

MINERALOGICAL MAGAZINE

VOLUME 37 NUMBER 292 DECEMBER 1970

Replacement of OH by OD in layer silicates, and identification of the vibrations of these groups in infra-red spectra

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SUMMARY. Conditions necessary for exchange between lattice OH groups and D₂O in expanding layer silicates are reported. From spectral changes in the 200–1200 cm⁻¹ region resulting from this exchange, in-plane librations of OH co-ordinated to (AlAl), (AlMg), (AlFe³⁺), and (MgMgMg) have been identified in montmorillonite, beidellite, saponite, hectorite, and vermiculite. Both in-plane and out-of-plane librations have been identified for pyrophyllite and celadonite, from comparison of synthetic specimens containing OD with natural or synthetic OH forms. Comparison of hydrogen and deuterium forms of Mg- and Ni-talcs leads to the identification of translational and librational OH vibrations.

TREATMENT of minerals with D₂O at room or higher temperatures leads to conversion of some or all of their OH groups to OD groups. The degree of exchange can be determined from the infra-red spectrum, and this technique has been applied to distinguish different kinds of hydroxyl group in clay minerals (Farmer, Russell, and Ahlrichs, 1968).

Such exchange reactions also serve to identify those infra-red absorption bands that arise from vibrations involving hydroxyl, and by this means Stubican and Roy (1961) established that the in-plane rocking vibration (libration) of hydroxyl linked to two aluminium ions, as in kaolinite and beidellite, lay in the 910–40 cm⁻¹ region, whereas libration of hydroxyl linked to two ferric ions, as in nontronite, lay at 827 cm⁻¹. They failed to find a libration of hydroxyl groups in talc or saponite.

In the present paper, the minimum conditions necessary to achieve complete replacement of OH by OD in expanding layer silicates have been investigated, and the deuterated products have been used to identify the librational frequencies of hydroxyl groups in dioctahedral and trioctahedral smectites. Preliminary reports on these

assignments have been published (Farmer, Russell, and Ahlrichs, 1968; Farmer *et al.*, 1967), but these earlier observations in the 1200–650 cm^{-1} region have now been extended to 300 or 200 cm^{-1} , and several vibrations involving hydroxyl have been found. To assist in characterizing these vibrations, OH and OD forms of pyrophyllite, celadonite, and talc have been prepared and examined. OH and OD forms of Ni-talc have also been prepared in an attempt to achieve a complete assignment for the talc spectrum.

Experimental

Replacement of lattice OH groups by OD groups in montmorillonite (Skyrvedalen, Wyoming, and Woburn Fuller's Earth), beidellite (Black Jack Mine, Idaho), saponite (Allt Ribhein, Skye), hectorite (Hector, California), and vermiculite (Loch Scye, Caithness) was readily achieved by heating self-supporting oriented films of NH_4 -saturated specimens in D_2O vapour at 300–400 °C in a cell, fitted with AgCl windows, similar to that described by Angell and Schaffer (1965). The cell was successively evacuated to 0.002 mm Hg and filled with D_2O vapour (17.5 mm Hg) six times at room temperature to ensure removal or complete exchange of interlayer water. This procedure also resulted in extensive (80–100 %) exchange of NH_4 ions in all but the vermiculite where about 50 % NH_4 still remained. After heating for 1–16 hours the cell was evacuated, refilled with fresh D_2O vapour, and the heating continued. This procedure was repeated until the infra-red spectrum showed no OH stretching vibrations.

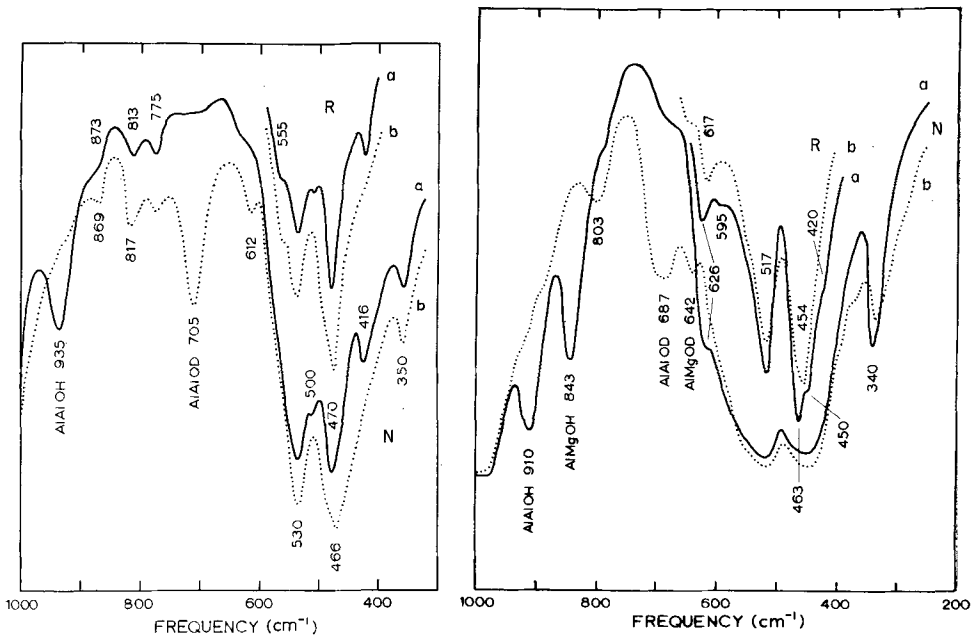
The comparative ease with which H–D exchange took place in the expanding layer silicates is worth noting: 3 one-hour treatments at 350 °C produced virtually complete deuteration of saponite, hectorite, vermiculite, and montmorillonite. Beidellite was slightly more resistant, requiring 4 treatments at 400 °C. Some exchange occurs even at 100 °C—about 7 % in beidellite and up to 25 % in montmorillonite. These results contrast sharply with those of Roy and Roy (1957) who achieved less than 50 % exchange in a hydrothermal treatment of montmorillonite (3 days at 370 °C and about 1.4 kb).

Synthetic deuterated specimens of pyrophyllite, talc, and celadonite were prepared hydrothermally from amorphous gels of the appropriate composition (Luth and Ingamells, 1965) and D_2O . The experimental conditions were: pyrophyllite, 27 days at 447 °C and 2 kb pressure; talc, 7 days at 640 °C and 1 kb; celadonite, 30 days at 360 °C and 1 kb. The composition of the celadonite, which was also prepared in the hydroxyl form, was $\text{KMgFe}^{3+}\text{Si}_4\text{O}_{10}(\text{OH})_2$.

Attempts at hydrothermal synthesis of OD pyrophyllite from either the natural material or its dehydroxylate and D_2O yielded only about 5 and 25 % respectively. The latter is close to the level of rehydroxylation of dehydroxylated pyrophyllite at 500 °C in steam at atmospheric pressure (Heller *et al.*, 1962).

Infra-red absorption spectra were recorded on a Grubb–Parsons Spectromaster over the range 4000–400 cm^{-1} and on a Perkin Elmer 225 down to 300 cm^{-1} or 200 cm^{-1} . Lattice OD groups are stable in air at ambient temperatures. Samples were in the form of oriented separated films, oriented deposits on CsI plates or polyethylene

or AgCl sheet, and were also incorporated in CsBr or CsI pressed discs (0.2–1.5 mg/250 mg, 12 mm diameter). Ishii, Shimanouchi, and Nakahira (1967) have published spectra of randomly oriented talc and pyrophyllite down to about 50 cm^{-1} , and Wilkins and Ito (1967) have studied Ni-talc to 400 cm^{-1} . Our spectra agree well with theirs.



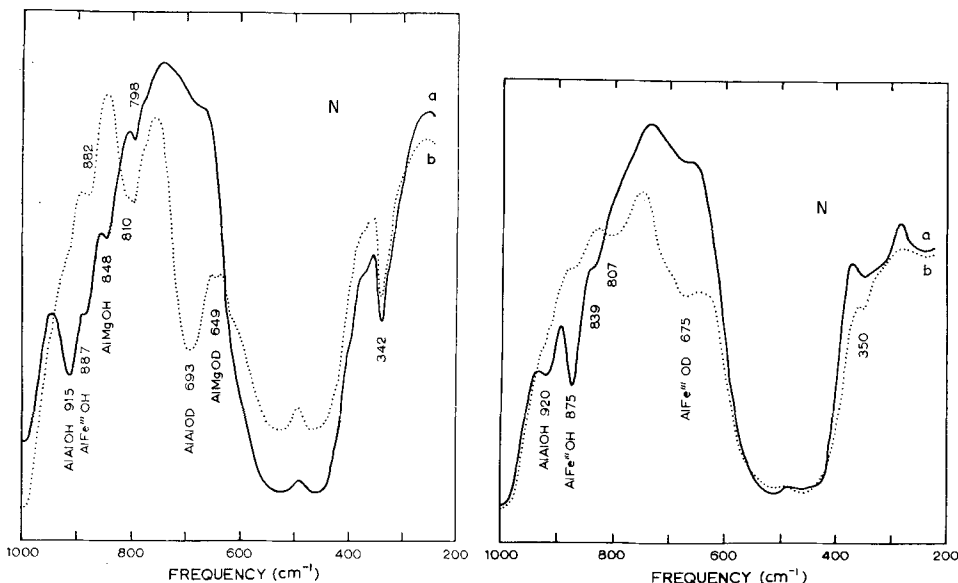
FIGS. 1 and 2: Fig. 1 (left). Infra-red spectrum of beidellite: (a) OH form, (b) OD form, N: film at normal incidence, R: randomly oriented sample in pressed disc. Fig. 2 (right). Infra-red spectrum of Skyrvedalen montmorillonite: symbols as in fig. 1.

Results and Discussion

The 2:1 dioctahedral layer silicates. When OD groups replace OH groups in dioctahedral layer silicates, the most striking changes in spectra below 1000 cm^{-1} are due to the displacement of the OH in-plane rocking vibration, or libration, to lower frequencies by a factor of 1.30–1.35. Thus the Al_2OH libration, lying at 935 cm^{-1} in OH-beidellite (fig. 1) is replaced by the Al_2OD libration at 705 cm^{-1} in OD-beidellite, as previously noted by Stubican and Roy (1961). Beidellite contains only aluminium ions in its octahedral layer, whereas montmorillonites have hydroxyl groups linked to both Al_2 and AlMg octahedral pairs. In all three montmorillonites (figs. 2, 3, 4) an Al_2OH libration can be identified at $910\text{--}20\text{ cm}^{-1}$, and an AlMgOH libration at $839\text{--}48\text{ cm}^{-1}$, by their displacement to lower frequencies in the OD-forms; these are the only librational frequencies in the iron-free Skyrvedalen montmorillonite (fig. 2).

Absorption bands at 887 cm^{-1} in Wyoming montmorillonite (fig. 3) and at 875 cm^{-1} in Woburn Fuller's Earth (fig. 4) have been ascribed to the libration of hydroxyl

co-ordinated to AlFe^{3+} pairs, on the grounds that their intensity is related to the iron content of the montmorillonites, and that they are readily eliminated from the spectrum under reducing conditions, for example by exposure of clay films to hydrazine vapour (Farmer and Russell, 1964, 1967). The displacement of the 875 cm^{-1} band of Woburn Fuller's Earth to lower frequencies on deuteration (fig. 4) confirms this assignment, but it is noteworthy that at least some of the $\text{AlFe}^{3+}\text{OH}$ groupings in



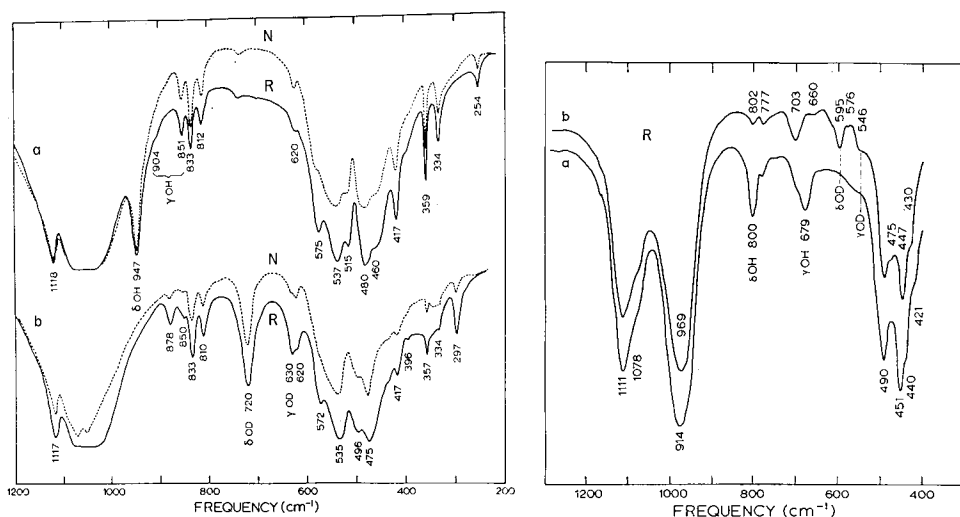
Figs. 3 and 4: Fig. 3 (left). Infra-red spectrum of Wyoming montmorillonite: symbols as in fig. 1. Fig. 4 (right). Infra-red spectrum of Woburn Fuller's Earth: symbols as in fig. 1.

Wyoming montmorillonite are resistant to deuteration, as the 887 cm^{-1} band persists at 882 cm^{-1} in the deuterated sample (fig. 3). The possibility that the residual 882 cm^{-1} band arises from a different type of vibration was eliminated by the finding that it disappeared when the deuterated mineral was exposed to hydrazine vapour.

Deuteration causes a number of other changes in the spectra, in addition to those associated with the in-plane libration. Thus in montmorillonites, replacement of OH by OD causes the appearance, or the very marked enhancement of a band at $800\text{--}10\text{ cm}^{-1}$, and bands near 620 and 460 cm^{-1} undergo slight shifts. In beidellite, bands at 416 and 500 cm^{-1} are lost, a band appears at 612 cm^{-1} , and bands at 470 , 813 , and 873 cm^{-1} undergo displacements.

There are two possible causes for these changes in spectra. Firstly, in addition to the in-plane libration of hydroxyl groups in dioctahedral layer silicates, a second, out-of-plane librational frequency should occur, with a dipole oscillation approximately perpendicular to the layer plane. Secondly, coupling between librational and translational vibrations of hydroxyl groups can occur, and so lead to frequency displacements.

In order to distinguish these possibilities under more favourable circumstances than those offered by smectite spectra, spectra of OH- and OD-pyrophyllite, which are sharper and better defined than those of smectites, have been examined (fig. 5). Further assistance in identification was given by comparing the spectra of oriented samples with those of randomly oriented samples; by this means it was possible to identify absorption bands that have a distinct component perpendicular to the layers and therefore appear weaker in the spectra of oriented samples (Farmer, 1958).



Figs. 5 and 6: Fig. 5 (left). Infra-red spectrum of pyrophyllite: symbols as in fig. 1. Fig. 6 (right). Infra-red spectrum of celadonite: symbols as in fig. 1.

In the pyrophyllite spectra, the in-plane OH libration at 947 cm^{-1} and the corresponding OD libration at 720 cm^{-1} are readily identified, but the out-of-plane libration is less obvious, as so many changes occur in the spectrum when OD substitutes for OH. Vedder and McDonald (1963) suggested that a band at 405 cm^{-1} in muscovite is the out-of-plane libration of OH, as it was absent from the spectrum of an OD-muscovite. This band of muscovite has clear analogues in beidellite and pyrophyllite, near 417 cm^{-1} , which weaken considerably in the deuterated forms.

A new band appears at 297 cm^{-1} in OD-pyrophyllite that could be interpreted as the out-of-plane libration of OD, corresponding to an OH libration at 417 cm^{-1} . Farmer (1968) has pointed out, however, that the 405 cm^{-1} band of muscovite has no component perpendicular to the layers, and this appears to be true also for the 417 cm^{-1} band of pyrophyllite; thus their assignment as out-of-plane librations is unlikely, and an alternative interpretation of the 297 cm^{-1} band in OD-pyrophyllite must be sought.

A much stronger candidate for the out-of-plane libration of OD-pyrophyllite is a band at 630 cm^{-1} , which has marked perpendicular polarization. The corresponding

OH libration must be considered to couple with a lattice vibration to give a pair of weak bands at 904 and 851 cm^{-1} . In the deuterated form these two bands are replaced by one uncoupled lattice vibration, which appears at the intermediate frequency, 878 cm^{-1} . Taking an estimated value of 880 cm^{-1} for the uncoupled OH-libration, a reasonable value (1.39) is obtained for $\gamma_{\text{OH}}/\gamma_{\text{OD}}$.

It will be noted that the changes in the 850–900 cm^{-1} region on substituting OD for OH in pyrophyllite cannot be ascribed to coupling between these vibrations and the in-plane libration at 947 cm^{-1} . No such coupling is possible, as the vibrations are of different symmetry species. The unit cell of a single pyrophyllite sheet has symmetry C_{2h} , and its infra-red-active vibrations have dipole oscillations either along the two-fold axis in the plane of the layers (A_u) or at right angles to the axis (B_u). The in-plane libration belongs to symmetry species A_u , whereas both the 851 cm^{-1} band of OH-pyrophyllite and the 878 cm^{-1} band of OD-pyrophyllite have components perpendicular to the layers, and so must belong to the same symmetry species, B_u , as the out-of-plane libration.

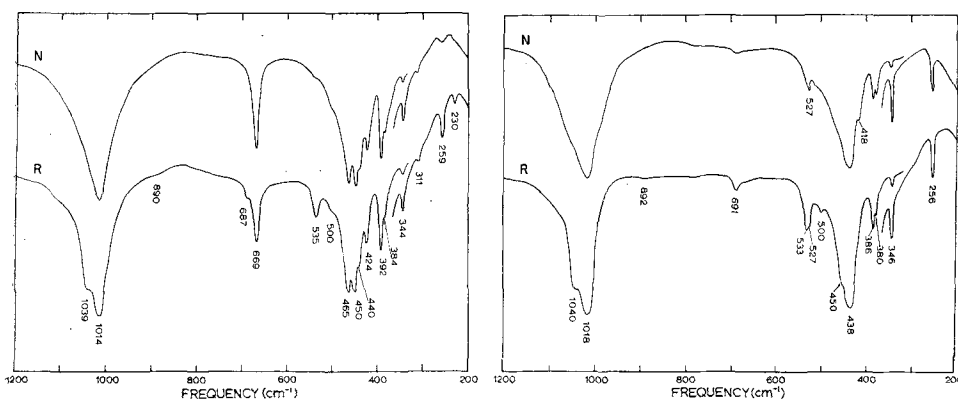
The diffuseness of the spectra of the clay minerals makes it impossible to get from them confirmation for the assignment of the OH out-of-plane vibration suggested by the pyrophyllite spectra, but support has been obtained from a comparison of the spectra of synthetic OH- and OD-celadonites (fig. 6) in which each hydroxyl is shared between an Mg^{2+} and an Fe^{3+} octahedral cation. This comparison indicates that the in-plane and out-of-plane librations of OH lie at 800 cm^{-1} and 679 cm^{-1} , and of OD at 595 and 546 cm^{-1} . The 679 cm^{-1} band of OH-celadonite has already been recognized as having a component perpendicular to the layers (Farmer and Russell, 1964), and this is now found to be true also for the 546 cm^{-1} band of OD-celadonite. Thus here again, as in pyrophyllite, the out-of-plane libration is not very much lower in frequency than the in-plane libration.

Returning now to the spectra of beidellite (fig. 1), it can be seen that the spectral changes following deuteration are very similar to those produced in pyrophyllite. The OD out-of-plane libration can be detected at 612 cm^{-1} , and there is also evidence of some band shifts in the 850–900 cm^{-1} region. On the other hand, the striking increase in intensity of absorption near 800 cm^{-1} when montmorillonites are deuterated (figs. 2, 3, 4) has no analogue in either pyrophyllite or celadonite. This absorption is polarized in the plane of the layers, and so cannot be ascribed to the out-of-plane libration of OD. The only alternative is that it is a lattice vibration involving hydroxyl groups, whose intensity and frequency are affected by replacing OH with OD. The presence of lattice vibrations in the 800–900 cm^{-1} region that couple with hydroxyl librations was previously noted in kaolinite spectra (Farmer and Russell, 1964) as well as in the present study of pyrophyllite.

The 2:1 trioctahedral layer silicates. In a previous study of talc, hectorite, and saponite (Farmer, 1958), a medium-intensity band, lying at 670 cm^{-1} in talc and at 655 cm^{-1} in saponite and hectorite, was assigned to an in-plane silicon–oxygen vibration; a possible alternative assignment of this band to an OH librational frequency was discounted, as this vibration in brucite lies near 460 cm^{-1} . However, neutron inelastic scattering

spectra of talc show proton vibrations near 650 and 490 cm^{-1} , which have been correlated with infra-red bands at 670 and 535 cm^{-1} and ascribed to librations of hydroxyl groups by Naumann, Safford, and Mumpton (1966). In addition, neutron scattering indicates a series of vibrations, ascribed to translatory motion of the OH groups, below 400 cm^{-1} .

Neutron inelastic scattering spectra, although they include vibrations that are active in the infra-red spectrum, also reflect all other vibrations of the crystal lattice that involve protons. It is difficult, therefore, to correlate such spectra with infra-red spectra unambiguously, and it seems desirable to search for librational frequencies in the infra-red spectrum of talc by study of a synthetic OD-talc.

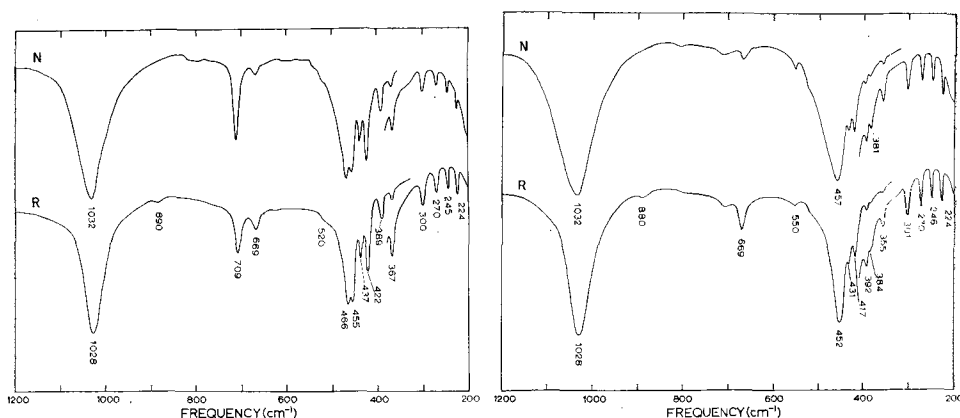


Figs. 7 and 8: Fig. 7 (left). Infra-red spectrum of MgOH-talc: symbols as in fig. 1. Fig. 8 (right). Infra-red spectrum of MgOD-talc: symbols as in fig. 1.

As the hydroxyl groups in talc are perpendicular to the layers and lie in sites that approximate closely to trigonal symmetry, their two librational motions form a degenerate pair and in the absence of coupling would give a single infra-red absorption band with a dipole change in the plane of the sheets. Comparison of MgOH- and MgOD-talc (figs. 7 and 8) confirms that the 669 cm^{-1} band is the OH libration, as it is replaced in the spectrum of MgOD-talc by the OD libration at 527 cm^{-1} . The ratio $\nu_{\text{OH}}/\nu_{\text{OD}}$ ($669/527$) is 1.27, which is significantly less than the theoretical value (1.37) for a purely librational frequency. This low value is explicable in terms of coupling between librational and translatory vibrations of OH and OD; the effect of this coupling can be seen in displacements of other vibrations, notably that at 465 cm^{-1} in MgOH talc, and also in some marked changes in intensity of absorption bands, when deuterium substitutes for hydrogen. It seems probable that the 465 cm^{-1} band of talc, and not the 535 cm^{-1} band, as suggested by Naumann, Safford, and Mumpton (1966), should be correlated with the neutron scattering peak at $487 \pm 23\text{ cm}^{-1}$, since the 465 cm^{-1} vibration obviously involves hydrogen, whereas the 535 cm^{-1} vibration is little affected by substituting deuterium for hydrogen.

Further guidance in the assignment of the absorption bands of talc can be obtained by comparison of the spectra of NiOH-talc and NiOD-talc with the corresponding

Mg-talcs and by comparison of the spectra of randomly oriented samples in CsBr discs with oriented samples deposited from suspension on CsI plates. On the basis of an approximate treatment of vibrations of the talc lattice, four vibrations with dipole oscillations perpendicular to the plane of the talc layer are expected, and these should be weak or absent in the spectra of oriented samples. Three of these have been identified in MgOH-talc at 1039, 687, and 535 cm^{-1} (Farmer, 1958) and these occur at almost identical frequencies in MgOD-talc (see figs. 7 and 8). In the present study, extension of the spectral range to 200 cm^{-1} indicates that the fourth perpendicular vibration lies at 259 cm^{-1} in MgOH-talc. It is anomalous, however, that the corresponding band of MgOD-talc, at 256 cm^{-1} , does not show obvious perpendicular polarization.



FIGS. 9 and 10: Fig. 9 (left). Infra-red spectrum of NiOH-talc: symbols as in fig. 1. Fig. 10 (right). Infra-red spectrum of NiOD-talc: symbols as in fig. 1.

Of the four perpendicular bands in Mg-talc, the two of higher frequency have been ascribed by Farmer (1958) to Si-O vibrations, and so should not be greatly perturbed by substitution of Ni for Mg in the octahedral layer. The other two perpendicular vibrations involve the octahedral cations and the hydroxyl groups, and these should be profoundly affected by substitution of Ni for Mg. These predictions are confirmed in the spectra of Ni-talc (figs. 9 and 10) although this synthetic material does not give such marked orientation effects as natural talc. The perpendicular band of highest frequency, an Si-O stretching vibration, must lie under the in-plane absorption at 1032 cm^{-1} , and the other perpendicular Si-O vibration can be identified with certainty at 669 cm^{-1} , only a little lower than in Mg-talc. The 535 cm^{-1} band of Mg-talc is totally absent from the spectrum of Ni-talc; its analogue in Ni-talc appears to lie at 455 cm^{-1} , as this band weakens relative to its neighbours in the spectrum of the oriented deposit. The fourth perpendicular band of Ni-talc could not be detected, and may lie below 200 cm^{-1} .

Simplified calculations, which treat the octahedral cations and hydroxyl groups as vibrating between the oxygens of a rigid silicon-oxygen lattice, indicate that the perpendicular vibrations of Mg-talc would lie at 535 and 272 cm^{-1} , while those of

Ni-talc would lie at 437 and 212 cm^{-1} . These rough calculations therefore support the assignments made.

It is more difficult, however, to rationalize the results for the in-plane vibrations of Mg- and Ni-talc. From the approximation that treats the silicate anion as having hexagonal symmetry, and the octahedral layer as trigonal, we expect six degenerate pairs of vibrations. Of these, the Si-O-Si stretch occurs at 1014 and 1032 cm^{-1} , and the OH librations at 669 and 709 cm^{-1} , for Mg- and Ni-talc respectively; for none of these vibrations is any splitting of the degeneracy detectable. Extending the notation used by Farmer (1958), the remaining four, which must all lie below 500 cm^{-1} , include: ν_4 , an angle-bending vibration of the Si-O-Si network; ν_5 , a vibration in which the octahedral oxygens and hydroxyls move in opposition to the octahedral cations; ν_6 , a vibration in which the octahedral cations move in phase with their adjacent oxygen layers, relative to the silicon and surface oxygen layers; and ν_7 , a translatory vibration of hydroxyl groups, out of phase with the other oxygens in this layer.

Of these ν_6 is necessarily of low frequency and has been reasonably assigned to a doublet near 170 cm^{-1} by Ishii, Shimanouchi, and Nakahira (1967). This leaves three, possibly degenerate, pairs of vibrations to be identified in the 500 to 200 cm^{-1} region. Examination of the spectra shows that the total number of absorption bands in both Mg- and Ni-talc (some nine or ten) considerably exceeds the number predicted. Thus the approximate treatment that satisfactorily accounts for the absorption pattern above 500 cm^{-1} breaks down for vibrations below 500 cm^{-1} . Nevertheless, some of the stronger bands in the talc spectrum should approximate to the types listed above.

A striking feature of all the talc spectra is the strong absorption near 450 cm^{-1} . Previous attempts to assign the two strong bands of MgOH-talc at 450 and 465 cm^{-1} have assumed that they represent a nearly degenerate pair of vibrations; that is, mutually perpendicular vibrations of the same type. The present spectra disprove this assumption, as the higher frequency band at 465 cm^{-1} in MgOH-talc is displaced to 438 cm^{-1} in MgOD-talc, whereas the 450 cm^{-1} band is not displaced; the two absorption bands therefore represent vibrations that differ in type. On the other hand, the 465 cm^{-1} bands of MgOH- and NiOH-talc are clearly of the same type, since both are displaced in the deuterated forms. The insensitivity of this vibration to the nature of the octahedral cation, and its sensitivity to substitution of deuterium for hydrogen, suggests that it be assigned to ν_7 above. Its relatively high frequency must then be ascribed to strong repulsive forces within the tightly packed oxygen layer in which the hydroxyl group lies.

The persistence of the 450 cm^{-1} vibration of MgOH-talc at 455 cm^{-1} in NiOH-talc has led Stubican and Roy (1961) and Wilkins and Ito (1967) to suggest that it must be an Si-O vibration, presumably ν_4 above. The present results indicate, however, that the 455 cm^{-1} band of NiOH talc either overlies a perpendicular band, or itself has some perpendicular character. If the latter interpretation is correct, then the 450 cm^{-1} band of MgOH-talc can be taken as being ν_5 , the in-plane vibration of the magnesium ions, whereas the 455 cm^{-1} band of NiOH-talc must be taken as a perpendicular vibration involving nickel and hydroxyl ions, corresponding to the 535 cm^{-1} band of MgOH-talc. The in-plane motion of the nickel ions probably contributes to the intensity of the

four bands of NiOH- and NiOD-talc in the 200–300 cm^{-1} region. Mg-talc shows only one strong band, at 259 cm^{-1} , in this region, and as this is a perpendicular band it cannot correspond to any of those of Ni-talc.

Conclusions

In the present study some progress has been made in the assignment of the vibrations of layer silicates. The identification of the OH libration in talc, saponite, and vermiculite as lying near 700 cm^{-1} provides a rational explanation for the strong absorption shown by serpentine and chlorites in this region (see, for example, Moenke,

TABLE I. *Calculated and experimental vibrational frequencies (cm^{-1}) of talc*

Type of vibration	Experimental		Calculated		
	Mg-talc	Ni-talc	Vedder (1964)	Ishii et al. (1967)	
Tetrahedral	$A_1 \nu_1$	1040	c. 1025	941	902
	$A_1 \nu_2$	687	669	554	613
	$E_1 \nu_3$	1014	1032	1041	1015
	$E_1 \nu_4$	< 460	< 460	482	543
Octahedral	δ (OH)	669	709		
	trans (OH) \parallel	465	466		
	(Mg,Ni) OH \perp	535	c. 455		
	(Mg,Ni) OH \perp	259	< 200		

1962), since these minerals have a higher concentration of hydroxyl linked to magnesium. In the dioctahedral minerals, the out-of-plane libration of the hydroxyl group has been plausibly identified in pyrophyllite and celadonite, but it seems that this vibration, unlike the in-plane libration, will be of little diagnostic value in characterizing the octahedral cations to which the hydroxyl group is linked.

The spectra of Ni- and Mg-talc have been assigned with some certainty down to 460 cm^{-1} , and it is now possible to make a comparison in this region between experimental results and the frequencies calculated for the vibrations of the tetrahedral layer (table I). The marked discrepancy between experimental and calculated frequencies for ν_1 , the perpendicular Si–O stretching vibration, can be explained by the effect of the coulombic forces that are associated with intense dipole oscillations perpendicular to the plane of a thin platy crystal, and which increase the vibrational frequencies markedly (Farmer and Russell, 1966). The second perpendicular vibration, ν_2 , is a much weaker absorber than ν_1 , so that here it is unlikely that coulombic forces can account for the discrepancy between observed and calculated frequencies. In calculations, the Si–O–Si stretching-force constant is adjusted to give agreement for ν_3 . The calculated frequency for in-plane Si–O–Si bending, ν_4 , is too high in the treatment of Ishii and co-workers.

For both talc and pyrophyllite, the region below 460 cm^{-1} is of considerable complexity, and it has not yet proved possible to assign the bands there to particular

vibrations with any certainty. Many bands in this region are affected in intensity and frequency by replacing hydrogen by deuterium in the structures; indeed even the direction of the transition moment of one band in talc appears to change on going from MgOH- to MgOD-talc. Apparently, the vibrations of the hydroxyl group are strongly coupled with those of other oxygens in the structure, as, indeed, neutron scattering studies have already indicated.

It is noteworthy, however, that the principal differences between the spectra of Mg- and Ni-talc occur in the 400 to 200 cm^{-1} region, confirming the expectation that this region will be of particular value in distinguishing isomorphous minerals.

Acknowledgements. The authors wish to thank Mr. A. R. Fraser for able technical assistance and Dr. D. C. McKean (Department of Chemistry, Aberdeen University) for making available the Perkin Elmer 225 spectrometer.

REFERENCES

- ANGELL (C. L.) and SCHAFER (P. C.), 1965. *Journ. phys. Chem.* **69**, 3463.
FARMER (V. C.), 1958. *Min. Mag.* **32**, 353.
— 1968. *Clay Minerals*, **7**, 373.
— and RUSSELL (J. D.), 1964. *Spectrochim. Acta*, **20**, 1149.
— — 1967. *Clays and Clay Min.* **15**, 121.
— — and AHLRICH (J. L.), 1968. *Trans. 9th Int. Congr. Soil Sci., Adelaide*, **3**, 101.
— — — and VELDE (B.), 1967. *Bull. Groupe franç. Argiles*, **19** (2), 5.
HELLER (L.), FARMER (V. C.), MACKENZIE (R. C.), MITCHELL (B. D.), and TAYLOR (H. F. W.), 1962. *Clay Min. Bull.* **5**, 56.
ISHII (M.), SHIMANOCHI (T.), and NAKAHIRA (M.), 1967. *Inorg. Chim. Acta*, **1**, 387.
LUTH (W. C.) and INGAMILLS (C. O.), 1965. *Amer. Min.* **50**, 255.
MOENKE (H.), 1962. *Mineralspektren*, Berlin (Akademie-Verlag).
NAUMANN (A. W.), SAFFORD (G. J.), and MUMPTON (F. A.), 1966. *Clays and Clay Min.* **14**, 367.
ROY (D. M.) and ROY (R.), 1957. *Geochimica Acta*, **11**, 72.
STUBICAN (V.) and ROY (R.), 1961. *Zeits. Krist.* **115**, 200.
VEDDER (W.), 1964. *Amer. Min.* **49**, 736.
— and McDONALD (R. S.), 1963. *Journ. chem. Phys.* **38**, 1583.
WILKINS (R. W. T.) and ITO (J.), 1967. *Amer. Min.* **52**, 1649.

[Manuscript received 24 November 1969]