

DETERMINATION OF TETRAHEDRAL SUBSTITUTIONS AND INTERLAYER SURFACE HETEROGENEITY FROM VIBRATIONAL SPECTRA OF AMMONIUM IN SMECTITES

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Abstract—Integrated intensities of the fundamental modes of vibrations of ammonium in heat-treated, NH_4^+ -exchanged swelling minerals permits (1) a quantitative determination of the amount of tetrahedral substitutions of Si^{4+} by M^{3+} in dioctahedral smectites, and (2) an estimate of the degree of interlayer surface heterogeneity in trioctahedral minerals to be made. This is possible because NH_4^+ cations balancing the negative charge of tetrahedral sites that are not influenced by an excess positive charge of the octahedral layer have a symmetry lower (probably C_{3v}) than the usual tetrahedral T_d symmetry of NH_4^+ . In C_{3v} symmetry the ν_1 band is infrared active whereas it is only Raman active in T_d symmetry. Protons left after deammoniating dioctahedral smectites with tetrahedral substitutions form interlayer silanol groups, the stretching vibration of which give a band that is distinct from that of octahedral OH-stretching modes.

Key Words—Ammonium, Hofmann-Klemen effect, Infrared spectroscopy, Smectite, Tetrahedral substitution.

INTRODUCTION

Phyllosilicates of the 2:1 type present an extraordinary diversity in chemical composition. Because they are either dioctahedral or trioctahedral, chemical analyses are always difficult to transform into structural formulae in which the cationic population of the tetrahedral or of the octahedral sheets is unambiguously established. Moreover, the presence of free amorphous oxides, such as SiO_2 , Al_2O_3 , or Fe_2O_3 even in small quantities, provokes large discrepancies in the interpretation of the chemical analysis.

It is, however, highly desirable to know accurately the amount of ionic substitution in the tetrahedral sheet, as this has a profound effect on the polarity of the oxygen atoms forming the interlayer surfaces and thus affects appreciably the chemical characteristics of these surfaces. For single crystals of micas, refined X-ray diffraction technique (Gatineau, 1964) have been applied to the localization of aluminum in the tetrahedral sheet, but such techniques are obviously impossible to use for fine particle-size materials, such as clays. Therefore, other experimental procedures have been investigated to obtain this type of information. Hofmann and Klemen (1950) observed that heating a Li-exchanged dioctahedral smectite to $\sim 200^\circ\text{C}$ decreased the lattice charge by an amount that depended upon the ratio of the charge originating from the octahedral sheet to the total charge. This observation was interpreted to be the result of small cations (e.g., Li^+) migrating toward free octahedral vacancies where they neutralized the charge arising from ionic substitutions (e.g., Al^{3+} by Mg^{2+}) in this sheet. Thus, the fraction of

the charge arising from ionic substitutions in the tetrahedral sheet is not modified by this treatment.

Glaeser and Mering (1967) observed that the cation-exchange capacity (CEC) of trioctahedral hectorite is not modified if the Li-exchanged clay is heated, whereas the CEC of a beidellite-type material is partially affected. Later, by applying what they called the Hofmann-Klemen (HK) effect to Li-Na-smectites, Glaeser *et al.* (1972) showed that the HK procedure permits an evaluation of the amount of Si^{4+} by Al^{3+} substitutions in dioctahedral smectites. However, Glaeser and Fripiat (1976) pointed out that the charge on the edges of the microcrystals perturbs to some extent this evaluation, and, of course, that the HK procedure is not applicable to trioctahedral smectites.

It was therefore tempting to search for a more general technique which could, on the one hand, check the results obtained as described above for dioctahedral smectites and, on the other hand, be equally applicable to trioctahedral clays. Also, in view of the importance of charge localization for rheological and other clay properties, it was desirable that this new procedure should not require too sophisticated a treatment so that it could be applied to a large number of industrial samples.

This paper proposes an experimental method which fulfills these requirements. It is based on the quantitative determination of integrated intensities of the infrared (IR) bands of the normal modes of vibration of NH_4^+ cations in clays which were totally exchanged by this cation. It involves recording the IR spectra in the 4000–1200 cm^{-1} range of clay films which were pro-

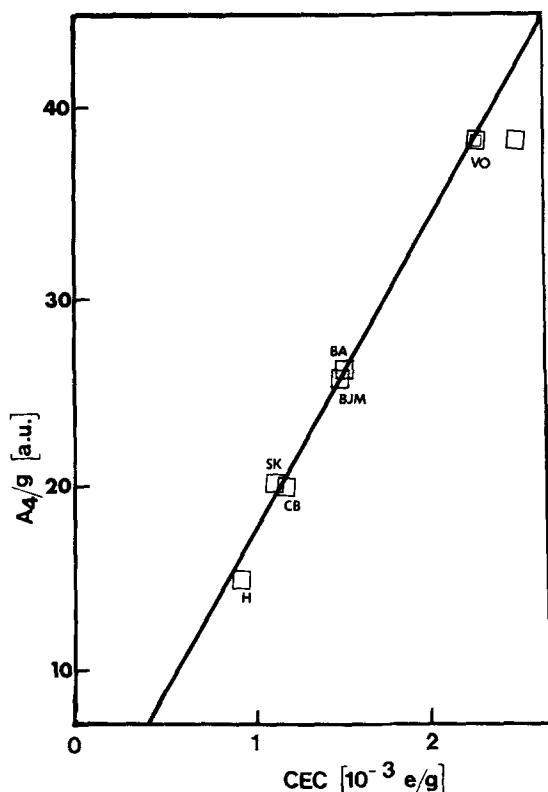


Figure 1. Integrated intensity (a.u. = arbitrary unit) of the deformation vibrational band of ammonium (A_4) per gram of clay film dried at 200°C vs. the cation-exchange capacity shown in Table 1. For VO, the value obtained by IR is about 10% less than that calculated from the chemical composition.

gressively heated from 200° to 600°C in vacuum. In addition, this paper discusses the fate of the protons left within the clay lattice on progressive removal of NH_3 at increasing temperature (deammoniation process).

MATERIALS

Six samples were chosen to cover a range of structures and chemical compositions as shown in Table 1. The Camp Berteau (CB) montmorillonite and the Black Jack mine (BJM) (USA) and Rupsroth (BA) (Germany) beidellites are dioctahedral smectites. The hectorite (H) (Hector, California), saponite (SK) (Kozakov, Czechoslovakia), and vermiculite (VO) (Santa Olalla, Spain) are trioctahedral minerals.

Each sample was exchanged with NH_4^+ by repeated contacts at room temperature with a 1 N NH_4Cl solution and its CEC calculated from the unit-cell composition and chemical analyses. As shown in Figure 1, the CECs were in good agreement with those predicted from the integrated intensity of the ν_4 deformation band of NH_4^+ (*vide infra*), showing that the exchange process was complete. This is, of course, an essential requirement for the validity of the technique that is proposed here.

EXPERIMENTAL

A vacuum-tight stainless steel cell fitted with NaCl windows was constructed to hold six samples. It contained one compartment where the samples mounted on a mobile sample holder could be heated and a second compartment where the IR spectrum of each sample

Table 1. Chemical characteristics of the studied samples.

Sample ¹	Tetrahedral composition ²	Octahedral composition ²	Charge/unit cell (eq)	p ³	References ⁴	r ⁵	CEC ⁶ (eq/g)
CB	$\text{Si}_{7.75}, \text{Ti}_{0.03}$ $(\text{Al}, \text{Fe})_{0.22}$	$(\text{Al}, \text{Fe})_{3.32}$ $\text{Mg}_{0.69}$	0.91	—	a	0	1.15
BA	$\text{Si}_{7.35}, \text{Ti}_{0.03}$ $(\text{Al}, \text{Fe})_{0.64}$	$(\text{Al}, \text{Fe})_{3.54}$ $\text{Mg}_{0.45}$	1.09	0.43	a b	0	1.48
BJM	$\text{Si}_{6.92}, \text{Al}_{1.08}$	$\text{Al}_{3.92} \text{Fe}_{0.08}$	1.08	1	c d	0	1.42
H	$\text{Si}_{8.0}$	$\text{Mg}_{5.45} \text{Li}_{0.55}$	0.55	0	e b	und.	0.92
SK	$\text{Si}_{6.6}, \text{Al}_{1.36}$ $\text{Fe}_{0.04}$	$\text{Mg}_{5.0} \text{Fe}_{0.48}$ $\text{Fe}^{2+}_{0.52}$	0.92	—	f	0.34	1.2
VO	$\text{Si}_{5.52} \text{Al}_{2.48}$	$\text{Mg}_{4.8} \text{Fe}_{0.8}$ $\text{Fe}^{2+}_{0.16} \text{Ti}_{0.10}$	1.76	—	f	0.29	2.4

¹ CB = Camp Berteau montmorillonite; BA = Rupsroth beidellite; BJM = Black Jack mine beidellite; H = hectorite; SK = Kozakov saponite; VO = Olalla vermiculite.

² Unless indicated Fe is Fe^{3+} .

³ p is experimentally obtained by the HK procedure.

⁴ a = Vielvoye (1975), b = Glaeser *et al.* (1972), c = Shannon (1924), d = Greene-Kelly (1953, 1955), e = Guedon (1963), f = Suquet (1978).

⁵ r is the excess positive charge of the octahedral layer divided by the number of tetrahedral substitutions.

⁶ The CEC was calculated from the charge/unit cell.

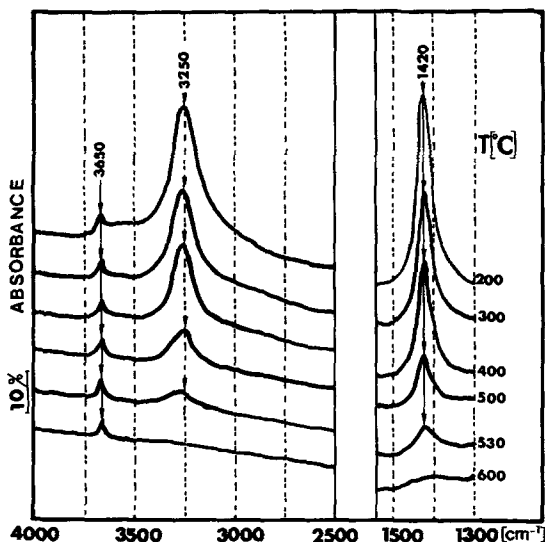


Figure 2. IR spectra recorded after pretreatment at the indicated temperature for hectorite (H).

could be recorded. A complete set of determinations for six samples required approximately three days. The IR spectra were scanned between 4000 and 2500 cm^{-1} and between 1600 and 1250 cm^{-1} , with approximate spectral slit widths of 1 and 0.5 cm^{-1} , respectively, at a rate of $\sim 1 \text{ cm}^{-1}/\text{sec}$ for samples which had been heated at 100°, 200°, 300°, 400°, 500°, and 600°C for at least 4 hr. The residual pressure in the cell was of the order of 10^{-4} torr.

RESULTS

Four sets of typical spectra are shown in Figures 2–5. Figure 2 shows the simplest one, namely that obtained for hectorite. Nearly symmetrical bands were observed at 3250 and 1420 cm^{-1} , corresponding to the ν_3 and ν_4 fundamental modes of vibrations of NH_4^+ (see next section). Recall that in hectorite there is no substitution in the tetrahedral layer, whereas the octahedral layer contains Mg^{2+} for Li^+ substitutions. After heating the samples in vacuum at increasing temperature, these two bands decreased progressively in intensity, and at 600°C they had practically disappeared. No bands were observed except the weak OH-stretching band at $\sim 3650 \text{ cm}^{-1}$.

Figure 3 shows a comparable set of spectra obtained for the Camp Berteau montmorillonite. The only difference is that the band at 3280 cm^{-1} is not as symmetrical. A shoulder is present on the low wave-number side which decreased with increasing temperature. Two bands at 3250 and 3040 cm^{-1} are present in the spectra of vermiculite (Figure 4) in addition to the 1430 cm^{-1} band. Here also, these two high frequency bands decreased in intensity at higher pretreatment temperatures. The decrease in absorbance between the lattice

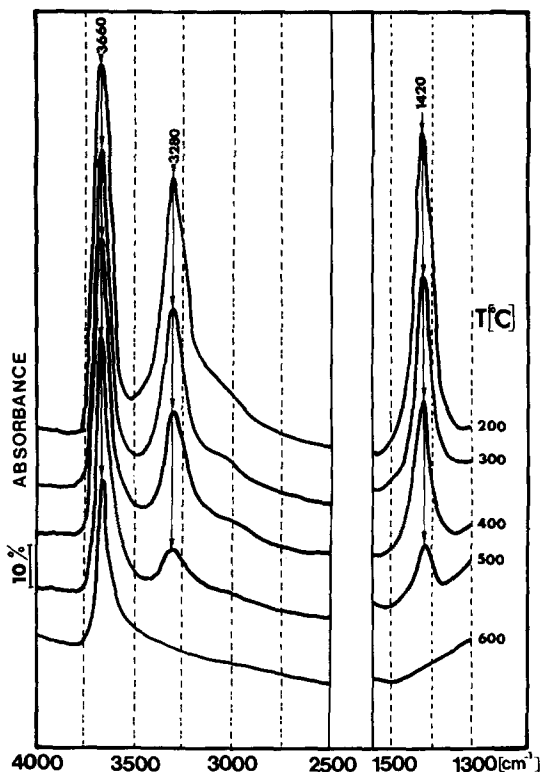


Figure 3. IR spectra recorded for the Camp Berteau montmorillonite (CB).

OH-stretching bands at 3650 and 3700 cm^{-1} and the band at 3250 cm^{-1} was due to the removal of residual hydration water. The evolution of the spectra recorded for saponite was very similar to that shown in Figure 4, except that only one OH lattice-stretching band is present at 3670 cm^{-1} , and the two high frequency bands of NH_4^+ are at 3280 and 3030 cm^{-1} . The bands at 3280 and 3030 cm^{-1} in the spectra of the Black Jack mine sample (Figure 5) are well defined but, when compared to Figure 4, a very interesting feature appeared between 3400 and 3500 cm^{-1} as deammoniation proceeded. In beidellite at 400°C, and above, two new well-defined bands appeared at 3500 and 3420 cm^{-1} , whereas the lattice-OH stretching band at 3655 cm^{-1} disappeared. The evolution of the spectra observed for the Rupsroth beidellite was similar. However, the 3030 cm^{-1} band, though well defined, was weaker than that observed for BJM in Figure 4. The new band observed above 400°C in the 3500 cm^{-1} range was also weaker.

In summary, for trioctahedral and dioctahedral smectites, the NH stretching (high frequency) band split into a well-defined doublet when Si^{4+} by M^{3+} (Al^{3+} mainly) ionic substitutions were present in the tetrahedral layer. With these same types of substitutions new bands appeared at $\sim 3500 \text{ cm}^{-1}$ upon deammoniation of dioctahedral smectites but not on deammoniation of trioctahedral minerals containing tetrahedral

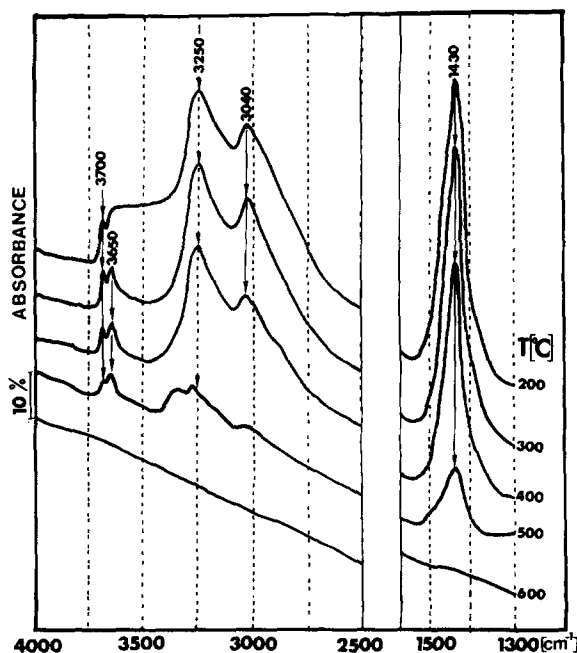


Figure 4. IR spectra recorded for the vermiculite (VO).

substitutions. Thus, the NH_4^+ cation appears to be a very sensitive probe of the atomic environment in the interlayer space. It was therefore worthwhile (1) to study its spectrum in detail, (2) to examine the quantitative information which can be obtained from the integrated intensities of its characteristic bands, and (3) to understand the significance of the new bands observed in the 3500 cm^{-1} region upon deammoniation.

It should be recognized that in the broad bands containing the stretching vibrations of water and ammonium in hydrated beidellite, saponite, and vermiculite, Farmer and Russell (1967) pointed out a shoulder in the 3030-cm^{-1} region. They assigned this band to hydrogen-bonded ammonium. Another explanation is proposed in the present report, although the slight shifts in frequency observed for the high frequency NH-stretching band are probably due to some variation in the strength of the hydrogen bonds of NH_4^+ with lattice oxygens.

AMMONIUM VIBRATIONAL SPECTRUM

Isolated NH_4^+ belongs to the symmetry group T_d . The triply degenerated ν_3 and ν_4 modes are IR active, and the corresponding bands are intense. The Raman active ν_1 mode is also intense, but ν_2 , equally Raman active, is weak. In a symmetrical environment the same IR spectrum with two strong bands can be observed but their frequencies are displaced to some extent, because of hydrogen bonding.

In a phyllosilicate where the charge originates exclusively from ionic substitutions in the octahedral sheet, the lattice charge is smeared out over all oxygens of the interlayer surface; therefore, the symmetry of interlay-

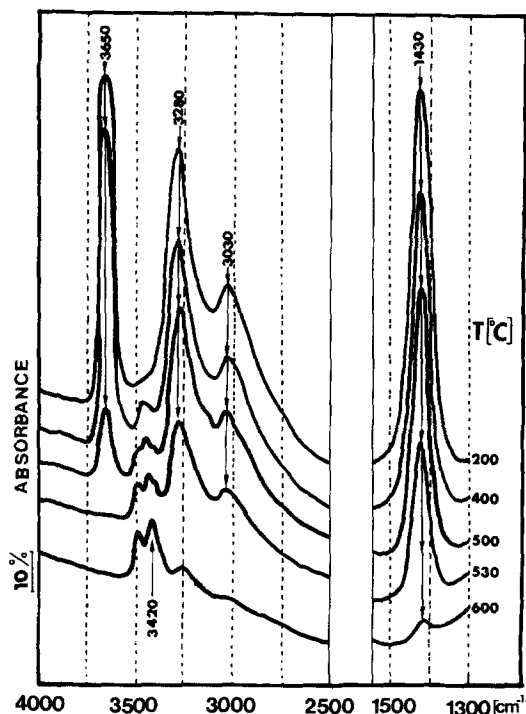


Figure 5. IR spectra recorded for the Black Jack mine beidellite (BJM).

er NH_4^+ should not be affected. Indeed, two well-defined and intense ν_1 and ν_3 bands were observed in the present study. If the tetrahedral symmetry is lost because of a structural distortion along one privileged axis, NH_4^+ takes the lower C_{3v} symmetry, and the transformations shown in Table 2 must occur (Herzberg, 1947). The six bands become IR active. In particular, the ν_1 mode should appear near 3040 cm^{-1} , which is the frequency of the corresponding Raman-active mode in T_d symmetry. The weak ν_2 should be observed near 1635 cm^{-1} , but it could possibly be obscured by the deformation band of H_2O and overtones of lattice vibrations in this region. ν_3' and ν_4' should be very close to ν_3 and ν_4 , respectively, because in CH_3D , $(\nu_3 - \nu_3')/\nu_3 = 0.016$ and $(\nu_4 - \nu_4')/\nu_4 = 0.11$. Because the reduced masses for these vibrations in C_{3v} NH_4^+ and in T_d NH_4^+ are the same, these ratios should be much less in going from the first to the second symmetry group, and the splittings may produce a very moderate broadening of these two bands. For these reasons the $T_3 \rightarrow C_{3v}$ symmetry transformation should be mainly observed by the splitting of the stretching band ν_3 into two bands, one near the ν_3 band characteristic of T_d , and the other near the frequency of the Raman T_d ν_1 .

This qualitative analysis accounts completely for the experimental results observed for phyllosilicates with an appreciable amount of ionic substitutions in the tetrahedral sheet, namely, the two beidellites, vermiculite, and saponite. Therefore, it is suggested that the

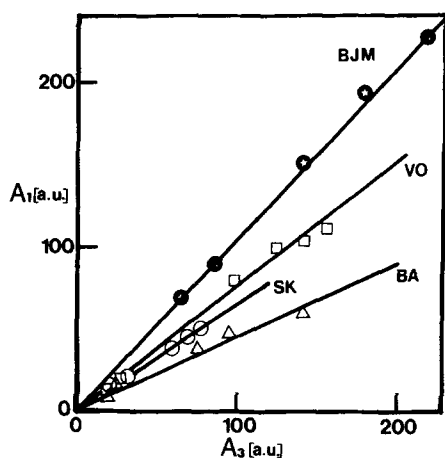


Figure 6. Plot of A_1 vs. A_3 . The arbitrary units (a.u.) for these two integrated intensities are the same.

splitting of the NH stretching into two bands, ν_1 and ν_3 , is due to NH_4^+ cations balancing the lattice charges due to ionic substitutions Si^{4+} by M^{3+} (Al^{3+} mainly) in the tetrahedral layer. The combination band, $\nu_2 + \nu_4$, which is IR active and should appear near 3000 cm^{-1} , could theoretically interfere with ν_1 . Because no absorption was observed in this region for clays without tetrahedral substitutions (e.g., hectorite), it must be concluded that this combination band is too weak to be observed. Thus, on a purely qualitative basis, the ν_1 stretching band at 3030 cm^{-1} can be assigned to the C_{3v} NH_4^+ cation. To check this hypothesis, a quantitative study was made of the intensity of the observed vibration bands as related to the amount of tetrahedral substitutions.

QUANTITATIVE DETERMINATION OF TETRAHEDRAL SUBSTITUTIONS

The integrated intensity, A , of an active IR vibrational band was defined by Rouxhet (1969) by the following general equation:

Table 3. Values of the dimensionless proportionality constants of Eq. 5-7.

Sample ¹	$k_{1,3}$	$k_{1,4}$	$k_{3,4}$
BJM	1.05	1.05	1.05
VO	0.77	0.64	0.81
SK	0.65	0.54	0.87
BA	0.45	0.44	1.0

¹ Samples are the same as listed in Table 1.

$$A = \text{NSC}\ell \quad (1)$$

where N is the number of vibrators per unit volume and ℓ is the film thickness. C is proportional to the square of the transition moment of the vibrational mode, and S is proportional to the square of the cosine of the angle between this moment and the direction of the electrical field of the exciting electromagnetic radiation. S may be considered as a constant because of the absence of dichroism for the observable 3 vibrational modes. The stretching bands were decomposed into their components, and the band areas were measured by planimetry. If U is a constant containing the arbitrarily chosen surface unit and S , three general equations may be written for each observed vibrational mode as follows:

$$\text{for } \nu_1, A_1 = U_v p N C_1 \ell \quad (2)$$

$$\text{for } \nu_3, A_3 = U_v N C_3 \ell \quad (3)$$

$$\text{for } \nu_4, A_4 = U_d N C_4 \ell \quad (4)$$

where N is the total number of ammonium cations in the clay film of thickness ℓ , and p is the fraction of C_{3v} ammonium cations. Note that $N\ell$ is the number of ammonium cations/ cm^2 of irradiated film.

The first quantitative check is the linear relationship shown in Figure 1 between A_4 and the CEC. The plots of A_1 vs. A_3 , A_1 vs. A_4 , and A_3 vs. A_4 for each sample pretreated at increasing temperature are, in all cases, perfectly linear. An example (A_1 vs. A_3) is shown in Figure 6. Thus, for each sample, relationships such as

Table 2. Frequencies of normal modes of vibration of NH_4^+ with T_d or C_{3v} symmetry.

T_d symmetry				C_{3v} symmetry		
Species	Activity	Frequency (cm^{-1})		Species	Activity	Frequency ² (cm^{-1})
		Free ¹	Adsorbed ²			
$A_1 : \nu_1$	R	3040	—	$A_1 \nu_1$	I, (R)	3030–3040
$E : \nu_2$	(R) ³	1680	—	$E \nu_2$	I, (R)	not observed
$F_2 : \nu_3$	I, R	3145	3250–3280	$\left\{ \begin{array}{l} E \nu_3 \\ A_1 \nu_3' \end{array} \right\}$	$\left\{ \begin{array}{l} I \\ I \end{array} \right\}$	3250
$F_2 : \nu_4$	I	1400	1420–1430	$\left\{ \begin{array}{l} E \nu_4 \\ A_1 \nu_4' \end{array} \right\}$	$\left\{ \begin{array}{l} I, (R) \\ I, (R) \end{array} \right\}$	1430

¹ Nakamoto (1963).

² Observed by IR in this work. For the symmetry transformation, see Herzberg (1947, p. 238).

³ The parentheses indicate a weak band.

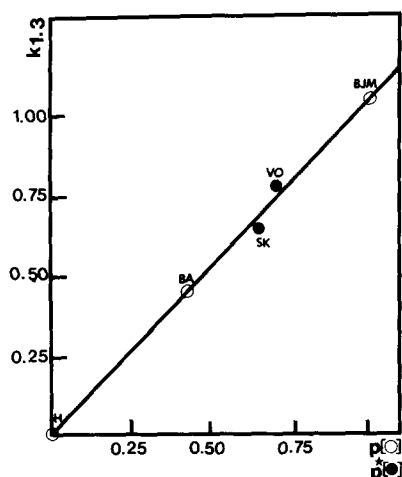


Figure 7. Linear relationship between $k_{1,3}$ and p , experimentally determined by the HK procedure (open circle). The closed circles are the values of $p^* = 1 - r$ (see text) for SK and VO.

$$A_1 = k_{1,3}A_3 \quad (5)$$

$$A_3 = k_{3,4}A_4 \quad (6)$$

$$A_1 = k_{1,4}A_4 \quad (7)$$

are obeyed. The constants $k_{1,3}$, $k_{3,4}$, and $k_{1,4}$ are shown in Table 3 and were obtained graphically by plotting A_i against A_j . Combining Eq. (2), (3), and (4) and Eq. (5), (6), and (7), these constants have the following significances

$$k_{1,3} = pC_1/C_3 \quad (8)$$

$$k_{1,4} = U_p C_1/U_d C_4 \quad (9)$$

$$k_{3,4} = U_v C_3/U_d C_4 \quad (10)$$

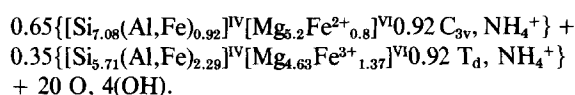
If C_1/C_3 could be calculated, $k_{1,3}$ would provide the possibility of measuring p . Unfortunately, the calculation of C_1/C_3 is a difficult task because environmental effects must be taken into account. It is, however, possible to obtain an experimental value for C_1/C_3 if $k_{1,3}$ is plotted against p , determined by the HK procedure for BJM, BA, and H. Note that no excess positive charge exists in the octahedral sheet of these minerals. As shown in Figure 7, a linear relationship was obtained from which it may be concluded that $C_1/C_3 = 1.05$. That $C_1 \approx C_3$ is not unexpected, because C_1 and C_3 are proportional to the square of transition moments of two stretching modes.

There is no reason to believe that C_1 would differ strongly from C_3 for ammonium in trioctahedral minerals; however, Table 3 shows that $k_{1,3}$ is noticeably smaller than 1 for SK and VO, i.e., for the two trioctahedral minerals with an excess positive charge in the octahedral sheet. Moreover, as shown in Figure 7, within experimental error, for these two minerals $k_{1,3} = p^* = 1 - r$, where r is the ratio of the excess positive charge in the octahedral sheet to the total number of tetrahedral substitutions (see Table 1). Therefore, r is

equal to the proportion of ammonium cations with the T_d symmetry, whereas p^* is the proportion of ammonium cations with the C_{3v} symmetry. Thus, there are two types of environment for the interlayer cations.

If the excess positive charge of the octahedral layer is localized around some of the net negative surface sites, assuming that the positive charge is on the oxygen atoms surrounding these sites, the structural perturbation on NH_4^+ might be too weak to induce the $T_d \rightarrow C_{3v}$ symmetry change. On the contrary, in domains without excess positive octahedral charge, the ammonium cations balancing the tetrahedral substitutions would be sufficiently perturbed to have the C_{3v} symmetry. This is the simplest explanation to explain the observation of the relationship between $k_{1,3}$ and p^* shown in Figure 7. Other explanations, such as those founded on structural characteristics of trioctahedral minerals (e.g., lesser trigonal distortion of the hexagonal holes) and NH_4^+ bonding to sheets, are also possible but the authors doubt that these types of perturbation could be sufficiently active to modify the effect of trioctahedral substitutions. Electronic effects acting on the surface oxygens seem more probable.

If this is the case, it would mean that $k_{1,3}$ is a parameter allowing some kind of measurement of the degree of interlayer surface heterogeneity in trioctahedral minerals. This heterogeneity could be the consequence of heterogeneity of the cationic compositions. To clarify this assumption, consider saponite as an example, with the following chemical formula:



The gross chemical composition shown in Table 1 is unchanged, but two types of domains have been defined where the charge-balancing ammonium cations have two different types of symmetry. In the first, the lattice charge is purely tetrahedral and localized on tetrahedra which are electrically balanced by $C_{3v} NH_4^+$. In the second, the positive charge of the octahedral sheet compensates partially for the negative charge of the substituted tetrahedra, and the symmetry of the exchangeable ammonium is T_d . Of course the splitting of the chemical composition into two idealized domains raises the question of the origin of the heterogeneity. From the present experimental data, it is impossible to determine whether the heterogeneity is confined to domains belonging to the same sheet or if there are alternating sheets with different compositions. For SK, Suquet *et al.* (1977) observed two swelling distances for this Ca-exchanged mineral, namely X-ray powder diffraction reflections at 15.4 and 18.6 Å. They interpreted this double swelling as a mixture of layers with low (~ 0.66 eq/unit cell) and higher charge density (~ 0.9 eq/unit cell). It is also possible that the two types of heterogeneity coexist.

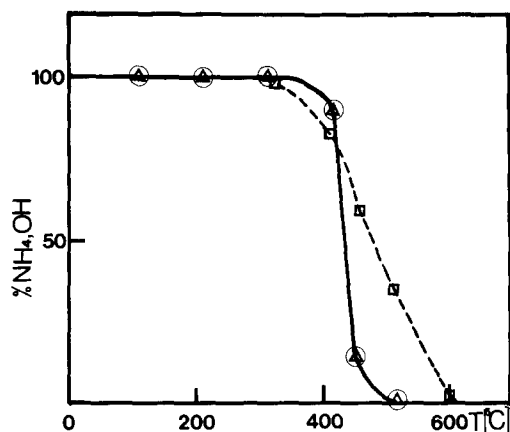
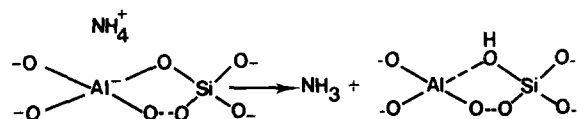


Figure 8. Relative contents of NH_4^+ (\square obtained from the ν_4 band) and of octahedral lattice OH for the ammonium BJM (Δ); and for the potassium BJM (\circ) vs. pretreatment temperature.

It is, of course, necessary to study more trioctahedral minerals to detect the potential use and limitations of the measurements of the degree of heterogeneity proposed here. The main difficulty is to obtain samples uncontaminated by other minerals. The authors are anxious to study samples of different origins meeting this requirement in order to check the validity of the IR technique proposed here.

PROTONIC TRANSFORMATION AND THERMAL STABILITY

The proton lost on deammoniation can either enter the structure where, at high temperature, it should combine with the OH of the octahedral sheet to form water or to break Si–O–M^{IV} bonds in the tetrahedral sheet, forming Si–OH bonds. In either way, it should affect the structure's thermal stability. In faujasite-type X and Y molecular sieves, Uytterhoeven *et al.* (1965) showed that the following transformation occurs between 200° and 350°C.



Two OH stretching bands were observed at 3650 and 3570 cm^{-1} corresponding to hydroxyls pointing toward the supercage or the framework, respectively (White *et al.*, 1966).

In the spectrum of the BJM beidellite the bands at 3420 and 3500 cm^{-1} and the single (weaker) band in the spectra of the BA beidellite at 3500 cm^{-1} observed upon deammoniation above, e.g., 300°C, can be assigned to silanol groups that are formed by protons breaking Si–O–Al linkages. Thus, the protons left after deammoniation were at least partially trapped by the oxygens of the interlayer surfaces. This is not surprising because

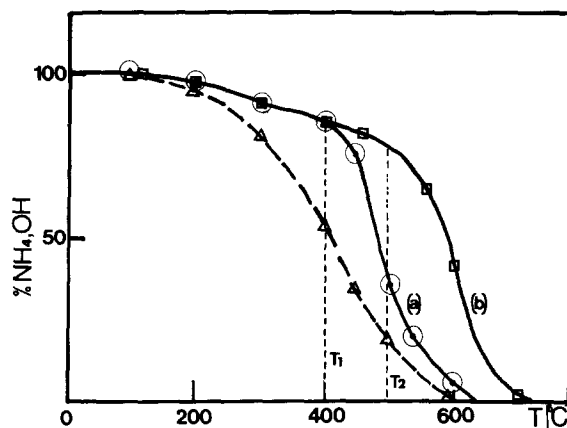


Figure 9. Relative contents of NH_4^+ (Δ obtained from the ν_4 band) and of octahedral lattice OH for the ammonium CB (\circ); and for the potassium CB (\square). The catalytic effect of the proton on the dehydroxylation process is shown by comparing the amount of OH lost in curves a and b at temperatures T_1 and T_2 to the loss of NH_3 in the same temperature range. In a, the loss of OH is larger than the loss of NH_3 .

these oxygens are negatively charged as a result of Si^{4+} by Al^{3+} (or Fe^{3+}) substitutions. Similar bands were observed by Farmer and Russell (1967) and by Russell and White (1966) in NH_4 -rectorite.

It may thus be anticipated that the thermal stability of NH_4 -exchanged and K-exchanged BJM should be about the same. As shown in Figure 8, this was actually observed because the relative loss of octahedral OH was the same for these two cation-exchange forms of BJM. As shown in Figure 9, the dehydroxylation and deammoniation phenomena were completely different for the CB montmorillonite. For this mineral, deammoniation was completed before the complete disappearance of the octahedral OH-stretching band, in contrast to what was observed for BJM, but in agreement with Farmer and Russell (1967).

In montmorillonite, the interlayer surface oxygens were apparently not negative enough to trap protons left after deammoniation even if a small amount of tetrahedral substitutions was present in this mineral, as suggested by the shoulder observed at $\sim 3030 \text{ cm}^{-1}$. The free protons migrated towards the octahedral sheet where they catalyzed the nucleation of water at the expense of the octahedral OH. This catalytic effect was evidenced by the greater thermal stability of K-CB as compared to that of NH_4 -CB. An intriguing question arises from the observation that trioctahedral minerals containing tetrahedral substitutions (vermiculite and saponite) which show no stretching band due to interlayer surface-silanol upon deammoniation. As mentioned above, the octahedral sheet of these minerals contains an excess positive charge which can drain electrons from oxygens of the tetrahedral sheet, thereby decreasing their affinity for the protons left by the

removal of ammonia. Thus, C_{3v} ammonium should behave as in beidellite and produce some surface OH. Perhaps proton migration on the surface and in the bulk precluded the formation of interlayer silanols, but this question requires further study.

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Резюме—Интегральные интенсивности основных типов колебаний аммония в обогреваемых набухающих минералах, насыщенных NH_4^+ , позволяют: (1) определить количество тетраэдрических замещений Si^{4+} на M^{3+} в диоктаэдрических смектитах и (2) оценить степень неоднородности поверхности промежуточных слоев в триоктаэдрических минералах. Это является возможным, так как катионы NH_4^+ , уравнивающие отрицательный заряд тетраэдрических мест, на которые не влияет избыток положительного заряда октаэдрического слоя, имеют симметрию (вероятно C_{3v}) ниже, чем обычная тетраэдрическая симметрия T_d для NH_4^+ . В симметрии C_{3v} полоса ν_1 инфракрасно активна в то время, как в симметрии T_d она является только рамановско активной. Протоны, оставленные после деаммонизирования диоктаэдрических смектитов с тетраэдрическими замещениями, образуют промежуточные силаноловые группы, растягивающие колебания которых дают полосу, отличающуюся от полосы октаэдрических OH-растягивающих колебаний. [E.C.]

Resümee—Die Fundamentalschwingungen des Ammonium in Hitze-behandelten NH_4^+ -ausgetauschten quellbaren Mineralen erlaubt (1) eine quantitative Bestimmung der Menge der tetraedrischen Substitution von Si^{4+} durch M^{3+} in dioktaedrischen Smektiten, und (2) eine Abschätzung des Heterogenitätsgrades der Zwischenschichtoberflächen in trioktaedrischen Mineralen. Dies ist möglich, da NH_4^+ , das die negative Ladung der Tetraederplätze ausgleicht, die nicht durch eine positive Überschlußladung der Oktaederlage beeinflusst werden, eine Symmetrie haben, die niedriger ist (wahrscheinlich C_{3v}) als die übliche tetraedrische T_d -Symmetrie von NH_4^+ . Bei einer C_{3v} -Symmetrie ist die ν_1 -Bande Infrarot-aktiv, während sie in der T_d -Symmetrie nur Raman-aktiv ist. Protonen gingen nach der Deammonisierung dioktaedrischer Smektite mit tetraedrischer Substitution aus zwischengelagerten Silanol-Gruppen. Die Streckschwingungen dieser Protonen ergeben eine Bande, die von denen oktaedrischer OH-Streckschwingungen verschieden ist. [U.W.]

Résumé—La mesure de l'intensité des bandes des modes fondamentaux de vibration de l'ion ammonium dans des minéraux argileux gonflants permet (1) une mesure quantitative du nombre de substitutions Si^{4+} par M^{3+} dans les smectites dioctaédriques, et (2) une estimation du degré d'hétérogénéité de la surface interlamellaire des phyllites gonflantes trioctaédriques. Le principe de cette technique repose sur le fait que les cations ammonium qui neutralisent les charges négatives des sites tétraédriques qui ne sont pas influencés par un excès de charge positive de la couche octaédrique ont une symétrie plus basse (probablement C_{3v}) que la symétrie habituelle de NH_4^+ (T_d). Pour la symétrie C_{3v} , la bande ν_1 est active dans l'infrarouge tandis qu'elle n'est active en Raman que pour la symétrie T_d . Les protons provenant du départ de l'ammoniac dans les smectites dioctaédriques contenant des substitutions tétraédriques forment des groupes silanols dans l'espace interlamellaire et la vibration de valence de ces groupes silanols se situe à une fréquence différente de celle des hydroxyles de la couche octaédrique.