionic radius of the *M*(1) and *M*(3) cations.

ACKNOWLEDGEMENTS

We greatly appreciate the comments of two anonymous referees. The work was supported by NSF grant EAR-8720666 to C.W.B.

REFERENCES

ABBOTT, R.N., JR. (1990): An improved empirical method for calculating short-range O-H potentials in minerals. *Geol. Soc. Am., Program Abstr.* **22**, A214.

______ (1991): A short-range O-H potential for amphiboles based on OH-stretching frequencies. *Can. Mineral.* **29**, 131-142.

BAERLOCHER, C., HEPP, A. & MEIER, W.M. (1976): *DLS-76: A Program for Simulation of Crystal Structures by Geometric Refinement.* Inst. für Kristallogr. und Petrogr., ETH, Zurich, Switzerland.

BISH, D.L. & BURNHAM, C.W. (1984): Structure energy calculations on optimum distance model structures: application to the silicate olivines. *Am. Mineral.* **69**, 1102-1109.

BORN, M. & HUANG, K. (1954): *Dynamical Theory of Crystal Lattices.* Oxford University Press, London, England.

BURNHAM, C.W. (1985): Mineral structure energetics and modeling using the ionic approach. *In* Microscopic to Macroscopic: Atomic Environments to Mineral Thermodynamics (S.W. Kieffer & A. Navrotsky, eds.). *Rev. Mineral.* **14**, 347-388.

BURNS, R.G. (1970): *Mineralogical Application of Crystal Field Theory*. Cambridge University Press, Cambridge, England.

BUSING, W.R. (1980): WMIN, a computer program to model molecules and crystals in terms of potential energy functions. *U.S. Nat. Tech. Inf. Serv.* **ORNL-5747.**

COOPER, J.E. (1981): *Introduction to PASCAL for Scientists*. John Wiley & Sons, New York.

HAWTHORNE, F.C. (1981): Amphibole spectroscopy. *In* Amphiboles and Other Hydrous Pyriboles - Mineralogy (D.R. Veblen, ed.). *Rev. Mineral.* **9A**, 103-139.

______ (1983): The crystal chemistry of the amphiboles. *Can. Mineral.* **21**, 173-480.

______ & GRUNDY, H.D. (1976): The crystal chemistry of the amphiboles. IV. X-ray and neutron refinements of the crystal structure of tremolite. *Can. Mineral.* **14**, 334-345.

LEVINE, I.N. (1970): *Quantum Chemistry. II. Molecular Spectroscopy*. Allyn & Bacon, Boston, Massachusetts.

MEIER, W.M. & VILLIGER, H. (1969): Die Methode der Abstandstandsverfeinerung zur Bestimmung der Atomkoordinaten Idealisierter Gerüststrukturen. *Z. Kristallogr.* **129**, 411-423.

RAUDSEPP, M., TURNOCK, A.C., HAWTHORNE, F.C., SHERRIFF, B.L. & HARTMAN, J.S. (1987): Characterization of synthetic pargasitic amphiboles ($NaCa_2Mg_4M^{3+}Si_6Al_2O_{22}(OH,F)_2$; M^{3+} = Al, Cr, Ga, Sc, In) by infrared spectroscopy, Rietveld structure refinement, and ^{27}Al, ^{29}Si, and ^{19}F MAS NMR spectroscopy. *Am. Mineral.* **72**, 580-593.

SEMET, M.P. (1973): A crystal-chemical study of synthetic magnesiohastingsite. *Am. Mineral.* **58**, 480-494.

SHEU, JUANG-LING & MCMILLAN, P. (1988): An *ab initio* study of the O-H stretching frequency in tremolite. *Phys. Chem. Miner.* **16**, 114-119.

SKOGBY, H. & ROSSMAN, G.R. (1991): The intensity of amphibole OH bands in the infrared absorption spectrum. *Phys. Chem. Miner.* **18**, 64-68.

STRENS, R.G.J. (1974): The common chain, ribbon, and ring silicates. *In* The Infrared Spectra of Minerals (V.C. Farmer, ed.). The Mineralogical Society, London, England (305-330).

Received April 3, 1991, revised manuscript accepted August 26, 1991.