Estimating mineral abundances of clay and gypsum mixtures using radiative transfer models applied to visible-near infrared reflectance spectra

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**Abstract**

Quantitative mineral abundances of lab derived clay–gypsum mixtures were estimated using a revised Hapke VIS-NIR and Shkuratov radiative transfer model. Montmorillonite–gypsum mixtures were used to test the effectiveness of the model in distinguishing between subtle differences in minor absorption features that are diagnostic of mineralogy in the presence of strong H2O absorptions that are not always diagnostic of distinct phases or mineral abundance. The optical constants (k-values) for both endmembers were determined from bi-directional reflectance spectra measured in RELAB as well as on an ASD FieldSpec3 in a controlled laboratory setting. Multiple size fractions were measured in order to derive a single k-value from optimization of the optical path length in the radiative transfer models. It is shown that with careful experimental conditions, optical constants can be accurately determined from powdered samples using a field spectrometer, consistent with previous studies. Variability in the montmorillonite hydration level increased the uncertainties in the derived k-values, but estimated modal abundances for the mixtures were still within 5% of the measured values. Results suggest that the Hapke model works well in distinguishing between hydrated phases that have overlapping H2O absorptions and it is able to detect gypsum and montmorillonite in these simple mixtures where they are present at levels of ~10%. Care must be taken however to derive k-values from a sample with appropriate H2O content relative to the modeled spectra. These initial results are promising for the potential quantitative analysis of orbital remote sensing data of hydrated minerals, including more complex clay and sulfate assemblages such as mudstones examined by the Curiosity rover in Gale crater.

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1. Introduction

Numerous occurrences of a wide variety of hydrated minerals have been identified on the surface of Mars through a combination of orbiter, lander and rover observations. Hydrated sulfates and clay minerals are the two dominant classes of hydrated minerals, both being more common in ancient Noachian and Hesperian terrains than in younger Amazonian terrains (Poulet et al., 2005; Gendrin et al., 2005; Bibring et al., 2006; Murchie et al., 2009; Ehmann et al., 2011; Carter et al., 2013). These minerals and their host rocks may record global climatic conditions and aqueous processes during the first billion years of Mars’ history (Bibring et al., 2005; Chevrier et al., 2007; Murchie et al., 2009; Ehmann et al., 2011) as well as discrete, localized aqueous conditions during later times (e.g., Mangold et al., 2010). However, in order to relate mineralogical observations to potential environmental conditions it is important to identify the specific mineral species as well as their relative, and preferably absolute, abundances.

Initial orbital observations from NASA’s Mars Reconnaissance Orbiter CRISM and ESA’s Mars Express OMEGA visible-near infrared (VIS-NIR) imaging spectrometers suggested sulfates and clays were largely segregated both temporally and spatially (e.g., Bibring et al., 2006, Poulet et al., 2005). However, subsequent global surveys and detailed local studies suggest there are numerous locations where these minerals coexist (e.g., Wray et al., 2010; Milliken et al., 2010; Roach et al., 2010; Ehmann et al., 2011; Noe Dobrea et al., 2012; Carter et al., 2013), either in discrete geologic units or possibly mixed below the ~18 m/pixel spatial scale of CRISM. Sulfate and clay assemblages are commonplace in many terrestrial settings (e.g., Baldridge et al., 2009), and it is not unexpected that the same may be true of Mars, particularly for alluvial/fluvial and lacustrine environments or rocks that have been subject to diagenesis. Indeed, recent results from the Curiosity rover at Gale crater provide excellent examples of strata that host both clay
minerals and sulfates, where both are believed to have formed in situ (Grotzinger et al., 2014; Vaniman et al., 2014). CheMin X-ray diffraction measurements of rock powders drilled from the Sheepbed mudstone indicate as much as 22% smectite and 3.6% Ca-sulfate (bassanite and anhydrite) may be present (Vaniman et al., 2014). However, the mudstone is crosscut by numerous veins and nodules filled with Ca-sulfate (Grotzinger et al., 2014), thus sulfates are likely a much more volumetrically important component of the unit as a whole than indicated solely by the XRD results. Intriguingly, no hydrated minerals were observed in CRISM orbital data for this region, likely due to the thin dust cover on the outcrops, though spectral signatures of both clay and sulfate minerals are present in other lower Mt. Sharp strata in Gale crater (Milliken et al., 2010). In the Sheepbed mudstone, the clays have been interpreted to be authigenic and the crosscutting, sulfate-filled veins are indicative of a later diagenetic event. Therefore, knowledge of the relative abundance of these phases can be used to assess the relative contribution of these two distinct processes, and similar concepts may apply to other clay and sulfate-bearing assemblages on Mars.

Therefore, methods that allow for absolute or relative estimates of clay and sulfate abundance from VIS-NIR reflectance spectra can help to constrain the type and extent of processes that may be responsible for the co-occurrence of these minerals. Assessing how abundances of clay and sulfate vary within a stratigraphic sequence can also provide important insight into temporal changes in local water chemistry, water–rock interaction, and paleoclimate. However, uniquely identifying individual components in mixtures of hydrated minerals using VIS-NIR reflectance spectroscopy can be complicated by overlapping or non-unique absorption features as well as mixing between strong and weakly absorbing (spectrally ‘neutral’) components. Qualitative methods that rely solely on the positions and/or widths of individual absorptions may be prone to missing the presence of volumetrically subordinate (yet geologically important) components, oversimplification of mineral identifications, or misidentification of minerals.

Hydrated salts (e.g., hydrated sulfates and chlorides) are an excellent example of the difficulties associated with qualitative spectral analyses, as VIS-NIR reflectance spectra for some of these minerals lack unique diagnostic absorptions. Examples of ‘polyhydrated’ sulfates on Mars (e.g., Gendrin et al., 2005; Birbing et al., 2006; Murchie et al., 2009; Carter et al., 2013) could represent complex mixtures of various sulfates/hydrated phases (e.g., Cloutis et al., 2006) or they could represent a single sulfate phase for which weaker diagnostic absorptions are masked or muted.

Spectral ‘unmixing’ of VIS-NIR reflectance spectra using radiative transfer models (RTMs) can help to constrain the mineralogy of complex assemblages through the simultaneous fitting of reflectance values at many wavelengths. RTMs are also advantageous in that they can provide estimates of the abundance and particle size of each component in a mixture. However, as noted in previous studies (e.g., Sklute et al., 2015), widespread application of these models to spectra of planetary surfaces has been somewhat limited, primarily due to the lack of accurate optical constants (real, n, and imaginary, k, components of the complex index of refraction) for appropriate minerals, which are required inputs to the models. This is particularly true for clay and sulfate minerals, and though optical constants at VIS-NIR wavelengths have been reported for montmorillonite (Roush, 2005), gypsum (Roush et al., 2007), bloedite, epsomite, hexahydrate (Dalton and Pitman, 2012), and select Fe-sulfates (Pitman et al., 2014; Sklute et al., 2015), they are not readily available for many other hydrated minerals that are of importance to Mars (e.g., nontronite, saponite, chloride, bassanite, kieserite, etc.) or for phases with variable H2O content. In addition, the application of these optical constants in radiative transfer models for well-controlled mineral mixtures has been very limited, particularly for minerals relevant to sedimentary environments and compositions (e.g., clays, sulfates, and other hydrated phases).

Two commonly used models in remote sensing applications for planetary bodies are those of Hapke (2005) and Shkuratov et al. (1999), both of which are considered in this study. Previous laboratory studies have tested the Hapke RTM for igneous materials with applications to the Moon and asteroids (Mustard and Pieters, 1987, 1989; Li and Milliken, 2015). Of relevance to Mars, laboratory mixtures of nontronite and various igneous materials (Ehmann et al., 2011) were recently analyzed using both Hapke (2005) and Shkuratov et al. (1999) models, and Stack and Milliken (2015) also used the Hapke model for a suite of clay and Mg-sulfate (epsomite) mixtures. In addition, Poulet et al. (2009) applied the Shkuratov model directly to OMEGA spectra of clay-bearing regions on Mars. This study yielded promising results, but a detailed and well-controlled laboratory study of how the Hapke and Shkuratov models perform for clay and sulfate mixtures when starting with optical constants is currently lacking. Although optical constants for montmorillonite and gypsum are available in the literature and both phases have been observed on Mars, to our knowledge these optical constants have not yet been tested in RTMs for laboratory mixtures of clay and sulfate. This is of course a necessary first step in order to understand and quantify potential uncertainties in modal mineralogy derived from such models when applied to actual reflectance spectra of Mars.

In this study we assess the efficacy of the Hapke model in estimating modal mineralogy of montmorillonite–gypsum mixtures at VIS-NIR wavelengths. We examine the effectiveness of the model in distinguishing subtle differences in moderate or weak absorption features that are diagnostic of mineralogy when they are in the presence of stronger, non-unique H2O absorptions, as typify many CRISM spectra of Mars. In addition, we derive independent estimates of the optical constants for montmorillonite and gypsum using two different spectrometers and compare our results to previously published values. The effectiveness of the ASD FieldSpec3 spectroradiometer is evaluated as a tool for performing Hapke modeling and is directly compared to the birefringent reflectance spectrometer. We present estimates of modal mineralogy derived from the Hapke RTM for a suite of binary mixtures that encompass a range in gypsum-to-montmorillonite ratios and particle sizes, and as a final step we compare these results to those derived from an implementation of the Shkuratov model. Though sedimentary rocks on Mars are likely composed of more than two mineral phases it is important to begin validation of RTMs with simple, well-controlled cases where variables can be minimized and/or isolated. The results presented here for binary sulfate–clay mixtures can provide a foundation for future application of Hapke and Shkuratov models to more complex lab mixtures, and ultimately to reflectance spectra of sedimentary deposits on Mars.

2. Methods

2.1. Sample preparation

The gypsum used in this study was coarse and poorly sorted gypsum sand collected near White Sands, NM, and the montmorillonite was sample SAz-2 obtained from the Clay Minerals Society (CMS). Though the CMS offers several different montmorillonite samples, the SAz-2 variety was chosen for this work because the bulk material arrived as large pieces, which allowed us to easily grind, sieve, and control the particle size of this component.

The gypsum sand and montmorillonite chips were ground in an agate mortar and pestle, wet sieved with H2O to remove clinging fines, and dried in air to make two separate groups of particle size fractions (Table 1). Group 1 consisted of four particle size ranges (25–32 μm, 38–45 μm, 63–75 μm and 125–150 μm) and each
Table 1
Particle sizes used in Groups 1 and 2 along with their respective measurements and analyses. The bulk of the Hapke modeling was performed on Group 1 whereas Group 2 was used to establish an empirical relationship between measured and modeled ‘effective’ particle size.

<table>
<thead>
<tr>
<th>Particle size Range (μm)</th>
<th>Instrument</th>
<th>Analyses for Specific Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gypsum</td>
<td>Clay</td>
</tr>
<tr>
<td>25–32</td>
<td>BDR, ASD</td>
<td>BDR, ASD</td>
</tr>
<tr>
<td>38–45</td>
<td>BDR, ASD</td>
<td>BDR, ASD</td>
</tr>
<tr>
<td>63–75</td>
<td>BDR, ASD</td>
<td>BDR, ASD</td>
</tr>
<tr>
<td>125–150</td>
<td>BDR, ASD</td>
<td>BDR, ASD</td>
</tr>
<tr>
<td>&lt; 5</td>
<td>ASD</td>
<td>ASD</td>
</tr>
<tr>
<td>90–106</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>106–125</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>150–180</td>
<td>-</td>
<td>ASD</td>
</tr>
<tr>
<td>180–212</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>180–250</td>
<td>-</td>
<td>ASD</td>
</tr>
<tr>
<td>212–250</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>250–300</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>300–500</td>
<td>ASD</td>
<td>-</td>
</tr>
<tr>
<td>chip</td>
<td>-</td>
<td>ASD</td>
</tr>
</tbody>
</table>

Table 2
Comparison of measured and modeled ‘effective’ particle sizes for the different size fractions of gypsum and montmorillonite for both RELAB BDR and ASD spectra.

<table>
<thead>
<tr>
<th>Gypsum size fraction</th>
<th>From microscope</th>
<th>k optimization</th>
<th>Modeled results using average k (BDR)</th>
<th>Modeled results using average k (ASD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125–150 μm</td>
<td>145</td>
<td>138</td>
<td>135</td>
<td>n/a</td>
</tr>
<tr>
<td>63–75 μm</td>
<td>85</td>
<td>69</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>38–45 μm</td>
<td>46</td>
<td>44</td>
<td>37</td>
<td>46</td>
</tr>
<tr>
<td>25–32 μm</td>
<td>39</td>
<td>39</td>
<td>39</td>
<td>40</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>125–150 μm</td>
<td>140</td>
<td>50</td>
<td>55</td>
<td>n/a</td>
</tr>
<tr>
<td>63–75 μm</td>
<td>62</td>
<td>42</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>38–45 μm</td>
<td>38</td>
<td>33</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>25–32 μm</td>
<td>31</td>
<td>25</td>
<td>25</td>
<td>24</td>
</tr>
</tbody>
</table>

sample was analyzed with two different VIS-NIR spectrometers (see Section 2.2). Additional size fractions, Group 2 (Table 1), were generated for both gypsum (<5 μm, 90–106 μm, 106–125 μm, 180–212 μm, 212–250 μm, 250–300 μm, 300–500 μm) and montmorillonite (<5 μm, 150–180 μm, 180–250 μm, 250–300 μm, chip) and were analyzed with the ASD spectrometer. This second suite of particle sizes was created to further compare measured particle sizes with those estimated from the models for the pure mineral endmembers.

The gypsum and montmorillonite endmembers for each size fraction (Groups 1 and 2) were analyzed with an Olympus optical microscope in order to assess the actual average particle size for comparison with the assumed average particle size based on the sieve size range (Table 2). Analysis was performed at 100X magnification with a pixel width of 0.15 μm allowing for the reliable identification of particles as small as 3 μm. Individual particles were measured with image processing software where the average of the smallest and longest axes was taken as the average particle size. In all cases, a minimum of 500 particles were measured for the particle size determination.

Aliquots of the pure gypsum and montmorillonite were weighed using a microbalance and mixed together by stirring and shaking to produce binary mixtures with 0, 10, 25, 50, 75, 90, and 100 wt. % gypsum for each size fraction in Group 1. These mixtures were kept under ambient conditions in the lab and measured with both spectrometers using the same procedures as for the pure mineral endmembers.

2.2. Spectral measurements

Reflectance spectra for all mixtures were measured in the NASA Reflectance Experiment LABoratory (RELAB) at Brown University using a custom built bi-directional reflectance (BDR) spectrometer that utilizes a monochromator, various light sources, and a combination of UV-VIS-NIR detectors. Details of this instrument and basic measurement procedures can be found in Pieters (1983) and the RELAB user manual, available on the RELAB website (currently hosted at [http://www.planetary.brown.edu/relab]). All samples were measured using the standard RELAB on-axis viewing geometry of incidence angle (ι) = 30°, emergence angle (ε) = 0°, and phase angle (g) = 30° from 0.35 μm to 2.6 μm. Sample dishes were spun during measurement to average out potential effects due to particle orientation, and pressed Halon was used as the reflectance standard.

Four reflectance spectra of each sample were also acquired using an ASD FieldSpec3 portable spectroradiometer. Unlike the BDR measurements, samples were not spun during the ASD measurements. Repeat measurements of each sample thus allowed us to evaluate potential uncertainties associated with sample heterogeneity, packing, particle orientation, and scattering effects. A fiber
optic light source with a QTH bulb was used to illuminate the sample and both the illuminating and receiving fiber optic bundles have a field of view of ~25°, which is much larger than the < 6° emergence angle for the BDR instrument. The fibers were positioned such that the central angle of each matched the viewing geometry of the BDR measurements (i = 30°, e = 0°, g = 30°), over a wavelength range of 0.35–2.5 μm allowing for a more direct comparison between the two types of spectral measurements. All samples were optically thick and the typical spot size was on the order of 4–6 mm. A small Spectralon® disk from Labsphere was used as a reflectance standard.

2.3. Radiative transfer model

The implementation of the Hapke (2005) and Shkuratov et al. (1999) radiative transfer models used in this study were developed by Li and Li (2011) and Li and Milliken (2015) which provide a more detailed description of the models, their parameterization, and how they are solved using inverse methods. Briefly, RTMs are typically used to describe how light intensity changes as it enters, interacts with, and exits a specific medium. Hapke’s model has been used in a number of previous studies for modeling spectra of laboratory mixtures and planetary surfaces (e.g., Hapke, 1981, 2005; Li and Li, 2011; Lucey, 1998; Mustard, 1987; Poulet, 2004; Li and Milliken, 2015). While Hapke’s model is designed for intimate mixtures of particulates, the Shkuratov RTM treats particles as one-dimensional layers. The Shkuratov model is computationally faster, which is favorable for spectral un-mixing of large datasets or image cubes acquired by instruments such as CRISM and OMEGA, but it does not explicitly account for the viewing geometry dependence of reflectance that is present in such image cubes (Poulet et al., 2002). In contrast, although the Hapke model may yield better estimates of mineralogy in some cases (e.g., Li and Milliken, 2015), it is at the expense of increased computation time.

In Hapke’s model, the reflectance can be described as a function of single scattering albedo (ω(λ), where λ is wavelength), solar incidence angle (i), emittance angle (e), backscattering function (Rg, φ), where g is the phase angle and φ is the filling factor), phase function (P(φ)), and multiple scattering function (H, for both down-welling and up-welling radiance). Reflectance can thus be described as:

\[ R = \frac{\omega_{ave}}{4\pi} \frac{\mu_0}{\mu_0 + \mu} \left( 1 + B(g)P(g) + H(\mu_0, \omega_{ave})H(\mu, \omega_{ave}) \right) - 1 \]

where,

\[ \omega_{ave} = \sum_i \frac{M_i \omega_i}{D_i \rho_i} / \sum_i \frac{M_i}{D_i \rho_i} \]

in which \( \rho \) = solid density, \( M \) = bulk density, and \( D \) = particle diameter. The particle diameter may be related to the optical path length, <D> - as described below. The single scattering albedo of an individual component, \( \omega_i \), is a function of the optical constants \( n = k \) through external and internal scattering terms \( (S_e, S_i, \text{respectively}) \) and the internal transmission factor, \( \Theta \) (Hapke, 1993). In its simplest form, \( \Theta \) is approximated by Beer’s Law (\( \Theta = e^{-\alpha <D>} \)) and single scattering albedo is thus boiled down to a transmission problem.

Therefore, each reflectance spectrum can be converted to a single scattering albedo spectrum that is the weighted linear combination of individual endmember single scattering albedo spectra. The fundamental inputs to the model are typically the optical constants, \( n(\lambda) \) and \( k(\lambda) \), and the solid density of each endmember mineral. An estimate of porosity is also commonly included. The final outputs of the model are an estimate of the abundance and particle size for each endmember component. In this study we assume \( B(g) = 0 \) and we adopt a constant value for \( n \) for the BDR and ASD wavelength range. The real indices of refraction can vary over the wavelength range (0.8 μm–2.5 μm) used in this study, but we adopt constant values of \( n = 1.51 \) for gypsum and \( n = 1.52 \) for montmorillonite, which are averages based on estimates from Roush (2005) and Roush et al. (2007). This is in contrast to the wavelength-dependent Kramers–Kronig solutions for \( n \) used in other studies (Roush, 2005; Roush et al., 2007; Sklute et al., 2015), which find that \( n \) may vary by up to 0.03 (e.g., Roush et al., 2007). However, for this study we make the assumptions that such differences are negligible and adopt a constant value over the wavelength range of interest. As will be shown below, our use of a wavelength-independent \( n \) yields results extremely similar to those of Roush (2005) and Roush et al. (2007) for these particular minerals, though we stress that this simplification may not be appropriate for other minerals with much stronger variations in \( k \) (and thus \( n \)).

We note that our implementation of the Hapke model is largely similar to that of Roush et al. (2007) and Sklute et al. (2015), with the exception that we estimate the phase function by using fixed values for the Legendre polynomial coefficients \( b = -0.4 \) and \( c = 0.25 \), based on values for silicates from Mustard and Pieters (1989) and consistent with moderate forward scattering. As a test of the sensitivity to these values, we varied the \( b \) and \( c \) parameters by ±0.3 and found that it changed the single scattering albedo values by only 1% (relative) and ultimately had a negligible effect on the modeling results. Therefore, we conclude that an assumption of moderate forward scattering is appropriate for the clay and gypsum examined in this work.

In addition, we do not include the additional variable of the internal scattering coefficient, \( s \), in the internal transmission factor because appropriate values for this variable are poorly constrained for different minerals and may be system-dependent (e.g., Roush et al., 2007; Sklute et al., 2015). Omission of the internal scattering coefficient typically results in a lower single scattering albedo, however the particles in our study may be considered optically thin (i.e., \( k \ll 1, D = \sim 10^{-5} \) microns), therefore the internal scattering effects are likely minimal (Hapke, 1981) and we prefer to minimize the number of unknown parameters in our model. We note that the omission of the \( s \) parameter forces all observed spectral behavior to be accommodated in the imaginary part of the index of refraction, \( k \), when deriving the optical constants from the radiative transfer model. All modeling was performed over a wavelength range of 0.8–2.5 μm for both the ASD and BDR data. This wavelength range was selected because we were more interested in testing the ability to model the subtle differences in the hydration bands than the slopes in the visible range, where the latter may be affected by the presence of Fe-bearing impurities (e.g., Fe-oxides in the clay samples).

2.4. \( k \)-values for mineral endmembers

In this study we first use Hapke’s model to solve for the imaginary part of the index of refraction (\( k \)) by using the reflectance spectra, a starting value for particle size, estimated porosity (1–\( \phi \)), and viewing geometry for the pure minerals as the inputs. By measuring the reflectance spectra for a number of different particle sizes of a given endmember (either gypsum or montmorillonite) it is possible to solve the equation using an inverse, least-squares approach. A best fit is obtained when the differences between measured and modeled reflectance spectra are minimized (a tolerance of 10−6 was used for each wavelength in this study when solving for \( k \)), and the associated \( k \) values that satisfy this for a single spectrum (or for spectra of all different particle sizes simultaneously) are taken to be the best estimates for the imaginary part of the complex index of refraction. During the derivation of the \( k \) values, the particle size was allowed to vary within
the sieved size range and smaller (given that smaller particles may have broken off of the clay aggregates during sample handling). When solving for a single k value for the different particle sizes simultaneously, the code was run with a tolerance between measured and modeled reflectance values of $10^{-6}$ and up to 10,000 iterations, whichever criterion was met first. The maximum number of iterations was not reached during the inversion, indicating that the tolerance between measured and modeled reflectance spectra was reached. Because the k values derived from radiative transfer models of reflectance spectra represent some kind of average over the different crystallographic axes and thus may differ from those derived from transmission (absorbance) spectra, it is perhaps more proper to think of the RTM-derived k values as ‘effective’ or ‘apparent’ optical constants.

The effective optical constants for each endmember are then used as the input to the model, and the mineral abundance and particle size of each component in our gypsum-montmorillonite mixtures can be solved using a similar inverse, least-squares approach. Again, a tolerance of $10^{-6}$ was used (between measured and modeled reflectance spectra for each wavelength) and particle size was allowed to vary within or below the sieved size range when modeling each mixture spectrum. It is worth noting that the particle diameter, D, may be related to the mean optical path length, $<D>$, by $<D> = 0.9 D$ for spherical particles and $<D> \approx 0.2 D$ for irregular particles (Li and Li, 2011). These values are based on lab results and Monte Carlo simulations taken from Shkuratov and Gryko (2005). In their paper, Shkuratov and Gryko suggest that the particle diameter-path length relationship is dependent on a small imaginary index of refraction. While they test different values of r (which inherently means different k values) they do not give exact values for imaginary index of refraction. In our case, while there is a 2 order magnitude of difference in the imaginary index associated with the absorption features, the maximum k-value does not exceed 0.01 therefore, it can still be assumed ‘small’.

In addition to the irregular particle size assumption, the real component of the optical constant (n-value) is incorporated into the path-length therefore, when using this model, any optical constants derived using the spherical model should be scaled down by (4.5/n) to account for these differences. Because modeled values of k will be inherently linked to values of $<D>$ (and by extension, D), and n = 1.51 and 1.52 for gypsum and montmorillonite respectively it can be seen that k values may differ by a factor of 3 depending on whether an assumption of irregular or spherical particles is adopted. We estimate k-values under both assumptions but ultimately model the binary mixtures assuming that particles are irregular, in accordance with tabular and platy crystals (appropriate for gypsum and montmorillonite) and with findings in previous RTM studies for other minerals (Hiroi and Pieters, 1992; Li and Milliken, 2015). Therefore, it can be demonstrated that if the solid density for each endmember is known then the unknown parameters are effectively the optical path length, $<D>$, and bulk density, $M_b$, for each component, which can be solved for using a least-squares approach and then easily converted to particle size and mass (or volume) fraction, respectively.

Imaginary refractive indices for the gypsum and montmorillonite were estimated independently using both the BDR and ASD spectra. The k-values for Group 1 were determined by optimizing the particle size input to the model in order to obtain a single, consistent k-value for all four particle sizes while simultaneously solving for the effective particle size. A starting value for the particle size was chosen for each size fraction (e.g., mean of sieve range or mean determined from optical microscope measurements) and these values were simultaneously adjusted using a least-squares approach until a best-fit was achieved. The resultant output was a single k-value with a range of particle sizes for each particle size range. For gypsum, there was no range needed, and the min-max particle sizes to yield the same k-value were almost identical. The clay needed a wider tolerance to accomplish this, giving a min-max particle size range. The values given (Table 2) are the average (median) value for that particle range. Although such a solution is non-unique, the resulting ‘effective’ particle sizes, which allow the model to yield a consistent k value for a given mineral, can be compared to the sieve size range and the mean particle size determined from the optical microscope measurements.

As a separate experiment, the montmorillonite endmembers in the 63–75 μm and 25–32 μm size fractions were systematically dehydrated and measured with the ASD in order to observe the variation of k-values relative to the degree of hydration (amount of interlayer H2O). Water content in hydrated minerals can have a large effect on estimates of optical constants, and for minerals such as smectites the water content can be highly variable. Indeed, the optical constants for montmorillonite determined by Rouss (2005) were for samples measured in a purged environment that was then filled with nitrogen, thus the samples likely had decreased interlayer H2O. Aliquots of our montmorillonite sample were heated in an oven from 25 °C to 350 °C and immediately transferred to the ASD FieldSpec3 for analysis. The dehydrated sample was then stored in a desiccator with drierite for 72 h and measured again to assess any potential changes in hydration state and to evaluate these effects on modeled k-values.

As a final step in this study we compared the results from the Hapke RTM with those derived from the Shkuratov RTM. Our implementation of the latter follows the procedures described by Li and Milliken (2015), and we refer the reader to that publication for a more detailed description of the methodology. Importantly, when estimating mineral abundances and particle sizes using the Shkuratov model we rely on the effective optical constants that were also derived with that model; for consistency within the models we do not use Hapke-derived optical constants in the Shkuratov model and vice versa (Li and Milliken, 2015). Differences in the (effective) optical constants derived from the two RTMs are discussed below.

3. Results

3.1. Endmember particle sizes

The particle size distribution, mean particle size, and aspect ratio for both gypsum and montmorillonite, as determined from the optical microscope measurements, are shown in Fig. 1 for all particle size fractions in Group 1. It is observed that the mean particle sizes for gypsum are larger than the estimated values from the sieve sizes, presumably due to the tabular nature of the gypsum particles. The large aspect ratio can allow individual particles to pass through the sieve lengthwise, skewing the particle size distribution to larger values. In contrast, the mean particle sizes for the clays are smaller than the sieve size range. Individual clay crystals are significantly smaller, and the particles we observe represent aggregates of many individual montmorillonite crystals. Even though the montmorillonite was well sieved, rinsed and carefully handled, there still remained some fine grains in the powder. The optical microscope used for the particle size distribution allowed for particles as small as 3 μm to be detected and counted. Therefore, the skew towards smaller values is possible due to the disaggregation during and after sieving. This effect is not as apparent for the 25–32 μm montmorillonite fraction, with the result being that the mean particle size for the 25–32 μm and 38–45 μm montmorillonite size fractions are very similar (31 and 38 μm, respectively).

We note that the SAz2 montmorillonite is reported as having elevated iron content as described in the Clay Minerals Society.
X-ray diffraction analysis of this sample revealed minor magnetite present in the ‘as-shipped’ clays (Chipera and Bish, 2001). Some care was taken to handpick the iron oxide from the sample however some impurities still remain. We speculate that the presence of these oxides may affect the overall albedo of the samples and the spectral slope of the montmorillonite samples at wavelengths < 1.3 μm (e.g., Fig. 2).

3.2. Bi-directional (BDR) reflectance spectra

Reflectance spectra of gypsum and montmorillonite endmembers for the four size fractions in Group 1 are presented in Fig. 2. The absolute reflectance values for the gypsum endmembers are consistent with trends typically associated with particle size variations, where reflectance values systematically increase with decreasing particle size. While the relationship between particle size and overall reflectance is non-linear, spectra for the two smallest size fractions (25–32 μm and 38–45 μm) exhibit similar reflectance values, in agreement with the measured particle sizes. Spectra for the montmorillonite endmembers exhibit a similar sequence of increasing reflectance associated with decreasing particle size (Fig. 2b). However, the absolute reflectance for the 38–45 μm fraction is somewhat lower than might be expected considering how similar the measured mean particle size is to that of the 25–32 μm size fraction.

A change in the spectral slope at wavelengths < 1.3 μm is also apparent between the different size fractions for the clay endmembers (Fig. 2b). The slope appears to become shallower with increasing particle size, which we speculate could be a result of lesser spectral influence or decreased relative abundance of the darker oxide particles in the coarser samples. This minor variability in the slope at short wavelengths has a surprisingly significant effect on the modal abundance estimates for the coarser size fractions, a factor that we discuss in more detail below.

The BDR reflectance spectra for the binary mixtures (Fig. 3) show the expected behavior in the absorption band depth and position for all mixtures for each particle size (gypsum absorptions systematically weaken with increasing montmorillonite abundance and vice-versa). There is also a large drop in reflectance values for the coarsest size fraction of gypsum (Fig. 2a), which results in a very small spread in the reflectance values for the 125–150 μm clay–gypsum mixtures (Fig. 3d).
3.3. ASD reflectance spectra

The ASD reflectance spectra were scaled to the absolute reflectance of the BDR data at 1.09 μm in order to account for any differences in absolute reflectance that may result from the ASD having a slightly different viewing geometry compared with the RELAB BDR instrument (e.g., large cone angles). In addition, this scaling allows direct comparison of ASD unmixing results with BDR results using the same optical constants. A single representative example is shown in Fig. 4 for the 63–75 μm size fraction of the 50–50 gypsum–montmorillonite mixture. This plot shows the spectral variability for the four repeat measurements of this mixture with the ASD compared with the BDR measurement of the mixture. The spectra are very similar, with most discrepancies associated with slight differences in the strength of H2O absorption features near ~1.4 and ~1.9 μm. The observed differences between individual ASD spectra and BDR spectra are likely due to variations in the hydration level and/or orientation of particles at the time of data collection. No attempt to control the ambient relative humidity was done, therefore some variation in adsorbed water may be expected between analyses. In addition, the BDR measurements were acquired while the sample dish was spinning, thus averaging over particle orientations. In contrast, each ASD spectrum represents a static and different orientation of the sample dish, thus any slight particle orientation effects may affect the spectra.

Despite these different measurement techniques and instruments, the differences between the ASD and BDR spectra were minimal and did not have a significant effect on the un-mixing results. However, it is important to note that extreme care was taken in the experimental setup of the ASD to attempt to reproduce the illumination, geometry, and other measurement conditions of the BDR spectrometer. In this case, for relatively homogenous particulate samples, the spectra are quite comparable, but given the large FOV of bare fiber of the ASD instrument this is unlikely to be true of very heterogeneous or non-particulate samples.

3.4. Derivation of optical constants

3.4.1. Bi-directional spectra

Endmember spectra for the four size fractions in Group 1 were used to generate k-values for both phases. A least squares minimization routine was independently applied to the Hapke model using the endmember BDR spectra and initial particle size estimates for the four size fractions. The model was iterated and particle sizes (D) were allowed to vary from 0 to the maximum measured value (Fig. 1) as a means of adjusting the optical path length, and iteration proceeded until k values for each size fraction started to converge. This optimization is necessary because, as demonstrated above, the mean sieve size range was not always an accurate predictor of the mean particle size or range. The end result is a set of k ‘spectra’, one for each particle size, that are within a specified tolerance of each other for all measured particle sizes (Fig. 5).

As evident from Fig. 5a, the k-values derived for gypsum over the full wavelength range (0.8–2.5 μm) are extremely similar for all wavelengths for all particle sizes, indicating a nearly unique
solution within our tested parameter space. Convergence was achieved where the min–max range for particle sizes was almost zero. However, we found that with the montmorillonite spectra, there was a lack of convergence and a wider particle range was required to obtain a single k-value. Values of $k(\lambda)$ for the clay are consistent at longer wavelengths (>1.3 $\mu$m), but a subtle difference is observed below this value for the 25–32 $\mu$m and 125–150 $\mu$m size fractions (see Fig. 5b). This is also represented in the original reflectance spectra (Fig. 2) where there is an increase in the slope at these wavelengths as the particle size decreases. The differences in slope could be attributed to increasing spectral influence of the iron oxide impurities or a scattering effect of unknown origin. This discrepancy has a surprisingly large effect on the un-mixing of the coarsest fraction, and is discussed below.

Though the modeled k-values are technically non-unique solutions (because they are dependent on $<D>$, which we are treating as a variable), by constraining the particle size to be within the known or expected range it was found that the range in k-values for a given wavelength was not large, particularly for the gypsum. The particle sizes derived from the k-optimization are compared with the values determined from the optical microscope measurements in Table 2. The measured and optimized values are consistent for the gypsum, whereas the particle sizes estimated for the montmorillonite are somewhat smaller than the measured values, particularly for the two largest size fractions. Due to the nature of the SA2-2 material, the particles contain significant porosity and are actually aggregates of much smaller clay crystallites, thus they are not solid particles. Therefore, the estimated particles sizes are best thought of as ‘effective’ particle sizes that are representative of average optical path length and not necessarily representative of measured particle sizes or size distributions. In addition, as described in Section 3.1, disaggregation will result in a smaller average particle size when compared to the sieved sizes. For this work, such ‘effective’ particle sizes are assumed related to measurable particle size in the same manner as for the gypsum endmember.

The average k-value solutions from the Group 1 particle size suites were used in all of the un-mixing results. These single k-values were calculated using Hapke’s model assuming both spherical and irregular particle shape and are compared to previously published values in Fig. 6. When assuming irregular particles, the k-values for gypsum are higher than those of Roush et al. (2007) by a factor of ∼3 (Fig. 6a), which, as stated above, is similar to the expected difference between irregular and regular particle shape models. Indeed, when assuming spherical particles our results are in excellent agreement, possibly because the Roush et al. (2007) study followed the model of the Roush (2005) study that relied on equivalent spherical diameters for the particle size.

The agreement between our results and those of Roush et al. (2007) (Fig. 6) also demonstrate that our use of a wavelength-independent value for n is justified for gypsum.

By contrast, our estimated k-values for montmorillonite show clear differences compared to those reported by Roush (2005) (Fig. 6b). Though our results under the assumption of
spherical particles are the same order of magnitude as the k-values of Roush (2005), there are notable differences in the overall slope at longer wavelengths as well as in the depths of the H$_2$O absorption features at 1.4 and 1.9 μm. This could be due to slight differences in clay chemistry between the samples used in these studies (SWy1 in Roush (2005) versus SAz-2 in this study), but it is more likely that the differences are due to sample texture and hydration level. Specifically, our SAz-2 samples consisted of single coherent particles that were washed to remove clumping fines. In contrast, the SWy-1 material is often supplied as a micromilled powder, and sieving this material causes clumping that leads to ‘particles’ that are actually aggregates of much smaller particles and crystalites (and the size of such ‘particles’ can be easily altered during sample handling).

In addition, our samples were measured under ambient (moderate to high humidity) conditions and those of Roush (2005) were measured under purified nitrogen gas, thus our samples contain significantly more interlayer H$_2$O. This difference in H$_2$O is likely a large factor in the observed differences in k-values at 1.4 and 1.9 μm as well as the stronger spectral slope towards the ∼3 μm ‘hydration’ region. This is examined in Fig. 6c, which compares the k-values for our dehydrated montmorillonite with those of Roush (2005). Dehydrated montmorillonite spectra were acquired via in-situ heating with the ASD instrument using the 25–32 μm size fraction. This resulted in the expected decrease in the H$_2$O absorption band depths as well as a decrease in the slope at short wavelengths for the k-values (Fig. 6c). The dehydrated k-values are in better agreement with those of Roush (2005), but there are still notable differences. Perhaps of most importance is the difference in k-values near the diagnostic Al–OH absorption at ∼2.2 μm, which will have important effects on modeled abundances of montmorillonite in mineral mixtures. Nevertheless, the fact that our results are of the same order of magnitude as those of Roush (2005) also provides confidence that our measurement and modeling approaches are yielding reasonable k-values.

While some differences may be expected due to different measurement techniques, different instrumentation, and different modeling approaches, these results illustrate a fundamental difficulty of determining unique or standard optical constants for minerals like clays and zeolites that can have highly variable amounts of H$_2$O. Any variability in the H$_2$O content of sulfates, like gypsum, results in a discrete phase transition with a new mineral structure containing a fixed amount of H$_2$O. Other hydrated phases, including clays, zeolites, opal, and palagonite, can vary significantly in H$_2$O content yet maintain the same crystal structure, which means that k-values for the H$_2$O absorptions are sample (and measurement) specific and cannot be uniquely tied to mineral abundance. Using k-values derived from a sample with an inappropriate H$_2$O content (e.g., lab measurements where samples were too wet or too dry compared to Mars-like conditions) can result in errors associated with modeled mineral abundances. While, not surprising, it is fundamentally important to ensure a proper representation of the materials measured in the orbital data. Future work in this area should look at the impact of using multiple k-values of variable hydration levels for the same mineral phases.

3.4.2. ASD spectra

A similar derivation of k-values was performed using the ASD reflectance data for all particle sizes in Groups 1 and 2. Each sample was measured multiple times with the ASD instrument to assess repeatability and the extent to which factors such as particle orientation may affect derived k-values. Fig. 7 shows the average k-values determined from the ASD spectra, as well as the standard deviations based on the repeat measurements, for the two mineral endmembers. There is very little variation in the gypsum optical constants for all size fractions, and the average is effectively identical to the BDR results, indicating the k-values for gypsum are very robust. The ASD results for montmorillonite exhibited larger variability (up to ∼15%), much of which is associated with the H$_2$O absorptions, but the average of the ASD values is still in extremely good agreement with the BDR-derived k-values. Despite the different measurement conditions of the two instruments, this agreement indicates that reliable k-values can be derived from ASD instruments if great care is taken to control illumination geometry and measurement conditions.

However, it is worth noting that the standard deviations of the repeat ASD measurements (gray regions in Fig. 7) imply that a single ASD measurement for a given sample may not yield as accurate of a result as the use of multiple measurements. Choosing one of the extreme values did not improve the modeling results equally at all wavelengths. Although an extreme may improve the spectral fit at some wavelengths, it is at the expense of other wavelengths for certain samples. The average value, which we have focused on, provided the best overall fit when considering the full wavelength range.

3.5. Estimates of particle size

The modeled ‘effective’ particle sizes for all size fractions in Group 2, which consisted primarily of particles > 90 μm, are
Fig. 7. The average k-values (black lines) for (a) gypsum and (b) montmorillonite as measured using the ASD compared with the average k-values (red stippled lines) as measured using the RELAB BDR spectrometer. The average k-values for the ASD spectra represent 5 repeat measurements for each of the 4 different size fractions, with the standard deviation from the repeat measurements shown in grey. The average k-values between the two instruments for both phases are in good agreement, with some minor variation observed in the $\mathrm{H_2O}$ absorption bands for the montmorillonite. These estimates relied on the assumption of irregular particle shape. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Fig. 8. Comparison of measured particle sizes with modeled effective particle size, assuming irregular particle shape, as determined from particle size optimization for both ASD data (black circles) and BDR data (red circles). (a) The gypsum values follow very closely to the 1:1 line (solid black line), whereas values for the (b) montmorillonite show a distinct offset in the effective particle size. The latter may be due to the much smaller crystallitles in the clay. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

compared with the measured particle sizes in Fig. 8 in order to establish an empirical relationship between actual particle size and optical path length. The ‘effective’ particle sizes for gypsum are similar to those determined from optical microscopy, even for large particles (Fig. 8a). In contrast, and as expected, the modeled effective particle sizes for montmorillonite are significantly smaller than measured values, particularly for particles > 50 $\mu$m. As noted above, this is likely due the clay particles being aggregates of much smaller crystallitles with significant porosity, therefore the mean optical path length ($<D>$) appears to decrease rapidly (and non-linearly) as actual particle size increases. Additional study is warranted to determine if this trend is true of clay minerals in general or is specific to our particular montmorillonite sample, though we suspect the former is likely correct.

3.6. Radiative transfer modeling

The un-mixing results presented here are all based on the average k-values for the gypsum and SAz-2 montmorillonite endmembers derived from the BDR data (which are nearly identical to the ASD results, as shown in Fig. 7). The average k-values were then used for the mixture modeling in the ASD and BDR data set. For all models the particle sizes were allowed to vary along with modal abundance (bulk density) and we used a least-squares approach...
to minimize the difference between measured and modeled reflectance spectra. Example spectral fits and associated residuals for select mixtures are presented in Fig. 9 with the average derived particle sizes shown in Table 2.

3.6.1. Mineral abundances from BDR spectra

Estimated minerals abundances for the BDR data are shown in Fig. 10 for the four size fractions from Group 1. The model results for the 25–32 μm, 38–45 μm and 63–75 μm size fractions show less than 5% deviation from the known values (Fig. 10a–c), suggesting the model can accurately account for any subtle differences that may occur in the H2O absorption bands for the two mineral endmembers. However, results for mixtures in the 125–150 μm size fraction show large deviations in the clay-dominated samples (Fig. 10d). As discussed above, the k-values for the 125–150 μm montmorillonite samples were coincident with an effective particle size of 50 μm, which gave the closest match to the average k-values determined from the other three particle sizes (Fig. 5).

A comparison between the k-values in Fig. 5 shows a subtle but distinct difference in the spectral slopes, with the most pronounced difference occurring at the shorter wavelengths (<1.3 μm). This difference can either be attributed to differences in the hydration level between the finest and coarsest grained fractions, an uneven distribution of the iron oxide particles or due to the incorrect grain size distribution (fine particles). Indeed, electronic absorptions due to iron are consistent with broad absorptions at these wavelengths (e.g., Burns, 1993). Regardless of the cause, it is apparent that these seemingly small differences in spectral slope result in the model trying to increase the optical path length (and thus effective particle size) of the brighter mineral (gypsum) for the short wavelengths in the 123–150 μm size fractions in order to match the observed higher reflectance values and as such it results in an overestimation of the gypsum abundance. In other words, it appears that the average k-values for the montmorillonite are too large (too absorbing) at the shorter wavelengths compared to the actual absorption properties of the 123–150 μm.
montmorillonite sample and associated mixtures. To compensate during the spectral fitting, the contribution from the more weakly absorbing gypsum is over-modeled.

This disproportionate effect of the shorter wavelengths is confirmed by running the model without the 1.3 μm wavelength region. In this case (gray points in Fig. 10d) the modeled mineral abundances are in better agreement with the measured values and nearly all points are within 5% absolute. Removing the shorter wavelength region may improve the unmixing results, and there are no pertinent absorption features in this region for the binary mixtures examined in this study, but it is still beneficial to account for this problem in order to develop a more universal model that can be applied to a wide range of mineral mixtures.

As noted above, it is possible that the variation in k-values for the montmorillonite size fractions is due to the presence of impurities in this mineral endmember (e.g., Fe-oxides). Additional endmembers were included in the model to account for any spectral darkening and slight slopes in the coarser size fractions. Synthetic optical constants were generated to simulate endmembers with linear positive and negative sloped reflectance spectra, which can help to account for variations in spectral slope not well-modeled by the mineral optical constants. The mineral abundance results for the models that used these endmembers were then normalized to include only the gypsum and clay abundances. The results of these ‘slope-corrected’ values for the 125–150 μm size fractions are presented as red points in Fig. 10d. Such linear slopes are not necessarily representative of the exact spectral properties of opaque minerals such as magnetite and other oxides, which may have shallow broad absorptions or slightly nonlinear spectral slopes in this region (e.g., Morris et al., 1985), but it allows for a first-order correction of these effects. A more robust approach would be to include optical constants of actual Fe-oxides, which will be examined in future work, but this simple correction produces results similar to those from the reduced wavelength range (gray points in Fig. 10d) on par with the three other size fractions.

3.6.2. Mineral abundances from ASD data

The un-mixing results for the ASD mineral mixture spectra for the four size fractions from Group 1 are presented in Fig. 11. Abundance estimates for the 63–75 μm and 38–45 μm size fractions are nearly all within 5% of measured values, and though most mixtures in the 25–32 μm size fraction were also within this range there is a general offset where most of the results underestimated the fraction of gypsum fraction (Fig. 11a). The 125–150 μm fraction also
showed good results (using the slope-corrected model described above) except for the 25 wt% gypsum mixture, for which the gypsum was overestimated. Given the decent results for other mixtures in this size fraction we suspect this is a result of heterogeneity in the mixture or other uncertainties in the `known' abundance of the minerals within the field of view of the ASD.

Overall, the ASD results are very promising when compared to the BDR data, even with the minor variability in the ASD measurements associated with repeat measurements of the same samples/mixtures. Though not shown here, the model fits to the ASD spectra are good, similar to the BDR results (Fig. 9), with the majority of the residuals associated with the H₂O absorptions. The particle size estimates from these un-mixing models are compared with the values obtained from k-value derivation as well as the measured values in Table 2.

3.6.3. Comparison of Hapke with Shkuratov mineral abundances

The model results presented in Figs. 9–11 and discussed above are all based on the Hapke model, and it is clear that this method is able to correctly estimate mineral abundances within ~5% of measured values for nearly all mixtures and particle sizes. For comparison, k-values for both the montmorillonite and gypsum endmembers were calculated using the Shkuratov model and were compared to the Hapke results, as well as those of Roush (Fig. 12). It is seen that the general spectral shape and properties of the optical constants are similar between the Hapke and Shkuratov methods, but the Shkuratov values are systematically lower, possibly related to the different implementation of the phase function between the two RTMs. This trend is also shown in Roush et al., (2007), however it becomes reversed at longer wavelengths.

Mineral abundance estimates for both Hapke and Shkuratov models are presented in Fig. 13. As with the Hapke-based results, the Shkuratov estimates are largely within 5% absolute mineral abundance, though there are larger deviations in the 50:50 mixtures for both the 25–32 µm and 63–75 µm size fractions. In general, we observe that the Hapke model yields slightly better estimates of mineral abundance for the mixtures examined here. Additional study is needed to determine if this is true for other minerals and mineral mixtures, though recent results for modeling of eucrite and diogenite meteorites suggest the Hapke model performs better in silicate-dominated mixtures as well (Li and Milliken, 2015). However, the Shkuratov model is computationally more efficient and the larger uncertainties may be acceptable in some applications where high accuracy is not necessary and processing speed is preferred.

3.7. Irregular versus spherical particles

The model results described above were based on the assumption of irregular particle shape such that $<D> \approx 0.2 \, D$. This has the effect the k-values will be larger than when derived under the assumption of spherical particles (Fig. 6). Though either assumption may be used, the choice may have an effect on the actual modeled mineral abundances. This is because once the k-values are fixed.
the only way to adjust absorption strengths to match observed values is to adjust $<D>$, which changes $D$ and the modeled bulk density, $M$, which ultimately affects the estimated mass or volume fractions.

It is possible that in a complex mixture a change in $<D>$ could be balanced by a change in $M$ to yield an accurate mass fraction for a given component regardless of which particle shape model is assumed, but this is not a given. Indeed, Li and Milliken (2015) recently demonstrated that the irregular particle assumption provided a better estimate between RTM-derived $k$-values and transmission-derived values for a pyroxene. For the present study, although the particle shapes are clearly non-spherical (particularly for the tabular gypsum crystals), the $k$-values derived for gypsum are more in line with previously published transmission measurements (e.g., Roush et al., 2007) if it is assumed the particles are spherical. Therefore, there are contradictory results as to whether it is more or appropriate to assume spherical or irregular particles, and indeed the assumption may vary from case to case depending on the mineral particles in question and how they are oriented with respect to the incident photons.

Interestingly, for the materials examined in this study the difference between assuming spherical or irregular particle shape seems to have little net effect on the cumulative results of the modeled mineral abundances for the gypsum–montmorillonite mixtures. This is demonstrated in Fig. 14, which compares modeled mineral abundances for both assumptions (results for the
38–45 μm size fraction are shown and are representative for the mixtures suites as a whole). From this comparison it is clear that model results are often better under one assumption versus the other for a given mixture, but for the mixture suite as a whole there is little difference between the two assumptions (that is, one model is not inherently better than the other for all or a majority of the mixtures). This is because whether or not particles are assumed to be irregular or spherical has a relatively minor effect on the corresponding modeled particle sizes (D), which in turn has little effect on the mineral abundances estimated for these mixtures. Perhaps this is not unexpected given other sources of uncertainty in the model and the fact that the difference in k-values between the two assumptions is less than an order of magnitude (only a factor of ~3).

However, the observation that the irregular particle assumption yields more accurate results in some cases and not others (e.g., Li and Milliken, 2015 versus this work), and the (possibly fortuitous?) result that k-values for non-spherical gypsum particles are in better agreement with transmission derived values when they are treated as spheres, deserves additional attention in future work. Specifically, an assessment of whether or not a spherical or irregular particle shape assumption is appropriate or necessary in other cases seems warranted, especially for other non-spherical particles. In more complicated mixtures it is likely that some minerals may be better approximated by a spherical assumption (volcanic or impact glass? olivine?). Therefore, it may be worth considering the use of mineral-specific relationships between D and <D> to achieve the best possible estimates of mineral abundance in more complicated mixtures. Most importantly, when using Hapke or Shkuratov RTMs it is critical to be self-consistent such that the k-values used as inputs to the model were derived using the same model and assumptions as what is being applied to the mixture spectra. That is, Hapke-derived k-values are not appropriate for Shkuratov modeling (and vice versa) and RTM-derived k-values under the assumption of irregular particles should not be used in a model that then assumes spherical particles (and vice versa).

4. Conclusions

We have examined a suite of binary gypsum–montmorillonite mixtures for a variety of particle sizes to understand the accuracy of Hapke and Shkuratov radiative transfer models for estimating mineral abundances when the imaginary indices of refraction are well-constrained. Key findings are as follows.

1. Estimated values of k(λ) derived from RTMs such as the Hapke model are in good agreement when using RELAB BDR spectral data and those acquired by an ASD FieldSpec instrument, provided care is taken when the latter is used for this purpose. Specifically, illumination and viewing geometry must be well-controlled (though need not be fixed at certain values) and multiple measurements of the sample should be acquired or samples should be spun during ASD measurements to average out preferential orientation/scattering effects.

2. Our estimates of k(λ) for gypsum at NIR wavelengths are in excellent agreement with results previously published by Roush et al. (2007) under the assumption of spherical particle shape. This is despite the fact that instrumentation, samples, and modeling codes were different between these studies, demonstrating that these k(λ) values for gypsum are robust at these wavelengths.

3. Our estimates of k(λ) for montmorillonite at NIR wavelengths are qualitatively similar to results previously published by Roush (2005) under the assumption of spherical particle shape. Some of the differences are further reduced when our dehydrated montmorillonite is used to derive k(λ). Key sources of the remaining differences may be the physical state of the particles, where our montmorillonite samples consisted of discrete particles (composed of smaller, cemented clay crystallites) that were washed to remove clingines, and remaining differences in hydration state. Despite these differences our k(λ) values are within the same order of magnitude as those of Roush (2005).

4. Though previous studies have used Hapke and Shkuratov RTMs to estimate values of k(λ) for clays and sulfates, in this study we have demonstrated that these k(λ) values are indeed appropriate for actual RTM modeling of simple mixtures with components that are of relevance to Mars and Earth. When using the RTM-derived optical constants to model a wide variety of gypsum–montmorillonite mixtures we find that estimated mineral abundances are typically within 5% (absolute) of measured values for the samples examined here, although a slope correction was required for the coarsest grain size due to issues with the montmorillonite. Overall, the Hapke model provides slightly better accuracy than the Shkuratov model for these mixtures. Future work will focus on applying these optical constants to more complex mineral mixtures as well as to gypsum and montmorillonite samples from different localities. The latter will provide information as to how ‘universal’ these k(λ) values may be.

5. Care must be used when relying on RTM-derived optical constants for modeling of spacecraft and lab reflectance spectra in order to understand which factors may be model-specific. The optical constants used as inputs to an radiative transfer model, for example, should be consistent with the assumptions of that model, as factors such as particle shape have the potential to introduce large uncertainties in mineral abundance if they are not consistent between the RTM used to derive k(λ) and the RTM used to model the mixture spectra.

6. When clay and gypsum were present in the mixtures at levels as low as 10% they were still detected with the RTMs, though the relative uncertainty in these modeled abundances is accordingly higher. This suggests that CRISM and OMEGA observations of simple clay and sulfate-dominated rocks on Mars may have similar detection limits (~10%),
though this aspect certainly warrants additional research. Future work will incorporate the optical constants reported here with those of other clays and primary silicates (olivine, pyroxene, feldspar) to model more complex mixtures that are directly relevant to the mudstone compositions observed in Gale crater by the Curiosity rover. Such higher fidelity tests will ultimately provide a more detailed understanding of the accuracies and limitations of deriving clay and sulfate mineral abundances on Mars using RTMs at VIS-NIR wavelengths.

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