

# INFRARED STUDY OF THE THERMAL DECOMPOSITION OF AMMONIUM RECTORITE\*

*by*

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## ABSTRACT

CHANGES in the infrared absorption spectrum of ammonium-saturated rectorite on heating suggest that the ammonium cations are hydrogen bonded to water molecules when the mineral is hydrated. Further spectral changes above 300°C indicate that lattice OH groups are perturbed by protons liberated from the decomposition of ammonium ions giving rise to an absorption doublet at 3500 and 3476  $\text{cm}^{-1}$ . The doublet attains maximal intensity when decomposition of ammonium cations and dehydroxylation of the mineral is complete at about 550°C.

The perturbation effect occurs only for swelling dioctahedral minerals which derive their layer charge from Al-for-Si substitution.

## INTRODUCTION

WHILE the existence of hydronium ions in clay minerals has been postulated several times (Brown and Norrish, 1952; Korolev, 1960; Bokii and Arkhipenko, 1962) their presence has never been unambiguously established. In their study of an artificially weathered muscovite White and Burns (1964) concluded from infrared and X-ray data that following hydrogen or ammonium saturation and heating, hydronium ions were produced. The present study is a further investigation of this problem in the mineral rectorite, whose structure has been established most recently (Brown and Weir, 1963) as a regular alternation of mica-like and montmorillonite-like layers. Uchiyama and Onikura (1956) have suggested that rectorite-type minerals are natural weathering products of muscovite and moreover that they may not be of uncommon occurrence.

## MATERIALS AND METHODS

The rectorite used was that designated "allevardite-B" by Brown and Weir (1963). It was saturated with  $\text{H}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  by treatment with

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appropriately saturated resin (Dowex 50W-X8) and was examined as films sedimented from aqueous suspension either unmounted or on quartz disks.

Heating of samples up to 700°C in vacuum was carried out in quartz infrared cells using a rotary vacuum pump capable of attaining  $10^{-2}$  mmHg. The cells were cooled under vacuum and infrared absorption spectra were recorded on a Perkin Elmer 421 double-beam spectrometer, with a matching quartz cell in the reference beam. Spectra were recorded over the range 4000–2000  $\text{cm}^{-1}$  where the matched cells gave a very flat absorption background and not less than 80% of the radiant energy was available: spectra were also recorded from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  with the samples in air.

X-ray diffraction patterns were recorded on a GE XRD5 diffractometer, heated samples being held over  $\text{P}_2\text{O}_5$  and flushed with dry nitrogen to minimize rehydration. The cation exchange capacity of  $\text{NH}_4^+$ -rectorite, determined by a conventional microkjeldahl method, was 59 m-equiv./100 g air-dry material.

Samples were deuterated by flushing them six times with the vapor from  $\text{D}_2\text{O}$  (99.7%; General Dynamics Corporation, San Carlos, California).

## RESULTS AND DISCUSSION

It can be concluded from Fig. 1 that exchangeable ammonium cations in the expanding layer of ammonium-saturated rectorite are hydrogen bonded to water molecules. The hydrogen bonded  $\text{NH}_4^+$  absorption bands at 3190, 3050, 2865, and 1450  $\text{cm}^{-1}$  shift to 3280 and 1430  $\text{cm}^{-1}$  on heating in vacuum to 200°C. These shifts are consistent with more freely rotating ammonium ions when interlayer water is removed from the sample and are analogous to the shifts observed on dehydrating  $\text{NH}_4^+$ -montmorillonite (Mortland *et al.*, 1963; Russell and Farmer, 1964). These observations support the conclusion of Brown and Weir (1963) that hydration water and exchangeable cations are associated in the expanding layer of rectorite, and that the expanding layer is montmorillonite-like. However, the lower intensity and greater width of the 1430  $\text{cm}^{-1}$   $\text{NH}_4^+$  deformation band in the dehydrated mineral compared with the 1440  $\text{cm}^{-1}$   $\text{NH}_4^+$  band in the hydrated mineral are anomalous. They seem to indicate that  $\text{NH}_4$  cations participate in a range of strengths of hydrogen bonds to surface oxygens in the dehydrated structure, and these bonds are probably the origin of the residual broad absorption between 3100 and 2800  $\text{cm}^{-1}$  (Fig. 1b).

On heating the  $\text{NH}_4^+$ -rectorite to higher temperatures in vacuum,  $\text{NH}_4$  and OH stretching bands decrease in intensity due to decomposition of  $\text{NH}_4$  and dehydroxylation of the mineral and a new absorption band develops at 3476  $\text{cm}^{-1}$  (Fig. 2). Maximum development of the band occurs at about 550°C when the mineral spectrum shows neither OH nor  $\text{NH}_4$  absorption bands.

Scale expansion of the 3476  $\text{cm}^{-1}$  band reveals some interesting fine structure (Fig. 3). At 300°C the principal 3476  $\text{cm}^{-1}$  band is accompanied by weaker

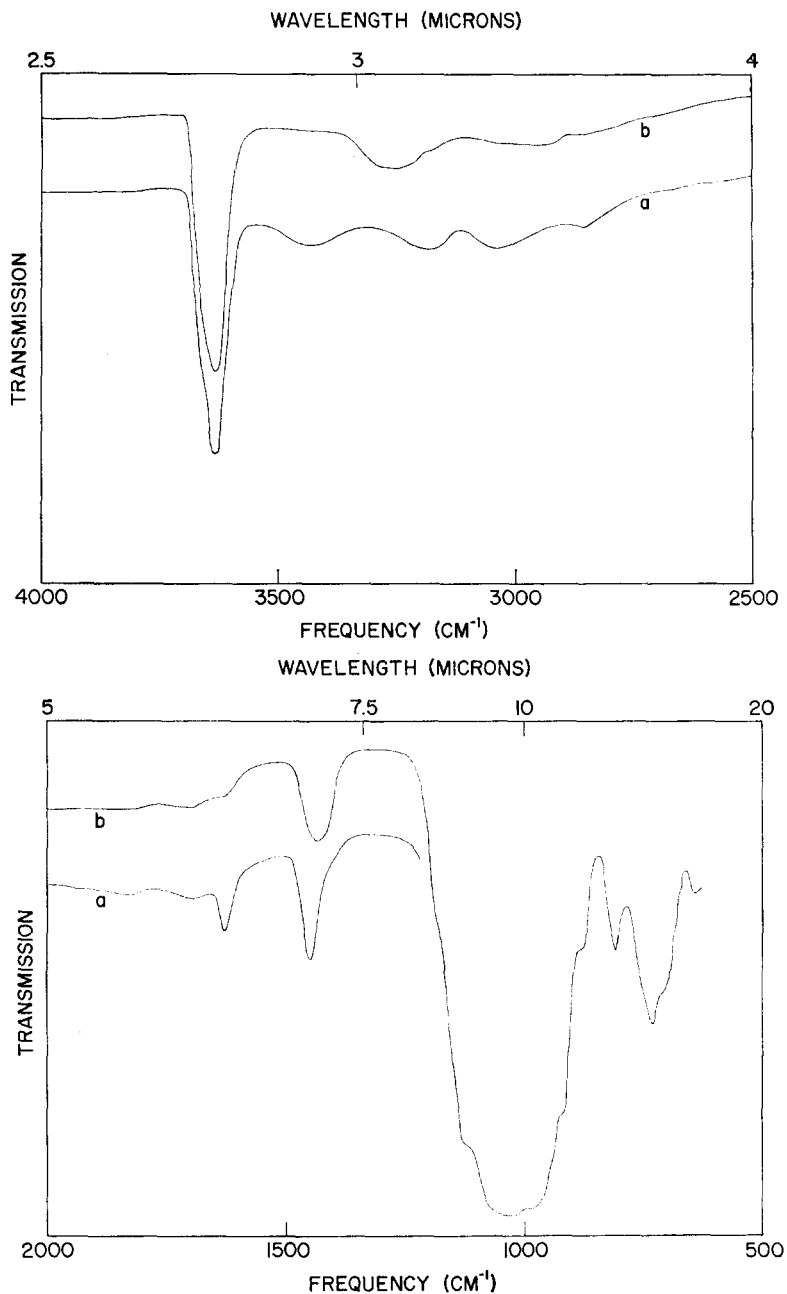


FIG. 1.—Infrared spectra of  $\text{NH}_4^+$ -rectorite film (a) air-dry, (b) dehydrated by evacuation to  $10^{-2}$  mmHg at room temperature.

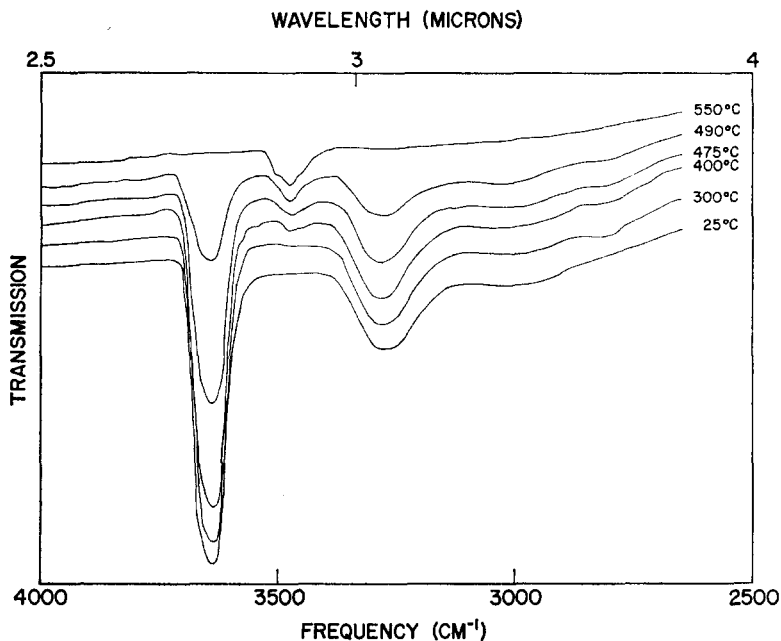


FIG. 2.—Infrared spectra of  $\text{NH}_4^+$ -rectorite film heated in vacuum to the temperatures shown, then cooled to room temperature in vacuum.

but quite distinct bands at  $3445$  and  $3415\text{ cm}^{-1}$ . With increasing temperature the  $3476\text{ cm}^{-1}$  band intensity increased at the expense of the  $3440$  and  $3410\text{ cm}^{-1}$  bands, until by  $475^\circ\text{C}$  only the  $3476\text{ cm}^{-1}$  band remained. Above  $500^\circ\text{C}$  a very sharp band developed at  $3500\text{ cm}^{-1}$  on the side of the  $3476\text{ cm}^{-1}$  band. This doublet was unchanged after heating the sample for 1 hr at  $850^\circ\text{C}$  in vacuum.  $\text{H}^+$ -saturated rectorite showed the same but weaker band development as  $\text{NH}_4^+$ -rectorite (Fig. 3), the weakness probably being due to replacement of protons by  $\text{Al}^{3+}$ .  $\text{H}^+$ -rectorite aged several months showed only a very weak  $3476\text{ cm}^{-1}$  band on heating to  $600^\circ\text{C}$ . Neither  $\text{Ca}^{2+}$ -saturated rectorite nor the natural mineral showed absorption bands in the  $3500$ – $3400\text{ cm}^{-1}$  region on heating.

The simple relationship between decreasing O–H and N–H absorption band intensities and increasing intensity of the  $3476\text{ cm}^{-1}$  band (Fig. 4) and the fact that the  $3476\text{ cm}^{-1}$  band only develops in the presence of protons suggests that the origin of the vibration lies in an interaction of protons with the lattice O–H groups. Two possible reactions are (a) direct perturbation of lattice OH groups by protons (either exchangeable  $\text{H}^+$  or  $\text{H}^+$  from decomposition of  $\text{NH}_4^+$  into  $\text{NH}_3$  and  $\text{H}^+$ ):



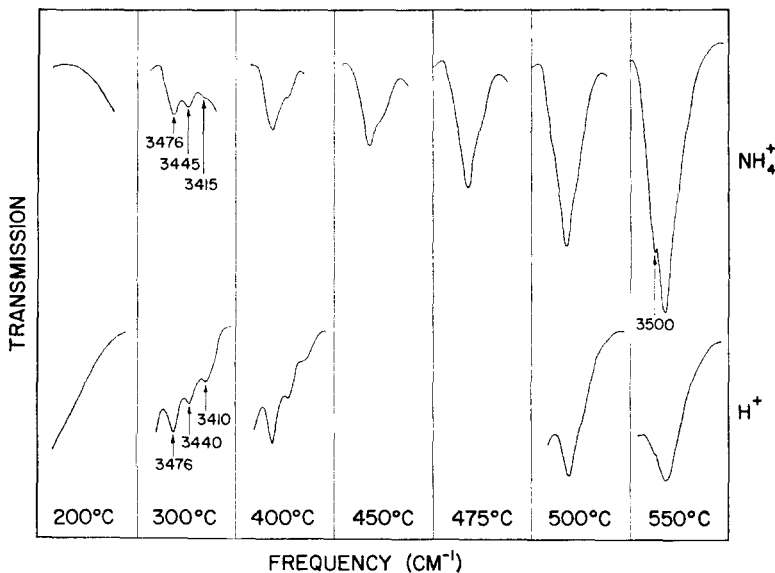
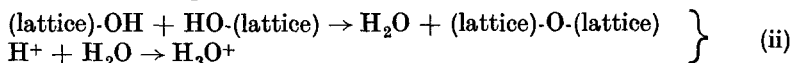


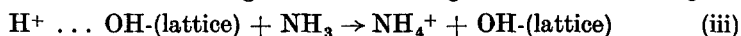
FIG. 3.—Development of the 3476  $\text{cm}^{-1}$  band complex ( $5\times$  scale expansion) in  $\text{NH}_4^+$ - and  $\text{H}^+$ - rectorites heated to the temperatures shown.

and (b) indirect formation of hydronium ions ( $\text{H}_3\text{O}^+$ ) from protons and a water molecule resulting from mutual condensation of two lattice OH groups:

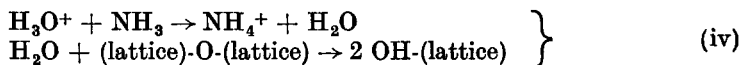


Exposure of the heated  $\text{NH}_4^+$ -rectorite to anhydrous ammonia causes the disappearance of the 3500, 3476  $\text{cm}^{-1}$  doublet and the reappearance of an  $\text{NH}_4$  stretching vibration at 3280  $\text{cm}^{-1}$  whose intensity was equal to that of the original  $\text{NH}_4$  band at this frequency, and an O-H stretching band in the range 3650–3630  $\text{cm}^{-1}$ , the optical density of which was 8.9% of that of the original O-H stretching band at 3630  $\text{cm}^{-1}$  (Fig. 5). Repeated  $\text{NH}_3$  treatments failed to cause an increase in either of the regenerated OH or  $\text{NH}_4$  band intensities.

On the basis of the structural formula of Brown and Weir (1963) for rectorite and of an ideal structural formula composed of montmorillonite and mica in a 1:1 ratio, protons equivalent to the exchange capacity of the mineral would associate with 9% of the lattice OH groups according to reaction (i) and 18% according to reaction (ii), i.e. 9% and 18% of the original OH content would be regenerated following treatment with  $\text{NH}_3$ :



and



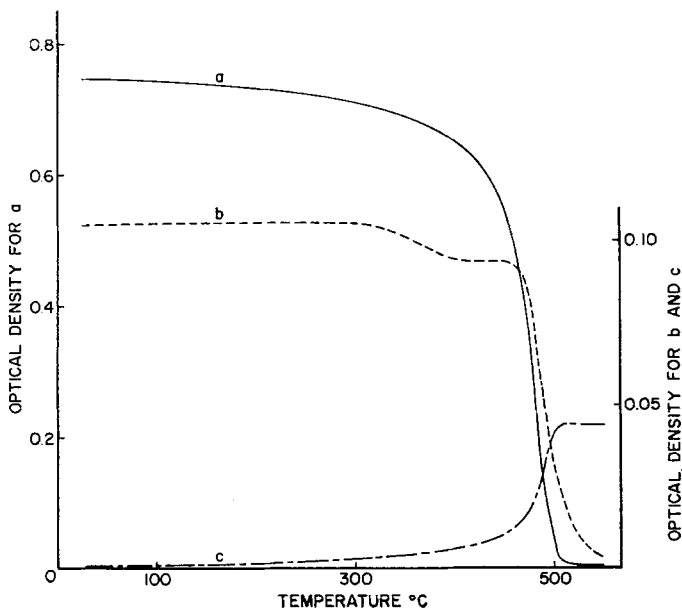


FIG. 4.—Variation with temperature of optical density of (a) lattice O—H stretching vibration, (b) N—H stretching vibration of  $\text{NH}_4^+$ , and (c)  $3476\text{ cm}^{-1}$  band in  $\text{NH}_4^+$ -rectorite.

The excellent agreement between observed and calculated values of the proportion of OH groups regenerated by  $\text{NH}_3$  treatment, 8.9 and 9.0% respectively, supports the assignment of the  $3500, 3476\text{ cm}^{-1}$  doublet to a proton-perturbed OH group. Moreover, a  $d(001)$  spacing of  $19.2\text{ \AA}$  for the  $\text{NH}_4^+$ -rectorite after heating to  $600^\circ\text{C}$  (Table 1) is smaller than might be expected if hydronium ions, with an ionic radius similar in size to potassium, occupied the interlayer space. Brown and Weir (1963) quoted a value of  $19.6\text{ \AA}$  for  $d(001)$  spacing of the natural rectorite (predominantly sodium-saturated) after heating to  $600^\circ\text{C}$ , although they observed a spacing of  $19.1\text{ \AA}$  following heating to  $300^\circ\text{C}$ . Table 1 shows the changes in  $d(001)$  spacing accompanying dehydration and heat treatment of  $\text{NH}_4^+$ -rectorite. The spacing of  $19.77\text{ \AA}$  at  $300^\circ\text{C}$ , which is in sharp contrast to the  $19.1\text{ \AA}$  observed by Brown and Weir (1963), is correlated with the appearance in the infrared absorption spectrum of the triplet at  $3476, 3445,$  and  $3415\text{ cm}^{-1}$  (Fig. 3) and the commencement of decomposition of  $\text{NH}_4^+$  into  $\text{NH}_3$  and  $\text{H}^+$ . A possible interpretation is that protons react transiently with isolated residual interlayer water molecules to form hydronium ions which prop the silicate sheets apart and give rise to the high spacing. The force field surrounding such hydronium ions is likely to be unsymmetrical and might account for the appearance of the three infrared absorption bands.

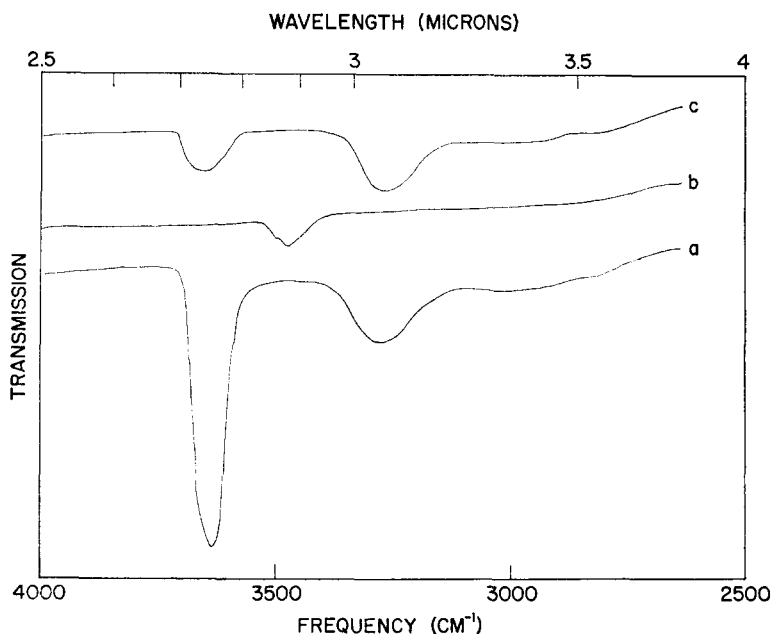


FIG. 5.—Infrared spectra of  $\text{NH}_4^+$ -rectorite film (a) heated to  $200^\circ\text{C}$  in vacuum then cooled to room temperature, (b) heated to  $550^\circ\text{C}$  in vacuum then cooled to room temperature, (c) sample (b) exposed to dry  $\text{NH}_3$  gas for several hours then evacuated.

TABLE 1.—BASAL SPACINGS FOR AMMONIUM-SATURATED RECTORITE

Treatment	88% Relative humidity	Dry $\text{N}_2$ $\text{P}_2\text{O}_5$	$200^\circ\text{C}^*$	$300^\circ\text{C}$	$400^\circ\text{C}$	$500^\circ\text{C}$	$600^\circ\text{C}$
$d(001)\text{\AA}$	21.37	19.62	19.53	19.77	19.42	19.17	19.20

\* The sample heated to the temperatures shown was held over  $\text{P}_2\text{O}_5$  and flushed with dry nitrogen gas while recording the diffraction pattern.

The progressive decrease in basal spacing from 19.77 to 19.20  $\text{\AA}$  with rising temperature must be the result of decomposition of these hydronium ions, the resulting protons and those formed from further decomposition of  $\text{NH}_4^+$  interacting with lattice OH groups as previously described [equation (i)] to give the 3500, 3476  $\text{cm}^{-1}$  doublet.

Treatment of  $\text{NH}_4^+$ -rectorite with  $\text{D}_2\text{O}$  vapor produced  $\text{ND}_4^+$ -rectorite in which no lattice OH-OD exchange had taken place. This is in agreement

with the inability, except at elevated temperatures, of OH groups in montmorillonite to undergo deuterium exchange. The isotopic ratio

$$\nu_3\text{ND}_4/\nu_3\text{NH}_4 = 0.750$$

is in good agreement with the value of 0.746 quoted by Mortland *et al.* (1963) for  $\text{ND}_3$ -treated  $\text{H}^+$ -montmorillonite. The infrared spectrum of  $\text{ND}_4^+$ -rectorite after heating to  $550^\circ\text{C}$  showed in addition to the 3500, 3476  $\text{cm}^{-1}$  doublet another doublet at 2585, 2565  $\text{cm}^{-1}$  (Fig. 6). The high frequency

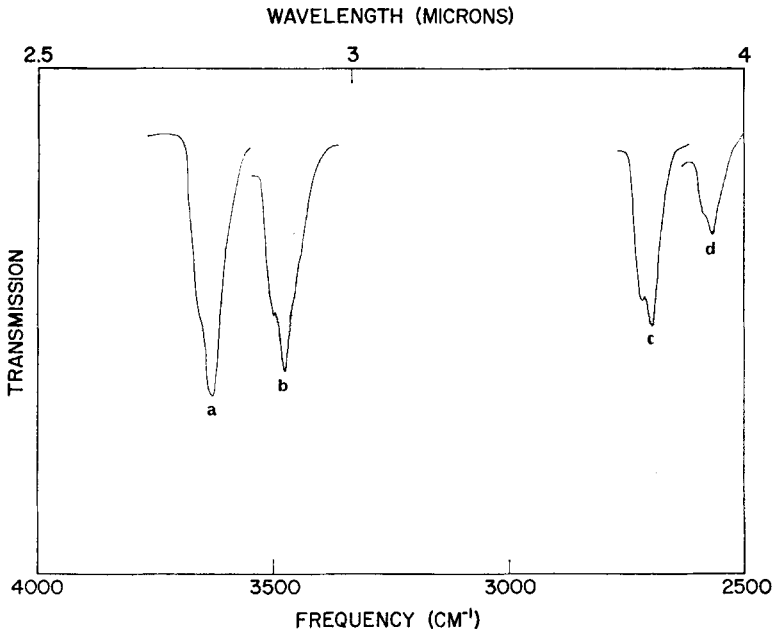


FIG. 6.—Normal and perturbed O-H and O-D stretching vibrations in  $\text{NH}_4^+$ -rectorite: (a) normal O-H, (b) perturbed O-H (in  $\text{NH}_4^+$ -rectorite heated to  $550^\circ\text{C}$ ), (c) normal O-D (in  $\text{NH}_4^+$ -rectorite heated to  $550^\circ\text{C}$ , exposed to  $\text{D}_2\text{O}$  vapor, then evacuated), and (d) perturbed O-D (in  $\text{NH}_4^+$ -rectorite exposed to  $\text{D}_2\text{O}$  vapor then heated to  $550^\circ\text{C}$ ).

doublet undoubtedly arises from proton perturbed lattice OH groups:  $\text{ND}_4^+$  would be partially reconverted to  $\text{NH}_4^+$  by  $\text{H}_2\text{O}$  liberated by dehydroxylation, subsequent decomposition of  $\text{NH}_4^+$  giving the doublet. The lower frequency doublet would appear to be due to perturbed lattice OD groups:  $\text{D}^+$  from decomposition of  $\text{ND}_4^+$  would perturb lattice OH groups, which, because of their proximity to  $\text{D}^+$  in the perturbation complex, would undergo H-D exchange. Thus the 2585, 2565  $\text{cm}^{-1}$  doublet is assigned to perturbed lattice OD groups and isotopic ratios,  $\nu\text{OD}/\nu\text{OH}$  (Table 2), close to those in



deuterated clay systems (Roy and Roy, 1956; Ledoux and White, 1964) and in ordinary and heavy ice (Ockman, 1958) support the assignment.

TABLE 2.—ISOTOPIC RATIOS OF STRETCHING FREQUENCIES OF OH AND OD IN AMMONIUM-SATURATED RECTORITE BEFORE AND AFTER HEATING AND D<sub>2</sub>O TREATMENT

Group	$\nu$ OH	$\nu$ OD	$\nu$ OD/ $\nu$ OH
Perturbed lattice	3500	2585	0.739
OH, OD	3476	2565	0.739
Lattice	3650	2720	0.745
OH, OD	3630	2695	0.743
Lattice			
OH, OD in montmorillonite			0.730*
Lattice			
OH, OD in kaolinite			0.739†
OH, OD in solid H <sub>2</sub> O and D <sub>2</sub> O			0.740‡

\* Roy and Roy (1956).

† Ledoux and White (1964).

‡ Ockman (1958).

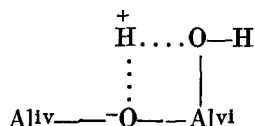
Contrary to the findings of previous investigations (Brindley, 1956) dehydroxylated rectorite can be partially rehydroxylated by exposure to water vapor at room temperature. It was possible then to introduce lattice OD groups into dehydroxylated rectorite by exposure to D<sub>2</sub>O vapor. A sample so treated showed a doublet at 2720, 2695 cm<sup>-1</sup> (Fig. 6). Isotopic ratios of these frequencies with the normal lattice OH frequencies at 3650 (a weak but distinct shoulder), and 3630 cm<sup>-1</sup> (Fig. 6) are satisfactory (Table 2) and support the assignment of the 2720, 2695 cm<sup>-1</sup> doublet to unperturbed lattice OD groups.

The doublet nature of the OH and OD stretching bands discussed above indicate that two different types of lattice OH groups exist in the rectorite structure. On the basis of the known structure of the mineral, "... a double-layer mineral made up of pairs of 2:1 type alumino-silicate layers. Alternate interlayers are mica-like ... and montmorillonite-like ..." (Brown and Weir, 1963), the two types of OH groups would be those adjacent to the mica-like region, and those adjacent to the montmorillonite-like region. Since the higher frequency member of the 3500, 3476 cm<sup>-1</sup> perturbed OH doublet only developed at high temperatures (Fig. 3) it can be reasonably concluded that the 3500 cm<sup>-1</sup> band arises from proton perturbation of OH groups adjacent to the mica-like layer: presumably more energy would be required to induce the proton to move into the neighborhood of the mica-like

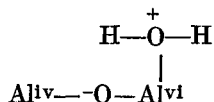
OH groups. Thus, the higher frequency members of the OH, OD doublets shown in Fig. 6 might arise from vibrations of mica-like OH or OD groups, while the lower frequency vibrations have their origin in montmorillonite-like OH or OD groups. There did not appear to be preferential loss of either of the two types of OH group during dehydroxylation.

The formation of proton-perturbed OH groups was observed only in dioctahedral minerals whose layer charge arises from Al-for-Si substitution in the tetrahedral layer: the effect was not observed in  $\text{NH}_4^+$ -saturated hectorite, saponite, and Wyoming montmorillonite. It occurred weakly and was of a transient nature in  $\text{NH}_4^+$ -saturated nontronite. A band at  $3472\text{ cm}^{-1}$  was observed by White and Burns (1964) in artificially expanded muscovite following  $\text{H}^+$  saturation and heating. The mineral is dioctahedral and has only tetrahedral substitution, and on this basis the band could arise from proton perturbation of lattice OH groups by analogy with  $\text{H}^+$ -hectorite. Jorgensen (1965) sought a possible explanation of the  $3472\text{ cm}^{-1}$  band in the stretching vibration of a lattice OH group with either two  $\text{Al}^{3+}$  ions and one  $\text{Li}^+$  ion or one  $\text{Al}^{3+}$ , one  $\text{Li}^+$  and one  $\text{Fe}^{2+}$  ions as neighbors by comparison with bands observed in high-lithium micas. However, the  $3472\text{ cm}^{-1}$  band was not observed in  $\text{Li}^+$  or  $\text{K}^+$  saturations of the muscovite following artificial expansion by treatment with molten lithium nitrate.

The proton-perturbed OH group which gives rise to the 3500,  $3476\text{ cm}^{-1}$  doublet in heated  $\text{NH}_4^+$ -hectorite is thermally very stable. The stability of the group can be explained in terms of its environment: the proton is held between a negatively charged apical oxygen and a hydroxyl group on an octahedral Al ion. This can be represented as



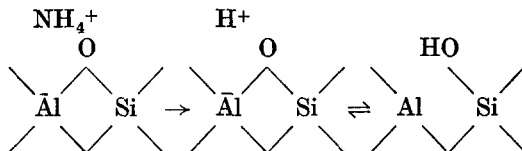
or in the extreme case



This latter arrangement would be expected to be very stable, final dehydroxylation leaving the charge deficiency on  $\text{Al}^{\text{IV}}$  internally balanced by a positive charge on  $\text{Al}^{\text{VI}}$ . Low stabilities of the proton-perturbed OH group in  $\text{NH}_4^+$ -nontronite would result from the higher electron affinity of octahedral  $\text{Fe}^{3+}$  compared with  $\text{Al}^{3+}$ . Normal dehydroxylation would result leaving the charge deficiency internally compensated by  $\text{H}^+$ . Another factor in the failure of  $\text{NH}_4^+$ -nontronite to develop the  $3476\text{ cm}^{-1}$  band strongly is that the mineral dehydroxylated at  $400^\circ\text{C}$  in vacuum at which temperature only 25% of the  $\text{NH}_4$  groups have decomposed. It is to be expected that a stable

proton-perturbed OH group would develop in  $\text{NH}_4^+$ -beidellite in which both octahedral and tetrahedral Al occur.

Recently it has been suggested from a study of thermal decomposition of ammonium zeolites (Uytterhoeven, *et al.*, 1965) that Si-OH groups absorbing at 3670 and 3585  $\text{cm}^{-1}$ , and trigonal Al ions are produced by rearrangement of a Brønsted acid site on the zeolite.



This scheme cannot account for the doublet observed in  $\text{NH}_4^+$ -rectorite since no regeneration of OH groups could take place on treating the heated sample with  $\text{NH}_3$ .

The authors would like to thank Dr. M. M. Mortland for helpful discussions.

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