NEAR-INFRARED REFLECTANCE SPECTRA OF MIXTURES OF KAOLIN-GROUP MINERALS: USE IN CLAY MINERAL STUDIES

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Abstract—Near-infrared (NIR) reflectance spectra for mixtures of ordered kaolinite and ordered dickite have been found to simulate the spectral response of disordered kaolinite. The amount of octahedral vacancy disorder in nine disordered kaolinite samples was estimated by comparing the sample spectra to the spectra of reference mixtures. The resulting estimates are consistent with previously published estimates of vacancy disorder for similar kaolin minerals that were modeled from calculated X-ray diffraction patterns. The ordered kaolinite and dickite samples used in the reference mixtures were carefully selected to avoid undesirable particle size effects that could bias the spectral results.

NIR spectra were also recorded for laboratory mixtures of ordered kaolinite and halloysite to assess whether the spectra could be potentially useful for determining mineral proportions in natural physical mixtures of these two clays. Although the kaolinite-halloysite proportions could only be roughly estimated from the mixture spectra, the halloysite component was evident even when halloysite was present in only minor amounts. A similar approach using NIR spectra for laboratory mixtures may have applications in other studies of natural clay mixtures.

Key Words—Dickite, Interstratification, Kaolinite, Near-infrared spectroscopy, Order-disorder, X-ray powder diffraction.

INTRODUCTION

X-ray powder diffraction (XRD) modeling techniques have been applied to a number of important clay mineral problems, including studies of structural disorder (Plançon and Tchoubar, 1977) and the determination of layer proportions in interstratified clay minerals (Reynolds, 1980). Some clay mineral characteristics, however, are inherently difficult to analyze by XRD methods, either because the diffraction features of interest are ambiguous, or because short-range structural phenomena are involved, which do not result in coherent X-ray scattering behavior. In this study, near-infrared reflectance spectra are used to address two such problems involving kaolin-group minerals. In each experiment spectral measurements were recorded for mineral mixtures that simulated natural clay materials. The first experiment dealt with the estimation of octahedral vacancy disorder in kaolinite, a question that has previously been addressed by XRD modeling techniques, but which has not been corroborated by other analytical methods (Plançon and Tchoubar, 1977). The second experiment involved the quantitative analysis of intimate mixtures of ordered kaolinite and halloysite, a problem that has not been resolved by XRD or other methods (Brindley *et al.,* 1963).

BACKGROUND

Infrared reflectance spectroscopy is not as widely used as infrared transmission spectroscopy, and the experimental considerations involved in planning reflectance work are probably less familiar to clay min-

eralogists. The use of spectral reflectance measurements in either the near-infrared (NIR, 0.8–2.5 μm) or the mid-infrared (MIR, 2.5–25 μm) wavelength regions avoids two significant problems associated with MIR transmission measurements of clay minerals. The first problem is that the grinding of samples to prepare extremely fine material for dispersion in KBr pellets can cause structural damage in clay minerals (Farmer and Palmieri, 1975). Lightly grinding samples in alcohol may minimize this damage; however, reflectance-IR measurements usually can be made without any sample grinding. For mineral mixtures, the extremely small quantity of sample examined in the MIR transmission analysis also raises the question of whether the sample being measured is representative of the material from which it came. Much larger sample amounts are analyzed in the reflectance-IR mode than in the transmission mode (Salisbury *et al.,* 1987).

The particle size of a sample significantly affects its reflectance spectrum. In relatively transparent materials, light is scattered out of fine-grained samples before much absorption takes place, resulting in spectra that have weak absorption bands and a bright background or "continuum" (Vincent and Hunt, 1968). Coarser samples commonly show more pronounced absorption bands, although in very coarse-grained materials both the continuum reflectance and the band depths can be reduced (Adams and Filice, 1967). Mineral mixtures present an additional complication, because the mixture constituents may have different particle sizes. Clark and Kierein (1988) showed that mixtures involving minerals having different particle

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sizes exhibit complex volume-scattering phenomena, in which the spectral properties of the coarser material typically predominate.

Certain clay minerals bear a spectroscopic resemblance to intimate mixtures of two (or more) minerals of equivalent small particle size. For example, disordered kaolinite resembles a mixture of ordered kaolinite and ordered dickite. Some clay minerals which are interstratifications of different layer types may also resemble intimate mixtures. Laboratory mixtures can be used to investigate these clay structural phenomena; however, it is important that the end member minerals used in such mixtures be selected to minimize any spectral predominance of one component over another due to particle size differences. Because clay samples consist of particle agglomerates of smaller crystallites, volume scattering in clay samples is a complex function of crystallite size, agglomerate size, and crystallite packing in the agglomerates; these are all attributes that are difficult to characterize. To avoid this analytical difficulty, we suggest the use of spectral band intensities and continuum brightness levels as the bases for selecting end member samples for use in reference mixtures. Simply stated, end member samples should be chosen that exhibit equal absorption-band intensities for spectral bands attributed to hydroxyl groups occurring in similar structural sites. For most phyllosilicate minerals, absorption bands related to the "inner-hydroxyl" groups located between the octahedral and tetrahedral sheets are suitable for this purpose. The discussion below for kaolinite-dickite mixtures illustrates such a sample-selection method.

A different use of reflectance spectra for mineral powder mixtures involves the characterization of mineral proportions in natural physical mixtures. For example, Brindley et al. (1963) determined that halloysite, if it is interspersed with ordered kaolinite, can be overlooked by X-ray powder diffraction analysis. Spectra for ordered kaolinite-halloysite mixtures are examined below to determine whether such spectra can be potentially useful for analyzing mineral proportions in unknown samples. As will be seen, this application raises special problems related to the particle size of the natural mixture constituents.

EXPERIMENTAL

The NIR reflectance spectra shown in this report were recorded using a Beckman Instruments, Inc., Model UV 5240 spectrophotometer, equipped with an integrating sphere attachment. The samples consisted of fine particulate agglomerates composed of <2-μm size material, which was concentrated by centrifugal separation of sonified clay samples. The samples were poured loosely into a sample cup (depth 5 mm) and should have had near-random orientation. The sample area measured by the spectrophotometer was about 1

cm by 0.5 mm. Pressed Halon was used as the reference material (Weidner and Hsia, 1981). All samples were analyzed by XRD using side-packed powder mounts to minimize sample orientation. Table 1 lists localities and other information for the samples used in this study.

To prepare the mixture series between kaolinite and dickite, samples were selected that showed 1.415-μm absorption bands having approximately equal integrated intensities (Table 2). The 1.415-μm bands in both minerals are related to "inner-hydroxyl" groups located between the octahedral and tetrahedral sheets. The inner-hydroxyl sites are similar, although not identical for the two minerals, as indicated by the different bandwidths for the 1.415-μm features (Figure 1A; see also, Brindley et al., 1986). Because the number of inner-hydroxyl groups per unit volume is the same for kaolinite as for dickite, absorption related to these groups presumably should be equal, except for variations in band intensity caused by differences in volume scattering. On this assumption, the integrated intensities of the 1.415-μm bands were used as an index for selecting the best pair of end member samples for the reference mixtures. The integrated band intensities were measured graphically, with each sample continuum used as a baseline. The samples chosen for the mixtures also had similar continuum brightnesses (Table 2). This condition was necessary to avoid any major spectral bias towards one end member caused by differing particle size or trace amounts of opaque impurities in the samples.

A series of kaolinite-halloysite mixtures was also prepared using end member samples that had roughly equal 1.415-μm band intensities. This procedure involved an implicit and not necessarily true assumption that natural kaolinite-halloysite mixtures consist of mineral components of equal particle size. This assumption must be verified by some other analytical method before laboratory mixtures can be used to estimate mineral proportions in natural mixtures.

RESULTS

Kaolinite-dickite mixtures

Figure 1A shows spectra for the series of ordered kaolinite and dickite reference mixtures. The spectra cover only a narrow portion of the NIR wavelength range and show absorption bands that result from the first overtone of the OH-stretching fundamental (Hunt and Salisbury, 1970). Bands positioned between 1.36 and 1.40 μm are attributed to hydrogen-bonded OH groups located on the exterior surfaces of the octahedral sheets, whereas the 1.415-μm bands were produced by the inner-hydroxyl groups. Brindley et al. (1986) gave a more detailed discussion of the OH absorption band assignments in kaolinite.

Figure 1B shows spectra for nine additional kaolinite

samples exhibiting various degrees of structural disorder (Table 1). Figure 2 is a plot of the relation between the 1.39/1.415 μm band-depth ratio and structural disorder as measured by the Hinckley index (Hinckley, 1963). Also shown on the upper axis of the same plot are the 1.39/1.415 μm band-depth ratios measured from the reference mixture spectra presented in Figure 1A. Comparison of the disordered kaolinite band depth ratios with those for the reference mixtures indicates that the proportion of a dickite-like component in the disordered kaolinite samples ranges from 0 to ~34%. A strong correlation exists between the Hinckley indexes and the band-depth ratios for the natural samples. Note that two samples (Mesa Alta and Keokuk) were slightly more ordered than the Murfreesboro kaolinite used in the reference mixtures and so plotted to the right of the zero line on the diagram.

Figure 3 shows XRD patterns for an ordered (3a) and a disordered kaolinite (3c). Also shown in the figure are XRD patterns calculated by Plançon and Tchoubar (1977) for ordered and highly disordered kaolinite (3b and 3d). The calculated and the measured XRD patterns match each other closely, except that the calculated patterns assumed perfectly random sample orientation, which caused the hk0 reflections near 0.225 $\mathring{A}^{-1}$ to appear somewhat more intense than those in the measured data. The 002 reflections were not modeled and are indicated by dashed lines in Figures 3b and 3d (Plançon and Tchoubar, 1977).

The model disordered kaolinite (Figure 3d) has 52% octahedral vacancies, whereas the measured comparison sample (sample 301, Table 1) is indicated by its 1.39/1.415 μm spectral band ratio to have about 34% vacancies. This discrepancy exists because the calculated XRD pattern does not include translational defects which also contribute to the diffraction characteristics of natural samples. Refining the calculated pattern to include these other defects would reduce the percentage of Al-vacancy displacement defects (Plançon and Tchoubar, 1977) to about the same values for the highly disordered kaolinite (30–40%) observed in the present study.

Kaolinite-halloysite mixtures

Figure 4A shows reflectance spectra for a series of mixtures between Murfreesboro kaolinite (ordered) and halloysite. A comparison of this figure with Figure 1 shows that the absorption bands at 1.415 and 1.385 μm in the halloysite-kaolinite mixtures have more nearly equal intensities than the bands in disordered kaolinite and that they are significantly broader than the bands in ordered kaolinite (Figure 1B; Table 1). Moreover, the individual spectra in the kaolinite-halloysite mixtures were strongly dominated by the absorption characteristics of the halloysite component, the exact reverse of the problem reported in XRD studies of such mixtures (Brindley *et al.*, 1963). Figure 4B
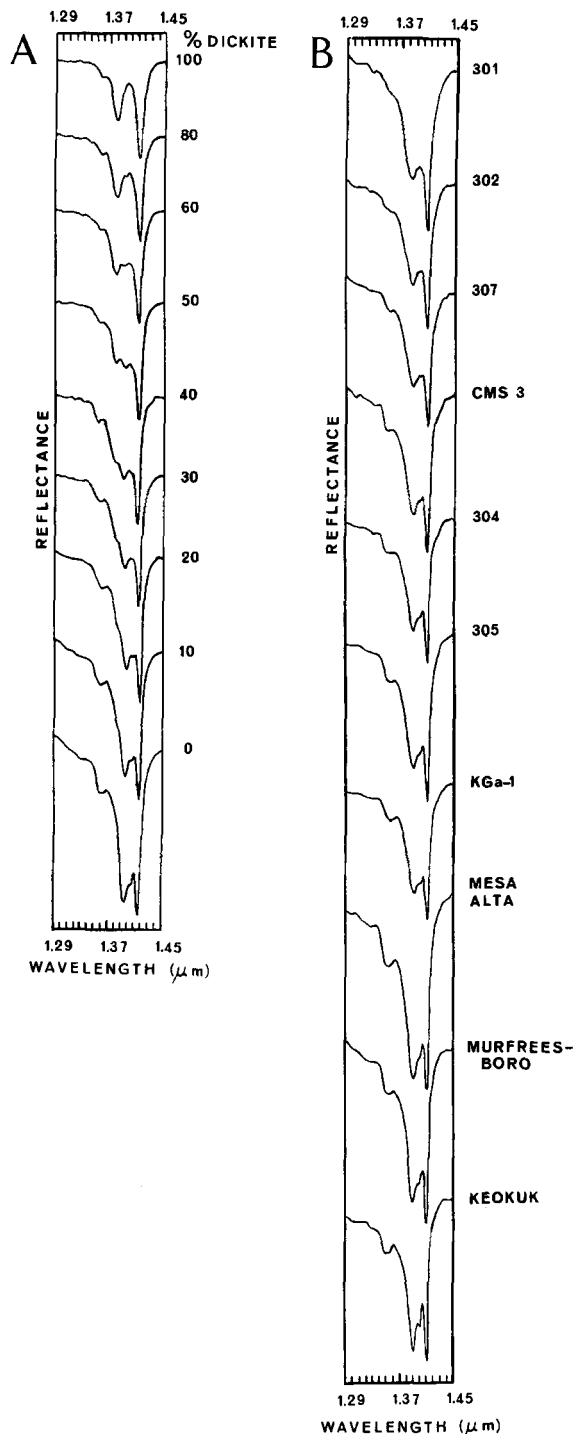

Figure 1. Near-infrared diffuse reflectance spectra for kaolin-group minerals measured against a Halon reference (wavelength range = 1.29–1.45 μm). Figure 1A shows spectra for reference mixtures of ordered dickite–ordered kaolinite. Figure 1B shows spectra for natural kaolinite samples exhibiting various degrees of disorder.

Table 1. Location, Hinckley index, and spectral band ratio of samples examined in this study.[1]

Sample mineralogy/number[2]	Locality	Hinckley index[3]	Spectral band ratio 1.39/1.415 μm
Kaolinite:			
Keokuk	Keokuk, Iowa	1.68	0.94
Murfreesboro	Murfreesboro, Arkansas	1.56	0.89
Mesa Alta	Mesa Alta, New Mexico	1.39	0.95
Kga-1[4]	Washington County, Georgia	0.91	0.80
305	Macon County, Georgia	0.73	0.81
304	Macon County, Georgia	0.64	0.79
Ward's No. 3[5]	Macon County, Georgia	0.50	0.76
307	Macon County, Georgia	0.43	0.71
302	Macon County, Georgia	0.14	0.71
301	Macon County, Georgia	<0.05	0.68
Dickite:			
NMNH #46967	Zuni Mine, Colorado	n.a.	n.a.
NMNH #106243	St. George, Utah	n.a.	n.a.
NMNH #92395-7	Cusihuiriachio, Mexico	n.a.	n.a.
NMNH #106242	Red Mountain, Colorado	n.a.	n.a.
Halloysite:			
NMNH #106237	Lawrence County, Indiana	n.a.	n.a.

[1] n.a. = not applicable.
[2] NMNH = National Museum of Natural History, Washington, D.C.
[3] Hinckley (1963).
[4] Source: Clays Repository of The Clay Minerals Society.
[5] Ward's Natural Science Establishment, Rochester, New York.

shows three mixtures, each consisting of a different ordered kaolinite sample mixed with halloysite in the same proportions (60% kaolinite, 40% halloysite). Despite the significant differences in absorption band intensity for the three pure kaolinite samples (Figure 1B), the spectra for the three mixtures in Figure 4B are virtually identical.

DISCUSSION

Structural disorder in kaolinite

Disorder in kaolinite can be the result of non-regular interlayer shifts, non-regular rotations of layers, or faults

Table 2. Data used to select ordered kaolinite and dickite samples for the reference mixture series.[1]

Sample mineralogy/number[2]	Hinckley index[3]	Continuum reflectance at 1.45 μm	Integrated 1.415-μm band intensity (arbitrary units)
Kaolinite:			
Murfreesboro[4]	1.56	82%	0.270
Keokuk	1.68	93%	0.219
Mesa Alta	1.39	80%	0.360
Dickite:			
NMNH #46967[4]	n.a.	84%	0.280
NMNH #106242	n.a.	87%	0.549
NMNH #106243	n.a.	93%	0.390
NMNH #92395-7	n.a.	93%	0.419

[1] n.a. = not applicable.
[2] See Table 1 for locations and sources of samples.
[3] Hinckley (1963).
[4] Denotes samples used in the reference mixtures.

involving the position of the vacancy in the octahedral sheet (Brindley, 1980). XRD studies by other workers have demonstrated that vacancy displacements within the octahedral sheet constitute the most important type of defect (Plançon and Tchoubar, 1977). Ordered kaolinite contains only B-site vacancies, whereas ordered dickite contains regularly alternating B- and C-site vacancies (the A sites are always occupied in both minerals). Thus, disordered kaolinite having vacancy disorder can be considered to contain small domains of ordered kaolinite and dickite. Barrios *et al.* (1977) reported the unpublished findings of C. Noel that spectra for disordered kaolinite can be considered as intermediate between spectra for ordered kaolinite and ordered dickite. The results here are consistent with this concept and indicate that it is possible to estimate the amount of octahedral vacancy disorder in disordered kaolinite by comparing its spectrum with spectra of mixtures of ordered kaolinite and ordered dickite.

Although the present study of octahedral vacancy disorder in kaolinite corroborates earlier published XRD modeling results, the spectroscopic data lack the versatility of XRD techniques for treating the other types of defects present in natural kaolin minerals. The use of mixtures for addressing structural disorder problems requires that suitable analog mineral structures (e.g., ordered kaolinite and dickite) be available for use in mixture preparations. No such analogs were available to simulate the translational and rotational defects found in disordered kaolinite. Also, the analog minerals must exhibit diagnostic spectral bands that permit
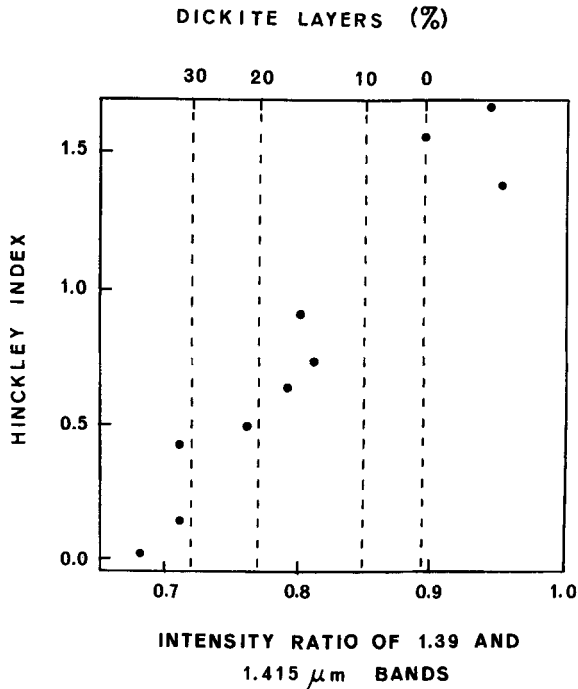
DICKITE LAYERS (%)

Figure 2. Scatter plot showing relation between Hinckley indexes for the kaolinites examined in this study and their 1.39/1.415 μm band intensity ratios measured from Figure 1B. Also shown on the upper axis are percent dickite values corresponding to the 1.39/1.415 μm band intensity ratios measured from the reference spectra in Figure 1A.

their distinction in mixture spectra. If the NIR spectra are ambiguous, MIR reflectance or transmission spectra might exhibit suitable bands for analyzing mixtures (Salisbury *et al.*, 1987).

Kaolinite-halloysite mixtures

Problems involved in characterizing physical mixtures of halloysite and ordered kaolinite were described by Brindley *et al.* (1963), who commented that as much as 60% halloysite in such a mixture could be overlooked by XRD analyses. These same authors also concluded that examination of crystal habits by scanning electron microscopy (SEM) was not a reliable means of distinguishing halloysite from other disordered forms of kaolinite. The present study indicates that NIR spectral measurements can be used to detect minor amounts of halloysite in physical mixtures with ordered kaolinite, even in samples in which the kaolinite is relatively coarse grained and absorbs strongly. The subtle spectral differences noted for different mixtures, however, were not sufficiently diagnostic to determine the relative proportions of the components. It is also important to note that the components in natural physical mixtures of kaolinite and halloysite, or other clay mixtures, need not have equivalent particle sizes.
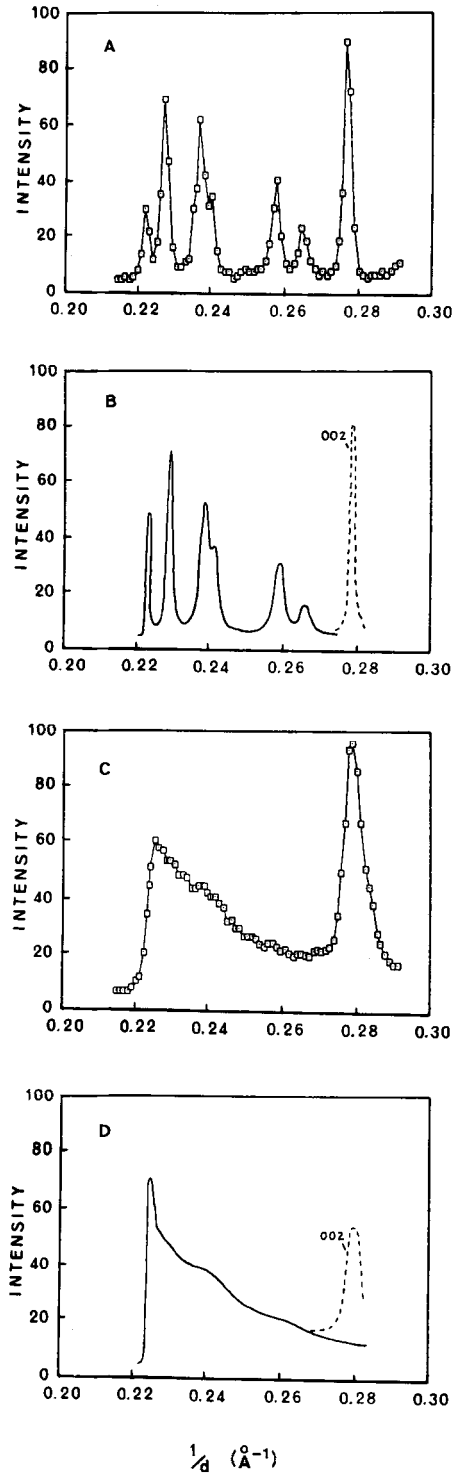

Figure 3. Comparison of measured X-ray powder diffraction patterns with calculated patterns adapted from Plancon and Tchoubar (1977). Figures 3A and 3B are measured and calculated patterns, respectively, for well-ordered kaolinite. Figures 3C and 3D are measured and calculated patterns for relatively disordered kaolinite. The measured patterns are for samples 301 and Keokuk listed in Table 1.
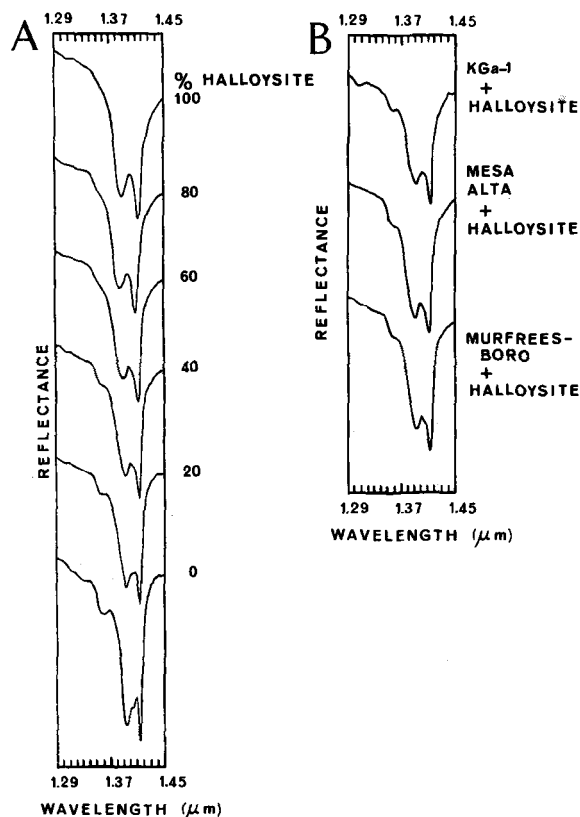
Figure 4. Near-infrared diffuse reflectance spectra for mixtures of ordered kaolinite and halloysite (wavelength range = 1.29–1.45 μm). Figure 4A shows spectra for a series of reference mixtures of Murfreesboro kaolinite and halloysite. Figure 4B shows spectra for three mixtures, each consisting of 40% halloysite and 60% kaolinite. Three different ordered kaolinites were used in these mixtures.

Thus, reference mixture spectra should be used cautiously for characterizing natural mixtures, and preferably should be interpreted in conjunction with SEM observations or other data to help address the particle-size question.

An approach using radiative transfer theory, as discussed by Clark and Kierein (1988), may avoid some of the experimental pitfalls mentioned above by calculating mixture spectra. Reflectance spectra can be calculated for any particle size-mixture combination using the optical constants (absorption coefficients and indices of refraction) of the end member minerals. The necessary optical constants are not presently available for clay minerals, but can, in principle, be measured. Relations between clay mineral particle size, as measured by SEM, and sample reflectance properties also have not been studied and must be better understood to ensure the validity of the modeling algorithms. If successfully developed, such a modeling approach would provide a spectroscopic analog to X-ray powder diffraction modeling techniques, and would be a powerful tool for clay mineral studies.

Other applications and refinements

Many clay mineral species exhibit NIR absorption bands related to structural hydroxyl groups that should be suitable for matching sample volume scattering properties. For example, the determination of layer proportions in mixed-layer clays, such as illite/smectite (I/S), may be regarded as a mixture problem similar to kaolin structural disorder. The smectite component in I/S clays, however, contains interlayer water molecules that produce absorption near 1.4 μm, which may preclude the use of the 1.415-μm inner-hydroxyl band for selecting reference mixture end members. Nonetheless, other structural OH absorption bands located in the 2.0–2.5-μm wavelength region (Hunt and Salisbury, 1970) should still be suitable for sample selection purposes, and would not suffer directly from molecular water interference effects. Because I/S minerals exhibit greater compositional variation than kaolin minerals, the reference mixture end members ideally should match the natural sample compositions.

CONCLUSIONS

Reflectance spectra recorded for reference mineral mixtures can be used to analyze certain clay mineral characteristics, including the amount of octahedral vacancy disorder in kaolinite. This use of mixtures is largely independent of XRD modeling techniques, but lacks the versatility of XRD methods for studying other types of disorder in kaolinite. In preparing the kaolinite-dickite reference mixtures to simulate disordered kaolinite, it was necessary to consider possible grain-size effects on the reflectance spectra by carefully matching the particle size-volume scattering properties of the mixture components. In this study, the matching was done by selecting samples that had inner-hydroxyl absorption bands of approximately equal integrated intensity.

Mixtures of kaolinite and halloysite were prepared to determine whether the reflectance spectra could be potentially useful in studies of natural physical mixtures of these minerals. In contrast with XRD results, the spectral data clearly revealed the presence of the halloysite component, even if the proportion of halloysite in a mixture was only 20 to 40%. Natural mixtures of kaolinite-halloysite, however, may have mineral components of unequal particle size, and the reference mixtures ideally should match the natural samples in particle size as well as composition. The question of sample particle-size distributions is common to all analytical problems involving intimate physical mixtures of clay minerals, and presents a practical problem insofar as suitable spectral reference samples may not always be available. Eventually, it may be possible to avoid this difficulty by calculating spectra for mineral mixtures through the use of radiative transfer modeling techniques.

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