

THE AMERICAN MINERALOGIST, VOL. 50, JANUARY-FEBRUARY, 1965

INFRARED ABSORPTION PATTERNS (OH REGION)  
OF SEVERAL CLAY MINERALS<sup>1</sup>ROGER G. WOLFF, *Department of Geology, University of  
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## INTRODUCTION

In a previous article (Wolff, 1963) the infrared absorption patterns (OH region) for kaolinite were presented and discussed. As a part of the same study, infrared absorption patterns covering the same region were also determined for several other clay minerals. The interpretive usefulness of these patterns with respect to structural OH orientations of the clay minerals under consideration here is considerably less than for kaolinite, however, they do provide some information.

The equipment used and sample preparation technique for infrared absorption and  $x$ -ray diffraction were the same as those used for the kaolinite study.

## SAMPLES USED

Table 1 is a listing of the samples used. Figure 1 presents the  $x$ -ray diffraction patterns for the same samples. With the exception of mont-

TABLE 1. DESCRIPTION OF SAMPLES USED

Sample Number	General Description	Collecting Locality
Allophane	Glassy allophane	Bedford, Indiana
Halloysite	Halloysite, some gibbsite	Eureka, Utah
Fithian Illite	Illite	Fithian, Illinois
F 66	Na montmorillonite	Mowry No. 2 Cret., Wyoming
GM No. 2	Ca montmorillonite	Wilcox formation Eocene, Arkansas
Kaolinite No. 1	Kaolinite, illite	Baker, commercial grade kaolinite

morillonite, only one sample of each mineral type was chosen for presentation. Because of some apparent differences in the infrared pattern, a "sodium" and "calcium" montmorillonite are included. The samples chosen for presentation are considered typical for each type studied.

Changing the angle of incidence of the infrared radiation did not result in significant absorption intensity changes for any of the samples listed, therefore, only the 90° pattern (incidence parallel to  $c$  axis) is presented.

<sup>1</sup> Publication authorized by Director, U. S. Geological Survey.<sup>2</sup> Present Address: U. S. Geol. Survey, Washington, D. C. 20242.

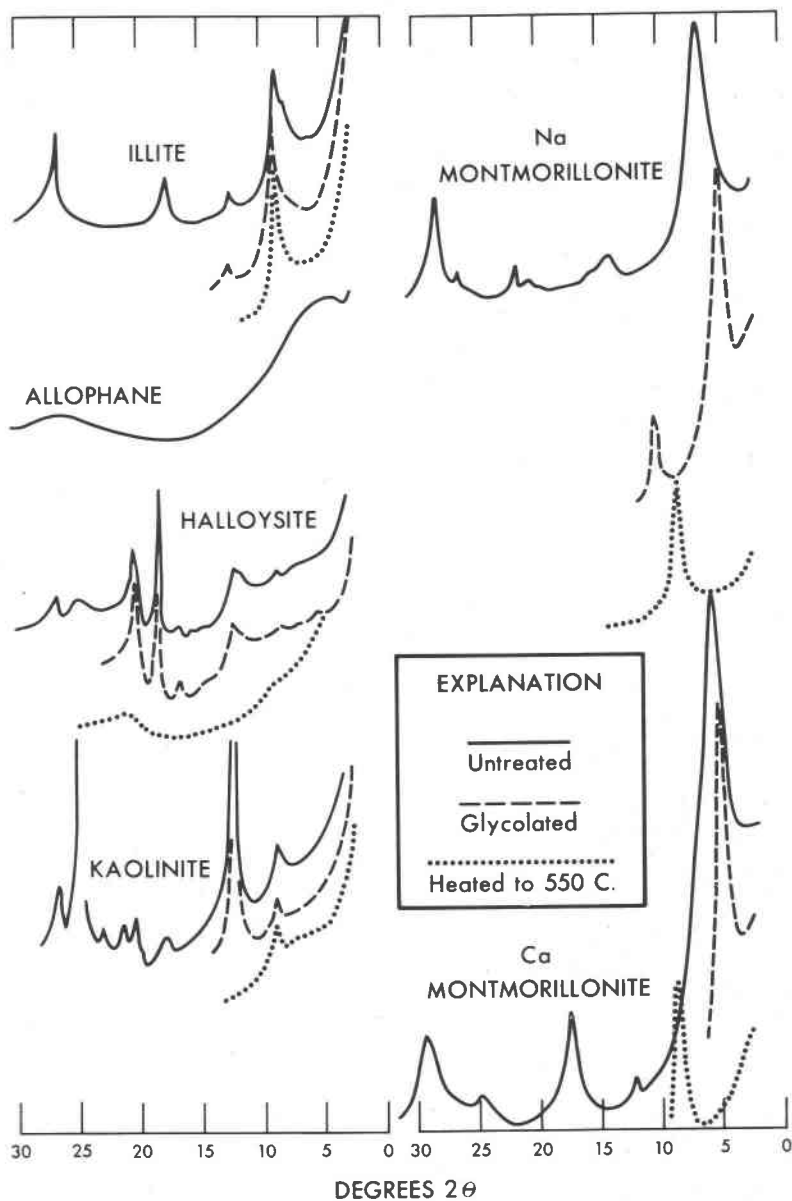


FIG. 1. Smoothed, x-ray diffraction patterns of oriented samples shown, using Cu K $\alpha$  radiation.

## RESULTS

Figure 2 shows the infrared absorption patterns for the samples listed. A pattern for kaolinite is included for comparison.

## DISCUSSION

*Allophane.* The particular sample used is amorphous to  $x$ -rays as well as infrared radiation in the region of interest. This indicates that the lack of order includes the O-H bonding.

Various concentrations of this material were used to assure that the apparent amorphous condition was not the result of insufficient material.

*Montmorillonites.* The band of absorption at  $3704\text{ cm}^{-1}$  has been suggested as indicating partial trioctahedral filling (Serratos and Bradley, 1958).

The most intense band of absorption ( $3635\text{ cm}^{-1}$ ) may be indicative of hydroxyl bonding in the octahedral portion of the structure, and in part due to adsorbed water as indicated by the decreased intensity after heating. The intensity of this band was not significantly changed by varying the angle of incident radiation, indicating it does not represent bonds

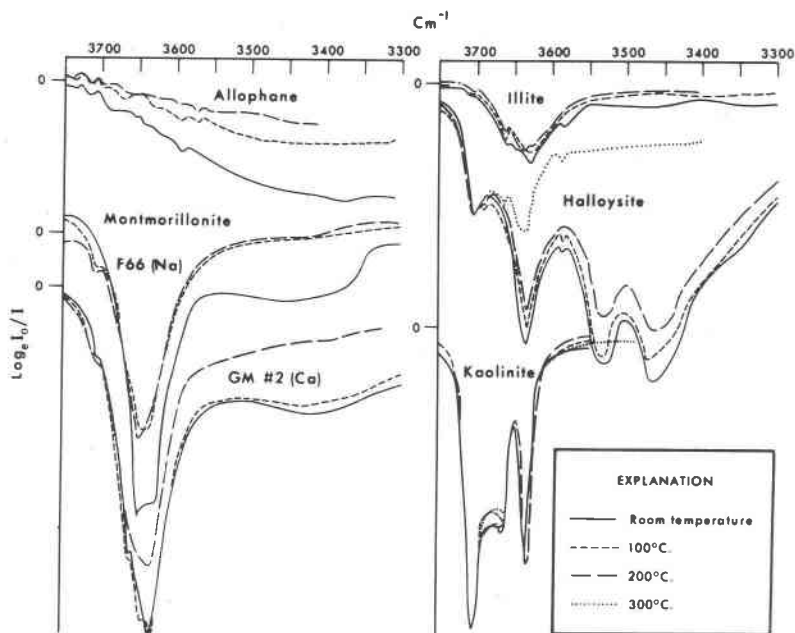


FIG. 2. Infrared absorption patterns of indicated clay minerals.

having a unique direction, which is in accord with the accepted structure of montmorillonite.

The broad bands of absorption around  $3440\text{ cm}^{-1}$  are indicative of adsorbed water, as indicated by their decreased intensity upon heating.

Based on patterns of the samples shown and on three other samples of both of the Na and Ca varieties, the evidence suggests that the adsorbed water has developed stronger bonds in the presence of calcium.<sup>1</sup> This observation is in accordance with the findings of several investigations cited by Grim (1953).

Since two bands are apparently the result of adsorbed water and because hydrogen bonding apparently occurs between water molecules and between water molecules and the clay mineral surface, the question arises: which bond is responsible for which type of band?

The concept of oriented water presented by Hendricks and Jefferson, as summarized by Grim (1953), positions alternate water molecules approximately over an oxygen of the basal layer of montmorillonite. This arrangement results in the availability of one-fourth of the hydrogens in the water for bonding to the oxygen of the clay mineral. Since such hydrogen bonding should have a relatively uniform bond length and strength, it should exhibit a relatively uniform vibration frequency. Therefore, the reduction of intensity of absorption at  $3635\text{ cm}^{-1}$  after heating may be due to the loss of these bonds; whereas the broad band at  $3440\text{ cm}^{-1}$  is probably due to OH bonds within the water itself. This latter theory agrees with the findings of Frohnsdorff and Kington (1958).

*Illites.* The spectrum of the illite sample is very similar to those of the montmorillonites, except for the absence of the broad band of absorption ( $3440\text{ cm}^{-1}$ ) credited to adsorbed water. As in the montmorillonites, there is no evidence for any high degree of bond orientation.

*Halloysite.* The band of absorption at  $3704\text{ cm}^{-1}$  can be considered indicative of free OH groups, similar to kaolinite (Wolff, 1963). No significant changes of absorption intensity occurred as a result of changing the angle of incidence. This is explained by the tubular shape of the particles, which prevents uniform orientation on the slide.

The infrared absorption patterns of this small region are not sufficiently distinctive for identification purposes. Relatively pure samples could be qualitatively identified if no other methods were available; however, the overlapping of absorption bands of the various clay minerals inhibits the method's use for quantitative application.

<sup>1</sup> Both types of samples were heated at the same time, eliminating time and temperature difference.

## SUMMARY AND CONCLUSIONS

The infrared absorption patterns covering the OH stretching frequencies of allophane, montmorillonite, illite and halloysite are presented.

The OH bond development in the allophane sample used is not sufficient to result in distinct bands of absorption.

As could be expected from the accepted structures of montmorillonite and illite, no evidence for unique OH bond directions was found. Indications are that a band of absorption at  $3704\text{ cm}^{-1}$  may be useful in determining the octahedral filling of montmorillonite and illite.

For montmorillonite, two bands of absorption are creditable to adsorbed water. A broad band at  $3440\text{ cm}^{-1}$  probably represents OH bonds within the water, whereas a relatively sharp band at  $3635\text{ cm}^{-1}$  is considered indicative of OH bonding between the clay mineral surface and the water. These bands of absorption disappear at lower temperatures in the presence of sodium than in the presence of calcium, which agrees with previous findings.

Halloysite morphology did not lend itself to the sample study technique used. The resultant pattern has little interpretive usefulness.

As presented here, individual mineral absorption patterns appear unique; however, the applicability of this method for identification is doubtful.

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CHEMICAL COMPOSITION OF DIAGENETIC ZEOLITES FROM TUFFACEOUS ROCKS OF THE MOJAVE DESERT AND VICINITY, CALIFORNIA<sup>1</sup>

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Zeolites are abundant rock-forming minerals in many tuffaceous rocks of Cenozoic age in the western United States. Some beds consist almost entirely of one or more zeolite (Deffeyes, 1959b; Regnier, 1960). In spite

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.