

DIFFUSE REFLECTANCE SPECTRA OF SEVERAL CLAY MINERALS

JAMES D. LINDBERG AND DAVID G. SNYDER, *Atmospheric Sciences
Laboratory, US Army Electronics Command, White Sands
Missile Range, New Mexico 88002*

ABSTRACT

The diffuse reflectance spectra in the 0.3 to 2.1 micrometer wavelength region have been measured for several samples of clay minerals sometimes found in the atmospheric aerosol. Examples of spectra are shown for different hydration states of several montmorillonite and kaolin group minerals. It was found that these clays show absorption features in the wavelength regions where liquid water absorbs. These absorption bands are removed by dehydration, as would be expected. It is concluded that the major features of the near infrared absorption spectra of montmorillonite and kaolin clays are determined primarily by the water present in the clay structures. In addition, the spectra show evidence of strong absorption in the near ultraviolet and short wavelength visible region. This latter absorption is a general feature of all the clay samples investigated.

INTRODUCTION

In connection with this laboratory's interest in the properties of atmospheric dust it has become necessary to obtain some information about the absorption spectra of several clay minerals in the near ultraviolet, visible, and near infrared spectral regions. Previous work (Hoidale and Blanco, 1969) has shown that the clay minerals montmorillonite, kaolinite, and illite are likely to be significant constituents of atmospheric dust, at least in arid desert regions. The spectra for most clay minerals have been determined by several workers¹ for wavelengths longer than about two micrometers, using alkali halide disk or liquid mull infrared spectroscopic techniques. However, no similar information is available for shorter wavelengths. The purpose of the work reported here was to determine the character of the absorption spectra, in the shorter wavelength region, of several representative clay minerals.

MEASUREMENT TECHNIQUE

Since clay samples always consist of aggregates of small particles whose dimensions are about the same as the wavelength of visible or near infrared light, most of the radiation incident on a sample is scattered. For this reason direct transmission spectroscopy using alkali halide pressed disks or similar

¹ Many examples of such spectra are available in Adler, H. H. *et al.* (1950) *Infrared Spectra of Reference Clay Minerals*. American Petroleum Institute Project 49 Preliminary Report No. 8, Columbia University, New York, 146 p.

techniques does not give very satisfactory results. Therefore, diffuse reflectance spectroscopy was chosen for use in this study, since the diffuse reflectance spectra of a powder is in general a very good representation of the qualitative character of the absorption spectra of the material. One must keep in mind, however, that the diffuse reflectance of a powder depends on particle size and refractive index of the substance, as well as on its absorption coefficient, so the two kinds of spectra are not equivalent in a quantitative sense. Excellent discussions of diffuse reflectance spectroscopy have been published by several authors (Wendlandt and Hecht, 1966; Kortüm, 1969).

The spectra reported here were made with a Cary Model 14 dual beam spectrophotometer, equipped with the manufacturer's *cell space* diffuse reflectance integrating spheres, recoated with aluminum oxide, as described by Sklensky, *et al.* (1967). These integrating spheres are also described by Wendlandt and Hecht (1966). Since the efficiency of the spheres is quite low, the spectrophotometer operates with somewhat wider slits than usual. The monochromator spectral band width varied from a few tenths of a nanometer in the visible to a maximum of about 10 nanometers at wavelengths near two micrometers.

The sample port is located on the top of the sample beam integrating sphere, so it was necessary to place the powdered mineral sample on a thin fused quartz plate for support. The reference material, which was barium sulphate,¹ was similarly mounted on the reference beam integrating sphere. The use of the quartz plates introduces a specular reflection component which causes a minor error in the diffuse reflectance measurement. A second small error occurs because separate spheres are used for the reference and sample beams in the spectrophotometer. Neither error is significant enough to affect the qualitative character of the spectra, so corrections have not been made in the curves presented here. The curves have, of course, been corrected for spectrometer baseline effects. The ordinate axis expresses the diffuse reflectance of the sample as a percentage of the diffuse reflectance of the barium sulphate white reflectance standard, which is very close to unity, except near two micrometers, where it is slightly lower.

CLAY MINERAL SAMPLES

The clay mineral samples used in this study were obtained from Ward's Natural Science Establishment. The supplier states that they were collected in 1955 by Dr. Ralph J. Holmes, of Columbia University, from sites as close as possible to those of the samples used in the American Petroleum Institute study of reference clay minerals, and that they have been checked against the original API reference specimens by X-ray diffraction and differential thermal analysis. In this report the identification numbers associated with clay samples correspond to the numbers used in the original series of API reference minerals. A few additional samples obtained from the US National Museum were also used.

Each sample was crushed (not ground) in a mortar, to remove any large lumps. No sieving was done, since there was no requirement to obtain a known particle size. Diffuse reflectance spectra were recorded for each clay mineral without further sample preparation.

In cases where it was desirable to obtain spectra after partial or nearly complete dehydration, the sample was heated in an open pyrex tube over an open

¹The reference material was *Eastman White Reflectance Standard*, a highly refined barium sulphate available from Eastman Kodak Company, Rochester, New York.

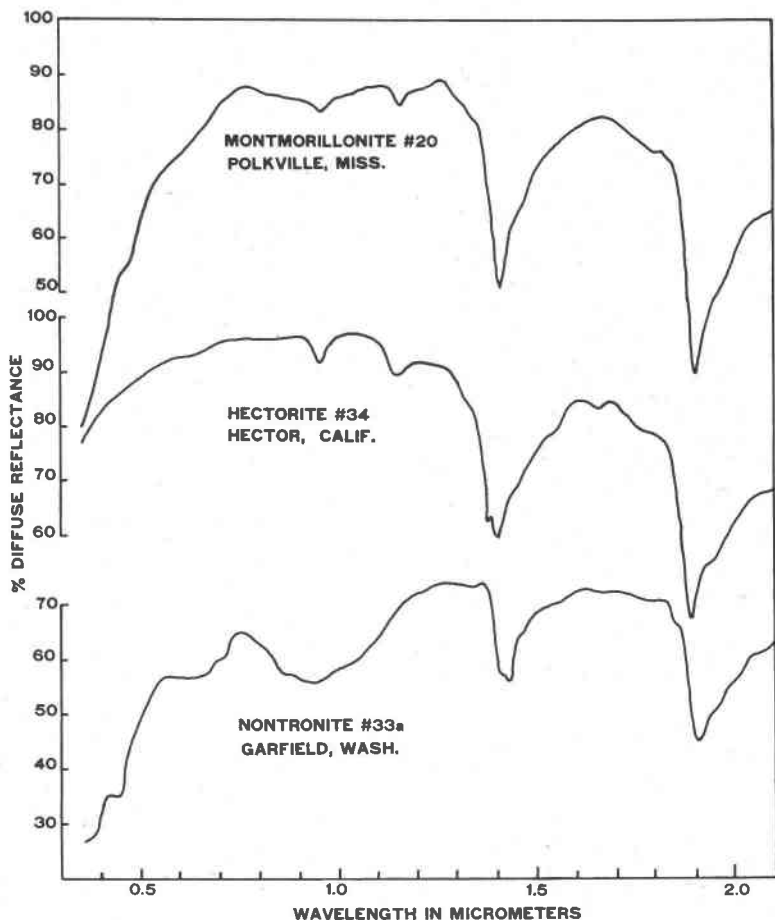


FIG. 1. Diffuse reflectance spectra of several montmorillonite group clay minerals.

flame, with frequent stirring of the powder. The sample was maintained at its elevated temperature for a period of a few minutes, that is, until no further obvious loss of moisture was apparent at that temperature. In a few cases partially dehydrated samples were *humidified* by sealing them in a closed container with an open beaker of water at room temperature for a period of two weeks.

RESULTS

Of the montmorillonite group of clay minerals, a total of eleven samples of montmorillonite, one of nontronite, and one of hectorite were examined. Spectra for three of these specimens are shown in Figure 1. The most typical feature of these minerals in this spectral region is the presence of two strong absorption bands (diffuse reflectance)

tance minima) at about 1.41 and 1.90 micrometers. Both bands have a characteristically asymmetrical shape caused by the presence of one or more unresolved lines at slightly longer wavelengths. Two other weak bands at 0.96 and 1.16 micrometers were often, but not always, observed in montmorillonite samples and were present in the hectorite sample as well. The first of these is not unique to this group of min-

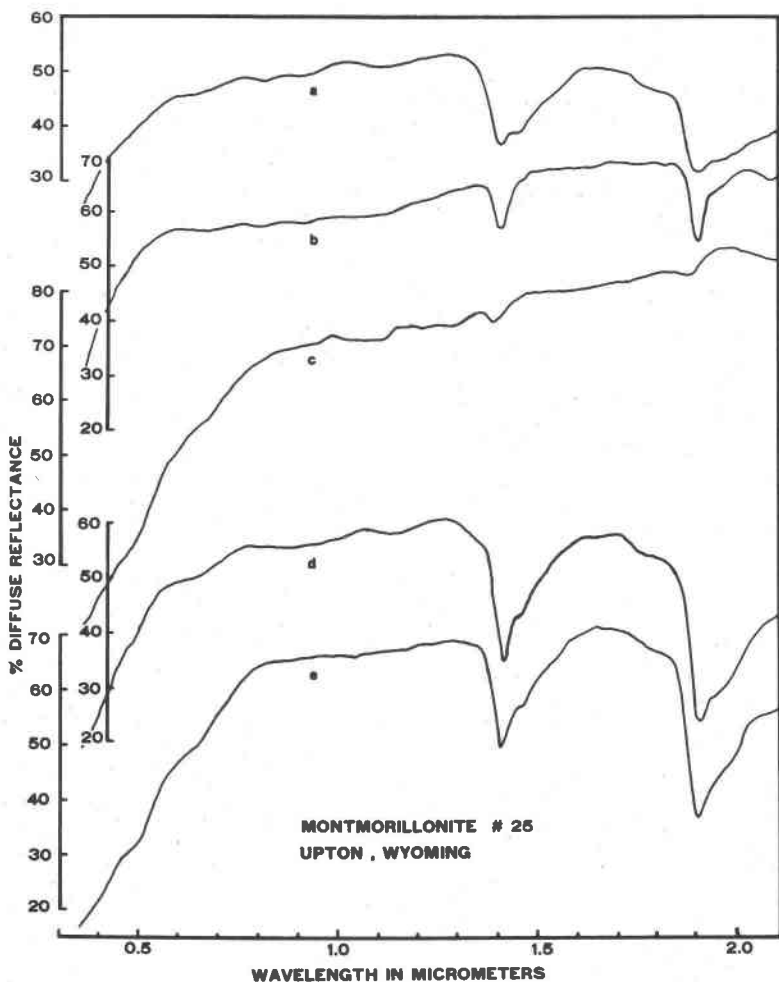


Fig. 2. Changes in the reflectance spectra of montmorillonite as a result of changes in hydration state. Curve (a) original sample; (b) sample after heating to 120°C; (c) sample after heating to 600°C; (d) sample from curve b after humidification for two weeks; (e) sample from curve c after humidification for two weeks.

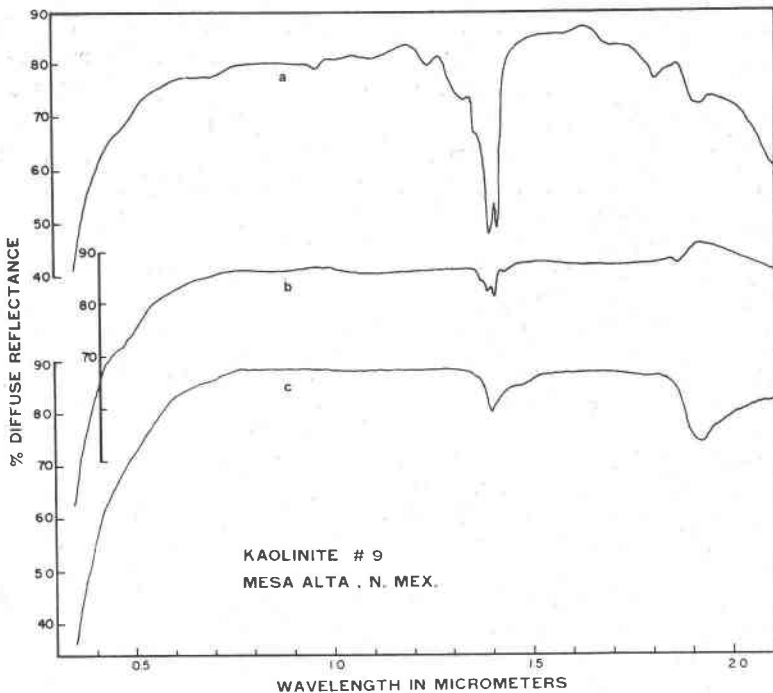


FIG. 3. Diffuse reflectance spectra of a sample kaolinite. Curve (a) original sample; (b) sample material after partial dehydration by heating to 600°C; (c) sample from curve b after humidification for two weeks.

erals; weak absorption at about 0.96 micrometers was also found in other clays. The absorption at 1.16 micrometers, however, does seem to be typical of the montmorillonite group. It was not found in any other clay mineral examined in this study.

Since the structures of clay minerals in general usually involve water in one form or another, it is reasonable to suspect that the absorption spectra shown in Figure 1 are caused primarily by the presence of water. This was verified for one montmorillonite sample by recording spectra before and after the material had been dehydrated by heat, and again after storage for two weeks in an environment of high relative humidity. The results of this test are shown in Figure 2. It is clear that the spectra of montmorillonite is highly dependent on the mineral's hydration state.

From the kaolin group of clays four samples of kaolinite, five of halloysite, and two of dickite were examined. Spectra of a typical example of kaolinite, as received, after partial dehydration, and after

humidification are shown in Figure 3. The structure around 1.4 micrometers consisting of a pair of strong lines accompanied by several poorly resolved lines at shorter wavelengths is a typical feature of these three kaolin clays.

Figure 4 shows the spectra of an example of halloysite, and some of the changes caused by dehydration and subsequent humidification.

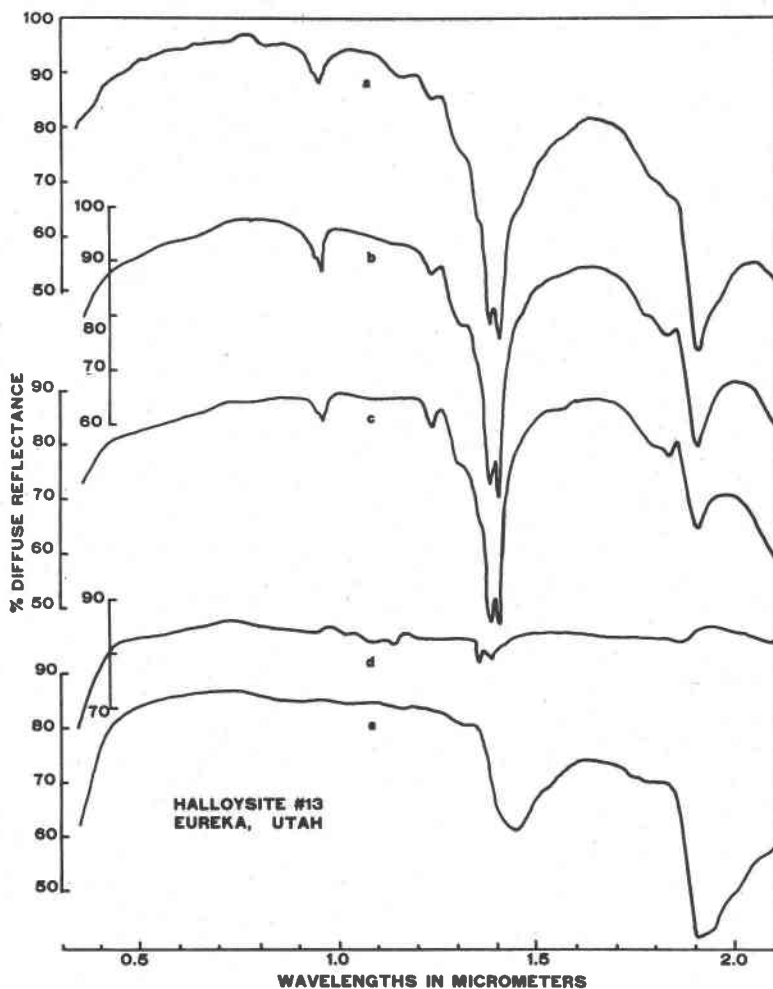


Fig. 4. Diffuse reflectance changes in halloysite. Curve (a) original sample; (b) spectra after heating to 90°C; (c) after heating to 210°C; (d) after further heating to 600°C; (e) spectra of sample from curve d after humidification for two weeks.

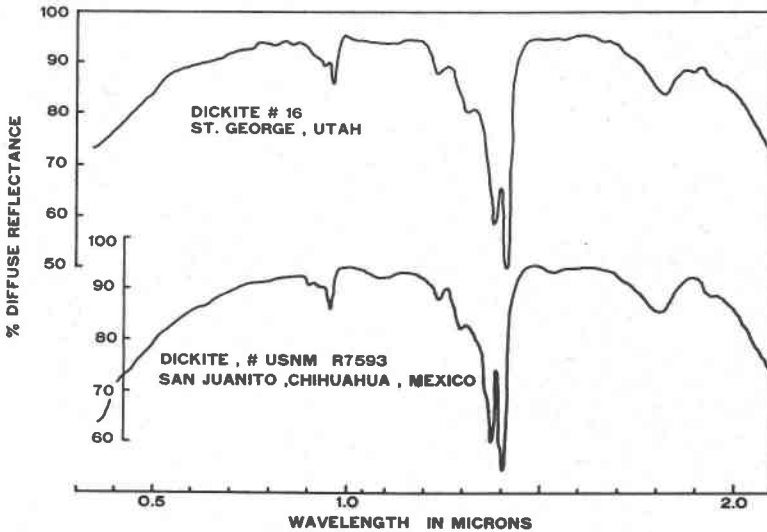


Fig. 5. Diffuse reflectance spectra of two samples of dickite.

This sample shows the same sort of structure at about 1.9 micrometers. In this sample of halloysite the weak absorption near one micrometer appears to be a poorly resolved doublet, with one reflection minimum at 0.94, and the other at 0.96 micrometers.

The only sample of dickite corresponding to the API series of reference clay minerals was #16, from St. George, Utah. The diffuse reflectance of this sample is shown in Figure 5, which also shows the spectra of a second dickite sample obtained from the US National Museum. The spectra of dickite strongly resemble those of kaolinite and halloysite, and show a similar behavior on dehydration.

Three samples of illite were examined, and it was found that their spectra were quite different from those of the montmorillonite or kaolin minerals. None of the illite samples showed any significant absorption bands at any well defined wavelengths. They showed a diffuse reflectance that decreased more or less smoothly from long wavelengths to shorter wavelengths. Since no detailed spectral structure was shown by the measurements on illite samples, curves are not included in this report.

DISCUSSION

Examination of the diffuse reflectance spectra of montmorillonite and kaolin group clay minerals shows that they have several features in common with the transmission spectra of liquid water. For a path

length of a fraction of a millimeter, water shows a strong absorption band at about 1.92 micrometers, and a slightly weaker one at 1.45 micrometers. A very weak band at about 1.78 micrometers can also be seen. For a path length of a few millimeters two weak absorption bands can be observed in transmission spectra of water, near wavelengths of 1.19 and 0.97 micrometers. All of the diffuse reflectance minima (absorption maxima) shown by the spectra of these clays in the near infrared can readily be accounted for by comparison with the transmission spectra of water. For the montmorillonite group the agreement is very good, even for the weak absorption near 1.16 micrometers. Since the major reflectance minima disappear when the sample is dehydrated, it is reasonable to conclude that from the red of the visible to about 2 micrometers these clay minerals owe the major features of their absorption spectra to the presence of water. Each of the major absorption bands in water is represented in these clays by a group of several absorption maxima. This results from the fact that the resonant frequencies involved are modified by the presence of the clay structure itself, and also depend on the manner in which the water is present in the clay sample.

Another very consistent feature of the diffuse reflectance spectra of all the clays examined here is the decrease in reflectance with decreasing wavelength in the visible spectrum. This indicates that the minerals have a higher absorption coefficient in the near ultraviolet and blue of the visible than in the red of the visible. This is of course consistent with the observation that most samples tend to have some degree of brown or yellow color. This apparent decrease in reflectance with decreasing wavelength is not dependent on the hydration state of the sample, and must be attributed to the silicate structure itself, or to the impurities inevitably present in clay samples.

As a result of this study it is expected that in the 0.3 to 2.1 micrometer spectral range these clay minerals, when present in sufficient quantities, will contribute to the absorption spectra of atmospheric dust, both in the near ultraviolet region, and at wavelengths near 1.4 and 1.9 micrometers, where liquid water has strong absorption bands. In the latter case, the actual absorption coefficient is highly dependent on the hydration state of the sample.

REFERENCES

- HODALE, G. B., AND A. J. BLANCO (1969) Infrared absorption spectra of atmospheric dust over an interior desert basin. *Pure Appl. Geophys.* 74, 151-164.
KORTÜM, G. (1969) *Reflectance Spectroscopy*. Springer-Verlag, New York, 366 p.
SELENSKY, A. F., J. H. ANDERSON JR., AND K. A. WICKERSHEIM (1967) Method

for obtaining improved diffuse reflectance spectra in the near infrared. *Appl. Spectr.* 21, 339-342.

WENDLANDT, W. W., AND H. G. HECHT (1966) *Reflectance Spectroscopy*. Interscience Publishers, New York, 298 p.

Manuscript received, October 26, 1971; accepted for publication, November 15, 1971.