GENERALIZATION OF THE CORRELATIONS BETWEEN HYDROXYL-STRETCHING WAVENUMBERS AND COMPOSITION OF MICAS IN THE SYSTEM K₂O-MgO-Al₂O₃-SiO₂-H₂O: A SINGLE MODEL FOR TRIOCTAHEDRAL AND DIOCTAHEDRAL MICAS

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ABSTRACT. This paper presents a model that integrates the observed correlations between OH-stretching wavenumbers and composition of trioctahedral and dioctahedral mica solid solutions in the system K₂O-MgO-Al₂O₃-SiO₂-H₂O. The vibrational properties of hydroxyls are measured by infrared absorption and Raman scattering spectrometries; both methods give the same OH-stretching wavenumbers within experimental errors.

Trioctahedral micas belong to phlogopite solid solutions; dioctahedral micas belong to the phengitic series. The variable Al⁹⁺ + Al⁴⁺ is used to represent mica compositions; OH-stretching bands are designated according to the usual nomenclature: N (OH bonded to 3 Mg), I (OH bonded to 2Mg, Al) and V (OH adjacent to an octahedral vacancy). N, I, and V bands are observed in phlogopite solid solutions, whereas in the phengitic series all OH bands belong to the V-type.

In a diagram $\nu$—OH versus Al⁹⁺ + Al⁴⁺ = Alₜ, the collection of points define four remarkable lines:

- line A: $\nu_N = -11.20 \text{ Al}_T + 3735 \text{ cm}^{-1}$, for Alₜ ≤ 1
- line B: $\nu_N = -22.56 \text{ Al}_T + 3748 \text{ cm}^{-1}$, for Alₜ > 1
- line C: $\nu_I = -37.30 \text{ Al}_T + 3732 \text{ cm}^{-1}$
- line D: $\nu_V = -11.45 \text{ Al}_T + 3592 \text{ cm}^{-1}$.

Lines A and C have almost the same origin; muscovite belongs to the intersection of lines C and D.

Local charge imbalances on oxygens of tetrahedra, generated by Si → Al substitutions, lead to weak OH • • • O bonds, responsible for the negative slopes of lines A, B, and C. Because of the tilting of the OH dipole away from the c* direction in I-type environments, the repulsive K⁺-H⁺ interaction is weakened, as Al⁹⁺ + Al⁴⁺ increases, which explains the steep slope of line C. In V-type environments, the charge imbalance on apical oxygen O(3) of tetrahedra is high if this oxygen is bonded to a (MgMg) pair; this generates strong OH • • • O(3) bonds and low $\nu_V$—OH: 3595 cm⁻¹ in K (Mg₂.₅□₀.₅)Si₄O₁₀(OH)₂. Underbonding on O(3) decreases with increasing aluminum content, explaining the outstanding positive slope of line D. High $\nu_N$ wavenumbers in low-Al trioctahedral micas correspond to the maximum K⁺-H⁺ repulsion and to the minimum OH • • • O interactions, low $\nu_V$ wavenumbers in high-Al dioctahedral micas correspond to the mini-

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mum $K^+H^+$ repulsion and to maximum OH...O interactions; line C (I-type bands) is the link between these two opposite situations.

The N-band and the I-band of the high-Al sodium mica preiswerkite Na(Mg$_2$Al)(Si$_2$Al$_2$)O$_{10}$(OH)$_2$ fit in with the model established for potassium micas.

The two extreme lines A and D get closer with increasing Al content of the mica, their calculated intersection is for $\text{Al}^{VI} + \text{Al}^{IV} = 6.31$, that is, close to the maximum Al content conceivable in a mica (7 Al a./f.u.); the structural formula of this hypothetical mica would be: KAl$_3^{VI}$Al$_1^{IV}$O$_{10}$(OH)$_2$.

Tetrahedral Si ordering around V-type OH groups occurs on the whole of the join tetrasilicic magnesium mica (Al-free mica)-phlogopite (Al$_r$ = 1); this ordering is required by the charge balance on apical oxygens O(3).

INTRODUCTION

Micas and other phyllosilicates have been extensively investigated by vibrational spectrometries, essentially by infrared absorption spectrometry, but only a few Raman data are available on the subject (Loh, 1973; Liu and others, 1987; Robert and others, 1987: Smith and others, 1987; and Tlili and others, 1987). A great deal of research concerns the characterization of the environment of hydroxyls:


4. effect of the orientation of the OH dipole (Serratos and Bradley, 1958) and influence of this orientation on the repulsive interaction between the hydroxyl hydrogen and the interlayer cation (Chaussidon, 1970: Kodama and others, 1974: Robert and others, 1983).

Most of the spectroscopic measurements have been performed on inevitably complex natural minerals, but, despite this intricacy, several reliable models have been established that allow at least a qualitative identification of the nearest environment of OH groups in mica structures; a quantitative determination of these environments could be achieved in some cases (Rouxhet, 1970: Slonimskaya and others, 1986).

More and more work deals with synthetic minerals obtained in simple, well characterized experimental systems; they allow refinements

The OH stretching bands are usually classified into three main types: we refer to the nomenclature of Vedder (1964) in this paper: N-bands (normal), due to OH groups bonded to three octahedrally coordinated divalent cations; I-bands (impurity), due to OH groups bonded to two divalent and one trivalent cation; and V-bands (vacancy), due to OH groups adjacent to an octahedral vacancy. Generally, N-type wavenumbers are the highest, around 3700 cm$^{-1}$ and V-type wavenumbers are the lowest, around 3600 cm$^{-1}$; I-type bands have usually intermediate wavenumbers. Hydroxyl-stretching wavenumbers fluctuate as a function of the mica composition, the influence of tetrahedral as well as octahedral layer compositions and distortions is recognized, but, in most cases, N, I, and V-type bands have been considered independently. Moreover, data concerning I-type band shifts are scarce, and the influence of the mica composition on V-type band wavenumbers is not clearly understood.

The aim of the present paper is to integrate all data concerning dioctahedral micas (N and I-bands) as well as dioctahedral micas (V-bands) of the system K$_2$O–MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O in order to establish a relatively simple relation between OH-stretching wavenumber and mica compositions. This system has been selected for several reasons:

1. Trioctahedral micas have a wide solid solution range, which allows the investigation of a great variety of compositions: in these micas, the three types of OH-stretching bands have been observed (Robert, 1976).

2. The band positions are variable. A marked decrease of N-band wavenumbers with increasing aluminum content of the mica has been observed and interpreted as the result of a modification of the charge distribution, around hydroxyls, over tetrahedral and octahedral layers (Robert, 1973); the same evolution was observed for I-bands in these solid solutions and interpreted in the same terms (Robert, ms, 1981 and 1986).

3. In this system a wide solid solution range exists in dioctahedral micas, that is, the phengitic series, in which only V-type bands can be observed (Velde, 1978).

In the system studied, some micas can have tetrahedrally coordinated Mg (Seifert and Schreyer, 1971)—they will be considered briefly in concluding remarks: infrared data on these micas are available in Tateyama, Shimoda, and Sudo (1976) and in Robert (ms, 1981).

SAMPLES STUDIED, SPECTROMETRIC ANALYSES

The trioctahedral micas investigated belong to phlogopite solutions; their composition is summarized by the general structural formula:
\[ K(Mg_{3-x/2-y/2}Al_{x/2}\square_{y/2})(Si_{3-x/2+y}Al_{1+x/2-y})O_{10}(OH)_2, \]

based on 11 oxygens per formula unit; \( x \) represents the rate of the Tschemark-type substitution \((Mg^{VI}, Si^{IV} \rightleftharpoons Al^{VI}, Al^{IV})\) which leads to aluminous phlogopites, for example, eastonite is for \( x = 1, y = 0 \); \( y \) represents the rate of the substitution \( Mg^{VI}, 2Al^{IV} \rightleftharpoons \square^{VI}, 2Si^{IV} \), which leads to the tetrasilicic magnesium mica (TMM): \( K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2 \), that is, \( x = 0, y = 1 \). A complete solid solution exists between phlogopite \((x = y = 0)\) and TMM (Seifert and Schreyer, 1971); likewise, a large phlogopite solid solution range can be obtained from combinations of \( x \) and \( y \) (Robert, 1976): one will refer to these works for experimental details about syntheses and characterization of micas (optics, cell dimensions, polymorphism, . . .). Owing to the sensitivity of OH-stretching wavenumbers to the presence of interlayer vacancies, the potassium content of synthetic micas was systematically controlled by wet chemical analysis, which showed a very good agreement between observed and expected values.

The dioctahedral micas considered in this work belong to the join muscovite,

\[ K(Al_2\square)(Si_3Al)O_{10}(OH)_2 - Mg-celadonite, K(AlMg\square)Si_4O_{10}(OH)_2: \]

they were synthesized and investigated by infrared absorption by Velde (1978); we use Velde’s data in the text and figures in this series.

Hydroxyl-stretching wavenumbers were measured by infrared absorption spectrometry: some Raman scattering data have also been obtained.

**Infrared.**—Infrared spectra have been recorded on two grating spectrometers, Beckman I.R. 12 and Perkin Elmer P.E. 180, using the usual KBr pellet method for the preparation of samples: the two spectrometers gave consistent results. The resolution was kept within the range 1 to 2 cm\(^{-1}\) for all samples.

In this work, only the major intensity bands are concerned: fine structures which frequently appear as shoulders (Farmer, 1974; Langer, Chatterjee, and Abraham, 1981) will not be discussed here: they are particularly numerous and complex in high-Al phlogopite solid solutions (Robert, 1981) and will be discussed separately.

Infrared data on phlogopite solid solutions are represented by black circles in figure 1; data relative to the phengitic series being those of Velde (1978), the line published by Velde is reproduced in figures 1 and 2 (continuous part of line D), without experimental points.

**Raman.**—Some Raman scattering spectra have been recorded on a monochannel Jobin-Yvon U 1000 microspectrometer equipped with an argon ion laser Coherent Innova 90; exciting line: \( \lambda_0 = 488 \) nm. The estimated accuracy of measurements is \( \pm 1 \) cm\(^{-1}\). OH-stretching wavenumbers measured by Raman spectrometry are identical to those measured by infrared spectrometry within experimental errors; therefore, open symbols representing Raman data coincide with black symbols representing infrared data in figure 1.
Fig. 1. Evolution of the OH-stretching wavenumbers (in cm⁻¹) of N-bands (OH bonded to 3Mg²⁺, lines A and B), I-bands (OH bonded to 2Mg²⁺, Al³⁺, line C) and V-bands (OH adjacent to an octahedral vacancy, line D) in trioctahedral and dioctahedral magnesian micas, as a function of the sum Al⁶⁺ + Al⁴⁺. The continuous part of line D is adapted from Velde (1978).

TMM: tetrasilicic magnesium mica, K(Mg₂Si₄O₁₀(OH))₂
Mus: muscovite endmember, KAl₆Si₄O₁₀(OH)₂
Prswk: preisswerkite, Na(Mg₂Al)(Si₂Al)₂O₁₀(OH)₂
Infrared data:
- potassium micas (Robert, ms, 1973)
- potassium micas (Robert, ms, 1981, and this work)
- preisswerkite (Liu and others, 1987)
Raman data:
- potassium micas (this work)
- preisswerkite (Liu and others, 1987)

RESULTS

Experimental results are grouped in figure 1. The variable used to characterize mica compositions is the total aluminum content Al_T = Al⁶⁺ + Al⁴⁺, as previously proposed in Robert (ms, 1973). The total aluminum content, Al_T, is given in atoms per formula unit (a./f.u.), based on 11 oxygens. The experimental data determine four remarkable lines: line A (up to Al_T = 1) and line B (for Al_T ≥ 1) concern N-bands, line C concerns I-bands, and line D represents V-bands. These
four lines may be expressed by the following respective equations:

\[ \text{line A: } \nu_{\text{N}} - \text{OH} = -11.20 \text{ Al}_T + 3735 \text{ cm}^{-1} \quad (r = 0.995) \]  \hspace{1cm} (1)

\[ \text{line B: } \nu_{\text{N}} - \text{OH} = -22.56 \text{ Al}_T + 3748 \text{ cm}^{-1} \quad (r = 0.976) \]  \hspace{1cm} (2)

\[ \text{line C: } \nu_{\text{I}} - \text{OH} = -37.30 \text{ Al}_T + 3732 \text{ cm}^{-1} \quad (r = 0.991) \]  \hspace{1cm} (3)

\[ \text{line D: } \nu_{\text{V}} - \text{OH} = 11.45 \text{ Al}_T + 3592 \text{ cm}^{-1} \quad (r = 0.960) \]  \hspace{1cm} (4)

with \( \text{Al}_T = \text{Al}^{\text{VI}} + \text{Al}^{\text{IV}} \) atoms per formula unit, based on 11 oxygens. The continuous parts of lines correspond to measurements: the dotted parts, to calculated extrapolations. On line C (I-bands), the dotted part visible on figures 1 and 2, for low aluminum contents, is due to the absence of I-type hydroxyls for \( 0 \leq \text{Al}_T \leq 1 \text{ a./f.u.} \), aluminum being exclusively located in tetrahedral sites: for \( \text{Al}_T > 1 \text{ a./f.u.} \), I-type hydroxyls exist since some Al is octahedrally coordinated, but, up to \( \text{Al}_T \approx 1.5 \text{ a./f.u.} \), this I-band is a shoulder in the N-band, its wavenumber cannot be measured with accuracy. The dotted part of line C for high Al\(_T\) contents (fig. 1) is due to the lack of phlogopite solid solution for \( \text{Al}_T > 2.275 \text{ a./f.u.} \) (Robert, 1976).

Line D (V-bands) also exhibits a dotted part for low Al\(_T\) contents, owing to the lack of experimental data on the join TMM (Al\(_T\) = 0) – Mg-celadonite (Al\(_T\) = 1).

In this study, N-bands and I-bands belong to phlogopite solid solutions, whereas V-bands belong to the phengitic series (including muscovite), except for the very low-wavenumber V-band, 3595 cm\(^{-1}\), which is from the TMM endmember (Kodama and others, 1974). The V-bands of phlogopite solid solutions are not included in this model, because they appear generally as broad, poorly resolved shoulders; for the highest Al contents, \( \nu_{\text{V}} - \text{OH} \) are around 3630 cm\(^{-1}\) in this solid
solutions (Robert, 1976), in agreement with the expected values from line D.

Figure 1 exhibits several outstanding features that deserve comments:

1. The slope of line A (N-bands) is negative and gentle; the slope of line B (N-bands) is nearly twice as great as that of line A; the break between lines A and B is for $A_{1\Gamma} = 1$, which corresponds to the phlogopite endmember $KMg_5(Si_3Al)O_{10}(OH)_2$.

2. Line C (I-bands) has the steepest slope; the origins of lines A and C are very close to each other $3735 \text{ cm}^{-1}$ for line A, $3732 \text{ cm}^{-1}$ for line C, from eqs (1) and (3).

3. The point representing the V-band of muscovite is located close to the intersection of lines C (I-bands) and D (V-bands); the coordinates of the calculated intersection of these two lines, from eqs (3) and (4), are $A_{1\Gamma} = 2.87$ a./f.u. and $\nu-\text{OH} = 3625 \text{ cm}^{-1}$, whereas the muscovite endmember corresponds to $A_{1\Gamma} = 3.00$ a./f.u., with the OH stretching wavenumber of its major intensity band lying within the narrow range $3625 \text{ cm}^{-1}$ (Loh, 1973) – $3630 \text{ cm}^{-1}$ (Velde, 1978).

4. The point representing the V-band of TMM, $\nu_V = 3595 \text{ cm}^{-1}$ definitely belongs to line D; this point was included in the calculation of eq (4);

5. The slopes of the two extreme lines A and D, are similar, but their signs are opposite.

6. Finally, the two extreme wavenumbers $3735 \text{ cm}^{-1}$ and $3595 \text{ cm}^{-1}$ were observed in the same mica (TMM).

The maximum Al content of phlogopite solid solutions is $A_{1\Gamma} = 2.275$ atoms per formula unit in the potassic system (Robert, 1976); this experimentally observed upper limit is set by the maximum possible ditrigonal rotation angle of tetrahedra, $\alpha = 14.5^\circ$ (Robert, ms, 1981), in close agreement with the predicted value, $\alpha = 14.7^\circ$ (Hewitt and Wones, 1975). These authors have shown that sodium, a smaller interlayer cation, allows a larger maximum ditrigonal rotation angle, $\alpha = 18.8^\circ$; this is reached in the high-Al sodium mica $Na(Mg_2Al)(Si_2Al_3)O_{10}(OH)_2$ (Hewitt and Wones, 1975), which is the preiswerkite endmember described by Keusen and Peters (1980). Although potassium micas are the main subject of the present paper, it seems worthwhile to compare spectroscopic data obtained on this high-aluminum triocahedral sodium mica with the set of observations on potassium micas.

Preiswerkite has the same bulk aluminum content as muscovite, 3 $A_{1\Gamma}$ per formula unit. Owing to its octahedral composition, only two types of cationic arrangements are expected around OH groups: N-type arrangement (3Mg—OH) and I-type arrangement (2Mg, Al—OH). Two bands are actually observed in the OH-stretching wavenumbers region of synthetic preiswerkite (Liu and others, 1987): a minor intensity N-type band: $3691 \text{ cm}^{-1}$ (infrared), $3692 \text{ cm}^{-1}$ (Raman) and a major intensity I-type band: $3627 \text{ cm}^{-1}$ (infrared), $3630 \text{ cm}^{-1}$ (Raman). The OH-stretching wavenumbers of preiswerkite are indicated by the square
symbols in figure 1. From eqs (2) and (3), the expected OH-stretching wavenumbers of preiswerkite are \( \nu_N\text{---OH} = 3680 \text{ cm}^{-1} \) and \( \nu_I\text{---OH} = 3620 \text{ cm}^{-1} \), which are very close to experimental data. It is noticeable that the I-band of preiswerkite and the V-band of muscovite have almost the same wavenumbers.

**INTERPRETATION AND DISCUSSION**

It should be remembered that \( \nu\text{---OH} \) depends on the O---H bond strength \( K_{OH} \), according to the relation

\[
\nu\text{---OH} = \frac{1}{2\pi c} \sqrt{K_{OH}/\mu_{OH}},
\]

where \( c \) is the speed of light in vacuum and \( \mu_{OH} \) the reduced mass of the O, H pair;

\[
\mu_{OH} = \frac{M_O \cdot M_H}{M_O + M_H}.
\]

Any \( \nu\text{---OH} \) band shift reflects changes in the environment of the OH dipole and modifications of the OH \( \cdots \) O interactions by hydrogen bonds. The usual models of hydrogen bond concern one-dimensional asymmetric bonds (Lippincott and Schroeder, 1955; Novak, 1979); in micas, owing to the geometry of layers and to the orientations of OH dipoles, these expected OH \( \cdots \) O bonds should be multiple and three-dimensional in most cases.

To interpret the results, we consider first the two extreme situations: high-wavenumber N-type bands (lines A and B) and low-wavenumber V-type bands (line D); an understanding of the evolution of OH-stretching wavenumbers in these two extreme situations will simplify the interpretation of phenomena responsible for the very peculiar characteristics of line C (I-bands).

As we have seen previously, the tetrasilicic magnesium mica, TMM endmember, possesses both the highest N-type wavenumber (3735 cm\(^{-1}\)) and the lowest V-type wavenumber (3595 cm\(^{-1}\)) among micas of the system studied; therefore, in each case, we analyze first the environments of OH groups in this peculiar mica.

**N-bands.**—The wavenumber of N-type OH groups are the highest (figs. 1 and 2) among all OH stretching wavenumbers of the micas presently concerned. This means that the O---H bond strengths in N-type bonds are the strongest among all. In TMM, each N-type OH group is bonded to 3Mg\(^{2+}\) and directed toward interlayer K\(^+\), which is the general situation of N-type hydroxyls: in TMM, the OH dipole is surrounded by a nearly regular hexagonal ring of (SiO\(_4\)) tetrahedra: the ditrigonal rotation angle \( \alpha \) is only 1.42° in the fluorine-TMM endmember (Toraya, Iwai, and Marumo, 1976); this angle is not known in the hydroxyl-TMM endmember, but it is certainly very close to this value. The environment of these hydroxyls can be symbolized as follows:
$3\text{Mg}^{2+} - \text{OH} \rightarrow (6\text{SiO}_4) - \text{K}^+$.

Owing to the purely siliceous composition of the tetrahedral layer, no excess negative charge is created on tetrahedra; the distance between OH and surrounding oxygens of tetrahedra is as large as possible ($\alpha$ is very small), and the K$^+$-H$^+$ repulsive interaction is high (Kodama and others, 1974). Therefore, the O—H bond strength is as high as possible, which explains the high OH stretching wavenumber $3735$ cm$^{-1}$ which corresponds to the minimum OH ··· O$_i$ interactions between the proton and the oxygens O$_i$ of surrounding tetrahedra.

In terms of bond valence, the oxygen of the OH group, O(4), receives $3 \times 2^+ / VI = 1$ valence unit (v.u.) from its three octahedrally coordinated Mg$^{2+}$ neighbors; in the absence of OH ··· O$_i$ interactions, one valence unit is also exchanged between O(4) and H inside the OH group, thus accounting for the strong O—H bond and the high observed $\nu_N$—OH. This calculation rests on the hypothesis of regular polyhedra; in the lack of accurate data on each individual M—O(OH) bond length in complex mica solid solutions, we simply use the quotient of the cationic charge by the coordination number (Donnay and Allmann, 1970) to estimate bond valences; this approximation is near enough for the present purpose.

A comparison of TMM with talc allows the measurement of the K$^+$-H$^+$ repulsive effect on N-type OH groups in TMM. In talc, OH is bonded to $3\text{Mg}^{2+}$ and surrounded by a nearly hexagonal ring of (SiO$_4$) tetrahedra, the ditrigonal rotation angle is $\alpha = 3.4^\circ$ (Rayner and Brown, 1973), similar to that of TMM; this environment can be symbolized as follows:

$$3\text{Mg}^{2+} - \text{OH} \rightarrow (6\text{SiO}_4) - \square^{\text{XII}}.$$  

The OH-stretching wavenumber of talc is only $3677$ cm$^{-1}$ (Wilkins and Ito, 1967). The wavenumber of the important positive $\nu_N$-band shift, 58 cm$^{-1}$, from talc to TMM is due to the K$^+$-H$^+$ repulsive interaction.

The evolution of mica compositions along the join tetrasilicic magnesium mica (TMM)-phlogopite (Phl), represented by line A in figures 1 and 2, does not change the repulsive interaction K$^+$-H$^+$ since the OH dipole remains nearly normal to (001), see the review by Giese (1979); but, on this join, the progressive replacement of Si$^{\text{IV}}$ by Al$^{\text{IV}}$ creates residual negative charges on oxygens of aluminous tetrahedra. This new type of environment of the OH group can be summarized:

$$3\text{Mg}^{2+} - \text{OH} \rightarrow [6(\text{Si, Al})\text{O}_4] - \text{K}^+.$$  

At the same time, the ditrigonal rotation angle $\alpha$ increases from $1.4^\circ$ in TMM to $7.5^\circ$ in phlogopite (Hazen and Burnham, 1973); this shortens the OH ··· O$_i$ distances. The superposition of these two phenomena favors the development of weak OH ··· O$_i$ bonds (hydrogen bonds) and weakens the O—H bond strength, thus accounting for the negative slope of line A. From a point charge model, Vedder (1964) calculates $\Delta\nu_{\text{OH}} = -11$ cm$^{-1}$ for the Si → Al substitution: this predicted shift is
observed on the join tetrasilicic magnesium mica (TMM)-phlogopite (Phl): 3735 cm\(^{-1}\) and 5724 cm\(^{-1}\) respectively, for the two endmembers.

Beyond the phlogopite endmember (Al\(_T\) = 1), the same phenomena continue: more and more tetrahedra become aluminous and the ditrigonal rotation angle \(\alpha\), calculated after the model of Donnay, Donnay, and Takeda (1964) continues to increase up to \(\alpha = 14.5^\circ\), reached for Al\(_T\) = 2.275 a./f.u.; the particular mica eastonite (Al\(_T\) = 2) has \(\alpha = 13.5^\circ\) (Robert, 1981). The break observed between lines A and B can be interpreted by considering the local effects of bulk compositional changes: owing to mica compositions on line A, the most probable maximum Al content of a pseudo-hexagonal ring of six tetrahedra surrounding an OH group is one out of six, that is, Si\(_5\)Al; beyond Al\(_T\) = 1, more and more rings of six tetrahedra can have the composition Si\(_4\)Al\(_2\) and even Si\(_5\)Al\(_3\) for the highest Al contents: this implies more and more residual negative charges on oxygens of tetrahedra and stronger OH \(\cdots\) O\(_i\) interactions. The increase in the number of arrangements of Si and Al around hydroxyls with increasing Al content is also responsible for broadenings and fine structures of the OH-stretching bands in high-aluminum phlogopite solid solutions (Robert, 1981).

The existence of these usually weak hydrogen bonds between hydroxyl hydrogen and oxygens of neighboring tetrahedra has been recognized for a long time in trioctahedral micas (Saksena, 1961; Vedder, 1964; Jørgensen, 1966): these OH \(\cdots\) O\(_i\) interactions are a major phenomenon in dioctahedral micas (V-bands).

**V-bands.**—Wavenumbers of V-type bands are lower (figs. 1 and 2) than those of N and I bands: this reflects weak O—H bond strengths. The fundamental characteristics of OH groups in V-type environments is the tilting of the OH dipole away from c* axis. The angle \(\rho\) between OH and (001) varies in the range 1.3° to 23.1° (Giese, 1979): owing to this tilting, H\(^+\) lies close to two apical oxygens O(3) of two adjacent (Si, Al)O\(_4\) tetrahedra: this can permit stronger OH \(\cdots\) O\(_i\) interactions, compared to N-type OH, which weakens the O—H bond strength inside the hydroxyl. This topic is abundantly documented: Jørgensen (1966), Loh (1973), Farmer (1974), Langer, Chatterjee, and Abraham (1981), Sanz, de la Calle, and Stone (1984).

Admittedly, the repulsive interaction between K\(^+\) and H\(^+\) is much weakened in that case (Farmer, 1974; Kodama and others, 1979), but it cannot be ignored (Soboleva and Mineeva, 1981).

The tilting of the OH vector is not sufficient to explain the behavior of V-type bands; however, comparing talc with pyrophyllite in this respect is interesting. Talc is trioctahedral [Mg\(_3\)Si\(_4\)O\(_{10}\)(OH)\(_2\)], with the OH dipole nearly perpendicular to (001), \(\rho = 91^\circ\), its ditrigonal rotation angle \(\alpha\) is only 3.4° and \(\nu_\text{N} - \text{OH} = 3677 \text{ cm}^{-1}\), whereas pyrophyllite is dioctahedral [(Al\(_5\)Si\(_4\)O\(_{10}\)(OH)\(_2\)], the angle between the OH dipole and (001) is \(\rho = 23.1^\circ\) and its ditrigonal rotation angle is \(\alpha \approx 10^\circ\) (Wardle and Brindley, 1972). Despite these major structural discrepancies, the OH stretching wavenumber of pyrophyllite is \(\nu_\text{N} - \text{OH} = 3675 \text{ cm}^{-1}\) (Farmer, 1974), very close to the OH-stretching
The analysis of the neighborhood of V-type OH groups in TMM points provides us with the interpretation of line D. In TMM, the OH groups in V-type environments are bonded to $2\text{Mg}^{2+}$ and adjacent to an octahedral vacant site. No value is available for the angle $\rho$ between OH and (001), but a previous study of pleochroism on oriented aggregates of TMM showed inclined V-type OH bonds, as in muscovite (Kodama and others, 1974). Therefore, the OH dipole, which is tilted toward the vacant site, is directed between two apical oxygens O(3) of two successive ($\text{SiO}_4$) tetrahedra adjacent to this octahedral vacancy. Such an environment can be symbolized by $(2\text{Mg}^{2+}, \Box) - \text{OH} \rightarrow (2\text{SiO}_4)$. Let us consider the local charge balance on the apical oxygen O(3) of a tetrahedron adjacent to an octahedral vacancy: this oxygen O(3) is bonded to $\text{Si}^{IV}$ and to $2\text{Mg}^{VI}$, it receives $(1 \times 4^+/IV) + (2 \times 2^+/VI) = 1.67$ v.u. from its three cation neighbors. It is evident that this oxygen O(3) is strongly underbonded. In fact, it displays the strongest underbonding that has been observed among any micas of the system studied. This underbonding provokes strong OH ··· O(3) interactions by hydrogen bonds, responsible for the low $\nu_r$—OH-stretching wavenumber in TMM (3595 cm$^{-1}$).

Here again, the calculation of bond valences assumes regular polyhedra; crystal structure determination of TMM has shown that strong distortions occur in both tetrahedra and octahedra: the salient feature is the shortening of Si—O(3) bond length (Toraya, Iwai, and Marumo, 1976), in response to charge imbalance on those apical oxygens O(3) adjacent to an octahedral vacancy.

The underbonded character of oxygen O(3) is progressively reduced by the replacement of (MgMg) pairs by (MgAl) and then by (AlAl) pairs bonded to O(3); therefore, the interactions OH ··· O(3) decrease with increasing Al content of the mica, which readily explains the positive slope of line D (figs. 1 and 2). This occurs in the phengitic series, represented by the continuous part of line D. The underbonded character of oxygen O(3) is minimum in muscovite, in which all apical oxygens of tetrahedra are bonded to $2\text{Al}^{VI}$; therefore, muscovite has the highest OH-stretching wavenumber, on line D.

These observations contradict the commonly admitted relations between the OH-stretching wavenumber and the number of cationic charges in the octahedral neighborhood of V-type hydroxyls; for example, Vedder (1964) proposes the sequence:

$\sim 3625$ cm$^{-1}$: OH $-(\Box, 2\text{Mg}^{2+})$

$\sim 3600$ cm$^{-1}$: OH $-(\Box, \text{M}^{2+}, \text{M}^{3+})$

$\sim 3560$ cm$^{-1}$: OH $-(\Box, 2\text{M}^{3+})$,

which seems very logical if the group constituted by hydroxyl and its two octahedral neighbors is considered as an independent entity, because
low-charge cationic neighbors imply charge imbalance on hydroxyl oxygen and thus high O—H bond strength, that is, high OH-stretching wavenumber. The fundamental result of the present study is the charge balance priority on apical oxygens O(3) of tetrahedra, which means that the sequence cited above is not true, in fact the reverse is true.

The charge balance on hydroxyl oxygen is restored by the shortening of M—OH bonds, in comparison with M—O bonds, which is a very general feature in micas (Robert, 1981).

Line A corresponds to weak OH ⋯ Oₜ interactions, which rise with increasing Al content (negative slope); line D corresponds to high OH ⋯ Oₜ interactions which decrease with increasing Al content (positive slope); the nearly perfect equality of the absolute values of slopes (see eqs 1 and 4) indicates that the variation of bulk charges imbalances on oxygens of tetrahedra, around each type of hydroxyl: increasing for N-type hydroxyls and decreasing for V-type hydroxyls, with increasing Al content, is very similar in both cases.

Because these extreme lines, A and D, get closer with increasing Al content, it is interesting to extrapolate them to their intersection, which is indicated by point P in figure 2. The calculated coordinates of point P are: Al⁶⁺ + Al⁴⁺ = 6.31; ν—OH = 3664 cm⁻¹, from eqs (1) and (4). One notes that the Al content corresponding to point P is not far from the maximum Al content theoretically conceivable in a mica composition (7Al a./f.u.): the structural formula of this purely hypothetical hyperaluminous mica would be KAl⁶⁺Al⁴⁺O₁₀(OH)₂; its position is indicated by the asterisk in figure 2. No known crystal structure can approximate such a compound, but it is interesting to notice that one of the OH-stretching wavenumbers of the layer aluminum hydroxide bayerite, Al(OH)₃, is 3660 cm⁻¹ (Farmer, 1974), which is very close to the value obtained for point P.

Ordering around hydroxyls in V-type environments.—Because of local charge balance requirements, hypotheses involving random distributions of heterovalent substitutions are not satisfactory. Ordering has been recognized in phengites (Velde, 1978, 1980) and interpreted in terms of charge balance (Soboleva and Mineeva, 1981; Bailey, 1984). The solid solution between the tetrasilicic magnesium mica (TMM) and phlogopite (Phl) exhibits an interesting case of ordering in tetrahedral sites around V-type hydroxyls. Figure 3 shows the evolution of the infrared absorption spectra in the region of hydroxyl stretching wavenumbers, along the join TMM–Phl. The decrease in wavenumber of the major intensity N-band (3735 cm⁻¹ in TMM) corresponds to line A in figures 1 and 2. Another, minor intensity N-band exists in TMM (3695 cm⁻¹): its wavenumber also decreases from TMM to Phl (fig. 3). This minor intensity band was observed and briefly discussed in a previous paper about TMM (Kodama and others, 1974): further considerations about its origin are beyond the scope of the present paper. The V-type band has a different behavior: its intensity decreases from TMM to Phl, in conformity with the progressive disappearance of octahedral vacan-
Fig. 3. Infrared absorption spectra of mica solid solutions on the join phlogopite (Phl)-tetrasilicic magnesium mica (TMM), in the region of OH-stretching wavenumbers; the compositions are given in mole percent. N: N-type OH bands; V: V-type OH band.
cies, but its wavenumber remains remarkably constant, 3595 cm\(^{-1}\). This means that the local cationic octahedral as well as tetrahedral environment of V-type hydroxyls in TMM is preserved along the joint TMM–Phl; it should be remembered that these V-type hydroxyls are bonded to 2Mg\(^{2+}\) and interact by hydrogen bonds with the apical oxygens of two successive (SiO\(_4\)) tetrahedra. In other words, Al\(^{IV}\) is excluded from the near environment of V-type hydroxyls on this joint; this is a consequence of local charge balance requirements on oxygens of tetrahedra.

I-bands.—The cationic environment of I-type hydroxyls is trioctahedral: OH – (2Mg, Al). Concerning the valence sum, the hydroxyl oxygen receives: (2 \(\times\) 2\(^+\)/VI) + (1 \(\times\) 3\(^+\)/VI) = 1.17 v.u. from the three octahedral cations: the required contribution of H\(^+\) to the charge balance on this oxygen is then 0.83 v.u. This low O—H bond valence is sufficient to explain the low \(\nu\) \(_L\) wavenumbers, inferior to \(\nu\) \(_N\). The charge imbalance on H\(^+\) (0.17 v.u.) is set off by OH \(\cdots\) O\(_i\) hydrogen bonds. Vedder (1964) predicts a negative band shift \(\Delta\nu = -34\) cm\(^{-1}\) for a Mg \(\rightarrow\) Al substitution: this shift adds to the shift provoked by the tetrahedral Si \(\rightarrow\) Al substitution (\(\Delta\nu = -11\) cm\(^{-1}\)), since the Tschermak-type substitution responsible for (2Mg, Al\(^{VI}\)) groups involves both the octahedral and the tetrahedral layer (Mg\(^{VI}\), Si\(^{IV}\) \(\leftrightarrow\) Al\(^{VI}\), Al\(^{IV}\)). The sum of these two shifts is \(\Delta\nu = -45\) cm\(^{-1}\), which is approximated in eastonite: \(\nu\) \(_N\) = 3702 cm\(^{-1}\) and \(\nu\) \(_L\) = 3653 cm\(^{-1}\), that is, \(\Delta\nu = -49\) cm\(^{-1}\). The difference between \(\nu\) \(_N\) and \(\nu\) \(_L\) is not constant: eqs (2) and (3) show a much steeper slope for line C (I-bands) than for line B (N-bands). This difference can be explained if the K\(^+\)–H\(^+\) repulsive interaction is taken into account. A neighbor trivalent ion tilts the OH dipole away from the c* direction, that is, away from the normal to (001), but this tilting angle does not exceed \(\approx 10^\circ\); Vedder (1964) predicts 6\(^\circ\) and most crystal structure determinations agree with the prediction, except for lepidolites (Giese, 1979); therefore, a quite similar magnitude of the K\(^+\)–H\(^+\) repulsion is expected for N-type and I-type hydroxyls. A previous study of phlogopite and eastonite (Robert and others, 1983) has shown a surprisingly different response of N-type and I-type hydroxyls to K-depletion: the N-type band shift is \(\Delta\nu = -46\) cm\(^{-1}\), whereas the I-type band shift is only \(\Delta\nu = -21\) cm\(^{-1}\); this significant difference has been interpreted in terms of K\(^+\)–H\(^+\) repulsion, strong for N-type hydroxyls and much weaker for I-type hydroxyls, owing to the tilting of the OH dipole. No data are available concerning the I-type bands of K-depleted micas on the join phlogopite–eastonite, but the observations on these two micas permit us to conclude that the variation of K\(^+\)–H\(^+\) interaction has a major influence on band shifts. Another consequence of the tilting of the OH dipole is the shortening of OH \(\cdots\) O\(_i\) distances, which strengthens the hydrogen bonds. The conclusions drawn about the effect of the variations of the ditrigonal rotation angle \(\alpha\) on N-bands remain valid for I-bands: increasing aluminum content increases \(\alpha\), which also shortens the OH \(\cdots\) O\(_i\) distances. On the whole, all these phenomena act and vary in the same way, as a function of the composition, that is, as a function of the variable Al\(^{VI}\) + Al\(^{IV}\).
Neither the common origin of lines A and C nor the position of the V-type band wavenumber of muscovite close to line C are coincidental. The ordinate of the origin of lines A and C corresponds to the ν\textsubscript{ν} band of TMM (3735 cm\textsuperscript{-1}); as we have seen previously, this highest wavenumber is due to the strongest K\textsuperscript{+}-H\textsuperscript{+} repulsion and to the weakest OH \cdots O\textsubscript{1} interactions in low-aluminum micas; on the contrary, muscovite represents the weakest K\textsuperscript{+}-H\textsuperscript{+} repulsion and the strongest OH \cdots O\textsubscript{1} interactions in high-aluminum micas: line C is the link between these two opposite situations in the system studied.

The similarity between ν\textsubscript{υ}—OH of muscovite and ν\textsubscript{ι}—OH of preiswerkrite reflects similar O—H bond strengths and makes highly desirable the crystal structure determination of preiswerkrite in order to measure the actual OH orientation in this high-aluminum trioctahedral mica.

**CONCLUDING REMARKS**

Among the different factors that can act on OH-stretching wavenumbers, that is on O—H bond strengths, the nature of the nearest cationic environment is fundamental because it controls both the charge balance on hydroxyl oxygen and the orientation of the OH dipole in the mica structure and therefore the repulsive interaction K\textsuperscript{+}—H\textsuperscript{+}, a major phenomenon. The other major factor is the charge balance on oxygens of tetrahedra: charge imbalances can have either a tetrahedral origin (that is, Si → Al substitution) or an octahedral origin (that is, octahedral vacancy) or both.

The lowest OH-stretching wavenumber observed in the system studied is 3595 cm\textsuperscript{-1}, for the V-type band of TMM, that is, OH—(2Mg, □): Slonimskaya and other. (1986) have observed a much lower ν\textsubscript{υ}—OH (3505 cm\textsuperscript{-1}) for hydroxyls in the same type of environment, in natural celadonites and glauconites: they interpret this difference in terms of distribution and octahedral vacancies over cis and trans sites. Low ν\textsubscript{υ}—OH can also be observed in micas with tetrahedrally coordinated divalent cations that produce strong charge imbalances on oxygens of tetrahedra. Tateyama, Shimoda, and Sudo (1976) indicate the value ν\textsubscript{υ}—OH = 3572 cm\textsuperscript{-1} for a mica having 0.34 Mg\textsuperscript{iv}.a./f.u. (based on 11 oxygens) and Robert (ms. 1981) observed ν\textsubscript{υ}—OH = 3565 cm\textsuperscript{-1} in a mica containing 0.37 Mg\textsuperscript{iv} per formula unit.

The highest OH-stretching wavenumber is observed for the N-band of TMM, 3735 cm\textsuperscript{-1}, which corresponds to the maximum O—H bond strength in the system studied: any change in the cationic environment of the OH dipole provokes a negative band shift, which is particularly strong if the charges increase in the near octahedral neighborhood of the OH group, that is (2Mg, Al)—OH in the present case. In trioctahedral environments, a decrease in the sum of cationic charges provokes the opposite phenomenon: in lepidolites, the stretching wavenumbers of OH groups bonded to (2Mg, Li) can reach \textasciitilde3755 cm\textsuperscript{-1} (Robert, ms. 1981 and 1986; Robert and others, 1987).
The characterization of a mica phase from OH-stretching wave-numbers requires the greatest caution because the ranges of $\nu$—OH overlap. This is particularly tricky for I-bands and V-bands in very high aluminum micas.

ACKNOWLEDGMENTS

The authors are indebted to J.-M. Beny and C. Beny for valuable assistance in the Raman work. Many conclusions expressed in this paper have benefited from helpful discussions with V. C. Farmer, J. Sanz, P. Tarte, and B. Velde.

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