INFRARED STUDY OF THE THERMAL DECOMPOSITION OF AMMONIUM RECTORITE*

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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 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 H^+, NH_4^+ and 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 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 cm^{-1} to 500 cm^{-1} with the samples in air.

X-ray diffraction patterns were recorded on a GE XRD5 diffractometer, heated samples being held over P_2O_5 and flushed with dry nitrogen to minimize rehydration. The cation exchange capacity of 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 D_2O (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 NH_4^+ absorption bands at 3190, 3050, 2865, and 1450 cm^{-1} shift to 3280 and 1430 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 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 cm^{-1} NH_4^+ deformation band in the dehydrated mineral compared with the 1440 cm^{-1} NH_4^+ band in the hydrated mineral are anomalous. They seem to indicate that 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 cm^{-1} (Fig. 1b).

On heating the NH_4^+-rectorite to higher temperatures in vacuum, NH_4 and OH stretching bands decrease in intensity due to decomposition of NH_4 and dehydroxylation of the mineral and a new absorption band develops at 3476 cm^{-1} (Fig. 2). Maximum development of the band occurs at about 550°C when the mineral spectrum shows neither OH nor NH_4 absorption bands.

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

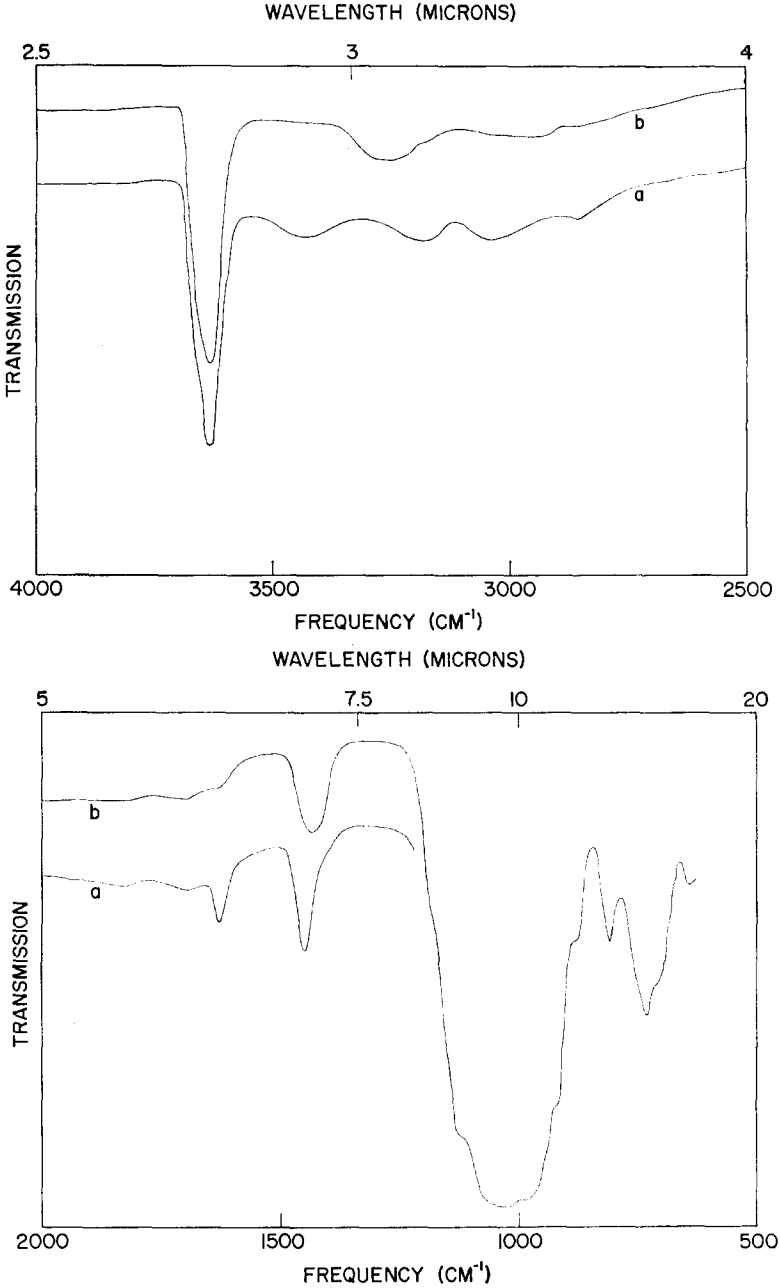


FIG. 1.—Infrared spectra of NH_4^+-rectorite film (a) air-dry, (b) dehydrated by evacuation to 10^{-2} mmHg at room temperature.

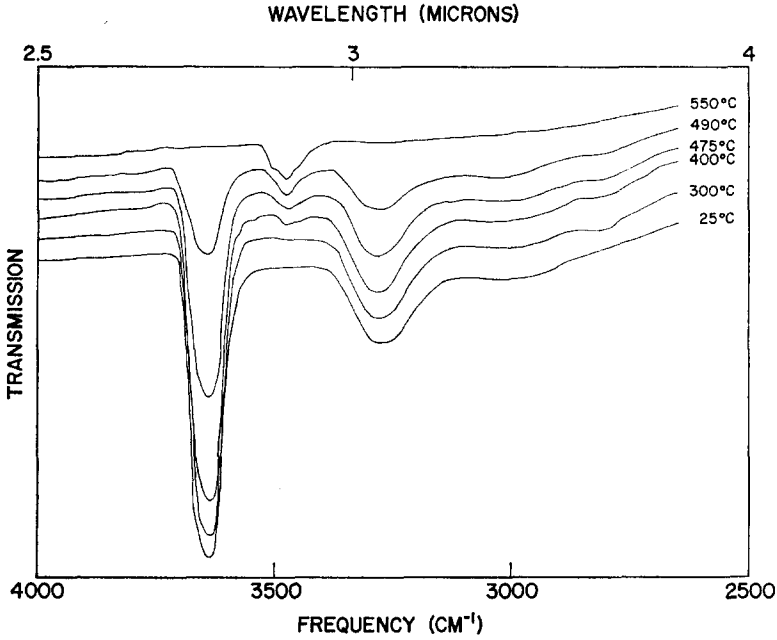


FIG. 2.—Infrared spectra of NH_4^+-rectorite film heated in vacuum to the temperatures shown, then cooled to room temperature in vacuum.

but quite distinct bands at 3445 and 3415 cm^{-1}. With increasing temperature the 3476 cm^{-1} band intensity increased at the expense of the 3440 and 3410 cm^{-1} bands, until by 475°C only the 3476 cm^{-1} band remained. Above 500°C a very sharp band developed at 3500 cm^{-1} on the side of the 3476 cm^{-1} band. This doublet was unchanged after heating the sample for 1 hr at 850°C in vacuum. H^+-saturated rectorite showed the same but weaker band development as NH_4^+-rectorite (Fig. 3), the weakness probably being due to replacement of protons by Al^{3+}. H^+—rectorite aged several months showed only a very weak 3476 cm^{-1} band on heating to 600°C. Neither Ca^{2+}-saturated rectorite nor the natural mineral showed absorption bands in the 3500–3400 cm^{-1} region on heating.

The simple relationship between decreasing O–H and N–H absorption band intensities and increasing intensity of the 3476 cm^{-1} band (Fig. 4) and the fact that the 3476 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 H^+ or H^+ from decomposition of NH_4^+ into NH_3 and H^+):

$$H^+ + \text{OH (lattice)} \rightarrow H^+ \ldots \text{OH (lattice)} \qquad \text{(i)}$$

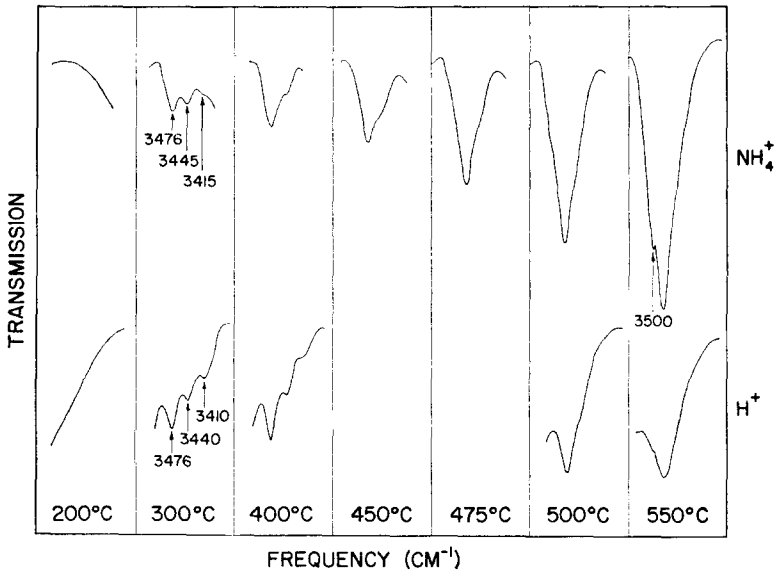


FIG. 3.—Development of the 3476 cm^{-1} band complex (5 × scale expansion) in NH_4^+- and H^+- rectorites heated to the temperatures shown.

and (b) indirect formation of hydronium ions (H_3O^+) from protons and a water molecule resulting from mutual condensation of two lattice OH groups:

$$\left.\begin{array}{l}\text{(lattice)-OH} + \text{HO-(lattice)} \rightarrow H_2O + \text{(lattice)-O-(lattice)} \\ H^+ + H_2O \rightarrow H_3O^+\end{array}\right\} \quad \text{(ii)}$$

Exposure of the heated NH_4^+—rectorite to anhydrous ammonia causes the disappearance of the 3500, 3476 cm^{-1} doublet and the reappearance of an NH_4 stretching vibration at 3280 cm^{-1} whose intensity was equal to that of the original NH_4 band at this frequency, and an O–H stretching band in the range 3650–3630 cm^{-1}, the optical density of which was 8.9% of that of the original O–H stretching band at 3630 cm^{-1} (Fig. 5). Repeated NH_3 treatments failed to cause an increase in either of the regenerated OH or 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 NH_3:

$$H^+ \ldots \text{OH-(lattice)} + NH_3 \rightarrow NH_4^+ + \text{OH-(lattice)} \quad \text{(iii)}$$

and

$$\left.\begin{array}{l}H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O \\ H_2O + \text{(lattice)-O-(lattice)} \rightarrow 2\ \text{OH-(lattice)}\end{array}\right\} \quad \text{(iv)}$$

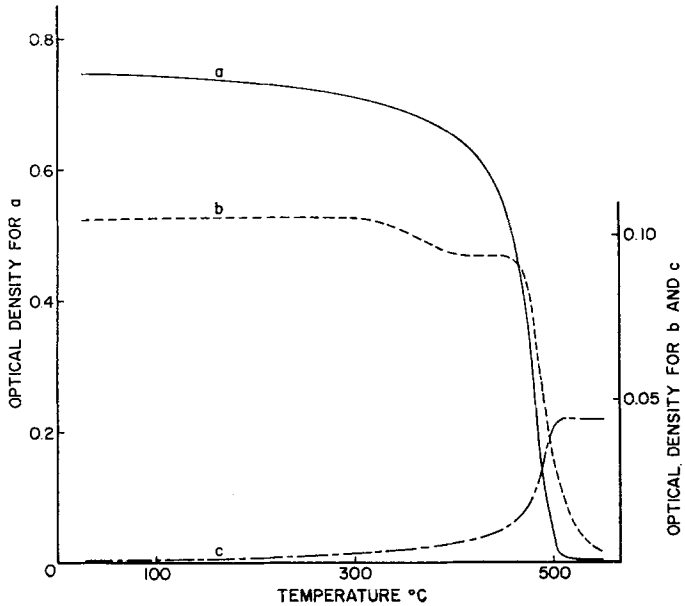


FIG. 4.—Variation with temperature of optical density of (a) lattice O–H stretching vibration, (b) N–H stretching vibration of NH_4, and (c) 3476 cm^{-1} band in NH_4^+-rectorite.

The excellent agreement between observed and calculated values of the proportion of OH groups regenerated by NH_3 treatment, 8.9 and 9.0% respectively, supports the assignment of the 3500, 3476 cm^{-1} doublet to a proton-perturbed OH group. Moreover, a $d(001)$ spacing of 19.2 Å for the NH_4^+-rectorite after heating to 600°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 Å for $d(001)$ spacing of the natural rectorite (predominantly sodium-saturated) after heating to 600°C, although they observed a spacing of 19.1 Å following heating to 300°C. Table 1 shows the changes in $d(001)$ spacing accompanying dehydration and heat treatment of NH_4^+-rectorite. The spacing of 19.77 Å at 300°C, which is in sharp contrast to the 19.1 Å observed by Brown and Weir (1963), is correlated with the appearance in the infrared absorption spectrum of the triplet at 3476, 3445, and 3415 cm^{-1} (Fig. 3) and the commencement of decomposition of NH_4^+ into NH_3 and 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.

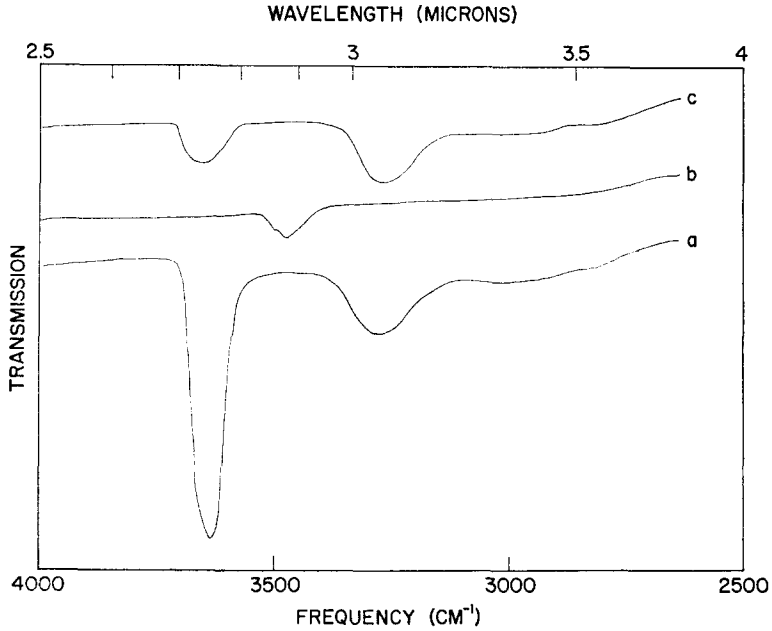


FIG. 5.—Infrared spectra of NH_4^+- rectorite film (a) heated to 200°C in vacuum then cooled to room temperature, (b) heated to 550°C in vacuum then cooled to room temperature, (c) sample (b) exposed to dry NH_3 gas for several hours then evacuated.

TABLE 1.—BASAL SPACINGS FOR AMMONIUM-SATURATED RECTORITE

Treatment	88% Relative humidity	Dry N_2 P_2O_5	200°C*	300°C	400°C	500°C	600°C
d(001)Å	21.37	19.62	19.53	19.77	19.42	19.17	19.20

* The sample heated to the temperatures shown was held over P_2O_5 and flushed with dry nitrogen gas while recording the diffraction pattern.

The progressive decrease in basal spacing from 19.77 to 19.20 Å with rising temperature must be the result of decomposition of these hydronium ions, the resulting protons and those formed from further decomposition of NH_4^+ interacting with lattice OH groups as previously described [equation (i)] to give the 3500, 3476 cm^{-1} doublet.

Treatment of NH_4^+-rectorite with D_2O vapor produced 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

$$\nu_3ND_4/\nu_3NH_4 = 0.750$$

is in good agreement with the value of 0.746 quoted by Mortland *et al.* (1963) for ND_3-treated H^+-montmorillonite. The infrared spectrum of ND_4^+-rectorite after heating to 550°C showed in addition to the 3500, 3476 cm^{-1} doublet another doublet at 2585, 2565 cm^{-1} (Fig. 6). The high frequency

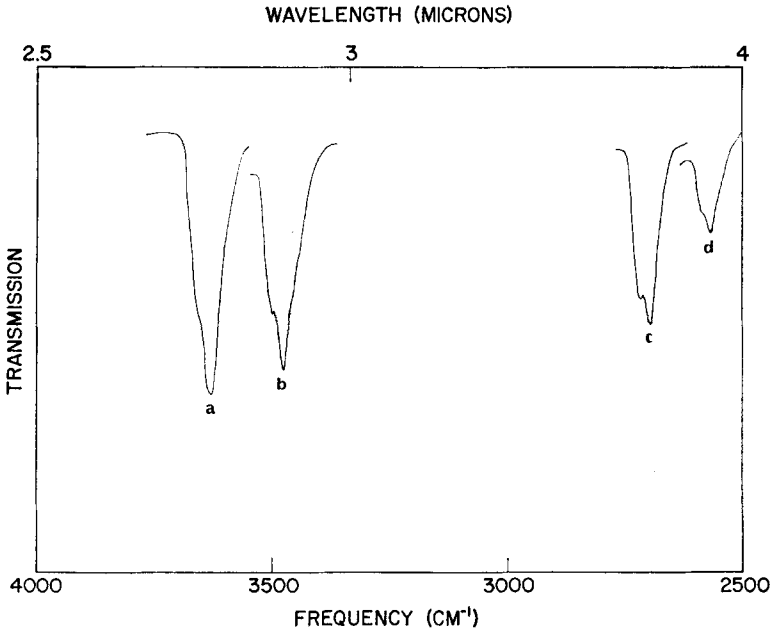


FIG. 6.—Normal and perturbed O–H and O–D stretching vibrations in NH_4^+—rectorite: (a) normal O–H, (b) perturbed O–H (in NH_4^+—rectorite heated to 550°C), (c) normal O–D (in NH_4^+—rectorite heated to 550°C, exposed to D_2O vapor, then evacuated), and (d) perturbed O–D (in NH_4^+—rectorite exposed to D_2O vapor then heated to 550°C).

doublet undoubtedly arises from proton perturbed lattice OH groups: ND_4^+ would be partially reconverted to NH_4^+ by H_2O liberated by dehydroxylation, subsequent decomposition of NH_4^+ giving the doublet. The lower frequency doublet would appear to be due to perturbed lattice OD groups: D^+ from decomposition of ND_4^+ would perturb lattice OH groups, which, because of their proximity to D^+ in the perturbation complex, would undergo H–D exchange. Thus the 2585, 2565 cm^{-1} doublet is assigned to perturbed lattice OD groups and isotopic ratios, $\nu OD/\nu OH$ (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_2O TREATMENT

Group	νOH	νOD	νOD/νOH
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_2O and D_2O			0.740‡

* Roy and Roy (1956).
† Ledoux and White (1964).
‡ Ockman (1958).

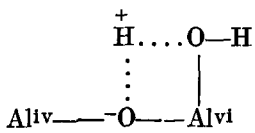
Contrary to the findings of previous investigations (Brindley, 1956) dehydroxylated rectorite can be partially rehydroxylated by exposure to water vapor at room temperature. It was possible then to introduce lattice OD groups into dehydroxylated rectorite by exposure to D_2O vapor. A sample so treated showed a doublet at 2720, 2695 cm^{-1} (Fig. 6). Isotopic ratios of these frequencies with the normal lattice OH frequencies at 3650 (a weak but distinct shoulder), and 3630 cm^{-1} (Fig. 6) are satisfactory (Table 2) and support the assignment of the 2720, 2695 cm^{-1} 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^{-1} perturbed OH doublet only developed at high temperatures (Fig. 3) it can be reasonably concluded that the 3500 cm^{-1} 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

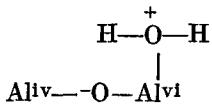
OH groups. Thus, the higher frequency members of the OH, OD doublets shown in Fig. 6 might arise from vibrations of mica-like OH or OD groups, while the lower frequency vibrations have their origin in montmorillonite-like OH or OD groups. There did not appear to be preferential loss of either of the 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 NH_4^+-saturated hectorite, saponite, and Wyoming montmorillonite. It occurred weakly and was of a transient nature in NH_4^+-saturated nontronite. A band at 3472 cm^{-1} was observed by White and Burns (1964) in artificially expanded muscovite following 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 H^+-rectorite. Jorgensen (1965) sought a possible explanation of the 3472 cm^{-1} band in the stretching vibration of a lattice OH group with either two Al^{3+} ions and one Li^+ ion or one Al^{3+}, one Li^+ and one Fe^{2+} ions as neighbors by comparison with bands observed in high-lithium micas. However, the 3472 cm^{-1} band was not observed in Li^+ or 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 cm^{-1} doublet in heated NH_4^+-rectorite 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



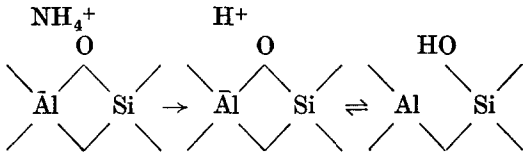
or in the extreme case



This latter arrangement would be expected to be very stable, final dehydroxylation leaving the charge deficiency on Al^{iv} internally balanced by a positive charge on Al^{vi}. Low stabilities of the proton-perturbed OH group in NH_4^+-nontronite would result from the higher electron affinity of octahedral Fe^{3+} compared with Al^{3+}. Normal dehydroxylation would result leaving the charge deficiency internally compensated by H^+. Another factor in the failure of NH_4^+-nontronite to develop the 3476 cm^{-1} band strongly is that the mineral dehydroxylated at 400°C in vacuum at which temperature only 25% of the NH_4 groups have decomposed. It is to be expected that a stable

proton-perturbed OH group would develop in 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 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 NH_4^+-rectorite since no regeneration of OH groups could take place on treating the heated sample with NH_3.

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