Mid-infrared (5–100 µm) reflectance spectra and optical constants of ten phyllosilicate minerals

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Abstract

We have derived the real and imaginary indices of refraction for 10 phyllosilicate minerals—montmorillonite, beidellite, nontronite, hectorite, saponite, illite, illite-smectite (60/40 interlayered) kaolinite, halloysite, and serpentine—from 100–2000 cm⁻¹ (5–100 µm) at 2 cm⁻¹ spectral sampling using classical Lorentz–Lorenz dispersion theory. We present the real and imaginary indices and the oscillator parameters with which they were modeled. Use of these optical constants will aid in the modeling of thermal infrared spectra of planets, asteroids, interplanetary and interstellar dust, and protoplanetary disks around nearby stars.

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1. Introduction

Silicates are an important component of the surface of Earth, Mars, and other planets, as well as interplanetary and interstellar dust particles, asteroids, and disks surrounding young stars. Studies using both visible/near-infrared (VNIR) and thermal infrared (TIR) spectroscopy have shown that crystalline, hydrous silicates are important phases in these bodies (Lebofsky, 1978; Barber, 1981; Vilas and Gaffey, 1989; Reach et al., 2003; Poulet et al., 2005; Bibring et al., 2005). An important factor in identifying the components of these materials in TIR spectra is the availability of suitable optical constants that allow modeling of scattering, transmission and absorption processes that affect the spectra. Here, we present the estimated optical constants of 10 hydrated phyllosilicates from 100–2000 cm⁻¹ (5–100 µm) which were determined by applying classical Lorentz–Lorenz dispersion analysis to high-quality laboratory reflectance spectra.

2. Background

2.1. Phyllosilicates on Mars

As discussed by Bell (1996), phyllosilicates have been detected in several martian meteorites (termed the SNC meteorites) indicating that these minerals once formed on Mars. Trieman et al. (1993) identified iddingsite (a mixture of ferrirhydrite and smectite clay) in the Lafayette meteorite, while Gooding and Meunow (1986), Gooding et al. (1991), and Gooding (1992) discussed the possible identification of illite/smectite mixed layer clays in the EETA79001 and Nahkla meteorites.

Until the discovery of phyllosilicates by the European Space Agency’s Observatoire pour la Minéralogie, l’Eau, les Glaces, et l’Activité (OMEGA) VNIR imaging spectrometer (Bibring et al., 2005; Poulet et al., 2005; Mustard et al., 2006), in the Mawrth Vallis and Nili Fossae regions of Mars, the presence of phyllosilicates on Mars at measurable quantities from remote sensing observations had been the subject of debate. Early evidence from VNIR telescopic and spacecraft observations showed only weak OH⁻ spectral features (Singer et al., 1979; McCord et al., 1982; Murchie et al., 1993; Bell et al., 1997) that could be interpreted as due to phyllosilicates. Particu-
lar emphasis was placed on the search for phyllosilicates in the martian bright regions and atmospheric dust—an effort which is summarized in detail by Hamilton et al. (2005). Early analysis of Mariner 9 Infrared Interferometer Spectrometer (IRIS) TIR spectra indicated that the composition of the dust could be modeled as montmorillonite (Hunt et al., 1973; Aronson and Emslie, 1975) or a combination of basalts and montmorillonite (Toon et al., 1977). More recent work has shown that palagonite, an amorphous weathering product of basaltic glass is a better match to the visible spectrum of the martian dust than crystalline phyllosilicates (Roush et al., 1993; Clancy et al., 1995) although it is not a good match to the TIR spectrum (Hamilton and Morris, 2003). From analysis of Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data, Hamilton et al. (2005) conclude that phyllosilicates are not a likely component of the martian dust.

There has also been some debate on the existence of phyllosilicates in the dark, less-dusty regions of Mars, as measured by TES. Initial TES results showed that the dark regions of Mars could be divided into two main surface types—basalt (surface Type 1; ST1) and basaltic andesite (surface Type 2; ST2) (Bandfield et al., 2000)—and that although some phyllosilicates are often present in linear deconvolution models of TES spectra, their presence does not dominate any particular geographic region of Mars (Bandfield, 2002). Wyatt and McSween (2002) showed that although a basaltic andesite mineralogy was still the best numerical fit to the TES ST2 surface shape, replacing primary volcanic glass with secondary phyllosilicate minerals also yielded an acceptable model fit. Thus, ST2 could also be interpreted as an altered basalt. Michalski et al. (2005, 2006) thoroughly investigated the spectral and crystal chemical properties of several phyllosilicates and concluded that, based on TES data, there was no unambiguous evidence for their presence in martian low albedo regions, and that poorly crystalline aluminosilicates may be more likely (e.g., Rogers and Christensen, 2007). This is in agreement with a search for phyllosilicates in TES data that concluded they are unlikely to be distributed globally (Ruff, 2003).

2.2. Phyllosilicates in the Solar System and extrasolar disks

The literature regarding aqueous alteration, and specifically phyllosilicate mineralogy of chondritic meteorites is vast, and demonstrates that phyllosilicate minerals are important components of these meteorites and their parent bodies. Carbonaceous chondrites show evidence of aqueous alteration in the form of phyllosilicate mineralogy ranging from pervasive to trace. Detailed reviews are given by Zolensky and McSween (1988), Buseck and Hua (1993), Rubin (1997), and Brearley (2006). CI chondrites, the most hydrated of the carbonaceous chondrites, contain serpentine and saponite within their matrices (Tomeoka and Buseck, 1988; Buseck and Hua, 1993). The phyllosilicate alteration phases of CM chondrites, on the other hand, are composed mostly of various serpentines (Barber, 1981; Richardson, 1981; MacKinnon, 1982; Zolensky et al., 1993; Laurentia et al., 2000; Hanowski and Brearley, 2001; Zega and Buseck, 2003), although crosstedite is also observed, and accounts for much of the matrix (Tomeoka and Buseck, 1982, 1985; Buseck and Hua, 1993; Zega et al., 2003). CR chondrites tend to be less altered than CI or CM chondrites, although there are some exceptions. The phyllosilicates that are present—primarily Al-rich chlorite, and Mg-poor saponite and serpentine—are finer grained than is generally seen in other meteorites (Weisberg and Prinz, 1991; Weisberg et al., 1993; Buseck and Hua, 1993; Abreu and Brearley, 2005).

In general, aqueous alteration has affected the CO and CV chondrites to a limited extent. There are, however, some exceptions. Tomeoka and Buseck (1990) found that the Mokia CV carbonaceous chondrite contains Fe-rich saponite, Na-rich phlogopite, and serpentine. This particular phyllosilicate assemblage differs considerably from phyllosilicates found in CI and CM chondrites, suggesting aqueous alteration of the parent bodies under differing conditions (Tomeoka and Buseck, 1990). The presence of fine-grained serpentine and chlorites has been reported in several CO chondrites (Ikeda, 1983; Keller and Buseck, 1990; Brearley, 1993; Itoh and Tomeoka, 2001). Finally, some unequilibrated ordinary chondrites also show evidence for aqueous alteration in the form of phyllosilicates (Hutchinson et al., 1987, 1998; Alexander et al., 1989; Grossman et al., 2000, 2002).

The extensive evidence for aqueous alteration in the carbonaceous chondrites has fueled efforts to identify alteration products in interplanetary dust particles (IDPs) and several types of asteroids to which they might be related. Most spectroscopic studies of asteroids have utilized the ultraviolet/visible (UVVIS) and VNIR portion of the spectrum. Numerous studies have indicated the presence of phyllosilicates on both main belt and outer belt asteroids (Lebofsky, 1978, 1980; Lebofsky et al., 1990; Vilas and Gaffey, 1989; King et al., 1992; Vilas et al., 1993; Vilas, 1994). Fewer studies have focused on the TIR to study asteroids, although that may change with acquisition of more data from the Spitzer Space Telescope, which launched in 2003. Recent Spitzer Infrared Spectrograph (IRS) observations of the Deep Impact encounter with Comet 9P/Temple 1 indicated the presence of nontronite (Lisse et al., 2006, 2007). In addition, Spitzer IRS observations of Trojan asteroids in the TIR have indicated that they are composed of fine-grained silicates (Emery et al., 2006). The best spectral matches for these asteroids are the CO3 chondrites, which contain some phyllosilicates. At smaller scales, Reach et al. (2003) find that a significant component of a hydrated silicate (likely montmorillonite) is needed to fit the TIR (5–16 µm) spectral shape of the dust particles composing the zodiacal light observed by the ISO-CAM instrument on the Infrared Space Observatory. This indicates that the parent bodies of the zodiacal light particles likely formed in the inner Solar System, where temperatures and pressures were high.

The zodiacal light is analogous to exozodiacal light which is responsible for most of the observed emission from other planetary systems and debris disks. Perhaps the most-studied disk is that surrounding the star β Pictoris. There have been numerous observations of β Pic in the infrared spectral region (Telesco et al., 1988; Chini et al., 1991; Telesco and Knacke, 1991; Aitken et al., 1993; Knacke et al., 1993; Lagage and Pantin, 2000).
are shown in Table 1. The minerals include aluminous, magnesium, and ferruginous phyllosilicates from the dioctahedral smectite, trioctahedral smectite, illite, kaolinite, and serpentine mineral groups. Seven of the 10 minerals used for this study are Clay Minerals Society source or special clays. These samples—nontronite, montmorillonite, beidellite, hectorite, kaolinite, illite, and illite–smectite mixed layer in a 60/40 ratio—as well as samples of saponite, halloysite, and serpentine from other sources were loaned to us by J. Michalski. Samples were originally prepared for studies by Michalski et al. (2005, 2006). The samples were placed in distilled water and centrifuged, and suspended fraction was then iteratively decanted and centrifuged again until the desired size fraction was attained. The final sample was then allowed to dry in air before analysis. X-ray characterizations of air-dried and ethylene glycol-treated samples were performed on oriented powder slide mounts according to the method of Moore and Reynolds (1997) which allowed Michalski et al. (2005, 2006) to identify both expandable and non-expandable layers. The major element chemistry of the Clay Mineral Society source clays (kaolinite, hectorite, and montmorillonite) was determined by Mermut and Cano (2001). The saponite, beidellite, nontronite, and serpentine samples were characterized by Eberl et al. (1982), Post et al. (1997), Keeling et al. (2000), and Piatak (1997), respectively. The structural formulae for illite–smectite, and halloysite are given by Michalski et al. (2006), and are shown here in Table 1. Each of these samples, except for the serpentine, which was also ground to a fine powder, are <2.0 or <0.2 µm size fractions that were pressed into pure pellets with mirror-like surfaces.

3. Methods

3.1. Sample descriptions

Details of the phyllosilicate minerals studied in this work are shown in Table 1. The minerals include aluminous, magnesium, and ferruginous phyllosilicates from the dioctahedral smectite, trioctahedral smectite, illite, kaolinite, and serpentine mineral groups. Seven of the 10 minerals used for this study are Clay Minerals Society source or special clays. These samples—nontronite, montmorillonite, beidellite, hectorite, kaolinite, illite, and illite–smectite mixed layer in a 60/40 ratio—as well as samples of saponite, halloysite, and serpentine from other sources were loaned to us by J. Michalski. Samples were originally prepared for studies by Michalski et al. (2005, 2006). The samples were placed in distilled water and centrifuged, and suspended fraction was then iteratively decanted and centrifuged again until the desired size fraction was attained. The final sample was then allowed to dry in air before analysis. X-ray characterizations of air-dried and ethylene glycol-treated samples were performed on oriented powder slide mounts according to the method of Moore and Reynolds (1997) which allowed Michalski et al. (2005, 2006) to identify both expandable and non-expandable layers. The major element chemistry of the Clay Mineral Society source clays (kaolinite, hectorite, and montmorillonite) was determined by Mermut and Cano (2001). The saponite, beidellite, nontronite, and serpentine samples were characterized by Eberl et al. (1982), Post et al. (1997), Keeling et al. (2000), and Piatak (1997), respectively. The structural formulae for illite–smectite, and halloysite are given by Michalski et al. (2006), and are shown here in Table 1. Each of these samples, except for the serpentine, which was also ground to a fine powder, are <2.0 or <0.2 µm size fractions that were pressed into pure pellets with mirror-like surfaces.

3.2. Collection and processing of spectra

Mid-infrared (100–2000 cm\(^{-1}\); 5–100 µm) reflectance spectra were acquired at 2 cm\(^{-1}\) spectral sampling on Caltech’s Nicolet Magna 860 Fourier Transform Infrared (FTIR) spectrometer equipped with a Perkin–Elmer micro-Fresnel reflection accessory with incidence and reflection angles of 20°. A schematic diagram of the reflectance accessory is shown in Fig. 1. An aluminum-coated front surface mirror was used as the reflectance standard and was assumed to have a reflectance of one. Samples were placed in a sample chamber purged of

![Fig. 1. Schematic diagram of the Perkin–Elmer reflectance accessory used for this study. Incidence and reflection angles are 20°.](image)

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample</th>
<th>Structural formula</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMS SWy-1</td>
<td></td>
<td>((0.21Al_{1.51}Mg_{0.27}Ti_{0.01})/(Al_{0.01}Si_{3.99})O_{10}(OH)_2)</td>
<td>Chester County, PA, USA</td>
</tr>
<tr>
<td>CMS SBld-1</td>
<td></td>
<td>((0.01Al_{1.70}Mg_{0.08}Ti_{0.05})/(Al_{0.23}Si_{3.77})O_{10}(OH)_2)</td>
<td>Idaho, USA</td>
</tr>
<tr>
<td>CMS NAd-1</td>
<td></td>
<td>((0.15Fe_{1.82}Mg_{0.02})/(Al_{0.51}Si_{3.49})O_{10}(OH)_2)</td>
<td>Uley Mine, South Australia</td>
</tr>
<tr>
<td>CMS SHCa-1</td>
<td></td>
<td>((0.70Mg_{2.30})/(Fe_{0.03}Al_{0.09}Si_{3.80})O_{10}(OH)_2)</td>
<td>San Bernardino County, CA, USA</td>
</tr>
<tr>
<td>D. SpNv-1</td>
<td></td>
<td>((0.05Mg_{0.72}Fe_{0.05}Si_{3.54})/(Al_{0.04}Si_{3.96})O_{10}(OH)_2)</td>
<td>Southern Nevada, USA</td>
</tr>
<tr>
<td>CMS IMt-1</td>
<td></td>
<td>((0.04Si_{0.04}K_{0.87})/(Al_{1.45}Fe_{3.03}Si_{3.87})O_{10}(OH)_2)</td>
<td>Silver Hill, MT, USA</td>
</tr>
<tr>
<td>CMS ISMt-1</td>
<td></td>
<td>((0.03Si_{0.04}K_{0.42})/(Al_{1.68}Fe_{3.03}Si_{3.87})O_{10}(OH)_2)</td>
<td>Mancos Shale, USA</td>
</tr>
<tr>
<td>CMS KGa-1a</td>
<td></td>
<td>((0.04Mg_{0.72}Fe_{0.05}Si_{3.54})/(Al_{0.04}Si_{3.96})O_{10}(OH)_2)</td>
<td>Washington County, GA, USA</td>
</tr>
<tr>
<td>Ward’s HWw-1</td>
<td></td>
<td>((0.00Si_{0.04}Fe_{0.05})/(Al_{1.95}Fe_{3.03}Si_{3.87})O_{10}(OH)_2)</td>
<td>Bedford, IN, USA</td>
</tr>
<tr>
<td>Burminco BUR-1690</td>
<td></td>
<td>((0.27Mg_{0.72}Fe_{0.05}Si_{3.87})/(Al_{0.04}Si_{3.96})O_{10}(OH)_2)</td>
<td>Mariposa County, CA, USA</td>
</tr>
</tbody>
</table>
CO₂ gas and H₂O vapor and spectra from two separate spectral regions were acquired for each sample. The viewing geometries for each set of spectra were identical. Mid-IR spectra were acquired from 400–4000 cm⁻¹ using a KBr beamsplitter and an uncooled deuterated triglycine sulfate (DTGS) pyroelectric detector with a KBr window. A total of 512 scans were averaged to produce each spectrum. Roush et al. (1991) point out that the assumption of single reflections from pellet surfaces is likely not accurate at shorter wavelengths. For this reason, spectra are analyzed only out to 2000 cm⁻¹. Far-IR spectra were acquired from 100–600 cm⁻¹ for each sample using a Nicolet Solid Substrate beamsplitter and an uncooled DTGS detector with a polyethylene window. Due to the lower signal to noise ratio (SNR) at long wavelengths, we averaged 1024 scans to produce each far-IR spectrum. Mid and Far-IR spectra of each sample were joined together near 500 cm⁻¹ for each set of spectra were identical. Mid-IR spectra were acquired from 400–4000 cm⁻¹ and up to 3000 cm⁻¹ for each set of spectra. Roush et al. (1991) note that the measured spectra were uncorrected for the KBr window. A total of 512 scans were averaged to produce each far-IR spectrum. Mid and Far-IR spectra of each sample had mid and far-IR spectra with slightly different spectral contrasts, perhaps due to measurement of different parts of the pellet. Differences in spectral contrast were commonly lower than 1% reflectance and never higher than 3%. In these cases, the far-IR spectrum was multiplicatively scaled to exhibit the same spectral contrast as the mid-IR spectrum.

3.3. Modeling of optical constants

To model the optical constants of the phyllosilicate minerals selected for this study, we make use of dispersion theory in combination with a Fresnel reflectance model using a non-linear least squares optimization routine. Mineral spectra are iteratively fit with a modeled spectrum produced using dispersion and Fresnel equations. When the best fit is achieved, the optical constants are determined.

Dispersion theory is a mathematical formulation that represents the vibration of a crystal lattice as the sum of the vibrations of two or more harmonic oscillators. Each vibrational mode in a mineral creates a moving dipole moment, which in turn produces the radiation that is measured in an infrared spectrum. Each model oscillator is defined by three parameters: ν, 4πρj, and γj, which represent the center frequency of the oscillation, the band strength, and damping coefficient, respectively. An additional term, ε0, is the high frequency dielectric constant, which is a bulk mineral property rather than an oscillator-dependent property and should be equal to n² measured in the visible part of the spectrum (Roush et al., 1991). Dispersion equations vary slightly in the literature (e.g., Spitzer and Kleinman, 1961; Onari et al., 1977; Roush et al., 1991; Esposito et al., 2000), but we adopt the formulation of Spitzer and Kleinman (1961), which is expressed in wavenumber space rather than wavelength space.

In the Spitzer and Kleinman (1961) formulation of the dispersion equations, n and k are related to the dispersion parameters via the following equations:

\[ n^2 - k^2 = \varepsilon_0 + \sum_j \frac{4\pi\rho_j\gamma_j^2}{(v_j^2 - v^2)^2 + (\gamma_j^2 v_j^2 v^2)} \]  \hspace{1cm} (1)

where \( n \) is the real index of refraction, \( k \) is the imaginary index of refraction, and \( j \) represents the \( j \)th oscillator. The input parameters (\( v_j, 4\pi\rho_j, \gamma_j, \) and \( \varepsilon_0 \)) are iteratively adjusted to solve for values of \( n \) and \( k \) which, when used as inputs into the Fresnel equations for non-normal incidence, produce a modeled spectrum that has the lowest RMS error compared to the measured spectrum. The total reflectance for non-normal incidence is described as follows:

\[ R_T = \frac{R_\parallel^2 + R_\perp^2}{2} \]  \hspace{1cm} (3)

where

\[ R_\parallel^2 = \frac{(\cos \theta - u)^2 + v^2}{(\cos \theta + u)^2 + v^2} \]  \hspace{1cm} (4)

\[ R_\perp^2 = \frac{[(n^2 - k^2)\cos \theta - u]^2 + (2nk\cos \theta - v)^2}{[(n^2 - k^2)\cos \theta + u]^2 + (2nk\cos \theta + v)^2} \]  \hspace{1cm} (5)

\[ u = \frac{(n^2 - k^2 - \sin^2 \theta) + [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2k^2]^1/2}{2} \]  \hspace{1cm} (6)

\[ v = \frac{-(n^2 - k^2 - \sin^2 \theta) + [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2k^2]^1/2}{2} \]  \hspace{1cm} (7)

and \( \theta \) is the angle of incident radiation measured from the surface normal (20° for our spectrometer setup). \( R_\parallel \) and \( R_\perp \) (vector components perpendicular and parallel to the plane of incidence) are amplitudes, and must be squared to get the fractional intensities, which are the measured parameters.

Non-linear least squares optimization is used to solve for the best-fitting dispersion parameters. Reasonable guesses for the dispersion parameters are entered as inputs, and the routine returns optimized parameters. Following the method of Roush et al. (1991), we first placed oscillators at positions of major restrahlen bands and then added additional oscillators as necessary to improve the quality of the fit. Our model treats each point in the measured spectrum equally. Although the major vibrational bands occur in the 100–1200 cm⁻¹ region, the 1200–2000 cm⁻¹ region is critical for correctly determining the value of \( \varepsilon_0 \).

Roush et al. (1991) estimated the errors for their optical constants by providing several values of \( \varepsilon_0 \) for each set of dispersion parameters and observing the resultant change in the optical constants. For our purposes, we let \( \varepsilon_0 \) vary with the other dispersion parameters until an optimized solution is achieved.

A successful dispersion analysis meets the following requirements: (1) the measured and modeled spectra agree within reasonable estimates of the experimental error, (2) the number of oscillators used in the analysis is the minimum that the data require, (3) the dispersion parameters are uniquely determined by fitting the modeled spectrum to the measured, and (4) all of the dispersion parameters have positive values (Spitzer and Kleinman, 1961; Roush et al., 1991).
Optical constants of phyllosilicates

4. Results

4.1. Estimates of measurement error

To assess the error associated with our laboratory reflectance measurements, we measured one sample (saponite SpNv-1) 20 times over 4 days. Each measurement was made after acquisition of a separate background spectrum. The average spectrum and associated 1σ errors are shown in Fig. 2. Errors are greatest at ~1050 cm⁻¹ and at wavenumbers <300 cm⁻¹. The maximum error is 0.0097 in reflectance at 1030 cm⁻¹, which corresponds to about 3% of the maximum spectral contrast of the spectrum. Over much of the spectrum, the error is ≪1%. These results show that there is great reproducibility of sample spectra with our spectrometer setup and lend confidence to the quality of the measured spectra as well as the accuracy of the derived optical constants.

4.2. Comparison of emissivity and reflectance spectra

We have acquired reflectance spectra of 10 pressed pellet phyllosilicate samples. Comparison of these reflectance spectra to emissivity spectra acquired by Michalski et al. (2005, 2006) of similar pressed pellets shows them to be generally consistent, although some differences are evident (Fig. 3). For purposes of direct comparison, the reflectance spectra were inverted and multiplicatively scaled to have similar spectral contrast to the emissivity spectra. Optical constants described in Section 4.3 were derived from the unscaled laboratory reflectance spectra. Assuming specular reflection, reflectance spectra can be converted to emissivity spectra via Kirchhoff’s law ε = 1 − R − T, where ε is emissivity, R is reflectance, and T is the transmittance. For a thick sample, the transmittance is zero, so the emissivity is 1 − R. Laboratory transmission measurements of several clay pellets confirm the assumption that the transmittance is ~0% over the wavelength range measured. The emissivity spectra were acquired by Michalski et al. (2005, 2006) from 300–1400 cm⁻¹, while reflectance spectra acquired at Caltech span 100–2000 cm⁻¹. While reflectance and emission spectra of all samples show the same major restrahlen bands indicative of Si–O stretching modes (700–1200 cm⁻¹) Si–O bending modes (150–600 cm⁻¹), and O–H bending modes (600–950 cm⁻¹) (Farmer, 1974), some differences between the spectra are immediately apparent. Reflectance and emissivity spectra of beidellite and kaolinite display different relative intensities between the Si–O stretching vibrations at and the Si–O bending modes (Figs. 3b, 3i). Reflectance and emissivity spectra of montmorillonite, hectorite, illite, illite-smectite, and kaolinite have different intensities in the OH-bending region from 600–950 cm⁻¹. Differences may be due to slightly different pellet preparation techniques or slight changes in the water content of the minerals over time. Despite the differences, the overall agreement between the reflectance and emissivity spectra is good and the optical constants derived from these spectra would be similar.

4.3. Optical constants of phyllosilicates

Here we show the measured and modeled spectra for each of the minerals discussed, along with the values of n and k derived from dispersion analysis. All measured and modeled spectra as well as derived values of n and k can be accessed at http://www.ms.cc.sunysb.edu/~tglotch/optical_constants.htm or by contacting the author.

4.3.1. Dioctahedral smectites

The measured and modeled spectra, along with the derived values of n and k for the dioctahedral smectites montmorillonite, beidellite, and nontronite are shown in Figs. 4, 5, and 6. The dispersion parameters used to model n and k are given in Table 2.
4.3.2. Trioctahedral smectites

The measured and modeled spectra, along with the derived values of $n$ and $k$ for the trioctahedral smectites hectorite and saponite are shown in Figs. 7 and 8. The dispersion parameters used to model $n$ and $k$ for these minerals are given in Table 3.

4.3.3. Illite group

The spectra, along with the derived values of $n$ and $k$ for the illite group minerals illite and illite–smectite are shown in Figs. 9 and 10. The dispersion parameters used to model $n$ and $k$ for these minerals are given in Table 4.

4.3.4. Kaolinite group

The spectra, along with the derived values of $n$ and $k$ for the kaolinite group minerals kaolinite and halloysite are shown in Figs. 11 and 12. The dispersion parameters used to model $n$ and $k$ for these minerals are given in Table 5.

4.3.5. Serpentinite group

The measured and modeled spectra and the derived values of $n$ and $k$ for serpentine are shown in Fig. 13. The dispersion parameters used to model $n$ and $k$ for serpentine are given in Table 6.

5. Discussion

5.1. Comparison to previous studies

Four of the samples for which we have modeled optical constants have been modeled previously in the literature at similar
Fig. 4. Reflectance spectrum and optical constants for montmorillonite SWy-1 from 100–2000 cm$^{-1}$. (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

Fig. 5. Reflectance spectrum and optical constants for beidellite SBId-1 from 100–2000 cm$^{-1}$. (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.
wavelengths, although our work extends further into the far-IR than most previous studies. The following sections detail the similarities and differences between our work and that of previous authors for the minerals montmorillonite, serpentine, saponite, and kaolinite.

5.1.1. Montmorillonite

Fig. 14 shows the optical constants of montmorillonite, serpentine, saponite, and kaolinite derived in this work compared to optical constants derived for these minerals in previous studies. The optical constants of montmorillonite have been previously determined by several authors (Toon et al., 1977; Koike and Shibai, 1990; Roush et al., 1991; Esposito et al., 2000). Koike and Shibai (1990) measured the extinction coefficients for montmorillonite and serpentine from 7–400 cm\(^{-1}\), and then modeled the optical constants assuming spherical particle shapes, which is likely to lead to errors in the reported values, as phyllosilicates have platy crystal habits. For this reason, we do not consider their work here. Toon et al. (1977) determined the optical constants of two montmorillonite samples from 250–2000 cm\(^{-1}\). In Figs. 14a and 14b, we show the optical constants determined for their sample 219b, which is most chemically similar to the Clay Mineral Society sample SWy-1 used in this work. Roush et al. (1991) determined the optical constants of montmorillonite from 400–2000 cm\(^{-1}\) at 4 cm\(^{-1}\) spectral sampling, and Esposito et al. determined the optical constants of a similar sample from 400–2500 cm\(^{-1}\) at 2 cm\(^{-1}\) spectral sampling. As can be seen in Figs. 14a and 14b, the optical constants of montmorillonite determined in this work and by other authors (Toon et al., 1977; Roush et al., 1991; Esposito et al., 2000) are in good agreement.

Although there is good agreement between the optical constants for montmorillonite derived in this and other work, there is some difference in the dispersion parameters used to model the optical constants. Roush et al. (1991) use 15 oscillators, and an \(\varepsilon_0\) value of 1.4050 to model the optical constants, while Esposito et al. (2000) use only 13 oscillators and an \(\varepsilon_0\) value of 1.928. In this work, we use a total of 30 oscillators, and an \(\varepsilon_0\) value of 2.2933 to model the optical constants of montmorillonite. In order to conduct a successful dispersion analysis, one must minimize the number of oscillators used to correctly describe the data. Thus, the use of more oscillators by our model is not in and of itself an improvement. Our data extend to 100 cm\(^{-1}\), as opposed to 400 cm\(^{-1}\) for the Roush et al. (1991) data and Esposito et al. (2000). We used 9 oscillators to model the optical constants from 100–400 cm\(^{-1}\), which was outside of the spectral range modeled by the other authors. Our data are also low noise (Fig. 2) due to long scan times, which allowed us to model weak bands, and weak features on the shoulders of strong bands that were not previously modeled. Finally, our non-linear least squares optimization model significantly reduced the time required to model many oscillators as compared to previous iterative approaches. This increases the feasibility of using additional oscillators to more accurately describe the data.

Fig. 15 shows the %RMS reflectance error between the measured and modeled spectra as a function of the number of oscillators used in model. Unsurprisingly, the error decreases with the number of oscillators used, and starts to flattens out (but is
still decreasing) as the final number of oscillators used is approached. We make use of the derived RMS error as well as qualitative evaluation of the measured and modeled spectra to determine the optimal number of oscillators.

### 5.1.2. Serpentine

Figs. 14c and 14d show the optical constants of serpentine determined in this work, and by Mooney and Knacke (1985) and Roush et al. (1991). There is good agreement between the optical constants derived in this work and by Roush et al. (1991), while the values determined by Mooney and Knacke (1985) are less consistent. This may be due to one or more of several factors. The optical constants derived from both this work and that of Roush et al. (1991) were determined from spectra of pressed pellets of serpentine fines. The optical constants derived by Mooney and Knacke (1985) were determined from spectra acquired of a polished serpentine-rich rock which contained 94% serpentine flakes in addition to 5% fine-grained magnetite and 1% dolomite. The presence of some magnetite in the sample of Mooney and Knacke (1985) could account for some of the observed difference in the 400–200 cm$^{-1}$ spectral region, where iron oxides have fundamental Fe–O stretching vibrations. Mooney and Knacke (1985) did not publish the dispersion parameters that they used for their work, but Roush et al. (1991) used 10 oscillators and an $\varepsilon_0$ value of 1.4000 to model the serpentine optical constants. For this work, we used 29 oscillators and an $\varepsilon_0$ value of 2.0581. Once again, 9 oscillators were used to model the optical constants from 100–400 cm$^{-1}$, a spectral range which was not modeled by Roush et al. (1991). Difficulty in modeling the structure of the large band centered at $\sim$1000 cm$^{-1}$ prompted us to use several oscillators to achieve a desirable fit.

### 5.1.3. Saponite

Roush et al. (1991) modeled the optical constants of saponite using 8 oscillators and an $\varepsilon_0$ value of 1.3134. We expanded the model of saponite optical constants using 27 oscillators and an $\varepsilon_0$ value of 1.8403. A comparison of the derived optical constants of saponite is shown in Figs. 14e and 14f, and some immediate differences are apparent. Roush et al. (1991) model only one hydration feature at 1620 cm$^{-1}$. Our saponite spectrum (Fig. 6) shows two distinct features at 1440 and
Fig. 7. Reflectance spectrum and optical constants for hectorite SHCa-1 from 100–2000 cm\(^{-1}\). (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

Fig. 8. Reflectance spectrum and optical constants for saponite SpNv-1 from 100–2000 cm\(^{-1}\). (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

1610 cm\(^{-1}\). The 1440 cm\(^{-1}\) feature is unlikely to be due to hydration, but there is another possibility. Ammonium (NH\(_4\)) is a common substitution ion in several types of minerals, including sulfates (Chourabi and Fripiat, 1981) and smectite clays (Altaner et al., 1988). Ammonium substitution could account for the presence of the 1440 cm\(^{-1}\) seen in the saponite spec-
trum. This additional oscillator in the high wavenumber region of the spectrum has the effect of raising the value of $k$ (Fig. 14f) compared to that determined by Roush et al. (1991).

5.1.4. Kaolinite

The kaolinite optical constants derived in this work are compared to those previously derived by Roush et al. (1991) in Figs. 14g and 14h. The comparison between the two is quite good, although as in previous cases, we require more oscillators (to model subtle features) and a higher value of $\varepsilon_0$ to model the spectrum. Roush et al. (1991) use 15 oscillators and an $\varepsilon_0$ value of 1.4400 to model the optical constants of kaolinite, while we find that 32 oscillators and an $\varepsilon_0$ value of 2.2221 are required to achieve the best model fit.

5.1.5. Discrepancies in the value of $\varepsilon_0$

The modeled values of $\varepsilon_0$ should be equal to the square of the visible index of refraction (Roush et al., 1991). Although our derived values of $\varepsilon_0$ are closer to the measured $n_{\text{vis}}^2$ than those derived by previous work (Mooney and Knacke, 1985; Roush et al., 1991; Esposito et al., 2000), for all samples except montmorillonite and hectorite, they generally fall below the values calculated from measured $n_{\text{vis}}$. As briefly discussed by Roush et al. (1991), this is consistent with a decreasing value of $n$ throughout the VNIR portion of the spectrum, past 2000 cm$^{-1}$ until $n$ approaches the initial dispersion region near 1200–1300 cm$^{-1}$. It is possible that our derived values of $\varepsilon_0$ are larger than those from previous work because we cover a larger portion of the infrared spectrum.

5.2. Implications for TIR remote sensing of phyllosilicates

As shown in Section 4.2, the reflectance spectra from which these optical constants are derived are consistent with emissivity spectra previously acquired by Michalski et al. (2005, 2006) over the wavelength range for which they overlap. Therefore, the optical constants derived here will be applicable to studies which make use of emissivity spectra of Mars, asteroids, other airless bodies, interplanetary and interstellar dust, and protoplanetary disks.

The role of volume scattering and its affect on the TIR spectra of fine particulates has been discussed extensively (Lyon, 1964; Hunt and Vincent, 1968; Vincent and Hunt, 1968; Arison and Emslie, 1973; Salisbury and Eastes, 1985; Salisbury and Wald, 1992; Wald and Salisbury, 1995) and optical constants are a critical component of any radiative transfer model that attempts to correctly model the scattering of small particulates in emissivity or reflectance spectra (e.g., Hapke, 1981, 1984, 1986, 1993a, 1993b, 1996a, 1996b; Moersch and Chris-
Much of the surface of Mars is covered by a finely particulate dust that has an estimated grain size of \(<10\ \mu m\) (Bandfield and Smith, 2003) or even \(<5\ \mu m\) (Pollack et al., 1979). In addition, spectra of the surfaces of the Moon and asteroids are dominated by fine-grained components (e.g., Pieters et al., 1993;
Fig. 11. Reflectance spectrum and optical constants for kaolinite KGa-1 from 100–2000 cm$^{-1}$. (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

Fig. 12. Reflectance spectrum and optical constants for halloysite HWw-1 from 100–2000 cm$^{-1}$. (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

Emery et al., 2006). Although phyllosilicates are not expected to form on the Moon, some evidence for their presence near the south polar region has been presented (Vilas et al., 1998). More robust detections have been made of phyllosilicates occurring on asteroids (Lebofsky, 1978, 1980; Lebofsky et al., 1990; Vilas and Gaffey, 1989; King et al., 1992; Vilas et al., 1993,
6. Conclusions

We have acquired mid-infrared (100–2000 cm$^{-1}$) reflectance spectra of 10 phyllosilicate samples, including montmorillonite, beidellite, nontronite, hectorite, saponite, illite, an illite-smectite interlayered clay consisting of 60% illite and 40% smectite, kaolinite, halloysite, and serpentine. From these spectra, we have determined the real and imaginary indices of refraction using classical Lorentz–Lorenz dispersion theory. The derived optical constants of montmorillonite, serpentine, saponite, and kaolinite compare favorably with the optical constants previously derived by other authors for these minerals (e.g., Toon et al., 1977; Mooney and Knacke, 1985; Roush et al., 1991; Esposito et al., 2000) over the regions in which they overlap. The high spectral resolution (2 cm$^{-1}$ sampling) of our data has allowed us to identify weak bands in the spectra that have not previously been modeled, and the increased spectral range has allowed us to generate robust optical constants of these clay minerals in the far infrared (400–100 cm$^{-1}$)—a region for which the optical constants of minerals have not commonly been determined. The optical constants for the clay minerals described here may aid in future work such as determining the mineralogy of interplanetary and interstellar dust, the fine-grained surfaces of airless bodies, protoplanetary disks surrounding young nearby stars, and the search for phyllosilicate minerals on Mars using the mid-IR portion of the spectrum.
Fig. 13. Reflectance spectrum and optical constants for serpentine BUR-1690 from 100–2000 cm$^{-1}$. (a) Measured and modeled reflectance spectrum. (b) Real index of refraction. (c) Imaginary index of refraction.

Fig. 14. Comparison of optical constants derived in this study to those derived in other studies. (a) The real index of refraction of montmorillonite derived in this study and by Roush et al. (1991), Esposito et al. (2000), and Toon et al. (1977). (b) The imaginary index of refraction of montmorillonite derived in this study and by Roush et al. (1991), Esposito et al. (2000), and Toon et al. (1977). (c) The real index of refraction of serpentine derived in this study and by Roush et al. (1991) and Mooney and Knacke (1985). (d) The imaginary index of refraction of serpentine derived in this study and by Roush et al. (1991) and Mooney and Knacke (1985). (e) The real index of refraction of saponite derived in this study and by Roush et al. (1991). (f) The imaginary index of refraction of saponite derived in this study and by Roush et al. (1991). (g) The real index of refraction of kaolinite derived in this study and by Roush et al. (1991). (h) The imaginary index of refraction of kaolinite derived in this study and by Roush et al. (1991).
Fig. 15. Percent root mean square (%RMS) reflectance error between the modeled and measured spectra of montmorillonite SWy-1 as a function of the number of oscillators used in the model.

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References


Optical constants of phyllosilicates


