

Effects of Very Fine Particle Size on Reflectance Spectra of Smectite and Palagonitic Soil

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A montmorillonite clay and a palagonitic soil sample were sieved to produce a series of size fractions in order to investigate the role that extremely fine particle sizes play on absorption strengths in martian analog materials. Significant decreases in band strength for both samples were observed as particle size decreased. The less than 5- μm fractions had 1.4-, 1.9-, and 2.2- μm bands that were approximately half the strength of the absorptions from the 45- to 75- μm size fractions. X-ray diffraction and loss on ignition measurements indicate that there are no significant changes in crystallinity, composition, or water content with particle size. Thus the reduction in spectral contrast is dominated by changes in the ratio of scattering to absorption with particle size. Furthermore, larger particles of montmorillonite clay are not individual crystals but are aggregates of much smaller particles. Nevertheless, the aggregate particles exhibit spectral properties consistent with the size of the aggregate, not the individual particles in the aggregate. This has important implications for the spectroscopic determination of the composition of the extremely fine martian dust. The abundance of very fine grained mineral phases such as phyllosilicates will be underestimated if comparisons to coarser or clumped laboratory samples are made.

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Key Words: Mars, surface; spectroscopy; mineralogy.

INTRODUCTION

It is well known that grain size affects the spectral characteristics of particulate materials (e.g., Lyon 1964, Lyon 1965, Vincent and Hunt 1968, Hunt and Vincent 1968, Pieters 1983, Crown and Pieters 1987, Gaffey *et al.* 1993). The classical example is the phenomenon of increasing albedo with decreasing particle size in weak absorbers (such as silicates) which stems from the increasing contribution of first surface scattering relative to volume scattering in very fine grained materials. Particle size also plays an important role in determining the strength of absorption features (cf. Hapke 1993), and this has important implications for the interpretation and understanding of remotely acquired spectral data.

The size of particulate matter will affect the strength of absorptions in two general ways. First, particles may have properties that affect the strength of absorptions and that, while not intrin-

sically linked to particle size, may vary as functions of particle size. Such properties include the composition of particles in naturally sorted soils, the amount of water adsorbed into the bulk particulate material, porosity, and the degree of crystallinity. Second, electromagnetic radiation will interact with particulate matter differently for different grain sizes as the ratio of surface to volume scattering changes (Hapke 1993). Also, as the sizes of particles begin to approach the wavelength of the light involved, the fundamental scattering behavior will change (van de Hulst 1957, Mustard and Hays 1997). These optical effects on absorption strengths are intrinsically linked to particle size. Both types of effects will be observed in any spectrum of very fine material, and it is therefore important to understand each effect independently to be able to compare laboratory and remotely acquired spectra.

In the case of Mars the surface may be dominated by very fine particles of dust (<5–10 μm). Thus the interpretation of near infrared water and hydroxyl bands and mid-infrared sheet silicate features must be grounded in a good understanding of the effects of extremely fine particle sizes on these spectral features. This study presents a careful analysis of the spectra of two spectral analogues of martian soil, a montmorillonite clay and a natural palagonitic soil from Hawaii. Both materials show broadly similar spectral characteristics in the near and mid-infrared. Analysis of the spectra of a variety of particle size fractions of each material under both ambient and purged (dry) conditions gives a good understanding of the systematic variations in spectra and the impact that particle size effects have on identification of martian surface materials from remotely acquired spectra. The purpose of this paper is to show that the strength of hydroxyl and water bands are dependent on the size of the particles being measured and are weaker with smaller particle sizes.

BACKGROUND

The silicate fraction is perhaps the most poorly constrained component of martian soils, yet it is essential when trying to understand the processes of weathering and alteration on the planet. The accurate characterization of this component is therefore critical. Smectite clays have long been regarded as good candidates

for the silicate component of the fine-grained martian dust. They have been observed in the SNC meteorites (Gooding *et al.* 1991), have been predicted as the alteration product of silicate glass based on thermodynamics (Gooding and Keil 1978), are present as minor components in some palagonitic soils (e.g., Golden *et al.* 1993), and match the elemental composition of the soil measured at the Viking lander sites (Baird *et al.* 1977). In terms of reflectance spectroscopy, iron-substituted smectite clays provide a good match to the visible to short wavelength infrared (0.4 to 1.2 μm) spectral properties of Mars (Banin *et al.* 1985, Bishop *et al.* 1993). However, in the near infrared most martian spectra lack a key feature that is characteristic of smectites, the 2.2- μm absorption due to a combination of stretching and bending of structural OH^- and metal-OH bonds. On the other hand, more recently acquired spectra appear to exhibit weak 2.2- μm features (Clark *et al.* 1990, Bell and Crisp 1993, Murchie *et al.* 1993, Beinroth and Arnold 1996). In order to determine the surface mineralogy of the planet, it is important to understand whether this absorption feature is missing due to the absence of smectite clays (e.g., Singer 1979, McCord *et al.* 1982) or instead is inherently weak and/or partially masked in character (e.g., Bishop 1993, Burns 1993, Bishop *et al.* 1998).

A typical smectite reflectance spectrum (SWy-1 montmorillonite) is shown in Fig. 1. In the near-infrared (NIR) region of the spectrum, smectite clays exhibit a number of absorption bands related to the presence of water and hydroxyl groups in and on the structure of the crystal lattice and mineral surfaces. The features at 1.4 and 1.9 μm are due to combinations of absorptions due to the vibrations of adsorbed and bound molecular water, with a contribution to the 1.4- μm feature from structural hydroxyl groups, while the feature at 2.2 μm is due solely to hydroxyls.

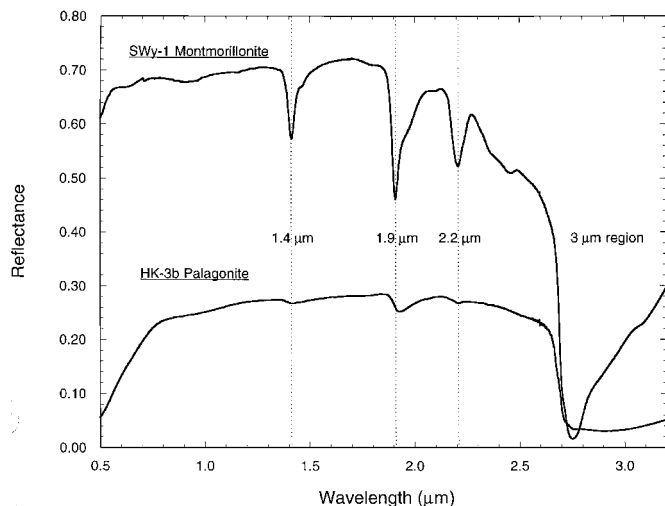


FIG. 1. A comparison of the near infrared reflectance spectra of the 25–45 μm size fractions of SWy-1 montmorillonite and HK-3b palagonitic soil showing the locations of near infrared absorption features discussed in the text. Spectra were obtained in the RELAB and Nicolet FTIR spectrometers and were spliced and scaled to the RELAB reflectance values at 2.3 μm . Absorptions are overtones and combinations that come from water and hydroxyl functional groups as listed in Table I.

TABLE I

Wavelength (μm)	Vibrational assignment
1.41	$2\nu_{\text{OH}}$
~ 1.41	$\nu'_{\text{w}} + 2\delta_{\text{w}}$
1.46	$\nu_{\text{w}} + 2\delta_{\text{w}}$
1.91	$\nu'_{\text{w}} + \delta_{\text{w}}$
1.97	$\nu_{\text{w}} + \delta_{\text{w}}$
2.20	$\nu_{\text{OH}} + \delta_{\text{AlMOH}}$
2.70	ν_{M2OH}
2.75	ν_{AlMOH}
2.76–2.78	ν'_{w3}
2.82–2.84	ν'_{w1}
~ 2.90	ν_{w3}
2.94–2.99	ν_{w1}
~ 3.10	$2\delta_{\text{w}}$

Note. Band assignments for water and hydroxyl for SWy-1 montmorillonite from Bishop *et al.* (1994). Vibrational assignments refer to stretching (ν) and bending (δ) modes. The subscripts w and OH refer to molecular water and structural hydroxyl groups, respectively. Al and M refer to aluminum and metal cations in the montmorillonite structure. The primed symbol ν'_{w} denotes stretching vibrations due to bound water, while unprimed ν_{w} are vibrations due to adsorbed water.

Martian spectra typically lack all three of these near-infrared absorptions but do exhibit a broad, strong absorption in the 3- μm region (e.g., Moroz 1964, Houck *et al.* 1973, Bibring *et al.* 1990, Calvin 1997). The numerous overlapping absorptions in this region are due to water and hydroxyl vibrations. Specific band assignments were studied by Bishop *et al.* (1994) for the near infrared absorptions in this particular clay and are listed in Table I. They found that changes in the amount of adsorbed water can strongly influence the strength and character of the 1.4- and 1.9- μm absorptions. Laboratory measurements of particulates under different environmental conditions or even on different days can be affected by variations in the amount of adsorbed water. The effects of this differential adsorption are twofold: absorptions due to vibrations in water molecules will be strengthened, and the location of the reflectance minima for these bands will shift. Shifts in band minima are due to the different coordination (and hence energy) environments around water molecules and have been documented for clays by Bishop *et al.* (1994), while effects of atmospheric pressure and composition on the strength of absorptions is explored by Bishop and Pieters (1995).

Recent Earth-based spectra (Clark *et al.* 1990, Bell and Crisp 1993) and spectra from the ISM NIR imaging spectrometer on the Russian *Phobos 2* spacecraft (Murchie *et al.* 1993) suggest that a weak absorption feature does exist around 2.2- μm . However, Dalton and Clark (1995) determined that the strength of this feature corresponds to not more than 0.5–1.0% clay by weight on the surface of Mars based on laboratory mixing studies. This abundance is clearly less than the 20–80% predicted on the basis of thermodynamics and the chemistry of martian soil (Banin *et al.* 1992).

Several explanations for the lack of the 2.2- μm feature in spectra of Mars have been proposed. First, many researchers believe that the dust is simply not smectite clay and prefer as analogs palagonitic soils with low abundances of phyllosilicates (Singer 1982, Morris *et al.* 1993). Palagonitic soils are an amorphous weathering product of basaltic glass that often have a similar bulk chemical composition to smectite clay-iron oxide/oxyhydroxide mixtures. Their mineralogy in general is variable and may reflect starting composition and the weathering environment (e.g., Singer 1982, Crisp and Bartholomew 1992, Orenberg and Handy 1992, Golden *et al.* 1993, Bishop *et al.* 1998). Visible to near infrared spectra of many palagonitic soils are close matches to remotely acquired spectra of Mars. Many of these samples have well-developed water features (1.4- and 1.9- μm absorptions) and often exhibit weak 2.2- μm absorptions due to the presence of smectite clays, allophane, or incipient phyllosilicates (e.g., Crisp and Bartholomew 1992, Orenberg and Handy 1992, Golden *et al.* 1993, 1998). The amorphous portion of Hawaiian soils is converted with time into phyllosilicates and other crystalline alteration products (Vitousek *et al.* 1997). In this light, the silicate portion of palagonitic soils may represent the amorphous or poorly crystalline endmembers of a continuum of crystallinities.

Second, a variety of methods of suppressing the 2.2- μm absorption in soils with abundant smectite have been proposed. Burns (1993) proposed that oxidized clays with O^{2-} substituted for OH^- should exhibit weakened structural hydroxyl absorptions. Mixtures of smectite clays with ferrihydrite or carbon black have been shown to exhibit diminished spectral contrast (Bishop *et al.* 1993). However, such physical mixtures fail to simultaneously match the albedo and spectral contrast observed in spectra of Mars across all wavelengths.

Third, a simpler explanation for the lack of observed hydroxyl features in the martian spectra that has not been fully examined is the role of particle size. As stated above, particle size plays a dominant role in determining albedo and spectral contrast of all materials, and additional effects are observed for extremely fine particles (Mustard and Hays 1997). While estimates of particle size for dust on Mars are not well constrained from material properties experiments carried out by landed spacecraft (dust diameters 2–10 μm , Moore *et al.* 1987; <10–18 μm , Ferguson *et al.* 1999; <40 μm , Moore *et al.* 1999), studies of aerosols provide tight constraints for the effective radii of airborne dust particles that range from 1.2 to 2.5 μm (Erard *et al.* 1994, Pollack *et al.* 1995, Tomasko *et al.* 1999). Studies of spectra of particulates coated with finer materials have shown that the finest fraction dominates the spectral properties of the bulk particulate (Salisbury *et al.* 1994, Johnson *et al.* 1998). Therefore, if a significant fraction of the number of particles on the martian surface is less than a few micrometers in size, the interpretation of remotely acquired spectra, either reflectance spectra in the visible to near infrared or emission spectra in the mid-infrared, will have to account for this extremely fine nature of the omnipresent dust.

The small particle sizes found in the martian dust will certainly affect the spectrum of light reflected or emitted from the surface.

Regardless of the actual composition of dust, it will have weaker absorption features than will coarser materials of the same composition measured in the laboratory. It is the understanding of this particle size effect and its impact on the interpretation of martian spectra that is of interest to us here, not the advocacy of a particular soil composition. By using both a smectite and a palagonitic soil in this laboratory study, we demonstrate the particle size weakening of near-infrared absorptions for both (1) well crystalline, mono-mineralic samples and (2) natural, poorly crystalline, polymineralic basalt alteration products.

EXPERIMENTAL METHODS

The preparation of very fine particle size separates through grinding and sieving may not adequately parallel natural processes for the production of fine grained particles. Light mechanical grinding will simply reduce large crystals to smaller sizes while maintaining their crystalline properties. In contrast, prolonged grinding may alter some minerals through frictional heating, such as the transformation of goethite to hematite reported by Rendón and Serna (1981). In addition, during grinding smaller naturally occurring particles with potentially different crystal properties may be mixed with the ground particles, producing an artificial, unrepresentative set of size fractions. Each of these effects of grinding combine to produce a set of particle sizes that are unlike those produced in natural weathering processes. In nature, crystallinities at different particle sizes may vary, with smaller fragments being less ordered than larger fragments. Alternatively, small pieces of glass may alter and crystallize more completely than larger pieces, producing more order in fine fractions. Analysis of artificially created particle size separates may therefore be misleading in assessing the strengths of absorption features in spectra of natural materials. Thus, rather than grinding and sieving, we simply sieved the two samples to separate the naturally occurring particle size fractions.

Our first sample was a smectite clay from the Clay Minerals Society, Source Clay Minerals Repository, sample SWy-1, a (Na, Ca) montmorillonite from Wyoming. The second sample was a palagonitic soil from Haleakala, Hawaii (sample HK-3b). The original sample contained unaltered basaltic glass as well as palagonitized material. Passing this material through a 250- μm sieve removed most of the darker (presumably less altered) material visible in the unsieved sample. These two materials exhibit broadly similar spectral properties (Cooper and Mustard 1997a, 1997b), suggesting that they differ in their degree of crystallinity but not in their basic coordination chemistry. The similarity in infrared spectra indicates that the types of bonds in the two materials are similar. In particular, the presence of a 2.2- μm absorption in the palagonitic material indicates that metal cations are bonded with OH^- ligands. Also, the shape of the 20- μm absorptions indicates silicon-oxygen coordination similar to that seen in montmorillonite (Farmer 1974, Cooper and Mustard 1997b). While the two materials probably incorporate the same bonds on a local scale, over larger scale lengths, they must have a very different degree of ordering, with the montmorillonite

being very crystalline and the palagonitic soil being poorly ordered. These properties match the observations of smectites and incipient phyllosilicates in other palagonite samples (Golden *et al.* 1993, 1998).

Both the palagonitic soil and the montmorillonite were sifted into particle size separates. Most previous studies of particle size effects have used particles sieved to less than 75 or 45 μm diameter for the finest fraction, the reason being that size distributions of particulates typically have a numerical majority of very fine (less than 5 micrometers) particles (Crown and Pieters 1987, Salisbury and Walter 1989, Salisbury and Wald 1992, Bishop *et al.* 1994). This study utilized more tightly defined particle diameter ranges to investigate the weakening of spectral contrast in greater detail. The size fractions for the palagonitic soil were 250–150, 150–75, 75–45, 45–25, 25–10, 10–5, and <5 μm , while for the montmorillonite, only fractions smaller than 75 μm were obtained. These size fractions were separated by passing the dry bulk materials through a series of wire and electroformed mesh (5, 10, and 15 μm) sieves purchased from the Gilson Company. Sieving was preferred over sedimentation because the particle sizes calculated using Stokes's Law are assumed to be those of spherical particles. Nonspherical particles such as clays settle more slowly than spherical particles of the same physical size. This leads to a calculated equivalent spherical diameter smaller than the actual size of the particle. Sieving does not underestimate particle sizes and better represents the physical dimensions of nonspherical particles. Because the interaction of light with particulate material depends critically upon the physical dimensions of the particles, we feel that sieving produces particles with nominal sizes that are a better match to the sizes that electromagnetic radiation "sees" when it interacts with these particles.

The sieve stack was placed in a Vibratory sieve shaker that has a built-in tap function to prevent the sieves from clogging. The sieves were periodically inspected visually for clogging and cleared when necessary. Microscopic observations of the palagonitic soil samples under reflected light showed that there were relatively few clinging fines, so samples were not washed. Similar success in removing clinging fines for some soils has been achieved by Johnson *et al.* (1998). However, the fine montmorillonite samples did have finer clinging particles, so they were wet sieved with ethanol. The larger size fractions of montmorillonite appeared to be spherical aggregate particles under low magnification in reflected light. These large particles deformed and disaggregated readily when compressed by a spatula. In contrast, the palagonitic soil particles were primarily single grains in each size fraction. Throughout this paper, we refer to the size of the particles that were separated by the sieving process, recognizing that for montmorillonite these are in fact aggregates of smaller particles. The implications for our analyses are treated in the discussion section.

For analysis, the midpoint of the particle size range defined by the sieve mesh size was used as the effective particle size. Previous work using these sieves with similar sample prepara-

tion methods (Mustard and Hays 1997) has shown that sieving produces a Gaussian distribution of particles with a volumetrically weighted mean that is well approximated by the midpoint of the particle size range.

Particle size fractions of both palagonitic soil and montmorillonite samples were characterized by x-ray diffraction measurements performed by D. C. Golden on a Scintag XDS2000 x-ray diffractometer using random powder mounts. A copper radiation source was used, and results were converted to lattice d spacings in nm using the Bragg equation. By constraining the mineralogical composition of the size fractions, we can assess whether changes in spectral properties with decreasing particle size are due to changes in mineralogy.

Reflectance spectra from each sample were obtained in the RELAB facility at Brown University (Pieters 1983). A Nicolet FTIR spectrometer was used to obtain data over the wavelength range from 0.9 to 26.0 μm relative to a diffuse gold standard. The atmosphere in the Nicolet sample chamber was purged of H_2O and CO_2 for 12 h with dry N_2 gas, which in addition to removing infrared active gasses from the atmosphere, also dried the samples in the chamber. Reflectance spectra were also obtained over the wavelength range from 0.35 to 2.6 μm using the RELAB bidirectional reflectance spectrometer that operates in an ambient atmosphere (Pieters 1983, Mustard and Pieters 1989). The environmental conditions in the room were controlled by air-conditioning and dehumidification and were stable over a measurement but may have varied from day to day. The standard viewing geometry of $i = 30^\circ$, $e = 0^\circ$ was used. The difference in atmospheres between the two spectrometers allows a comparison between changes in absorptions due to varying amounts of adsorbed water and effects that arise solely from the interaction of light with fine particulate material.

Additional information on the water and hydroxyl content of the samples was obtained from loss on ignition measurements. Crucibles were washed, oven-dried, and weighed and then had samples placed in them. Following weighing in the crucibles, the samples were dried in a convection oven for 14 h at 100°C to remove adsorbed water. These samples were then weighed again to find the mass of lost adsorbed water. Following this, samples were ignited in a muffle furnace for 4 h at 950°C . The calculated mass lost after ignition represents the volatile components of the samples including any organics present, any trace carbonates, and the bound water and hydroxyl in the samples.

Samples were prepared for reflectance measurements by filling sample holders, tapping the holder to cause the sample to settle, and then adding more material. This was repeated until the material did not settle anymore. Then additional material was added to the sample holder, and the surface was scraped by a straight-edged spatula angled away from the direction of motion to prepare a uniform textured, randomly oriented, non-packed surface.

Band strengths were calculated by first fitting a linear continuum over the region on either side of an absorption. The band strength is the difference between the continuum reflectance and

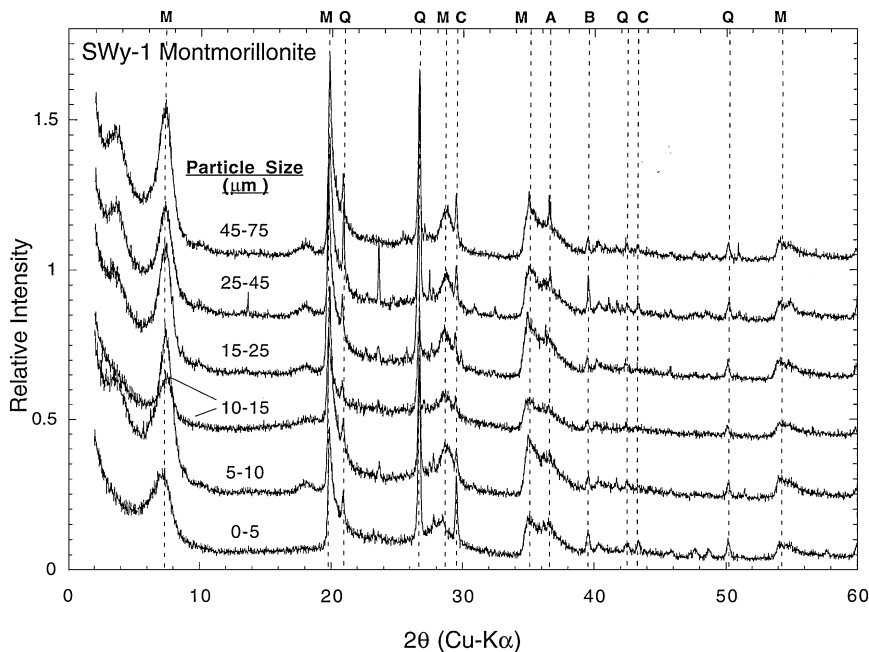


FIG. 2. X-ray diffraction spectrum of SWy-1 montmorillonite samples as a function of diffraction angle 2θ . Spectra are offset for clarity with coarsest size fraction (45–75 μm) at top, finest (0–5 μm) at bottom. Large, broad peaks are due to montmorillonite (M). Smaller peaks are due to contaminants calcite (C) and quartz (Q). Overlapping peak at $\sim 36.5^\circ$ (A) is montmorillonite and quartz. Overlapping peak at $\sim 39.5^\circ$ (B) is quartz and calcite.

the measured reflectance at the band minimum divided by the continuum reflectance (Clark and Roush 1984).

RESULTS

XRD

X-ray diffraction measurements of the montmorillonite are shown in Fig. 2 and display nearly constant diffraction patterns. Broad smectite peaks dominate the spectrum, while contamination from minor amounts of calcite and quartz is indicated by the weak but sharper peaks. Contamination levels appear fairly constant and are not a function of particle size. A weaker broad line around $3.6^\circ 2\theta$ (d spacing of ~ 2.4 nm) is apparent in all samples except for the 0–5 and 10–15 μm diameter size fractions, although the 10–15 μm fraction does show a subtle rise along the continuum. This line may result from the presence of corrensite, a chlorite/smectite mixed layer clay that has a basal spacing of approximately 2.2 nm (Moore and Reynolds 1997). The 0–5 and 10–15 μm size fractions also have slightly weaker clay features than the other fractions. These two size fractions had a very limited amount of sample available, and the weaker clay features are probably a measurement artifact, although they could also be due to a lower degree of crystallinity. The lack of any trend across all particle size ranges indicates that neither composition nor crystallinity controls the systematic changes in near infrared band strengths with particle size in montmorillonite. Additionally, measurements of the FWHM of the basal peak at $7.4^\circ 2\theta$ were made for each of the size fractions. Peak widths are $1.18 \pm 0.03^\circ 2\theta$ excluding the 0–5 μm fraction, which

has a peak width of $1.72^\circ 2\theta$. With the exception of the finest size fraction, there is no trend in the width of the peak, indicating that the crystallinity is not changing.

The palagonitic soil sample does exhibit some compositional sorting with particle size. The XRD patterns in Fig. 3 show that minor amounts of plagioclase, pyroxene, and spinel (Fe, Ti-magnetite) appear in all samples, with a slightly greater concentration in the coarser fractions. Because these materials do not exhibit water- and hydroxyl-related near infrared absorptions, any decreases in the small amounts present in the finer size fractions will not weaken the near infrared spectral features. A peak attributable to incipient phyllosilicates at a d spacing of 0.44 nm ($2\theta = 20.15^\circ$) (Kawano *et al.* 1997, Golden *et al.* 1998) is observed in all palagonitic soil size fractions. No well-crystalline smectites are observed. Weak, broad peaks near 0.25 and 0.15 nm (35.88° , 62.4°) have been interpreted by Morris *et al.* (1993) as being due to nanophase ferric oxides or ferrihydrite. Although sharper peaks due to spinel overlap these peaks, the broad peak appears to be nearly constant in strength in all of the size fractions, while the sharper spinel peaks decline, strengthening the ferric oxide assignment. A very broad rise around 0.37 nm (24°) in the XRD spectra of the two finest size fractions is probably due to allophane (Farmer 1997), which was also observed in other palagonite samples by Golden *et al.* (1998). However, no broad allophane peak near 0.23 nm (39°) is seen. So although the two finest size fractions of the palagonitic soil may have a slightly larger proportion of poorly crystalline allophane in them, no continuous trend in crystallinity is seen across all of the particle size fractions.

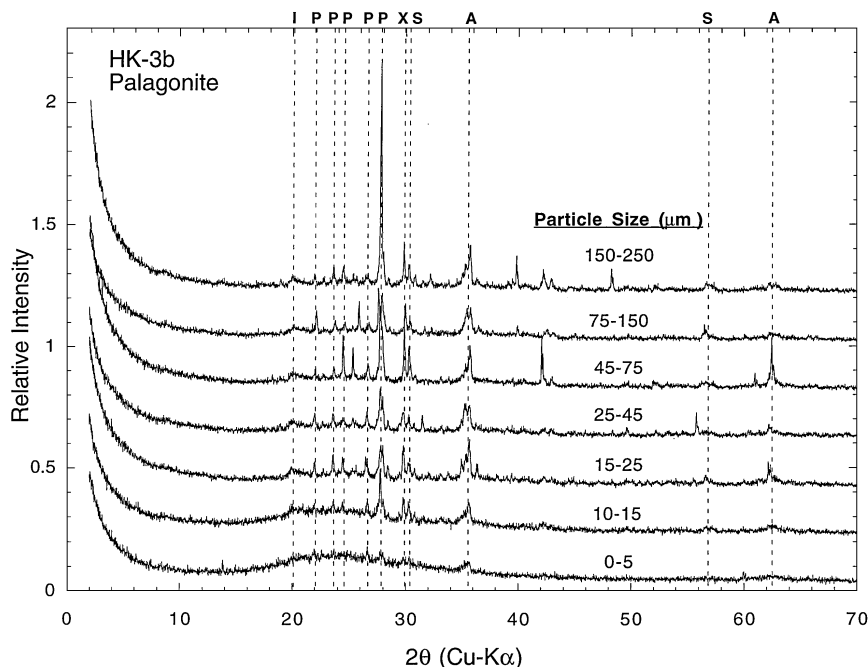


FIG. 3. X-ray diffraction spectrum of HK-3b palagonitic soil samples as a function of diffraction angle 2θ . As in Fig. 1, the coarsest size fraction (150–250 μm) is at the top, the finest (0–5 μm) is at the bottom. Spectra are offset for clarity. Peaks due to various minor phases including plagioclase (P), pyroxene (X), magnetite/spinel (S), nanophase iron oxides (O), incipient phyllosilicates (I), and a combination of spinel and nanophase oxides (A). The very broad peak near $24^\circ 2\theta$ in the two finest fractions has been attributed to allophane (Golden *et al.* 1998).

Near-Infrared

In the near-infrared (NIR) region of the spectrum, clays exhibit a number of absorption bands related to the presence of water and hydroxyl groups in and on the structure of the crystal lattice. Spectroscopic analysis of the palagonitic soil reveals similar absorptions not only at 1.4 and 1.9 μm where physically bound water is also important but also at 2.2 μm (Fig. 1), demonstrating that metal- OH^- functional groups are being formed in the palagonitic soil. Compared to montmorillonite, all of the absorptions in this region are considerably weaker and less well defined in the palagonitic soil. The 1.4- and 1.9- μm bands are rounded and relatively symmetric compared to the same montmorillonite features.

Figure 4 shows the variations in the near infrared band strengths as a function of particle size. Each band decreases monotonically in strength with decreasing particle sizes for both materials when measured in a purged environment. Under ambient conditions, the RELAB data show the same results for the palagonitic soil with continuous decreases in band strength down to the smallest fraction. In the case of the montmorillonite, though, the trends in band strength are more variable. The 5–10 and 10–15 μm particle size fractions have stronger 1.4 and 1.9 μm bands superimposed on an otherwise decreasing trend. In contrast to the two water bands, the montmorillonite 2.2- μm OH^- absorption does decrease monotonically in strength as particle size decreases.

The deviation in the trend for the 1.4- and 1.9- μm bands may be explained by variation in the humidity between the days the samples were measured. The three smallest particle size fractions were measured on a different day from the three larger size fractions and may have experienced different, presumably moister, environmental conditions at the time of measurement. Although environmental conditions were not recorded on the days when spectral measurements were taken, the behavior of the three near-infrared bands is consistent with environmental moisture variations. Since the 2.2- μm absorption is caused by structurally bound OH^- and metal- OH bonds, it should not be directly affected by the humidity of the environment. Secondary changes in the band strength may result however from changes in the longer wavelength continuum around the band by the broader 3- μm water absorption (Bishop *et al.* 1998). The fact that the 2.2- μm band does not show the same anomalies in RELAB measurements as the other two bands supports the hypothesis that the anomalies in the 1.4- and 1.9- μm band strengths are due to changes in adsorbed moisture caused by environmental conditions. Furthermore, since the 1.4- μm band is caused by combinations of water and hydroxyl absorptions, it should be less affected by environmental differences than the 1.9- μm band, which is due to water only. These systematics in 1.4- and 1.9- μm band strengths clearly illustrate both the importance of environmental conditions on the character of reflectance spectra and the role of particle size in determining band strength, as noted by other workers (*i.e.*, Bishop *et al.* 1993). The 2.2- μm

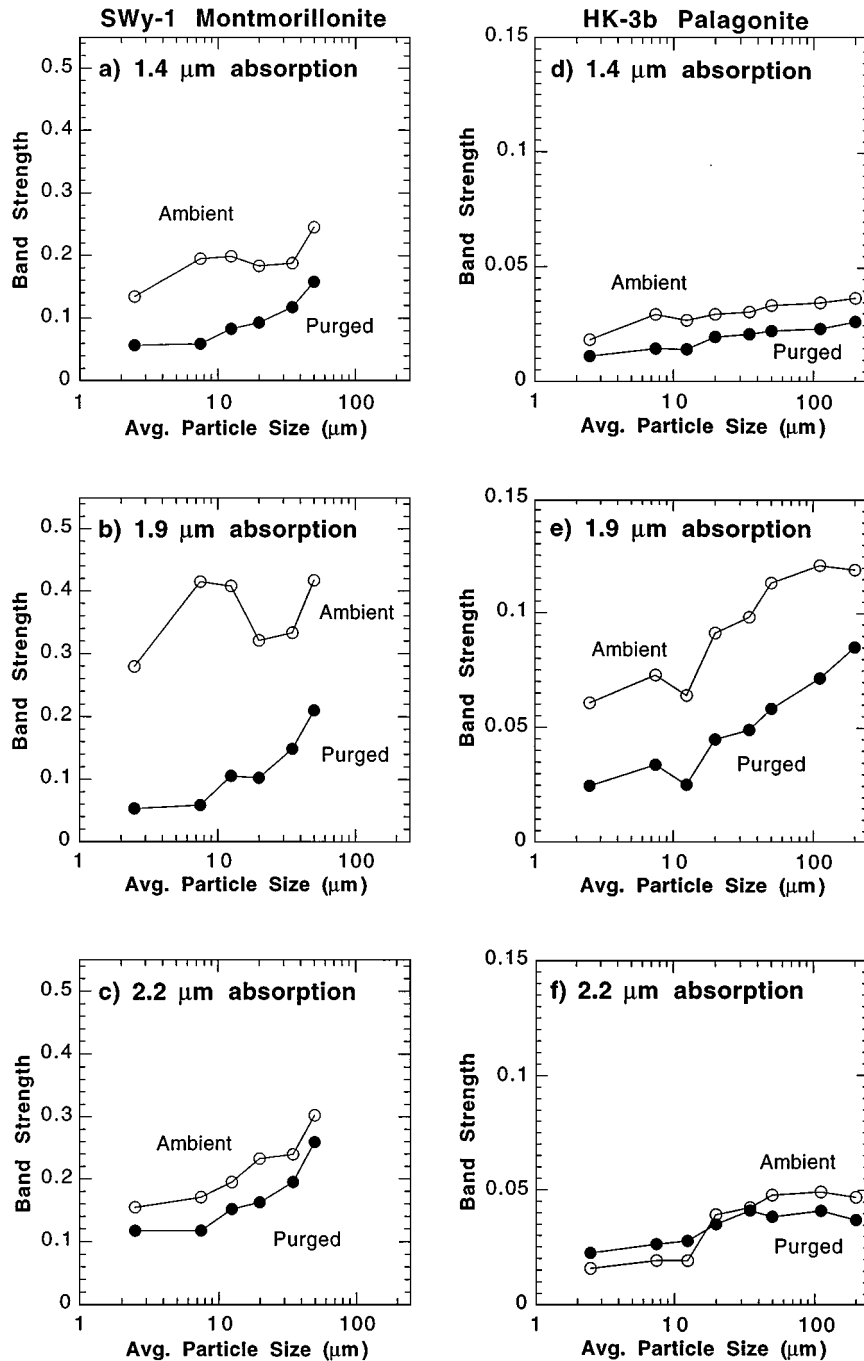


FIG. 4. Behavior of near infrared absorption band strengths in both ambient and purged environments as functions of particle size. SWy-1 montmorillonite 1.4, 1.9, and 2.2 μm bands are shown in (a)–(c), HK-3b palagonite bands in HK-3b palagonitic soils are shown in (d)–(f). Note difference in scale between montmorillonite and palagonitic soil band strengths.

band illustrates the particle size trend that is otherwise obscured in the shorter wavelength absorptions.

Measurements in the purged (Nicolet) and unpurged (RELAB) environments show considerable differences in the strength of the 1.4- and 1.9- μm bands of both the montmorillonite and palagonitic soil (Fig. 4). At all particle sizes, the 1.4- and 1.9- μm bands are weaker when measured in the dry, purged

atmosphere of the Nicolet instrument. However, the 2.2- μm band exhibits relatively little decrease in strength between the purged and unpurged measurement conditions. The variations in the strength of the 2.2- μm band are thus not due to changes in the amount of adsorbed water but are instead due to instrumental differences. The biconical reflectance measurement of the Nicolet may contain a greater Fresnel component than the bidirectional

reflectance of the RELAB instrument. This will decrease contrast and thus band strengths in the Nicolet. However, it should affect all particle sizes equally and would not contribute to trends seen related to particle size. Because the $2.2\text{-}\mu\text{m}$ band exhibits a relatively small decrease in strength in the purged compared to the ambient environment, we feel that the larger part of the decreases in band strength of the 1.4- and $1.9\text{-}\mu\text{m}$ absorptions between RELAB and Nicolet measurements is due to the purged nature of the measurement. The variations in the strength of the $2.2\text{-}\mu\text{m}$ band are due to greater Fresnel reflectance in the Nicolet. These general observations agree with the expectation that in the purged environment samples will lose adsorbed water, and therefore the absorptions caused by water at 1.4 and $1.9\text{ }\mu\text{m}$ will decrease in strength while the hydroxyl absorptions will be unaffected.

LOI

As a first hypothesis, it could be thought that differences in water and hydroxyl content among the samples could control the particle size trend in band strengths. Finer particles could have proportionally more water adsorbed on the larger surface area. To address this possibility, measurements of loss on ignition (LOI) for each sample were performed.

The montmorillonite samples lost $7.3 \pm 0.9\%$ mass on drying at 100°C with no dependence on particle size. Similarly, the palagonitic soils had a $6.1 \pm 1.3\%$ mass loss on average with no relation to particle size. Loss on ignition was also independent of particle size for both samples. The montmorillonite lost another $7.2 \pm 0.9\%$ mass relative to the dry mass after ignition at 950°C , while the palagonitic soil lost $14.6 \pm 1.4\%$. The amount of adsorbed water was measured on multiple days to test whether it was dependent on the humidity in the atmosphere. On a cool, dry day the amount of adsorbed water lost was around 6.8% for the montmorillonite and 5.2% for the palagonitic soils, compared with the above numbers which were measured on a hot, damp day.

The independence of LOI and particle size show that the decreases in $2.2\text{-}\mu\text{m}$ band strength cannot be due to a lower abundance of hydroxyl species in the finer size fractions. Furthermore, the 1.4- and $1.9\text{-}\mu\text{m}$ bands also decrease in strength at finer particle sizes for a reason other than water content as neither the adsorbed water content nor LOI decreased at the finer particle sizes. However, the variations in the trend of decreasing strength in the RELAB measurements on the two days of measurements could reasonably be due to variations in atmospheric humidity as this does affect the amount of adsorbed water on these samples.

Mid-Infrared

Mid-infrared spectra were measured in the Nicolet spectrometer. Small sample sizes hampered some measurements, but enough good spectra were obtained to illustrate the effects of particle sizes on band strengths in this wavelength region. The

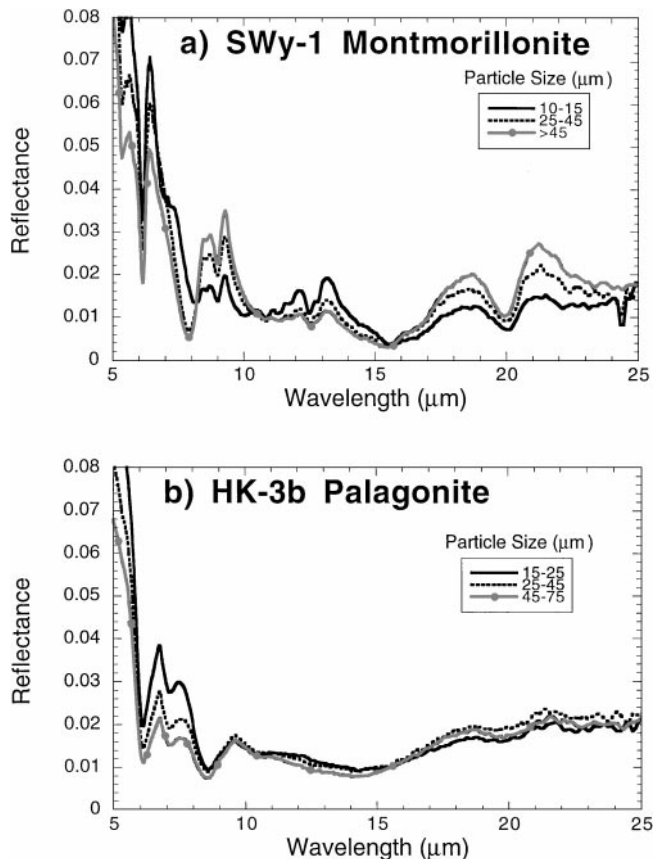


FIG. 5. Comparison of the mid-infrared spectra of three particle size separates of (a) Swy-1 montmorillonite and (b) HK-3b palagonitic soil. Note the gross similarity in spectral shapes of the two materials and the decrease in spectral contrast in the $8\text{-}10$ and $16\text{-}24\text{ }\mu\text{m}$ ranges.

HK-3b palagonitic soil shares some general spectral properties in the mid-infrared with montmorillonite (Fig. 5). Both materials exhibit a broad absorption at $6\text{ }\mu\text{m}$, which is due to the H–O–H bending vibration (Salisbury *et al.* 1991). Superimposed on this are sharper individual absorptions due to metal–hydroxyl species. Both the montmorillonite and the palagonitic soil have a Christiansen feature near $8\text{ }\mu\text{m}$, where the feature occurs at wavelengths longer than $8\text{ }\mu\text{m}$ in the palagonitic soils and at wavelengths just short of $8\text{ }\mu\text{m}$ in the montmorillonite. Reststrahlen bands that decrease in strength as particle size decreases are seen between 9 and $10\text{ }\mu\text{m}$ in the spectra of the palagonitic soil, while they are located between 8 and $10\text{ }\mu\text{m}$ in the case of the montmorillonite. These bands are attributed to asymmetric Si–O–Si stretching vibrations (Salisbury *et al.* 1991). Volume scattering is observed in both materials between 11 and $14\text{ }\mu\text{m}$, as is evidenced by the increase in reflectance with decreases in particle size. Absorptions in this region are due to $M_2\text{OH}$, Si–O–Si, and Al–O–Si vibrations (M = cation, Farmer 1974, Salisbury *et al.* 1991) and give structure to the transparency region. The sharp features between 12.5 and $13\text{ }\mu\text{m}$ are due to silica or quartz contaminants which are also seen in XRD. However, both the reststrahlen and transparency bands in the palagonitic soil

are much broader and less structured than their counterparts in the montmorillonite spectra. At 20 μm there is a double-humped feature that decreases in contrast with decreasing particle size for both montmorillonite and the palagonitic soil. The half at 18.9 μm is due to an Al–O–Si vibration and the half at 21.3 μm is due to a Si–O–Si vibration (Farmer 1974, Madejova *et al.* 1993). The gross similarities between the mid-infrared spectra of the palagonitic soil and the montmorillonite and comparisons with other montmorillonite spectra (van der Marel and Beutelspacher 1976, Madejova *et al.* 1993, Piatek and Christensen 1998) suggest that silicon–oxygen coordination is similar in the two materials.

The kinds of spectral changes with particle size seen in these samples are similar to those documented by Mustard and Hays (1997) in quartz and pyroxene. A general trend of decreased spectral contrast in finer particulates is observed across most of this wavelength range. In particular, the weakening of the restrahlen bands and the 20- μm feature would make spectroscopic detection of clays more difficult for fine particle sizes, particularly when comparisons to unsieved samples are made.

DISCUSSION

The observed decreases in near-infrared band strengths with decreasing particle size could be due to changes with particle size of mineral composition, adsorbed water content, crystallinity, or optical behavior. If the varying interaction of photons with different size particles is the dominant phenomenon, then interpretations of remotely acquired martian spectra should include the effects of particle size. These effects can play an important role in quantitative mineralogical abundance measurements as they may lead to underestimation of the amount of an absorbing species (such as clay minerals) in fine particulates due to the optically weaker absorptions. In order to verify that particle size is optically affecting the band strengths, the other possible sources of weaker band strengths must be ruled out.

Composition

The near-infrared band strength decreases are not caused by changes in the mineralogical composition of either material as a function of particle size. The XRD patterns for montmorillonite confirm that the composition of this reference clay is essentially constant at all particle sizes. No fundamental dilution or contamination of the clay in the finer particle sizes is seen, nor is any evidence for a lower degree of crystallinity present. This clearly means that the band strength decreases in the finer fractions are due to another cause.

The observed decreases in the band strengths for the palagonitic soil are also not due to compositional variation with particle size. Although some contaminant phases (plagioclase, pyroxene, and magnetite) are linked to particle size, these contaminants decrease in abundance as particle size decreases and thus cannot cause the 1.4-, 1.9-, or 2.2- μm bands to weaken in the finest fractions. Because these minerals are anhydrous, the only influ-

ence they would exert on water and hydroxyl absorptions would be to dilute their strengths when larger quantities of the contaminant phases are present. This would, if anything, decrease the band strengths in the *coarser* size fractions which contain more unaltered contaminant minerals, exactly the opposite phenomenon as observed. However, it is likely that no dilution is occurring because of the relatively small changes in abundance with particle size.

Crystallinity

The XRD data show that crystallinity does not change with particle size in either the montmorillonite or the palagonitic soil. The increase in an amorphous allophane phase in the two finest fractions of the palagonitic soil could dilute its near infrared bands, but no changes in the allophane content are observed in any of the other size fractions. Since the reference clay exhibits the same band strength decreases and appears to be uniformly crystalline (constant XRD peak widths) across all particle diameter ranges greater than 5 μm , factors other than crystallinity must dominate the changes in band strength in these materials.

Water Content

The 1.4- and 1.9- μm absorption bands are each composed of multiple absorptions that arise from bending and stretching vibrations and overtones of molecular water (and structural OH⁻ in the case of the 1.4- μm band). The molecular water may be in the form of molecules that are coordinated to the metal cations in the clay structure, or they may be hydrogen bonded to either the mineral surface or to other water molecules. The energy associated with a vibrational mode will vary depending on how the water is bound. Bishop *et al.* (1994) demonstrated that water molecules coordinated to metal cations in montmorillonite have a higher energy absorption (shorter wavelength) than the absorption arising from water that is hydrogen-bonded to other water molecules (physisorbed water). A summary of their band assignments appears in Table I.

In more humid environments where larger amounts of water are adsorbed to the surfaces of the clay particles, strong, broad, longer wavelength absorptions develop around 1.46 and 1.97 μm . Figure 6 shows the 1.9- μm absorption band measured in the RELAB spectrometer for each particle size fraction of the SWy-1 montmorillonite. The anomalously strong 1.4- and 1.9- μm absorptions in the 5–10 and 10–15 μm fractions of montmorillonite occur in conjunction with stronger 1.46- and 1.97- μm wings (Fig. 6a). We also observe a slight variation in the position of the band minima of these bands that correlates with the strength of the adsorbed water wings. The wetter samples have slightly shorter wavelength (1.410 and 1.905 μm) band minima (see also Table II) than the drier ones (1.415 and 1.910 μm). Whether this is simply due to instrumental noise or is instead caused by slight changes in the bond energetics of water molecules bonded to the surface (as opposed to water molecules hydrogen bonded to each other in a wetter surface

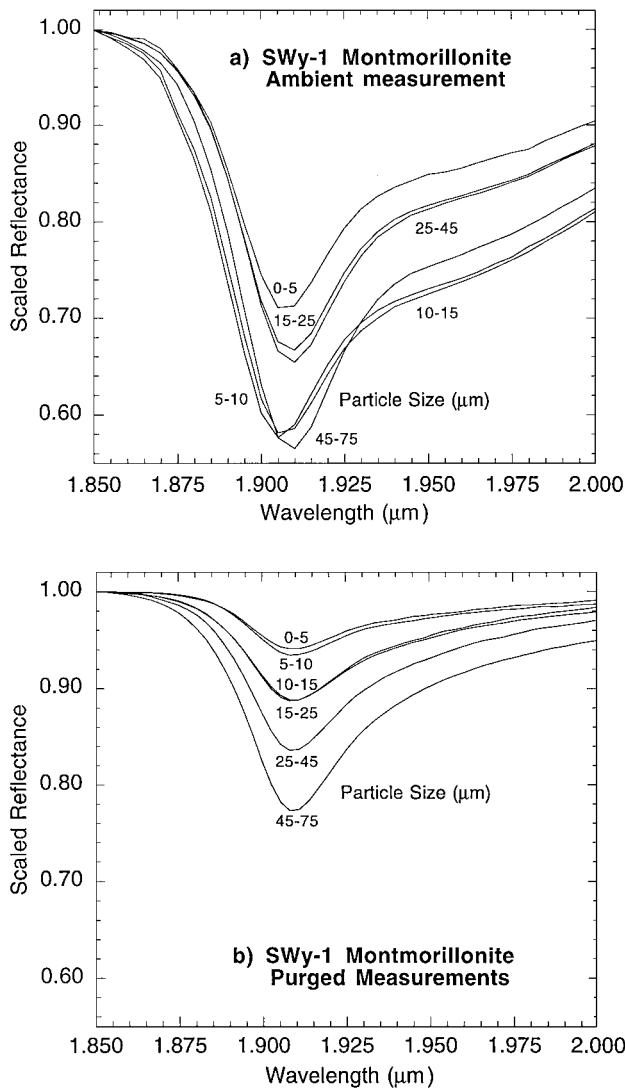


FIG. 6. Comparisons of the strength and shape of the 1.9- μm absorption in SWy-1 montmorillonite. Reflectance is scaled to unity at 1.850 μm . (a) A strong 1.97- μm wing indicates the importance of adsorbed water on this absorption when measured in an ambient atmosphere. Band strength does not follow a perfect particle size trend because some smaller samples were measured on a different day and were wetter, as indicated by their stronger long wavelength wings. (b) Under purged conditions, most adsorbed water is removed and the 1.97- μm wing disappears. Additionally, the band strength order follows particle size.

environment) is unclear. In any case, reflectance spectra taken in the purged, dry environment of the Nicolet do not show this subtle variation in band position. Also missing are the longer wavelength wings (Fig. 6b) in the 1.4- and 1.9- μm absorption bands due to adsorbed water (Bishop *et al.* 1994). Adsorbed water thus contributes only minimally to these spectra making them more useful for judging the fundamental optical effects of particle size on the band strengths of the 1.4- and 1.9- μm absorptions. Furthermore, water content does not play a role in 2.2- μm band strengths even in the ambient environment mea-

surements. Figure 7 shows the variations in the 2.2- μm band for montmorillonite. Its shape and strength only changes minimally between RELAB and Nicolet measurements, as expected due to the fact that the absorption comes from hydroxyl groups that are part of the crystal lattice and are not related to adsorbed water molecules.

The palagonitic soil samples have band minima at 1.415–1.425 and 1.920–1.935 μm in RELAB spectra (Table II). Golden *et al.* (1998) ascribe the longer wavelength locations of the band minima relative to smectite clays to the presence of adsorbed water and the lack of crystalline phyllosilicates (and hence water coordinated to regular cation centers) in their palagonites. However, these wavelengths are still short of the positions of the wings in the montmorillonite samples due to adsorbed water (Bishop *et al.* 1994). The intermediate position of the bands in the palagonitic soils instead indicates contributions from both adsorbed water and water bound in the crystal structure. These overlapping absorptions combine to give the intermediate wavelength band centers. Alternatively, the different position may indicate energetically different sites for adsorption of water in the palagonitic soil and the montmorillonite. In the Nicolet measurements in the purged environment, the band centers are at the lower end of the above ranges (Table II), in agreement with a weaker contribution from adsorbed water and a more important contribution from water coordinated to more regular (but possibly energetically different) crystal sites.

Because groups of samples were measured on different days with the RELAB spectrometer, the environmental conditions at the time of measurement were probably different. This is likely the cause of the offset in 1.4- and 1.9- μm band strength between the three finest and three coarsest size fractions of the montmorillonite. The LOI measurements show that all size fractions hold the same proportion of adsorbed water under a given set of conditions, so water content cannot explain band strength variations among samples measured under the same environment (purged Nicolet or single day of RELAB measurements). Instead, particle size appears to be controlling band strengths directly.

Particle Size Effects

With composition, crystallinity, and water content approximately constant in the samples measured in the purged atmosphere of the Nicolet, the cause of the significant variations with particle size in all three near infrared absorption bands must be the changing interactions of electromagnetic radiation with the different size particles. Mustard and Hays (1997) observed a marked decrease in spectral contrast in the volume scattering absorptions of olivine and quartz as particle sizes decreased. The explanation proposed there applies to these samples as well. For larger particles (~ 250 μm) in a wavelength regime where the real part of the complex index of refraction n is greater than 1 and the imaginary part k is small ($\ll 1$), reflectance is low and absorption strengths are moderate (Vincent and Hunt 1968, Moersch and Christensen 1995). When particle

TABLE II

Band identity	Ambient atmosphere			Purged atmosphere		
	1.4 μm	1.9 μm	2.2 μm	1.4 μm	1.9 μm	2.2 μm
	Average particle size (μm)					
SWy-1 montmorillonite						
2.5	1.410	1.905	2.205	1.412	1.908	2.207
7.5	1.410	1.905	2.205	1.410	1.908	2.207
13	1.415	1.905	2.205	1.412	1.908	2.207
20	1.415	1.910	2.210	1.412	1.908	2.207
35	1.415	1.910	2.210	1.412	1.908	2.207
50	1.415	1.910	2.210	1.412	1.908	2.207
HK-3b palagonitic soil						
2.5	1.415	1.925	2.210	1.419	1.922	2.209
7.5	1.410	1.920	2.205	1.412	1.920	2.207
13	1.415	1.920	2.205	1.415	1.922	2.207
20	1.415	1.925	2.210	1.415	1.920	2.207
35	1.415	1.930	2.210	1.413	1.922	2.207
50	1.420	1.930	2.210	1.413	1.922	2.207
113	1.420	1.930	2.210	1.413	1.925	2.206
200	1.425	1.935	2.213	1.419	1.922	2.207

Note. Band minima locations in μm for montmorillonite and the palagonitic soil size fractions as measured under both ambient and purged conditions.

sizes decrease, the number of first surface reflections and multiple scatters increases, increasing the reflectance. The band strengths of these absorptions increase with decreasing particle size until the absorption path length ($\sim\lambda/(4\pi k)$) equals the mean optical path length (Hapke 1993). Further decreases in particle size cause the absorptions to weaken as volume scattering plays a diminishing role relative to first surface interactions.

The observed decreases in water and hydroxyl combination and overtone absorption strengths in the near infrared fit this pattern of behavior. With the extremely small particle sizes tested, we observe decreases in band strengths as the dimensions of the particles decrease and first surface scattering becomes more dominant. For the finest particle size fractions, the absorptions are one-half to one-third the strength of the absorptions in the coarsest size fractions. These finest sizes are more typical (if perhaps still larger) of the particles found in the global bright red dust on Mars. For a given concentration of clay or altered, palagonitic material in a particulate mixture, the fine particle sizes will produce a weaker set of absorptions and thus will lead to underestimations of the fraction of such species from remotely sensed data interpreted with only the knowledge of the behavior of coarser particles of the same composition.

As noted earlier, the change in sieved particle size in the montmorillonite is in fact a change in the size of aggregate particles, not a change in the actual size of each individual mineral grain. Yet the behavior of the various sieve separates are best explained as the effects of optical interactions with particles of these larger sizes. This has important implications for understanding laboratory measurements and their application to remote sensing data.

In order for a given particle to behave optically as an individual grain, the separation between it and other particles must

exceed some distance, likely proportional to the wavelength of light involved. The interface must present a coherent surface in order for the light to either reflect or transmit. If the separation distance is less than this undefined threshold, then the light only interacts with the grain as if it is a continuum of an absorbing medium with no interfaces (Mustard and Hays 1997, see Fig. 8). As an extreme case, mineral grains in an aggregated particle may orient preferentially along a crystallographic axis with small voids existing at grain junctions. In this case, the small voids within the aggregate particle act as sources of internal scattering, but the mean optical path length is greater than in the case where each individual mineral grain is randomly oriented.

This set of behaviors is analogous to the observations in the mid-IR where sample preparation has a strong affect on reflectance and emissivity (Salisbury and Wald 1992, Salisbury *et al.* 1994). The reduction of spectral contrast for restrahten bands at small particle sizes was found to be related to the porosity or separation between the particles (Salisbury and Wald 1992). Very fine particles separated by spaces more than a wavelength in size act as individual fine particles, whereas in more tightly packed, less porous cases, the particles scatter coherently, behaving as if they were larger particles.

Salisbury and Wald (1992) conclude that the martian regolith, with its considerable portion of fines, may display mid-infrared emission spectra that are very different from spectra of coarse materials. From the work presented here, the near-infrared reflectance spectra will also be affected by particle sizes. In particular, absorption bands will be significantly weakened. At particle sizes less than 5 μm , the band strengths may be only half those of particles around 50 μm in diameter.

IMPLICATIONS AND CONCLUSIONS

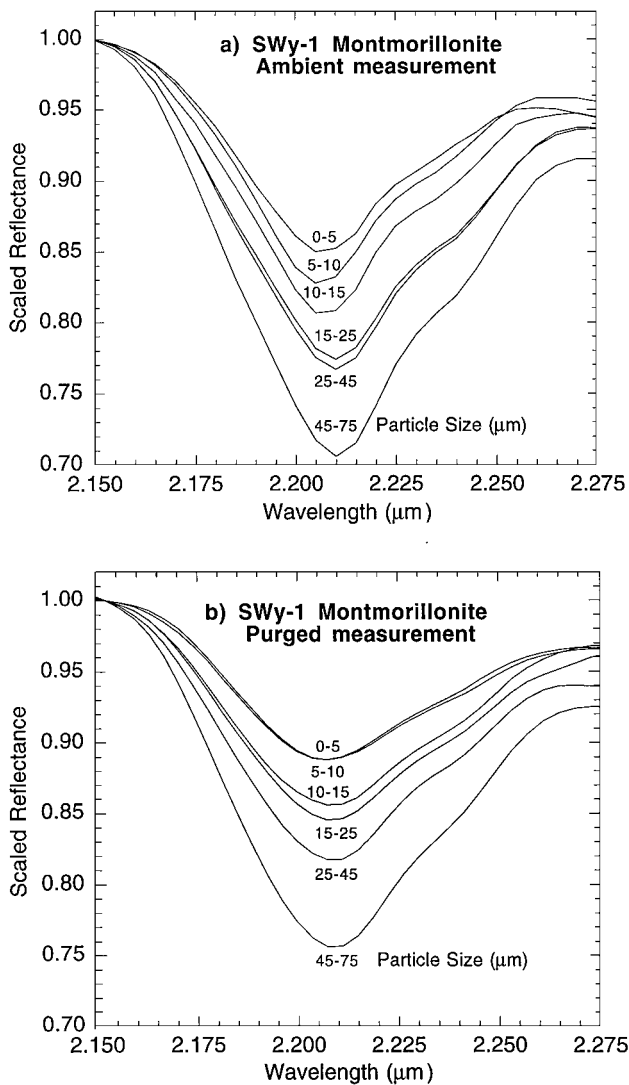


FIG. 7. Comparisons of the strength and shape of the $2.2\text{-}\mu\text{m}$ absorption in SWy-1 montmorillonite. Unlike the $1.9\text{-}\mu\text{m}$ absorption in Fig. 5, the $2.2\text{-}\mu\text{m}$ feature does not show significant change between ambient and purged measurement conditions. Band strength is a function of particle size even in (a) where the amounts of adsorbed water do not vary regularly as indicated by the 1.4- and $1.9\text{-}\mu\text{m}$ absorptions.

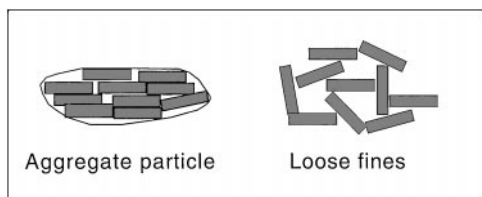


FIG. 8. Behavior of aggregated and loose fine particles. Fine particles aggregated together behave optically as a single larger particle, while separated fine particles behave individually.

By preparing particle size separates of nearly constant mineralogical composition of both a palagonitic soil and a montmorillonite clay and measuring them in dry environments, we have been able to isolate particle size as the main cause for the systematic decreases in band strength with particle size seen in near infrared spectra of these materials. Furthermore, mid-infrared spectra of these materials show the same loss of contrast for finer particle sizes. The measured band strengths are sensitive to the physical size of the particles. Solid aggregations of material such as clays behave as larger single particles. This means that physical particle size such as determined by sieving, and not crystal grain size, is the parameter that governs the way that radiation interacts with the particulate material.

Interpretations of remotely acquired spectra of the ubiquitous fine dust on Mars must reflect the fact that this dust will have inherently weaker near infrared absorptions. Researchers have used the absence of a strong $2.2\text{-}\mu\text{m}$ feature to place upper limits on the abundance of clays on the surface of Mars (e.g., Orenberg and Handy 1992, Dalton and Clark 1995). If analog materials with inappropriate particle sizes or crystallinities are used then estimates of phyllosilicate or other component abundances will be inaccurate. Observations by Pathfinder indicates that fine dust coats most surfaces (Greeley *et al.* 1999). Because particle sizes on Mars are around $1\text{-}2\text{ }\mu\text{m}$, martian materials do not appear to be aggregated and will display weaker absorption bands. Potential clay bands will only be half the strength of the bands measured in typical reference clays without sieving. Mixing models failing to account for particle size will potentially underestimate the abundance of these clays by a factor of two. Upper limits of any absorbing species should reflect the particle size expected (or measured) for that material.

If the martian dust is fine, nonaggregated clay, then why does it not clump in the manner of terrestrial clays? This question requires a knowledge of the causes of clumping of clays on Earth, but it seems likely that humidity may play a role. In this case, clays on Mars would naturally be expected to be disaggregated by the action of the wind in the absence of the moisture needed to hold clumps together. Other possibilities for clumping mechanisms include cementation by salts or carbonates and electrostatic attraction of particles.

If the martian dust is a palagonite-like alteration product and not a crystalline clay, its properties may still be different than otherwise thought if particle sizes are not taken into account. The weakness in the absorption features caused by the fine particle sizes might be misinterpreted as a lower degree of crystallinity than is actually the case. Estimates of the degree of weathering based on degree of crystallinity as derived spectroscopically should first factor out particle size effects.

Use of near-infrared band strengths as a measure of soil water content must also take particle size effects into account. Finer particulate materials with their inherently weaker absorption bands will appear to have a lower water content than coarser

soils. Therefore particle sizes should be ascertained first, and a correction to the band strengths derived from experiments with reference materials of varying particle sizes should be applied before conclusions about water content are made. A good example is the work of Yen *et al.* (1998), in which they converted reflectance into apparent absorbance in an attempt to minimize particle size effects in measuring water content with the 3- μm band.

For particle sizes less than 5 μm , the 2.2- μm band strength of montmorillonite is 11%. A 10% mixture of montmorillonite with a neutral material should therefore have a band strength of $\sim 1.1\%$, which is equal to the deepest 2.2- μm band observed by the ISM instrument in bright regions on Mars (Murchie *et al.* 1993). This means that if the absorption is caused by a smectite clay, the limit on the abundance of the clay in the dust is 10%, much higher than proposed by Dalton and Clark (1995). The estimates presented here are higher than previous ones because of the very fine particle size of the analog materials measured, which is more appropriate for comparison to the ubiquitous martian dust. Alternatively, the absorption could be due to phyllosilicates or incipient phyllosilicates in a palagonitic soil. The strength of the 2.2- μm band in the palagonitic soil measured here is 1.5–2.0%, meaning the finest fraction of this palagonitic soil could easily make up half to two-thirds of the dust on Mars. In either case, the importance of using analog materials with appropriate particle sizes is clearly demonstrated. Particle size plays a major role in determining infrared band strengths in fine grained material.

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