

## THE I.R. SPECTRUM OF STRUCTURAL HYDROXYLS OF K-DEPLETED BIOTITES

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**Abstract**—The i.r. spectrum of K depleted biotites (structural OH stretching range) has been studied with monocrystals equilibrated at various water contents. Prior to spectroscopic measurements, the samples were submitted to deuteration treatments which displaced the hydration water spectrum to the OD region and made it possible to observe the behaviour of the structural hydroxyls without interference from hydration water.

In these conditions it was shown that the high frequency absorption of K depleted biotites (N + I bands) is the sum of two absorptions: the first corresponds to the initial mica spectrum, the second corresponds to the hydrated phase in which component bands (according to Vedder and Wilkins) are shifted by  $36\text{ cm}^{-1}$  towards low frequencies.

Simultaneously it was shown that low frequency bands (V bands) decreased in intensity. This unexpected observation has been explained by a partial deuteration of structural OH, which takes place during the preliminary contacts of the samples with  $\text{D}_2\text{O}$  vapour.

### INTRODUCTION

THE STRUCTURAL OH stretching region of the i.r. spectrum of biotite micas has received considerable attention during the past five years. As of now, it can be considered that the interpretations proposed by Vedder and Wilkins (Vedder, 1964; Wilkins, 1967; Vedder and Wilkins, 1969) constitute a good basis for the band assignments, and they will be used for the discussion of the spectra of K-depleted biotites examined in this study.

Prior to experimental results discussion, it is necessary to review Vedder and Wilkins assignments. These authors consider that three main types of structural OH can be found in a biotite mica:

OH bound to 3 divalent cations, responsible for 4 bands designated N

OH bound to 1 trivalent and 2 divalents cations, responsible for 3 bands designated I

OH bound to 2 cations and in the vicinity of 1 vacancy, responsible for 3 bands designated V.

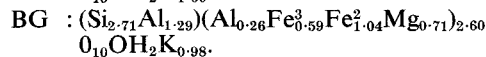
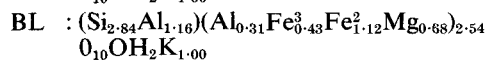
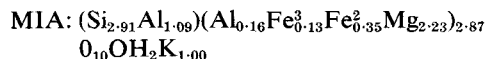
N and I bands due to a locally trioctahedral structure are dichroic when tilting the crystal in the beam, whereas V bands are not dichroic.

Table 1 summarizes the detailed assignments proposed by Vedder and Wilkins.

### MATERIALS AND METHODS

The three biotite samples examined in this study are designated by MIA, BL and BG respectively.

Structural formulas are as follows:



The cleavage flakes of these micas were treated with 2N  $\text{NaNO}_3$  at  $90^\circ\text{C}$  for periods of time greater than 15 days. This treatment yields a mineral which is partially K-depleted and thus hydrated. It was not possible to completely exchange K for Na, because resulting delamination and fracture would render it impossible to compare quantitatively initial and K-depleted mica. Great care was taken in reproducing the positions of crystals in the beam. Spectra were recorded either at normal or oblique incidence (generally  $45^\circ$ ), in unpolarized light.

The spectroscopic study of structural OH groups is greatly facilitated by complete replacement of hydration by  $\text{D}_2\text{O}$ . This isotopic exchange was accomplished by numerous exposures to  $\text{D}_2\text{O}$  vapor at spectrometer temperature, followed by evacuation; as will be seen later, this methodology may be responsible for some of the unexpected observations. Unless otherwise stated, it must be kept in mind that the results and discussions refer to systems which have been deuterated in this manner.

Table 1

Notation	Occupation of closest octahedral sites	Vibration frequency (cm <sup>-1</sup> )
N <sub>A</sub>	Mg, Mg, Mg	3712
N <sub>B</sub>	Mg, Mg, Fe <sup>2+</sup>	3696
N <sub>C</sub>	Mg, Fe <sup>2+</sup> , Fe <sup>2+</sup>	3680
N <sub>D</sub>	Fe <sup>2+</sup> , Fe <sup>2+</sup> , Fe <sup>2+</sup>	3664
I <sub>A</sub>	Mg, Mg, R <sup>3+</sup>	3668
I <sub>B</sub>	Mg, Fe <sup>2+</sup> , R <sup>3+</sup>	3652
I <sub>C</sub>	Fe <sup>2+</sup> , Fe <sup>2+</sup> , R <sup>3+</sup>	3636
V <sub>A</sub>	R <sup>2+</sup> , R <sup>2+</sup> , V	~3625
V <sub>B</sub>	R <sup>2+</sup> , R <sup>3+</sup> , V	~3600
V <sub>C</sub>	R <sup>3+</sup> , R <sup>3+</sup> , V	~3560

R<sup>2+</sup> = Mg, Fe<sup>2+</sup>; R<sup>3+</sup> = Al, Fe<sup>3+</sup>; V = vacancy.

### RESULTS

Within these experimental conditions (strong deuteration), differences between unaltered and K-depleted micas can be summarized as follows:

(1) The total integrated absorption of structural OH decreases when K depletion increases.

(2) The low frequency bands attributed by Vedder (1969) to hydroxyls in dioctahedral environment (V bands) do not change in frequency. However, their absorption decreases significantly when K depletion increases.

(3) The high frequency bands attributed by Vedder (1969) to hydroxyls in trioctahedral environment (N and I bands) show a complex behaviour: unaltered mica frequencies show decreases in absorption whereas the lower frequencies in this group show increases in absorption.

(4) For a given state of alteration, increasing dehydration of the mica results in increases in absorption at unaltered mica frequencies. This effect is reversible upon increasing hydration. By contrast, no changes could be detected for V bands either in frequency or in absorption.

These results are illustrated in Figs. 1–3.

### DISCUSSION

#### High frequency bands (N+I bands)

At first sight, results 3 and 4 are qualitatively similar to those obtained with phlogopite or vermiculite (Chaussidon, 1970; Fernandez *et al.*, 1970). It was thus assumed that the frequencies of N and I bands depended upon the water content, this being due to the variation of the effective perturbation exerted by interlayer cations on hydroxyls. This perturbation is practically suppressed when the cation is removed from the hexagonal cavity by hydration, whereas, in the dehydrated state, the perturbation increases again tending to restore

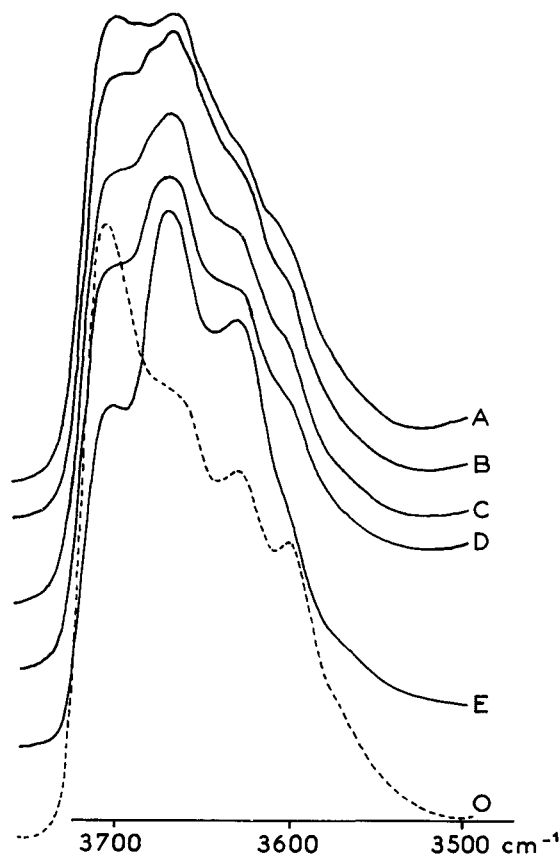


Fig. 1. MIA biotite, incidence angle: 45°. Spectra A to E refer to the same alteration state, hydration increasing from A to E. O—initial crystal before alteration.

a force field similar to that present in unaltered mica.

The quantitative treatment of this effect requires a knowledge of the background contribution under the absorption band. Even for a narrow band, this background is not necessarily as simple as the straight line drawn tangent to the two wings of the band. In our case, the question is still more complicated because; (1) the band is not narrow, and (2) the high frequency wing of adsorbed HOD remaining in the driest samples interfere with structural OH bands up to 3600 cm<sup>-1</sup>. Thus, only a plot which preserves the trend of background evolution on both sides of the spectrum and which confers on the HOD band a profile in agreement with results on the adsorbed water spectrum, may be considered as acceptable. It usually has a sigmoid shape.

We showed previously (Chaussidon, 1970) that the integrated absorption for a phlogopite crystal

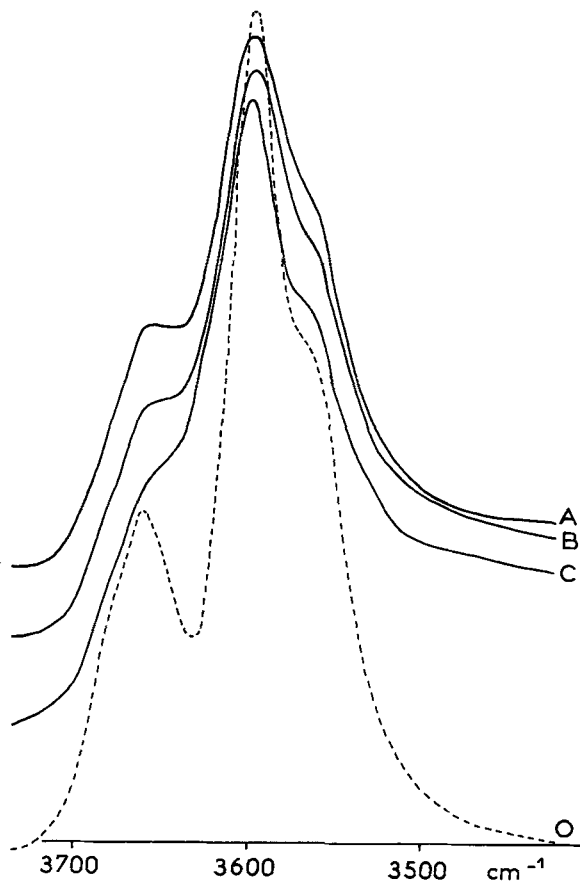


Fig. 2. BL biotite, incidence angle:  $45^\circ$ . Spectra A to C refer to the same alteration state, hydration increasing from A to C. O—initial crystal before alteration.

in a given alteration state was practically constant regardless of the water content. With a little experience and a few minor adjustments, the empirical drawing of the background produced spectra of biotites which differed by no more than 1 or 2% in integrated intensities. In spite of the arbitrariness of this procedure, it serves as a useful basis for an attempt to analyze these systems in a quantitative manner. It is thought that the perturbation due to water is faint in the  $3650\text{--}3700\text{ cm}^{-1}$  region and that the choice of a background as outlined above does not introduce too much uncertainty in the estimation of the absorbance of dichroic high frequency bands.

The second hypothesis concerns the composition of a complex spectrum where several bands obviously contribute to the total absorption. In our case, the relationships and assignments proposed by Vedder and Wilkins (1969) could be applied to each sample without any

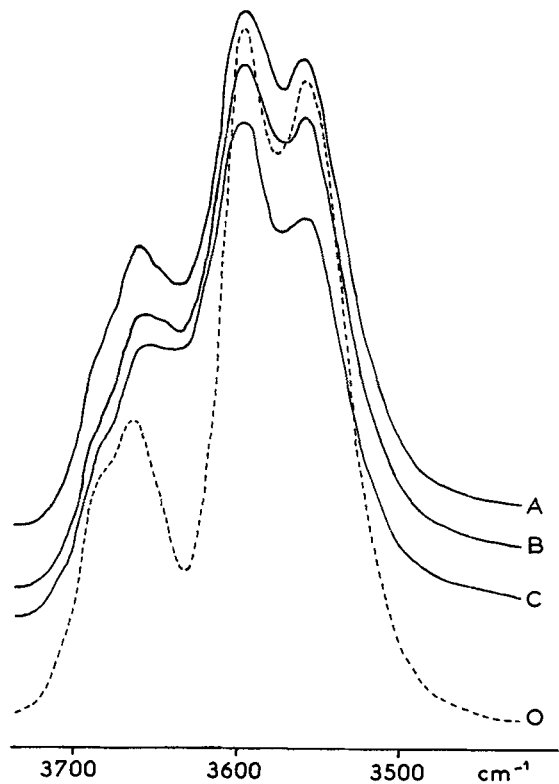


Fig. 3. BG biotite, incidence angle:  $45^\circ$ . Spectra A to C refer to the same alteration state, hydration increasing from A to C. O—initial crystal before alteration.

difficulty. All the initial mica spectra could be recalculated with gaussian bands located at the frequencies and with the parameters quoted by Wilkins (1967). The crude application of Wilkins (1967) formulas generally gives a calculated spectrum which requires only small corrections in peak heights in order to obtain a satisfactory fit. Although we know that from a strict mathematical view point such a fit is not a definite proof of the uniqueness of the decomposition, we have considered that when it was reached we had a reasonable basis for discussion.

The results of these calculations appear in Figs. 4–6. In each case, the low frequency side of dichroic bands has been obtained by calculation. In order to check the calculated values, we used the fact that low frequency bands do not show any appreciable variation of intensity when crystals are examined either at normal or oblique incidence. Figures 4–6 show that the low frequency band calculated by subtracting high frequency bands computed according to Wilkins (1967) from experimental spectrum at oblique incidence fit fairly

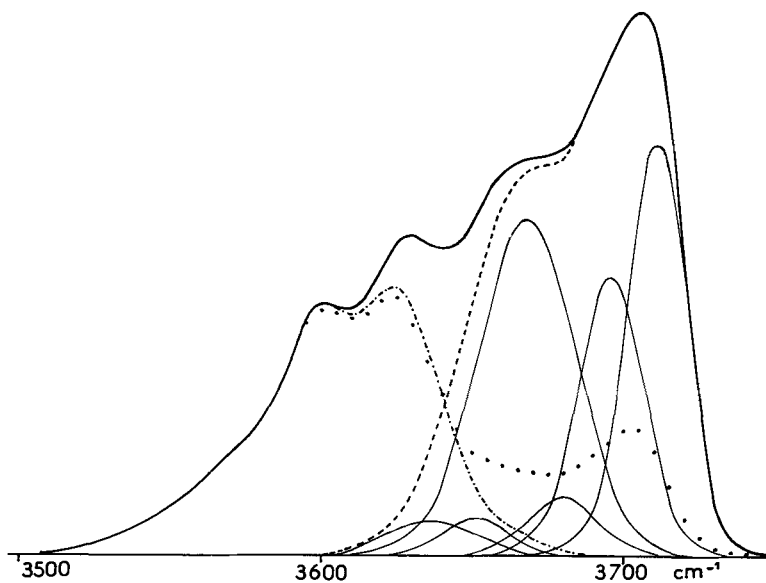


Fig. 4. MIA biotite. (a) Incidence angle  $45^\circ$ . — experimental spectrum; — component bands computed according to Vedder; ---- computed dichroic spectrum; - · - · - computed low frequency bands. (b) Normal incidence, · · · · · experimental spectrum.

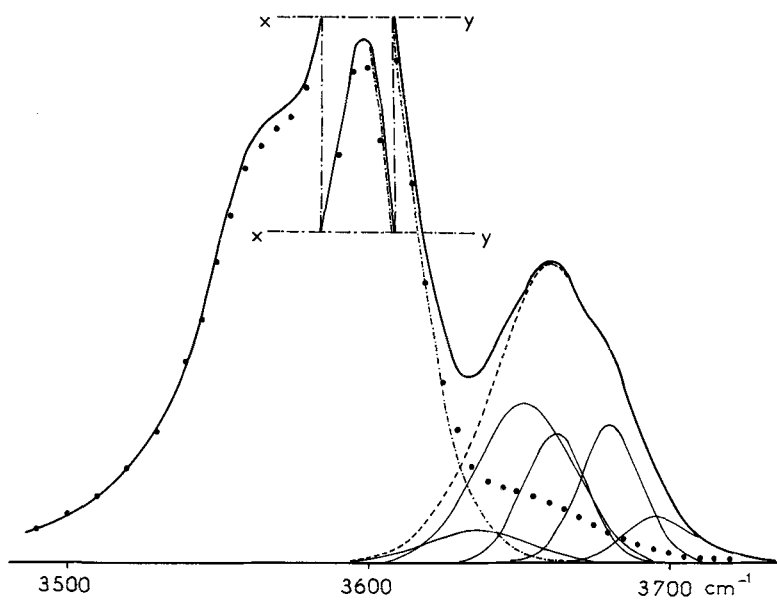


Fig. 5. BL biotite. (a) Incidence angle  $45^\circ$ . — experimental spectrum; — component bands computed according to Vedder; ---- computed dichroic spectrum; - · - · - computed low frequency bands. (b) Normal incidence, · · · · · experimental spectrum. The top of low frequency band above XY axis has been translated downwards.

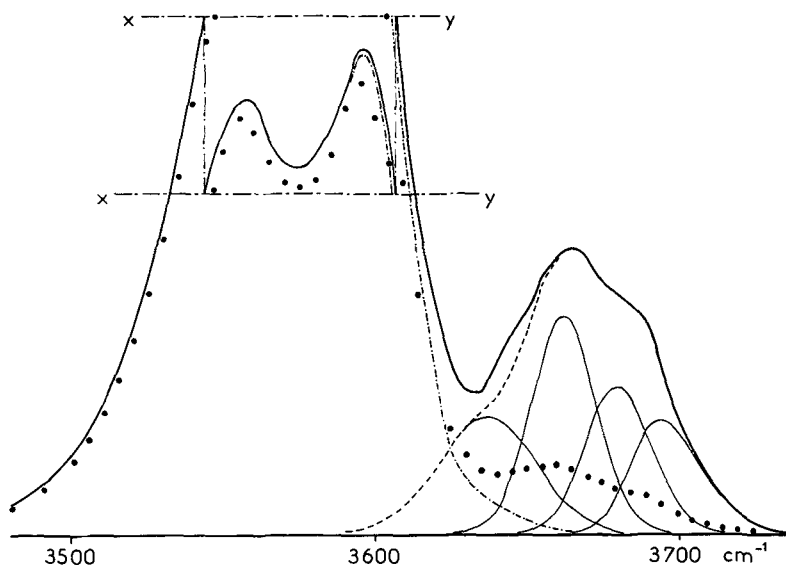


Fig. 6. BG biotite. (a) Incidence angle  $45^\circ$ . — experimental spectrum; — component bands computed according to Vedder; - - - - computed dichroic spectrum; ····· computed low frequency bands. (b) Normal incidence. ····· experimental spectrum. The top of low frequency band above XY axis has been translated downwards.

well the experimental low frequency bands at normal incidence; this observation means that within the scope of the foregoing assumptions, high frequency absorption is approximated by the dashed lines of Figs. 4–6.

Wilkins (1967) calculations have been applied to spectra recorded at oblique incidence ( $45^\circ$ ); these decompositions define thus only the respective intensities of elementary bands in a given set of experimental conditions. The assumption made is that, for an altered mica, the orientation of a given OH dipole moment does not change appreciably in the collapsed and expanded states.

It is then possible to compare spectra of a K-depleted sample at various water contents with the spectrum of the same crystal in its original form. This appears in Figs. 7–9, in which, for the present, we consider only the thick lines. In each figure three spectra are drawn: the original mica (full line) and two different hydration states of altered mica (dashed lines and dotted and dashed lines).

The total spectra of altered mica intersect the dichroic spectrum of original mica at the same point. When one considers the total spectrum of original mica, the slight variation for a unique intersection point is due to the high frequency wing of low frequency bands, which is still noticeable in K-mica, and negligible in altered samples.

This result, presented here on a very limited number of examples, was in fact checked on

several tens of measurements performed under widely varying conditions, and suggests strongly the occurrence of an isosbestic point, already noticed for hectorite and K-depleted phlogopites (Chaussidon, 1970). In this work, we have attempted to analyze the physical meaning of such an isosbestic point.

Let us consider Fig. 10a. It shows that if a given contour representing a complex absorption band changes in total surface by a simultaneous variation of all component bands in the same ratio, the straight line AJ parallel to the frequency axis, will define two frequencies O and H at which corresponding intensities on other spectra, B and I or C and K are respectively equal (result a).

Let  $S'$  be a spectrum deduced from  $S$  by a translation  $\vec{t}$  (Fig. 10b). Each point of  $S'$  corresponds to one point of  $S$  by this translation; the intersection point of  $S$  and  $S'$  agrees with this condition. This point, considered on curve  $S$ , is also one end of a chord parallel to the frequency axis and of the same length as the translation vector. This intersection point may be unique or multiple, according to the shape of  $S$  and the length of  $\vec{t}$  (result b).

In Fig. 10c are represented a spectrum  $S$  and a second one  $S'$ , made of the superposition of an untranslated fraction of  $S$ ,  $S_2$ , and a translated fraction  $S'_1$ , such as  $S'_1 + S_2 = S' = S$ ;  $S'_2 = S_2$  and  $S_1 = S'_1$  are also indicated. Let  $A$  be the end of the translation vector (frequency 0). From the foregoing

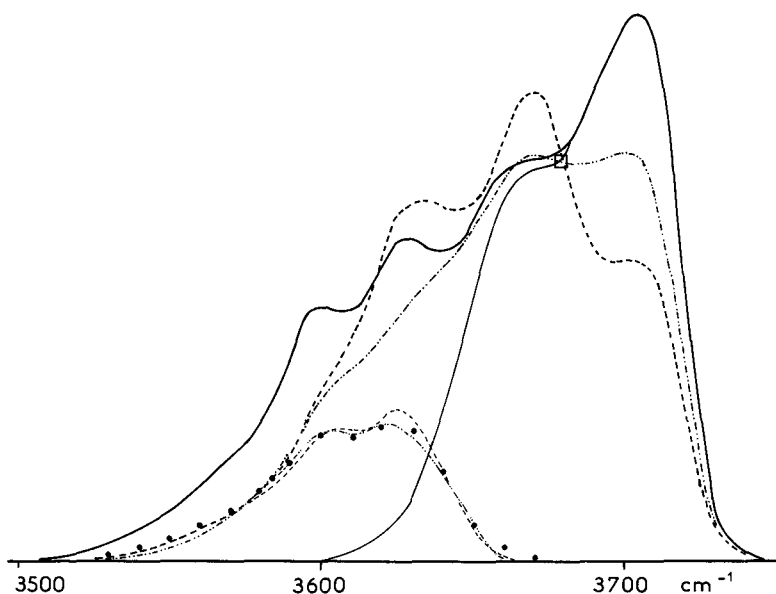


Fig. 7. MIA biotite. Experimental spectra: — initial mica; ----- and -·-·-· two different states of hydration of K-depleted crystal. Calculated spectra: — dichroic part of the spectrum of initial mica; ----- and -·-·-· low frequency bands at two different states of hydration of K-depleted mica; ······ low frequency bands of initial mica after contraction.

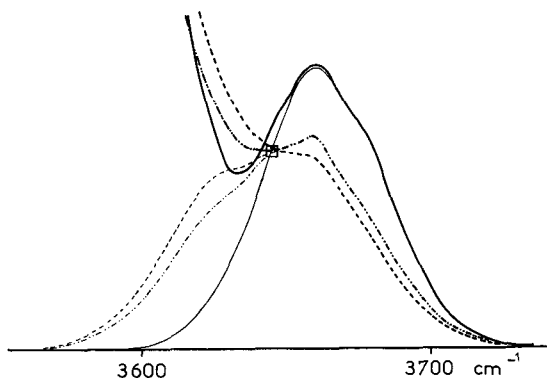


Fig. 8. BL biotite. Experimental spectra: — initial mica; ----- and -·-·-· two different states of hydration of K-depleted crystal. Calculated spectra: — dichroic part of the spectrum of initial mica; ----- and -·-·-· dichroic part of the spectrum of K-depleted mica at two different states of hydration.

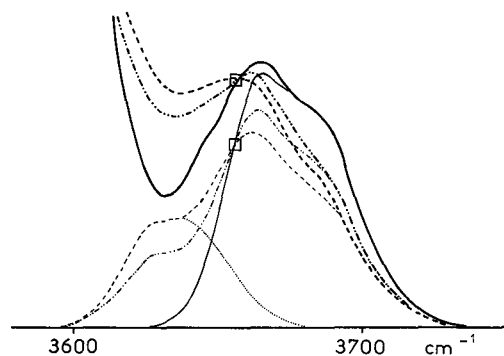


Fig. 9. BG biotite. Experimental spectra: — initial mica; ----- and -·-·-· two different states of hydration of K-depleted crystal. Calculated spectra: — dichroic part of the spectrum of initial mica; ----- and -·-·-· dichroic part of the spectrum of K-depleted mica at two different states of hydration; ······ residual dichroic absorption band (see text).

results, it is clear that  $S_2$  and  $S'_2$  intersect at  $B$  so that  $BI$  is equal and parallel to  $AJ$ ; the same is true for  $C$  and  $CK$ .

Now, the optical density at frequency  $O$  in spectrum  $S'$  is  $OA' = OC + OB$ . As  $OC = HK$  and  $OB = HI$ , it follows that  $OA' = HJ = OA$  which means that points  $A$  and  $A'$  are mixed, or, in other words, that the intersection point of spec-

tra  $S$  and  $S'$  is one end of the chord, drawn on  $S$ , parallel to the frequency axis and of the same length as the translation vector (result  $c$ ).

It is obvious that the frequency and optical density of this point is independent of the ratio translated/untranslated areas. Thus, it has the characteristics of an isosbestic point.

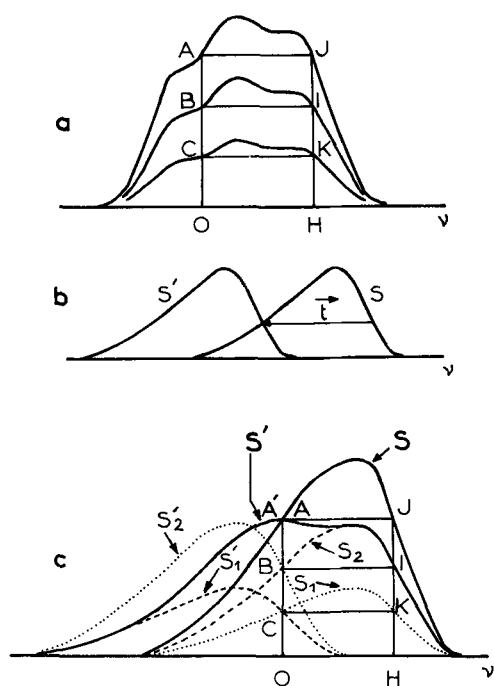


Fig. 10. The isosbestic point (see text).

Upon examination of Figs. 7–9, it can be seen that the length of the translation vector, as defined above, is  $36\text{ cm}^{-1}$ , the same as that found previously with K-depleted phlogopites.

From result *b*, several isosbestic points should be theoretically found in biotite BG and BL, because it is possible to draw several  $36\text{ cm}^{-1}$  chords. However, all possible chords, except for one of them located inside the high frequency band, have at least one end on the low frequency absorption band, which makes this treatment meaningless. Result *b* explains also why one point is found in biotite MIA (only one chord can be drawn).

These observations tend to indicate that in K-depleted biotites (at least up to K-depletion levels investigated) the dichroic high frequency absorption is constant but made of an untranslated part of the initial spectrum corresponding to the collapsed phase, and of a translated part corresponding to the expanded phase. The relative proportions of these parts vary with water content, the translated part increasing with increasing hydration.

In Fig. 7 we have drawn also, for K depleted samples, the residual absorption located in the low frequency range. At the same frequencies is drawn (dotted line) the low frequency profile deduced by contraction from dotted and dashed line of Fig. 4, which gives the low frequency absorption bands of

initial mica. The fit between between these three curves seems very reasonable. The same result is obtained for each biotite, which shows that in the investigated systems, hydroxyls in a dioctahedral environment decrease gradually but uniformly.

In the case of MIA and BL (Figs. 7 and 8) the experimental isosbestic point corresponds to the shift of a certain fraction of dichroic absorption as a whole; all the dichroic bands are affected to the same extent by hydration.

BG biotite seems to behave differently. The isosbestic point is observed experimentally at  $3656\text{ cm}^{-1}$ , whereas the predicted value with a  $36\text{ cm}^{-1}$  translation vector is  $3651\text{ cm}^{-1}$ . It can be stated that if the translation is applied only to  $N_B + N_C + N_D$  bands (dotted line, Fig. 11), the isosbestic point appears at the experimental frequency. This would suggest that an obviously dichroic band (see Fig. 6) located at  $3636\text{ cm}^{-1}$  would not be involved in the perturbation process.

#### Low frequency bands (V bands)

It has been already pointed out (result No. 2) that K depletion induces an apparent decrease of low frequency absorption. One could be tempted to generalize the shift observed with trioctahedral OH to dioctahedral OH; in this case the shift should be directed towards high frequency when mica is hydrated. Now, it is impossible to detect in the high frequency domain, any extra absorption which could be attributed to vacancy hydroxyls. From another view point, it is also very difficult to invoke a structural change: in the alteration states which were reached no noticeable modifications of charge of  $\text{Fe}^{2+}$  content could be observed. It was then assumed that the decrease of vacancy bands was a kind of artifact due to the deuteration of some dioctahedral hydroxyls taking place during the preliminary replacing of  $\text{H}_2\text{O}$  by  $\text{D}_2\text{O}$ . This hypothesis was checked with the well known Bancroft biotite which shows only one V band at  $3550\text{ cm}^{-1}$ .

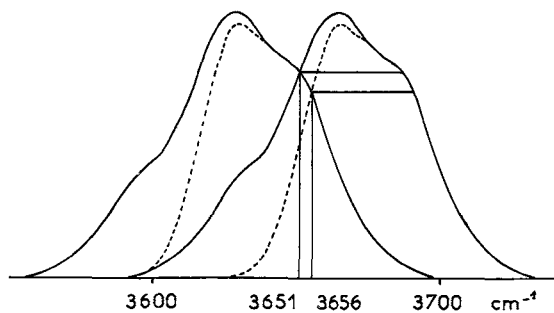


Fig. 11. BG biotite. Computed and observed isosbestic point (see text).

It is clear that the absorption of water at 3550 is not zero. On the contrary, the absorption of structural low frequency OH is negligible at 3460  $\text{cm}^{-1}$  which is the frequency of one resolved maximum of water. Thus the optical density at 3550  $\text{cm}^{-1}$  is the sum of structural OH absorption and of an absorption of water which can be expected to vary proportionally to the absorption at 3460  $\text{cm}^{-1}$ . A plot  $A_{3550} = f(A_{3460})$  must then be a straight line which intersects the  $A_{3550}$  axis at the value of structural OH absorbance. The same is true in the OD region where the classical deuteration ratio of 1.35 leads to the assignment of the OD frequencies 2620 and 2550  $\text{cm}^{-1}$  to structural OD and hydration water OD, respectively.

Figure 12 shows that for a slight deuteration the plot  $A_{2620} = f(A_{2550})$  goes through the origin which means that no noticeable structural OH deuteration occurs. At the same time, the plot  $A_{3550} = f(A_{3460})$ , strongly suggests the same result in spite of the arbitrariness of the extrapolation. On the contrary, for a strong deuteration, the plot  $A_{3550} = f(A_{3460})$  is markedly lower indicating a decrease in structural OH content.

Figure 13 shows the simultaneous plots  $A_{3550} = f(A_{3460})$  and  $A_{2620} = f(A_{2550})$ . The crude addition of the two intercepts, respectively  $0.15 + 0.14 = 0.29$  yields a value similar to the absorbance of structural OH before treatment with  $\text{NaNO}_3$ , which was 0.33. This comparison seems to be another argument for the dioctahedral OH deuteration.

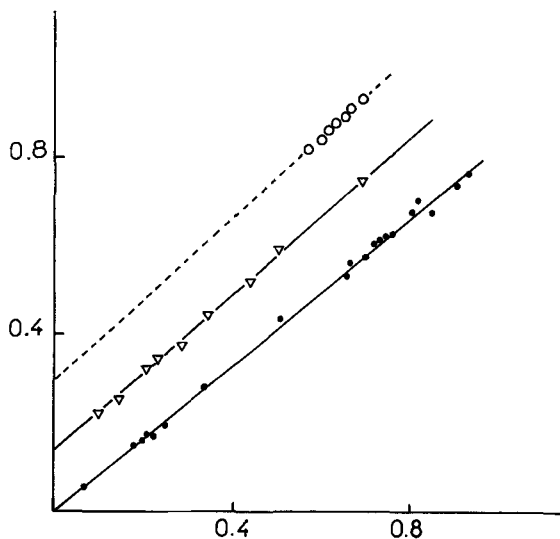


Fig. 12. Bancroft biotite.  $\circ$ :  $A_{3550} = f(A_{3460})$  slight deuteration;  $\bullet$ :  $A_{2620} = f(A_{2550})$  slight deuteration;  $\nabla$ :  $A_{3550} = f(A_{3460})$  strong deuteration.

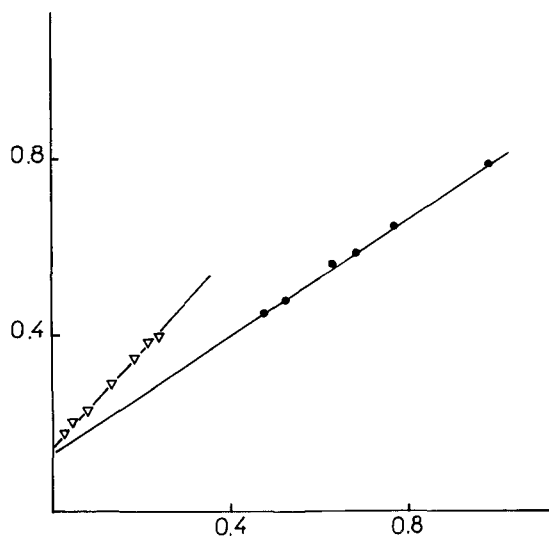


Fig. 13. Bancroft biotite.  $\nabla$ :  $A_{3550} = f(A_{3460})$  strong deuteration;  $\bullet$ :  $A_{2620} = f(A_{2550})$  strong deuteration.

#### CONCLUSION

It seems possible to extend previous results obtained with phlogopite to biotites at least for dichroic structural OH bands. The explanation which is proposed is an indirect argument for the validity of the theory of Vedder (1969) and Wilkins (1967); it is reasonable to think that chemical changes within the structure, i.e. oxidation of  $\text{Fe}^{2+}$ , can be interpreted on the same basis. It is thus readily expected that natural weathering of biotite, which involves K depletion, oxidation of  $\text{Fe}^{2+}$ , and hydration, will lead to minerals whose spectra are poorly resolved and show an increase in apparent band width and a marked shift towards low frequencies.

The "decrease" of low frequency bands has been interpreted as a consequence of the experimental process. It is tempting to parallel this result with the well-known tendency of a dioctahedral structure to dehydroxylate more readily than a trioctahedral structure upon heating. It must be kept in mind, however, that the both effects are at first sight different, since one of them concerns a H-D exchange, whereas the other one concerns the loss of a  $\text{H}_2\text{O}$  molecule.

Finally, it was not possible to observe a shift towards high frequency of the V-band in the hydrated state. The reverse effect has been observed by Russell and Farmer (1964) with a montmorillonite thoroughly dehydrated by heating. We think that this absence of apparent sensitivity of dioctahedral OH is due to the fact that extreme conditions—completely K depleted mica and/



or completely dehydrated systems—have never been reached in our experiments.

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**Résumé**—Le spectre infrarouge (domaine des vibrations d'élongation des OH du réseau) de biotites appauvries en K a été étudié avec des monocristaux équilibrés à différents teneurs en eau. Avant les déterminations spectroscopiques, les échantillons étaient soumis à une deutération destinée à déplacer le spectre de l'eau d'hydratation dans la région OD, pour rendre possible l'observation du comportement des hydroxyles du réseau sans que les spectres soient perturbés par l'eau d'hydratation.

Dans ces conditions on a montré que l'absorption haute fréquence des biotites appauvries en K (bandes N et I) est la somme de deux absorptions: la première correspond au spectre du mica initial alors que la seconde correspond à la phase hydratée dans laquelle les bandes composantes (d'après Vedder et Wilkins) sont déplacées de  $36\text{ cm}^{-1}$  vers les basses fréquences.

En même temps, on a montré que les bandes basse fréquence (bandes V) voient leur intensité diminuer. Cette observation inattendue a été expliquée par une deutération partielle des OH du réseau, qui s'établit durant les contacts préliminaires entre les échantillons et la vapeur de  $\text{D}_2\text{O}$ .

**Kurzreferat**—Das Ultrarotspektrum von K-armen Biotiten (Gefüge-OH Spannbereich) wurde mittels Monokristallen, die bei verschiedenen Wassergehalten im Gleichgewicht gehalten wurden, studiert. Vor den spektroskopischen Messungen wurden die Proben Deuteriumbehandlungen unterworfen wobei das Hydrationswasserspektrum zum OD Bereich hin verschoben wurde und das Verhalten des Gefügehydroxyls ohne Beeinflussung durch Hydrationswasser beobachtet werden konnte.

Unter diesen Bedingungen wurde gezeigt, dass die Hochfrequenzabsorption von K-armen Biotiten (N + I Bänder) die Summe zweier Absorptionen darstellt: die erste entspricht dem anfänglichen Glimmerspektrum, während die zweite der hydratisierten Phase entspricht in welcher Bestandteilstreifen (nach Vedder und Wilkins) um  $36\text{ cm}^{-1}$  gegen niedrigere Frequenzen verschoben werden.

Gleichzeitig wurde dargelegt, dass niedrige Frequenzbänder (V Bänder) an Intensität abnahmen. Diese unerwartete Beobachtung wurde durch eine teilweise Deuteriumbestückung des Gefüge-OH erklärt, die im Laufe der vorläufigen Kontakte der Proben mit dem  $\text{D}_2\text{O}$ -Dampf stattfindet.

**Резюме** — Изучены ИК-спектры обедненных K биотитов (в области валентных колебаний структурных OH) на монокристаллах, находящихся в равновесии с различным количеством воды. Перед спектроскопическим исследованием образцы подвергались дейтеризации, которая приводила к смещению спектра гидратационной воды в область OD и делала возможным наблюдение характеристик структурных гидроксиллов без наложения спектра от гидратационной воды.

Показано, что высокая частота поглощения обедненных K биотитов (N + I полос) обусловлена двумя поглощениями, первое из которых соответствует спектру исходной слюды, а второе спектру гидратированной фазы, в котором составляющие полосы (в соответствии с Веддером и Уилкинсом) смещены на  $36\text{ cm}^{-1}$  в сторону низких частот.

Одновременно установлено, что интенсивность низкочастотных полос (V-полос) уменьшилась. Этот непредвиденный факт объясняется частичной дейтеризацией структурных OH, под действием на образцы паров  $\text{D}_2\text{O}$ .