

I.R. SPECTROSCOPIC EVIDENCE FOR INTERACTION BETWEEN HYDRONIUM IONS AND LATTICE OH GROUPS IN MONTMORILLONITE

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Abstract—At low levels of hydration, exchangeable D^+ in montmorillonite interacts with lattice OH groups and quantitatively converts $AlMgOH$ groups to $AlMgOD$. Hydroxyl groups coordinated to two Al ions undergo a slower exchange, the extent of which is restricted by octahedral Fe^{3+} ions.

The OH stretching vibration of $AlMgOH$ groups in montmorillonite is assigned an unusually high frequency (3687 cm^{-1}) compared with that of the same group in phengites (3602 cm^{-1}).

INTRODUCTION

THE IMPORTANCE of the surface acidity of clay minerals in controlling adsorption of both organic and inorganic molecules has been outlined by Mortland (1968). While infrared spectroscopy has demonstrated protonation of species adsorbed on H- or Al-montmorillonite (Russell, 1965; Mortland, 1966; Tahoun and Mortland, 1966) the properties of acid clays themselves have not been investigated by this technique. Mortland (1966) suggested that, on dehydration of protonated urea adsorbed on montmorillonite, H^+ becomes dissociated from the protonated species and can migrate into the clay lattice towards negative charge sites in the structure. A consequence of such migration might be seen in perturbation of the lattice OH groups. This paper describes an investigation by i.r. spectroscopy into this possibility using acid montmorillonites of different octahedral compositions.

EXPERIMENTAL

The resin column method described by Barshad (1969) was used to prepare H-montmorillonites although it was subsequently found that these preparations apparently had no advantage in terms of stability over those prepared by a conventional H-resin method. Al, Mg and Na saturations were carried out either on appropriate resin columns or using salt solutions. Oriented films of the montmorillonites whose compositions and origin are shown in Table 1 were prepared by sedimentation on polyethylene sheet; these films were evacuated to 0.002 mm Hg , flushed with D_2O vapour at about 17 mm Hg , and re-evacuated in an i.r. cell similar to that described by Angell and Schaffer (1965).

RESULTS AND INTERPRETATION

Spectra of air-dry films of all the H-montmorillonites investigated show broad absorption near 2900 cm^{-1} . This is illustrated for the samples from Crook County (Fig. 1a) and Chambers (Fig. 2a). The 2900 cm^{-1} band, which is lost after evacuation at room temperature (Figs. 1b, 2b) and a band at about 1700 cm^{-1} (not shown) are thought to be due to the hydronium ion (Falk and Giguere, 1957). Although the 1700 cm^{-1} band is not appreciably affected when the H-montmorillonite is evacuated or flushed with D_2O vapour, it is removed by treatment with gaseous NH_3 . The apparent failure of the 1700 cm^{-1} band to respond to D_2O may be due to its replacement by a deuterium band of different origin, at the same frequency.

H-montmorillonite loses most of its interlayer water in vacuum at 20°C (Figs. 1b, 2b). Residual molecules, showing absorption bands near 3380 and 3645 cm^{-1} which shift to 2492 and 2703 cm^{-1} after D_2O treatment (Fig. 1), are thought to have one of their OH groups weakly hydrogen-bonded to surface oxygens (Russell and Farmer, 1964; Farmer and Mortland, 1966). The 3382 cm^{-1} water band may indicate replacement of some H by Al in the H-montmorillonite, since Parfitt and Mortland (1968) observed a band near 3400 cm^{-1} in the spectrum of evacuated Al-montmorillonite.

In addition to the bands of residual water, spectra of evacuated H-montmorillonites show a weak absorption band near 3530 cm^{-1} , shifting to about 2610 cm^{-1} after D_2O treatment (Figs. 1 and 2), which may arise from perturbation of some of the

Table 1. Source and composition of montmorillonites investigated

Source	Composition	Ref.
Chambers, Arizona	$0.93M^+(Si_{7.98}Al_{0.02})(Al_{2.92}Fe_{0.16}^{3+}Mg_{0.92})O_{20}(OH)_4$	Roberson <i>et al.</i> (1968)
Umiat, Alaska	$0.92M^+(Si_{7.84}Al_{0.16})(Al_{2.96}Fe_{0.36}^{3+}Mg_{0.84})O_{20}(OH)_4$	Anderson and Reynolds (1967)
Wyoming	$0.93M^+(Si_{7.70}Al_{0.30})(Al_{3.12}Fe_{0.37}^{3+}Mg_{0.38})O_{20}(OH)_4$	Heller <i>et al.</i> (1962)
Crook County, Wyoming	$0.54M^+(Si_{7.68}Al_{0.32})(Al_{2.97}Fe_{0.83}^{3+}Mg_{0.45})O_{20}(OH)_4$	Roberson <i>et al.</i> (1968)

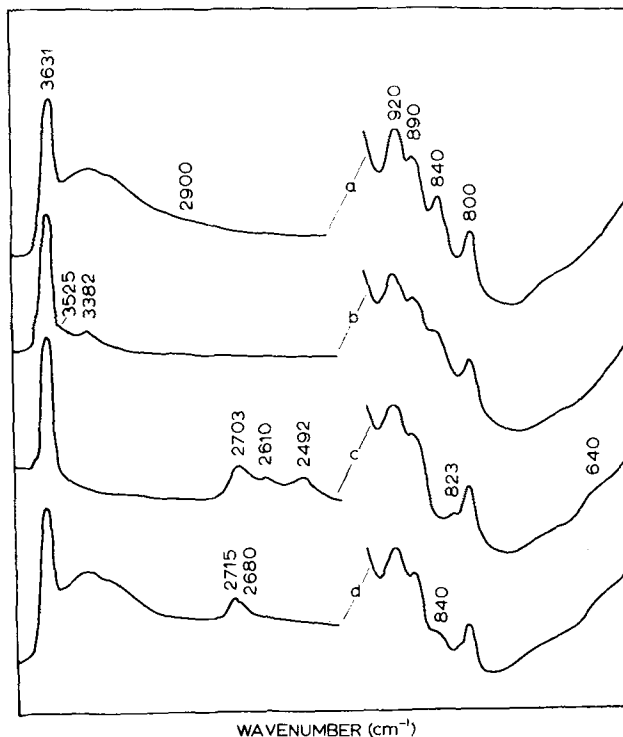


Fig. 1. I.R. spectra of H^+ -montmorillonite from Crook County, Wyoming: (a) untreated; (b) evacuated to 0.002 mm Hg; (c) flushed with D_2O vapour at 17 mm Hg, then evacuated to 0.002 mm Hg; (d) exposed to air at 20°C and 40% relative humidity following treatment (c).

lattice OH groups by H^+ . Similar perturbation by Ca and Mg are thought to produce weak bands at 3533 cm^{-1} in Ca- and at 3496 cm^{-1} in Mg-montmorillonite following dehydration (Russell and Farmer, 1964). The band observed by Rosenqvist and Jorgensen (1964) at 3520 cm^{-1} in NH_4 -montmorillonite heated above the decomposition temperature of NH_4 ions may also be due to a perturbed lattice OH group.

Although the OH stretching region indicates an interaction between H^+ and OH groups, there is no evidence of this from the OH librational frequencies. Bands due to $AlAlOH$ at 920 cm^{-1} ,

$AlFe^{3+}OH$ at 890 cm^{-1} and $AlMgOH$ at 840 cm^{-1} (Russell *et al.*, 1970) show reductions in their intensities (Figs. 1b, 2b) which are not significantly different from those observed for several other cation-saturated montmorillonites (Russell and Farmer, 1964). However, after treatment with D_2O vapour, which in itself produces no change in pattern on the $950\text{--}800\text{ cm}^{-1}$ region, evacuation leads to the replacement of the 840 cm^{-1} band of $AlMgOH$ by the $AlMgOD$ frequency at 640 cm^{-1} (Figs. 1c, 2c). Partial regeneration of the 840 cm^{-1} band occurs on exposure of the treated specimens to air humidity and is complete after subsequent

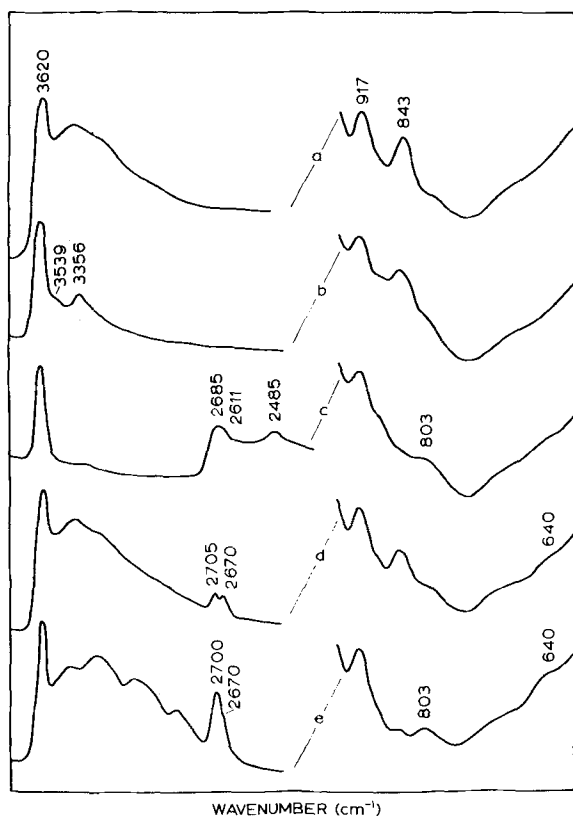


Fig. 2. I.R. spectra of H^+ -montmorillonite from Chambers, Arizona: (a) untreated; (b) evacuated to 0.002 mm Hg; (c) flushed with D_2O vapour at 17 mm Hg, then evacuated to 0.002 mm Hg; (d) exposed to air at 20°C and 40% relative humidity following treatment (c); (e) exposed to NH_3 at atmospheric pressure then air following treatment (c).

evacuation. Regeneration in air is greater for the Chambers sample (Fig. 2d) than for the specimen from Crook County (Fig. 1d). The Chambers sample has a lower iron content and less Al-for-Si substitution. Re-exchange of the AlMgOD group in air was minimized when, following D_2O flushing and evacuation, the montmorillonites were treated with gaseous NH_3 without exposure to air. This rapidly converted D^+ to NH_4^+ , thereby immobilizing the proton. The spectrum of the Chambers montmorillonite after this D_2O/NH_3 treatment (Fig. 2e) shows a very weak AlMgOH band at 840 cm^{-1} , a well-developed AlMgOD band at 640 cm^{-1} and a pronounced band at 2700 cm^{-1} with an inflexion at 2670 cm^{-1} . From its position and its inverse intensity relationship with the 840 cm^{-1} AlMgOH band, the 2700 cm^{-1} absorption must be due to the stretching vibration of the

AlMgOD group. The band of the corresponding AlMgOH vibration, which should occur in the range 3700–3650 cm^{-1} , was found at 3687 cm^{-1} in the montmorillonite from Crook County (Fig. 3) and at 3677 cm^{-1} in that from Chambers. Compared with the frequencies of AlAlOH vibrations, the AlMgOH frequencies in montmorillonite are some 56 cm^{-1} higher, while in phengites they are about 30 cm^{-1} lower (Farmer *et al.*, 1967).

Following D_2O treatment the principal AlAlOH stretching frequency at 3631 cm^{-1} in the Crook County montmorillonite suffers a small (<5 per cent) drop in intensity (Fig. 3) which can be correlated with the appearance of a weak AlAlOD stretching frequency at 2680 cm^{-1} (Fig. 1d). The weak band at 2670 cm^{-1} in spectra of the Chambers montmorillonite is similarly related to the original AlAlOH stretching frequency at 3620 cm^{-1} . The intensity of the 2670–2680 cm^{-1} AlAlOD band increases with the time of exposure of the sample to D^+ , more rapidly in the low-iron Chambers sample than in the Crook County specimen.

Spectra of D_2O -treated montmorillonites show, in addition to AlMgOD stretching and librational frequencies, a weak absorption band in the 800–825 cm^{-1} region. Assignment of this band to an OD bending vibration is uncertain since the corresponding OH vibration (assuming an average isotopic shift ratio) would be masked by the intense Si–O stretching vibration near 1050 cm^{-1} . However, the band is clearly due to translatory or librational vibrations of OD linked to Al and Mg, whose frequency appears to be dependent on neighbouring octahedral cations: it occurs at 803 cm^{-1} in the Chambers sample (Fig. 2e), 818 cm^{-1} in the Wyoming and Umiat samples (not shown) and 823 cm^{-1} in the sample from

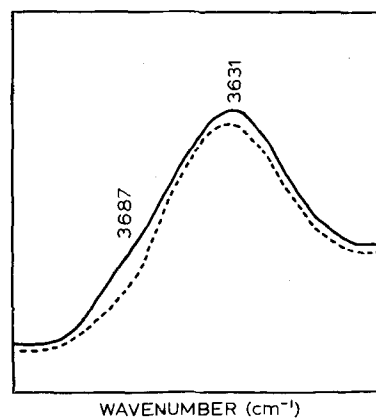


Fig. 3. Hydroxyl stretching vibration of H^+ -montmorillonite from Crook County, Wyoming: full line, original; broken line, evacuated, flushed with D_2O vapour, evacuated to 0.002 mm Hg then exposed to air.

Crook County (Fig. 1c), i.e. at frequencies which increase with increasing iron content. Fully deuterated montmorillonites have been found to absorb at $803\text{--}805\text{ cm}^{-1}$ with an inflexion on the high-frequency side of the band for the more iron-rich compositions (Russell *et al.*, 1970).

Even though the H-saturated montmorillonites investigated were freshly prepared before use, they will contain exchangeable Al as a result of proton attack on the structure. The presence of exchangeable Al in the montmorillonite does not affect the interpretation of the results of deuteration since it has been found that Al-montmorillonites behave like H-montmorillonites in their ability to undergo deuteration. Consequently, the bands observed at 2704 and 2688 cm^{-1} by Ahlrichs (1968) in Al-montmorillonite treated with D_2O may be re-assigned to AlMgOD and AlAlOD groups respectively.

Deuteration of lattice OH groups is very much slower in Mg-montmorillonites than in the H or Al forms, and can not be detected in Na-montmorillonite. These observations are in accord with the concept of the acidity of water molecules coordinated to exchange cations in montmorillonite (Mortland, 1968).

DISCUSSION

Replacement of Al by Mg in the octahedral layer of the montmorillonite structure results in incomplete neutralization of negative charges on the apical oxygens and OH groups coordinated to Mg. Small, mobile, positively charged ions should be capable of migrating to the vicinity of the negative charge. Although several investigators, among them Rosenqvist and Jorgensen (1964), have postulated that the apical oxygens readily accept protons and generate new lattice OH groups, the present findings do not support this contention.

Direct spectroscopic evidence for the migration of protons in H-montmorillonites may be found in the band near 3530 cm^{-1} which is thought to arise from perturbation of some of the lattice OH groups by protons. More convincing evidence is provided by montmorillonites containing D^+ and D_2O , in that the conversion of AlMgOH groups to AlMgOD must involve migration of D^+ and interaction with OH groups. By implication, interaction and exchange of H^+ with OH groups must also occur.

While protons and deuterons migrate principally to negatively charged AlMgOH groups in montmorillonite, migration to uncharged AlAlOH groups also occurs as shown by the appearance of AlAlOD groups. The latter type of migration appears to be diffusion controlled and may be

blocked by octahedral Fe^{3+} : it has been found that Al Fe^{3+} OH groups in montmorillonite are not deuterated even at 400°C (Russell *et al.*, 1970).

The mechanism by which protons (and deuterons) migrate from the interlayer to lattice OH groups is linked to the state of hydration of the proton, rapid migration occurring when excess adsorbed H_2O (or D_2O) has been removed. The H^+ (or D^+) species thereby achieve sufficient mobility or a suitably small cross-section to approach the lattice OH groups. Zundel and Metzger (1968) drew similar conclusions from resin systems, claiming that when the number of water molecules coordinated to a proton falls below two, the proton becomes dissociated and migrates to the anion. It is unlikely that the migrating species in the interlayer space of H-montmorillonite is the free proton because the energy of hydration of the proton is very high. The mobile species produced by partial dehydration of the montmorillonite is probably H_3O^+ or H_5O_2^+ from which H^+ is transferred to lattice OH by a low-energy mechanism. Two possibilities are: (i) transfer via the surface oxygens and apical oxygens to the OH group; (ii) direct transfer from the hydronium species. Both mechanisms involve large ($3.0\text{--}3.2\text{ \AA}$) oxygen-oxygen separations over which the transfer has to be made, but the second may be more practicable if the hexagonal hole were to expand slightly allowing the hydronium species a closer approach to the OH group.

Although the mechanism is speculative, spectroscopic evidence for migration of protons in H-montmorillonite and interaction and exchange with lattice OH groups is conclusive. Because of the ease with which the exchange reaction with D^+ occurs in montmorillonites saturated with strongly polarizing cations, care is required in interpreting spectra of smectites with synthetic interlayers, for which treatment with D_2O has been used to distinguish the OH absorption bands of the interlayer species from those of the smectites.

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Résumé—A tous les niveaux d'hydratation, le D^+ interchangeable dans la montmorillonite réagit sur les groupes OH croisés et, quantitativement, transforme les groupes $AlMgOH$ en $AlMgOD$. Les groupes hydroxyles coordonnés aux deux ions Al subissent un échange plus lent, dont l'étendue est restreinte par les ions octaédriques de Fe^{3+} . La vibration tendant à OH des groupes $AlMgOH$ dans montmorillonite a une haute fréquence inhabituelle (3687 cm^{-1}) par comparaison avec celle du même groupe dans les phengites (3602 cm^{-1}).

Kurzreferat—Auf zwei Ebenen der Hydratation reagiert austauschbares D^+ in Montmorillonit mit Gitter-OH Gruppen und verwandelt quantitativ $AlMgOH$ Gruppen in $AlMgOD$ Gruppen. Hydroxylgruppen, die mit zwei Al Ionen koordiniert sind erfahren langsameren Austausch, wobei das Ausmass desselben durch oktaedrische Fe^{3+} Ionen begrenzt wird.

Der OH Dehnvibration von $AlMgOH$ Gruppen in Montmorillonit wird eine Frequenz (3687 cm^{-1}) zugeschrieben, die im Vergleich mit der derselben Gruppe in Phengiten (3602 cm^{-1}) ungewöhnlich hoch ist.

Резюме — При низких степенях гидратации обменный ион D^+ в монтмориллоните взаимодействует с группами OH, входящими в кристаллическую решетку, и количественно переводит группы $AlMgOH$ в $AlMgOD$. Гидроксильные группы, координированные двумя ионами Al, подвергаются более медленному обмену, степень которого ограничена октаэдрическими ионами Fe^{3+} .

Деформационные колебания OH в группах $AlMgOH$ в монтмориллоните имеют необычно высокую частоту (3687 см^{-1}) по сравнению с частотой колебания этих групп в фенгитах (3602 см^{-1}).