

INFRARED SPECTROSCOPY STUDY OF TETRAHEDRAL AND OCTAHEDRAL SUBSTITUTIONS IN AN INTERSTRATIFIED ILLITE-SMECTITE CLAY

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Abstract—Infrared spectroscopy is used to distinguish between octahedral and tetrahedral substitutions in an interstratified illite-smectite clay. The Hofmann-Klemen (Li) test suggests that the AlMg□ and FeMg□ octahedral vacancies are preferentially occupied by Li after thermal treatment at 250°C. The ammonium (Chourabi-Fripiat) test reveals the beidellitic character by the formation of two OH stretching modes upon deammonation. The illitic layers are not affected since K is not exchangeable.

Key Words—Chourabi-Fripiat test, Hofmann-Klemen effect, Illite, Infrared spectroscopy, Interstratified, Smectite, Tetrahedral substitution.

INTRODUCTION

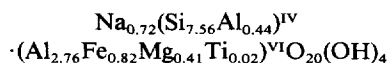
Most natural 2:1 phyllosilicates are either mixtures of swelling and nonswelling clays or they consist of regularly or irregularly interstratified illitic or smectitic sheets. While continuous variation in the composition of trioctahedral clays seems to be well established (Suquet and Pezerat, 1988), such a continuity has not been reported for the dioctahedral family. Within dioctahedral clays, montmorillonite has only octahedral isomorphous substitutions while beidellite has a layer charge attributable to tetrahedral substitutions. Moreover an intermediate situation can exist where both kinds of substitutions occur. In that case, the mean total charge is the sum of the tetrahedral and octahedral layer charges. The minerals in which this intermediate situation exists can be studied semi-quantitatively by chemical analysis and CEC measurements, on Li saturated samples, before and after heating at about 300°C (Hoffmann and Klemen, 1950). However, it is highly desirable to use additional techniques such as nuclear magnetic resonance or infrared spectroscopy because they are sensitive to short-range ordering and they can, therefore, shed light on local environments in the octahedral and tetrahedral layers.

The aim of this contribution is in the application of infrared techniques to a bentonite deposit recently discovered in Tunisia.

An extensive study of a large number of representative samples revealed that this mineral was an irregular interstratified illite-smectite with about 20% impurities (Srasra *et al.*, 1988).

SAMPLES

From the samples studied previously (Srasra, 1987), we have chosen a characteristic one which has the following formula (after repeated Na⁺ exchange):



The contribution of an illitic phase with an ideal composition similar to that given by Bailey *et al.*, (1986) has been subtracted by using the amount of non-exchangeable potassium, as representative of the illitic component. This phase represents 13 wt. % of the sample.

The overall CEC of the interstratified illite-smectite mineral is about 100 meq/100 g of calcined material. Its BET specific surface area, determined by nitrogen adsorption (N₂) after outgassing overnight at 100°C, is 119 m²/g. The internal surface area measured by ethylene glycol adsorption (Fripiat *et al.*, 1971) is 550 m²/g. This corresponds approximately to 85 wt. % of a swelling clay, in agreement with the 13 wt. % of non-swelling compound estimated from the chemical analysis. For the sake of comparison, an illite from Compagnie Française de MOKTA (France) has been used.

METHODS

The Na-exchanged sample was purified by sedimentation, the particles smaller than 2 μm being retained. Further exchanges with Li⁺ and NH₄⁺ in 1N chloride solutions were performed.

Infrared spectra of the sodium-, lithium-, and ammonium-exchanged samples were obtained by using either KBr pellets or self-supporting films (2 mg/cm²) and were recorded with a Perkin Elmer 180 dispersive spectrophotometer from 4000 to 200 cm⁻¹. The spectral resolution is between 2.5 and 1.7 cm⁻¹ in the range of the OH stretching vibrations and about 1.3 cm⁻¹ in the range of the OH bending vibrations. Oriented films were heated in vacuum in a cell equipped with NaCl windows.

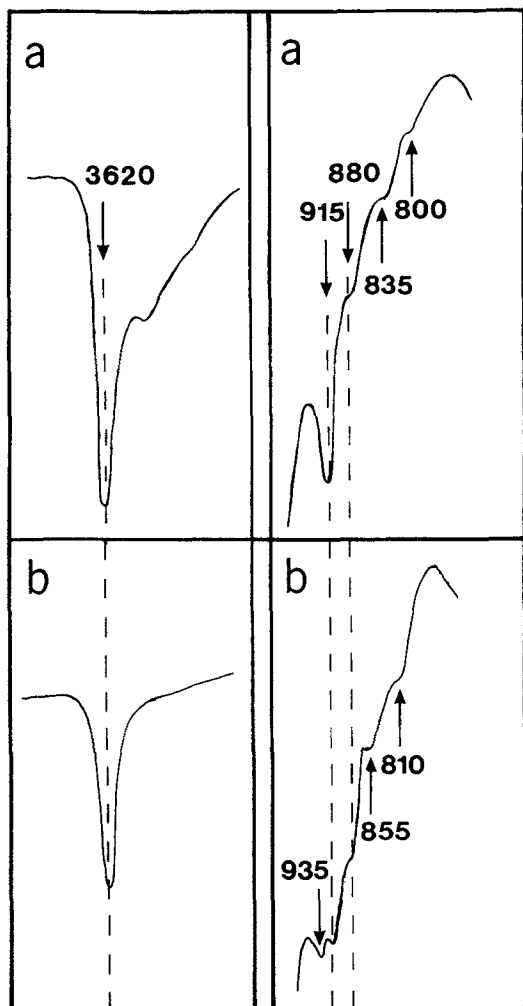


Figure 1. Infrared spectra of Li^+ -exchanged illite-smectite sample: a) air-dried at room temperature and b) dried at 250°C in vacuum.

EXPERIMENTAL RESULTS

Crude and Na- purified samples

The infrared absorption bands of phyllosilicates can generally be decomposed into three groups:

- 1) Stretching (between 3750 and 3400 cm^{-1}) and bending (between 950 and 600 cm^{-1}) vibrations frequencies of the structural OH groups.
- 2) Stretching (between 1200 and 700 cm^{-1}) vibrations of the lattice.
- 3) The bands due to adsorbed species. These bands can overlap those attributable to lattice vibration. For instance the OH stretching of the hydration water may obscure the 3640 and 3400 cm^{-1} spectral domain. The OH bending frequencies of water between 1650 and 1610 cm^{-1} may overlap with a combination band of the silicate lattice (Farmer, 1974; Kodama, 1985).

The infrared spectra of the air-dried Na samples before and after purification are similar. The shoulder at 3695 cm^{-1} and the weak band at 695 cm^{-1} suggest the presence of less than 5 wt. % of kaolinite. The non-clay impurity which is easily removed by sedimentation is essentially quartz detected by the doublet at 800 and 780 cm^{-1} (Farmer, 1974). The Al–Al–OH stretching frequency is observed at 3620 cm^{-1} , while the bending frequency is at 915 cm^{-1} . This can be considered as characteristic of a dioctahedral clay (Caillière *et al.*, 1982) and, more precisely a dioctahedral smectite (Borchardt, 1977). The intense bands at 1110 and 1020 cm^{-1} are those of the Si–O stretching frequencies. The tetrahedral bending modes are at 530 cm^{-1} for Si–O–Al, at 470 cm^{-1} for Si–O–Mg, and at 428 cm^{-1} for Si–O–Si (Van Der Marel and Beutelspacher, 1976).

We note that the intensity of the band at 470 cm^{-1} is higher than that observed normally for a dioctahedral smectite poor in Mg. This difference is probably due to the presence of 13 wt. % illite with the ideal formula, $\text{K}_{1.5}(\text{Si}_7\text{Al})(\text{Al}_{3.5}\text{Mg}_{0.5})\text{O}_{20}\text{OH}_4$, which is richer in Mg than the ideal montmorillonite (Weaver and Pollard, 1973).

The factors that affect the OH stretching frequencies in the dioctahedral 2:1 layer silicates are less clearly defined than are those in their trioctahedral counterparts. Generally, the bending frequencies give clearer information on the octahedral composition in the former than in the latter. Farmer (1974) suggested the following assignments for the OH bending frequencies in dioctahedral 2:1 layers silicates:

- 1) $\text{Al}^{\text{III}}\text{--Al}^{\text{III}}\text{--OH}$ near 915 cm^{-1} ;
- 2) $\text{Fe}^{\text{III}}\text{--Al}^{\text{III}}\text{--OH}$ near 880 cm^{-1} ;
- 3) $\text{Mg}^{\text{II}}\text{--Al}^{\text{III}}\text{--OH}$ near 835 cm^{-1} ; and
- 4) $\text{Mg}^{\text{II}}\text{--Fe}^{\text{III}}\text{--OH}$ near 795 cm^{-1} .

Li exchanged samples: Hoffmann-Klemen effect

Hoffmann and Klemen (1950) have shown that a dioctahedral clay saturated with small cations such as Li^+ (ionic radius 0.68 \AA) loses its CEC and its swelling capacity after heating at 250°C for 24 hr. The suggested interpretation is the migration of Li^+ cations toward the vacant octahedral sites with appreciable reduction of the octahedral layer charge. Furthermore, Glaeser and Mering (1967) have shown that this effect does not occur in hectorite (a trioctahedral clay) and that charge reduction is only partial in clays with Si by Al substitutions in the tetrahedral layer, such as beidellite. The additional electrostatic barrier in the tetrahedral layer probably opposes the Li migration. In summary, the three conditions necessary to obtain the so-called Hoffmann Klemen effect are:

- 1) exchangeable cation with radius smaller than 0.7 \AA ;
- 2) vacancies in the octahedral sheets; and

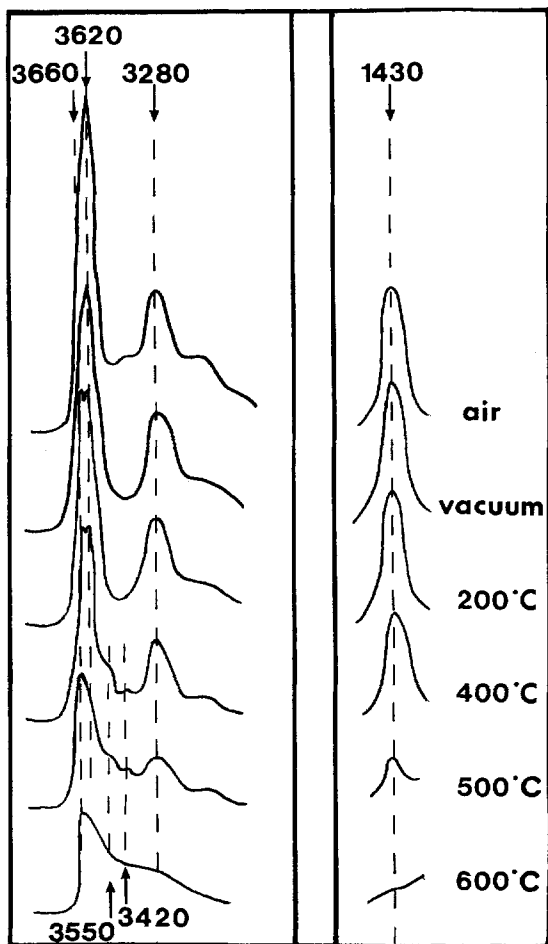


Figure 2. Infrared spectra of NH_4^+ -exchanged illite-smectite sample after treatment at the indicated temperatures.

3) at least a fraction of the lattice charge originating from substitution in the octahedral sheet.

The IR spectrum of the Li-exchanged unheated sample (Figure 1) is similar to that of the Na sample. However after heating at 250°C in a vacuum, three new bands appear at 935 , 855 , and 810 cm^{-1} which could be characteristic of bending frequencies in the environments AlAlLiOH , MgAlLiOH , and MgFeLiOH , respectively (Calvet and Prost, 1971). The residual intensity of the AlAlOH vibration at 915 cm^{-1} and of the FeAlOH vibration at 880 cm^{-1} after heating suggests that a fraction of the octahedral vacancies is not occupied by Li cations in the heated samples. Since the total number of compensating cations is 0.8 per unit cell, while the number of vacancies is 2, this observation is not surprising. What was unexpected is the disappearance of the bands at 835 cm^{-1} and at 800 cm^{-1} . Hence, the vacancies near Mg atoms ($\text{AlMg}\square\text{OH}$ and $\text{FeMg}\square\text{OH}$) to which these bands were assigned are preferentially occupied by Li. Indeed the vibration

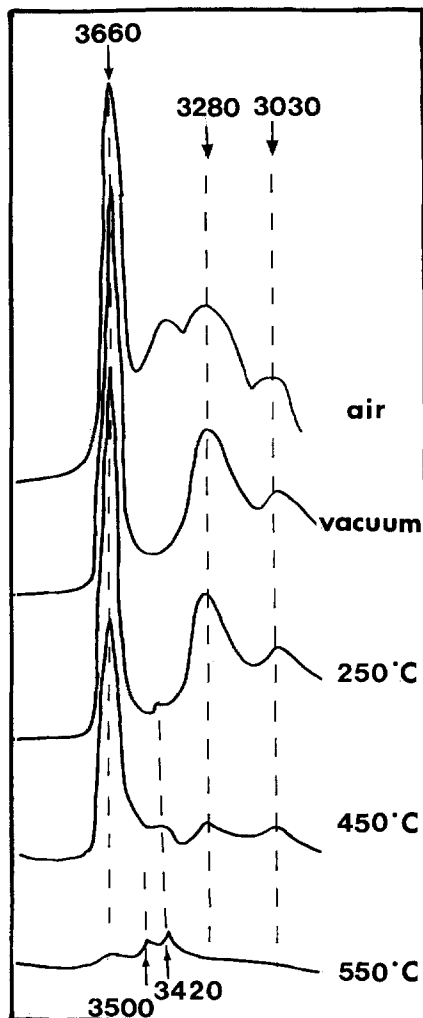


Figure 3. Infrared spectra of NH_4^+ -exchanged beidellite sample after treatment at the indicated temperatures.

$\text{FeAl}\square\text{OH}$ at 880 cm^{-1} is much less affected. Evidently, these conclusions are questionable to the extent that the bending bands, but those at 915 cm^{-1} and 935 cm^{-1} appear as shoulders on the low frequency wing of the SiO stretching.

NH_4^+ exchanged samples: Chourabi-Fripiat test

IR spectra of NH_4^+ exchanged samples heated at different temperatures and in vacuum are shown in Figure 2. This procedure has been proposed as a tool for detecting tetrahedral substitutions by Chourabi and Fripiat (1981). They have shown that an additional band assigned to the stretching mode of the NH_4^+ in C_{3v} symmetry induced by tetrahedral substitution appears in the beidellite (Black Jack Mine) but not in the montmorillonite (Camp Berteau). We have successfully reproduced this test on a beidellite of an unknown

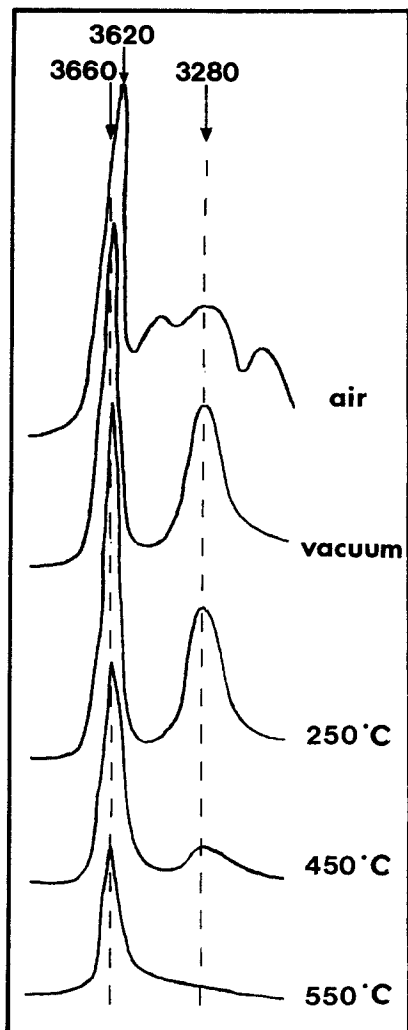


Figure 4. Infrared spectra of NH_4^+ -exchanged Wyoming montmorillonite sample after treatment at the indicated temperatures.

origin and a Wyoming montmorillonite (Figures 3 and 4).

Two bands at 3420 cm^{-1} and 3500 cm^{-1} appear in the IR spectrum of the beidellite heated at 550°C but are not observed in the IR spectrum of montmorillonite. The structural OH vibration at 3660 cm^{-1} in beidellite has completely disappeared at this temperature. The band from structural OH at 3620 cm^{-1} of NH_4^+ -exchanged montmorillonite shifts to 3660 cm^{-1} under vacuum, but it is still observable after heating at 550°C . In Figure 3, the two structural OH bands at 3620 cm^{-1} and 3660 cm^{-1} are distinguishable after heating at 200°C under vacuum, and the former disappears at 500°C (as in the set of spectra observed for illite). The partial beidellitic character of the montmorillonite is evidenced also by the 3550 cm^{-1} and 3420 cm^{-1} residual bands appearing between 400 and 500°C . The broad

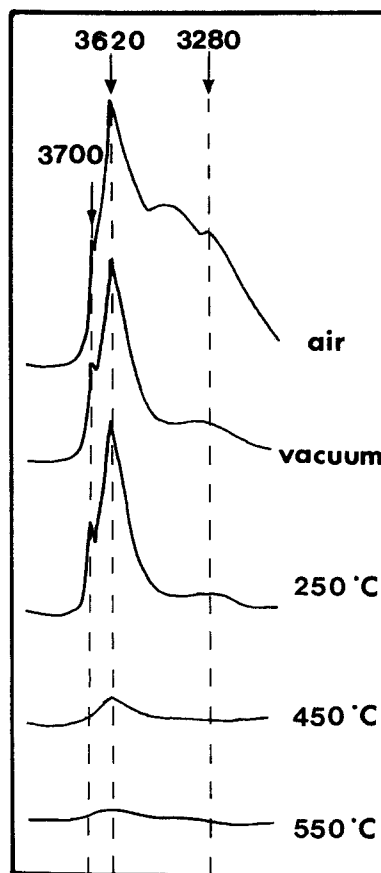


Figure 5. Infrared spectra of illite sample after unsuccessful NH_4^+ exchange and treatment at the indicated temperatures.

peak at 3660 cm^{-1} overlaps with the ca 3550 cm^{-1} peak. The fact that the band at 3660 cm^{-1} does not completely disappear at 600°C is additional evidence for a smectite with a partial beidellitic and montmorillonitic character.

It is also interesting to compare the behavior of a NH_4^+ exchanged illite in the same range of temperature (Figure 5). This test leads to the following conclusions:

- 1) Illite is less thermally stable than the smectites. The intensity of the OH stretching vibration at 3620 cm^{-1} decreases dramatically below 400°C .
- 2) The NH_4^+ stretching band near 3030 cm^{-1} observed in unheated beidellite is not observed in illite, the K-illite being not exchanged by ammonium except on the external surfaces. Hence, the band expected at 3030 cm^{-1} for the $\text{C}3\text{v}$ symmetry must be very weak.

CONCLUSION

From the experimental data described above, the main conclusion is that IR spectroscopy is a valuable tool for studying a complex natural smectite that con-

tains either illite or an interstratified illite-montmorillonite by using the Hofmann-Klemen and the Chourabi-Fripiat tests. The limitation is in the fact that an interstratified mineral cannot be distinguished from a mixture of minerals. This limitation is evident since infrared spectroscopy probes short-range ordering.

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