

A possible surprise for the Mars rover “Opportunity”: The inferred coarse hematite may instead be fine-grained, consolidated hematite

L. E. Kirkland^{1,2}, K. C. Herr², P. M. Adams²

¹Lunar and Planetary Institute; ²The Aerospace Corporation

Contact information: L. E. Kirkland, 3600 Bay Area Blvd., Houston, TX 77058
email: kirkland@lpi.usra.edu; phone: 281-486-2112

Abstract. Since 2001, there have been two, parallel interpretations of Mars Global Surveyor Thermal Emission Spectrometer (TES) observations of Sinus Meridiani, which are: (1) coarse hematite is the only spectral match; and (2) fine-grained hematite with particles closer than \sim wavelength (“fine-intimate hematite”, e.g., coating, ferricrete) is a better match, but coarse hematite is also viable. The TES team interpreted the spectra as consistent only with a large deposit (\sim 750 km x 350 km) of coarse hematite (>5 – 10 μ m grain size). Coarse hematite is considered strong evidence for longstanding water, which led to the decision to land the rover Opportunity there. On the other hand, the Aerospace/LPI remote sensing team argued that fine-intimate hematite (e.g., a coating) can better match TES spectra. A thin coating (\sim 5– 10 μ m thick) and a low exposure ($<5\%$) could cause the observed signatures. The distinction is important because: (1) It is unknown whether fine-grained hematite implies abundant water; (2) Fine-intimate hematite may explain the non-detection of coexisting aqueous alteration minerals and the lack of hematite wind streaks; (3) Current “hematite abundance maps” may instead map the surface texture; (4) Coatings may be of astrobiology interest; (5) Studies are needed to determine whether visible-infrared spectra can definitively distinguish fine-intimate from coarse hematite.

Background

TES measures spectra over the \sim 6– 50 μ m spectral range. TES spectra of Sinus Meridiani exhibit \sim 18, 23, and 33 μ m bands that are broadly consistent with hematite [Christensen *et al.*, 2000a; Christensen *et al.*, 2001; Estep-Barnes, 1977; Onari *et al.*, 1977]. The 23 μ m band has an observed spectral contrast of \sim 2%. Fig. 1 illustrates the definition of band contrast.

Strong bands such as hematite may exhibit at 18, 23, and 33 μ m are called “reststrahlen bands.” When reststrahlen bands troughs exhibit spectral contrast greater than \sim 1–5%, that indicates the presence of some smooth-surfaced material in one of two broad

forms: (1) fine-intimate material or (2) coarse particles.

“Fine-intimate material” is material composed of fine particles or grains that are closer than \sim wavelength together. Closely-spaced particles or grains may occur because the material formed that way (e.g., precipitate coating) or was consolidated or cemented (e.g., closely packed fines, duricrust, ferricrete, desert varnish).

Spectrally, “coarse particles” (e.g., coarse hematite) means large enough to be optically thick (high opacity) [Salisbury *et al.*, 1987], which for hematite is greater than \sim 1– 5 μ m over the \sim 15– 50 μ m range [Estep-Barnes, 1972]. The size at which a material becomes optically thick is tied to the absorptivity. Hematite absorptivity ranges from \sim 5000–10000 per centimeter for the 18, 23, and 33 μ m bands [Estep-Barnes, 1972]. The penetration depth is given by absorbance/(weight percent of the material*absorptivity). For pure hematite, the weight percent is 100. For absorbance=1 (i.e., transmission=10%), and absorptivity of 10000 and 5000 per centimeter, the penetration depth is 1 and 5 μ m, respectively.

Scattering effects explain why both fine-intimate and coarse hematite are consistent with the TES data. Material can scatter light through surface or volume scattering [Vincent and Hunt, 1968; Hapke, 1993]. A strong absorption causes high opacity, and the resulting mirror-like surface reflectance (“surface scattering”) causes a clear emissivity trough (a spectral band) because radiance exiting the material is reflected inward (Figure 1, “solid surface”) [Planck, 1914].

On the other hand, when unconsolidated particles are small enough for light to survive passage through the material, volume absorption (volume scattering) occurs. Volume scattering causes a reststrahlen band emission peak, (Figure 1, lower trace), which counters the surface scattering trough, and thus causes low spectral contrast (Figure 1, upper trace) [Vincent and Hunt, 1968; Salisbury *et al.*, 1991; Salisbury and Wald, 1992].

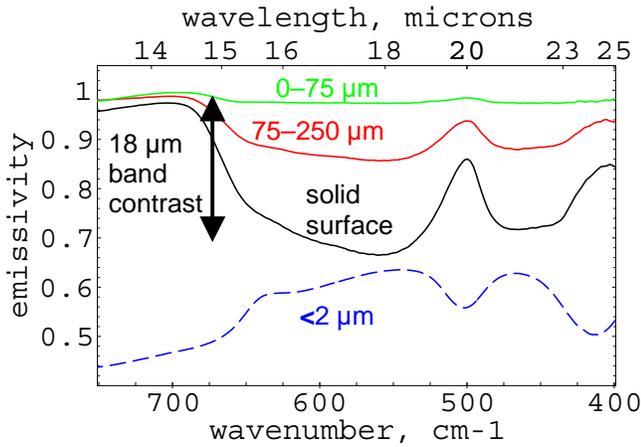


Figure 1. Unconsolidated, small particles can have poor spectral contrast. Surface scattering dominates a smooth surface, causing reststrahlen emissivity troughs (“solid surface” above). The arrow illustrates the approximate 18 μm band contrast. Band contrast is measured from the spectral continuum to the band center. Volume scattering dominates the optically thin, $<2 \mu\text{m}$ particles, causing reststrahlen emissivity peaks. Increasing volume scattering toward smaller particle size shifts the spectra toward the volume scattering spectral shape. Conversely, as packing or cementation places small particles closer than \sim wavelength together, the spectral shape shifts back toward that of the “solid surface” spectrum. The spectra are from *Salisbury et al.* [1991], sample “hematite.1”, as 1-biconical reflectance (upper traces) or one - transmission (lower trace).

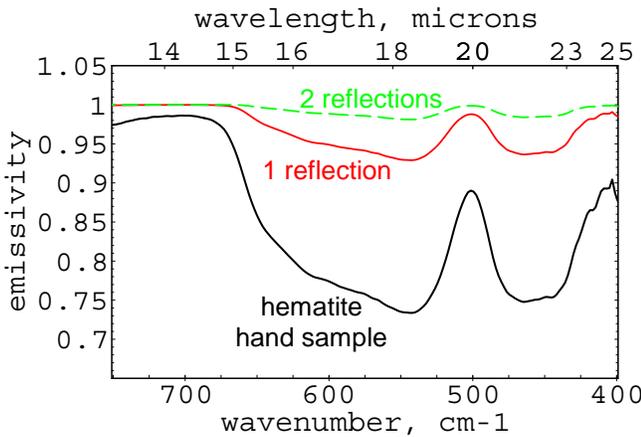


Figure 2. Surface roughness can reduce spectral contrast. The lower trace shows the spectrum measured of a hematite hand sample (“grhemfrhr”). The middle and upper traces simulate one and two surface reflections, as may result from surface roughness, as $\epsilon_e = 1 - (1 - \epsilon)(\xi + 1)$, where ϵ_e =emissivity; ϵ =true emissivity (lower trace), and ξ =number of reflections [Fraden, 1993; Kirkland et al., 2002a]. The spectrum was measured at The Aerospace Corporation in hemispherical reflectance.

However, when particles are less than \sim wavelength together, they behave optically like large particles [Salisbury and Wald, 1992]. Thus fine-intimate material behaves spectrally in a manner similar to larger particles.

In addition, if good spectral contrast is observed, then that means some smooth surfaces are present. Rough surfaces cause multiple reflections that reduce the spectral contrast. In general, the smoother the surface, the higher the spectral contrast, and the more readily the material is detected (Figure 2). Roughness at the grain scale can be an important cause of reduced contrast [Kirkland et al., 2002a; Kirkland et al., 2003a].

Band contrast has been used to map hematite abundance [Christensen et al., 2000a]. However, decreasing particle size and increasing roughness can cause a nearly identical spectral trend (Figures 1 and 2). That similarity makes it problematic to determine whether increasing band contrast actually maps increasing particle size, increasing fine-intimate behavior, increasing abundance, or increasing surface smoothness.

Christensen et al. [2000a] did not include spectra measured of hematite coatings. However, they concluded that a spectrum of hand-packed hematite powder did not match TES data, and thereby ruled out a hematite coating composed of <5 – $10 \mu\text{m}$ particles as a spectral match.

Figure 3 shows that a packed material is a poor spectral analog to a coating for two reasons. First, the hand-packed sample still exhibits volume scattering because the particles are not sufficiently close together. Second, packing can preferentially orient hematite crystals and cause the loss of the small, 26 μm trough, as occurred in the Figure 3 packed spectrum [Onari et al., 1977; Pecharoman and Inglesias, 2000]. Thus volume scattering and orientation effects can cause a packed material to exhibit different spectral band shapes, centers, and contrasts than a coating.

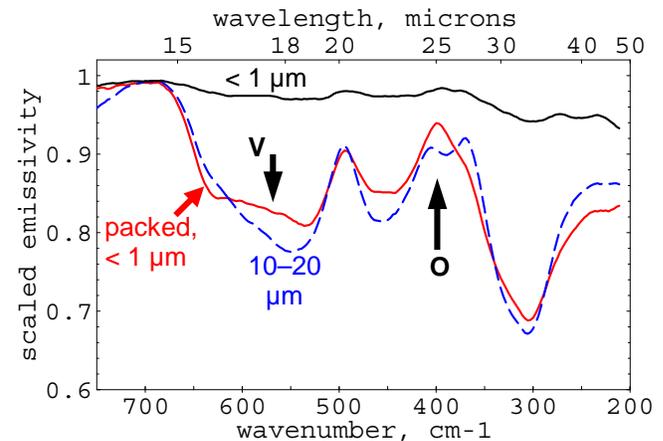


Figure 3. A packed sample is a poor spectral analog to a consolidated coating. The dashed spectrum is of 10–20 μm hematite particles, which are large enough that surface scattering dominates. The upper, black spectrum is of $<1 \mu\text{m}$, unpacked hematite particles, and the lower, solid red trace is of $<1 \mu\text{m}$, packed hematite particles. The arrow “V” notes the inflection of the packed sample from volume scattering. The arrow “O” notes where packing preferentially oriented the particles, causing loss of the 26 μm trough. The spectra are after Fig. 7 of Christensen et al. [2000a], measured in biconical reflectance at the U.S. Geological Survey.

Comparison to TES Data

Figure 4 shows spectra of coarse hematite, hematite coating, and TES data. The hematite coatings were characterized using X-ray Diffraction, Energy Dispersive X-ray Spectroscopy, Scanning Electron Microscopy, and the spectra. The Figure 4 coating spectra were measured in biconical reflectance (14–150 μm range) and converted to emissivity using Kirchhoff's Law (emissivity equals one minus reflectance) [Salisbury *et al.*, 1994]. Biconical spectra accurately record the spectral shape, but not the absolute contrast, while hemispherical spectra record the absolute spectral shape and contrast [Salisbury *et al.*, 1991]. We also measured hemispherical spectra of the 2.5–25 μm range, and the spectra had the same shape and band centers as the biconical spectra. Kirkland *et al.* [2002a] detail the instrumentation. Those laboratory and the TES spectra were measured at 4 cm^{-1} and 20 cm^{-1} spectral resolution, respectively. The coarse hematite spectrum was measured at the TES laboratory [Christensen *et al.*, 2000b]. Christensen *et al.* [2001] and Kirkland *et al.* [2001] detail the TES calibration and sensitivity.

Hematite coatings offer an improved match to TES spectra: (1) The “gray hematite” exhibits a wider 18 μm band and a different 23 μm band shape than TES data. The hematite coatings match the TES spectral bands. (2) The “gray hematite” band centers are consistently offset, while the hematite coatings have band centers that match the TES data [Kirkland *et al.*, 1999; Kirkland *et al.*, 2001a, Kirkland *et al.*, 2002b].

The trough near 26 μm in the Figure 4 TES spectrum is difficult to assess because it is weak and defined by one point. Lane *et al.* [2002] conclude that it is not present, which if correct indicates preferentially oriented crystals (e.g., Figure 3) [Onari *et al.*, 1977; Pecharoman and Inglesias, 2000]. Some coatings exhibit a 26 μm feature and others do not, which indicates variations in preferred crystal growth [Onari *et al.*, 1977; Pecharoman and Inglesias, 2000]. Potential causes of other spectral variations include scattering, optical, and preferred crystal orientation effects, and contaminants [Vincent and Hunt, 1968; Estep-Barnes, 1977; Onari *et al.*, 1977; Pecharoman and Inglesias, 2000; Estep-Barnes, 1972; Salisbury *et al.*, 1991; Lane *et al.*, 2002]. Those effects have received almost no attention for a hematite coating.

Visible Data

Christensen *et al.* [2000] concluded that hematite will be red for particles <5–10 μm (“red hematite”). They concluded that Hubble Space Telescope did not observe visible spectral features at Sinus Meridiani that “red hematite” should exhibit, and thereby that the material must be coarse (“gray”) hematite.

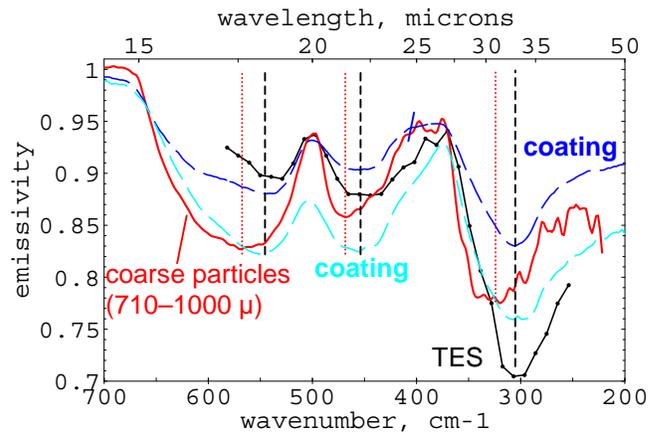


Figure 4. A hematite coating matches the TES spectral shape and band centers, while coarse material exhibits mismatches. The two dashed spectra show hematite coating signatures, and the solid trace shows coarsely particulate hematite. The TES spectrum is scaled to a similar spectral contrast for comparison of the band shapes. The dashed vertical lines illustrate the band centers of the coarse hematite (red vertical lines) vs. the coatings and TES spectra (black vertical lines). The offsets show the mismatch of the coarse hematite vs. the TES signature. The coatings are: blue=“bhm3_blk_a”; blue-green = “bhm4_blk_b”, as 1-biconical reflectance, measured at The Aerospace Corporation. The TES Sinus Meridiani spectrum is an average of 11 spectra (ICK 643888002 to -024, detector 5), in apparent emissivity, with an atmospheric compensation [Kirkland *et al.*, 2002a; Young *et al.*, 2003], scaled as $(3 \times x) - 2$. The “coarse particles” spectrum is “bur2600”, measured in emission at the TES team laboratory [Christensen *et al.*, 2000b], with a 3-point boxcar smoothing.

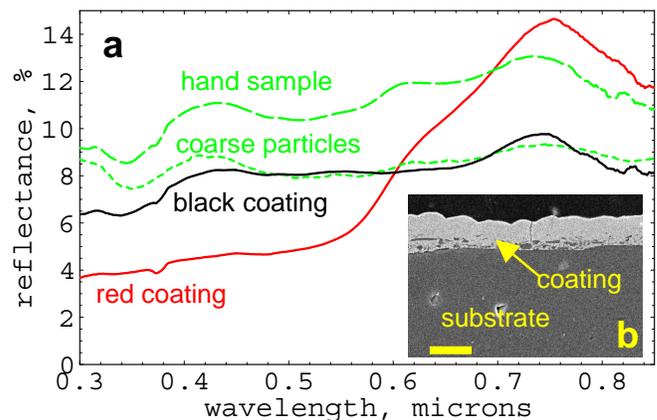


Figure 5. Visible and near-infrared reflectance spectra and a hematite coating cross-section. (a) The upper spectrum is of a hand sample (“gry_hem”); the black trace is of a black hematite coating (“bhm3”); and the red trace is of a red hematite coating (“bhm1”), all measured at The Aerospace Corporation. The coarse particles (150–250 μm) are from Clark *et al.* [1993] (“gds_69_a150-250u”). (b) Scanning Electron Microscope cross-section of a hematite film that formed on a quartz substrate, from near Bunker Hill Mine, eastern Inyo Mountains, California. Scale bar=20 μm .

Contrary to that line of reasoning, Figure 5a illustrates that a black hematite coating can be essentially indistinguishable from coarse hematite at visible wavelengths, even though the coating is not coarse hematite. Hematite coatings examined included smooth, matte, black, and red examples, and a ferricrete sample was also studied [Kirkland *et al.*, 2002b]. Figure 5a shows an example red coating spectrum, which has a different spectral shape than the black coating. Visible measurements used a Perkin-Elmer Lambda-9 spectrometer.

Discussion

A thin coating (~5–10 μm) can mask the substrate. However, a sufficiently thin coating can have a distorted spectral signature because the coating opacity varies with wavelength. Some of the coatings tested are optically thick over the 18–50 μm range, yet slightly translucent in the ~7–13 μm range, so that a subtle substrate signature appears at some wavelengths but not others. An even thinner coating can become reddish, yet retain the 18, 23, and 33 μm bands.

Smooth coatings can exhibit notably high spectral band contrast, because optically smooth surfaces are the best case for few surface reflections and thus little cavity effect [Kirkland *et al.*, 2001b; Kirkland *et al.*, 2002a; Kirkland *et al.*, 2003a]. A typical sample exhibited a 23 μm band depth of ~45%. TES Sinus Meridiani spectra exhibit a 23 μm spectral band depth of ~2%. For this case, and an optically thick coating, that translates to an aerial exposure of ~4% [Thomson and Salisbury, 1993; Kirkland *et al.*, 2002].

It may be that optically smooth coatings shed fine dust better than a rougher surface. If so, then exposure may explain why the signature is observed. Conversely, rougher coatings could be common but remain undetected. The hematite signatures thus may mark locations with a rare surface texture, rather than a rare material. In addition, it is unknown whether a hematite coating may form preferentially on certain substrates, and thereby preferentially conceal or indirectly mark them.

Little is known about potential formation pathways for fine-intimate hematite materials, especially the role of water. Thus a potential irony would be if a hematite spectral signature actually marks areas that had an unusually dry history. Whatever the formation pathway, it has to explain why no correlated aqueous alteration minerals are detected at Sinus Meridiani (e.g., silica phases, hydrous sheet silicates). In addition, whether a hematite coating could be biologically mediated would keenly interest astrobiology researchers.

Finally, Christensen *et al.* [2000] propose that the Sinus Meridiani deposit is a hematite lag exposed by

aeolian stripping. Aeolian movement of material can cause wind streaks. If the hematite is instead immobile (e.g., a coating, ferricrete), that may explain why TES has not observed hematite wind streaks.

Those effects and gaps in understanding illustrate the importance of fine-intimate materials for geologic, climatic, and astrobiology disciplines. However, the “coarse-only” conclusion discouraged researchers from spending scarce resources to study fine-hematite.

Conclusions

We have shown that the Sinus Meridiani “coarse-only” hematite interpretation is incomplete: (1) Scattering effects can cause fine, consolidated material to mimic coarse material; (2) Specifically, spectra of naturally occurring hematite coatings broadly match visible and infrared spectra of coarse hematite; (3) Spectra of coatings can match TES spectra better than coarse hematite does; and (4) A hematite coating can exhibit a very strong spectral signature, so a small exposure (<5%) of thin material (~5–10 μm) may fit the observations.

Issues currently unknown are: (1) The role of water for formation and preservation of fine-intimate hematite on Mars. It is thus unconstrained in range from requiring abundant water to a relatively dry history; (2) The impact of coating thickness and scattering properties on data recorded by rover instruments; (3) Whether current “hematite abundance maps” actually map abundance or surface texture; (4) Whether smooth surfaces would better shed fine dust, thereby enhancing detection of smooth vs. rough coatings; (5) Whether immobile hematite (e.g., coating) may explain the lack of other aqueous alteration minerals and hematite wind streaks at Sinus Meridiani; (6) Whether coatings may preferentially form on certain substrates; (7) Whether the spectral differences observed between fine-intimate and coarse hematite (Figure 4) can definitively discriminate them. A study of this question is in progress.

Those interpretations and uncertainties were not widely acknowledged, including during landing site selection. It is possible that “coarse-only” presentations dominated in number because an interpretation that points to abundant, longstanding water may be perceived as more stimulating. However, discussion of all reasonable hypotheses should be an important element of the landing site selection process. For example, fine-intimate hematite (especially a coating), may have primary implications for Mars (e.g., for astrobiology) that are vastly more remarkable than “coarse hematite.”

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References

- Christensen, P. R. et al., Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: Evidence for near-surface water, *J. Geophys. Res.*, *105*, 9623–9642, 2000a.
- Christensen, P. R. et al., A thermal emission spectral library of rock-forming minerals, *J. Geophys. Res.*, *105*, 9735–9739, 2000b.
- Christensen, P. R. et al. Mars Global Surveyor Thermal Emission Spectrometer experiment: Investigation description and surface science results, *J. Geophys. Res.*, *106*, 23823–23871, 2001.
- Clark, R. N., G. A. Swayze, A. J. Gallagher, T. V. V. King, and W. M. Calvin, The U. S. Geological Survey Digital Spectral Library: Version 1: 0.2 to 3.0 microns, U.S.G.S. Open File Report 93-592, 1993.
- Estep-Barnes, P. A., Infrared Spectroscopic Studies of Hematite, Masters Thesis, West Virginia University, 1972.
- Estep-Barnes, P. A., Infrared Spectroscopy, ch.11 in *Physical Methods in Determinative Mineralogy*, ed. J. Zussman, 2nd ed., 1977.
- Fraden, J., *AIP Handbook of Modern Sensors*, p.136, AIP, New York, Yew York, 1993.
- Hapke, B., *Theory of Reflectance and Emittance Spectroscopy*, Cambridge UP, 1993.
- Kirkland, L. E., K. C. Herr, P. B. Forney, and J. W. Salisbury, 1969 Mariner 7 Infrared Spectrometer: Data recovery and comparison to TES, *LPSC XXX*, abs. 1693, 1999.
- Kirkland, L. E., K. C. Herr, and P. M. Adams, Searching for an improved spectral match to TES and IRIS Sinus Meridiani spectra: Coatings and cemented materials, *Eos Trans. AGU*, *82*(20), abstract, S242, 2001a.
- Kirkland, L. E., K. C. Herr, and J. W. Salisbury, Thermal infrared spectral band detection limits for unidentified surface materials, *Appl. Optics*, *40*, 4852–4862, 2001b.
- Kirkland, L. E., K. C. Herr, E. R. Keim, P. M. Adams, J. W. Salisbury, J. A. Hackwell, A. Treiman, First Use of an Airborne Thermal Infrared Hyperspectral Scanner for Compositional Mapping, *Remote Sens. Environ.*, *80*, 447–459, 2002a.
- Kirkland, L. E., K. C. Herr, P. M. Adams, F. Westall, J. W. Salisbury, Spectra of Cemented, Hematite-Rich Material and TES Spectra of Sinus Meridiani, Mars, *LPSC XXXIII*, abstract 1218, 2002b.
- Kirkland L. E., Herr K. C., Adams P. M., Infrared stealthy surfaces: Why TES and THEMIS may miss some substantial mineral deposits on Mars and implications for remote sensing of planetary surfaces, *J. Geophys. Res.*, *10.1029/2003JE002105*, 108(E12), 2003a.
- Kirkland, L.E., K. C. Herr, P. M. Adams, and J. W. Salisbury, Hematite coatings match TES spectra of Sinus Meridiani, Mars, *LPSC XXXIV*, abstract 1944, 2003b.
- Lane, M. D.; R. V. Morris, S. A. Mertzman, P. R. Christensen, Evidence for platy hematite grains in Sinus Meridiani, Mars, *J. Geophys. Res.*, *107*, Issue E12, pp. 9-1, 2002.
- Onari, S., Arai, T. & Kudo, K. Infrared lattice vibrations and dielectric dispersion in $\alpha\text{-Fe}_2\text{O}_3$, *Physical Review B* *16*, 1717–1721, 1977.
- Pecharromán, C. and J. E. Inglesias, Effect of particle shape on the IR reflectance spectra of pressed powders of anisotropic materials, *Appl. Spectroscopy*, *54*, 634–638, 2000.
- Planck, M, The Theory of Heat Radiation, (translation by M. Masius), AIP, 1914.
- Salisbury, J. W., B. Hapke, and J. W. Eastes, Usefulness of weak bands in midinfrared remote sensing of particulate planetary surfaces, *J. Geophys. Res.*, *92*, 702–710, 1987.
- Salisbury, J. W., L. S. Walter, N. Vergo, D. M. D’Aria, *Infrared (2.1–25 μm) Spectra of Minerals*, Johns Hopkins UP, Baltimore, 1991.
- Salisbury, J. W. and A. Wald, The role of volume scattering in reducing spectral contrast of reststrahlen bands in spectra of powdered minerals, *Icarus*, *96*, 121–128, 1992.
- Thomson, J. L. and J. W. Salisbury, The mid-infrared reflectance of mineral mixtures (7–14 μm), *Remote Sens. of Environ.*, *45*, 1–13, 1993.
- Vincent, R. K. and Hunt, G. R., Infrared reflectance from mat surfaces. *Appl. Optics*, *7*, 53–58, 1968.
- Young, S. J., B. R. Johnson, and J. A. Hackwell, An in-scene method for atmospheric compensation of thermal hyperspectral data, *J. Geophys. Res.*, *107*, D24, ACH14, 2002.