

INFRARED STUDY OF STRUCTURAL OH IN KAOLINITE, DICKITE, NACRITE, AND POORLY CRYSTALLINE KAOLINITE AT 5 TO 600 K

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Abstract—The resolution of the infrared spectra of structural OH in kaolin-group minerals increases with decreasing temperature. Poorly crystalline kaolinite gives typical infrared spectra, which suggest the existence of kaolinite-, dickite-, and nacrite-like configurations. The relative amount dickite- and nacrite-like configurations compared with kaolinite-like configurations increases with decreasing crystallinity. Low-temperature infrared spectroscopy is a more sensitive means of estimating the degree of order of poorly crystalline kaolinite than is X-ray powder diffraction.

Key Words—Crystallinity, Dickite, Infrared spectroscopy, Kaolinite, Nacrite, X-ray powder diffraction.

INTRODUCTION

The physicochemical properties of kaolin-group minerals are strongly dependent on their crystallinity. The concept of crystallinity as defined by Hinckley (1963) comes from variations observed in the X-ray powder diffraction (XRD) $hk0$ lines of kaolinite samples. Using changes in the relative intensities of these peaks, Hinckley (1963) defined a crystallinity index which is commonly used. Cruz-Complido *et al.* (1982) established a relationship between this index and the proportions of layers expanded by hydrazine.

Relationships have also been found between the Hinckley index and the infrared (IR) absorption bands of structural-OH groups in various kaolinite samples (Brindley *et al.*, 1986; Muller and Bocquier, 1987). These relationships are based on changes in the position and in the relative absorbance of the OH-stretching or the OH-bending bands. Prost *et al.* (1987) showed that the resolution of the IR spectra of the structural-OH groups of kaolinite, dickite, and nacrite is a function of temperature; that property is used here to obtain a better understanding of the modifications that occur in the stretching modes as a function of the crystallinity of kaolin-group minerals.

MATERIALS AND METHODS

The samples used are (see Table 1) from kaolin deposits, except for the Keokuk kaolinite, which comes from a geode, and from soil toposequences. On the basis of literature data, the Keokuk kaolinite, the Wisconsin dickite, and the Swedish nacrite used in this work are good reference samples. Kaolinite samples from soil toposequences were carefully extracted from soil samples to avoid mixing with other components. The JY (yellow clayey matrix) and KR (ferruginous nodules) samples from a lateritic profile in Cameroon are respectively very well and poorly crystalline kaolinite (Muller and Bocquier, 1986, 1987). Red and

beige kaolinite samples from a ferralitic soil toposequence in Casamance are poorly crystalline (Chauvel, 1977). The red kaolinite from Manaus, Brazil, is poorly crystalline (Lucas *et al.*, 1987).

IR spectra were recorded between 5 and 300 K on a Perkin-Elmer 580 spectrophotometer equipped with a microcomputer using a helium cryostat with KRS 5 windows built by the Oxford Instrument Company and between 300 and 600 K using a heating cell equipped with BaF₂ windows built by the Specac Limited Company. These cells made it possible to control the temperature of the sample to a precision of ± 1 K. Samples were studied in KBr discs. Due to the effect of grinding on the stacking of kaolin layers (Miller and Oulton, 1970; De Luca and Slaughter, 1985) samples were gently ground in KBr.

RESULTS

Figures 1a–1c show IR spectra of the stretching vibration of structural-OH groups of the kaolinite, dickite, and nacrite reference samples between 5 and 600 K. The bending spectra of the structural-OH groups of kaolinite, dickite, and nacrite between 5 and 300 K were reported by Prost *et al.* (1987). Figure 2 shows the spectra of the stretching vibration of structural-OH groups of the JY and KR and the red and beige Casamance kaolinite samples, also at 5, 300, and 600 K.

For all these samples the increase of temperature from 5 to 600 K induced opposite shifts of the low- and high-frequency components of the absorption bands of the structural-OH groups. Prost *et al.* (1987) already commented on the spectra of the reference samples obtained between 5 and 300 K. At 600 K the IR spectra of all the kaolinite samples (Figures 1a and 2) are very similar. Three bands at 3623, 3650, and 3677 cm^{-1} are visible. At 600 K the spectra of dickite and nacrite are also characterized by three stretching components at 3623, 3650, and 3683 cm^{-1} , but the 3650- cm^{-1} band

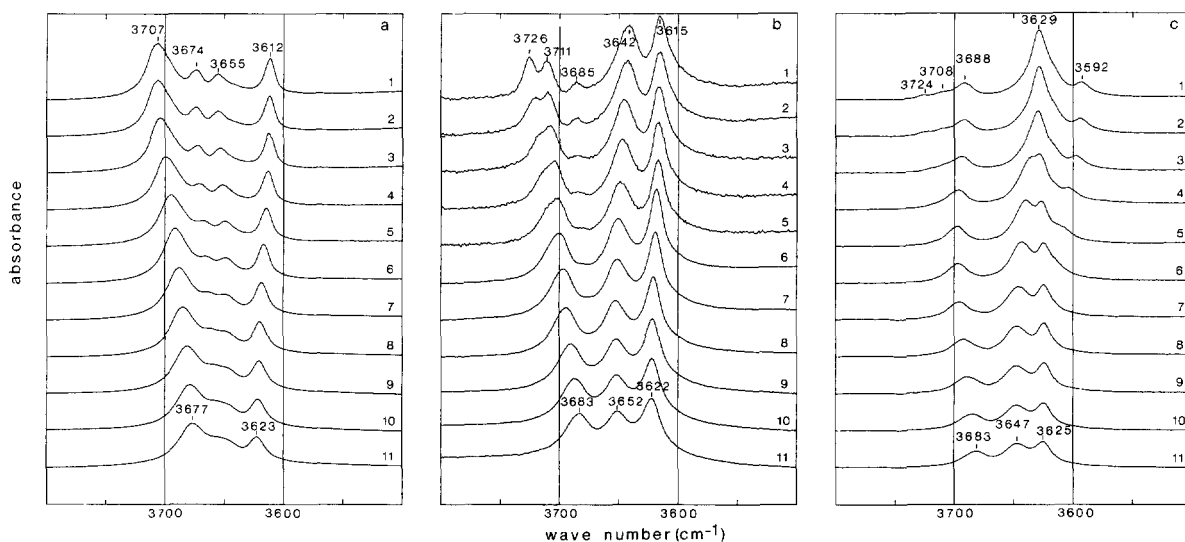


Figure 1. Infrared spectra of (a) kaolinite, (b) dickite, and (c) nacrite in KBr vs. temperature. Numbers from 1 to 11 correspond to increasing temperatures from 5 to 60, 120, . . . , 600 K by steps of 60 K.

is better resolved than that of the kaolinite samples. At 5 K the resolution of the spectra of the structural-OH groups of all samples (Figure 1) is improved due to the opposite shifts of the low- and the high-frequency components of the spectra. At this temperature the IR spectra of Keokuk kaolinite and the dickite and nacrite samples are absolutely characteristic for each sample. The IR spectra of kaolinite samples from soil toposequences show the same absorption bands as the well-

crystallized samples at 3612, 3656, 3675, and 3707 cm^{-1} and an additional band at 3630 cm^{-1} .

Figure 3 shows the IR spectra of structural-OH groups of the Pugu D kaolinite and of kaolinite samples from the soil toposequences (Table 1) at 5 K. Although a difference in the relative intensity of the 3707- and 3612- cm^{-1} bands (I_{3707}/I_{3612}) is apparent between the JY and Keokuk samples (Figures 1a and 2a), both are highly crystalline (Muller and Bocquier, 1986). The IR

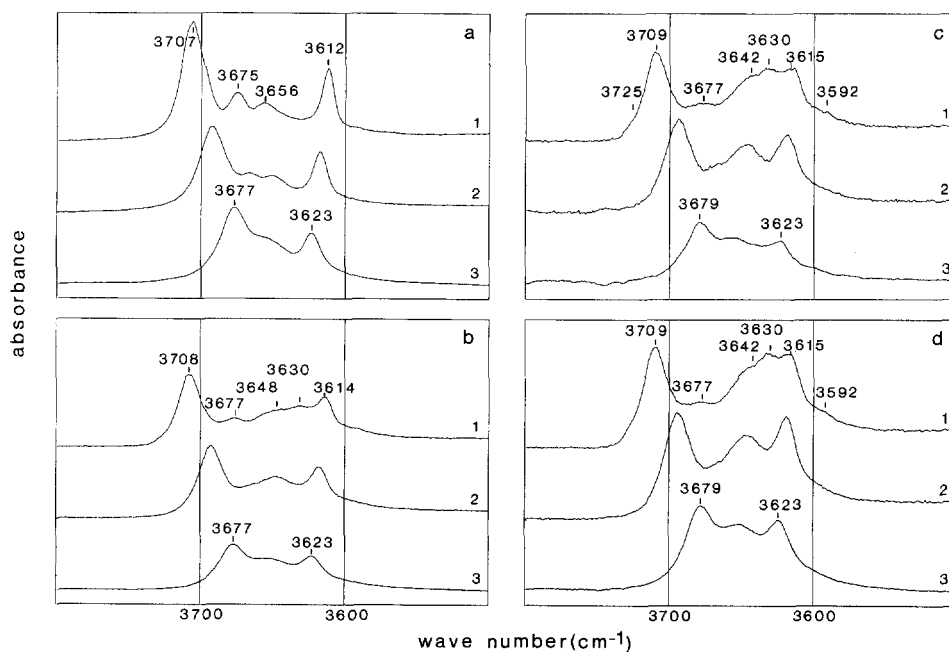


Figure 2. Infrared spectra of (a) JY kaolinite, (b) KR kaolinite, (c) beige Casamance kaolinite, and (d) red Casamance kaolinite in KBr vs. temperature. Numbers 1, 2, and 3 correspond to 5, 300, and 600 K. See Table 1 for sample descriptions.

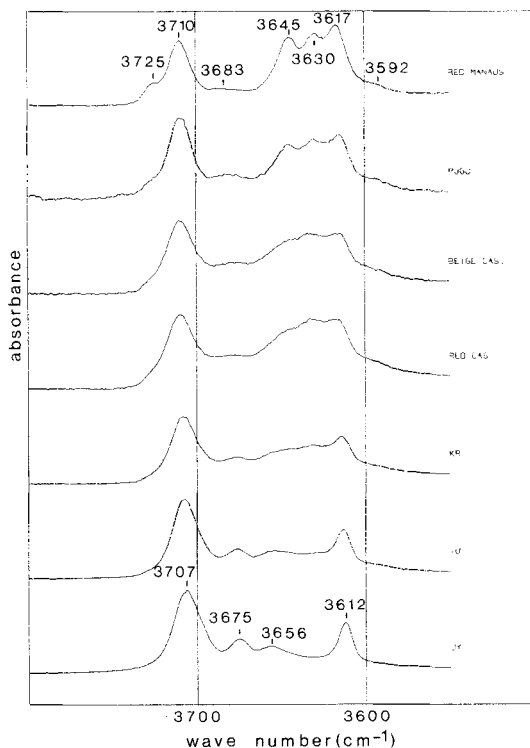


Figure 3. Infrared spectra of kaolinite samples from soil toposequences in KBr at 5 K. The order is a function of the "crystallinity"; JY and red Manaus are very well and poorly crystalline kaolinite, respectively.

spectra of the KR, the red and beige Casamance, and the red Manaus samples (Figure 2) show additional absorption bands at 3592, 3630, and 3725 cm^{-1} . These bands are also visible in the spectrum of the Pugu D kaolinite and are well resolved in the spectrum of the Manaus sample.

DISCUSSION

The spectra in Figures 1a–1c show that the stretching bands of the structural-OH groups of kaolinite, dickite, and nacrite progressively shift as the temperature increases from 5 to 600 K. The same shift can be seen for the IR bands of poorly crystalline kaolinite samples shown in Figure 2. The progressive and reversible shifts observed with changing temperature suggest that no phase change occurred. The frequency shift of the stretching modes of external OH groups, located between the layers, is larger than for internal OH groups. Indeed, the frequency of the external OH groups of kaolinite (Figure 1a) shifted from 3707 to 3677 cm^{-1} as the temperature increased from 5 to 600 K, but the frequency of internal OH groups of kaolinite (Figure 1a) shifted only from 3612 to 3623 cm^{-1} over the same temperature range. The shift could also have been a consequence of perturbations in the local electric field

Table 1. Location and source of samples studied.¹

Sample	Locality	Source
Kaolinite	Keokuk, Iowa	W. D. Keller
Dickite	Wisconsin	C. B. Roth
Nacrite	Sweden	A. M. Brusewitz
Kaolinite	Pugu D	D. Morgan
JY	Cameroon	(Muller and
KR	(lateritic profile)	Bocquier, 1986)
Casamance beige	Casamance,	(Chauvel, 1977)
Casamance red	Senegal, fer- ralitic soil toposequence	
Manaus red	Manaus, Brazil	(Lucas <i>et al.</i> , 1987)

¹ Papers given as references give more details about the location and origin of soil kaolinites.

surrounding the OH oscillators due to small changes with temperature in the location of the atoms in the structure. XRD data for kaolinite and dickite at 96, 298, and 573 K show a shift of all peaks to higher angles (i.e., lower d-values) as temperature is decreased, which is simply a manifestation of thermal expansion of the kaolinite and dickite structures (D. L. Bish, Los Alamos National Laboratory, Los Alamos, New Mexico, personal communication).

The shift of the high-frequency components to higher frequencies and of the low-frequency components to lower frequencies as the temperature decreases from 600 to 5 K leads to changes in the resolution (Prost *et al.*, 1987). As a result of the differing temperature shifts of the various peaks, spectra characteristic of the material may be taken at any temperature according to the resolution required. Except for nacrite (Figure 1c), the best resolution, i.e., the greatest number of bands visible on the spectra, was obtained from spectra recorded at 5 K.

The comparison of the spectra of the minerals obtained at 5 K (Figures 1a and 1c) shows that the Keokuk kaolinite, the Wisconsin dickite, and the Swedish nacrite have characteristic infrared absorption spectra for their structural-OH groups that can be used unambiguously as "finger prints" (Prost, 1984). The Pugu D kaolinite and the kaolinite samples from the soil toposequences have a different set of absorption bands at 3592, 3617, 3630, 3645, 3683, 3710, and 3725 cm^{-1} (Figure 3), which are characteristic of these poorly crystalline minerals. The intensity of the bands at 3592, 3630, 3645, and 3725 cm^{-1} decreased as the crystallinity increased (Figure 3).

These data suggest that poorly crystalline kaolinite samples have a specific IR spectrum of their structural-OH groups, meaning that the structural-OH groups of these minerals are, at the molecular scale, in specific configurations. These configurations are the same for the IU, the KR Cameroon, the beige and red Casa-

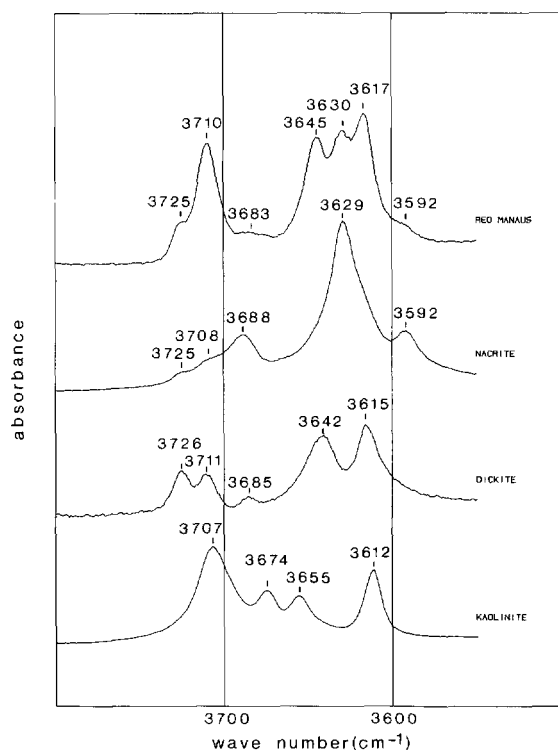


Figure 4. Infrared spectra of kaolinite, dickite, nacrite, and poorly crystallized kaolinite (red Manaus) in KBr at 5 K.

mance, the Pugu D, and the red Manaus samples (Figure 3).

Remarkably, the absorption band frequencies of poorly crystalline kaolinite samples were very close to those of kaolinite (3617, 3710 cm^{-1}), dickite (3645, 3726 cm^{-1}), and nacrite (3592, 3629 cm^{-1}) (Figure 4). Farmer and Russell (1964) and Lombardi *et al.* (1987) suggested the existence of dickite- and nacrite-like configurations in poorly crystalline kaolinite samples. This is supported in our work by the development, with decreasing temperature, of the 3645–3726- cm^{-1} and 3592–3630- cm^{-1} components, which are characteristic of dickite and nacrite (Figure 4).

The shift from 3707 to 3710 cm^{-1} observed as the crystallinity of the samples decreased can be explained by the increasing contribution of dickite-like configurations and the overlapping with the 3707- cm^{-1} component of kaolinite of the 3711- cm^{-1} component of dickite. The same explanation can be given for the 3612- cm^{-1} band which shifts to 3617 cm^{-1} due to the overlapping of the 3612- cm^{-1} band with the 3615 and 3629- cm^{-1} components.

SUMMARY AND CONCLUSIONS

Comparison of the low-temperature IR spectra of Keokuk kaolinite, Wisconsin dickite, and Swedish nacrite with the IR spectra of poorly crystalline ka-

olinite samples showed that kaolinite configurations co-exist with dickite- and nacrite-like configurations in the latter materials.

The existence of dickite-like configurations in these poorly crystalline kaolinite samples was already suggested by Cruz-Complido *et al.* (1982), on the basis of the partial expansion of these minerals with hydrazine. These dickite-like configurations were not detectable by X-ray powder diffraction; a study of the structural-OH groups at a molecular level, using low-temperature IR, was necessary to demonstrate their existence. Thus, low-temperature IR appears to be a more sensitive tool than X-ray powder diffraction for the estimate of the "crystallinity", as it was defined by Hinckley (1963). Low-temperature IR spectra showed that the relative amount of dickite- and nacrite-like configurations, compared with kaolinite-like configurations, increased with decreasing "crystallinity".

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