SYMPOSIUM ON SPECTROSCOPIC TECHNIQUES

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INFRARED ABSORPTION SPECTROMETRY IN CLAY STUDIES

by

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ABSTRACT

THE relationships between spectrum and structure in layer-silicates are reviewed, and applied in the study of structural changes occurring during the heating of montmorillonites up to dehydroxylation, and their subsequent rehydroxylation. Information given by infrared spectroscopy on the binding of water in expanding layer silicates is presented, and the physical and chemical processes associated with entry of basic, neutral and acidic molecules into the interlayer space of these minerals are illustrated for ammonia, ethylamine, pyridine, nitrobenzene, and benzoic acid. Problems associated with the study of soil clays, which are often complex mixtures including poorly ordered and amorphous constituents, frequently firmly combined with organic matter, are discussed.

New evidence is presented concerning the environment of the two types of hydroxyl group in beidellite. The thermal stabilities of NH_4^+ and lattice OH in montmorillonite and beidellite, and the properties of their dehydroxylates, are contrasted. The nature of the collapsed phase formed in Li-, Mg-, and NH_4-montmorillonite at 300–500°C is discussed. The presence of weak hydrogen bonds between lattice oxygens and interlayer water is established, although it is shown that the strength of hydrogen bonds formed between NH_4^+ and lattice oxygens is dependent on the sites of substitution in the layer lattice.

INTRODUCTION

INFRARED studies on clays at the Macaulay Institute have been directed towards characterizing the types of clay mineral that occur naturally in soils, and to obtaining information on the surface properties and reactivity of these minerals. As with all physical methods of investigation, the achievement of these aims has required the solution of many problems of technique and interpretation that are raised by the method of investigation itself. On the one hand, infrared methods have the potential to solve many problems in clay studies, if techniques capable of yielding unambiguous results were available. On the other hand, the infrared spectrum has been found to contain a considerable amount of information which cannot yet be fully interpreted.

This paper is concerned with problems of interpretation that have arisen in the course of infrared studies at the Macaulay Institute during the last

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ten years and includes some new observations amplifying previously published work. These studies fall naturally into two parts: namely, studies of the vibrations of the hydroxy-silicate structure, and studies of the binding of water and of other molecules and ions in the interlayer space of expanding silicates.

Acknowledgment must be made here to the many collaborators and assistants who have participated in the work, but particularly to Dr. R. L. Mitchell, who recognized so early the potentialities of infrared spectroscopy in soil studies, and who has given the work his continuous support, and to Dr. R. C. Mackenzie, who made his knowledge of clay mineralogy and his collection of well-characterized clay minerals freely available.

THE HYDROXY-SILICATE LATTICE

Vibrations of the Hydroxyl Group

OH stretching.—Vibrations involving the proton, that is, OH stretching and bending vibrations, are very largely independent of the vibrations of silicon and oxygen in the rest of the lattice. These proton vibrations are directly affected by the immediate environment of the proton and can yield information on this environment. The importance of their study was early recognized, but the OH stretching region could not be adequately examined until grating spectrometers giving well resolved spectra such as those in Figs. 1–3 (Farmer and Russell, 1964) became available. Not all the differences in spectra are as yet adequately understood. Perhaps the most striking anomaly is that the OH groups in pyrophyllite absorb at 3675 cm^{-1} whereas the inner OH groups in the kaolin minerals, which apparently have the same environment, absorb at 3620 cm^{-1}. In the dioctahedral series, substitution of Al for Si in the lattice causes a marked broadening in the absorption bands, as in the muscovite and beidellite spectra. The two components in the beidellite spectrum, at 3660 cm^{-1} and 3630 cm^{-1}, must arise from two types of OH, differing, perhaps, with respect to the site of Al-for-Si substitution in neighboring tetrahedra. The lower frequency component weakens considerably when interlayer water is removed from beidellite, indicating that the interlayer cation moves into close proximity with these OH groups. The divalent cation Ca^{2+} has a greater effect than monovalent cations and gives rise to a perturbed OH vibration near 3550 cm^{-1} (Farmer and Russell, 1966). Similar perturbed OH bands appear in the spectra of Ca- and Mg-montmorillonite following dehydration (Russell and Farmer, 1964).

A recent observation made on oriented beidellite films is that the OH group absorbing at 3660 cm^{-1} lies more nearly parallel to the layer sheets than does the OH group absorbing at 3630 cm^{-1}. It may be that the proton of the latter OH is attracted out of the oxygen layer in which it lies, towards an oxygen associated with a site of Al-for-Si substitution in the tetrahedral sheet on the opposite side of the octahedral sandwich. Coordination of the

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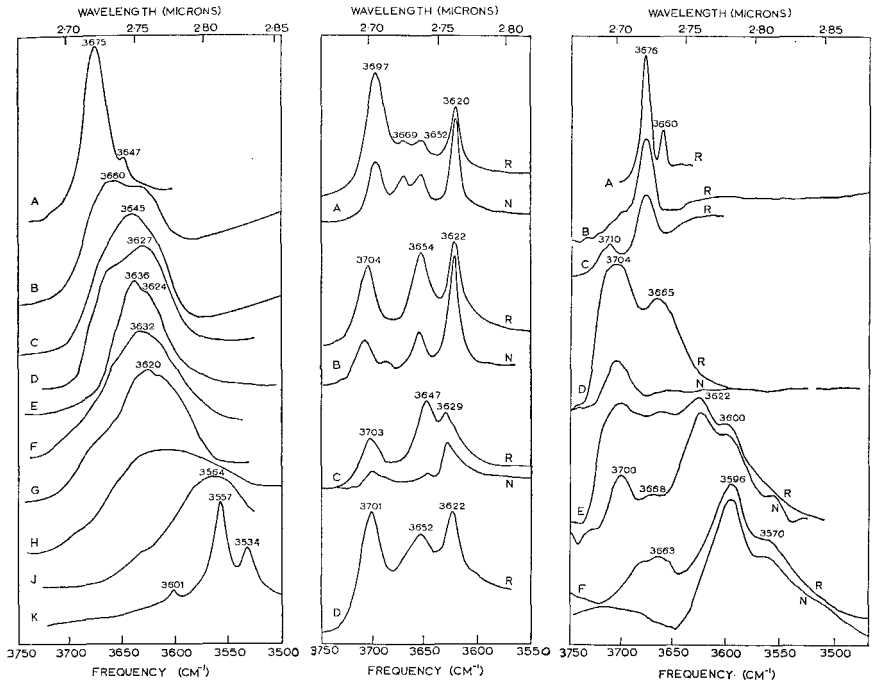


FIG. 1 FIG. 2 FIG. 3

FIG. 1. Hydroxyl absorption bands of randomly oriented samples of A—pyrophyllite, B—beidellite, C—rectorite, D—muscovite or paragonite, E—margarite, F—Wyoming montmorillonite, G—Skyrvedalen montmorillonite, H—Woburn montmorillonite, J—nontronite and K—ferric celadonite.

FIG. 2. Hydroxyl absorption bands of A—kaolinite, B—dickite, C—nacrite, D—Pugu D kaolinite. R indicates randomly oriented specimens, and N films at normal incidence.

FIG. 3. Hydroxyl absorption bands of A—talc, B—hectorite, C—saponite, D—phlogopite (126 μ), E—green biotite (115 μ), and F—dark brown biotite (25 μ). The mica spectra were obtained from single flakes of the thickness indicated at normal (N) and 45° incidence (R).

exchangeable cation to this OH can then assist in transmitting the cation charge through the silicate lattice when water is removed.

Substitution of Fe^{3+} for octahedral Al^{3+}, as in nontronite and celadonite, causes a striking shift of the OH band to lower frequencies. The extreme sharpness of the OH stretching bands in ferric celadonite can probably be correlated with the absence of Al-for-Si substitution, and with the regularity of the octahedral substitution, as each OH is coordinated to a divalent and a trivalent ion. The two bands at 3557 and 3534 cm^{-1} may arise from OH

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groups associated with Fe^{3+}—Mg^{2+} and Fe^{3+}—Fe^{2+}, respectively. Other celadonites and glauconites examined give less sharp spectra, with additional strong OH absorption near 3603 and 3577 cm^{-1}. The additional bands may be correlated with the presence of Al^{3+} in the octahedral layer, and the greater breadth of the bands with Al-for-Si substitution in the lattice. The sharp celadonite spectrum contrasts strikingly with those of montmorillonites, in which substitution is also principally in the octahedral layer. The diffuseness of montmorillonite spectra may be due to the irregularity of the substitution pattern in this mineral.

The spectra of the kaolin minerals (Fig. 2) have provoked a long-continuing discussion, as the problems to be resolved increased with increasing resolving power of the spectrometers used in their study. Considerations based solely on the known lengths of the hydrogen bonds in this mineral lead to the assignment of the highest frequency band to the inner OH group of the kaolinite structure, but Ledoux and White (1964) have conclusively established that the lowest frequency band arises from the inner hydroxyl and that the three higher frequency bands arise from the hydroxyls on the surface of the kaolinite layer. Clearly factors other than hydrogen-bond lengths are important in determining OH stretching frequencies.

Again, the assumption that each absorption band arises from a distinct type of OH implies that there are three different types of surface OH: one type oriented perpendicular to the sheets giving the 3697 cm^{-1} band and two others oriented more nearly parallel to the sheets, giving rise to the 3669 and 3652 cm^{-1} bands. The spectrum can, however, be satisfactorily explained in terms of the structure indicated by X-ray diffraction, in which the surface OH groups are all nearly normal to the layers. Coupling between the three, nearly equivalent, surface OH groups in the unit cell can be expected to give one in-phase vibration with strong absorption perpendicular to the layers, and two out-of-phase vibrations with weak absorption in the plane of the layers (Farmer and Russell, 1964; Farmer, 1964). Figure 4 illustrates the operation of these coupling forces in the simpler case of two OH groups related by a plane of symmetry and a two-fold axis of symmetry. The symmetric vibration (Fig. 4*a*) has a change in dipole moment along the two-fold axis while the anti-symmetric vibration (Fig. 4*b*) has its dipole change perpendicular to the axis. Because of coupling through the electric fields associated with the vibrating protons the symmetric vibration would have a higher frequency.

The rather different pattern given by nacrite and dickite implies that the surface OH groups in these minerals are less nearly equivalent than those in kaolinite. Small amounts of dickite- and nacrite-type stacking in kaolinite crystals would be expected to give stronger absorption near 3650 cm^{-1} than is found in regularly stacked kaolinites. Such absorption is in fact a common feature of kaolinites from many localities, although the stacking irregularities are not sufficiently numerous to be obvious in the X-ray pattern. This band is strongly developed in Pugu D kaolinite (Fig. 2D) where the stacking

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irregularities lead to a *b*-axis disordered type of X-ray diffraction pattern. The infrared spectrum suggests, therefore, that the disorder in this mineral arises from a random sequence of kaolinite-type and either dickite- or nacrite-type stacking.

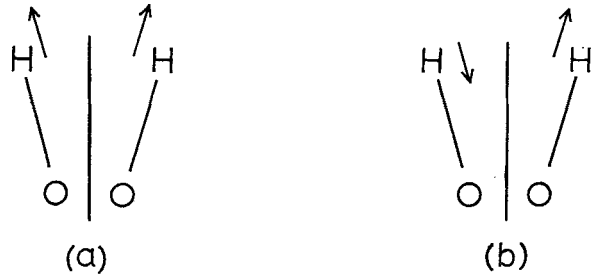


FIG. 4. The symmetrical (*a*) and antisymmetrical (*b*) vibrations of two hydroxyl groups related by a plane of symmetry and a two-fold axis of symmetry, lying in the plane.

In the trioctahedral minerals, Al-for-Si substitution, as in saponite, and Li-for-Mg substitution, as in hectorite, have little apparent effect on the OH stretching frequency. The higher frequency band of saponite at 3710–20 cm^{-1} has been found to appear only when interlayer water is removed from this mineral, and only when it is saturated with the monovalent cations, K^+, Na^+ or NH_4^+ (Farmer and Russell, 1966). It must be ascribed to OH groups whose vibrations are perturbed by the electric field of these monovalent ions, which are positioned directly over OH groups in the anhydrous state. This effect can therefore account for the higher frequency of the principal OH absorption band of phlogopites, near 3704 cm^{-1} (Fig. 3D). Vedder (1964) has suggested that substitution of Fe^{2+} for Mg^{2+} in talc causes a low-frequency shift in the OH vibration, and our study of a series of analysed phlogopites and biotites indicates that a similar effect can be detected in these minerals, so that OH groups associated with ($Mg_2^{2+}Fe^{2+}$) groupings absorb at 3685 cm^{-1}, and those associated with ($Fe_2^{2+}Mg^{2+}$) groupings absorb near 3660 cm^{-1} (see also Jørgensen, 1966). These bands are much broader in biotites than in talc, and so overlap to a considerable extent. This effect cannot, of course, account for the 3665 cm^{-1} band which appears in most phlogopites, where Fe^{2+} is low or absent; this band may arise from ($Al^{3+}Mg_2^{2+}$) groupings (Vedder, 1964).

The group of lower frequency bands in biotites in the 3530–3620 cm^{-1} region are almost certainly associated with vacancies in the octahedral layer, but assignment of the individual components can still not be considered satisfactory. The marked effect of Fe^{3+} on the OH stretching frequencies in the dioctahedral layer silicates suggests that this ion may be associated with the lower frequency bands in biotites, while Al^{3+} is associated with the higher frequency bands.

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OH bending.—The OH bending or rocking vibration has not yet been identified in the trioctahedral minerals. In the dioctahedral minerals two OH bending vibrations are to be expected, one with the change in dipole moment in the plane of the sheets, and one nearly perpendicular to this plane, but only the in-plane type has been identified, lying in the 800–950 cm^{-1} region. A band near 400 cm^{-1} has been ascribed to the out-of-plane vibration of the OH group in muscovite (Vedder and McDonald, 1963), but, according to spectra shown in a later publication (Vedder, 1964), this band does not show the appropriate polarization behaviour.

In the montmorillonite group, the bending vibration of OH groups associated with two Al^{3+} ions occurs near 920 cm^{-1}; those associated with two Fe^{3+} ions absorb near 820 cm^{-1}, while vibrations associated with an Al^{3+}—Fe^{3+} pair appear to absorb in the region 845–890 cm^{-1}. This last band is dominant in a montmorillonite (Woburn Fuller's Earth; Heller *et al.*, 1962) which had a particularly high iron content, but is commonly present as a subsidiary band in most published spectra of montmorillonites. Exceptions are montmorillonites from Cheto (Grim and Kulbicki, 1961) and Skyrvedalen (Farmer and Russell, 1964) which are very low in iron. This band is characterized by its ready elimination from the spectrum under reducing conditions (Farmer and Russell, 1964): indeed, simple exposure to hydrazine vapor has been found to be sufficient (Russell, Munsus, and White, unpublished). By this treatment, the spectrum of Wyoming montmorillonite becomes identical with that of Cheto montmorillonite, suggesting that the only difference between these species is the iron content of the former.

Vibrations of the Silicate Anion

The OH stretching and bending vibrations are localized on the proton, but none of the vibrations involving silicon, oxygen, and the octahedral cations can be localized on any one of these atoms. The silicate anion itself gives rise to eighteen vibrations, and the lower frequency vibrations of this structure, especially those of the inner oxygen layer, can be expected to be mechanically coupled with translational vibrations of the octahedral cations and of the OH groups, whose presence contribute another six vibrations. The problem of assignment of the absorption bands is therefore of some complexity (Farmer and Russell, 1964; Vedder, 1964). The high symmetry of the talc structure simplifies the problem, as many of its vibrations are inactive in the infrared. The silicate anion then gives only five absorption bands, two of which have dipole moments perpendicular to the sheets, and three parallel to the sheets. Oriented preparations permit the in-plane vibrations to be distinguished from the perpendicular vibrations (Fig. 5), and a reasonable assignment can be made for trioctahedral layer silicates on this basis (Farmer, 1958). The in-plane Si—O—Si stretching vibrations are degenerate in talc, giving a single band near 1020 cm^{-1}, but are split into two components in the dioctahedral series of layer silicates because of distortion of the tetrahedral layer (Fig. 6, Farmer and Russell, 1964). This distortion

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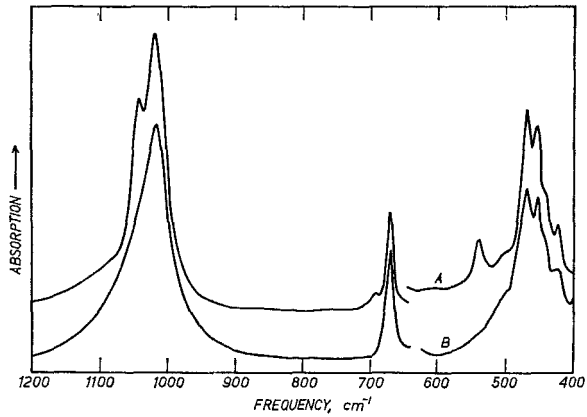


FIG. 5. Infrared spectrum of talc. A—sample in KBr pressed disk; B—oriented film on KBr window.

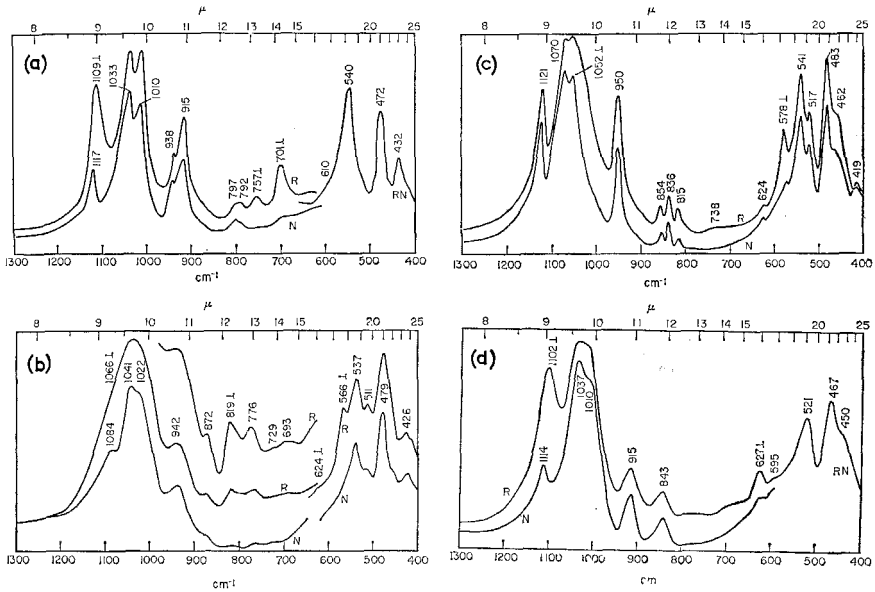


FIG. 6. Infrared spectra of (*a*) kaolinite, (*b*) beidellite, (*c*) pyrophyllite, and (*d*) Skyrvedalen montmorillonite. R indicates randomly oriented samples, N films at normal incidence, and RN spectra independent of orientation.

also causes a band near 1100 cm^{-1} to appear, arising from an in-plane vibration which is inactive in talc. The high frequency of this vibration is rather surprising, as is also that of the perpendicular Si—O^- vibration, which appears in the 1050–1110 cm^{-1} region; they are certainly not accounted for

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in terms of the force-constants of the bonds involved. In these vibrations, which are associated with the development of strong dipole moments, account must be taken of the electric fields produced by the oscillating dipoles. Stretching of the Si—O^- bonds causes the thin plates of the layer silicate crystals to become electrically polarized like the dielectric in a parallel-plate condenser. The resultant field, acting on the vibrating ions, can account for the high frequency of the perpendicular Si—O^- stretching vibration. The maximum effect is apparent only for very thin crystals of thickness 0.1 μ or less. With thicknesses of the order of 1 μ, such as occur in crystals of dickite, nacrite, and some kaolinites, the Si—O^- stretching vibration is shifted to a significantly lower frequency (Farmer and Russell, 1966).

The Characterization of Clay Structures and their Reactions

The infrared spectrum is determined by the atomic masses, and by the geometry and force-constants of the interatomic bonds within the individual layers of a layer silicate. It therefore reflects aspects of the structure different from those which determine X-ray diffraction patterns and thermal curves, and gives results largely complementary to these techniques. Thus different types of montmorillonite, such as Cheto, Wyoming, Woburn Fuller's Earth, and beidellite, are readily distinguished by their infrared pattern, although indistinguishable by X-ray diffraction (Farmer and Russell, 1964).

It is illuminating, therefore, to re-examine the thermal reactions of montmorillonites by infrared techniques. Montmorillonite when saturated with Li^+ and Mg^{2+} has been long known to collapse to a 9.5 Å phase after heating at 300–550°C (Greene-Kelly, 1953). This behaviour was ascribed to migration of these small cations into the octahedral layer, giving a pyrophyllite-like structure. The infrared spectrum clearly distinguishes the charged montmorillonite structure from the neutral pyrophyllite structure, and examination of heated montmorillonite samples showed that the pyrophyllite pattern did not develop under these conditions (Russell and Farmer, 1964), but only appeared after montmorillonite had been completely dehydroxylated at 750°C and then rehydroxylated in steam (Heller *et al.*, 1962). The spectra of Li-, Mg-, and NH_4-montmorillonite heated to 350°C did, however, show certain features in common, not shown by Na- or Ca-montmorillonite, and this led to a search for other common properties. As a result it was established that these collapsed montmorillonites all gave strongly acid reactions with indicators in ethylene glycol, and that they could be completely re-expanded by treatment with NH_3 vapor, with the formation of NH_4^+ ions in the interlayer space (Russell and Farmer, 1964).

The development of acidity in NH_4–montmorillonite is clearly due to thermal decomposition of NH_4^+, with loss of NH_3 and liberation of a proton. With Mg- and Li-montmorillonite, protons can only be liberated by reaction of the interlayer cations either with residual water molecules or with lattice OH groups.

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Recent results obtained with samples which have been re-expanded with NH_3 (Table 1) indicate that just over half of the original lithium content is no longer exchangeable and has presumably migrated into vacant octahedral sites. There it effectively neutralizes the negative lattice charge and the exchange capacity is correspondingly reduced. Two-thirds of the magnesium ions are no longer exchangeable but the exchange capacity is only reduced by about one-third. Possibly the excess positive charge arising from migration of Mg^{2+} into an octahedral site causes ionization of an overlying lattice OH group. Much of the original acidity indicated by the high NH_4^+ contents immediately after NH_3 treatment is lost after the samples have been equilibrated with ammonium acetate solution.

TABLE 1.—CATION CONTENTS (meq/100 g) OF MONTMORILLONITES, RE-EXPANDED WITH NH_3 FOLLOWING HEATING TO 400°C

Exchangeable cation (a)	NH_4 content after treatment (b)	Exchange capacity (c)	Li and Mg displaced (d)
Li^+	45	45	39
Mg^{2+}	84	54	32
NH_4^+	105	84	

(a) Initial content of 90 meq/100 g.
(b) NH_4^+ content immediately after re-expansion with NH_3.
(c) NH_4^+ content after equilibrating re-expanded samples with neutral ammonium acetate.
(d) Amounts of Li and Mg displaced by ammonium acetate solution.

These results imply, for Li-montmorillonite, that part of the exchangeable Li migrates into the octahedral layer and becomes fixed there, but does not liberate a proton, while the remainder reacts with interlayer water or lattice hydroxyl to yield a proton, but remains in, or close to, the interlayer space. The latter reaction is reversed when the collapsed phase is re-expanded and equilibrated with ammonium acetate, and the lithium ions involved then become exchangeable. A similar process probably proceeds in Mg-montmorillonite although in this instance each Mg^{2+} which migrates into the octahedral layer also liberates a proton.

Beidellite is commonly distinguished from montmorillonite by the fact that Li-beidellite does not collapse after heating to 300°C. Our observations indicate that these minerals are also distinguished by the very different thermal stability of NH_4^+ on the exchange sites. Thermal decomposition of NH_4^+ and loss of lattice OH is readily followed by infrared spectroscopy, and the results (Fig. 7) show that NH_4^+ begins to decompose in montmorillonite at about 150°C, and that decomposition is completed before dehydroxylation of the mineral is complete. In beidellite the NH_4^+ does not begin to decompose until dehydroxylation begins, and is not complete till after dehydroxylation is complete. In montmorillonite the spectrum gives no

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indication of the presence of the proton liberated by decomposition of the NH_4^+, but in beidellite an OH doublet develops near 3450 cm^{-1} and persists to over 800°C, although normal lattice OH is eliminated by 650°C. A similar band develops when NH_4-rectorite (Russell and White, 1966) and NH_4-muscovite (White and Burns, 1963) are heated, so its appearance is clearly associated with Al-for-Si substitution in dioctahedral minerals. No such

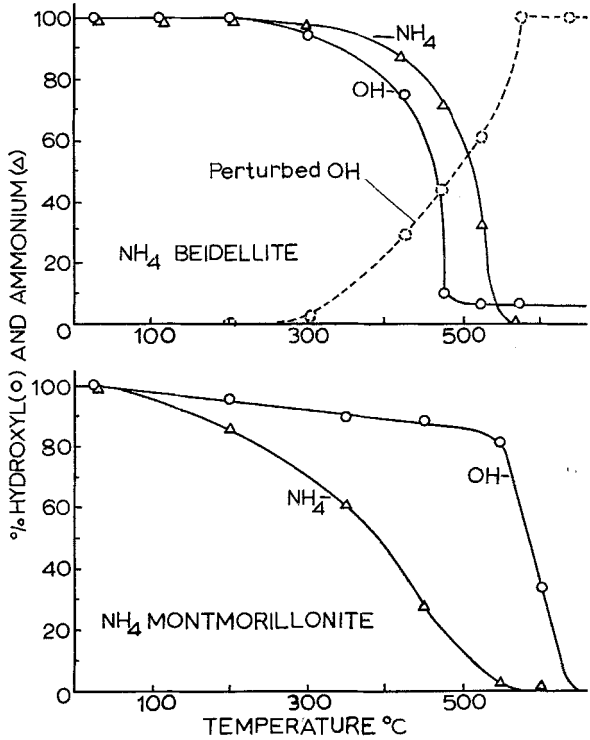


FIG. 7. Loss of (*a*) ammonium and (*b*) lattice hydroxyl groups from montmorillonite and beidellite. Dashed line indicates the development of an OH band near 3450 cm^{-1} in beidellite.

band appears in saponite or hectorite when NH_4^+ in these clays is thermally decomposed. Although the work on rectorite has suggested that the proton liberated by decomposition of NH_4^+ associates with an OH group in the vicinity of tetrahedral Al^{3+} to form an $H^+ \cdots$ OH grouping, the persistence of the OH doublet at temperatures over 800°C is more consistent with an SiOH or AlOH group.

Like the SiOH group formed when NH_4^+ in zeolites is thermally decomposed, the OH group in beidellite reacts with NH_3 to form NH_4^+, and the

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3450 cm^{-1} doublet is then eliminated. No NH_4^+ is formed when NH_4-montmorillonite is dehydroxylated and the product is exposed to ammonia, suggesting that the protons liberated in NH_4^+-montmorillonite are eliminated during dehydroxylation. This requires that these protons can migrate through the lattice so that two can associate with a lattice oxygen to form water.

Dehydroxylated montmorillonite has been found to rehydroxylate in steam at 400–500°C to give a neutral pyrophyllite-like structure (Heller *et al.*, 1962). Recent work has shown that dehydroxylated beidellite also partially rehydroxylates under these conditions but the product retains its layer charge. Thus Ca-beidellite is largely regenerated in its original form, while NH_4-beidellite yields a product in which NH_4^+ is formed on treatment with NH_3 gas. The ready rehydroxylation of the 2:1 dioctahedral layer silicates indicates strongly that dehydroxylation and rehydroxylation are homogeneous reactions in these minerals.

POLAR MOLECULES IN THE INTERLAYER SPACE OF SMECTITES

Interlayer Water

The typical interlayer molecule of expanding layer silicates is water, and an understanding of the structure of this water layer has been sought by many techniques. The infrared absorption spectrum provides information on the strengths of hydrogen bonds formed in the water layer but the results are complicated by overlapping of the broad absorption bands of water in inner and outer spheres of coordination, and by the band of lattice OH in montmorillonite. There are considerable advantages in working with the trioctahedral minerals, whose lattice OH bands are sharp, weak, and lie at higher frequencies than the water bands. It is then possible to see that water in hectorite containing the non-polar tetramethylammonium ion (Fig. 8) gives two distinct bands at 3630 and 3425 cm^{-1}. Studies with oriented clay films show that the high-frequency band corresponds to a weak hydrogen bond to oxygens of the silicate lattice, and the lower frequency band to water–water hydrogen bonding. A shoulder at 3240 cm^{-1} cannot be taken as evidence for a still stronger hydrogen bond, as it could be the overtone of the HOH angle deformation band at 1630 cm^{-1}. A very similar pattern of absorption (Fig. 8) is given by water in hectorites containing the ammonium and the hexammino-cobalt(III) cation, even though there is clear evidence from the spectra that these cations form hydrogen bonds with water molecules surrounding them (i.e. NH absorption bands of NH_4^+ at 3063 and 2850 cm^{-1}, and of $Co(NH_3)_6^{3+}$ at 3230 cm^{-1}). Accordingly, this pattern of hydrogen bonding can be considered typical of water in outer spheres of coordination round more polar cations. In K-hectorite (Fig. 8) the increased intensity of the 3425 cm^{-1} absorption band indicates that water directly coordinated to the cation forms hydrogen bonds with surrounding water molecules rather

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than with the silicate lattice. In Mg- and Cu-hectorite, water coordinated to these more polarizing cations is more acidic and forms stronger hydrogen bonds to water in outer spheres of coordination, as evidenced by the development of strong broad bands in the region below 3300 cm^{-1}. Similar bands which appear both in aqueous solutions of aluminium chloride (Fripiat, Cauwelaert, and Bosmans, 1965) and in Al-montmorillonite must also have the same origin.

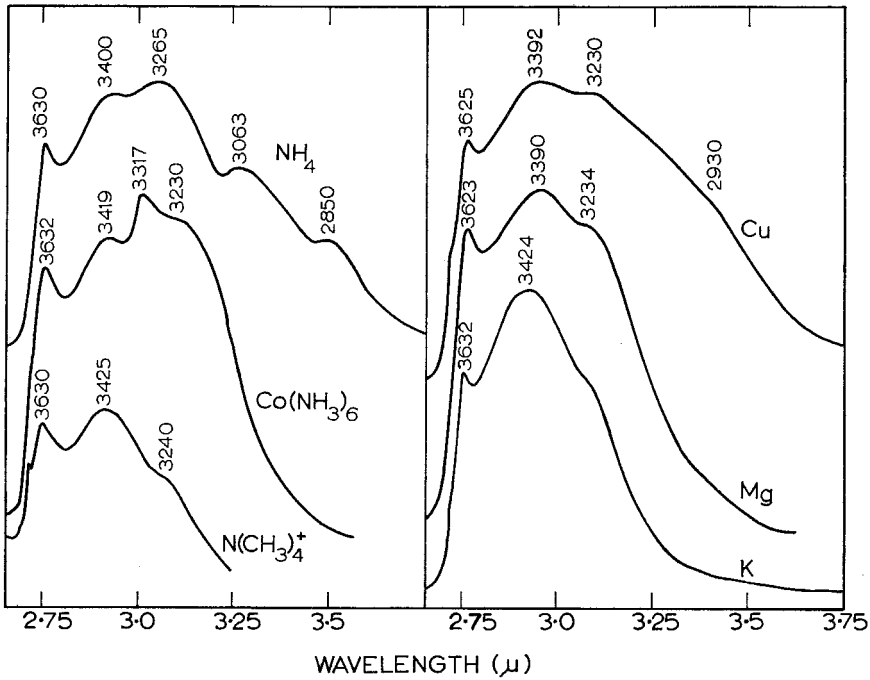


FIG. 8. Stretching vibrations of water in hectorite saturated with various exchangeable cations.

Absorption bands of water directly coordinated to the cation are seen more clearly when water in outer spheres of coordination is removed by heating and evacuation, or displaced by other polar molecules, but the environment of the coordinated water is then very different from that in the normal hydrated state. Thus isolated water molecules remaining in saponite after heating and evacuation can form hydrogen bonds only with the silicate lattice. The strength of hydrogen bonding is again a function of the polarizing power of the cation but the bonds are very much weaker than those formed with water in outer spheres of coordination (Russell and Farmer, 1964). This

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investigation showed that the broad absorption near 3200 cm^{-1} in Mg-saponite persists up to at least 200°C, suggesting that a structure of the type



Mg^{2+}- - -O—H- - -O—H is particularly stable in this mineral. The divalent cation cannot in general effectively neutralize two negative lattice sites without the assistance of such water bridges, except when chance brings the sites on adjacent silicate layers directly opposite each other.

Polar organic molecules such as pyridine and nitrobenzene readily displace water in outer spheres of coordination round divalent cations and the smaller monovalent cations, where they then form hydrogen bonds with directly coordinated water (Farmer and Mortland, 1966; Yariv, Russell and Farmer, 1966). The strength of hydrogen bonding is then a function of the polarizing power of the cation, the basicity of the organic molecule, and the packing of the organic molecules round the hydrated cation. Thus Mg-hectorite, like Mg-montmorillonite (Farmer and Mortland, 1966), is largely expanded to a 23 Å spacing when freshly removed from pyridine, and in this phase both protons of coordinated water form hydrogen bonds with pyridine, giving a band near 3050 cm^{-1} (Fig. 9). This phase rapidly loses pyridine in air to give a 14.8 Å phase in which packing considerations allow only one proton of each water molecule to form a hydrogen bond to pyridine. The development of a band at 3630 cm^{-1} shows that the other OH group is generally only weakly bonded to the oxygens of the silicate lattice.

It seems likely that hydrogen bonds to those silicate oxygens which carry the negative lattice charge will be rather stronger than hydrogen bonds to uncharged oxygens, and some evidence for this can be seen in the nitrobenzene complex of Mg-hectorite (Fig. 9). Hydrogen-bonding of coordinated water molecules to the oxygens of the nitro group is much weaker than to pyridine, and gives a band near 3500 cm^{-1}. In this complex, the high-frequency band at 3607 cm^{-1} is weakly developed, and is removed simply by evacuation at room temperature. As it seems unlikely that the coordinated water molecules form hydrogen bonds only to nitrobenzene, it is concluded that in this case water hydrogen-bonded to the silicate lattice absorbs below 3600 cm^{-1}.

The negative charge associated with Al-for-Si substitution in the tetrahedral layer should be localized on the three surface oxygens attached to Al^{3+}, whereas the charge associated with substitution in the octahedral layer (Mg for Al, or Li for Mg) can be expected to be more diffusely spread over the surface oxygens. In consequence, stronger hydrogen bonds to surface oxygens associated with Al-for-Si substitution would be anticipated. The infrared spectra of anhydrous smectites containing NH_4^+ do give evidence for this (Table 2). An NH_4 absorption band in the 3025–3050 cm^{-1} region, appearing in the spectra of saponite, vermiculite, and beidellite, indicates hydrogen bonding to surface oxygens, whereas absorption in this region of the spectra of NH_4^+-montmorillonite and hectorite is weaker and more diffuse.

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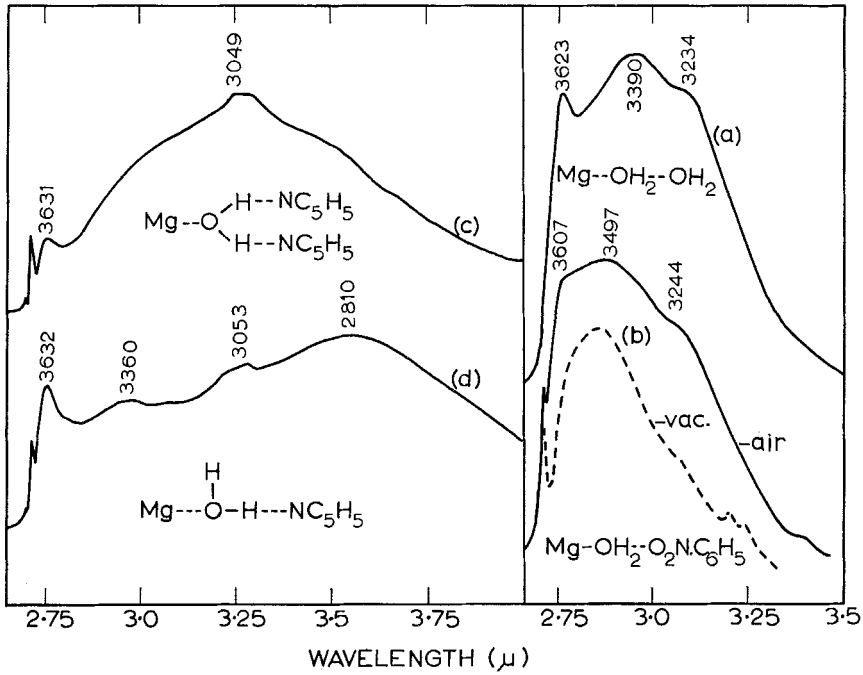


FIG. 9. Water absorption bands in Mg-hectorite, (*a*) normal hydrated state, (*b*) nitrobenzene complex, (*c*) 23 Å pyridine complex, (*d*) 14.8 Å pyridine complex.

TABLE 2.—NH_4^+ ABSORPTION BANDS IN ANHYDROUS LAYER SILICATES

	Frequencies, cm^{-1}
Montmorillonite	3270
Beidellite	3286, 3026
Muscovite*	3300, 3042
Hectorite	3262, (3062 v.w.)
Saponite	3270, 3045
Vermiculite	3255, 3045

* Vedder, 1965; v.w.: very weak.

Interlayer Molecules other than Water

Polar molecules have long been known to substitute for water in the interlayer space of expanding layer silicates, but only by the application of infrared methods has it been possible to get direct evidence of the mechanism of adsorption. In studying the adsorption of ammonia (Russell, 1965), ethylamine (Farmer and Mortland, 1965), pyridine (Farmer and Mortland,

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1966), nitrobenzene, and benzoic acid (Yariv, Russell, and Farmer, 1966) several different mechanisms of adsorption have been distinguished, in all of which the exchangeable cation plays a predominant role.

Protonated cations in smectites can form hydrogen bonds with lone-pair electrons in polar molecules. Thus N—H vibrations of ammonium, ethylammonium and pyridinium ions are strongly perturbed by hydrogen bonding to the corresponding free bases. The formation of discrete base–cation dimers of the type ($B:\overset{+}{H}:B$) has been postulated for the ethylamine–ethylammonium and pyridine–pyridinium systems. In the former, evidence was obtained for the formation of a symmetrical hydrogen bond, leading to complete suppression of the typical absorption bands of the ethylammonium cation. The weakly polar nitrobenzene molecule, however, leaves the ammonium ion unperturbed and freely rotating in montmorillonite, as it is in the collapsed anhydrous state.

Nitrobenzene and pyridine readily displace water in outer spheres of coordination round Na^+, Ca^{2+}, and Mg^{2+}, and these molecules then form hydrogen bonds with the directly coordinated water molecules (Fig. 9). Benzoic acid enters the interlayer space as the unionized monomer, and its behavior is then similar to that of the structurally analogous nitrobenzene molecule. Pyridine forms a strong coordinate bond with exchangeable Cu^{2+} which is resistant to hydrolysis by water, but part of the pyridine is also indirectly coordinated through a bridging water molecule. Nitrobenzene and benzoic acid do not readily displace coordinated water round Cu^{2+}. Generally, directly coordinated water can be reversibly removed by heating and evacuation, and polar molecules which were in outer spheres of coordination then coordinate directly with the cation. Changes in the spectrum of interlayer benzoic acid indicate that the oxygens of both the carbonyl group and the hydroxyl group become coordinated to the cation. At 150°C in vacuum benzoic acid around divalent cations is converted to benzoic anhydride which is also coordinated with the cation. Attempts to remove directly coordinated water from the magnesium–water–pyridine system leads to ionization of residual water molecules, thus forming pyridinium ions and magnesium hydroxide in the interlayer space.

Ammonia and ethylamine both form tetra-coordination complexes with Cu^{2+}, displacing water entirely; NH_3 readily displaces water round Na^+ and Li^+ and coordinates directly with the cation. Evidence for coordination of NH_3 to Ca^{2+} has also been obtained, but with this cation the principal reaction involves transfer of a proton from coordinated water, giving $Ca(OH)_2$ and NH_4^+ in the interlayer space. Al^{3+} and Mg^{2+} in montmorillonite are quantitatively converted to their hydroxides, and an equivalent amount of NH_4^+ is formed.

Formation of the protonated cations when free bases are adsorbed on montmorillonite has been frequently reported (Mortland *et al.*, 1963; Fripiat, Servais, and Leonard, 1962; Swoboda and Kunze, 1966). In many instances no special role need be ascribed to the montmorillonite environment; for

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example, NH_3 will precipitate aluminium and magnesium hydroxides from aqueous solutions of their salts, as well as in Al- and Mg-montmorillonite. Again, the tetra-amminocopper(II) complex readily hydrolyses in neutral solution to give copper hydroxide and ammonium ions: this hydrolysis also occurs in montmorillonite when excess NH_3 is displaced by water.

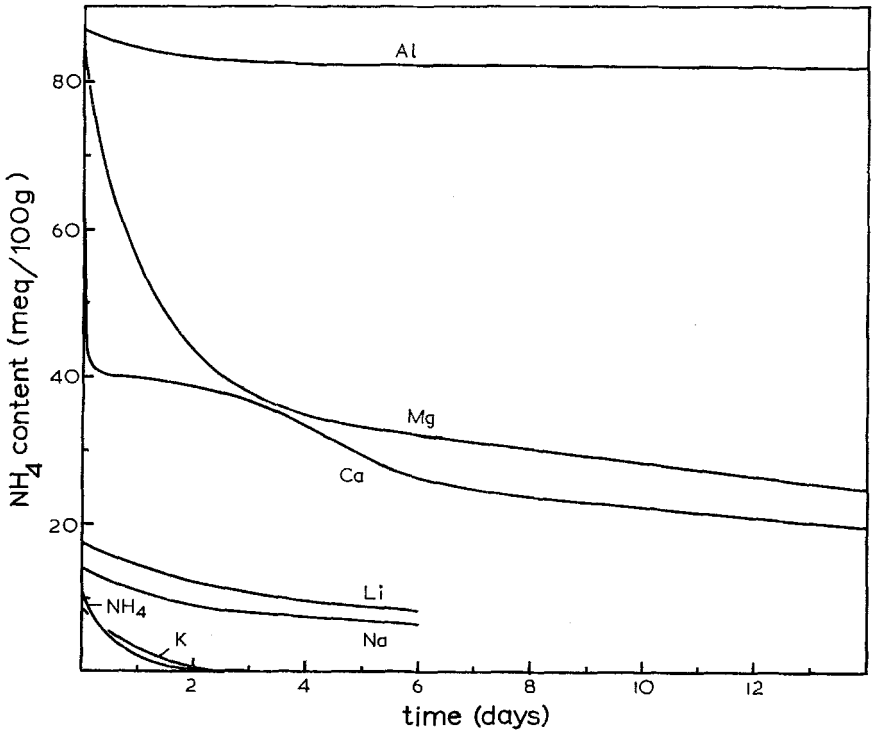


FIG. 10. Decrease, with exposure to air at about 40% relative humidity, of the NH_4 formed by NH_3 treatment of montmorillonites containing the exchangeable cations indicated. NH_4 content estimated from the optical density of the 1440 cm^{-1} infrared absorption band of the NH_4 cation.

On the other hand, the montmorillonite environment must be responsible for the formation of 17 meq NH_4/100 g when Li- and Na-montmorillonite are treated with NH_3, especially as about 10 meq/100 g is retained after long exposure to the atmosphere (Fig. 10). Similarly, the montmorillonite environment must be involved in the formation of pyridinium ion (10 meq/100 g) when pyridine is adsorbed on Na-montmorillonite. The principal cause in both instances appears to be strong preferential adsorption of the protonated cation in the interlayer space of montmorillonite. Inorganic cations do not readily displace pyridinium ion completely from montmorillonite (Farmer

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and Mortland, 1966), and montmorillonites have been shown (Alexiades and Jackson, 1966) to have a few sites like those in vermiculite from which NH_4^+ would be displaced only with some difficulty.

A previous discussion of the formation of protonated species when bases are adsorbed on montmorillonite has ascribed the effect to increased acidity of residual water molecules in the interlayer space (Fripiat, 1964), but such increased acidity would not be expected in Na-montmorillonite at normal humidities. The role of preferential adsorption of the protonated cation in the interlayer space should also be considered in other systems.

The formation of ionic species is also possible when acids are adsorbed on smectites, but, in fact, no formation of benzoate anion could be detected in montmorillonite containing monovalent exchangeable cations except after long exposure to the acid. With divalent cations, 13 to 25 meq/100 g of benzoate ion are formed, and the infrared spectra indicated that the anion is associated with the exchangeable cation, rather than with the silicate lattice.

Infrared studies on oriented montmorillonite films also give information on the orientation of interlayer molecules. The results (Farmer and Mortland, 1966; Serratosa, 1966; Yariv, Russell, and Farmer, 1966) confirm Greene-Kelly's conclusion from X-ray studies (1953) that aromatic molecules in their 15 Å complexes lie with the plane of the aromatic ring at a high angle to the silicate layers. There is evidence, however, that the plane of the ring might not be strictly perpendicular to the layers.

THE INFRARED SPECTRA OF SOIL CLAYS

A pure mineral species can often be more quickly and more fully defined in structure and composition by its infrared spectrum than by any other single technique, but few, if any, soil clays are single mineral species. In general, they are complex mixtures which may include several layer silicates (either interstratified or as separate species) feldspars, various forms of silica, oxides and hydroxides of iron and aluminium, carbonates, sulphates, and phosphates. These minerals may be poorly ordered, and associated with varying amounts of amorphous material. As isolated, the clays may contain considerable amounts of organic matter. Infrared spectroscopy can best contribute to the characterization of soil clays if certain precautions are taken in the pre-treatment and preparation of samples.

Soil organic matter has a considerable hydroxyl content, and retains adsorbed water strongly. It also gives rise to strong, broad absorption near 1600 and 1400 cm^{-1} due to carboxylate groups, which are probably the principal site of binding to the inorganic constituents. As these bands overlap those of the mineral component, removal of the organic material is necessary. Hydrogen peroxide, which is commonly used, can leave troublesome oxalate residues (Farmer and Mitchell, 1963). A preliminary treatment with hypochlorite (Anderson, 1963) or hypobromite (Troell, 1931) (which do not leave

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oxalate residues but are less effective) followed by hydrogen peroxide is probably the most satisfactory procedure.

Absorption bands of water overlap the OH absorption bands of several mineral species. Water associated with exchangeable cations can be reduced in amount by saturating the exchange complex with potassium ions. Ammonium is an alternative that permits an estimate of the exchange capacity from the intensity of its absorption bands, but these bands complicate the interpretation, as they overlap absorption of other possible components such as goethite and carbonate minerals.

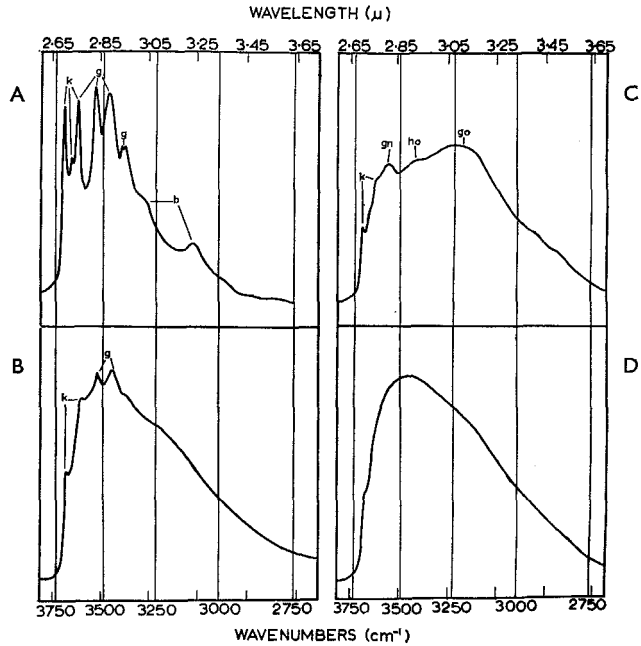


FIG. 11. OH stretching absorption of: A—highly crystalline clay deposit containing kaolinite (k), gibbsite (g) and boehmite (b); B—soil clay containing kaolinite (k), gibbsite (g), and amorphous hydrated oxides; C—soil clay containing kaolinite (k), glauconite–nontronite (gn), goethite (go), and amorphous hydrated oxides (ho); D—soil clay containing principally amorphous hydrated oxides.

The potassium bromide pressed disk technique is a suitable semiquantitative technique for examining clays. It is desirable to use two sample concentrations: 2 mg in a 12.5 mm disk containing 170 mg KBr is generally suitable for examining the OH stretching region and the weaker absorption bands in other regions of the spectrum; but the stronger absorption around 1000 cm^{-1} and 500 cm^{-1} requires only 0.3 mg. Drying the prepared disk at 100°C

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reduces to a low level any water adsorbed on the KBr, or held in the interlayer space of smectites containing potassium ions.

Some labeled spectra of soil clays are shown in Figs. 11 and 12. The distinctive bands of kaolin minerals at 3697 and 3620 cm^{-1} can be detected at very low levels. The infrared evidence is of particular value when the 7 Å diffraction line of kaolinite is overlain by second-order diffraction of 14 Å layer silicates. Gibbsite can often be detected at lower levels by its hydroxyl

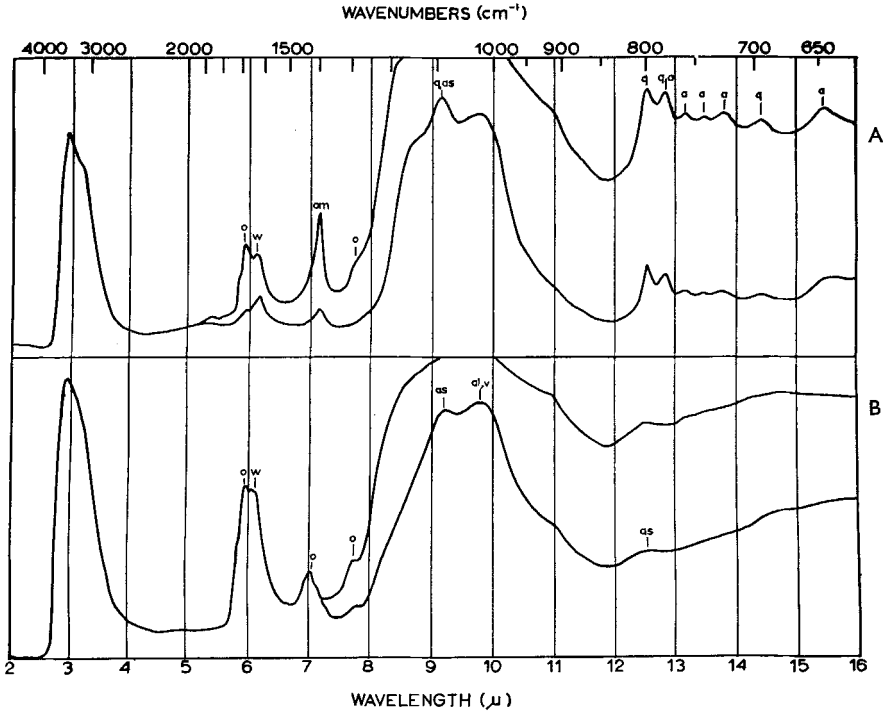


FIG. 12. Infrared spectra of: A—soil clay from sand dunes containing quartz (q), albite (a) and amorphous silica (as); B—soil clay containing amorphous silica (as), vermiculite (v) and allophane (al). Bands of NH_4^+ (am), water (w), and adsorbed oxalate (o) are also indicated.

stretching bands than by X-ray techniques (Wilson, 1966). Nontronite and glauconite have *b*-axis spacings close to those of trioctahedral minerals, but can readily be distinguished in the OH stretching region. Amorphous inorganic materials absorb as strongly in the infrared as do the crystalline species, and their presence in admixture with crystalline components is less readily overlooked in the infrared spectra of soil clays than in X-ray diffraction patterns (Mitchell and Farmer, 1962). Further, the infrared spectrum

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clearly distinguishes amorphous silica present as a separate phase from silica in combination with alumina and iron oxides, as in allophanes (Mitchell, Farmer, and McHardy, 1964).

While use of high resolution grating spectrometers has greatly increased the information obtainable in the study of OH groups in clays, there is still a considerable amount of overlapping of the absorption bands of different mineral species. Further clarification of this region can be obtained by progressive thermal decomposition of the hydroxyl-containing components. Mitchell and Farmer (1962) have shown, for example, that allophanes are largely dehydroxylated by heating pressed disks containing them to 300°C. Several other dehydration and dehydroxylation reactions have been followed in alkali-halide pressed disks, but these reactions occur at rather higher temperatures in disks than when the powdered minerals are heated in air (Farmer, 1966).

Looking to the future, it is clearly desirable to develop a convenient technique whereby the spectra of minerals can be followed as the samples are progressively heated. Further assistance in the differentiation of clays can be expected from the accumulating information on the spectral changes associated with adsorption of organic and inorganic compounds on clays. The study of adsorption mechanisms on clay surfaces are also important for an understanding of many reactions which occur in soil. Thus study of the adsorption of NH_3 on clays clarifies the processes occurring when anhydrous NH_3, used as a fertilizer, is injected into soils. Again, the interactions between minerals and organic constituents in soils are illuminated by investigation of the adsorption of simpler organic compounds on pure clay specimens. For example, a recent report by Schnitzer and Kodama (1966) that fulvic acid is preferentially adsorbed in montmorillonite under acid conditions would be anticipated from the work on benzoic acid, which shows that unionized carboxylic acid groups behave like neutral polar substituents. Previous investigations (Emerson, 1955) had indicated that although synthetic polymeric alcohols were adsorbed in the interlayer space of montmorillonite, polymeric acids were not. However, Emerson used partially neutralized preparations of the polymeric acids, and the presence of negatively charged carboxylate ions would tend to inhibit interlayer penetration.

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