The hydroxyl-stretching region of the biotite mica spectrum[1]

By R. W. T. Wilkins, M.Sc., Ph.D.

Department of Geological Sciences, Harvard University, Cambridge, Massachusetts

[Taken as read 25 September 1967]

Summary. An interpretation of part of the hydroxyl-stretching region of the infra-red absorption spectrum of biotite is proposed. A consideration of band shapes enables the interpretation to be quantified and tested against a series of natural biotites. The equation derived may be used to determine the atomic ratio $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ in biotites but the necessary assumptions and simplifications make it unlikely that the method will be very useful in practice.

Vedder (1964) has established the main features of the infra-red spectrum of biotite. Three major bands were distinguished in the hydroxyl-stretching region and these were termed N, I, and V from high to low frequency. They were interpreted to represent hydroxyl ions vibrating adjacent to three divalent ions, to two divalent and one trivalent ion, and to a vacancy respectively. With increasing concentration of Fe^{2+} in the octahedral layer, the N band was observed to be displaced to lower frequencies.

Although others working independently (Saksena, 1964; Jorgensen, 1966) have come to different conclusions, in neither case can the suggested interpretations explain all the features of the region, especially the relative intensities of the observed bands and the presence of an I band in some biotites that are almost iron-free.

An adequate interpretation of this part of the spectrum is important if it is to be used to study the mechanism of the many reactions involving biotite including the biotite–oxybiotite, biotite–vermiculite, and biotite–chlorite transformations. An examination of the spectra of 15 analysed biotites by the present writer as a starting-point to the study of these reactions indicated that a more detailed analysis of the N–I region was desirable. For this purpose a discussion of the spectrum of talc (Farmer, 1958; Vedder, 1964; Wilkins and Ito, 1967) is a convenient starting-point.

---

[1] Published under the auspices of the Committee on Experimental Geology and Geophysics at Harvard University.

Talc, $Mg_3Si_4O_{10}(OH)_2$, is theoretically free from Al^{3+} for Si^{4+} substitution in the tetrahedral layer. Analyses indicate that there is, indeed, little substitution in this layer in the natural material. The average talc shows two sharp bands in its spectrum at about 3676 and 3660 cm^{-1}, the former being by far the more intense. The rare talc that has at least one in ten of its octahedral Mg^{2+} replaced by Fe^{2+} has an additional band at about 3644 cm^{-1}.

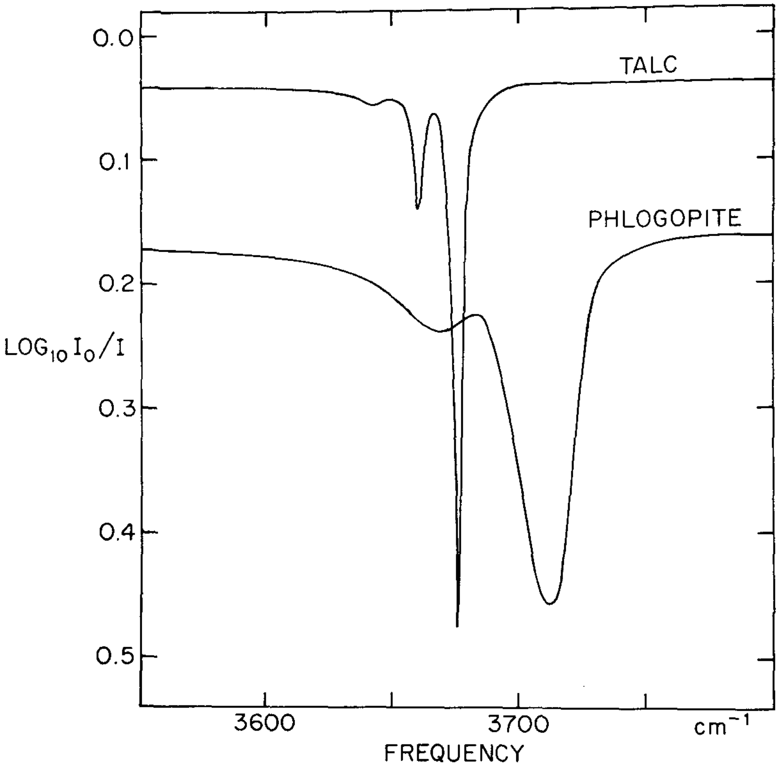


FIG. 1. OH-stretching vibrations in a talc (Chester, Vermont) and a phlogopite (M#1, Vedder, 1964). KBr disks.

The three bands are most readily explained as representing hydroxyl ions vibrating adjacent to three Mg^{2+} ions, $2Mg^{2+}+1Fe^{2+}$ ions, and $2Fe^{2+}+1Mg^{2+}$ ions in that order. Since the perturbation is small, the effect of substituting two Fe^{2+} and three Fe^{2+} in a Mg triad is about two and three times the effect of substituting one Fe^{2+}. Following this argument an iron analogue of talc should have a strong peak at about 3628 cm^{-1}, all of the hydroxyl ions being situated close to three Fe^{2+} ions. Four hydroxyl absorption bands corresponding to the four possible combinations of Mg^{2+} and Fe^{2+} have been identified in some amphiboles (Burns and Strens, 1966; Strens, 1966).

Since the features of the spectrum in this region are primarily determined by the details of the octahedral layer, the biotite spectrum must have a similar origin. The two essential differences between talc and biotite, however, each have their effect on the spectrum. This may be illustrated by fig. 1, which compares the spectrum of a particularly pure phlogopite with that of a talc. The intense bands at 3712 cm^{-1} for the phlogopite and at 3676 cm^{-1} for the talc represent hydroxyl ions vibrating close to three Mg^{2+} ions. The displacement of the same band in talc to a higher frequency in the mica is at least in part due to the effect of potassium between the silicate layers, causing a compression of the OH bond and a resulting increase in frequency (Farmer and Russell, 1966).

The second difference is in the width of the absorption bands. In talc $\Delta\nu_{\frac{1}{2}}$ is 3 to 6 cm^{-1} while in biotite it is 20 to 25 cm^{-1}. This is probably the result of Al for Si substitution in the tetrahedral layer of the mica. The effects of K and Al substitutions differ because in the former case the influence on the proton is largely along the OH bond direction while in the latter case it is largely normal to the OH bond direction.

The additional band at 3668 cm^{-1} in the phlogopite spectrum of fig. 1 is Vedder's I-band. In this case it represents hydroxyl ions vibrating close to $2Mg^{2+}+1Al^{3+}$ ions. This comparison of talc and biotite leads to the postulate that in biotite, as in talc, the replacement of each Mg^{2+} by Fe^{2+} in the triad of adjacent octahedral ions leads to a 16 cm^{-1} decrease in the hydroxyl-ion vibration frequency for both N and I bands. The extension of the perturbation scheme to the I band is readily justified because it has been shown (Vedder, 1964) that the I-type OH bonds have very similar orientation characteristics to those of N type. The scheme of vibration frequencies and the notation that will be used to describe them are shown in table I.

Method of sample preparation. For detailed study of this region of the infra-red spectrum considerable care has been taken in the preparation of the samples in order to ensure little distortion of the spectra. The biotite samples were filed to < 200 mesh, moistened with *iso*-propyl alcohol, and then ground in a mortar. The resultant powder was sedimented in water and the $< 2\,\mu$ diameter fraction removed and dried. It was observed that very little biotite $< 0{\cdot}5\,\mu$ diameter was produced. 20–30 mg of the $< 2\,\mu$ powder was intimately ground with 0·8 g KBr of infra-red quality in a mortar. The introduction of water by adsorption on the KBr was of no consequence at this stage. The mixture was then pressed into a 1-in. diameter opaque disk at 30 tons/sq. in. pressure, then placed in an oven at 250° C for a few hours and pressed again under the same conditions. This resulted in an almost water-free transparent disk. The spectra prepared in this manner have the advantage of having a much reduced Christiansen effect. Oxidation of the biotite does not take place to an appreciable extent under these conditions.

TABLE I. Associations of octahedrally coordinated cations close to hydroxyl ions in biotite

Closest three cations	Notation	Vibration frequency	Closest three cations	Notation	Vibration frequency
$Mg^{2+}Mg^{2+}Mg^{2+}$	N_A	3712	$Mg^{2+}Mg^{2+}R^{3+}$	I_A	3668
$Mg^{2+}Mg^{2+}Fe^{2+}$	N_B	3696	$Mg^{2+}Fe^{2+}R^{3+}$	I_B	3652
$Mg^{2+}Fe^{2+}Fe^{2+}$	N_C	3680	$Fe^{2+}Fe^{2+}R^{3+}$	I_C	3636
$Fe^{2+}Fe^{2+}Fe^{2+}$	N_D	3664			

Provided the disk is quickly pressed after removal from the oven, the broad water band centred at about 3400 cm^{-1} has little intensity and it may easily be corrected for by comparing the spectra of similarly prepared biotite-free disks.

The spectra were run on a Cary-White 90 infra-red spectrophotometer using a scanning speed of 0·5 cm^{-1}/min and a pen period 0·3 sec. The optimum slit width was found to be 4 cm^{-1}, no detectable change in band shape being observed with narrower slits.

Band shape characteristics. An examination of the N band of phlogopite M#1 obtained from a single crystal with unpolarized radiation at normal incidence to the sheet indicates that it would probably need a Voigt function (Seshadri and Jones, 1963) to properly describe the shape of the band. For the polycrystalline mount, however, the shape of the N band is close to Gaussian, though graphical separation of the N and I components establishes that the N band is slightly asymmetrical with a low frequency tail. 0·15 % FeO was found in the powder from which the disk was prepared, showing that the contribution of the N_B band to the asymmetry was negligible.

It has been shown (Wilkins and Ito, 1967) that in synthetic substituted talc asymmetry of the OH-stretching bands increases with both ionic radius of the divalent ion substituting for Mg^{2+} and its concentration relative to Mg^{2+} in the octahedral layer. It must be assumed, though it cannot be proved with the material at hand, that the same factors influence the asymmetry of individual hydroxyl bands in the spectrum of biotite micas. Since a quantitative correction cannot be applied at the present time, it will be assumed for simplicity that all bands are Gaussian in shape.

It may also be noted by analogy to synthetic talc that band *frequencies* also depend to some extent on ionic radius and concentration of the substituting ion, but errors due to neglecting this factor are in the opposite sense to those occasioned by neglecting the asymmetry so that a good description may be expected at least for biotites with $Mg^{2+}/(Mg^{2+}+Fe^{2+}) > 0{\cdot}50$.

Intensity distribution in the N–I region. With the chosen model it is necessary to relate intensity distribution amongst the four N bands with that amongst the three I bands. Assuming a random distribution of Fe^{2+} and Mg^{2+} among the two crystallographically non-equivalent octahedral sites, the result of substituting a trivalent ion into each N association in turn may be shown schematically:

$$\begin{array}{ll} \mathrm{N_A} & \\ & P_{\mathrm{I_A}} = K(3P_{\mathrm{N_A}}+P_{\mathrm{N_B}}) \\ \mathrm{N_B} & \\ & P_{\mathrm{I_B}} = K(2P_{\mathrm{N_B}}+2P_{\mathrm{N_C}}) \\ \mathrm{N_C} & \\ & P_{\mathrm{I_C}} = K(P_{\mathrm{N_C}}+3P_{\mathrm{N_D}}) \\ \mathrm{N_D} & \end{array}$$

$P_{\mathrm{N}i}$ is the probability of forming the N_i association and $P_{\mathrm{I}i}$ is the probability of forming the I_i association in the octahedral layer. K, for any biotite, is a constant related to the concentration of trivalent ions in the octahedral layer.

For a Gaussian distribution of intensity, peak height is proportional to integrated intensity. The relative intensity of $\mathrm{N_A}$, $\mathrm{N_B}$, $\mathrm{N_C}$, and $\mathrm{N_D}$ bands is given by $p^3:3p^2q:3pq^2:q^3$ in that order, where p is the probability that an Mg^{2+} ion will be found in an N association and q is the probability that an Fe^{2+} ion will be found in an N association.

If x and y are peak heights of $\mathrm{N_A}$ and $\mathrm{N_B}$ bands respectively, then $p^3 \propto x$, $3p^2q \propto y$, $3pq^2 \propto y^2/(3x)$, and $q^3 \propto y^3/(27x^2)$. The absorbance at any frequency in the hydroxyl band system is the sum of the absorbances due to neighbouring bands overlapping at that frequency. For any family of Gaussian absorption bands with the same width at half height, the absorbances at a specified frequency interval from centres of the bands are a constant fraction of the heights of the bands. Let a, c, and m be the fractions of peak heights representing absorbance at 16 cm^{-1} from the centre of an N band and 28 and 12 cm^{-1} from the centre of an I band. Neglecting small contributions from distant bands,

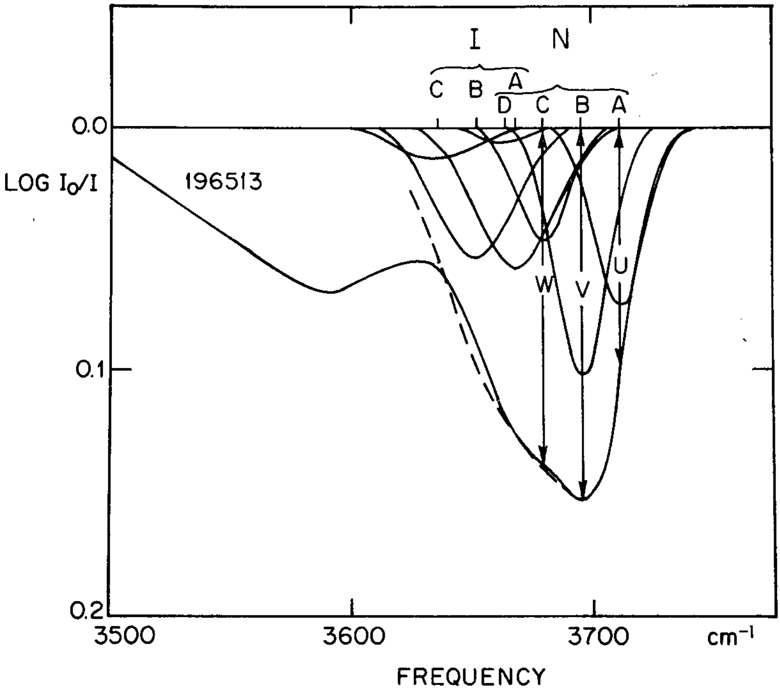


FIG. 2. OH-stretching region of biotite 196513, resolved into N and I bands by calculations based on measurement of the ordinates U, V, and W. The dashed line gives the calculated band envelope for comparison with the actual spectrum.

three equations may be written for the ordinates U, V, and W of the band system at 3712, 3696, and 3680 cm^{-1}:

$$U = x+ay,$$

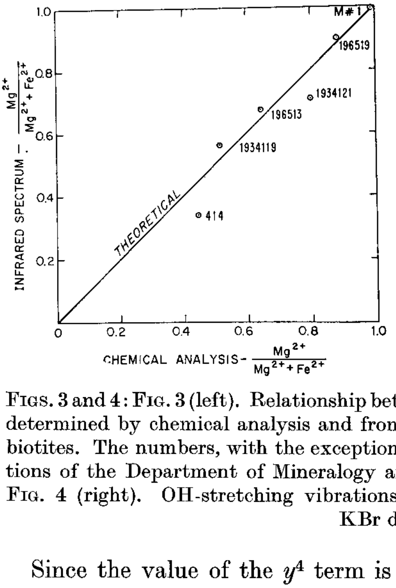
$$V = y+ax+ay^2/(3x)+cK(3x+y),$$

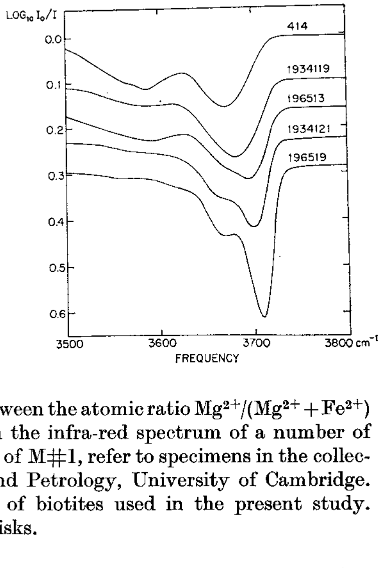
$$W = ay+y^2/(3x)+ay^3/(27x^2)+mK(3x+y)+cK(2y+2y^2/3x).$$

The parameters characterizing N and I bands probably vary somewhat from biotite to biotite but on the basis of the spectrum of phlogopite M#1, $\Delta\nu_{\frac{1}{2}}$ has been chosen as 25 cm^{-1} for all N bands and 38 cm^{-1}

for all I bands. For these parameters the relevant values of the constants a, c, and m are 0·320, 0·223, and 0·755 (van de Hulst and Reesinck, 1947). Under these conditions y may be obtained from the equation:

$$\begin{aligned}0{\cdot}00323y^4+(-0{\cdot}369U+0{\cdot}00534V-0{\cdot}00410W)y^3+\\+(3{\cdot}124U^2+0{\cdot}340UV-0{\cdot}282UW)y^2+\\+(-6{\cdot}760U^3-4{\cdot}365VU^2+1{\cdot}880WU^2)y+\\+10{\cdot}16VU^3-3WU^3-3{\cdot}250U^4=0.\end{aligned}$$





FIGS. 3 and 4: FIG. 3 (left). Relationship between the atomic ratio $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ determined by chemical analysis and from the infra-red spectrum of a number of biotites. The numbers, with the exception of M#1, refer to specimens in the collections of the Department of Mineralogy and Petrology, University of Cambridge. FIG. 4 (right). OH-stretching vibrations of biotites used in the present study. KBr disks.

Since the value of the y^4 term is always small, an acceptable value for y is given by the smallest positive root of the cubic equation. The probability that an Mg^{2+} or Fe^{2+} ion will be found in an N association is proportional to the concentration of Mg^{2+} and Fe^{2+} in N type associations in the octahedral layer so that the $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratio for the N associations is given by $x/(x+y/3)$. Provided neither Mg^{2+} nor Fe^{2+} is favoured in I or V type associations, this is also the ratio for the whole biotite.

In fig. 2 the spectrum of biotite 196513 has been resolved into its component N and I bands. The contribution of the lower-frequency V band, not considered in the present treatment, to the absorption in the OH-stretching region is also apparent.

The results of the determination of the $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratio for six biotites chosen to cover a wide range of composition are shown in fig. 3, plotted against the same atomic ratio derived from chemical analysis. The actual spectra are shown in fig. 4.

The analyses were performed on small flakes using an electron-probe micro-analyser supplemented by determination of alkalis, ferrous iron, fluorine, and H_2O^+ on separate portions of the mineral powder. The magnitude of the errors involved makes it uncertain whether such lack of agreement as there is results from error in the chemical analysis or in the spectrum analysis. Considering the difficulties involved in a thorough quantitative treatment, however, the data may be considered to give reasonable support to the suggested interpretation.

Discussion and conclusion. During the derivation of the above relationships several implicit assumptions have been made. F^-, for example, which commonly replaces a substantial proportion of OH ions in biotites, must be assumed to have no preference for any of the N or I type sites and to be proportionately distributed amongst them. Further, Fe^{2+} and Mg^{2+} must be randomly distributed between M_I and M_3, the two non-equivalent octahedral sites, although it can be shown that with many ranges of composition the over-all effect of ordering on this part of the absorption spectrum is small. In addition, the exact effect of the natural variation in tetrahedral Al on the width of the absorption bands can only be guessed at present. These assumptions, together with the approximations of Gaussian band shape, neglecting of overlap from distant bands, and other matters of detail (Wilkins and Ito, 1967), make a truly satisfactory description difficult to obtain.

For these reasons and also because the procedure requires a comparison of two small quantities for the more ferrous-iron-rich biotites, resulting in low accuracy, it is thought that the method will have restricted value for the rapid determination of $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratios in biotites although it probably does as well as any X-ray method at present proposed (Franzini and Schiaffino, 1965). In this respect its peculiar advantages are that Fe^{3+} in octahedral or tetrahedral positions has no effect on the determination, and the atomic ratio $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ is determined direct from the spectrum without the necessity of any other analytical determinations on the sample. Mn^{2+} and any other divalent transition element ion will be determined as Fe^{2+}.

On the other hand, where the chemical analysis of the specimen is known and the proposed description fits well, the hydroxyl stretching vibrations will be a useful tool for studying the details of mineralogical transformations involving biotite.

Acknowledgements. The author is much indebted to Dr. J. D. C. McConnell and particularly to Dr. W. Vedder for discussion and many helpful comments on the subject of this paper. He also has to thank Dr. J. F. Turner of the Department of Chemistry, University of Cambridge, and Dr. G. Dudek of the Department of Chemistry, Harvard University, for providing instrumental facilities and for help in many other ways. Financial support was provided by the Committee on Experimental Geology and Geophysics, Harvard University. The specimens used in this study were kindly provided by Dr. S. Agrell and Dr. W. Vedder.

References

Burns (R. G.) and Strens (R. G. J.) 1966. Science, vol. 153, p. 890.
Farmer (V. C.), 1958. Min. Mag., vol. 31, p. 829.
—— and Russell (J. D.), 1966. Spectrochimica Acta, vol. 22, p. 389.
Franzini (M.) and Schiaffino (L.), 1965. Zeits. Krist., vol. 122, p. 100.
van de Hulst (H. C.) and Reesinck (J. J. M.), 1947. Astrophys. Journ., vol. 106, p. 121.
Jorgensen (P.), 1966. Clays and Clay Minerals, 13th Conf., 1964, p. 263.
Saksena (B. D.), 1964. Trans. Faraday Soc., vol. 60, p. 1715.
Seshadri (K. S.) and Jones (R. N.), 1963. Spectrochimica Acta, vol. 19, p. 1013.
Strens (R. G. J.), 1966. Chem. Comm., p. 519.
Vedder (W.), 1964. Amer. Min., vol. 49, p. 736.
Wilkins (R. W. T.) and Ito (J.), 1967. In preparation.

[*Manuscript received 6 February 1967*]