STRUCTURAL ASPECTS OF KAOLINITE
USING INFRARED ABSORPTION

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ABSTRACT

Using a single beam infrared spectrometer equipped with LiF optics, the OH stretching vibrations of kaolinites were studied. Using oriented aggregates, spectra were obtained for each sample with the slide positioned at 0°, 15°, 30° and 45° to the incident radiation. Each sample was heated to 100° C. and 200° C. After each heating the above spectral determinations were repeated.

Three distinct bands of absorption are present. In order of decreasing absorption intensity they are: 3704 cm^{-1}, 3635 cm^{-1} and 3663 cm^{-1}. Heating did not significantly affect the absorption intensity or frequency of any of the bands. Increasing the angle of incidence resulted in a significant increase of absorption intensity of the band at 3704 cm^{-1}. These results indicate that a majority of the "free" hydroxyl bonds having a vibration frequency of 3704 cm^{-1} are oriented perpendicular to the basal plane. The bands at 3663 cm^{-1} and 3635 cm^{-1} are probably indicative of interlayer hydroxyl bonding and hydroxyl bonds pointing into vacant octahedral sites respectively.

INTRODUCTION

Early investigators using infrared spectrometry to study minerals were interested primarily in using the tool as a means of "fingerprinting." As instrumentation and techniques improved the method became useful as an aid in studying the structure of minerals. The early, and to a large extent the present, clay mineral analytical work using infrared spectrometry was concerned with that portion of the electromagnetic spectrum which encompasses the stretching and bending vibrations of Si-O-Al bonds.

This report concerns a detailed survey of a relatively small portion of the electromagnetic spectrum encompassing the characteristic O-H stretching vibrations of kaolinite.

PROCEDURE

Using a single beam, double pass infrared spectrometer equipped with LiF optics, the OH stretching vibrations (3800 cm^{-1} − 3200 cm^{-1}) of kaolinite were studied. Oriented aggregates of the less than two micron diameter size fraction (based on Stoke's Law) were prepared in the conventional manner. Normal mounting slides were not useable because of excessive absorption. Peels of oriented clay minerals as described by Serratosa (1962) were not feasible because of the resultant high energy losses. Various organic materials (Saran wrap, cellophane, scotch tape) were shown to have absorption bands interfering with those of interest

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in the clay minerals. The mounting material found most suitable was a cover glass—Corning 22 mm square, No. 0 thickness. The cover glass absorbed approximately five per cent of the incident radiation at 3900 cm^{-1} and had no interference bands in the region of interest.

Using the goniometer shown in Fig. 1, three sets of spectra were determined for each sample, these were: unheated, heated to 100° C. and heated to 200° C. The heating procedure consisted of placing the sample
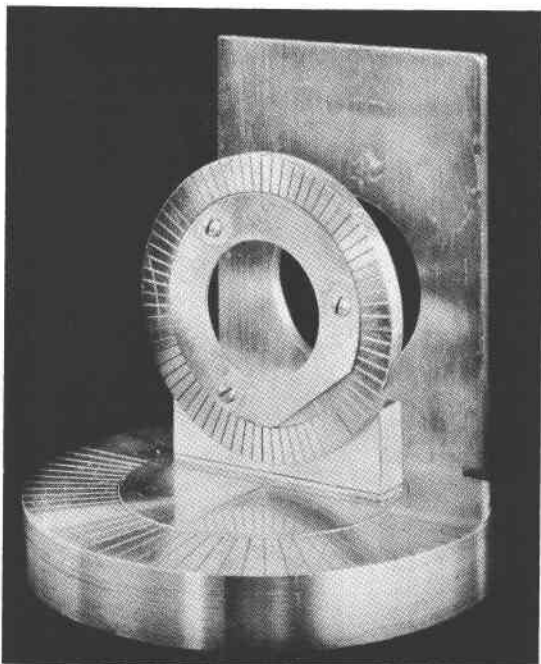

FIG. 1. Goniometer used to orient samples in the infrared beam (modeled after a similar goniometer built by Dr. J. M. Serratosa).

in a cool oven, heating the oven to the desired temperature as rapidly as possible, permitting the samples to soak at that temperature for one hour and removing the samples to a desiccator to cool where they remained until immediately before subjection to infrared study. Each set of spectra consists of four individual determinations: the mounting medium oriented at 0°, 15°, 30° and 45° to the incident radiation.

The same sample slide was used for each determination, heated and unheated, thereby eliminating intensity variations due to concentration differences except as the concentration may vary from point to point on the slide.

A background determination was made following each succession of

four incidence angle determinations. The background was determined by using a blank cover glass, which was shuttered to the desired intensity of transmission at the starting point with silver foil, and by using the same instrument control settings as used for the oriented aggregate. For the background determinations of heated samples a cover glass which had been heated with that sample was used.

Attempts were made to decrease, if not eliminate, the absorption bands of atmospheric H_2O and CO_2, which occur in the spectral range of interest, by flushing the sample area with anhydrous nitrogen which had been passed through a drying column and by placing silica gel and Ascarite under the covers of the instrument. However, after opening the sample area to insert the blank cover glass for background determination it was essentially impossible to achieve the same degree of flushing. Therefore, the operation was conducted without flushing in a room which was thermostatically controlled and which was kept at relatively constant humidity by an oversize room dehumidifier. Because the clay mineral spectra and the background spectra are influenced by the same atmospheric absorption it was assumed that for all practical purposes the effects of the atmosphere cancelled.

The plotting procedure used is $\mathrm{Log_e}\ I_0/I$ (where I_0 is the background absorbancy and I is the absorbancy of background plus material of interest) versus wave number (cm^{-1}). Corrections were applied for the loss of energy due to reflection as the angle of incidence was increased.

SAMPLES USED

Table 1 is a list of samples used for this study. Figure 2 shows the x-ray diffraction data for each sample used.

TABLE 1. LIST OF SAMPLES USED

Sample #	General Description	Sample Source
1	Kaolinite, some quartz, illite	Baker commercial grade kaolinite
2	Essentially pure kaolinite	McIntyre, Georgia

As shown, sample #1 contains minor amounts of quartz and illite in addition to kaolinite. Sample #2 is essentially pure kaolinite except for possibly a small amount of montmorillonite. Also, as shown by the diffraction patterns, only the peaks representing basal plane reflections are present for sample #2 whereas, for sample #1 peaks representative of planes other than basal are also present indicating that the degree of orientation of particles on the slide is considerably better for sample #2 than for sample #1.
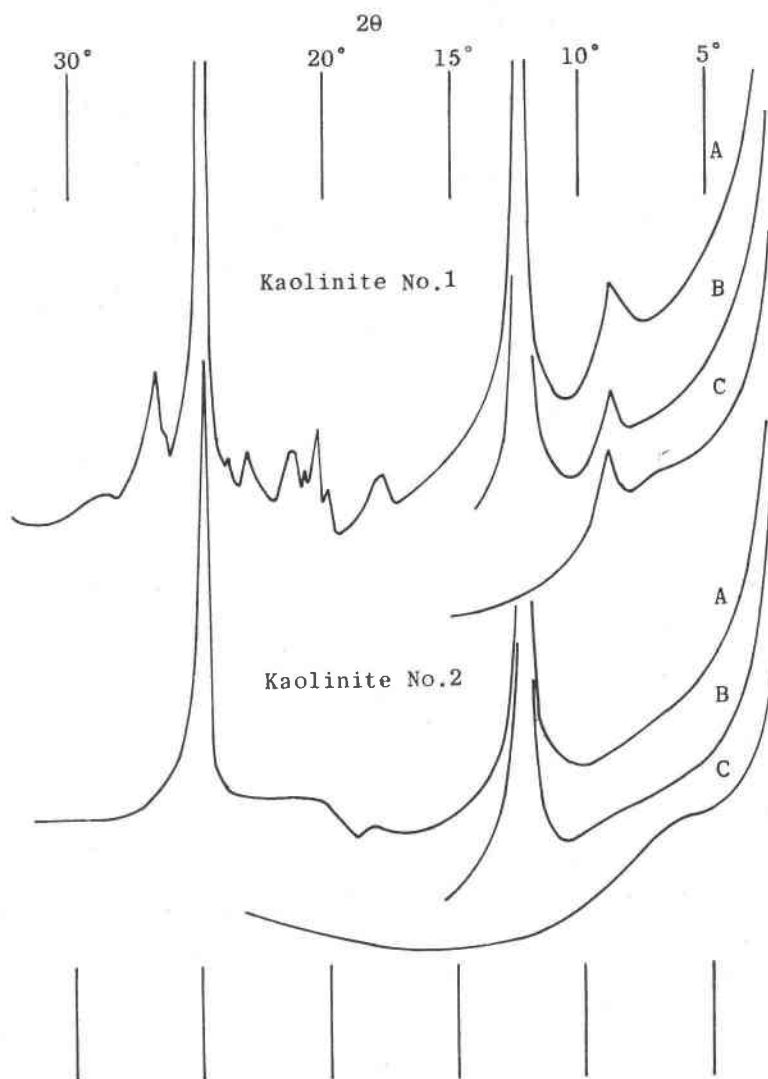
FIG. 2. X-ray diffraction patterns of oriented samples using Cu Kα radiation.
A=untreated, B=glycolated, C=heated at 550° C. for 1 hr.

Experimental Data and Results

Figure 3 presents the infrared absorption spectra for the kaolinites used.

Discussion

The use of infrared spectrometry to determine bond directions has been clearly described by Bassett (1960). Briefly, in order for infrared absorption to occur it is necessary that a dipole moment exist. Polarized radiation interacts with the molecules of oriented crystals only when the electric vector of the radiation makes an angle different from 90° with the dipole moment of the atomic group absorbing at the frequency of the radiation. Maximum absorption occurs when the vibration direction of the dipole moment is parallel to the vibration direction of the incident radiation.

Figure 3 shows three distinct bands of absorption, the frequencies of which correspond closely to those observed by: Roy and Roy (1957), 3705 cm^{-1}, 3663 cm^{-1}; Fripiat and Toussiant (1960), 3700 cm^{-1}, 3663 cm^{-1}, 3627 cm^{-1}; Van Der Marel and Zweirs (1958), 3698 cm^{-1}, 3660 cm^{-1}, 3630 cm^{-1}; and Serratosa *et al.* (1962), 3695 cm^{-1}, 3670 cm^{-1}, 3650 cm^{-1}, 3620 cm^{-1}. All three bands observed in this study exhibit an apparent increase of absorption intensity as the angle of incident radiation is increased; however, the change of absorption intensity of the band at 3704 cm^{-1} is significantly greater than that of the other two bands for equal variations of the angle of incidence.

For bands of absorption at the same frequency the change of absorption intensity for equal variations of the angle of incidence is greater for sample #2 than for sample #1. This difference is assignable, in part at least, to the difference of perfection of particle orientation on the slide as described earlier.

The following discussion of the possible structural locations of OH bonds which satisfy the frequency and directional evidence of the infrared spectra is based on the kaolinite structure depicted by Fig. 4.

The band of absorption at 3704 cm^{-1} is the frequency considered characteristic of "free" OH bonds, *i.e.*, OH groups in which the oxygen-hydrogen bond is the only bond affecting the hydrogen (Serratosa and Bradley, 1958; Newnham, 1961).

Because the intensity of absorption of this band increases as the angle of incident radiation is increased, it follows that in the samples oriented at 0° some of the free OH bonds are oriented parallel to the direction of incident radiation. Assuming the aggregate is perfectly oriented on the slide, these bonds are perpendicular to the basal plane.

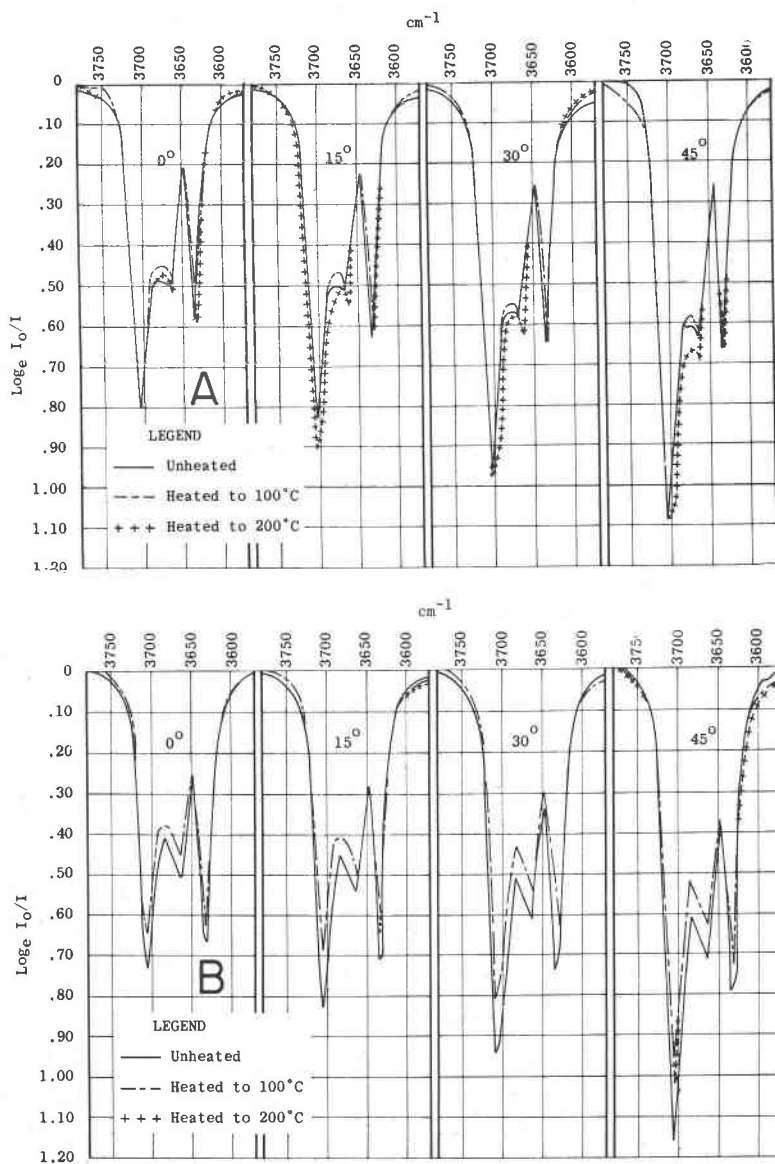Structurally, the most conceivable positions of OH groups meeting

FIG. 3. Infrared absorption spectra of kaolinites (degree values refer to angle of incidence). A. Kaolinite #1. B. Kaolinite #2 (due to instrumental failure the 200° C. spectra for 0° and 30° are not available).

the 3704 cm^{-1} "free" frequency requirement are the OH groups in the layer common to the octahedral and tetrahedral sheets with the proton end pointing toward the hole formed by the oxygens in the basal tetrahedral sheet. Also hydroxyl groups located in the basal octahedral layer of an opposing sheet which are pointing away from the octahedral layer toward the same hole from the opposite side, would essentially meet the free requirement. The difference in "freedom" afforded by these two locations has been cited by Serratosa *et al.* (1962) to account for the broad-
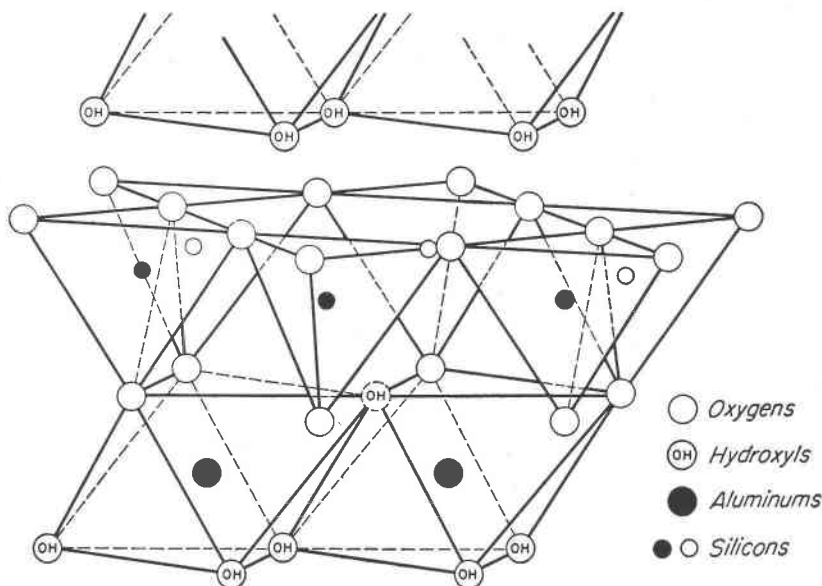

Fig. 4. Diagrammatic sketch of the structure of kaolinite (after Gruner in *Clay Mineralogy* by Ralph E. Grim, 1953, McGraw-Hill Book Company, by permission).

ness of the absorption peak at 3704 cm^{-1}. Both of these positions provide orientations conforming to the requirements for increasing absorption intensity as the angle of incidence is increased.

OH groups located at the edges and in fractures of plates, although relatively very few in number, may account for a very small percentage of the absorption at 3704 cm^{-1}.

The bands of absorption at 3663 cm^{-1} and 3635 cm^{-1} may be analogous to bands at 3644 cm^{-1} and 3617 cm^{-1} observed by Newnham (1961) studying dickite. Newnham credits the band of absorption at 3644 cm^{-1} to a bond between a basal hydroxyl of one sheet and the "puckered" oxygen of the next sheet. Newnham visualizes the puckering to be the result of shortened shared edges in the layer common to the octahedral-

tetrahedral layer causing "tilting" of the silica tetrahedra. The effect of the tilting is to lower two of the basal oxygens while elevating the remaining basal oxygen of a silica tetrahedron.

Newnham credits the band at 3617 cm^{-1} to interlayer hydrogen bonding involving two basal hydroxyls of one sheet and the remaining two oxygens of an opposing silica tetrahedron.

A possible alternative assignment of the observed band at 3635 cm^{-1} is based on the observations by Serratosa and Bradley (1958) and Bassett (1960) in which they noted that dioctahedral micas (muscovite) have a band of absorption at approximately 3620 cm^{-1} whereas, trioctahedral micas (phlogopite) have a band of absorption at approximately 3700 cm^{-1}. These observations suggest that the band of absorption at 3620 cm^{-1} is indicative of hydroxyl groups of which the proton end is probably pointing into vacant octahedral sites. A hydroxyl bond with a proton end pointing into the vacant octahedral site would have its major directional component parallel to the basal plane. Such a bond orientation should have little or no effect on the absorption intensity as the angle of incident radiation is increased, which conforms with the results of this study and that by Bassett (1960). A similar conclusion is cited by Serratosa *et al.* (1962).

The frequency difference between hydroxyl groups having hydrogen ends pointing into oxygen holes (3700 cm^{-1}) and hydroxyl groups having hydrogen ends pointing into vacant octahedral sites (3635 cm^{-1}) is best accounted for by the proximity of other atoms in the latter case, possibly another proton pointing into the same vacant site from an opposing position.

The band of absorption at 3663 cm^{-1} is probably indicative of interlayer hydrogen bonding. As shown by the absorption spectra, the change of absorption intensity with increasing angle of incidence of the band at 3663 cm^{-1} appears to be significant when compared to the intensity change of the band at 3635 cm^{-1}. This indicates that a component of the bonding represented by the absorption band at 3663 cm^{-1} is perpendicular to the basal plane.

The relative intensity of absorption of the three bands observed in kaolinites can be explained by the number of possible hydrogens available for each type of bond described. In the kaolinite structure, positions are available for eight hydroxyl groups per unit cell. Ideally these positions are distributed as follows, based on the direction in which the hydrogen end is pointing and therefore located: none in the oxygen layer of the tetrahedral layer; two in the layer common to the tetrahedral-octahedral layer; and six in the basal octahedral layer. However, this distribution is not fixed as shown by Fripiat and Toussiant (1960). Two hydroxyls can

be pointing toward the basal layer of the tetrahedral sheet, four can be pointing toward the layer common to the tetrahedral-octahedral layer and six can be pointing away from the basal octahedral layer. Because only a total of eight can be accommodated, it follows that the maximum number cannot be present simultaneously at each of the possible locations.

Because of the plotting procedure used for this study, the relative number of hydroxyl groups represented by each absorption band cannot be correlated directly to the area under the peak. However, indications are that the majority of OH bonds are in positions described as meeting the 3704 cm^{-1} frequency requirement. The remaining OH groups appear to be about equally divided between interlayer bonding and pointing into vacant octahedral sites.

Based on absorption peak areas of randomly oriented samples, Serratosa *et al.* (1962) have assigned four OH bonds to the band of absorption at 3700 cm^{-1} and two to the band at 3635 cm^{-1}. The two remaining bonds are assigned to interlayer bonding represented by bands of absorption at 3650 cm^{-1} and 3670 cm^{-1}. The results of this study appear to be in good agreement with these assignments.

SUMMARY AND CONCLUSIONS

Infrared absorption spectra of the OH region of kaolinites show three distinct bands of absorption at 3704 cm^{-1}, 3663 cm^{-1}, and 3635 cm^{-1}. The spectra are shown to be reproducible both with respect to frequency and intensity.

Heating to 200° C. had no significant effect on the spectra. Variation of the angle of incident radiation resulted in significant increases of absorption intensity of the bands at 3704 cm^{-1} and 3663 cm^{-1}.

The observed bands of absorption have been assigned as follows:

1. Band at 3704 cm^{-1}—indicative of "free" OH bonds with the hydrogen end pointing toward the hole of oxygens in the basal tetrahedral layer from the common octahedral-tetrahedral layer and from opposing basal octahedral layers resulting in a preferred bond orientation of which a major component is perpendicular to the basal plane. A very few bonds vibrating at this frequency may be located at the edges and in fractures of plates.

2. Band at 3663 cm^{-1}—indicative of interlayer hydrogen bonding in which a major component of the bonding is perpendicular to the basal plane.

3. Band at 3635 cm^{-1}—indicative of OH bonds in which the hydrogen end is pointing into vacant octahedral sites resulting in a bond orientation for which the major component is parallel to the basal plane.

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