cosmic radiation on Lake Michigan was found to be 4.4 ± 0.2 μr/hr. The dose rate from U, Th, and K on the Argonne site amounted to 8.0 ± 0.3 μr/hr. From September 1962 through October 1963 the dose rate from fission products on the site ranged from a low of 2.0 μr/hr to a high of 7.5 μr/hr. The decrease in terrestrial dose rate with height from the surface to 35 m was attributed to absorption and scattering of photons of energy greater than 0.5 Mev.

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Infrared Study of Selective Deuteration of Kaolinite and Halloysite at Room Temperature

Abstract. *Deuteration of expanded hydrazine-kaolinite complex at room temperature shifts the infrared stretching frequencies of the inner-surface hydroxyls from 3695, 3670, and 3650 cm^{-1} to 2725, 2710, and 2698 cm^{-1}, respectively, and the inner hydroxyls absorbing at 3620 cm^{-1} to 2675 cm^{-1}. The OH-OD exchange for the inner-surface hydroxyls varies from 60 to 67 percent, whereas it is only 22 percent for the inner hydroxyls.*

Assignment of infrared absorption bands to specific groups is facilitated by the use of isotopes. Deuterium exchange is particularly helpful for assignment to OH stretching vibrations —ν(OH)—where the hydrogen is exchangeable. At room temperature and at atmospheric pressure the internal hydroxyls of nonexpanded kaolinite are not sufficiently exchangeable for deuteroxyls to yield any ν(OD) absorption band (*1*). However, when koalinite was exposed to D_2O vapor at 180°C during a period of 3 months, 36 percent of the internal hydroxyls were exchanged (*2*). When the kaolinite-D_2O system is submitted to hydrothermal conditions, that is, at temperatures of 300° to 400°C and at pressures of 700 to 2100 bars (*3*), the OH-OD exchange reaches about 50 percent. Stubican (*4*) accomplished complete OH-OD exchange only by resynthesis of kaolinite and halloysite with D_2O from heated specimens at 1000°C.

Hydrothermal deuteration of kaolinite has indicated that the 3800 to 3000 cm^{-1} region is not the only region where OH absorptions occur. A comparison of the infrared spectra of OH and OD kaolinite shows that the absorption doublet at 938 and 910 cm^{-1} is shifted to 720 and 687 cm^{-1}; the dependence of this doublet on the cations suggests it is an OH-Al vibration (*5*). However, the hydrothermal deuteration does not provide any evidence for the assignment of the ν(OH) absorption frequencies to different OH sites in the lattice of kaolinite. The relative intensities of the absorption bands are the same in the OD region (2800 to 2200 cm^{-1}) as in the original OH region (3800 to 3000 cm^{-1}) (*3*). The only exchange mechanism that would provide evidence for a correlation of the ν(OH) to lattice sites should selectively deuterate the hydroxyls according to their accessibility for the exchange reaction. The "outer hydroxyls" (*6*) are readily accessible for deuteroxyl exchange but they do not yield any ν(OD) absorption band. The remaining hydroxyls are located inside the microcrystals and are not easily exchangeable. However, it has been shown by Ledoux and White (*6*) that the expansion of kaolinite with potassium acetate greatly facilitates the exchange of the internal hydroxyls. Our study is an attempt to show that the expansion of kaolinite and halloysite allows selective deuteration of internal hydroxyls and to provide evidence for the assignments of ν(OH)−ν(OD) shifts.

Three kaolinite samples (*7*) were intersalated with potassium acetate; one was washed three times with pure formamide, another with a saturated solution of urea, and the last sample with anhydrous hydrazine. X-ray diffraction (*8*) of oriented film specimens on a glass slide showed that the largest amount of expansion was obtained with hydrazine. A small portion (2 ml) of the expanded hydrazine-kaolinite complex (10.4 Å) was washed twice with 1 ml of D_2O; the residue was redispersed in 3 ml of D_2O and was allowed to remain in contact 30 minutes. A 1-ml portion of the D_2O suspension was evaporated at 110°C on an Irtran window (*9*) and the spectrum of the oriented clay film was determined by x-ray diffraction and infrared spectroscopy. The x-ray pattern of the D_2O-treated kaolinite shows that the mineral has collapsed to its original spacing, 7.13 Å. Figure 1 shows a comparison of the infrared spectra (*10*) of natural kaolinite with the D_2O-treated sample; the spectra were determined with two orientations of the clay film. In the infrared spectrum of natural kaolinite (Fig. 1*a*), four ν(OH) absorption frequencies are observed at 3695, 3670, 3650, and 3620 cm^{-1}. Both absorptions at 3695 and 3620 cm^{-1} are more intense than the 3670 and 3650 cm^{-1}. The spectrum of deuterated kaolinite (Fig. 1*b*) shows a reduction in the intensity of the 3695, 3670, and 3650 cm^{-1} absorptions, and the occurrence of strong bands at 2725 and 2698 cm^{-1} and weak absorptions at 2710 and 2675 cm^{-1}; the intensity of the 3620 cm^{-1} band is not

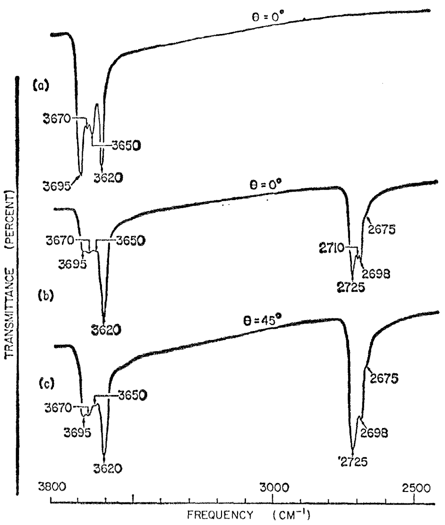

Fig. 1. Infrared spectra of (*a*) natural kaolinite heated to 110°C, concentration 1.20 mg/cm^2; (*b*) deuterated kaolinite heated at 110°C, the oriented film is at right angle to the infrared beam, concentration 1.15 mg/cm^2; (*c*) sample (*b*) rotated 45°. Scale, ×1.

significantly affected by the deuteration process.

The observed intensity of an infrared absorption band depends on the angle between the direction of the alteration of the dipole moment and the direction of vibration of the radiation. If the dipole moment change is parallel to the direction of "propagation" of the infrared light, no absorption takes place; if they lie at right angles to one another, maximum absorption occurs; between the two cases there is a gradual transition. Bassett (*11*) has clearly described the interaction of the infrared beam with the hydroxyls of micas.

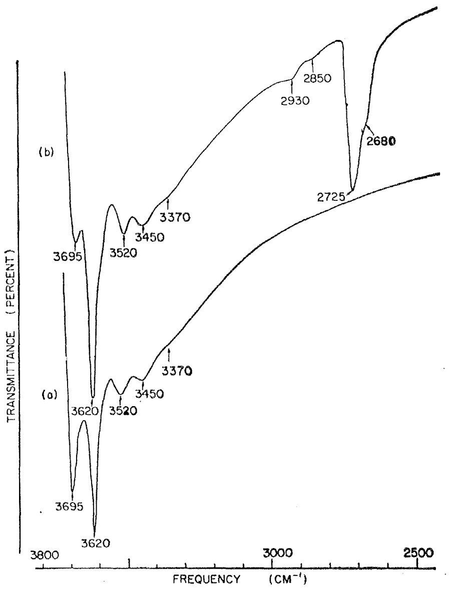

Fig. 2. Infrared spectra of (*a*) natural halloysite with gibbsite impurity, heated at 110°C, concentration 2.10 mg/cm^2; (*b*) deuterated halloysite-gibbsite heated at 110°C, concentration 1.92 mg/cm^2. Scale, ×5.

A rotation of 45 deg of the deuterated kaolinite film in the infrared beam produces considerable increase in the intensity of all the absorption bands, except that of the 3620 cm^{-1} (Fig. 1*c*). The differences between the background line absorption and the minimum transmittance (Table 1) indicate no change at all in the intensity of the 3620 cm^{-1} absorption band. The pleochroic effect on the oriented kaolinite film indicates that the direction of the dipole change of OH groups absorbing at 3695 and 3670 cm^{-1} and of OD groups absorbing at 2725 and 2689 cm^{-1} is nearly at right angles to the basal plane (001); for the 3650 and 2675 cm^{-1} bands the angle is large but less than 90 deg. The direction in dipole moment change of the OH groups absorbing at 3620 cm^{-1} makes an angle of 16 deg with the *ab* cleavage plane (*12*).

Similar observations were previously reported (*13*) and the pleochroic absorption band at 3695 cm^{-1} was interpreted as indicative of OH-bond axes at right angles to the (001) plane, whereas the nonpleochroic absorption at 3620 cm^{-1} was associated with OH groups in which the proton end was pointing into vacant octahedral sites. The measurements in pleochroic studies indicate only the direction of the dipole moment change and not essentially the direction of the vibrating bond. The direction of the dipole moment change and the bond axis may not be parallel because of crystalline perturbations or because of intramolecular interactions with other parts of the molecule. For instance, the ν(CO) stretching mode of the peptide group has been shown experimentally and theoretically to have a transition moment making an angle of about 20 deg with the axis of the (C=O) bond (*14*). Thus, caution must be exercised in making structural deductions from pleochroic studies. According to Huggins and Pimentel (*15*), the interpretation of the pleochroism in terms of bond orientations is acceptable only for linear hydrogen bonds for which the stretching modes are enhanced by the dipole change induced along the bond.

In this study an attempt was made to relate the average (O-H · · · O) distance of 3.02 Å reported by Radoslovich (*16*) for muscovite and the usually observed absorption frequency at 3620 cm^{-1}, and also the (O-H · · · O) values obtained by Newnham (*17*) for dickite, 3.12 Å, 2.97 Å, and 2.94 Å, with the absorption frequencies 3700, 3644, and 3617 cm^{-1}. When the above values were plotted and compared with the correlation curve, ν(OH) frequencies versus (O · · · O) distances for a one-dimensional model of the hydrogen bond (*18*), it was found that the values for muscovite and dickite fall considerably below the curve. The most probable interpretation is that the (O-H · · · O) bonds are of the bent type. It has been shown by neutron diffraction (*19*) that in diaspore the H atom in (O-H · · · O) lies 12 deg off the O-O axis of the hydrogen bond. Since the linearity of the (O-H · · · O) bonds in kaolinite has not been established, the parallelism of the direction of the dipole moment change and the OH-bond axis is uncertain.

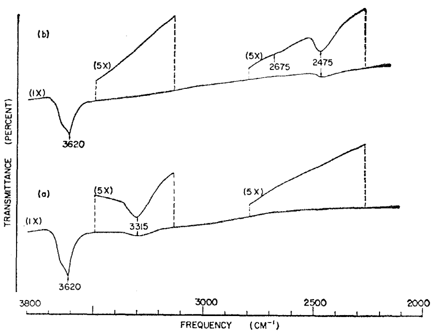

Fig. 3. Infrared spectra of (*a*) artificially expanded muscovite washed with H_2O and heated at 110°C, concentration 0.40 mg/cm^2; (*b*) artificially expanded muscovite washed with D_2O and heated at 110°C, concentration 0.35 mg/cm^2. Scale, ×1 and ×5.

A comparison of the Δ(45°–0°) values (Table 1) of the ν(OH) and ν(OD) intensities clearly shows, that for the same angle of rotation, the pleochroism is more intense in the ν(OD) region than in the ν(OH) region. This indicates that partial deuteration perturbs the direction of the OD dipole moment change with respect to the initial OH orientation; the net result is the formation of larger angles between the direction of the OD dipole moment changes and the basal plane (001) with respect to the angles that existed for OH before deuteration.

It has been shown (*6*) that the 3695 cm^{-1} absorption band corresponds to OH groups in inner-surface positions; the high percentages of the OH-OD exchange (Table 2) for the hydroxyls absorbing at 3670 and 3650 cm^{-1} suggest that they occupy identical positions. The hydroxyls absorbing at 3620

cm^{-1} are less completely deuterated; they should therefore be located in inner positions. This selective deuteration of inner-surface and inner hydroxyls suggests the following OH-OD shift assignments: 3695 cm^{-1} to 2725 cm^{-1}, 3670 cm^{-1} to 2710 cm^{-1}, 3650 cm^{-1} to 2698 cm^{-1}, and 3620 cm^{-1} to 2675 cm^{-1}. Although the 2675 cm^{-1} absorption frequency is slightly pleochroic and the 3620 cm^{-1} frequency is nonpleochroic, the OH-OD shift assignment 3620 cm^{-1} to 2675 cm^{-1} is reasonable since the angle of the OD transition moment with the *ab* cleavage plane is larger than the original angle for the OH group.

A sample of halloysite (*20*) was deuterated by the procedure used for kaolinite. The infrared spectrum of the natural halloysite (Fig. 2*a*) shows two strong absorption bands at 3695 and 3620 cm^{-1} and three weak absorptions at 3520, 3450, and 3370 cm^{-1}. The deuterated sample (Fig. 2*b*) shows a large reduction in the intensity of the 3695 cm^{-1}, a strong absorption at 2725 cm^{-1}, a shoulder at 2680 cm^{-1}, and weaker bands at 2930 and 2850 cm^{-1}. The shift of the 3695 cm^{-1} frequency to 2725 cm^{-1} is identical to the observed shift in kaolinite. The 2680 cm^{-1} absorption band results from the deuteration of hyroxyls absorbing at 3620 cm^{-1}. The absorption bands at 3520, 3450, and 3370 cm^{-1} are the $\nu(OH)$ of gibbsite (*21*). The presence of gibbsite was confirmed by the x-ray reflections at 4.79 and 4.39 Å. Intersalation, followed by hydrazine treatment, has expanded the halloysite but did not form complexes with gibbsite. The microcrystals of gibbsite were not expanded, and consequently no OH-OD exchange took place. Although the intersalated halloysite has been washed three times with hydrazine, a small amount of (CH_3COOK) remained in interlayer positions; this was indicated by a weak x-ray reflection at 14.2 Å, the $\nu(CH)$ at 2930 cm^{-1} and the $\nu(COO)$ at 1410 and 1560 cm^{-1} (*22*). Because of the tubular crystal habit of halloysite, the rotation of the deuterated clay film did not produce the pleochroic effect observed in kaolinite.

Table 1. Intensities of the hydroxyl and deuteroxyl stretching frequencies of kaolinite obtained from the difference between the background absorption line and the minimum percentage of transmittance (Θ = angle of rotation, Δ = difference between rotated and initial angles).

$\nu(OH)$ cm^{-1}	$\theta = 0$ deg	$\theta = 45$ deg	Δ(45 deg − 0 deg)
	Hydroxyl		
3695	16.0	26.0	10.0
3670	17.0	26.5	9.5
3650	16.5	23.0	6.5
3620	41.5	41.5	0.0
	Deuteroxyl		
2725	32.5	48.5	16.0
2710			
2698	27.5	37.0	9.5
2675	11.5	18.0	6.5

Table 2. Ratios of hydroxl to deuteroxyl stretching frequencies and percentages of OH-OD exchange in kaolinite.

$\nu(cm^{-1})$		$\frac{\nu(OH)}{\nu(OD)}$	OH-OD exchange (%)
OH	OD		
3695	2725	1,3559	66.8
3670	2710	1.3542	59.6
3650	2698	1.3528	62.2
3620	2675	1.3532	22.0

In order to investigate more closely the extent of deuteration of the inner lattice hydroxyls absorbing at 3620 cm^{-1}, we washed one sample of artificially expanded mica (*23*) three times with H_2O and a second sample with D_2O. After 15 hours of contact, a 1-ml portion of each suspension was evaporated on an Irtran window in an oven at 110°C. The infrared spectrum of the mica washed with H_2O (Fig. 3*a*) shows a strong absorption at 3620 cm^{-1} due to the $\nu(OH)$ of inner lattice hydroxyls and a weak absorption band at 3315 cm^{-1} corresponding to the $\nu(OH)$ of adsorbed water molecules. The mica washed with D_2O (Fig. 3*b*) shows the same absorption frequency at 3620 cm^{-1} and a weak band at 2475 cm^{-1} which corresponds to the $\nu(OD)$ of adsorbed deuterium oxide molecules. The isotope ratio of the OH-OD shift of the adsorbed water is 1.339. If we assume that the isotope ratio of the inner lattice hydroxyls is 1.35, the 3620 cm^{-1} absorption band should be shifted to 2675 cm^{-1} by deuteration. The very weak absorption band near 2675 cm^{-1} (Fig. 3*b*) shows that the inner hydroxyls absorbing at 3620 cm^{-1} are not readily exchangeable at room temperature.

Thus, deuteration of expanded kaolinite and halloysite at room temperature has shown that the inner-surface hyroxyls are more easily exchanged than the inner OH groups. The OH-OD exchanges for the hydroxyls absorbing at 3695, 3670, and 3650 cm^{-1} in kaolinite are 67, 60, and 62 percent, respectively, and 22 percent in the case of the 3620 cm^{-1} absorption. The infrared spectra of deuterated halloysite and $LiNO_3$-treated muscovite also indicate small OH-OD exchange of the hydroxyls which absorb at 3620 cm^{-1}, thus supporting their assignment to inner OH sites. The selective deuteration at room temperature of lattice hydroxyls confirms the hypothesis advanced by Fripiat (*3*) that the high and the medium frequencies are correlated predominantly to inner-surface hydroxyls and that the low stretching frequency is related to inner hydroxyls.

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9. Irtran No. 2 window is made of polycrystalline zinc sulfide and is transparent to infrared rays between 1 to 14 μ. The first x-ray reflection is at $2\theta = 28.5$ deg.
10. A Perkin-Elmer double beam spectrophotometer, model 421, was used for recording the infrared spectra.
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