

THE NEAR-INFRARED COMBINATION BAND FREQUENCIES OF DIOCTAHEDRAL SMECTITES, MICAS, AND ILLITES

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Abstract—The highest frequency near-infrared (NIR) combination bands for specimens of four species of mica—montmorillonite-beidellite, illite, chlorite, and kaolinite—were correlated with respect to Al_2O_3 content. A direct linear correlation was found between the combination band positions and the Al_2O_3 contents of the montmorillonite-beidellite series, which may be given as: $\bar{\nu} \text{ cm}^{-1} = (5.38 \pm 0.04) (\% \text{ Al}_2\text{O}_3) + (4412.8 \pm 0.9)$. A similar linear correlation for muscovite is: $\bar{\nu} \text{ cm}^{-1} = (6.10 \pm 0.25) (\% \text{ Al}_2\text{O}_3) + (4434.1 \pm 8.3)$.

Possible NIR band interferences are shown for different mineral mixtures, along with the correlation of different illites with muscovite. No combination bands were found in the frequency region 4425 cm^{-1} to 4625 cm^{-1} for specimens in which the Al_2O_3 content was only in the tetrahedral layer sites.

Key Words—Al content, Dioctahedral smectites, Micas, NIR spectra.

INTRODUCTION

This investigation began as a study of the near-infrared (NIR) spectra of micas to determine whether micas could be readily identified and differentiated by the use of diffuse reflectance in the laboratory. The NIR spectral range is particularly useful both for identifying clay minerals and micas and for determining the dominant weathering products present at the surface when mapping land by remote sensing. The linear relationship of the highest frequency combination band of Muscovite with Al_2O_3 content became apparent, and the study was expanded to include other clay minerals, such as smectites, illites, chlorites, and kaolinite. The problem of spectral band interference in mineral mixtures was also investigated. Then, the linear relationship of the sole combination band frequency of dioctahedral smectite with Al_2O_3 content was detected. It now appears possible to identify specific mineral species from the smectite group and to estimate the Al_2O_3 content of these smectite minerals from their NIR spectral band frequencies. Moreover, illites formed in different geologic environments have different NIR spectral band frequencies and may be studied in this manner.

For this study, the spectra are presented by wave number, ranging from $4750\text{--}4000 \text{ cm}^{-1}$ ($2105\text{--}2500 \text{ nm}$) in the NIR spectrum, because this is a “window” in the atmospheric absorption spectrum where the different vibrational mode frequencies of water are unlikely to interfere with the spectral response. The spectral patterns (bands) observed are related to the OH part of the crystalline structure of the minerals (Higgins and Streitz, 1988). These band frequencies consist of the sum of OH stretching and bending effects (Clark *et al.*, 1990) representing specific resonant bonds in a crystal structure, such as Al–OH bonding. The fre-

quency of the bands varies as cation substitutions in the structure vary because different cation radii change bond lengths and alter the structural geometry. The small changes in stretching and bending band positions are additive in the combination bands, making them more readily differentiated.

Most clay minerals and micas can be identified by their unique NIR spectral bands, and some of the particular bands have been assigned, such as the Al–OH combination band in muscovite near wave number 4540 cm^{-1} (2200 nm) (Vedder, 1964). A summary of band assignments is given in Hunt (1977).

The history of the development of NIR reflectance spectroscopy is given by Clark *et al.* (1990), including a summary of NIR spectra for selected common minerals. An NIR mineral database was established by Hunt (1977) and is now being updated by the USGS Spectroscopy Lab located in Denver, Colorado.

Identification of the NIR absorption bands for Camontmorillonite was verified by Cariati *et al.* (1981), with additional data concerning the effects of exchange cations (Cariati *et al.*, 1983a) and layer charge (Cariati *et al.*, 1983b) as well as the spectra of hectorite, nontronite, and vermiculite. More recently, a practical application of the use of field measurement of reflectance spectra was given for delineating gold deposits in the Carlin Trend (Kral, 1990).

EXPERIMENTAL METHODS

A total of 22 samples were studied (Table 1), of which 11 were smectite specimens. Chemical analyses for five smectites were previously published. Four illites and one kaolinite (Kga-1) were included to determine possible NIR spectral interference. Six smectite specimens and four illite specimens were analyzed by X-ray spectrographic methods, and all results are pre-

Table 1. Sources, composition and near-infrared reflectance absorption bands of minerals investigated.

No.	Specimen	Al ₂ O ₃	Fe ₂ O ₃	MgO	Absorption bands, cm ⁻¹
		% by wt.			
Montmorillonite					
1	Amory, MS, API 22 ¹	24.3	5.9	2.1	4545m
2	Uri, Italy	22.5			4533
3	Upton, WY, API 256 ²	21.3	3.4	3.4	4529, 4480sh
4	Otay, CA, API 24	19.8	1.0	7.0	4518s, 4485sh
Fe-smectite					
5	Flagstaff Hill, CA	8.4	19.4	3.8	4458w, 4363m
Beidellite					
6	CP-6, DeLamar Mine, ID	25.0	3.2	0.9	4548m
7	GS-3 Bench, DeLamar Mine, ID	29.0	0.8	1.4	4568m
8	Blaine Tunnel, ID	30.6	2.1	0.8	4577s
9	GS-3 Vein, DeLamar Mine, ID	30.6	2.1	0.8	4585m
10	Crown Point Mine, ID	32.1	1.0	0.3	4585s
11	Black Jack Mine, ID	33.9	0.6	0.2	4603 (estim.)
Illite					
12	Occidental Mine, NV	27.5	4.1	3.1	4533s, 4252w, 4085w
13	Black Jack Mine, ID	27.3	4.0	0.5	4534s, 4249w, 4095m
14	Phillips Mine, ID	35.5	1.2	0.4	4550s, 4261m, 4098m
15	Empire Mine, ID	35.8	1.5	0.6	4547s, 4256m, 4099m
Muscovite					
16	Isinglass Mine, CA	35.3	3.4	0.2	4548s, 4460sh, 4260m, 4104w
Phlogopite					
17	SUNY, Buffalo, NY	16.8	3.2 ⁴	24.3	4448m, 4297s, 4200m, 4100w
Biotite					
18	Nashville Trail, CA	16.3	22.4 ⁴	10.1	4435s, 4255s, 4175m
Roscolite ³					
19	Coloma, CA	11.9	1.2 ⁴	1.5	4428w, 4350s, 4220m
Ripidolite					
20	Flagstaff Hill, CA	19.8	25.3 ⁴	16.6	4444m, 4340w, 4270s
Kaolinite					
21	Source Clay KGa ⁻¹	39.2	0.2	0.1	4529s
Nontronite					
22	Panamint Valley, CA	8.1	29.6	2.1	4364m, 4170w

Band strength: s—strong; m—moderate; w—weak; sh—shoulder.

¹ From Hunt and Salisbury (1970).

² From Hunt *et al.* (1973).

³ Roscolite specimen contains 20.7% V₂O₅.

⁴ Iron content given as FeO.

References for chemical analyses of clay minerals involved in this study include kaolinite (Jepson and Rowse, 1975); beidellite (Shannon, 1923, and Weir and Greene-Kelly, 1962); and montmorillonite (Pietracaprina *et al.*, 1972, and Weaver and Pollard, 1973). The Isinglass Mine muscovite was chemically analyzed by Post (1988), the roscolite by Post and Burnett (1985), and the biotite is from Nashville Crossing, El Dorado County, California. In Figure 2, the Otay bentonite and Flagstaff Hill ripidolite are from the Source Clay collection, and the phlogopite was analyzed by Lin and Clemency (1981).

sented as oxide wt. % recalculated on an H₂O-free basis. The smectite oxide analyses were further adjusted to exclude adsorbed water content at 110°C because adsorbed water loss between 110°C and 300°C varies from about 2%–4% by weight for different Al smectites. The precise methods of XRF analysis used are given by Post and Austin (1993).

The NIR spectra and partial mid-IR spectra (4000–3500 cm⁻¹ or 2500–2857 nm) were obtained using a

Perkin-Elmer Model 1800 FTIR with a diffuse reflectance (DRIFT) accessory. The spectra were acquired using low-energy mode, with 4 cm⁻¹ resolution and eight cycles of signal averaging. Undiluted specimens gave satisfactory spectra in the range above 2000 cm⁻¹ (5000 nm), but interference occurs in the 1400–1100 cm⁻¹ (7143–9091 nm) frequency range in the form of a broad absorption band that obscures other bands present. The broad band occurs when the refractive

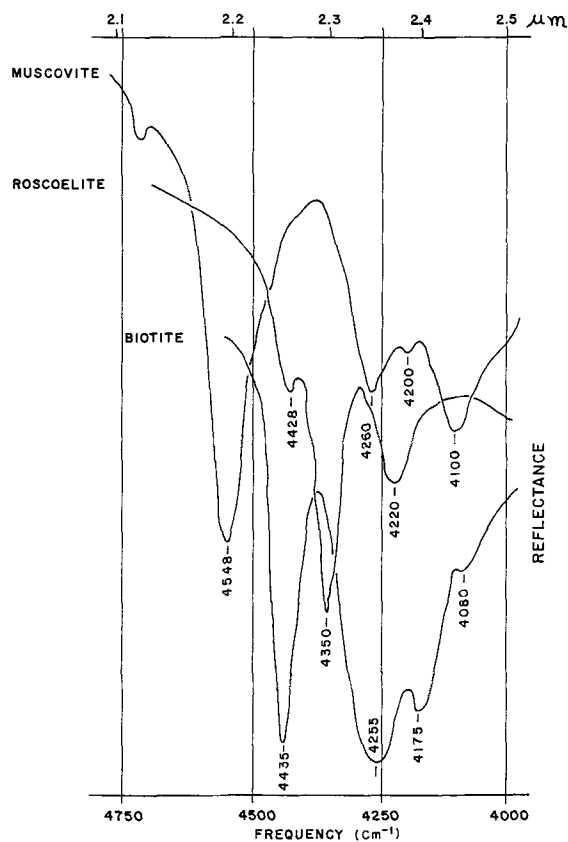


Figure 1. Near infrared spectrum of muscovite, roscoelite, and biotite. Sample locations detailed in Table 1.

index of the material matches that of the surrounding medium, known as the principal Christiansen frequency (Logan *et al.*, 1973). A mixture consisting of 5 wt. % sample in powdered KBr gave well-resolved reflectance spectra below 1500 cm^{-1} if mid-IR spectra were desired without resorting to transmission techniques. In a few instances, the KBr mixtures also facilitated the detection of poorly resolved shoulders on the intense OH stretching band in the $4000\text{--}3000\text{ cm}^{-1}$ region. Mid-IR spectra may be utilized to compare the two component bands comprising the NIR combination band, even though as much as a 5 cm^{-1} frequency difference between the combination band position and the sum of the measured mid-IR fundamentals was observed.

RESULTS

The Al_2O_3 , Fe_2O_3 or FeO and MgO contents, along with NIR and OH stretching vibration maxima are given in Table 1. All oxide compositions are given on the basis of X-ray spectroscopic analysis, with no adjustment for adsorbed water. The illite specimens showed no weight loss when heated from 110°C – 300°C . The NIR spectra investigated consist of combination bands, such as the six examples of mineral spectra

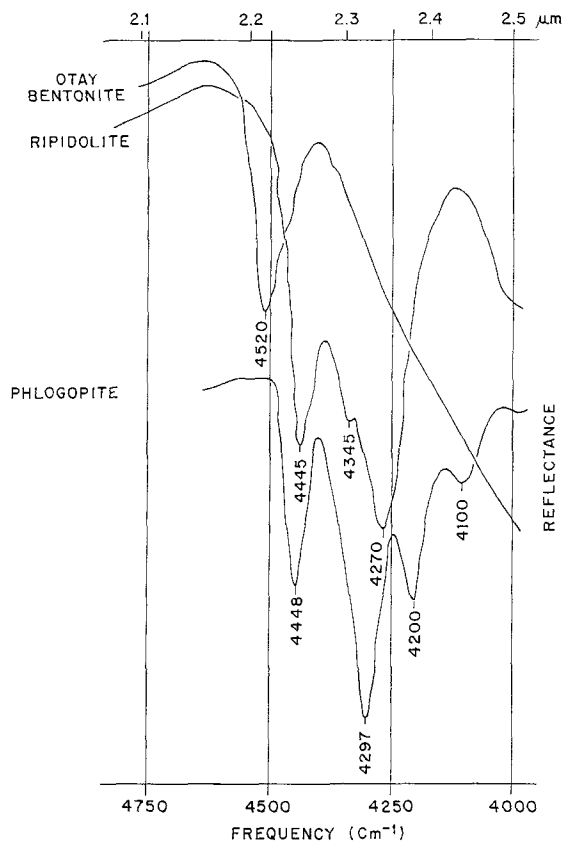


Figure 2. Near-infrared spectrum of Otay bentonite, ripidolite, and phlogopite. Sample locations detailed in Table 1.

shown in Figures 1 and 2. The six spectra were chosen to illustrate the range in variation of NIR bands for different micas and clays, and their juxtaposition suggests possible band interferences that result when mineral combinations are present.

The random powder XRD patterns of muscovite and roscoelite are nearly identical, but the NIR spectra are completely different (Figure 1). The muscovite band at 4548 cm^{-1} is assigned as an Al–OH band (Vedder, 1964), but the remaining bands are not assigned. It is possible that the roscoelite band at 4350 cm^{-1} is due to $\text{V}^{3+}\text{--OH}$, because it does not appear in the other mica spectra.

Stubican and Roy (1961) showed that there was a correlation of IR band positions with isomorphous substitution of cations for tetrahedral coordinated Al in hydrous layered silicates, but these mid-IR bands are often difficult to see because of chemical heterogeneities and interference from adjacent bands. The frequencies of the first NIR spectral bands assigned to Al–OH combination modes are given in Figure 3 for the smectites, illites, and kaolinite. The highest frequency bands present in this NIR spectral range are plotted for the other micas and chlorites, but they have no band assignments.

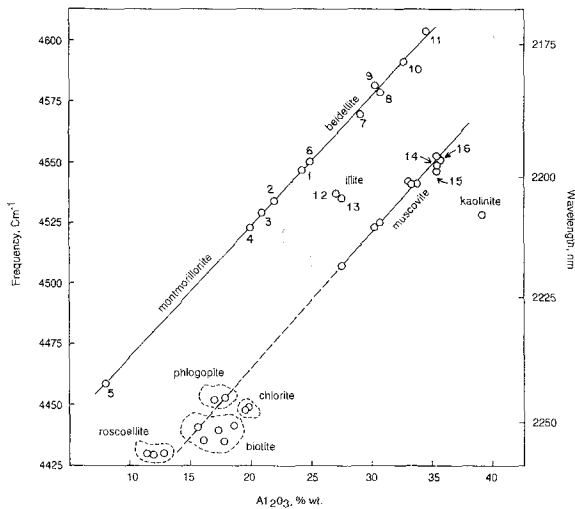


Figure 3. The correlation of the primary Al-OH near-infrared combination bands and Al_2O_3 contents for different smectites and illites, plus muscovite, phlogopite, biotite, roscoelite, kaolinite, and chlorite. Points 1-4 are montmorillonite, and 5 is Fe-smectite. Points 6-11 are beidellite. The sources of the four illite specimens and one kaolinite are described in Table 1.

There is a direct linear correlation between band position and Al content for the dioctahedral smectite series, including the montmorillonite and beidellite minerals. Similar correlations are found for other minerals, such as muscovite. The regression analyses for the two linear relations shown in Figure 3 are:

montmorillonite-beidellite

$$\text{cm}^{-1} = (5.38 \pm 0.04)(\% \text{Al}_2\text{O}_3) + (4412.8 \pm 0.9)$$

muscovite

$$\text{cm}^{-1} = (6.10 \pm 0.25)(\% \text{Al}_2\text{O}_3) + (4434.1 \pm 8.3)$$

The beidellite specimens were taken from an area of Al-rich clays around the DeLamar Silver Mine and Florida Mountain in southwestern Idaho near Silver City adjacent to the source of the well-known Black Jack Mine beidellite (Lindgren, 1899; Piper and Laney, 1926). The mid-IR spectrum of the Black Jack beidellite (Farmer, 1974) has a hydroxyl fundamental stretching band at 3660 cm^{-1} and an Al-OH bending band at 942 cm^{-1} , giving a combination band of 4602 cm^{-1} . In comparison, the Crown Point beidellite has an OH stretching band at 3650 cm^{-1} and an Al-O band at 940 cm^{-1} , giving a measured combination band of 4585 cm^{-1} . The NIR spectra for five dioctahedral smectites are shown in Figure 4.

The spectral bands for the dioctahedral smectite specimens are well defined, except for the Fe-smectite from Flagstaff Hill, California. The four spectra reveal the shift in band position with differing Al contents. The Fe-smectite and nontronite show Fe-OH bands at

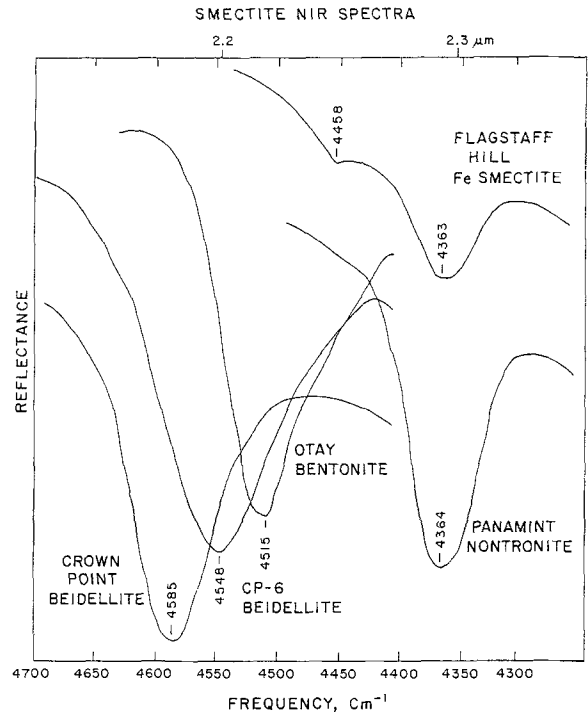


Figure 4. NIR spectral bands are shown for four smectites with different Al contents and for one nontronite specimen. Locations for the samples are described in Table 1.

a frequency of about 4364 cm^{-1} . Nontronite and saponite minerals tend to contain small amounts of Al, mainly in the tetrahedral layers, and their spectra generally do not include an Al-OH band. The Fe smectite appears to contain Al mainly in the octahedral layer, with a weak combination band at 4458 cm^{-1} . The biotite bands, at about 4440 cm^{-1} , occur at higher frequency with increase in octahedral Al content; that band is not present when Al fills only the tetrahedral sites in the unit cell, as with trioctahedral smectites such as saponite. The calculated octahedral Al ions in the unit half-cells of the five biotites given (Figure 3) ranged from 0.12 to 0.40.

DISCUSSION

Illite formed as an alteration product tends to be Si-rich, whereas degraded muscovite retains its Al_2O_3 content. This distinction can be useful in surface reflectance mapping (Kral, 1990). Specimens 12 and 13 (Figure 3) are examples of Si-rich illite. The illite specimens tested have formed from the hydrothermal alteration of K-feldspar in rhyolite. Two specimens from Florida Mountain, Nos. 14 and 15 (Figure 3), are unusual in that they appear to be a mixture of 1M and $2M_1$ illite, but they contain from 8.5 to 9.1% K_2O .

The NIR spectra of hydrous layered silicates are quite useful in a number of ways in addition to surface mapping by remote sensing. The Al_2O_3 content of mus-

covite and montmorillonite, and possibly a number of other minerals such as chlorite, may be readily determined and the type of illite in ore bodies may be identified using laboratory or field apparatus. Also, the NIR spectra may be useful in assigning infrared spectral bands previously unknown, such as unique V^{3+} bands (Figure 1).

Mixtures of discrete clay minerals may cause interference with the identification of dioctahedral smectite NIR bands. For example, the most common clays in the DeLamar-Florida Mountain area are illite, kaolinite, and beidellite. The strong kaolinite band may overlap montmorillonite bands, and illite bands may overlap beidellite bands; however, in most cases, mixtures of hydrous layer silicates may be directly investigated. For example, the Al content of dioctahedral smectite in the DeLamar-Florida Mountain area may be determined without removing any quartz or feldspar because there are no interfering spectral bands and the kaolinite band occurs at a lower frequency (4529 cm^{-1}) than the beidellite bands.

NIR combination band frequencies have also been assigned for Fe-OH as shown for Panamint nontronite (4364 cm^{-1}) in Figure 4 (Cariati *et al.*, 1983b) and for Mg-OH as shown for phlogopite (4297 cm^{-1}) in Figure 2 (Hunt, 1977).

The shift in band position for dioctahedral smectites with varying Al content appears to be related to the dimensions of the smectite unit cell. MacEwan (1951 and 1961) showed that the b-axis dimension of the smectite unit cell is a linear function of the amount of isomorphous substitution of Fe and Mg for octahedral Al, that most of the Fe content is in the form of Fe^{3+} , and that the cation radius of Mg^{2+} (0.66 \AA) is nearly the same as Fe^{3+} (0.64 \AA). The smectite unit cell becomes smaller with increased Al content to the end member beidellite with a b-axis dimension of 8.93 \AA , as calculated by Weir and Greene-Kelly (1962). The NIR Al-OH band position of dioctahedral smectite also appears to be a linear function of Al content, as its frequency increases as the size of the unit cell decreases. The same sort of relationship appears to hold for muscovites (Figure 3), and other micas have varied lower band frequencies. A table of comparable b-cell parameters for some smectites, talc, and pyrophyllite, is given by Deer *et al.* (1962).

CONCLUSION

The direct correlation between the combination band positions and Al_2O_3 contents of the montmorillonite-beidellite series is useful for determining the Al_2O_3 content of unanalyzed specimens. The band frequency may be measured without removing any quartz or feldspar present. A similar linear correlation exists for muscovite. The main band interference for the clays commonly found together is from a mixture of kaolinite and montmorillonite containing considerable Fe in

its structure. The montmorillonite-beidellite series appears to be continuously uniform without break, so it is possible to estimate the b-axis dimension of an unknown specimen by determining its NIR combination band frequency in respect to specimens with known unit cell dimensions.

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