# Visible and Near-Infrared Absorption Coefficients of Montmorillonite and Related Clays

JAMES B. GILLESPIE, JAMES D. LINDBERG, AND MICHAEL S. SMITH

Atmospheric Sciences Laboratory, U.S. Army Electronics Command, White Sands Missile Range, New Mexico 88002

# Abstract

Estimates of the optical absorption coefficients for montmorillonite, hectorite, nontronite, metabentonite, illite, and attapulgite clay minerals were made by the application of diffuse reflectance spectroscopy in the spectral region from 0.4 to 2.4  $\mu$ m. These clay minerals are weak absorbers over this spectral range, with the primary absorption occurring in the 1.4- $\mu$ m and 1.9- $\mu$ m water bands. Values of the absorption coefficients were on the order of 10 to 20 cm<sup>-1</sup> in the 1.4- $\mu$ m band and 20 to 30 cm<sup>-1</sup> in the 1.9- $\mu$ m band with the exception of the metabentonite, which gave an absorption coefficient of about 80 cm<sup>-1</sup> in the 1.9- $\mu$ m band. The absorption coefficient increased rapidly as the near-ultraviolet region was approached. Absorption maxima between 0.9 and 2.1  $\mu$ m were determined. Weak bands were found at 0.95  $\mu$ m and 1.15  $\mu$ m. These bands were too weak to appear in the plotted absorption coefficient data.

#### Introduction

Montmorillonite-type clays are common soil minerals and are therefore often found in samples of atmospheric dust. By infrared analysis of dust samples, Hoidale and Blanco (1969) have found that clay minerals make up a significant portion of the atmospheric dust by weight. Because of our laboratory's interest in the effects of atmospheric aerosol upon the propagation of electromagnetic energy, it is necessary to know the absorption coefficient of such minerals. In a previous paper Lindberg and Smith (1974) reported the Kubelka-Munk absorption coefficients of kaolinite and related clays. This paper continues that work and reports the absorption coefficients of montmorillonite-type clays.

The clays selected for this study are of the threelayer crystalline type, which includes the montmorillonite group (montmorillonite, hectorite, nontronite, and metabentonite) and the illite group. A chain structure-type clay, attapulgite, was also chosen because of its visible and near-infrared spectral similarity to the montmorillonte-type clays.

The equipment and measurement techniques used in this work are the same as those described in Lindberg and Smith (1974). The calculations of the Kubelka-Munk absorption coefficients were performed as described by Lindberg and Snyder (1973).

#### **Results**

The nine clay samples investigated in this report 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 (API) study of reference clay minerals (Adler et al, 1950), and that they have been checked against the original API reference samples by X-ray diffraction and differential thermal analysis. The nine samples were montmorillonite #20, montmorillonite #22a, montmorillonite #25, hectorite #34, nontronite #33a, metabentonite #42, illite #35, illite #36, and attapulgite #44. The identifications were rechecked in this laboratory by both X-ray diffraction and infrared potassium bromide (KBr) pellet spectroscopy. One sample, hectorite #34, could not be verified by X-ray diffraction; however, the infrared analysis indicated that the sample was predominately hectorite.

The calculated Kubelka-Munk absorption coefficients are shown for each sample from 0.4  $\mu$ m to about 2.4  $\mu$ m in Figures 1 through 9. The absorption coefficients vary from a fraction of 1 cm<sup>-1</sup> to 10 cm<sup>-1</sup> in regions outside the major water bands, and range from about 10 cm<sup>-1</sup> to about 20 cm<sup>-1</sup> in the 1.4- $\mu$ m water band. In the several spectrometer scans of each



FIG. 1. Kubelka-Munk absorption coefficient of montmorillonite #20 from Polkville, Mississippi, as determined from diffuse reflectance measurements on a powdered sample.

clay, it was observed in the  $1.9-\mu m$  water band that the values of the absorption coefficient varied with the hydration state of the clay. These values were typically on the order of 20 cm<sup>-1</sup> to 30 cm<sup>-1</sup> except for metabentonite #42, which had a value on the order of 80 cm<sup>-1</sup>. The data from 2.1  $\mu m$  to 2.5  $\mu m$ could not be adequately resolved due to the low signal-to-noise ratio. These data are qualitatively shown by dashed lines in this region.

The 1.4- $\mu$ m band shows little or no structure for the clays considered in this report. The two illite clays only weakly showed the 1.4- $\mu$ m band; this is in contrast to the kaolinite-type clays which show considerable structure in this band (Lindberg and Smith, 1974). The montmorillonite-type clays also lacked the strong 2.2- $\mu$ m band observed in the kaolinite-type clays; however, in some of the clays (montmorillonite

TABLE 1. Wavelengths of the Absorption Coefficient Maxima for the 0.9 to 2.1 Micrometer Region of the Montmorillonite-Type Clays\*

Montmorillonite			Hectorite		Nontronite
#20	#22a	#25	#34		#33a
1.904	1.945	1.902	1.900		1.907
1.413	1.904	1.412	1.410		1.435
1.155	1.407		1.15		0.930
0.967	0.912		0.950		
Metabentonite			Illite		Attapulgite
#42		#35	#36	#44	
	1,908		1.941	1.945	1.915
	1.414		1.410	1.410	1.417
	0.915				

\*The above results were obtained from the diffuse reflectance of a thick layer of each powdered clay.



FIG. 2. Kubelka-Munk absorption coefficient of montmorillonite #22a from Amory, Mississippi, as determined from diffuse reflectance measurements on a powdered sample.

#20, metabentonite #42, hectorite #34, illite #35, and illite #36), there was a qualitative indication of some structure in the 2.1 to  $2.4-\mu m$  region. This could have been caused by the poor signal-to-noise in this region or by slight impurities in the samples.

A peak analysis of the absorption coefficient maxima was made for each clay for the spectral interval 0.9 to 2.1  $\mu$ m. The results are shown in Table 1. Peaks below 0.9  $\mu$ m were not tabulated because such peaks were broad and weak compared to the general absorption in this region. Peaks beyond 2.1  $\mu$ m were not recorded because the poor signal-to-noise ratio prevented accurate values. The values in Table 1 were obtained from the diffuse reflectance of a very



FIG. 3. Kubelka-Munk absorption coefficient of montmorillonite #25 from Upton, Wyoming, as determined from diffuse reflectance measurements on a powdered sample.



FIG. 4. Kubelka-Munk absorption coefficient of hectorite #34 from Hector, California, as determined from diffuse reflectance measurements on a powdered sample.

thick layer (2 to 3 mm) of the sample clay. The spectra were corrected for baseline effects and for the BaSO<sub>4</sub> Reflectance Standard and recorded by a Spectrosystem 100 minicomputer at 10 Å intervals. These results were then listed and the peaks were tabulated. From this analysis most of the clays showed the two major water bands to be centered about 1.41  $\mu$ m and 1.905  $\mu$ m; however, the two illites had their 1.9- $\mu$ m band centered closer to 1.94, and montmorillonite #22a showed a doublet structure at 1.945 and 1.903. The 1.4- $\mu$ m band in nontronite was shifted to 1.435  $\mu$ m. An extremely weak band centered at 0.95  $\mu$ m was observed in montmorillonite #20 and hectorite #34. This weak band



FIG. 5. Kubelka-Munk absorption coefficient of nontronite #33A from Garfield, Washington, as determined from diffuse reflectance measurements on a powdered sample.



FIG. 6. Kubelka-Munk absorption coefficient of metabentonite #42 from High Ridge, Kentucky, as determined from diffuse reflectance measurements on a powdered sample.

was not sufficiently resolved to be seen in the data presented in Figures 1 and 4.

The bulk samples of the nine clays were visibly inspected to qualitatively compare their colors to the visible absorption calculated. Montmorillonite #20 is a very pale yellow; montmorillonite #22a is a reddish-brown; montmorillonite #25 is a very light gray; hectorite #34 is a bright white; nontronite #33a is a medium green color; attapulgite #44 is white; metabentonite #42 is a light beige color; and both illites are dark gray. These qualitative observations are consistent with the spectra obtained in Figures 1–9. The materials with the brighter appearance have the lower absorption coefficients.



FIG. 7. Kubelka-Munk absorption coefficient of illite #35 from Fithian, Illinois, as determined from diffuse reflectance measurements on a powdered sample.

HAS HELENGTH IN MICROMETERS

FIG. 8. Kubelka-Munk absorption coefficient of illite #36 from Morris, Illinois, as determined from diffuse reflectance measurements on a powdered sample.

# **Concluding Remarks**

This report presents the Kubelka-Munk absorption coefficient for several montmorillonite and related clays for the 0.4 to 2.4- $\mu$ m spectral region. In general, the absorption coefficients are on the order of 1 to 10 cm<sup>-1</sup> except in the 1.4-µm and 1.9-µm water bands. In these regions the absorption is sharply peaked, and is on the order of 10 to 20 cm<sup>-1</sup> in the 1.4- $\mu$ m band and 20 to 30 cm<sup>-1</sup> for the 1.9- $\mu$ m band. However, the two illite clay samples are an exception; they show only a slight increase in absorption coefficient in these bands. The metabentonite clay, while of the same spectral shape as the montmorillonites, is much more strongly absorbing in the water bands. It was also noted that the 1.9-µm band caused by presence of molecular water was highly variable in intensity, depending on the hydration state of the clay sample.



FIG. 9. Kubelka-Munk absorption coefficient of attapulgite #44 from Attapulgus, Georgia, as determined from diffuse reflectance measurements on a powdered sample.

# Acknowledgment

The authors wish to thank Gayle S. Rinehart of the Atmospheric Sciences Laboratory for performing the X-ray diffraction tests to verify the identity of the samples used in this work.

### References

- 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.
- HOIDALE, G. B., AND A. J. BLANCO (1969) Infrared absorption spectra of atmospheric dust over an interior desert basin. *Pure Appl. Geophys.* 74, 151–164.
- LINDBERG, J. D., AND M. S. SMITH (1974) Visible and near infrared absorption coefficients of kaolinite and related clays. Am. Mineral. 59, 274–279.

, AND D. G. SNYDER (1973) Determination of the optical absorption coefficient of powdered materials whose particle size distribution and refractive indices are unknown. *Appl. Opt.* **12**, 573–578.

Manuscript received, March 26, 1974; accepted for publication, May 1, 1974.