to be in evidence for 17 years, the lower bones constituted quarry No. 2, and contained the partial burned skeletal parts of a young mammoth which I excavated in 1946. On the opposite side of the erosional channel are several fire areas in which erratic chips, which may be discards of tool making, or, in some cases, thermal fractures, occur in considerable numbers.

This tool is made from a beach cobble naturally rounded on all sides except where it is bifacially chipped by percussion. The upper side (as it lay in the ground) has six distinct chips, the lower side has one large chip and two smaller ones. There is evidence of some retouching.

Numerous chipped-stone implements have been found on the surface, some in association with weathered mammoth bones. Other chipped stones have been found with buried mammoth bones, but are controversial as to whether they were "thermal fractures" or man-made. There is no doubt that this last find is man-made, and *in situ* in the mammoth beds.

While no radiocarbon age can as yet be assigned to this particular specimen, it lies stratigraphically about 120 m east of Lamont's L. 290-T, 12,500 years old, made on charcoal from a mammoth "kill," and at an equal distance west of sample UCLA 141, made from carbon in an Indian midden and dated as 12,620 years ago. From about 90 m away and slightly higher stratigraphically, charcoal from a buried midden was dated at 11,900 years ago (sample UCLA 661).

Further dating and excavation will be carried out in the future, and this and other artifacts will be described elsewhere.

PHIL C. ORR
*Santa Barbara Museum of Natural History, Santa Barbara, California*

**References and Notes**

1. Conducted by the Santa Barbara Museum of Natural History and the Western Speleological Institute, Inc.
2. P. C. Orr, *Science* **135**, 219 (1962).
3. K. P. Oakley, *ibid.* **141**, 1172 (1963).
4. Of the Institute of Geophysics and Planetary Physics, University of California, Los Angeles.
5. P. C. Orr, *Bull. Geol. Soc. Am.* **61**, 1113 (1960).
6. Contribution of the Western Speleological Institute, No. 20.

15 November 1963

■

# Infrared Study of the OH Groups in Expanded Kaolinite

Abstract. *Expansion of kaolinite with potassium acetate and with hydrazine followed by deuteration, shifts the absorption frequency at 3695 $cm^{-1}$ to lower values, but does not affect the intensity of the 3620-$cm^{-1}$ absorption band. The band at 3695 $cm^{-1}$ is correlated predominantly to inner-surface hydroxyls with the dipole at right angles to the basal plane and the band at 3620 $cm^{-1}$ is related to inner hydroxyls with the dipole inclined toward empty octahedral sites.*

In spite of a rather considerable amount of work done with infrared spectroscopy, only limited correlations have been made between the hydroxyl stretching frequencies and the hydroxyl sites in the clay lattices. Our report includes results obtained with infrared spectroscopy on expanded kaolinite complexes and suggests absorption band assignments for the hydroxyl groups.

The terminology used to specify the OH groups in kaolinite structure (Fig. 1) is as follows. "Outer hydroxyls" refer to structural OH groups at the surface of micro crystals, including both hydroxyls at the broken edges (*A*), and hydroxyls of the octahedral sheet found at the upper surface denoted by (*B*). "Inner-surface hydroxyls" refer to OH groups located at the surface of the octahedral sheets opposite the tetrahedral oxygens of the adjacent kaolinite layer and having their OH dipole normal or nearly normal to the (001) plane; they are indicated by (*C*). "Inner hydroxyls" are designated by (*D*) and refer to the OH groups in the plane common to octahedral and tetrahedral sheets and to OH groups at 4.37 Å, both having their dipole directed towards an empty octahedral site.

Each oxygen atom not bonded to Si has two free orbitals which can interact with one proton to form an OH group. The choice of the specific oxygen orbitals interacting with the protons was based upon consideration of (i) the length and the proportion of each type of oriented O-H ⋯ O bond necessary to account for the number and the relative intensity of the infrared absorption bands, and (ii) the electrostatic repulsion between the aluminum and the proton. The probability of finding a proton associated with the remaining free orbitals is small.

We have attempted to correlate the OH absorption frequencies to the OH sites in the lattice of kaolinite by studying the manner in which the OH vibration frequencies are affected when the mineral is expanded by intersalation and then deuterated.

Andrew *et al.* (*1*) expanded kaolinite from 7 Å to 14 Å simply by grinding and hydrating a mixture of potassium acetate ($CH_3COOK$) and kaolinite, and proposed the term "intersalation" for the phenomena of entrance of such salts between lattice layers of clay minerals. The intersalated kaolinite for our study was prepared by grinding a 1 g sample of the mineral (*2*) with 15 mmoles of ($CH_3COOK$) for 20 minutes in a Fisher mechanical mortar-and-pestle grinder and allowing the mixture to stand overnight over a water bath. A large proportion of the kaolinite crystals were expanded, although a significant amount remained in the collapsed state. The specimens were prepared so that it would be possible to record the infrared spectra and the x-ray patterns, and to allow dipole orientation studies. A small portion of the hydrated ($CH_3COOK$)-kaolinite complex was dispersed in distilled water and a film specimen was prepared by evaporating, in a desiccator, 1 ml of suspension that had been placed on a cover glass (*3*). The cover glass with the mounted specimen was inserted as a window into a cylindrical infrared cell with the specimen surface inside the cell. Thin cover glasses are very suitable window material; excellent compensation is easily obtained between 4000 and 2400 $cm^{-1}$ by using four matched windows in the reference and sample cells. Since the specimen had to be removed from the cell for x-ray determination, a mark was made on the edge of the cover glass to insure replacement of the sample in exactly the same position.

The infrared spectra (*4*) were obtained after the sample and the reference cells had been heated at 110°C. The sample was removed from the cell, reheated at 110°C for 1 hour, and an x-ray diffraction pattern was recorded (see *4*) while a stream of dry nitrogen was passed through the sample chamber.

In the infrared spectrum of pure

Table 1. Ratios of hydroxyl to deuteroyl stretching frequencies in kaolinite complexes.

| $\nu$(cm$^{-1}$) | | $\nu$OH |
|---|---|---|
| OH | OD | $\nu$OD |
| 3695 | 2725 | 1.356 |
| 3650 | 2700 | 1.352 |
| 3620 | 2675 | 1.353 |
| 3600 | 2650 | 1.358 |

kaolinite (Fig. 2*a*), four stretching absorption bands are observed at 3695, 3670, 3650, and 3620 cm$^{-1}$. The four absorption bands observed in this study correspond exactly to those previously reported (*5*). The absorption bands at 3695 and 3620 cm$^{-1}$ are very strong and have about the same intensity, whereas those at 3670 and 3650 cm$^{-1}$ are much less intense. The ($CH_3COOK$)-kaolinite complex (Fig. 2*b*) shows four transmittance minima in the OH-stretching region at 3695, 3650, 3620, and 3600 cm$^{-1}$ (the OH-stretching region of most clay minerals is from 3710 to 3600 cm$^{-1}$).

The intersalation of the kaolinite resulted in the disappearance of the 3670-cm$^{-1}$ absorption and also the occurrence of additional bands at 3600, 3470, 3000, 2970, and 2930 cm$^{-1}$. The absorption intensities of the bands at 3695 and 3650 cm$^{-1}$ were considerably reduced whereas that of the band at 3620 cm$^{-1}$ was not significantly affected. The absorption at 3470 cm$^{-1}$ in Fig. 2*b* may be due to remaining interlayer-water molecules. The stretching vibration frequency of the CH group—$\nu$(CH)—of the acetate anion is responsible for the absorptions at 3000, 2970, and 2930 cm$^{-1}$ (*6*).

The x-ray peak at 11.6 Å in Fig. 3*b* (*7*) for the ($CH_3COOK$)-kaolinite complex indicates the presence of ($CH_3COOK$) molecules in interlayer positions (*8*). When the acetate anion is situated in an interlayer position, there is a decrease in intensity of the 3695-cm$^{-1}$ absorption band and an additional absorption appears at 3600 cm$^{-1}$. The strong negative oxygens of the acetate anions would form hydrogen bonds with surficial and inner-surface hydroxyls, thus shifting their frequencies toward lower values; the outer hydroxyls would contribute very little because of their relatively small number. Improvement in the orientation of the clay particles would produce a similar effect, but deuteration and treatment with hydrazine show that expansion and interlayer ions are responsible for the decrease in intensity.

Deuteration has been widely used to investigate the hydroxyls of kaolinite. The exchange of outer hydroxyls for deuteroxyls in a kaolinite-$D_2O$ mixture is very small at room temperature and at atmospheric pressure (*9, 10*). Fripiat *et al.* (*11*), by dehydrating kaolinite under vacuum and allowing $D_2O$ vapor to circulate over the mineral, were able to show that only the outer hydroxyls can be exchanged at room temperature; however, they did not study the isotopic exchange with infrared spectroscopy. It was found (*10*) that at room temperature a kaolinite-$D_2O$ mixture showed less than ½ percent replacement of OH for OD in as long as 5 days, but the infrared spectra did not show any equivalent absorption. Considerable exchange of the inner surface and inner hydroxyls was obtained only by submitting the kaolinite-$D_2O$ system to high temperatures and pressures (*12*).

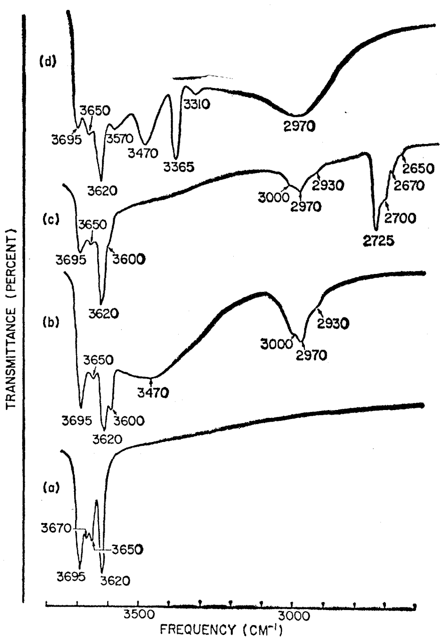

Fig. 2. Infrared spectra of (*a*) kaolinite at 110°C, (*b*) ($CH_3COOK$)-kaolinite complex at 110°C, (*c*) deuterated ($CH_3COOK$)-kaolinite complex at 110°C, and (*d*) hydrazine-kaolinite complex at 25°C.

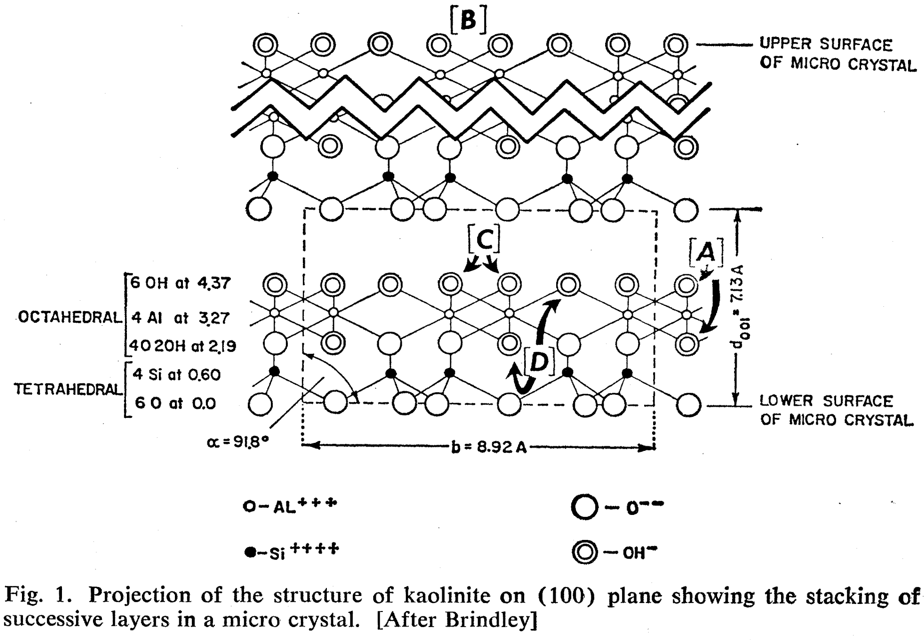

Fig. 1. Projection of the structure of kaolinite on (100) plane showing the stacking of successive layers in a micro crystal. [After Brindley]

In order to deuterate the mineral in our experiment, the cell containing the expanded ($CH_3COOK$)-kaolinite complex was heated at 200°C for 2 hours to remove most of the $H_2O$ molecules. The heated cell was immediately evacuated and filled with $D_2O$ vapor. The sample was allowed to cool and to rehydrate in $D_2O$ vapor for 1 hour and then it was heated at 110°C for 30 minutes before recording the infrared spectrum. The infrared spectrum of the deuterated ($CH_3COOK$)-kaolinite complex (Fig. 2*c*) showed reduction in the intensity of the absorptions at 3695 and 3650 cm$^{-1}$, complete disappearance of the 3600-cm$^{-1}$ absorption band, and the occurrence of a strong asymmetrical band between 2750 and 2600 cm$^{-1}$. The deuterated ($CH_3COOK$)-kaolinite complex absorptions at 2725, 2700, 2675, and 2650 cm$^{-1}$ correspond to an OH-OD shift as indicated by the ratios of the isotopes (Table 1). The shift of the 3695-cm$^{-1}$ absorption band to 2725 cm$^{-1}$ caused by the substitution of protons by deuterons has resulted in a considerable decrease in intensity of the 3695 cm$^{-1}$ band. This shift assignment is strongly supported not only by the ratio of $\nu$OH/$\nu$OD, but also by our observation of the OD dipole oriented at right angles to the basal plane.

In order to ascertain that the decrease in intensity of the 3695 cm$^{-1}$ absorption was related to expansion of the clay and not primarily to the preferential orientation of the clay particles, we washed the ($CH_3COOK$) out of the intersalated kaolinite and re-expanded the clay by shaking the mineral in an excess of anhydrous hydrazine (*13*). The x-ray diffraction pattern (Fig. 3*d*) indicates that nearly all of the clay particles are expanded to 10.4 Å, and the infrared spectrum (Fig. 2*d*) (*14*) shows that the intensity of the 3695 cm$^{-1}$ absorption has attained a minimum value.

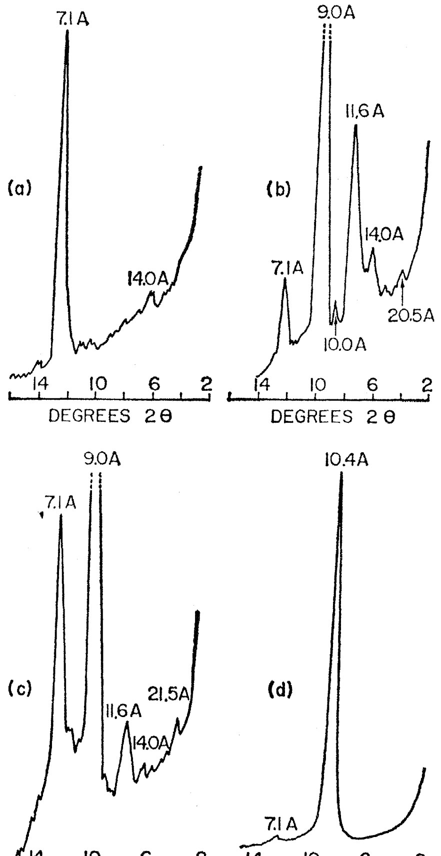

Fig. 3. X-ray diffraction patterns of (*a*) kaolinite at 110°C, (*b*) ($CH_3COOK$)-kaolinite complex at 110°C, (*c*) deuterated ($CH_3COOK$)-kaolinite complex at 110°C, and (*d*) hydrazine-kaolinite complex at 25°C.

The explanation that the decrease in intensity of the 3695 cm$^{-1}$ absorption would result entirely from reorientation, or different degrees in orientation of the particles, must be disregarded because intersalation has resulted in the shift of the 3695 cm$^{-1}$ absorption to 3600 cm$^{-1}$; in addition, treatment with $D_2O$ has also shifted the 3695 cm$^{-1}$ band to a lower frequency, but this time to 2725 cm$^{-1}$.

The correlation between the intensity of the 3695$^{-1}$ cm$^{-1}$ absorption and the intensity of the x-ray peak at 7.1 Å of (i) the pure kaolinite, (ii) the ($CH_3COOK$)-kaolinite complex, and (iii) the hydrazine-kaolinite complex favors the interpretation that expansion and interaction of interlayer materials with the hydroxyls are the factors primarily responsible for the decrease in intensity of the 3695-cm$^{-1}$ absorption band.

The formation of a hydrogen bond O-H ··· ($CH_3COO$) is proposed on the basis that interaction of the acetate anion with inner-surface hydroxyls has resulted in the shift of the 3695 cm$^{-1}$ to 3600 cm$^{-1}$, and that the 3600 cm$^{-1}$ absorption shifted to 2650 cm$^{-1}$ as a result of deuteration, thus forming a similar bond type O-D ··· ($CH_3COO$). The stretching vibration frequency $\nu$(CH) at 2970 cm$^{-1}$ is still present after deuteration (Fig. 2*c*) and indicates that the protons remain in the acetate anions.

Two reasons can be advanced to explain the weak intensity of the 2650-cm$^{-1}$ absorption band compared to that at 3600 cm$^{-1}$. (i) They are the possible formation of a bond O-D ··· ($CD_3COO$) which would vibrate at a frequency lower than 2650 cm$^{-1}$ thus being located beyond our range of observation; and (ii) the x-ray diffraction pattern of the deuterated complex (Fig. 3*c*) indicates only a small portion of expanded kaolinite at 11.6 Å and a larger amount collapsed to 7.1 Å. When the intersalated complex was bathed in an excess of $D_2O$ vapor, a large amount of interlayer ($CH_3COOK$) molecules were removed, and most of the particles collapsed to 7.1 Å on heating to 110°C. The large number of collapsed kaolinite particles would explain the strong intensity of the absorption band at 2725 cm$^{-1}$, whereas the small proportion of expanded particles at 11.6 Å would yield a weak absorption at 2650 cm$^{-1}$.

Thus, a large proportion of the OH groups absorbing at 3695 cm$^{-1}$ is in inner-surface positions with the dipole normal or nearly normal to the (001) plane, and the 3620-cm$^{-1}$ absorption band, which is not significantly affected by the interlayer anions, corresponds to inner hydroxyls with a dipole pointing towards an empty octahedral site. Serratosa *et al.* (*5*) compared the intensity of the 3695 cm$^{-1}$ absorption of expanded and nonexpanded halloysite, and they also concluded, without direct proof for the case of kaolinite, that a part of the OH groups is in inner-surface positions. We have demonstrated that many of the inner-surface hydroxyls in kaolinite have been exchanged for deuteroxyls at a temperature below 200°C, at atmospheric pressure, in a period of time not exceeding 1 hour.

ROBERT L. LEDOUX
JOE L. WHITE
*Department of Agronomy, Purdue University, Lafayette, Indiana*

### References and Notes

1. R. W. Andrew, M. L. Jackson, K. Wada, *Soil Sci. Soc. Am. Proc.* **24**, 422 (1960).
2. Hydrite No. 10, Georgia Kaolin Co.
3. Corning 22-mm circle, No. 2 thickness.
4. Perkin-Elmer double-beam spectrophotometer was used for spectra; a GE XRD-5 diffractometer was used for x-ray diffraction.
5. J. M. Serratosa, A. Hidalgo, J. M. Vinas, *International Clay Conference 1963, Sweden* (Pergamon Press, New York, 1963), vol. 1, pp. 17–26.
6. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963), p. 199.
7. Potassium acetate salt shows a very strong x-ray reflection at 9.0 Å and weak reflections at 10.0, 20.5, and 21.5 Å.
8. K. Wada, *Am. Mineralogist* **46**, 78 (1961).
9. C. D. McAuliffe, M. S. Hall, L. A. Dean, S. B. Hendricks, *Soil Sci. Soc. Am. Proc.* **12**, 119 (1947); J. A. Faucher and H. C. Thomas, *J. Phys. Chem.* **59**, 189 (1955).
10. D. M. Roy and R. Roy, *Clays and Clay Minerals*, Natl. Acad. Sci.–Natl. Res. Council Publ. No. 456 (1956), pp. 82–84.
11. J. J. Fripiat, M. C. Gastuche, G. Vancompernolle, *Cinquième Congrès International de la Science du Sol*, Léopoldville (1954), vol. 11, pp. 401–422. J. J. Fripiat and M. C. Gastuche, *Bull. Soc. Chim. France* **1958**, 626 (1958).
12. L. A. Romo, *J. Phys. Chem.* **60**, 987 (1956); D. M. Roy and R. Roy, *Geochim. Cosmochim Acta* **11**, 72 (1957).
13. V. A. Weiss, W. Thielepape, W. Ritter, H. Schafer, G. Goring, *Z. Anorg. Allgem. Chem.* **320**, 1 (1963).
14. The 3365 and 3310 cm$^{-1}$ absorptions correspond to stretching vibration of NH groups in hydrazine [P. A. Giguère and I. D. Liu, *J. Chem. Phys.* **20**, 136 (1962)]. No assignment is provided for 3570, 3470 and 2970 cm$^{-1}$ absorptions.
15. Supported by grants from the National Science Foundation (GP-1219) and the National Institutes of Health (EF 00055) made through the Purdue Research Foundation. Journal paper No. 2230 of the Purdue University Agricultural Experiment Station. We thank Dr. W. F. Bradley and Dr. J. J. Fripiat for helpful discussions.

10 October 1963