Canadian Mineralogist
Vol. 27, pp. 225-235 (1989)

CHARACTERIZATION OF LEPIDOLITES BY RAMAN AND INFRARED SPECTROMETRIES.
I. RELATIONSHIPS BETWEEN OH-STRETCHING WAVENUMBERS AND COMPOSITION

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ABSTRACT

Four partial solid-solutions that affect lepidolite compositions have been investigated by Raman scattering and infrared absorption spectrometries, in the wavenumber range of the OH-stretching vibration (ν - OH); in every case, both methods gave the same values, within experimental errors. The compositions synthesized belong to the solid solutions between phlogopite and each of the end members: taeniolite, trilithionite and polylithionite (all purely trioctahedral) and to the join tetrasilicic magnesium mica - taeniolite, which exhibits a partial dioctahedral character. On the first three joins, changes in the evolution of spectra reflect the compositional evolution and especially the increase in lithium content; all the bands observed belong to the trioctahedral type. Three subtypes are characterized by the bulk number of charges of the three adjacent cations: "5-charge bands", due to OH groups bonded to Mg_2Li or Li_2Al (range 3755–3740 cm^{-1}); "6-charge bands", due to OH groups bonded to Mg_3 or AlMgLi (range 3740–3715 cm^{-1}) and "7-charge bands", due to OH groups bonded to Mg_2Al or Al_2Li ($\nu < 3700$ cm^{-1}). On the basis of these observations, a new nomenclature is proposed, relevant to any mica. On the join tetrasilicic magnesium mica - taeniolite, an additional dioctahedral-type band observed at 3595 cm^{-1} is due to OH groups bonded to 2Mg and adjacent to an octahedral vacancy. This wavenumber is constant along the join, indicating the exclusion of Li^+ from the proximity of these hydroxyl groups. For all the trioctahedral-type bands, a systematic shift is observed toward low wavenumbers, as the bulk aluminum content (Al_{tot}) increases in the mica. This phenomenon, already known in phlogopite solid-solutions, is related to change in mica composition and is explained by changes in OH...O interactions by weak hydrogen bonding between the hydroxyl proton and the apical oxygen atoms of surrounding tetrahedra. These variations can be expressed by three equations, valid for light elements: (1) $\nu = -9.33Al_{tot} + 3754$ (5-charge bands); (2) $\nu = -16.95Al_{tot} + 3741$ (6-charge bands), and (3) $\nu = -29.66Al_{tot} + 3719$ (7-charge bands). The latter equation includes all the available values concerning K-bearing micas (lepidolite and phlogopite solid-solutions) and Na-bearing micas (preiswerkite and ephesite). The highest known ν - OH value (3755 cm^{-1}) corresponds to hydroxyl groups free of any OH...O interaction.

Keywords: Raman scattering, infrared absorption, hydroxyl stretching, lepidolite, synthetic micas.

SOMMAIRE

Quatre solutions solides partielles de lépidolites hydroxylées ont été étudiées par diffusion Raman et absorption infrarouge, dans le domaine des vibrations d'élongation des groupements hydroxyles (ν - OH); dans tous les cas, les valeurs de nombre d'ondes obtenues par les deux méthodes sont les mêmes, aux incertitudes expérimentales près. Ces lépidolites appartiennent aux solutions solides entre la phlogopite et chacun des pôles lépidolitiques taeniolite, trilithionite et polylithionite (ces micas sont tous purement trioctaédriques), ainsi qu'au joint mica tétrasilicique magnésien - taeniolite, qui possède un caractère partiellement dioctaédrique. Sur les trois premiers joints, l'évolution des spectres reflète l'évolution des compositions et en particulier l'augmentation de la teneur en lithium; toutes les bandes observées sont de type trioctaédrique. On montre que ces bandes appartiennent à trois sous-types, caractérisés par le nombre de charges portées par les trois cations liés à OH: bandes de type "5 charges", dues à des OH liés à Mg_2Li ou Li_2Al (domaine 3755–3740 cm^{-1}); bandes de type "6 charges", dues à des OH liés à Mg_3 ou AlMgLi (domaine 3740–3715 cm^{-1}), et bandes de type "7 charges" pour les OH liés à Mg_2Al ou Al_2Li (<3700 cm^{-1}). Cette observation sert de base à une nouvelle nomenclature, valable pour tout mica. Sur le joint mica tétrasilicique magnésien - taeniolite, on observe en plus, une bande caractéristique d'un environnement dioctaédrique (OH liés à 2Mg et adjacents à une lacune octaédrique), à très bas nombre d'ondes: 3595 cm^{-1}. La constance de ce nombre d'ondes, le long du joint, indique que le cation Li^+ est exclu de l'environnement de ces groupements hydroxyles. Pour l'ensemble des bandes de type trioctaédrique, on observe un glissement systématique vers les basses valeurs de nombre d'ondes lorsque la teneur globale en aluminium

(Al_{tot}) augmente dans le mica. Ce phénomène déjà connu dans les solutions solides de la phlogopite est expliqué par la modification des interactions OH...O par liaison hydrogène faible, entre le proton et les atomes d'oxygène apicaux des tétraèdres, lorsque les compositions évoluent. Trois équations relient les nombres d'ondes aux compositions des micas, exprimées par Al_{tot} (1) $\nu = -9.33Al_{tot} + 3754$ (bandes à 5 charges); (2) $\nu = -16.95Al_{tot} + 3741$ (bandes à 6 charges); (3) $\nu = -29.66Al_{tot} + 3719$ (bandes à 7 charges). Cette dernière équation inclut l'ensemble des données disponibles, relatives aux micas potassiques (lépidolites et solutions solides de la phlogopite), ainsi qu'aux micas sodiques (preiswerkite et éphésite). La plus haute valeur connue de ν - OH (3755 cm^{-1}) a été observée au cours de cette dernière étude; elle correspond à des groupes hydroxyles libres de toute interaction OH...O.

Mots-clés: diffusion Raman, absorption infrarouge, hydroxyle, lépidolite, micas de synthèse.

INTRODUCTION

Naturally occurring lepidolites generally have a high fluorine content; therefore, little is known about the spectroscopic properties of hydroxyl groups in this group of micas. The limited infrared absorption data available on the environments of hydroxyl in lithium micas pertain to lepidolite samples compositionally close to three theoretical end-members (trilithionite, zinnwaldite, polylithionite: Jørgensen 1966), lithian montmorillonites (Calvet & Prost 1971), the rare trioctahedral sodium mica ephesite $Na(Al_2Li)(Si_2Al_2)O_{10}(OH)_2$ (Farmer & Velde 1973), the partial solid solution between the tetrasilicic magnesian mica (TMM) $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$ and taeniolite $K(Mg_2Li)Si_4O_{10}(OH)_2$ (Robert 1981), and peculiar synthetic lithian micas containing Li as an interstitial cation in the interlayer space (Robert *et al.* 1983). The salient features of these findings are: (1) the presence of a high-wavenumber OH-stretching band (ν - OH 3750 cm^{-1}), attributed to OH groups bonded to (Mg_2Li), in the spectrum of taeniolite-like micas (Robert 1981), and (2) the existence of a low-wavenumber OH-stretching band, around 3600 cm^{-1} in the spectrum of ephesite (Farmer & Velde 1973) and below 3500 cm^{-1} in the spectrum of high-Li lepidolites (Jørgensen 1966), attributed to OH groups bonded to (Al_2Li). Thus, it is obvious that the nature of the neighboring cations and the bulk composition of the mica influence the OH-stretching wavenumber, *i.e.*, the O–H bond constant.

The aim of the present paper is to identify the octahedrally coordinated cations bonded to each type of hydroxyl, with special attention to lithium, and to analyze the role of the different crystal-chemical factors that influence the OH-stretching wavenumbers. For this purpose, four series of synthetic hydroxyl-bearing lepidolites were investigated by vibrational spectrometries, Raman scattering and infrared absorption. Three of the four lepidolitic series investigated here are purely trioctahedral: phlogopite–polylithionite, phlogopite–trilithionite (Robert & Volfinger 1979), and phlogopite–taeniolite (Robert 1981); the fourth series has a partial dioctahedral character and belongs to the join tetrasilicic magnesian mica - taeniolite (Robert 1981). A comparison with data available on synthetic phlogopite solid-solutions (Li-free trioctahedral micas) (Robert & Kodama 1988) also is presented.

SAMPLES STUDIED

The samples studied were prepared by hydrothermal synthesis. The starting products used were gels of appropriate compositions. Experimental details are given in Robert & Volfinger (1979). The maximum extent of solid solution occurs at low temperature. For this reason, samples were obtained at 500°C and below, at 2 kbar $P(H_2O)$; X-ray-diffraction results indicate excellent crystallinity despite the relatively low temperature of synthesis.

On the join phlogopite (Phl) $KMg_3(Si_3Al)O_{10}(OH)_2$ - taeniolite (Tae) $K(Mg_2Li)Si_4O_{10}(OH)_2$, the range of solid solution is extensive. The most Li-rich mica has the composition Phl_{10}–Tae_{90} (mole %) at 400°C (Robert 1981). On this join, lithium micas are systematically accompanied by a minor to trace amount of quartz (certainly less than 5%). These micas are characterized by a variable content of both the tetrahedral and octahedral layers, but this lepidolitic series has the simplest octahedral composition, from Mg_3 in the phlogopite end-member to (Mg_2Li) in the theoretical taeniolite end-member. Therefore, the presentation and the discussion of results will start with this join.

On the join phlogopite–trilithionite (Tril) $K(Al_{1.5}Li_{1.5})(Si_3Al)O_{10}(OH)_2$, solid solution extends to Phl_{40}–$Tril_{60}$ at 500°C (Robert & Volfinger 1979). The peculiar composition $Phl_{1/3}$–$Tril_{2/3}$ corresponds to the hydroxyl-bearing magnesian equivalent of zinnwaldite $K(AlMgLi)(Si_3Al)O_{10}(OH)_2$, but this composition yields the assemblage mica + α–eucryptite + kalsilite + sanidine under the experimental conditions used. The composition of the tetrahedral layer remains constant (Si_3Al) along the join, but that of the octahedral layer is complicated owing to the presence of the three cations, Al, Mg and Li.

On the join phlogopite–polylithionite (Poly) $K(Li_2Al)Si_4O_{10}(OH)_2$, the range in solid solution does not exceed the composition Phl_{75}–$Poly_{25}$ at 500°C and Phl_{70}–$Poly_{30}$ at 400°C. The composition of both tetrahedral and octahedral layers is variable, and the complexity in the octahedral layer is qualitatively identical to that along the join phlogopite - trilithionite. On the join phlogopite - polylithionite, the bulk aluminum content remains constant, and only the coordination of aluminum changes from fourfold in phlogopite and sixfold in polylithionite.

On the join tetrasilicic magnesium mica (TMM) $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$ - taeniolite, the range in solid solution is large and can extend to TMM_{20}–Tae_{80} at 500°C (Robert 1981). The composition of the tetrahedral layer is constant (Si_4) along the join. This solid solution exhibits a partial dioctahedral character owing to the presence of octahedral vacancies. The local relations between lithium and vacant octahedral sites will deserve special attention.

OH GROUPS IN MICAS

The OH group in micas is adjacent to three cationic octahedral sites. In trioctahedral micas, these three sites are occupied by a cation (Al, Mg or Li in the lepidolite compositions investigated in this work). The O–H vector is nearly perpendicular to (001) in most cases, but it can exhibit a higher angle of tilt in lepidolites (Giese 1979, Lin & Guggenheim 1983). Owing to this orientation, the repulsion between the hydroxyl proton and the interlayer cation is strong; the $OH...O_t$ interactions between the hydroxyl proton and the oxygen atoms of surrounding tetrahedra are usually weak (Robert & Kodama 1988). Therefore, the OH stretching wavenumber ν - OH, which reflects the O–H bond constant k ($\nu \simeq k^{1/2}$), is usually high in such environments.

The bond strength k can be approximated by the bond valence exchanged between the hydroxyl proton and the oxygen of the OH group. Vedder (1964) proposed the following band nomenclature: N-bands (N for normal) for OH stretching bands due to hydroxyl groups bonded to Mg_3, and I-bands (I for impurity) for hydroxyl groups bonded to Mg_2Al. The ν_N–OH wavenumbers commonly lie within the range 3735–3700 cm^{-1} in trioctahedral magnesium micas (Farmer 1974, Robert 1973, 1981, Robert & Kodama 1988), whereas ν_I–OH wavenumbers lie within the range 3670–3640 cm^{-1} in the same micas. This difference can be interpreted in terms of charge balance on the oxygen atoms of the hydroxyl groups.

Based on the observations and conclusions drawn in the present work, a new system of nomenclature suitable for the chemically complex octahedral environments of the OH group is proposed.

In dioctahedral environments, the hydroxyl is bonded to two cations and is adjacent to an octahedral vacant site; the OH dipole is tilted toward the vacancy and is nearly parallel to (001) (see Giese 1979 for a review of OH dipole orientations). The K^+ (or Na^+) - H^+ repulsion is weak in that case, and $OH...O_t$ interactions can occur between the hydroxyl proton and apical oxygen atoms of surrounding tetrahedra, controlled by the charge imbalances on the apical oxygen atoms. The $OH...O_t$ interactions are responsible for the systematically low OH-stretching wavenumbers in dioctahedral environments, usually below 3630 cm^{-1} (Robert & Kodama 1988). These OH groups and related OH-stretching bands belong to the V-type (V for vacancy), according to the nomenclature of Vedder (1964).

EXPERIMENTAL METHOD

Raman scattering spectra were recorded at room temperature, on compacted powders (average grain-size 1 μm), with a single-channel Jobin–Yvon U1000 microspectrometer equipped with an argon ion laser (Coherent Innova 90, exciting line λ_o = 488 nm). The estimated accuracy of measurements is ± 1 cm^{-1} for the high-intensity bands and certainly no better than ± 3 cm^{-1} for low-intensity bands and shoulders. Infrared (IR) absorption spectra were recorded at room temperature with a Perkin–Elmer PE180 grating spectrometer, using KBr pellets. A high-purity polystyrene foil was used as a standard for calibration. Resolution was kept within the range 1–2 cm^{-1} for all measurements.

In every case, OH-stretching wavenumbers obtained by Raman and IR are equal within experimental error, as was previously observed for trioctahedral and dioctahedral Li-free micas (Robert & Kodama 1988). The spectroscopic source of data is not specified in the text, but is indicated in the figures.

RESULTS AND INTERPRETATION

Join phlogopite (Phl) - taeniolite (Tae)

In the phlogopite end member, a well-known OH stretching band observed at 3724 ± 1 cm^{-1} is due to OH groups bonded to three octahedrally coordinated divalent cations, *i.e.*, the 6 cationic charges from Mg_3. On the join phlogopite - taeniolite a high-wavenumber band (ν <3740 cm^{-1}) increases progressively as the taeniolite (Li) content increases in the solid solution (Fig. 1). Considering the change in the octahedral occupancy on this join, from Mg_3 (Phl) to Mg_2Li (Tae), the most likely source of this new high-wavenumber band is the low-charge cationic environment caused by Mg_2Li (*i.e.*, 5 cationic charges), adjacent to an OH group. In Vedder's (1964) nomenclature, this high-wavenumber band can be considered as a special case of an impurity band, since it concerns OH groups that are not bonded to three divalent cations in a trioctahedral environment.

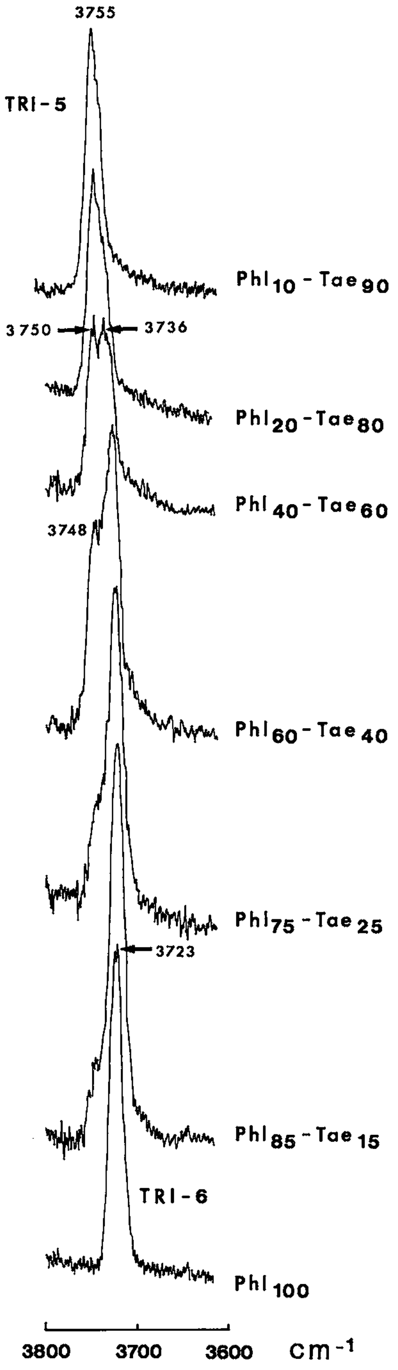

FIG. 1. Raman spectra of lepidolite compositions along the join phlogopite (Phl) - taeniolite (Tae) in the region of ν-OH wavenumbers. TRI-5: OH bonded to Mg_2Li; TRI-6: OH bonded to Mg_3.

Along the Phl–Tae join, the OH-stretching wavenumbers increase from Phl to Tae as the Al content decreases. This increase is in accord with the previous observations on phlogopite solid-solutions (Li-free trioctahedral micas). Note that the OH-stretching wavenumber of the hydroxyl group bonded to Mg_2Li in the mica Phl_{10}–Tae_{90} is the highest recorded for any mica (3755 cm^{-1}), and apparently for any compound.

Join phlogopite (Phl) - trilithionite (Tril)

The outstanding feature of the Phl–Tril join is the growth of two low-intensity, poorly resolved satellite bands, one on each side of the high-intensity band (Fig. 2). The high-intensity band broadens simultaneously from a half-height width of 17 cm^{-1} in Phl_{100} to 37 cm^{-1} in Phl_{50}–$Tril_{50}$; for the highest trilithionite contents, a slight splitting of this high-intensity band is observed (Fig. 2).

Join phlogopite (Phl) - polylithionite (Poly)

Raman spectra for Phl–Poly in the region of OH-stretching wavenumber (Fig. 3) are very similar to those observed for Phl–Tril. In particular, the two satellite low-intensity bands are clearly observed, a high wavenumber band at ν = 3746 cm^{-1} and a low wavenumber band at ν = 3686 cm^{-1}. The central high-intensity band also broadens as the Poly component increases in the solid solution.

The set of data concerning the Phl–Tril and Phl–Poly joins can be readily explained by considering the change in octahedral compositions of micas along these two joins. The octahedral position contains Mg_3 in the Phl end-member, in which each OH group is bonded to $3Mg^{2+}$; the octahedral composition becomes $(Al_{1.5}Li_{1.5})$ in theoretical Tril end-member and (Li_2Al) in the theoretical Poly end-member. Apart from the end-members, any mica composition located on the joins Phl–Tril and Phl–Poly possesses all three cations Al, Mg and Li in the octahedral layer.

Table 1 gives the ten combinations of these three cations around an OH group in a trioctahedral environment (first column); the corresponding number of cationic charges is given in the second column. The stability of any phase requires local charge-equilibrium both on cations and anions. The bond valence exchanged in a M–OH bond, calculated here as the quotient of the cationic charge by the coordination number, amounts to the calculated ideal bond-valence of Donnay & Allmann (1970). The calculation assumes regular octahedra; for lack of knowledge of each actual M–O(H) bond length, we must use this approximation. The bond-valence sum

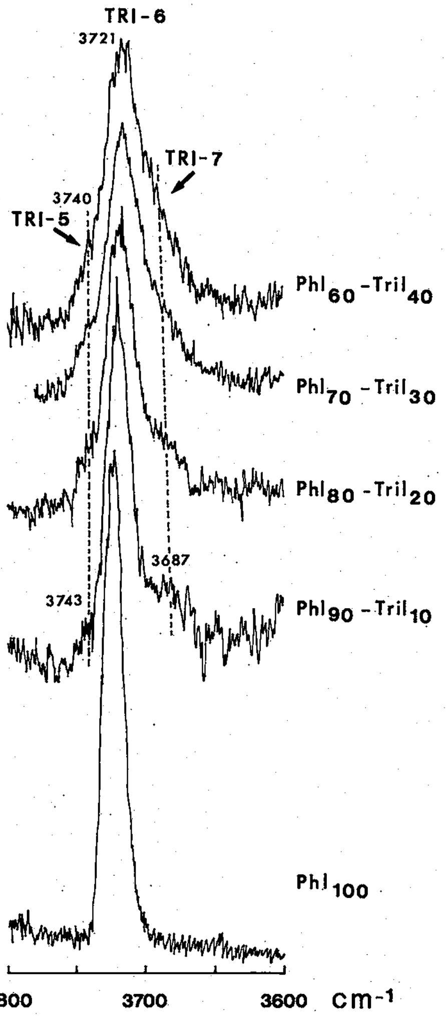

FIG. 2. Raman spectra of lepidolite compositions along the join phlogopite (Phl) - trilithionite (Tril), in the region of ν-OH wavenumbers. TRI-5: OH bonded to Mg_2Li or Li_2Al; TRI-6: OH bonded to Mg_3 or AlMgLi; TRI-7: OH bonded to Mg_2Al or Al_2Li.

theoretically received by the hydroxyl oxygen from the three adjacent octahedrally coordinated cations, expressed in valence units (v.u.), is given in the third column of Table 1. The two negative charges of the hydroxyl oxygen must be compensated both by the three cations and the hydroxyl proton. The higher the bond-valence sum received by the hydroxyl oxygen from its three adjacent cations, the lower the bond valence exchanged within the O–H group (*i.e.*, the bond constant *k*), and thus the lower the OH-stretching wavenumber ν. Table 1, adapted from Monier (1987), also indicates those cationic arrangements that are permitted; examples of mica end-members that exhibit the permitted cationic arrangements are given in the last column.

Note that in Table 1, the two cationic arrangements Li_3 and Li_2Mg are forbidden because their bulk charge is much too low, 3 and 4 charges, respectively, corresponding to the valence sums 0.5 and 0.67 v.u., instead of 1 v.u. in the ideal case. Although these arrangements are unknown in any trioctahedral mica, the four-charge environment ($Mg_2\square$) exists in the tetrasilicic magnesium mica $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$; there, the OH group belongs to a dioctahedral environment.

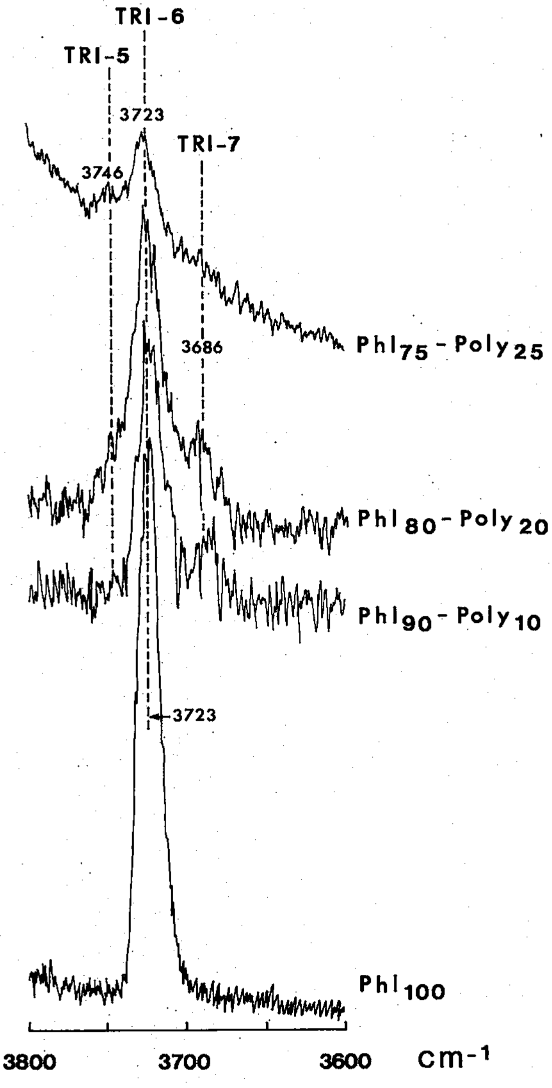

FIG. 3. Raman spectra of lepidolite compositions, along the join phlogopite (Phl) – polylithionite (Poly), in the region of ν–OH wavenumbers. TRI-5, TRI-6 and TRI-7 as in Figure 2.

TABLE 1. PERMITTED AND FORBIDDEN ARRANGEMENTS OF Al, Mg and Li AROUND A TRIOCTAHEDRAL-TYPE HYDROXYL

Cationic arrangement	N° of charges	Valence sum in M-OH bonds	Permitted	Forbidden	Examples
Al_3	9	1.5		**	
Mg_3	6	1.0	**		phlogopite
Li_3	3	0.5		**	
Al_2Mg	8	1.33		**	
Al_2Li	7	1.17	**		ephesite, bityite
Mg_2Al	7	1.17	**		eastonite, preiswerkite
Mg_2Li	5	0.83	**		taeniolite
Li_2Al	5	0.83	**		polylithionite
Li_2Mg	4	0.67		**	
AlMgLi	6	1.0	**		zinnwaldite

The ten cationic arrangements of Al, Mg and Li around a trioctahedral-type hydroxyl (first column); corresponding sum of positive charges (second column) and valence sum exchanged in the three M-OH bonds (third column). The last column gives examples of theoretical mica end members which exhibit the permitted arrangements.

phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$; ephesite $Na(Al_2Li)(Si_2Al_2)O_{10}(OH)_2$; bityite $Ca(Al_2Li)(Si_2AlBe)O_{10}(OH)_2$; eastonite $K(Mg_{2.5}Al_{0.5})(Si_{2.5}Al_{1.5})O_{10}(OH)_2$; preiswerkite $Na(Mg_2Al)(Si_2Al_2)O_{10}(OH)_2$; taeniolite $K(Mg_2Li)Si_4O_{10}(OH)_2$; polylithionite $K(Li_2Al)Si_4O_{10}(OH)_2$; zinnwaldite $K(AlMgLi)(Si_3Al)O_{10}(OH)_2$.

The group Al_3, unknown in any compound, is forbidden because its bulk charge is too high (9 charges); it would correspond to a valence sum of 1.5 v.u. exchanged between the hydroxyl oxygen and the three adjacent cations. Similarly, the group Al_2Mg (8 charges) is unknown in micas and is considered here as a forbidden group; however, the 8-charge group Mg_2Ti is well known in titanium-bearing phlogopite (Robert 1976, 1981).

Considering Table 1, the evolution of spectra on the joins phlogopite–trilithionite and phlogopite–polylithionite can be interpreted easily. The low-intensity, high-wavenumber band observed on the joins Phl–Tril (Fig. 2) and Phl–Poly (Fig. 3) is due to a 5-cationic-charge environment of the OH group. Examples are Mg_2Li, previously observed on the join Phl–Tae within the same wavenumber range (Fig. 1), and Li_2Al, known in polylithionite. Similarly, the second low-intensity satellite band observed at low wavenumbers (ν-OH < 3700 cm^{-1}) is due to a 7-charge environment of the OH group. Examples are Al_2Li, known in several mica end-members (ephesite, bityite), and Mg_2Al, found in phlogopite solid-solutions (*e.g.*, the K-mica eastonite and the Na-mica preiswerkite).

Finally, the broadening of the central high-intensity band (a 6-charge band, due to OH groups bonded to $3Mg^{2+}$ in the phlogopite end-member), particularly evident on the join Phl–Tril, can be attributed to the existence of a second 6-charge band whose intensity increases along the joins with increasing Li-contents. The only possible cationic arrangement compatible with this conclusion is AlMgLi (Table 1). This seems very reasonable considering the change in octahedral occupancy along the joins Phl–Tril and Phl–Poly. Note that the octahedral occupancy is $Al_{0.9}Mg_{1.2}Li_{0.9}$ in the most Li- (and Al-) rich mica stable on the Phl–Tril join. The atomic proportion is close to 1/1/1, *i.e.*, close to the composition AlMgLi in the octahedral layer of this mica.

As in the solid solution Phl–Tae, the OH-stretching wavenumbers along Phl–Tril are not constant; a regular negative shift in wavenumber from Phl to Tril is observed for all the bands. However, no band shift is observed along Phl–Poly. Considering previous studies of the effect of the bulk Al content on OH-stretching wavenumbers (Robert 1973, 1981, Robert & Kodama 1988), this constancy is quite predictable, since the bulk Al content remains constant along this join.

Join tetrasilicic magnesium mica (TMM) – taeniolite (Tae)

In the TMM end-member, $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$, two types of OH-stretching bands are observed: (1) trioctahedral-type bands, *i.e.*, OH bonded to 3Mg, at 3735 cm^{-1} (high-intensity band) and 3695 cm^{-1} (low-intensity band), and (2) dioctahedral-type band, *i.e.*, OH bonded to 2Mg and adjacent to an octahedral vacancy, at 3595 cm^{-1}. Note that the minor-intensity band at 3695 cm^{-1} is unexpected, considering the octahedral makeup of TMM. In a previous IR study at different angles of incidence, TMM was found to exhibit the same pleochroism as the high-wavenumber (3735 cm^{-1}) OH-stretching band (Kodama *et al.* 1974); therefore, the band at 3695 cm^{-1} was considered as a trioctahedral-type band, perturbed by a secondary effect, the peculiar distribution of octahedrally coordinated cations and vacancies around this trioctahedral-type OH group.

Along the join TMM–Tae, the behavior of these two main band-types is very different. The salient feature concerning each trioctahedral-type band is the growth of a new high-wavenumber band, whose intensity increases as the Li content increases along the join. The wavenumbers of these new OH-stretching bands are 3755 ± 1 cm^{-1} (corresponding to the band at 3735 cm^{-1} in TMM) and 3710 ± 1 cm^{-1} (corresponding to the band at 3695 cm^{-1}) (Figs. 4a,b). This phenomenon, which is the same as that previously observed on the join Phl – Tae (Fig. 1), can be interpreted similarly; the two new bands are due to OH groups bonded to Mg_2Li, *i.e.*, to a 5-charge cationic group. The wavenumbers of these bands remain constant, within experimental uncertainties, along the join. The similar behavior of the two bands at 3735 cm^{-1} and 3695 cm^{-1} supports the proposed assignment.

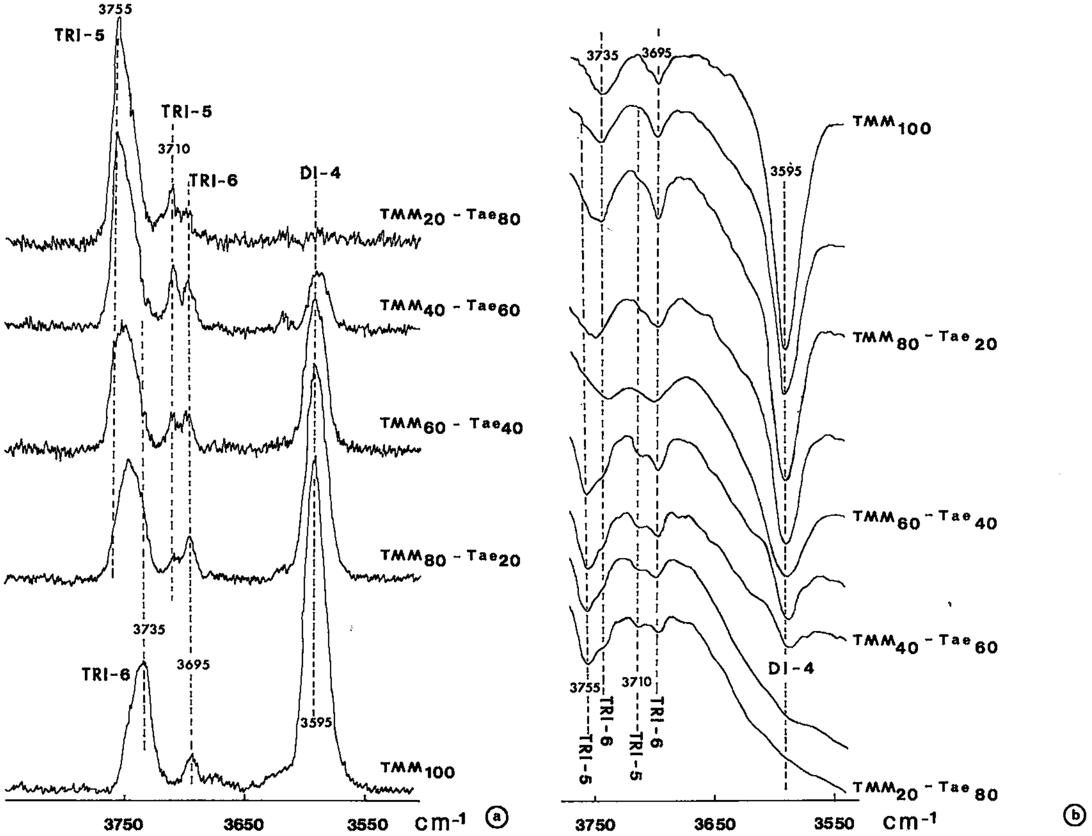

FIG. 4. Raman (a) and IR spectra (b) along the join tetrasilicic magnesium mica (TMM) – taeniolite (Tae), in the region of ν–OH wavenumbers. TRI–5 and TRI–6, as in Figure 1. DI–4: OH bonded to Mg_2 and adjacent to an octahedral vacancy.

On the other hand, the high-intensity band at 3595 cm^{-1}, which is a dioctahedral-type band (OH bonded to $2Mg^{2+}$ and adjacent to an octahedral vacancy), progressively vanishes from TMM to Tae, in response to the progressive disappearance of the octahedral vacancies. Here again, no band shift is observed along the join, indicating that the initial environment of this OH group remains unchanged from TMM to Tae, in fact to TMM_{20} – Tae_{80}, the limit of the solid solution. In other words, Li^+ is excluded from the vicinity of an OH group that belongs to this dioctahedral environment. The hydroxyl oxygen, therefore, would be bonded to MgLi, *i.e.*, to a 3-charge cationic group; the sum of bond valences received by this hydroxyl oxygen would be only 0.5 valence unit, which is much too low (compare with the forbidden trioctahedral environment Li_3 in Table 1).

This is the second example of ordering, in fact of cationic exclusion, observed for this kind of dioctahedral-type hydroxyl. The first example known was observed on the join TMM–Phl, and concerned the exclusion of ^{IV}Al from this environment (Robert & Kodama 1988). Both examples are a consequence of local charge-balance requirements on the oxygen atoms.

THE NEW SYSTEM OF NOMENCLATURE OF OH-STRETCHING BANDS

The present study has shown several ambiguities in the use of the previous system of nomenclature: (1) the OH-stretching band due to hydroxyl groups bonded to AlMgLi has almost the same wavenumber as the OH band arising from hydroxyl groups bonded to Mg_3. Acccording to Vedder (1964), (1) the first band should be considered as a special case of an impurity band, whereas the second is a typical normal band; (2) similarly, the high-wavenumber band of OH groups bonded to Mg_2Li should be considered as an other impurity band, but on the commonly accepted wavenumber scale, the impurity bands have low wavenumbers; and (3) the same remarks apply to the vacancy bands. In the present study, all OH groups in a dioctahedral environment are bonded to $2Mg^{2+}$, but OH groups bonded to $Al^{3+}Mg^{2+}$ are known in phengite and OH groups bonded to $2Al^{3+}$ are typical of muscovite, paragonite and pyrophyllite. Therefore, in order to clarify this nomenclature and to minimize the proliferation of suffixes, a new system suitable for any case is proposed. The results obtained on lepidolite solid solutions confirm the fundamental role of the bulk cationic charges adjacent to the OH group. Therefore, this number of charges must appear in the nomenclature. On the other hand, the only two types of OH groups that need to be considered are those that belong to a trioctahedral environment and those that belong to a dioctahedral one. Consequently, the new system of nomenclature is built as follows : TRI or DI designate trioctahedral- or dioctahedral-type OH-stretching bands (we use capital letters to prevent confusion with the abbreviations such as Tril). The number of cationic charges bonded to the hydroxyl is added to the symbol.

Considering Table 1, there are only three possibilities for the nomenclature of trioctahedral-type band: TRI–5 (OH bonded to Mg_2Li or Li_2Al), TRI–6 (OH bonded to Mg_3 or AlMgLi), and TRI–7 (OH bonded to Mg_2Al or Al_2Li). Similarly, the dioctahedral-type band of TMM is named DI–4 (OH bonded to Mg_2); in muscovite, this band would be named DI–6 (OH bonded to Al_2). This nomenclature is used in the Figures.

DEPENDENCE OF OH-STRETCHING WAVENUMBERS ON COMPOSITION

No band shift is observed on the joins Phl–Poly and TMM–Tae. On the first join, the bulk aluminum content is constant; on the second join, all the micas are Al-free. On the joins Phl–Tae and Phl–Tril, a systematic band-shift is observed for all the OH-stretching bands. In both series, the Al content is variable, and the OH-stretching wavenumbers decrease as total aluminum (Al_{tot}) increases. The same relationship is known in Li-free trioctahedral mica solid-solutions (Robert 1973, 1981, Robert & Kodama 1988).

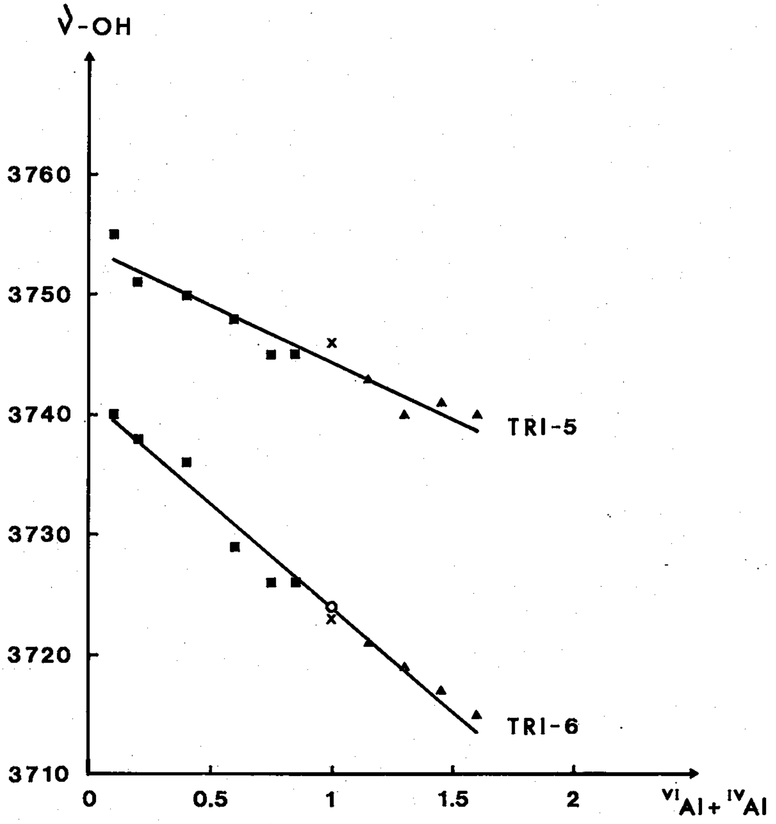

Fig. 5. Change of the OH-stretching wavenumbers (in cm^{-1}) of TRI–5 and TRI–6 bands, in lepidolite compositions (Raman data), as a function of the sum ^{VI}Al + ^{IV}Al. Open circle: phlogopite end-member; solid squares: join Phl–Tae; solid triangles: join Phl–Tril; X: join Phl–Poly.

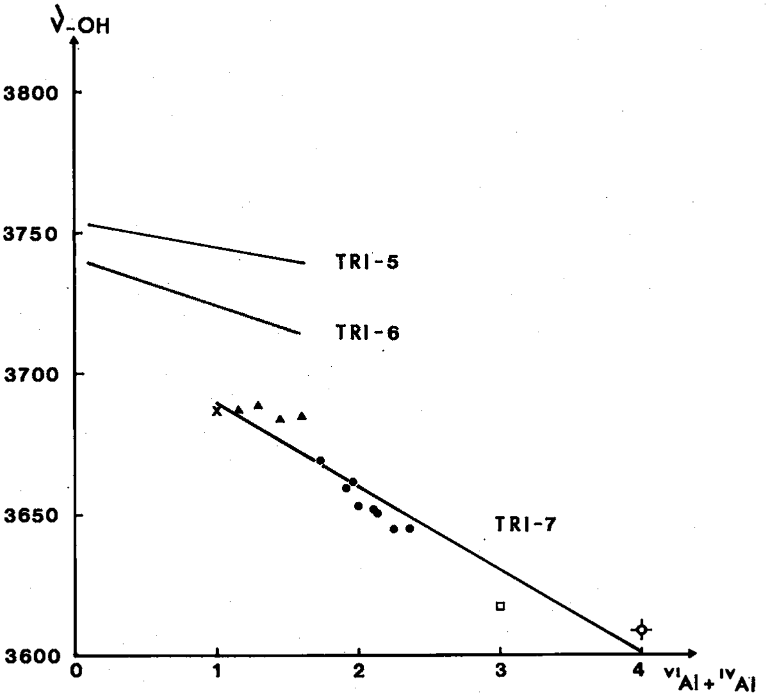

Fig. 6. Change of the OH-stretching wavenumbers (in cm^{-1}) of TRI-7 bands in lepidolite compositions as a function of $^{VI}Al + {}^{IV}Al$. Solid triangles: join Phl–Tril (Raman); X: join Phl–Poly (Raman); open square: preiswerkite (Raman), after Liu *et al.* (1987); starred circle: ephesite (IR), after Farmer & Velde (1973); solid circle: Li-free phlogopite solid-solutions (IR), after Robert & Kodama (1988). Lines TRI-5 and TRI-6 are from Figure 5.

TRI-5 and TRI-6 OH-stretching bands

The trends for TRI-5 and TRI-6 OH-stretching wavenumbers are given in Figure 5. The data points plot continuously along two lines whose equations are:

(1) line TRI-5: ν-OH = -9.33 Al_{tot} + 3754 (r = 0.964)

(2) line TRI-6: ν-OH = -16.95 Al_{tot} + 3741 (r = 0.990)

For the Phl–Poly join, the OH-stretching values of 3746 cm^{-1} for the TRI-5 band and 3723 cm^{-1} for the TRI-6 band were included in the calculation of these two equations.

TRI-7 OH-stretching band

In the lepidolite solid-solutions investigated in this work, the TRI-7 OH-stretching band is observed on the joins Phl–Tril ($3684 \le \nu \le 3689$ cm^{-1}) and Phl–Poly (ν = 3686 cm^{-1}). The corresponding data-points (Fig. 6) pertain to the narrow composition range $1.0 \le Al_{tot} \le 1.6$. Ephesite $Na(Al_2Li)(Si_2Al_2)O_{10}(OH)_2$, whose total Al content is 4, also possesses OH groups in a 7-charge environment, Al_2Li, with the OH-stretching wavenumber ν – OH = 3609 cm^{-1} (Farmer & Velde 1973). Including this value in the present study is justified, because the type of interlayer alkali cation has no detectable effect on OH-stretching wavenumbers. For example, the data for the high-Al trioctahedral sodium mica preiswerkite, $Na(Mg_2Al)(Si_2Al_2)O_{10}(OH)_2$, are in line with those obtained in phlogopite solid-solutions (Robert & Kodama 1988).

No solid solution is known between the low-Al K-bearing lepidolites (Phl–Tril and Phl–Poly) and the high-Al sodium-bearing lepidolite (ephesite). The gap between the corresponding OH-stretching wavenumbers can be easily filled by considering the second set of data, relative to a 7-charge environment of the hydroxyl, Mg_2Al (see Table 1), known in phlogopite solid-solutions (Robert 1981, Robert & Kodama 1988).

The equation of the line TRI-7 (Fig. 6), calculated from all the data relative to an OH group in a 7-charge environment, Al_2Li or Mg_2Al, is:

(3) ν-OH = -29.66Al_{tot} + 3719 (r = 0.962)

The quality of this fit supports the band assignments and emphasizes that the bulk cationic charge adjacent to the hydroxyl fundamentally influences the OH-stretching wavenumber.

CONCLUDING REMARKS

The observations presented here fit well with the assignments previously proposed for phlogopite solid-solutions (Robert & Kodama 1988). On the wavenumber scale, the classification of OH-stretching bands depends on the bulk charge carried by the three adjacent cations (first-neighbor effect): TRI-5 bands, high wavenumbers; TRI-6 bands, medium wavenumbers, and TRI-7 bands, low wavenumbers. Within each band type, the OH-stretching wavenumbers depend on the intensity of OH...O interactions between the hydroxyl proton and O(3), the apical oxygen atom of the tetrahedra. Charge imbalances on oxygen O(3) control these weak hydrogen bonds; they increase as the Al content increases.

This study also confirms that the gap between the different band-types increases as Al_{tot} increases (Fig. 6). From equations (1), (2) and (3), it is apparent that the slopes approximately double from line TRI-5 to line TRI-6 (ratio 1.82) and approximately double again, from line TRI-6 to line TRI-7 (ratio 1.75). In other words, OH groups in which the hydroxyl proton has little interaction with the surrounding oxygen atoms are little perturbed by changes in their environment (*e.g.*, TRI-5 bands). In contrast, hydroxyl groups involved in strong $OH...O_t$ interactions (*e.g.*, TRI-7 bands) are more strongly affected by these modifications. This aspect will be discussed in a forthcoming paper.

The very high ν - OH observed at 3755 cm^{-1} for the mica compositions Phl_{10}–Tae_{90} and along the join TMM–Tae can be explained readily. It results from a hydroxyl group in the lowest possible charge in a trioctahedral environment (5 charges); this hydroxyl is oriented toward a ring of $6(SiO_4)$ tetrahedra, which is the highest possible tetrahedral charge around an OH group. Therefore, this environment implies the weakest possible OH...O interactions and, thus, the maximum value of the bond constant k.

Compounds that exhibit very high OH-stretching wavenumbers are rare. Such a wavenumber (3749 cm^{-1}) is known in isolated surface silanol groups, Si-OH, free of hydrogen bonding, observed in high-temperature amorphous silica (McDonald 1957). The very high OH-stretching wavenumber, 3755 cm^{-1}, observed in the present work closely corresponds to the ν_3 stretching wavenumber (IR) of the free water molecule at 3755.79 cm^{-1}, registered under very low pressure, *i.e.*, the conditions of the minimum OH...O interactions (Sverdlov *et al.* 1970).

Calvet & Prost (1971) proposed the values 3700, 3670 and 3640 cm^{-1} for OH groups adjacent to Mg_2Li, AlMgLi and Al_2Li, respectively, in Li-bearing montmorillonite. These three OH-stretching bands are approximately 50 cm^{-1} below the values observed in the present work. This apparent discrepancy can be attributed to the lack of repulsive interaction between the hydroxyl proton and an interlayer cation; in this Li-bearing montmorillonite, about 2/3 of interlayer sites are vacant. This repulsive effect could be quantified by comparing the OH-stretching wavenumber of the TRI-6 band of TMM, a true mica (3735 cm^{-1}), to the OH-stretching wavenumber of talc (3677 cm^{-1}), in which the interlayer space is empty. The corresponding band-shift is 58 cm^{-1}, in satisfactory agreement with the present observations.

ACKNOWLEDGEMENTS

Thanks are due to Drs. J.L. Jambor, H. Kodama, R.F. Martin and to the referees for their constructive criticism.

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Received March, 21, 1988, revised manuscript accepted July 31, 1988.