

STRETCHING FREQUENCIES OF STRUCTURAL HYDROXYLS OF HECTORITE AND K-DEPLETED PHLOGOPITE AS INFLUENCED BY INTERLAYER CATION AND HYDRATION

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Abstract—The frequencies of structural OH stretching vibrations in swelling trioctahedral minerals such as hectorite or K-depleted phlogopite depend on the ionic form and hydration of the sample. The trioctahedral structure is evidently a suitable case for the observation of spectral changes, since hydroxyl groups are in conditions of high reactivity with the surrounding medium. These changes are attributed to the field which originates either from the cations or the residual water molecules, and the joint analysis of spectroscopic and X-ray diffraction data permits an interpretation that frequencies quoted for unaltered mica are only perturbed frequencies.

INTRODUCTION

INFRARED studies of silicas and zeolites (McDonald 1957; Angell *et al.* 1965; and White *et al.* 1967) have extensively shown a close relationship between frequencies of structural OH vibrations and the nature of the surrounding medium.

In the case of trioctahedral layer silicates, the dipole moments of structural OH are nearly normal to the basal plane. These OH groups have a non negligible sensitivity to external conditions. This property, already pointed out by Farmer *et al.* 1967 is studied here in a more systematic way.

MATERIALS AND METHODS

The materials studied were a hectorite clay (from Hector Calif) and a K-depleted mica (from Madagascar).

Structural formulas

Hectorite: $\text{Si}_4(\text{Mg}_{2.73}\text{Li}_{0.27})\text{O}_{10}(\text{OH}_1\text{F}_1)\text{M}^+$

Phlogopite: $[\text{Si}_{2.64}\text{Al}_{1.36}][\text{Mg}_{2.07}\text{Fe}_{0.26}\text{Al}_{0.62}\text{Ti}_{0.05}]\text{O}_{10}[\text{OH}_{1.85}\text{F}_{0.15}]\text{K}_{0.78}\text{Na}_{0.04}$

The less than 2μ size fraction of the Li, Na, K, Ca and Mg homoionic forms of hectorite were investigated. Oriented films were prepared by slow evaporation of a suspension and self supporting films are used for i.r. spectroscopy. Samples for X-ray diffraction were oriented deposits upon a glass slide.

K-depleted mica was obtained by treating flakes

of phlogopite in a 2N NaNO_3 solution at 90°C ; numerous pin holes in the flake and frequent renewals of NaNO_3 ensured a rapid ionic exchange. Measurements were generally made after a 1 month treatment, by which time the original mica is transformed into a swelling minerals in which any 10 Å phase has disappeared in the wet state and which behaves as a vermiculite for X-ray diffraction and water sorption isotherms. The exchange capacity of this K-depleted mica was 215 me/100 g. Li, K, Ca and Mg homoionic samples were obtained by ion exchange from the Na form produced by the potassium removal treatment. The flakes (2 cm × 2 cm) make self supporting samples for i.r. spectroscopy and X-ray diffraction.

Samples were examined in a double cell fitted with CaF_2 windows. They may be tilted with respect to the i.r. beam, heated up to 250°C and exposed to any atmosphere between saturating water vapour and vacuum (10^{-2} mm Hg).

Clay films or mica flakes were exposed several times to D_2O vapour followed by pumping in order to exchange as thoroughly as possible initial hydration H_2O . After this treatment at room temperature, structural OH are very easily observed as they are not deuterated.

Spectra were recorded starting from a fully hydrated phase (D_2O condensed in the coldest parts of the cell); these conditions correspond at least to a double water layer. Dehydration was then increased stepwise by pumping and heating. Hectorite spectra given in this paper were generally

recorded at normal incidence, whereas for K-depleted micas, samples were tilted with respect to the beam by an angle of the order of 30°.

RESULTS

A. Hectorite

(1) *I.R. spectra.* I.R. spectra show two bands, whose approximate frequencies are 3680 and 3710 cm^{-1} . The former is always stronger than the latter. However, these frequencies are not fixed, but vary noticeably with experimental conditions. Figures 1, 2 and 3 give some examples of these modifications, and general observations are the following:

(a) Modifications of lattice OH spectra are reversible with water content (b) If one designates the band near 3680 cm^{-1} as *LF* and the band near 3710 cm^{-1} as *HF*, it can be seen that *LF* and *HF* split, respectively, into two components *LF1*, *LF2* and *HF1*, *HF2*, when the clay water content changes. In intermediate states between fully hydrated and dehydrated, these four bands coexist (see for instances Fig. 1, curves 2 and 4 and Fig. 3, curves 2–5). Extreme frequencies observed, were dependent upon the exchangeable cation only in the case of the dehydrated mineral; they are given in Table I.

Table I. Limit frequencies of hectorite (cm^{-1})

State	Cation	Na, K	Li	Ca, Mg
Hydrated	<i>LF1</i>	3695	3695	3695
	<i>HF1</i>	3717	3717	3717
	<i>LF2</i>	—	—	—
	<i>HF2</i>	—	—	—
Dehydrated	<i>LF1</i>	—	—	—
	<i>HF1</i>	—	—	—
	<i>LF2</i>	3685	3681	3677
	<i>HF2</i>	3709	3706	3704

—: Not observed.

"Hydrated": D_2O condensed in the cold parts of the cell.

"Dehydrated": Samples heated to 250°C under vacuum. Spectra recorded after cooling the sample.

(c) With strongly hydrated cations (Li and Mg particularly), lattice OH deuteration begins as soon as the temperature reaches nearly 120°C. This heating under vacuum evidently decreases the hydration D_2O content, but simultaneously the hydration H_2O band increases, which points out the stability of cation hydration (Fig. 4).

(2) *X-ray diffraction.* Dehydration under a vacuum collapses K and Na clays but produce interstratification in Li, Mg and Ca clays. All the clays heated to 250°C collapsed at room atmosphere. Table 2 gives the spacings for dehydrated minerals.

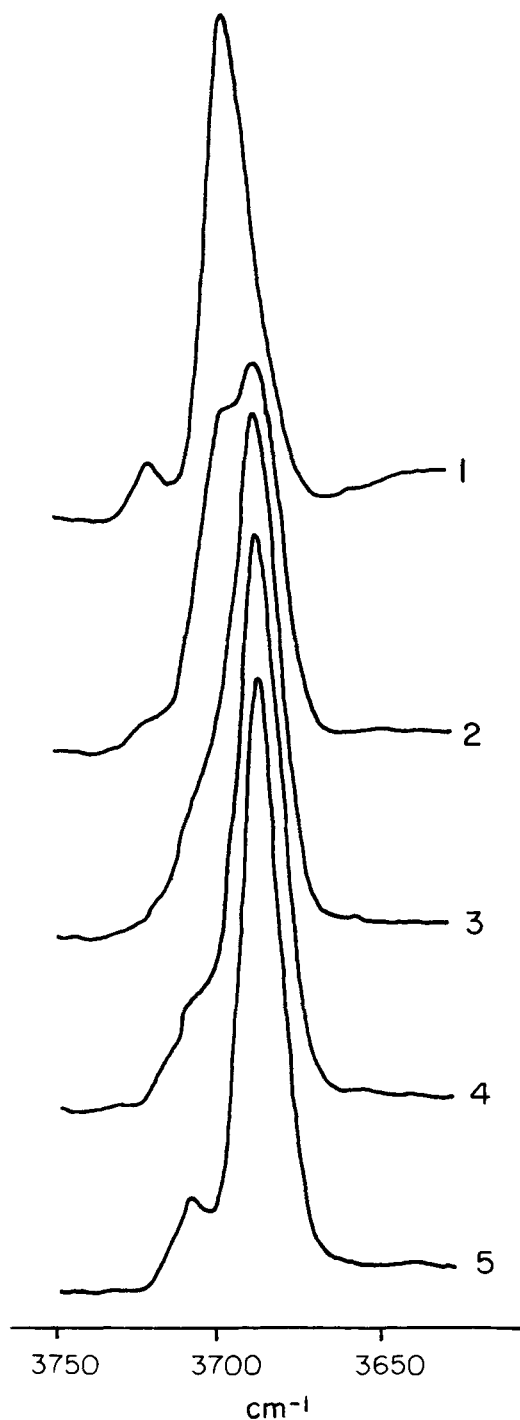


Fig. 1. Na-Hectorite. Structural OH spectra (dehydration increases from 1 to 5).

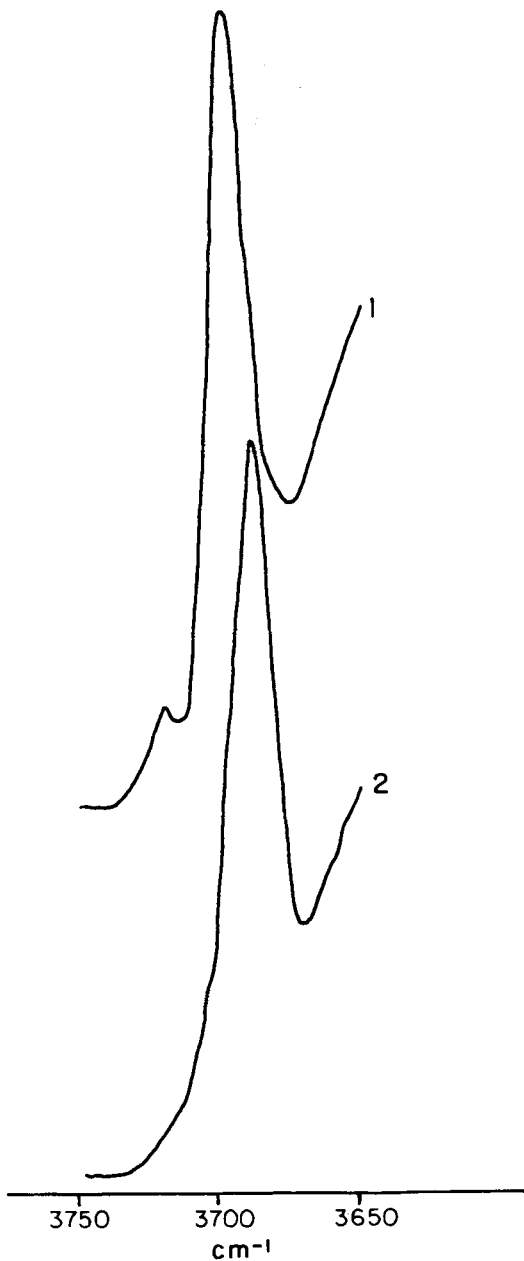


Fig. 2. Li-Hectorite. Structural OH spectra (1: hydrated, 2: dehydrated).

B. K-depleted phlogopites

(1) *I.R. spectra.* The initial K mica shows two resolved bands at 3712 and 3669 cm^{-1} ; as the iron content of the sample is low, these bands correspond very likely to the bands noted N_A and I_A by Vedder, 1964; and Vedder *et al.* 1969.

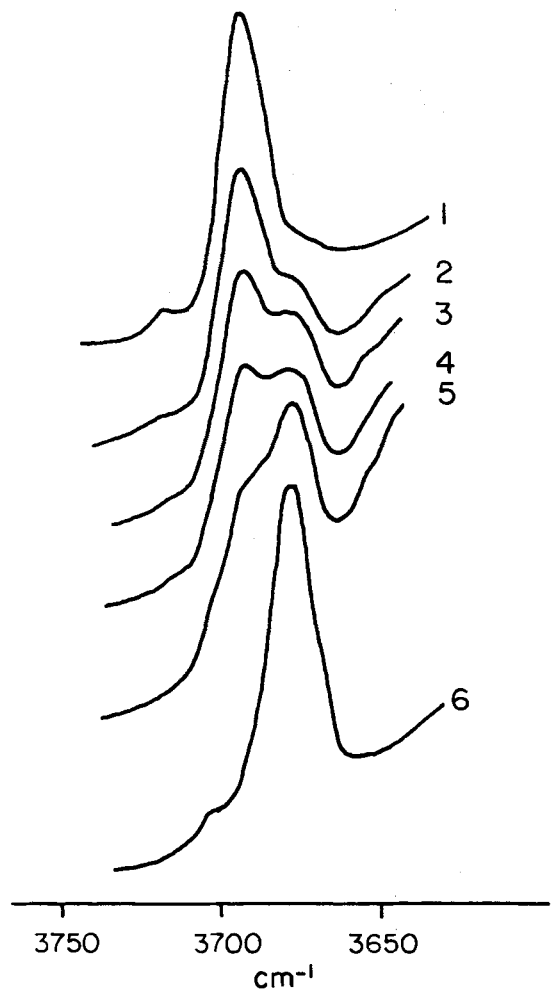


Fig. 3. Mg-Hectorite. Structural OH spectra (dehydration increases from 1 to 6).

Table 2. 001 spacings of dehydrated hectorite (\AA)

Cation	d_{001}
Li	9.73
Na	9.73
K	10.22
Mg	10.07
Ca	9.92

When interlayer potassium is removed, the spectrum changes. In the hydrated state, two resolved maxima are still present, but they appear at 3677 and 3635 cm^{-1} for the Na, Mg and Ca saturated samples. For the Li sample, the low

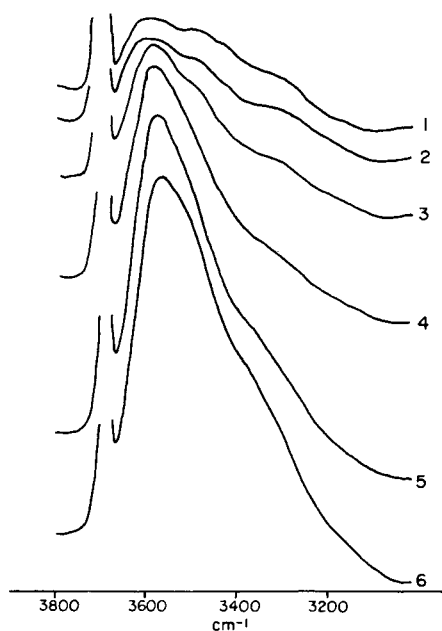


Fig. 4. Mg-Hectorite. Hydration H_2O spectra (samples heated under vacuum; temperatures increasing from 1 to 6).

frequency maximum appears at 3645 cm^{-1} , whereas K samples, obtained from Na samples by ion exchange, exhibit in the hydrated state practically the same spectrum as the initial mica.

The general shape of the spectra of initial phlogopite and K-depleted minerals is roughly similar. However, it cannot be precluded that some unknown components are present which would explain the appearance of shoulders in some hydrated samples. Anyway, as it cannot be ascertained that K depleted mica is rigorously free from H_2O in the D_2O hydrated state, interpretation of weak bands is very questionable and in the following discussion, only resolved maxima will be taken into account in the description of spectra.

Dehydration of K-depleted micas leads to results quite different from those obtained with hectorite. Reversibility along hydration-dehydration cycles and mixing of extreme configurations are still observed, but the influence of the cation seems more specific and each case will be reported separately. For brevity, the K-depleted forms will be noted Na-V, Li-V etc, and the initial phlogopite, K-P.

(a) Na-V (Fig. 5)

Starting with the D_2O fully hydrated sample, no appreciable changes can be detected during

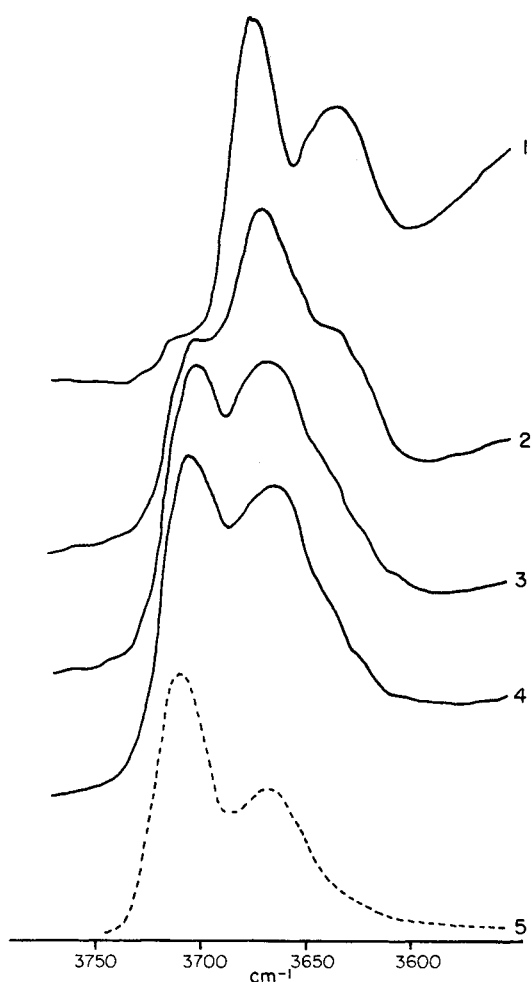


Fig. 5. Na-V. Structural OH spectra (dehydration increases from 1 to 4. 5: K-P spectrum).

evacuation at spectrometer temperature. As soon as the sample is heated to 100°C under vacuum, two bands located at K-P frequencies (3712 and 3669 cm^{-1}) appear, and replace gradually the Na-V bands when dehydration increases.

(b) Li-V (Fig. 6)

When the sample is dehydrated, a new set of two bands develops at 3661 and 3630 cm^{-1} , and structural OH deuterate very easily upon heating. Intermediate states are not so easily observed as with Na-V, but dehydration gives a system in which the frequencies are the lowest of all.

(c) Mg-V (Fig. 7)

With this ionic form, no changes occur in structural OH stretching spectrum even for

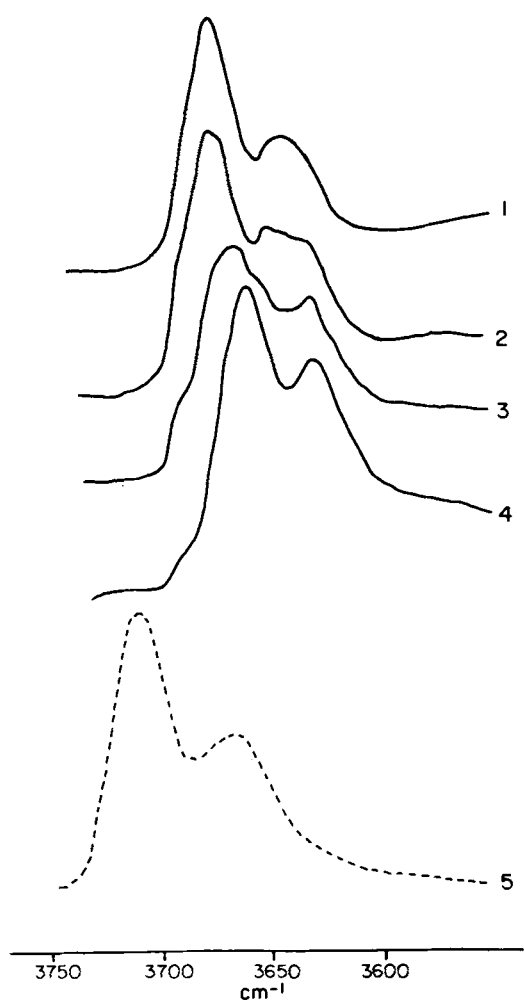


Fig. 6. Li-V. Structural OH spectra (dehydration increases from 1 to 4. 5: K-P spectrum).

samples heated to 250°C under vacuum; residual water content remains significant. Since the K-depleted phlogopite may be considered as a "vermiculite", this is not surprising and points out the optimal stability of the hydrated Mg-mineral. Unfortunately it was impossible to reach a temperature higher than 250°C in the cell, which would perhaps have induced changes in the spectra.

(d) Ca-V (Fig. 8(A) and 8(B))

Dehydration by heating under a vacuum induces a continuous decrease of structural OH absorbance without any important frequency displacement (Fig. 8(A)). The same phenomenon occurs for structural OD (Fig. 8(B)). Flattened structural



Fig. 7. Mg-V. Structural OH spectra (1: hydrated- 2: heated to 250°C under vacuum).

OH spectra (Fig. 8(A) curve 4, for instance) correspond very likely to a system in which structural deuteration is very important. However structural OD cannot be observed at the same time because of the overlapping by residual hydration D₂O (Spectra of Fig. 8(B) were obtained by hydrating the sample with H₂O).

(e) K-V (Fig. 9(A) and 9(B))

When the Na-V is converted into K-V, the spectrum is essentially the same as that of K-P with resolved maxima at 3712 and 3669 cm⁻¹ (Fig. 9(A)). However a band due to H₂O is present and does not disappear after heating to 250°C under vacuum. In one of the investigated samples the structural hydroxyls were partially deuterated before K saturation. It should be noted that the ion exchange treatment did not rehydroxylate the structural OD groups. These OD bands could then

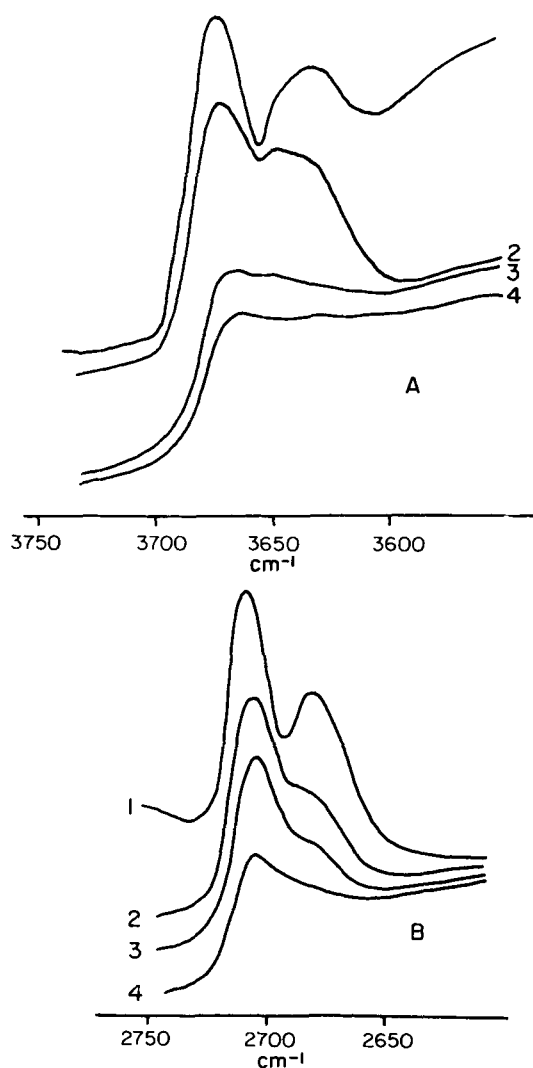


Fig. 8. Ca-V. 8(A): structural OH spectra. 8(B): structural OD spectra (in each case, dehydration increases from 1 to 4).

be easily studied, and a very small shift (of the order of 7 cm^{-1}) towards low frequencies was observed for the heated sample (Fig. 9(B)). The conversion from Na-V to K-V develops very likely from the edges towards the center. As K-V is collapsed, the observations made suggest that some interlayer volumes can be isolated from the surrounding medium by a continuous collapsed zone.

Table 3 summarizes these observations.

(2) *X-ray diffraction*. These measurements confirm that at the highest temperature reached

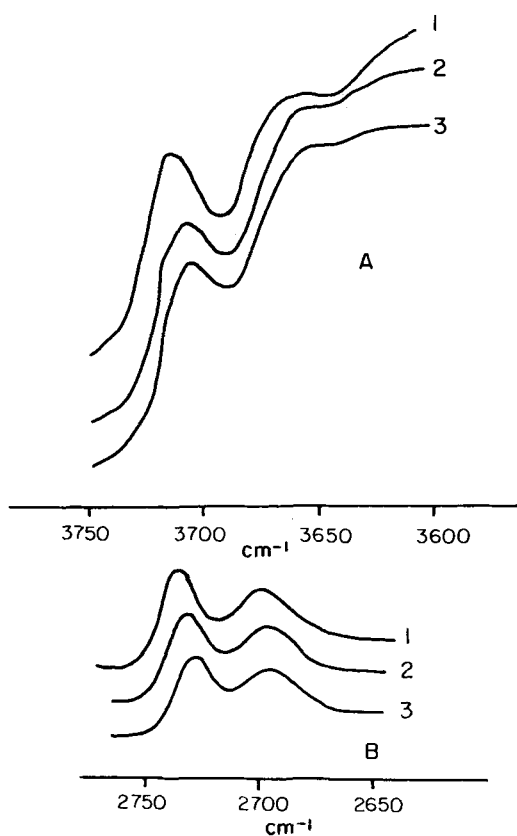


Fig. 9. K-V. 8(A): structural OH spectra. 8(B): structural OD spectra (in each case: 1: hydrated, 2: under vacuum at spectrometer temperature, 3: heated to 250°C under vacuum).

in the cell, Mg-V is not fully dehydrated. Table 4 summarizes some results.

DISCUSSION

A. Hectorite

Chemical analysis of hectorite reveals that 10 per cent of octahedral sites are occupied by lithium. The immediate vicinity of a hydroxyl may thus be $[\text{Mg}_3]$ (type I) and $[\text{Mg}_2\text{Li}]$ or $[\text{MgLi}_2]$ or $[\text{Li}_3]$ (type II). The theoretical percentages involving the type I and one of the type II arrangements are calculated in Table 5.

It can be anticipated that OH (I) and OH (II) do not have the same vibration frequency, type I giving the lower value due to the reduction of negative field around the proton. Moreover, if one assumes that absorption coefficients for OH (I) and OH (II) are nearly the same, values given in Table 5 determine the order of magnitude of *HF* and *LF* band absorbances.

Table 3. Limit frequencies of K depleted phlogopites (cm^{-1})

Sample	State	Hydrated		Dehydrated	
Na-V		3677	3635	3712	3669
Li-V		3677	3645	3661	3630
Mg-V		3677	3635	3677	3635
Ca-V		3677	3635	vanishing	
K-V		3712	~3639	~3712	~3699
K-P				3712	3669

The term "dehydrated" refers to experimental conditions and has not necessarily an absolute meaning.

Table 4. 001 spacings of K depleted phlogopites (\AA)

Sample	d_{001}
Na-V hydrated	14.87
Li-V hydrated	14.25
Mg-V hydrated	14.40
Na-V dehydrated 65°C	11.90
Na-V dehydrated 95°C	9.70
Na-V dehydrated 130°C	9.55
Li-V dehydrated 150°C	10.07
Li-V dehydrated 220°C	10.07
Mg-V dehydrated 250°C	11.28
Mg-V dehydrated 380°C	9.87

Table 5. Octahedral environment of hectorite structural OH

Type I (%)	Type II (%)
Mg ₃ OH 73	Mg ₂ LiOH 27
Mg ₃ OH 86.5	MgLi ₂ OH 13.5
Mg ₃ OH 91	Li ₃ OH 9

Experimental spectra were recalculated after background subtraction (Figs. 10 and 11 for instance). This empirical procedure involves unavoidable errors and must be used very cautiously; its use is necessary however for a comparative study. These spectra, in which an isosbestic point appears clearly, were decomposed on the basis of four component bands located at extreme frequencies quoted in Table 1. Throughout a given set of decompositions, the parameters of each band were kept as constant as possible and the areas were measured. When dealing with a given sample in which only the water content varied, one finds that the sum of areas $LF1+LF2$ is practically constant, representing an average percentage of

85 per cent of total absorbance. Keeping in mind the approximations involved in the decompositions and the fact that percentages calculated in Table 5 can only be taken as indicative, one can think that the value found for $LF1+LF2$ absorbance is not in disagreement with the hypothesis.

If two sets of bands exist, $LF1$ and $HF1$ on the one hand and $LF2$ and $HF2$ on the other, and if their simultaneous occurrence corresponds to an equilibrium state (which seems confirmed by the stability of i.r. spectra when no change is made in the water content of the clay), two isosbestic points should appear. As a matter of fact, only one such point is observed; this is due to the relative weakness of bands $HF1$ and $HF2$, which precludes any sensitivity in the high frequency region.

Values of Table 2 show that for all the investigated cations, the dehydrated form is collapsed.

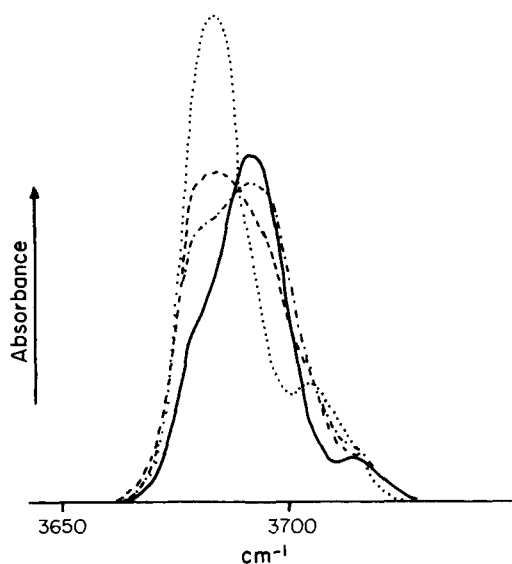


Fig. 10. Na-Hectorite. Recalculated structural OH spectra.

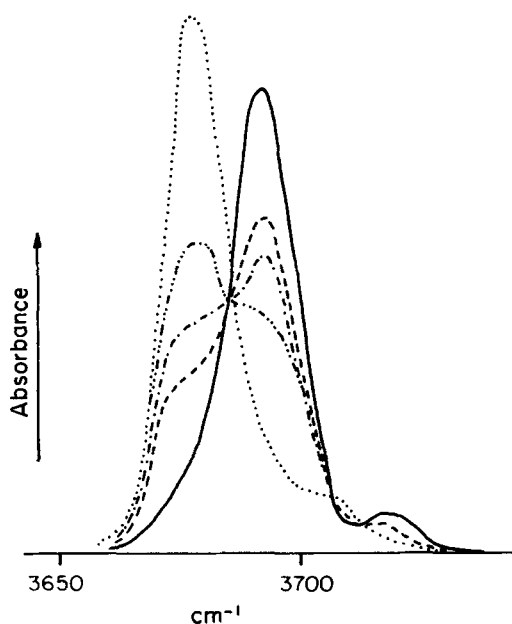


Fig. 11. Mg-Hectorite. Recalculated structural OH spectra.

These values preclude any configuration of the interlayer space in which at least one hexagonal cavity does not face the cation. If cations are located in front of OH cavities, the perturbation of the underlying OH will appear as a shift towards high frequencies. Since this displacement is always observed towards low frequencies it is concluded that in the dehydrated mineral cations face fluorine cavities, which are roughly in the same number as OH cavities. It can also be presumed that bringing

the cation close to the lattice will increase locally the positive charge of the layer, which would explain *LF2* and *HF2* bands. From this viewpoint, the observed order, $\text{Na} = \text{K} < \text{Li} < \text{Ca} = \text{Mg}$, can be explained both by ionic radius and electric charge.

Finally, frequencies of *LF1* and *HF1* bands observed in the hydrated minerals do not depend upon the nature of the cation. This is due to the strong hydration (two water layers at least) which overrides specific short range actions between cations and the clay layer. These values are a good approximation for the unperturbed OH stretching frequencies of an hectorite lattice.

B. K-depleted phlogopites

In this case, conclusions cannot be the same as previously because of the specific behaviour of each cationic form. The main discussion will concern Na-V and Li-V samples.

In addition to the observations previously reported, Li-V and Na-V differ as to the spectra of residual water still present when the modifications of structural OH spectra are already noticeable. Figure 12(A) shows that OH stretching vibrations of Li-V residual water are presumably not dichroic. However the water band most likely to show orientation lies in the $3620\text{--}3640\text{ cm}^{-1}$ range and could be obscured by the structural OH vibrations at $\approx 3640\text{ cm}^{-1}$. Figure 12(B) shows the residual water band for a Li-V sample which was heated in D_2O vapour at 230°C and where structural OH were noticeably deuterated. In this case the structural OH vibrations which are very weak cannot perturb the water band, and one can see that spectrum 1 (incidence 45°) and spectrum 2

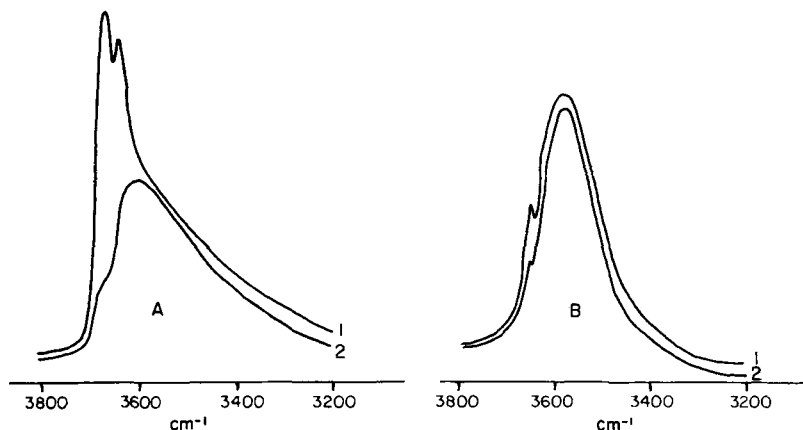


Fig. 12. Li-V. 12(A): residual H_2O spectra (1: incidence 45° , 2: normal incidence) 12(B): residual H_2O spectra after structural OH deuteration (1: incidence 45° , 2: normal incidence).

(normal incidence) coincide almost perfectly. These results indicate that water molecules are roughly lying flat upon the clay surface. It must be noted also that residual water is present in large amount. On the contrary, Na-V can be almost entirely dehydrated, and OH stretching vibrations of water molecules are significantly dichroic, which means that the dipole moments of OH groups are nearly perpendicular to the clay surface (Fig. 13).

Table 6. Upper frequency of K-depleted phlogopite (cm^{-1})

Frequency	Sample
3712	K-P (unaltered)
	Na-V (dehydrated)
3677	Na-V (hydrated)
	Li-V (hydrated)
3661	Li-V (dehydrated)

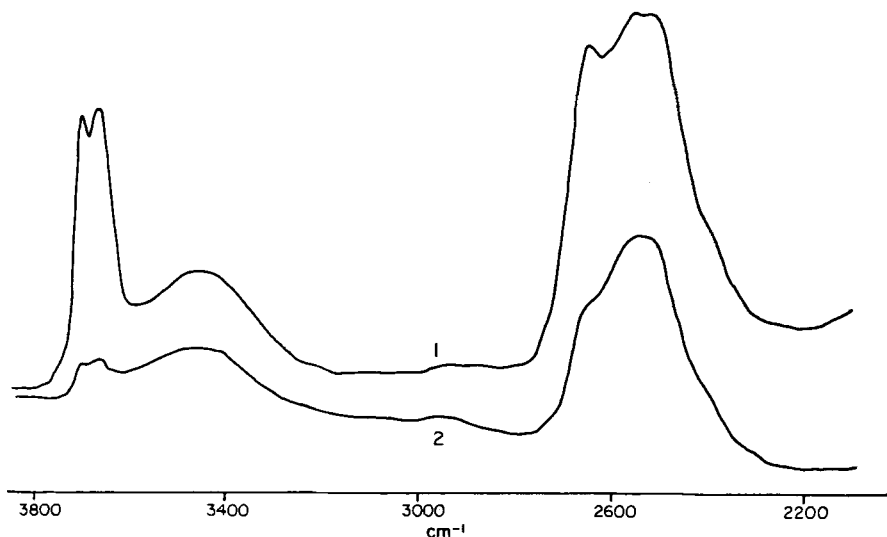


Fig. 13. Na-V. Residual H_2O and D_2O spectra (1: incidence 45° , 2: normal incidence).

These observations are compatible with the hypothesis that residual water molecules of Li-V turn a negative charge (from the oxygen atom) towards the hydrogen of structural OH; the orientation of water molecules and intensity of the binding between clay and water are further evidence in support of this hypothesis.

When comparing spectra of the same cationic form at various water contents after background subtraction, isobestic points can be detected as with hectorite. Figure 14 gives one example for Na-V. In this case, two isobestic points appear resulting from the fact that two corresponding bands *LF* and *HF* have an absorbance of the same order of magnitude. This means that an equilibrium state exists between hydrated and dehydrated forms and confirms the existence of two sets of bands, *LF1*, *HF1* and *LF2*, *HF2*, in opposition with the notion of a continuous shift.

If one considers the highest frequencies recorded for structural OH, three different values are found which correspond to well defined systems (Table 6).

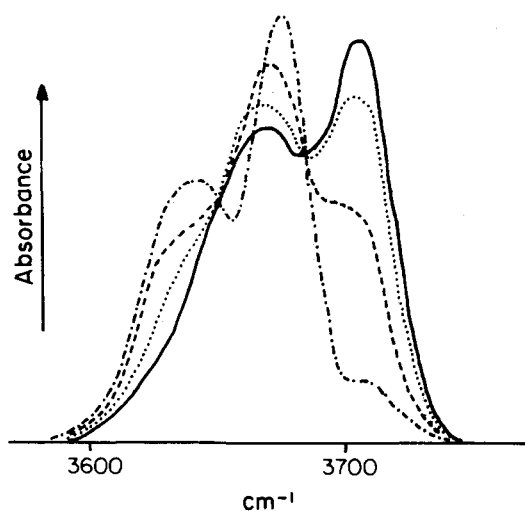


Fig. 14. Na-V. Recalculated structural OH spectra.

The structural OH stretching frequencies of uncharged micas (talc and pyrophyllite) are, respectively, 3676 and 3675 cm^{-1} (Farmer *et al.* 1964, Farmer *et al.* 1967). As soon as a charge exists, which induces the presence of potassium ions, OH frequency increases to 3712 cm^{-1} for phlogopite and decreases to 3630 cm^{-1} for muscovite. This fact points out the role of a cation in the interlayer space: as a first approximation, a cation close to an hexagonal cavity increases the OH stretching force constant in a trioctahedral mineral, whereas, in a dioctahedral mineral, where structural OH oxygen atoms turn a negative charge towards the cavity, the interlayer cation decreases the force constant.

It can thus be thought that in K-depleted phlogopites, either 3712 cm^{-1} or 3661 cm^{-1} are perturbed frequencies with respect to 3677 cm^{-1} which corresponds to hydrated minerals (and which is also the talc frequency); 3712 cm^{-1} would be due to the presence of a cation (K in the unaltered mica or Na in the Na-V dehydrated form) and 3661 cm^{-1} would be due to an increase of the negative field acting upon the structural OH proton resulting from the orientation of residual water molecules.

This scheme does not disagree with X ray diffraction, which shows (Table 4) that dehydrated Na-V collapses to 9.55 Å whereas Li-V collapses to 10.07 Å. The first value indicates that in Na-V basal oxygen planes are adjacent; the Li-V spacing on the contrary is only compatible with the presence of "wedges". These "wedges" cannot be lithium ions facing two trigonal arrays of basal oxygen atoms (the spacing would then be ~ 9.6 Å), but could be residual water molecules, the oxygen atoms of which ensure the system a spacing somewhat smaller than that of the initial K-mica. Anyway, the position of Li ion facing an hexagonal cavity seems very unlikely when considering the frequency displacement occurring with dehydration.

It is possible to calculate according to Coggeshall 1950 and White *et al.* 1967, the perturbing field E acting upon structural OH. Let 3750 cm^{-1} be the reference frequency for a free OH and 110 K cal/mole the dissociation energy. With a free proton charge of $0.2 \cdot 10^{-10}$ e.s.u. (Burnelle *et al.* 1957) one gets (Table 7):

Values found for E are of the same order as the field calculated by White at the lattice point occupied by the proton in the supercage of deca-cationated Y-zeolites.

It is very difficult to check the significance of results presented in Table 7 because of the lack of information concerning charge distribution in cation-mica or cation-water bonds. However, if one considers that the positive incremental field

Table 7. Electrostatic field perturbing OH frequency

Frequency (cm^{-1})	Field	
	e.s.u./cm	(V/Å)
3712	$1.165 \cdot 10^6$	3.50
3677	$2.233 \cdot 10^6$	6.70
3661	$2.719 \cdot 10^6$	8.16

ΔE , increasing the frequency from 3677 to 3712 cm^{-1} ($\Delta E = 1.068 \cdot 10^6$ e.s.u./cm) is due to the influence of the cation, it is possible to calculate the cationic charge involved in the cation-mica bond.

The basal spacing of initial K-phlogopite is 10.12 Å. The distance between potassium and lattice OH proton is of the order of 3 Å. Assuming a free protonic charge of $0.2 \cdot 10^{-10}$ e.s.u. and a simple electrostatic point charge model, the charge for potassium in one mica layer is calculated to be $2.33 \cdot 10^{-10}$ e.s.u., which has to be compared with a theoretical $4.8 \cdot 10^{-10} / 2 = 2.4 \cdot 10^{-10}$ e.s.u. Insofar as such a result is not purely accidental, it can be considered as an argument for the interpretation given previously.

CONCLUSION

When one modifies the nature of the interlayer medium of swelling trioctahedral minerals, structural OH stretching frequencies change; this effect has a more or less marked specificity which depends upon the nature of the exchangeable cation and the water content. It has been assumed that these variations are due to an electrostatic perturbation arising from the presence of charges (borne by cations or water molecules) in the close vicinity of the clay layer. The discussion shows that the lattice OH frequency, free from any influence other than the lattice, is observed in well determined cases. A high hydration which insures the cation removal from the clay surface appears as a necessary condition, and it can be noted that frequencies are then the same ones as in uncharged minerals. This statement is strictly valid for K-depleted micas only for which reference minerals exist. Taking into account the difference of unit cell charge, it is likely that this is also true of hectorite for which the "unperturbed" lattice OH frequency would be roughly 20 cm^{-1} higher than for K-depleted micas. It follows thus from these observations that the general theory concerning the influence of local atomic configurations of the unit cell on spectroscopic properties can be extended to the interlayer ions or molecules,

which could provide new information regarding the origin of the i.r. spectra of layer minerals.

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Résumé — Les fréquences des vibrations d'allongement de OH structural dans des minéraux gonflement triocétaédriques tels que l'hectorite ou la phlogopite appauvrie en K dépendent de la forme ionique et de l'hydratation de l'échantillon. La structure triocétaédrique est évidemment appropriée à l'observation des changements spectraux, puisque les groupes hydroxyles sont en condition de forte réactivité avec le milieu ambiant. Ces changements sont attribués au champ créé soit par des cations, soit par des molécules d'eau résiduelles et l'analyse des données spectroscopiques et de diffraction des rayons X permet d'avancer que les fréquences cotées pour le mica inaltéré ne sont que des fréquences perturbées.

Kurzreferat — Die Frequenz struktureller OH Spannungsschwingungen in aufquellenden trioktaedrischen Mineralen wie etwa Hectorit oder K-armem Phlogopit hängen von der ionischen Form und der Hydratation der Probe ab. Die trioktaedrische Struktur ist offenbar ein geeigneter Fall für die Beobachtung spektraler Veränderungen, da sich die Hydroxylgruppen in einem Zustand hoher Reaktivität mit der Umgebung befinden. Diese Veränderungen werden dem entweder aus den Kationen oder aus den Restwassermolekülen entstehenden Feld zugeschrieben, und die gemeinsame Analyse spektroskopischer Daten sowie Röntgenbeugungsdaten erlaubt die Annahme, dass die für unveränderten Glimmer angegebenen Frequenzen nur gestörte Frequenzen sind.

Резюме — Частота колебаний структурных гидроксидов в набухающих триоктаэдрических минералах — гекторите или флогопите с пониженным содержанием К — зависит от ионной формы и гидратации образца. Очевидно, триоктаэдрическая структура подходит для наблюдения спектральных изменений, так как гидроксильные ионы находятся в условиях высокой реакционной способности с окружающей средой. Эти спектральные изменения приписываются полю, которое возникает или от катионов, или от остаточных молекул воды. Комплексный спектральный и рентгеновский анализ позволяет считать, что частоты колебаний, указываемые для неизменной слюды, являются только нарушенными.