

RAMAN AND INFRARED SPECTROSCOPIC INVESTIGATION OF THE CATION DISTRIBUTIONS IN AMPHIBOLES

A. WANG, P. DHAMELINCOURT and G. TURRELL

LASIR (LP 2641, C.N.R.S.), Université de Lille Flandres Artois, Bât. C5
59655 Villeneuve d'Ascq Cedex, France

ABSTRACT

Micro-Raman spectra of a series of amphiboles have allowed an analysis of the cation distributions to be made. In addition, the micro-infrared absorption spectrum of Cummingtonite, one mineral in the series, has made possible the determination of both principal and interaction OH force constants. The results are interpreted in terms of the electronegativities of the cations occupying nearby sites.

INTRODUCTION

The cation distribution in amphiboles is a subject that has been of interest to mineralogists for at least 20 years. Numerous spectroscopic methods, including Mössbauer, visible-UV absorption and IR, have been used in combination with chemical analysis to study this question. However, it appears that Raman spectroscopy has not been applied previously because many amphibole samples exhibit strong fluorescence which usually masks the Raman scattering. At the present time with the use of Raman microspectroscopy, a very small, and hence less fluorescent sample (area $\approx 1\mu\text{m}^2$) can be chosen which yields Raman spectra of excellent quality.

RAMAN SPECTRA AND STRUCTURE OF THE AMPHIBOLES

The amphiboles have the general formula $A_{0-1}B_2C_5Si_8O_{22}(OH^-, F^-, Cl^-)_2$, where $A = Na^+, K^+$; $B = Na^+, Li^+, Ca^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+}$ and $C = Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Ti^{4+}$. Most of them are monoclinic crystals of space group $C2/m=C_{2h}^3$. The structure is shown in Fig. 1, where it can be seen that the OH nearest neighbors are the cations M_3 and the two cations M_1 . A calculation based on refined structure data indicates that the OH group is very nearly equidistant from these three ions and thus occupies a pseudo-trigonal site. Accordingly, the vibrational frequency of an OH group is dependent on the distribution of cations on the three sites.

As each of the three nearest-neighbor sites can be occupied by one of several different cations, a number of possible distributions can be defined, as given in Table I. Each distribution corresponds to a particular vibrational frequency of the OH group. Inversely, the probability of occupancy of a particular site by a given ion can be evaluated from the intensities of the OH Raman bands,

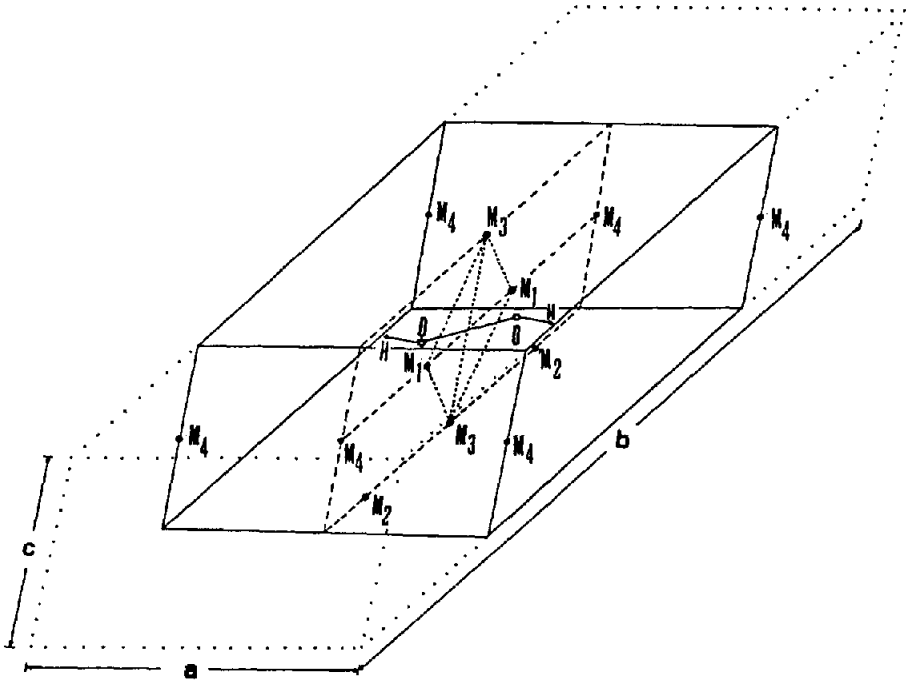


Fig. 1. Structure of monoclinic amphiboles.

assuming that the scattering tensor of that group is not modified by cation substitution. Reference to Table I shows, for example, that in a ternary system consisting of ions Mg^{2+} , Fe^{2+} and Fe^{3+} , the Mg^{2+} occupancy of the M_3 site is given by

$$\nu_3 = I_A + 2I_{B''} + I_{C'} + 2I_{E''} + I_{G'} + 2I_{F_2''} , \quad (1)$$

where I_A is the normalized integrated intensity of band A, etc., and the coefficient in each term is taken from the corresponding column of Table 1.

The micro-Raman spectra of the OH stretching region of four amphibole samples which were recorded in this work are shown in Fig. 2. The deconvolution of these spectral features allows a number of bands due to various cation distributions to be assigned. However, bands attributable to distributions such as B' and B'', C' and C'', etc., cannot be distinguished. This result is consistent with the pseudo-trigonal environment of the OH group which was pointed out above. Thus, only the total occupancy of cation sites $2M_1+M_3$ can be determined from the experimental data. For example, the Fe^{2+} occupancy of $2M_1+M_3$ sites in a quaternary system is obtained from the relation

$$2\phi_1 + \phi_3 = I_B + 2I_C + 3I_D + I_F + 2I_H + I_I + 2I_M + I_O + I_L + I_Q , \quad (2)$$

TABLE 1

Occupation of M_1 , M_3 sites

SYSTEM	(OH) ⁻ STRETCHING BAND	CONFIGURATION	OCCUPANCY OF SITE BY CATIONS													
			M_1		M_3		M_3^{2+}		Fe^{2+}		Fe^{3+}		Al^{3+}			
			M_1	M_3	M_1	M_3	M_1	M_3	M_1	M_3	M_1	M_3	M_1	M_3		
BINARY	A	$3M_3^{2+}$	○	○	○		2	1								
	B	$2M_3^{2+}Fe^{2+}$	⊕	○	⊕		2	2	2	1						
	C	$M_3^{2+}2Fe^{2+}$	⊕	⊕	⊕		2	1	2	2						
	D	$3Fe^{2+}$	⊕	⊕	⊕				2	1						
TERNARY	E	$2M_3^{2+}Fe^{3+}$	○	○	⊗		2	2			2	1				
	G	$M_3^{2+}2Fe^{3+}$	○	○	⊗		2	1			2	2				
	F	$M_3^{2+}Fe^{2+}Fe^{3+}$	⊕	⊗	⊗		2	2	2	2	2	2				
	H	$2Fe^{2+}Fe^{3+}$	⊕	⊗	⊗				2	2	2	1				
QUATERNARY	I	$Fe^{2+}2Fe^{3+}$	⊕	⊗	⊗				2	1	2	2				
	J	$3Fe^{3+}$	⊗	⊗	⊗						2	1				
	K	$2M_3^{2+}Al^{3+}$	○	○	●		2	2					2	1		
	N	$M_3^{2+}2Al^{3+}$	○	○	●		2	1					2	2	2	
	M	$2Fe^{2+}Al^{3+}$	⊕	⊕	●				2	2			2	1		
	O	$Fe^{2+}2Al^{3+}$	⊕	●	●				2	1			2	2	2	
	S	$2Fe^{3+}Al^{3+}$	⊗	⊗	●						2	2	2	2	1	
	R	$Fe^{3+}2Al^{3+}$	⊗	●	●						2	1	2	2	2	
	P	$M_3^{2+}Al^{3+}Fe^{3+}$	○	⊗	●		2	2			2	2		2	2	
	L	$M_3^{2+}Al^{3+}Fe^{2+}$	⊕	⊗	●		2	2	2		2			2	2	
	Q	$Fe^{2+}Al^{3+}Fe^{3+}$	⊕	⊗	●				2	2	2		2	2	2	
	T	$3Al^{3+}$	●	●	●								2	1		

as given in Table 1. If it can be assumed that $I_B = I_C$, $I_E = I_G$, etc., the specific occupancy of each site can be estimated (Table 2).

VIBRATIONAL FREQUENCIES OF THE OH GROUPS IN CUMMINGTONITE

A factor-group analysis based on the C_{2h}^3 space group of the amphiboles shows that there are 123 optical frequencies divided between gerade and ungerade species. Thus, the infrared and Raman spectra of these compounds are very rich. No attempt has been made at complete assignments, although the OH stretching bands can be easily identified. The existence of a center of inversion precludes the

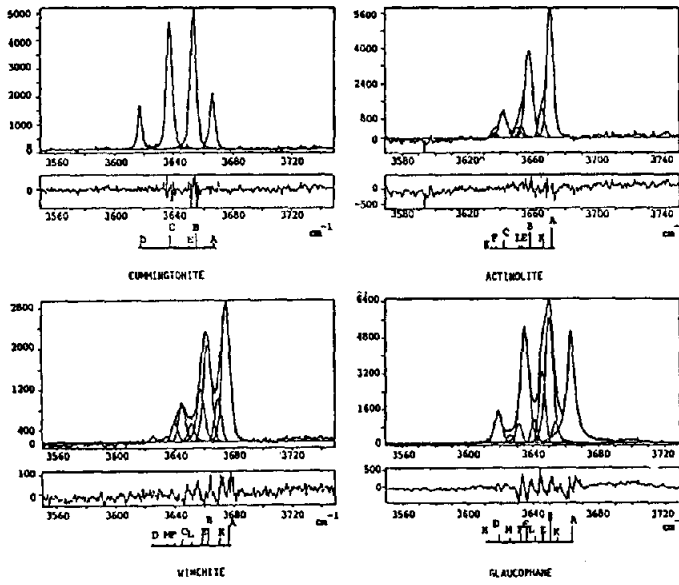


Fig. 2. Raman spectra of amphiboles in the OH-stretching region.

TABLE 2.
Cation site occupancies in the amphiboles.

		CUMINGTONITE	ACTINOLITE	WINCHITE	GLAUCOPHANE
M_1^{2+}	TOTAL	1.5752	2.2732	2.1839	1.8600
	μ_1	1.0746	1.7426	1.7177	1.3403
	μ_2	0.5006	0.5306	0.4661	0.5197
M_2^{2+}	TOTAL	1.4199	0.5594	0.5050	0.9361
	μ_1	0.9254	0.2279	0.2337	0.6229
	μ_2	0.4945	0.3315	0.2714	0.3132
M_3^{3+}	TOTAL	0.0049	0.0498	0.1743	0.1328
	μ_1		0.0074	0.0239	0.0153
	μ_2	0.0049	0.0424	0.1510	0.1175
Al	TOTAL		0.1176	0.1326	0.0711
	ξ_1		0.0222	0.0247	0.0215
	ξ_2		0.0955	0.1115	0.0496

coincidence of the two OH-stretching vibrations in the infrared and Raman spectra.

Application of the GF method leads to the expressions

$$f = 2\pi^2 c^2 (\bar{\nu}_R^2 + \bar{\nu}_{IR}^2) / (\mu_H + \mu_O) \tag{3}$$

and

$$f' = 2\pi^2 c^2 (\bar{\nu}_R^2 + \bar{\nu}_{IR}^2) / (\mu_H + \mu_O), \quad (4)$$

where f and f' are the principal force constant and coupling constant for the OH bonds. The observed OH-bond wavenumbers in the infrared and Raman spectra are $\bar{\nu}_{IR}$ and $\bar{\nu}_R$, the reciprocal atomic masses are μ_H and μ_O , and c is the velocity of light. From Eq. (4) it is clear that very accurate frequency data are necessary in order to determine the interaction constant, f' .

In the present work micro-Raman and micro-infrared spectra were measured on the same crystallite of Cummingtonite. The results obtained are given in Table 3, along with the force constants calculated from Eqs. (3) and (4). It is noted that f changes monotonically through the configuration order A,B,C,D, while f' has a more complex behavior. However, the latter variation is not illogical if it is assumed that the distance between the oxygen atoms of the two OH groups (and hence f') is determined by the electronegativities of the cations on sites M_1 and M_3 . This distance is plotted in Fig. 3 for different values of d , the displacement of an oxygen atom in the direction of a given substituted cation site.

TABLE 3
Observed OH frequencies and force constants.

CONFIGURATION	FREQUENCY OF VIBRATIONAL BAND			FORCE CONSTANT	
	ν_{IR} (cm ⁻¹)	ν_R (cm ⁻¹)	$2\nu \cdot \nu_{IR} - \nu_R$ (cm ⁻¹)	f (m dyne/Å)	f' (m dyne/Å)
A	3655.92	3655.91	- 0.99	7.5189	- 0.0020
B	3652.56	3653.14	- 0.58	7.4634	- 0.0012
C	3636.14	3637.74	- 1.60	7.3995	- 0.0035
D	3617.19	3618.61	- 1.42	7.3212	- 0.0029

LOW-TEMPERATURE STUDIES

An attempt was made to resolve the OH Raman bands associated with cation distributions of the type B'-B'', C'-C'', etc. by lowering the temperature in order to reduce line widths. However, it was found that the observed bands become broader at lower temperatures (Fig. 4). This unexpected behavior is, however, consistent with the argument introduced above which is based on the increase in interionic forces with decreasing temperature, resulting in an increased splitting between (unresolved) components such as B' and B'', leading to an increase in the apparent width of the band assigned to the B-type distribution (Fig. 5).

CONCLUSIONS

A detailed analysis of the micro-Raman spectra of the amphiboles in the OH-stretching region leads to the determination of the cation occupancies in nearby

sites. In cummingtonite, for which micro-infrared spectra were observed, a force-constant calculation yields OH stretching and interaction constants which are found to be simple functions of the cation electronegativities and distances.

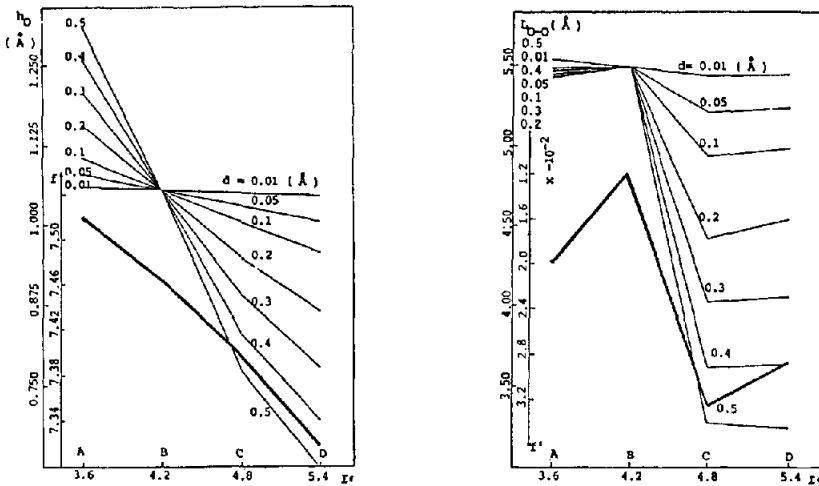


Fig. 3. Variations in force constants and distances in Cummingtonite as functions of the total cation electronegativity.

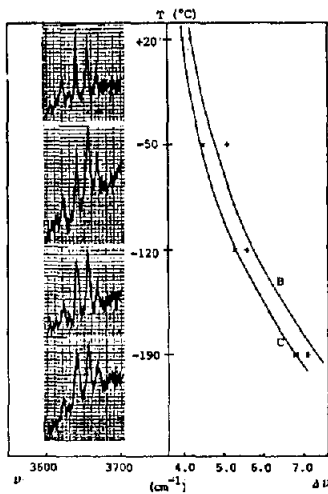


Fig. 4. Bandwidths vs. temperature.

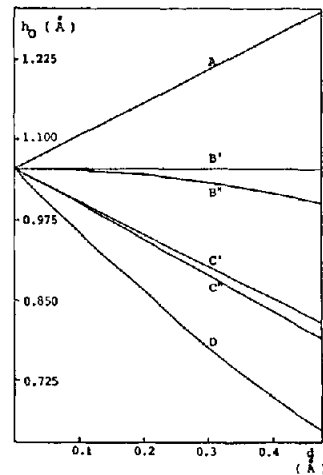


Fig. 5. Distance changes with cation substitution.

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