Estimating the water content of hydrated minerals using reflectance spectroscopy
II. Effects of particle size

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Abstract
Visible-near infrared reflectance spectra for five particle size fractions of a Hawaiian palagonite (HWMK101) and a nontronite (ferruginous smectite, Clay Minerals Society source clay SWa-1) were measured under ambient, purged, and heated conditions to characterize the effects of surface and volume scattering on the relationship between absolute H2O content and the strength of the 3 µm absorption feature. Both materials were ground and dry sieved to particle sizes of <25, 25–45, 45–75, 75–125, and 125–250 µm. Particles of the bulk palagonite have an approximate bimodal distribution consisting of small, amorphous particles <5 µm in diameter mixed with crystalline and glass particles <1 mm in diameter, whereas the nontronite particles are polycrystalline aggregates. We find that band parameters value relating the strength of the 3 µm hydration feature to water content increase with particle size for a given water content, regardless of whether reflectance or single scattering albedo spectra are used. Spectra generally increase in reflectance as particle size decreases, a result of the relative increase in volume to surface scattering. Spectra of large particles are commonly saturated in the 3 µm region due to an increase in optical path length, making an accurate estimate of water content indeterminate until the samples dehydrate to the volume-scattering regime. We find that the presence of fines in several of the size fractions of palagonite cause their spectra to be representative of the finest fraction rather than the mean particle size. The nontronite spectra appear to be representative of an effective particle size within the range of the sieved size fractions. Many planetary surfaces are expected to have a large number of small particles which can dominate their spectral signature. Our results for particles <45 µm provide a reasonable model for estimating the H2O content of hydrated asteroids and regions of Mars.

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1. Introduction
The shape and strength of water absorption bands in minerals are likely controlled by three primary factors: mineral composition and structure, albedo, and particle size. Previously, we showed that it was possible to estimate the absolute water content of a variety of hydrated minerals within approximately ±1 wt% H2O using visible-near infrared (VIS-NIR) reflectance spectra (Milliken and Mustard, 2005; Milliken and Mustard, 2007). We found that converting reflectance spectra to single scattering albedo, removing a continuum slope, and using Hapke’s (1993) effective single-particle absorption-thickness (ES-PAT) parameter yielded the best results for different compositions (Milliken and Mustard, 2005) and albedo values (Milliken and Mustard, 2007). Our model is applicable to all reflectance spectra that include the water absorptions centered near 3 µm (asymmetric and symmetric fundamental O–H stretches near 2.8–2.9 µm and overtone of the H2O bend near 3.1 µm), but we are primarily interested in how this model may be applied to high spatial-spectral resolution VIS-NIR data for Mars [OMEGA on Mars Express (Bibring et al., 2004) and CRISM on Mars Reconnaissance Orbiter (Murchie et al., 2003)].

All of our previous reflectance spectra were derived from samples composed of particles <45 µm in diameter or poly-

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crystalline aggregates <45 µm in diameter composed of much smaller individual grains. Understanding the relationship between band strength and particle size is important for both laboratory reflectance spectra as well as remotely-sensed spectra of planetary surfaces, though the particle size range of the former is commonly better constrained than the latter. Mustard and Pieters (1989) and Johnson et al. (1992) were able to model reflectance spectra of mixtures reasonably well with a priori knowledge of particle size, but this parameter is typically an unknown for planetary surfaces. The goals of this study are to (1) examine how assumptions about texture and particle size of planetary surfaces will manifest themselves in estimates of absolute water content, (2) determine the uncertainties in our model as they pertain to particle size, and (3) understand the relationship between particle size and albedo on the relative proportions of scattering and absorption as observed in reflectance spectra.

In this paper we examine the effects of particle size on our model using five size fractions for palagonite (altered volcanic material) and nontronite (ferruginous smectite), both of which may be present on the martian surface (Allen et al., 1981; Singer, 1982; Morris et al., 2001; Poulet et al., 2005). These results, combined with in situ observations of the texture and particle size distribution of the surface by the Microscopic Imager on the Mars Exploration Rovers (Herkenhoff et al., 2004), will help to constrain our model for application to current and future reflectance spectra of the martian surface.

2. Background

The effects of particle size on reflectance spectra in the VIS-NIR and IR (we generalize these definitions to mean wavelengths approximately shorter and longer than ~6 µm, respectively, for this discussion) have been documented by many workers over the past several decades, including Lyon (1964), Hovis and Callahan (1966), Adams and Filice (1967), Vincent and Hunt (1968, Hunt and Vincent (1968), Aronsn and Emslie (1973), Pieters (1983), Salisbury and Walter (1989), Salisbury and Wald (1992), Hiroi and Pieters (1992), Pieters et al. (1993a), Mustard and Hays (1997), Cooper and Mustard (1999), and Piatek et al. (2004) to name a few. Different particle sizes cause two primary changes in reflectance spectra: changes in absolute reflectance values and changes in the spectral contrast of absorption features (i.e., band depth). Modeling (e.g., Hapke, 1993) and observations [e.g., Gaffey et al. (1993) and Mustard and Hays (1997)] show that the spectral contrast of an absorption is maximized at an ‘optimum’ particle size. The spectral contrast of reflectance peaks and troughs over VIS-NIR wavelengths tend to decrease as particles become smaller than this value (Lyon, 1964; Adams and Filice, 1967; Vincent and Hunt, 1968; Pieters, 1983; Salisbury and Wald, 1992). It has also been shown that smaller particles may result in lower absolute reflectance values for reststrahlen bands in the IR (Hovis and Callahan, 1966; Aronsn and Emslie, 1973; Salisbury and Walter, 1989) but higher absolute reflectance values in the VIS-NIR (Adams and Filice, 1967; Pieters, 1983; Pieters et al., 1993a; Mustard and Hays, 1997). These general observations can be further complicated by surface asperities or changes in porosity (Aronson and Emslie, 1973; Salisbury and Wald, 1992; Hapke, 1993), particle sizes similar to or smaller than the wavelength (Mustard and Hays, 1997; Piatek et al., 2004), and particles that are aggregates of fine-grained material (Cooper and Mustard, 1999; Milliken and Mustard, 2007).

Reflectance spectra of particulate materials result from two types of scattered light. The first type, referred to as surface scattering (sometimes referred to as specular reflection or Fresnel reflection), is composed of incident rays (photons) that have never passed through a particle and have only interacted with the surfaces of particles before being redirected to the observer. Surface scattering is governed by the Fresnel equations (see Hapke, 1993, for a review), which are functions of both the real (n) and imaginary (k) parts of the complex index of refraction. Therefore, surface scattering will be present in reflectance data for all materials that have an index of refraction different from their surrounding medium. Thus even dark, strongly absorbing materials such as ilmenite have detectable reflectance values due to first-surface reflection (Hapke, 1993).

Volume scattering is composed of rays that have passed through one or more particles before being reflected off of surfaces and redirected to the observer. Volume scattering is the component that gives rise to absorption features and is governed by the absorption coefficient (α) of the material and the mean path length (⟨D⟩). The mean path length may be considered the average distance traveled by all rays that traverse the particle once without being internally scattered. The value of ⟨D⟩ is partially dependent on the index of refraction as well as the average diameter, D, of the absorbing particles. This relationship is expressed clearly when using the equivalent slab model as an approximation to model the reflectance and transmission of a perfect sphere (Hapke, 1993; Eq. (5.41)).

Though it may seem odd that the mean path length is only dependent on n and not α (and thus k), this is because ⟨D⟩ is defined as the equivalent thickness of a slab needed to achieve the same value of the internal transmission factor, Θ, as is observed for a sphere as α → 0 (Hapke, 1993). The internal transmission factor is “the fraction of light entering the particle that reaches another surface after one transit” (Hapke, 1993) and represents the portion of light that is not absorbed as it travels through the particle. The internal transmission factor can take several forms and can be directly related to the scattering efficiency (Qs) or single scattering albedo (w) by accounting for the internal and external scattering coefficients (S_i and S_e, respectively) (Hapke, 1993). Milliken and Mustard (2005) provide a full description of how these parameters are considered for the various band parameters used to quantify the hydration state of minerals. For the work presented here, we chose to use a simple exponential model for the internal transmission factor, similar to our previous work (Milliken and Mustard, 2005).

As the value of n increases the average distance a refracted photon travels through a particle before encountering another internal scattering surface also increases, thus increasing the mean path length. On the other hand, the mean path length,
(\(D\)), is linearly proportional to the particle diameter, \(D\), and a decrease in particle size will cause a decrease in the mean path length if \(n\) is held constant. The mean path length will be some fraction, \(x\), of the average particle diameter (described by \(\langle D \rangle = xD\)) and is thus often referred to as the 'effective' particle size (Hiroi and Pieters, 1992). Hapke (1993) showed that \(\langle D \rangle = 0.9D\) for a perfect sphere, but irregularities, imperfections, and changes in shape will typically result in smaller values of \(\langle D \rangle\). The effects of surface asperities and particle shape were observed by Aronson and Emslie (1973), whereas later work by Hiroi and Pieters (1992, 1994) examined the effects of particle size and shape on modeling reflectance spectra.

For particulate materials with an average particle diameter larger than the wavelength, the total reflectance in the VIS-NIR wavelength region is typically dominated by the volume scattering component, resulting in reflectance troughs in regions of increased \(\alpha\). Conversely, the total reflectance in the IR region for similar sized particles is often dominated by the surface scattering component, resulting in reflectance peaks in regions of increased \(\alpha\) (e.g., reststrahlen peaks) (Vincent and Hunt, 1968; Hunt and Vincent, 1968). Decreasing the particle size increases the number of scattering interfaces a photon encounters after having traveled a given distance through the medium. Therefore, the observed reflectance spectrum is composed of a greater number of photons that have passed through particles without having been absorbed and the relative proportion of the volume scattering component has increased. The range of \(\alpha/\langle D \rangle\) for which this holds true is known as the volume scattering region and has the characteristic that a decrease in particle size will result in an increase in absolute reflectance in the VIS-NIR, even within an absorption band. The surface scattering component becomes proportionally greater as \(\alpha/\langle D \rangle\) increases and will eventually result in an absorption band becoming saturated at its center. A decrease in particle size may cause an increase in reflectance outside of the band but not in the center, where \(\alpha\) is large, resulting in larger band depths for smaller particles. This means there is an optimum particle size for an absorption that will maximize its spectral contrast (Gaffey et al., 1993; Mustard and Hays, 1997). At the extreme, reflectance spectra of materials with very large absorption coefficients will be dominated by surface scattering with only a minor component of volume scattering, as is observed for metals.

It is obvious from this discussion that relating changes in reflectance spectra directly to changes in particle size is quite complex, especially if both the absorption coefficient and particle size of the material are unknown. This is the case for most planetary surfaces, however, and it is important to understand that absolute reflectance values and absorption strengths are affected by factors such as the particle size, porosity, surface texture, and the absorption coefficient of the material in question. Furthermore, attempting to derive parameters such as absorption coefficients from reflectance spectra is exceedingly difficult since absorption is not a direct measurement, but rather inferred by the absence of reflectance and may be complicated by the scattering effects mentioned above. The goal of this study is to characterize the effects of particle size on our model for estimating absolute \(\text{H}_2\text{O}\) content and to place these results within the context of applications to planetary surfaces such as Mars and asteroids, for which precise values of these parameters are largely unknown.

3. Methods

3.1. Sample description

We chose two materials for testing the effects of particle size on our model. The first sample is a ferruginous smectite/nontronite from Washington (Clay Minerals Society source clay SWa-1), provided by Dave Bish, Indiana University. Nontronite is an Fe-rich smectite capable of holding variable amounts of water in interlayer regions. Poulet et al. (2005) recently detected the presence of nontronite on Mars using Mars Express OMEGA data, making it a reasonable candidate for this project. The sample used for this study originally consisted of particles 0–1 cm in diameter and was subsequently crushed and sieved by hand to five particle size separates of <25, 25–45, 45–75, 75–125, and 125–250 \(\mu m\). We point out that the nontronite size separates are polycrystalline aggregates and not individual grains. Individual crystals of clay minerals are commonly only a few micrometers in diameter, yet Cooper and Mustard (1999) showed that the effective particle size for spectra of clay mineral aggregates tends to be more representative of the aggregate diameter than the diameter of individual crystals. Therefore, we believe the effective particle sizes for our different nontronite size fractions are better represented by the mean diameter of the sieve range used for each fraction (e.g., mean size of 35 \(\mu m\) for the 25–45 \(\mu m\) size fraction) than the true mean diameter of the individual nontronite crystals.

The second sample is the palagonite used in our previous work (Milliken and Mustard, 2005; Milliken and Mustard, 2007), HWMK-101, provided by Richard Morris, Johnson Space Center. This palagonite is a hydrated, devitrified basaltic glass collected in the same location as the HWMK-919 palagonite described in detail by Morris et al. (2001). Palagonite has been suggested as a possible compositional and spectral analog for the fine-grained oxidized materials on the martian surface (Allen et al., 1981; Singer, 1982; Orenberg and Handy, 1992; Morris et al., 2001). The amorphous alteration phase of this sample is predominantly in the <5 \(\mu m\) size fraction, which accounts for \(\sim 15\) wt% of the <1 mm size fraction. The >5 \(\mu m\) size fraction presumably contains a greater proportion of unaltered or weakly altered crystalline material, consisting primarily of plagioclase feldspar, magnetite, and lesser amounts of pyroxene, hematite, and glass (Morris et al., 2001). The original sample (<1 mm) was sieved, without grinding or crushing, to the same size fractions as the nontronite (<25, 25–45, 45–75, 75–125, and 125–250 \(\mu m\)).

All size fractions for both materials were sieved dry, not washed, to avoid changing their hydration state or amount of adsorbed/interlayer \(\text{H}_2\text{O}\). This is necessary for direct comparison of \(\text{H}_2\text{O}\) estimates between samples and size fractions but creates the potential for the large size fractions to contain particles with clinging fines. This effect is likely greater for the palagonite, which was sieved from a bulk material that
contained a large weight percent of fines <5 µm in diameter (Morris et al., 2001). The bulk nontronite, however, was composed primarily of particles greater than our largest size fraction (>250 µm) and it is not expected that a significant portion of fines will remain in the larger size fractions through clinging and electrostatic charges. This was verified by visually inspecting the size fractions with a microscope. Many of the larger palagonite particles are coated with fines whereas the larger nontronite particles are not. These effects are discussed further below.

3.2. VIS-NIR spectra

Reflectance spectra were acquired from 0.3–2.5 µm under ambient conditions for each size fraction using an ASD FieldSpec® spectrometer (Fig. 1). Reflectance spectra were also acquired from 1–4.5 µm using a Nicolet Nexus 870 FTIR spectrometer fitted with a Pike Technologies bi-conical attachment (AutoDIFF™) in RELAB at Brown University. A sample of each size fraction was also measured under a purged atmosphere (filtered for CO2 and H2O) at intervals of 5 min for half an hour and at 60 min. The sample was then heated in a benchtop furnace for 15 min at predetermined temperatures, measured in the spectrometer, and weighed with a balance to determine the weight loss (assumed to be due to loss of H2O and/or OH−). These steps are identical to those used in our previous studies and provide us with multiple data points corresponding to different water contents for each sample. Milliken and Mustard (2005) provide a full description of the experimental procedures, associated uncertainties, and potential effects of rehydration. All FTIR spectra were scaled such that their maximum reflectance value would match the maximum reflectance value observed in the ASD FieldSpec® measurements. Reflectance spectra were converted to single scattering albedo following the method of Hapke (1993). We assume incidence and emergence angles of 30°, an isotropic phase function of \( p(g) = 1 \), and negligible opposition effect \( B(g) = 0 \), identical to our previous work.

The nontronite samples were heated from 100–500 °C in 50° increments whereas the palagonite samples were heated from 100–800 °C in 50° increments. The nontronite begins to dehydroxylate at temperatures \( \geq 450 °C \), making it impossible to differentiate weight changes due to loss of H2O from weight changes due to loss of OH−. The focus of our model is to estimate H2O content, therefore data for higher temperatures were unnecessary (though it is understood that not all H2O may be removed at temperatures <500 °C). The palagonite also contains OH−, as evident from the presence of a 2.2 µm Al–O–H absorption, but this is believed to be a minor contribution to the total weight loss and samples were heated to higher temperatures to remove all H2O from the structure. The heated samples were then left under ambient conditions for 1–2 weeks and measured again using the ASD FieldSpec® (Fig. 1). It is clear from Fig. 1b that the nontronite samples heated to 500 °C have oxidized and experienced a change in structure due to the dehydroxylation. The Fe absorptions near 0.75 and 1 µm have increased in width to form a large absorption spanning from 0.85–1.7 µm and centered near 1.15 µm, likely a result of oxidation. The 2.28 µm metal–OH band is significantly weaker due to the loss of hydroxyls and the 1.4 µm OH− overtone appears as a weak band superimposed on the strong 1 µm Fe absorption. Again, these oxidation and structural changes only occur at temperatures >400 °C and will not affect the data used in our analyses.

![Fig. 1. VIS-NIR reflectance spectra for various size fractions of SWa-1 nontronite (a) before heating and (b) after heating to 500 °C and HWMK-101 palagonite (a) before heating and (b) after heating to 800 °C. The <25 and 25–45 µm size fractions in (c) are indistinguishable. Spectra were measured with an ASD FieldSpec® spectrometer.](image-url)
3.3. Band parameters

Band depth (BD), integrated band depth (IBD), normalized optical path length (NOPL), mean optical path length (MOPL), and effective single-particle absorption-thickness (ESPAT) band parameter values were calculated for the 3 μm water absorption using both reflectance spectra, $R$, and single scattering albedo spectra, $w$. We calculated these parameters using the same methods as presented by Milliken and Mustard (2005) and Milliken and Mustard (2007). When necessary, a continuum fit was determined using the method of Milliken and Mustard (2007). The nontronite spectra exhibit a distinct decrease in the strength of 2.28 μm band for a given size fraction at temperatures $>$400°C, evidence that loss of hydroxyls constitutes some fraction of the measured weight loss. Band parameter values corresponding to these spectra were not included in our analysis.

As an additional test for minimizing grain size effects, we also calculated band parameters from $w$ spectra that had been divided by a continuum fit prior to conversion from $R$ to $w$. This procedure provides different results for $w$ spectra because the conversion from reflectance to single scattering albedo is highly nonlinear over a wide range of reflectance values. All band parameter values were plotted against their correspond-

![Fig. 2. Plots of band depth (BD) versus wt% H$_2$O for the 3 μm absorption. Nontronite values are derived from (a) $R$ spectra, (b) $w$ spectra, continuum removed after conversion, and (c) $w$ spectra, continuum removed prior to conversion. Palagonite values are derived from (d) $R$ spectra, (e) $w$ spectra, continuum removed after conversion, and (f) $w$ spectra, continuum removed prior to conversion.](image-url)
Estimating hydration: Effects of particle size

4. Results

4.1. Nontronite size fractions

4.1.1. Spectral observations

As discussed previously, decreasing the particle size will result in an increase in absolute reflectance and either an increase or decrease in the spectral contrast of absorption bands in the VIS-NIR (depending on whether the particle size is larger or smaller than the ‘optimum’ particle size). It is preferable to compare spectra of similar water contents in order to examine these effects for the 3 µm water absorption. One spectrum from each particle size fraction of nontronite, corresponding

Fig. 3. Plots of normalized optical path length (NOPL) versus wt% H₂O for the 3 µm absorption. Nontronite values are derived from (a) \( R \) spectra, (b) \( w \) spectra, continuum removed after conversion, and (c) \( w \) spectra, continuum removed prior to conversion. Palagonite values are derived from (d) \( R \) spectra, (e) \( w \) spectra, continuum removed after conversion, and (f) \( w \) spectra, continuum removed prior to conversion.
to $\sim$8 wt% H$_2$O, is presented in Fig. 6. These spectra are the 10-min purging spectrum for the <25 µm fraction, the 30-min purging spectrum for the 25–45 µm fraction, and the 60-min purging spectra for the three larger size fractions. If we assume that all differences observed in these spectra are caused by differences in particle size, then Fig. 6 confirms that absolute reflectance values increase as particle size decreases. Additionally, the spectral contrast decreases for the 1.9, 2.2, and 3 µm absorption bands with decreasing particle size for the particle size range examined here. A continuum slope with endpoints defined by reflectance values at $\sim$1.6 and 3.9 µm becomes steeper with increasing particle size (Fig. 6). This may be a result of wavelength dependent scattering, the magnitude of which will change with particle size, the nonlinear changes in $\alpha$ with wavelength, or a combination of the two. Regardless of the cause, simply correcting for this difference in continuum slope over the 3 µm band will not account for all differences in spectral contrast between the various particle sizes.

The minimum reflectance value in the 3 µm region increases with decreasing particle size for the <25 and 25–45 µm size fractions, suggesting the value of $\alpha(D)$ is within the volume scattering region, whereas the band is saturated for the 75–125 and 125–250 µm size fractions, implying the value of $\alpha(D)$ is in the surface scattering region. The intermediate particle size of 45–75 µm falls somewhere between these two scattering regimes. The observed reflectance values for saturated
3 µm bands are at the limit of the FTIR detector and may exhibit minor differences caused by low signal-to-noise. These small differences may become exaggerated when the data are scaled to match the ASD spectra or when reflectance spectra are converted to single scattering albedo, therefore caution must be used when comparing absolute or relative values for...
Table 2
Measured weight losses and estimates of total H2O content corresponding to each purging and heating spectrum for various size fractions of HWMK-101 palagonite

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Fig. 6. FTIR spectra of different nontronite size fractions with similar water contents, ~8 wt, in (a) reflectance and (b) single scattering albedo. Heating and purging times corresponding to each spectrum are given in the text.

saturated bands. It is also important to note that we have attempted to isolate the water absorption by removing the continuum slope prior to calculating our band parameters, therefore ⟨D⟩ is more closely related to the mean path length of the absorbing species (H2O) in the sample and not necessarily the mean particle size. This is why ⟨D⟩ decreases as a sample dehydrates (see the MOPL values in Fig. 4). The 1.9 and 2.2 µm absorptions have much smaller absorption coefficients and are within the volume scattering region for all particle sizes examined here.

4.1.2. Band parameter observations

Nontronite band parameter values derived from reflectance spectra generally increase with increasing particle size, a direct result of the associated increase in spectral contrast for the 3 µm band (Figs. 2a–4a). These trends are more pronounced in the band parameters calculated from the continuum-removed single scattering albedo spectra (Figs. 2b–4b, 5a). For a given water content, the largest differences in band parameter values occur between the <25 and 25–45 µm size fractions and the 25–45 and 45–75 µm size fractions. Values for the two largest size fractions are quite similar for each of the band parameters except when these samples are fully hydrated, suggesting the particle size is approaching the optimum value for maximizing the spectral contrast. This is especially clear in the MOPL and ESPAT parameters, each of which has approximately constant values for water contents >6 wt% for these two size fractions due to a saturation of the 3 µm band. The value of ⟨D⟩ decreases as the samples dehydrate and the absorption eventually transitions from the surface scattering to volume scattering regime, similar to the smaller size fractions. We note that hydrated
phases such as these will likely be only partially, not fully, hydrated under current Mars surface conditions (Bish et al., 2003; Fialips et al., 2005), therefore it is unlikely that the 3 µm absorption will be complicated by saturation issues in reflectance spectra of the martian surface.

Unlike our results for low-albedo mixtures (Milliken and Mustard, 2007), none of the band parameters derived from single scattering albedo (or reflectance) show a unique correlation to water content all of for the different particle sizes of nontronite. Our preferred method for calculating band parameters from spectra is to divide by the continuum after converting \( R \) to \( w \). We also derived band parameters using \( w \) spectra that had their continuum removed prior to converting \( R \) to \( w \), however, as an additional test for ways to minimize scattering effects caused by changes in particle size (Figs. 2c–4c, 5b). This method resulted in a slightly higher correlation to water content for the size fractions as a group but it is still evident that there is no unique correlation for all particle sizes.

4.2. Palagonite size fractions

4.2.1. Spectral observations

The post-heating spectra of the various palagonite size fractions are quite similar to their pre-heating counterparts, with the noticeable exception that the former have higher reflectance. All FTIR spectra were scaled to the maximum reflectance value of the pre-heated sample as measured by the ASD spectrometer. Band parameters derived from reflectance spectra are based on continuum-removed reflectance values and will not be affected by uncertainties introduced by an incorrect scaling factor. Parameters derived from \( w \) spectra, however, are dependent on absolute reflectance values and will be affected by incorrect scaling. Fortunately, the increase in pre-scaled FTIR reflectance spectra during heating occurs only at the highest temperatures when most \( H_2O \) has already been removed from the sample and band parameter values are small. Major trends between water content and band parameters are well established without the measurement of these data points, making uncertainties introduced by including these values negligible for our analyses.

Similar to the nontronite samples, we have selected one spectrum from the heating series of each palagonite size fraction to compare spectra of similar water contents. We have chosen the 450, 400, 350, 300, and 250 °C spectra for the 0–25, 25–45, 45–75, 75–125, and 125–250 µm size fractions, respectively. These spectra correspond to \( \sim 2.3 \) wt% \( H_2O \) and are presented in Fig. 7. It was noted that the smaller size fractions of nontronite increased in reflectance near 2.9–3.1 µm relative to the larger particles. This trend is not as pronounced for the fully hydrated palagonite, in which the 3 µm band is near saturation for all size fractions. It is very clear, however, in reflectance and single scattering albedo spectra of the partially dehydrated palagonite (Fig. 7). The palagonite appears to be in the surface scattering region when fully hydrated and only transitions into the volume scattering region when \( \alpha(D) \) decreases via dehydration.

Unlike the nontronite, the different size fractions of palagonite also represent different bulk compositions. The larger size fractions of palagonite contain a relatively higher proportion of unaltered or weakly altered volcanic material, whereas the smaller size fractions are dominated by the hydrated amorphous alteration products (Morris et al., 2001). Furthermore, the similarity in the VIS-NIR spectra for the three smaller size fractions suggests that this fine-grained material is a significant component of the 25–45 and 45–75 µm size fractions (Fig. 1). Or, at the very least, the finer fraction is dominating the spectral signature. This effect has been well documented for lunar soils and laboratory mixtures that contain a large number of small particles (Adams and Filice, 1967; Pieters, 1983; Salisbury and Wald, 1992; Pieters et al., 1993a; Mustard et al., 1993). Differences in bulk composition for the palagonite size fractions are also evident by comparing their total water contents. Unlike the nontronite, which has similar water contents for the various size fractions, the water content of the palagonite decreases with increasing particle size (Table 2). This is expected since the fine-grained amorphous material is the primary hydrated phase, whereas the larger crystalline and glassy phases are mostly anhydrous.

Differences between the palagonite spectra may result from differences in particle size, composition, and water content. Our previous results of estimating water content for mixtures of montmorillonite, zeolite, and palagonite with ilmenite, how-
ever, suggest that mixtures of hydrous and relatively anhydrous materials will yield similar band parameter values for similar water contents (Milliken and Mustard, 2007). Data for physical mixtures of hydrous–anhydrous materials by Yen et al. (1998) suggest similar trends. Here we assume that differences in composition due to an increased abundance of an anhydrous component will not affect the strength of water absorptions in the 3 µm region. In other words, differences in absolute \( w \) values and spectral contrast between the various palagonite spectra are primarily related to differences in particle size and water content, not composition. Additionally, this suggests that our current model is only capable of estimating the water content of the bulk material and cannot determine the water content of individual hydrated phases in a mixture of hydrous and anhydrous materials.

4.2.2. Band parameter observations

None of the band parameters derived from reflectance spectra exhibit a unique correlation to water content for the five different size fractions of palagonite as a group (Figs. 2d–4d). There is significantly less scatter than observed in the nontronite data, however, and individual size fractions exhibit distinct trends that could be used to estimate \( \text{H}_2\text{O} \) content if particle size were a known parameter. Again, band parameter values (and spectral contrast in \( w \) spectra) increase with increasing particle size for a given water content, suggesting these size fractions are below the optimum particle size. We believe this is because the hydration bands are always associated with the smallest particles, even for the large size fractions. All palagonite parameters derived from \( w \) spectra show significantly more scatter than their reflectance-derived counterparts (Figs. 2e–4e). This is an effect of the nonlinear conversion from reflectance to single scattering albedo. The single scattering albedo spectra, however, are more representative of the true absorption strength of the bulk material and cannot determine the water content of individual hydrated phases in a mixture of hydrous and anhydrous materials.

5. Discussion

Changes in albedo and changes in particle size will affect both the relative proportions of volume scattering and surface scattering contributing to the total observed reflectance. Decreasing the albedo of a material by adding strong absorbers such as carbon black will increase absorption and decrease the volume scattering component. The external scattering coefficient is dependent on both \( n \) and \( k \) (Hapke, 1993), thus increasing \( k \) will also increase surface scattering. Similarly, increasing the particle size will decrease the relative proportion of volume scattering (Vincent and Hunt, 1968). We plotted the reflectance from 1.5–2.9 µm of the four largest size fractions of nontronite against the reflectance of the ~25 µm size fraction to further examine these effects. Fig. 8a shows that as particle size increases, reflectance values decrease nonlinearly relative to the smallest size fraction, representing a decrease in volume scattering. If the particle size were to continue to increase, the reflectance would eventually decrease to some nonzero value representing only the surface scattering component. This is more clearly visible when plotted in terms of single scattering albedo and may explain why the lowest reflectance values increase for the larger size fractions (Fig. 8b).

In order to apply our model for estimating water content to planetary surfaces, for which the absorption coefficients and particle size distributions of the components are unknown, it is necessary to find ways to minimize or account for the competing effects of albedo and particle size on the strength of the 3 µm absorption. The results of Milliken and Mustard (2007) suggest converting to single scattering albedo, removing a continuum slope, and calculating the ESPAT or MOPL parameter provides the best estimates of \( \text{H}_2\text{O} \) content over a wide albedo range of mixtures. Results from our current study suggest these same techniques will not account for scattering effects attributed to particle size. If these steps had, in fact, isolated the water absorption from the scattering and absorption effects of the surrounding host mineral, then the MOPL values for the 3 µm
band should be the same for a given water content regardless of particle size. It is clear from Fig. 4, however, that this is not the case. Using the correlation between the MOPL (or ESPAT) values and H2O for the <25 µm fraction would overestimate the water content of larger particles and vice versa. It was discussed above that removing the continuum prior to converting reflectance spectra to single scattering albedo reduced differences between particle sizes but at the cost of introducing effects correlated to albedo. Therefore, it is not possible to separate changes in spectral contrast (scattering) of the 3 µm band into relative contributions from albedo and particle size when neither the absorption coefficient nor particle size distribution of the bulk material is known.

This may seem discouraging for application to planetary surfaces, but the regolith of planetary surfaces lacking a thick atmosphere, such as the Moon or asteroids, likely contain a large number of small particles due to micrometeorite impacts. Pieters et al. (1993a) found that the <25 µm fraction accounted for ~25% of the bulk (<1 mm) material for several lunar soils, and that this ‘finest fraction’ dominated the spectral signature of the bulk soil. We note that this disproportionate effect for lunar soils was due partly to the effects of space weathering on such small particles and not caused solely by the smaller size of the particles (Pieters et al., 1993a).

Though space weathering and micrometeorite impacts are not dominant processes on Mars (due to the presence of a thicker atmosphere), other studies have shown that the presence of a large number of small particles or the coating of large particles by small particles will also dominate the spectral signature of mixtures whose mean particle size may be much larger (Adams and Filice, 1967; Aronson and Emslie, 1973; Pieters, 1983; Salisbury and Wald, 1992; Pieters et al., 1993a; Mustard et al., 1993; Pieters et al., 1993b). Therefore, the presence of fine particles in a mixture or natural surface can have an effect on the VIS-NIR spectral signature that is disproportionate to their volumetric abundance.

These effects were also observed in our three smallest size fractions of palagonite, all of which contain a significant number of small particles (which coat the larger particles in the larger size fractions) and have similar VIS-NIR reflectance spectra. Though we do not know the true particle size distributions for soils on Mars, images from the Viking, Pathfinder, and Mars Exploration Rover missions show that most rocks present on the surface are coated by fine-grained dust and have been etched, scoured, and pitted by weathering processes. An increase in surface roughness or surface asperities will increase the number of scattering surfaces and can cause a weathered rock to appear spectrally similar to smaller particles. At the opposite extreme, the ubiquitous airborne dust on Mars is <3 µm in diameter (Erard et al., 1994). Particles equal to or smaller than the wavelength of incident light cannot be modeled accurately by geometric optics and often exhibit scattering effects quite different than those discussed here (Mustard and Hays, 1997; Piatek et al., 2004). Fortunately, these small particles likely clump together to form larger aggregates on the surface (Ferguson et al., 1999; Moore et al., 1999), and Cooper and Mustard (1999) have shown that spectra of such materials are more representative of the aggregate particle size and not the smaller individual grains. Recent laboratory data by Piatek et al. (2004) for particulate samples of fine-grained material suggest similar results.

As mentioned previously, various bright and dark regions on Mars likely have different particle size distributions. Estimates of thermal inertia derived from Thermal Emission Spectrometer (TES) and Thermal Emission Imaging System (THEMIS) data can be used to constrain the particle size range of these regions (Mellon et al., 2000; Ruff and Christensen, 2002; Christensen et al., 2003; Putzig et al., 2005), but the solution is often nonunique. Thermal inertia values for bright, dusty regions are consistent with an average particle size <40 µm in diameter (Mellon et al., 2000; Christensen et al., 2003; Putzig et al., 2005), whereas low-albedo regions commonly have higher thermal inertia values, lower dust cover, and are consistent with a larger average particle size (Mellon et al., 2000; Ruff and Christensen, 2002; Putzig et al., 2005). How-
ever, Jakosky and Mellon (2001) and Putzig et al. (2005) showed that thermal inertia values were lower for the Viking lander sites than the Pathfinder site, even though images acquired on the surface suggest similar rock abundances. Therefore, it is difficult to uniquely determine the mean particle size or particle size range of surface materials from thermal inertia. Induration of surface materials, the presence of duricrust, and the particle size distribution of fines can affect the observed thermal inertia (Putzig et al., 2005) as well as the VIS-NIR reflectance spectra for complex natural surfaces.

With these considerations in mind, using thermal inertia to determine a mean particle size for different regions of Mars for use in our hydration model is somewhat impractical, especially when considering that it is the ‘effective’ particle size or particle size distribution that best describes reflectance spectra in the VIS-NIR (Hiroi and Pieters, 1992; Hiroi and Pieters, 1994; Mustard and Hays, 1997). Given that small particles will have a strong influence on reflectance spectra of mixtures and that natural surfaces may contain a large number of small particles and weathered rocks with surface asperities and small individual scattering facets, we believe our results for the <45 size fractions will provide reasonable estimates for the water content of many remotely sensed planetary surfaces, including many regions of Mars. An abundance of large smooth particles, decrease in surface roughness, or dearth of small particles will all decrease the validity of this assumption.

It is also worth noting that a decrease in porosity may cause a decrease in volume scattering, such that even small particles may be spectrally similar to larger particles if they are packed close together (Aronson and Emslie, 1973; Salisbury and Wald, 1992). This may be a reason why aggregates composed of individual small grains are spectrally similar to the size of the aggregate; groups of small particles may have a lower porosity when they are aggregates rather than a loose powder, thus interacting with photons as if they were larger particles. Any of these factors may lead to overestimating the water content by a factor of 2–3 based on the range of MOPL and ESPAT values observed for our samples (Figs. 4–5). Particulate samples measured in the laboratory are often dry sieved to a specific size range, making an accurate estimate of the mean particle size and ‘effective’ particle size more important. This is especially true for particles ~45–125 µm in diameter, which exhibit a significantly different ESPAT–H2O trends than smaller size fractions.

In an attempt to find a relationship between the slope of the ESPAT–H2O correlation and mean particle size, we fit a line to the data points corresponding to nonsaturated ESPAT values for each of the five nontronite size fractions (Fig. 9a). The slopes of these fits were then plotted against the mean particle size of each fraction, assuming any remaining small particles of nontronite would only increase the mean aggregate size and not act as ‘clinging fines’ (Fig. 9b). The same assumption is not possible for the palagonite, which is clearly dominated by fines in several size fractions and for which mean particle size is too unconstrained to determine a relationship with slopes of linear fits. The slope of the linear fit between ESPAT values and wt% H2O decreases exponentially as particle size increases (Fig. 9b). It appears that the slope approaches a constant value once particles become large enough that surface scattering is dominating the observed reflectance. The slope derived from this exponential fit will only be valid while the value of α⟨D⟩ for the water component is within the volume scattering region. That is, derived values of wt% H2O are only valid when the 3 µm band is not saturated. Hapke (1993) states that the volume scattering region corresponds to approximately α⟨D⟩ ≤ 3, which corresponds to a maximum ⟨D⟩H2O of ~2.5 µm for the 3 µm absorption for a maximum αH2O value of ~1.2 µm⁻¹. The exact value of ⟨D⟩ will depend on the true value of α for the water in the mineral, which likely varies for different mineral structures. Data for particle sizes of other minerals and rock powders are needed to determine if this exponential fit is unique or sample-specific.

6. Conclusions

We have calculated band parameters derived from reflectance and single scattering albedo spectra of the <25,
25–45, 45–75, 75–125, and 125–250 μm size fractions of nontronite (SWa-1) and palagonite (HWMK-101) for the 3 μm hydration band. The palagonite is complicated by the presence of clinging fines and changes in bulk composition with particle size, whereas the nontronite particles are aggregates of much smaller individual grains (<2 μm). Though particle size is not the only variable for different size fractions of these two materials, many natural surfaces are equally complex and we believe the textures of these samples are representative of materials that may exist on planetary surfaces such as Mars. We observe that increasing the particle size results in an increase in band parameter values for similar water contents, but none of the band parameters examined here exhibit a unique correlation to H2O content for the size fractions as a group for either material. The single scattering albedo MOPL and ESPAT parameters increase linearly with water content for all size fractions when α(D) is in the volume-scattering region and the 3 μm band is not saturated. All other parameters increase exponentially with water content.

Scattering theory predicts that absorption strength is dependent on both the absorption coefficient and mean path length. Our results suggest that converting reflectance spectra to single scattering albedo and removing the continuum does not isolate the 3 μm absorption feature of the H2O component in a hydrated mineral from the absorption and scattering effects of the non-H2O component. The mean path length of the H2O component is not equal when derived for different size fractions of a material with similar water content. Instead, it is related to the particle size of the host mineral. This is inherently different from our observations of modeling water contents of low-albedo mixtures. Both particle size and albedo will affect the relative proportions of absorption and scattering, but it is apparently easier to account for the effects of changing the absorption coefficient (e.g., adding a strong absorber such as carbon black) of a hydrated mineral or mixture than the effects of changing the path length (e.g., increasing or decreasing particle size). However, it is possible to determine a unique correlation between ESPAT values and water content if particle size and composition are well constrained. Thus the accuracy of this model can improve greatly for laboratory measurements under controlled conditions.

Combining our results for low-albedo mixtures and particle size separates, we find that a direct correlation between wt% H2O and single scattering albedo MOPL or ESPAT values exists over a wide albedo range if some estimate or assumption can be made for the effective particle size. Many planetary surfaces such as the Moon and asteroids likely have a large number of fine particles (<45 μm), which will in turn dominate spectral signatures due to the greater cumulative effects of their relative cross-sectional areas. This is observed in our palagonite size fractions of <25 μm, 25–45 μm, and 45–75 μm, all of which are spectrally similar, contain a large proportion of particles <5 μm in diameter, and follow the same ESPAT–H2O trend. The presence of bright and dark regions on Mars, however, implies that particle size distributions of surface materials may be quite variable. Impacts, dust storms, erosion by wind, and aggregation of fines will create and mobilize small particles on a global scale, thus we believe our data for small particle size fractions will be a viable analog for regions of Mars that contain a large number of fine particles or rocks coated with fine-grained dust. Future work will focus on combining VIS-NIR reflectance data returned by the OMEGA and CRISM spectrometers and estimates of particle size derived from thermal inertia with our hydration model. The methods presented in this paper are applicable to both laboratory and spacecraft data and we hope they will provide a valuable tool for evaluating the water content of Mars, asteroids, meteorites and the origin of hydrated materials in the Solar System.

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