GEOPHYSICAL RESEARCH LETTERS, VOL. 34, L10204, doi:10.1029/2007GL029602, 2007

Basaltic andesite, altered basalt, and a TES-based search for smectite clay minerals on Mars

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Received 8 February 2007; revised 28 March 2007; accepted 17 April 2007; published 23 May 2007.

[1] The global-scale surface type 2 unit first identified with the Mars Global Surveyor Thermal Emission Spectrometer (TES) remains enigmatic. Competing hypotheses suggest that it represents either basaltic andesite or some form of altered basalt rich in dioctahedral smectite clay minerals and/or spectrally similar amorphous silica phases. Common dioctahedral smectites contain a diagnostic feature in a portion of TES spectra that has been excluded in previous studies because of atmospheric CO_2 absorption. We exploit the relative transparency of this spectral region to develop two indices that in tandem, distinguish between certain smectites and amorphous phases. Smectites are not detected in northern lowlands type 2 settings, consistent with other datasets, but the case for primary or secondary amorphous silica phases is strengthened. Separately, one index reveals an abundance of isolated type 2 occurrences in the southern high-latitudes (>50°) associated with dunes, the other shows olivine concentrations between −40° and +30°. **Citation:** Ruff, S. W., and P. R. Christensen (2007), Basaltic andesite, altered basalt, and a TES-based search for smectite clay minerals on Mars, *Geophys. Res. Lett.*, *34*, L10204, doi:10.1029/2007GL029602.

1. Introduction

[2] One of the legacies of the TES experiment is the identification of two global-scale thermal infrared (TIR) spectral units in low albedo regions of Mars [*Bandfield et al.*, 2000b]. Surface type 1 (ST1) has the spectral characteristics of plagioclase- and clinopyroxene-rich basalt and is found mostly in the southern highlands. Surface type 2 (ST2), which is concentrated in the northern lowlands but distributed across the highlands as well, has been characterized as a plagioclase- and volcanic-glass-rich basaltic andesite [*Bandfield et al.*, 2000b]. Recent analysis of TES spectra by *Rogers et al.* [2007] has subdivided the two global-scale units, but the ST2 unit largely remains undivided. However, high concentrations of ST2 appear increasingly limited to the northern lowlands and specifically to northern Acidalia Planitia with a small occurrence in Solis Planum.

[3] Although the basaltic interpretation of ST1 is widely accepted and is maintained even with the new divisions [*Rogers et al.*, 2007], the andesitic interpretation of ST2 remains contentious. Several competing hypotheses have emerged demonstrating that alteration of a precursor basalt could yield a spectrum that resembles the ST2 spectrum [*Minitti et al.*, 2002; *Wyatt and McSween*, 2002; *Kraft et al.*, 2003; *Morris et al.*, 2003; *Ruff*, 2004; *Michalski et al.*, 2005]. The ambiguity arises because of the significant spectral overlap at TIR wavelengths of primary and secondary amorphous silica phases with some clay minerals, zeolites, and palagonites.

[4] The mineralogy of ST2 material is enigmatic in visible/near infrared (VNIR) wavelengths as well. Smectites have been identified in isolated locations on Mars using VNIR spectra from the Mars Express OMEGA instrument [*Bibring et al.*, 2005; *Poulet et al.*, 2005], but none in Acidalia Planitia, the location of the greatest concentration of ST2 material. Evidence for hydrated phases as well as mafic minerals is notably absent in OMEGA spectra of ST2 terrains [*Mustard et al.*, 2005]. OMEGA results would seem to preclude the suggestion by *Wyatt and McSween* [2002] for the origin of ST2 as smectite-rich weathered basalt. However, *Milliken and Mustard* [2005] cautioned that the 1.9 μm hydration feature found in smectites, and used to search for them [*Poulet et al.*, 2005], may be weak in poorly crystalline phases. Additionally, *Michalski et al.* [2006] demonstrated that textural effects in some cases can mask the VNIR signature of clay minerals.

[5] In this work, we seek to resolve outstanding uncertainties about the presence of smectites in ST2 material and contribute new details about its mineralogy. As first demonstrated by *Ruff* [2003], we exploit a portion of TES spectra that has been excluded in previous studies because of absorption by atmospheric CO_2 but which is sufficiently transparent to yield new information.

2. Methods

[6] The spectra of ST1 and ST2 identified by *Bandfield et al.* [2000b] are shown in Figure 1 along with laboratory spectra of candidate components in ST2. *Wyatt and McSween* [2002] demonstrated that if volcanic glass is excluded from the spectral library, up to 30% clay minerals/sheet silicates could be modeled in the CO_2-excluded ST2 spectrum, with montmorillonite and Fe-smectite as the dominant phases. We have reconstructed their modeled results to include the full spectral range spanning the CO_2 region (Figure 1). The result shows a spectral "doublet" with minima at ~530 cm^{-1} and ~465 cm^{-1} that arises from the modeled smectites. We have developed two spectral indices to test whether the doublet is actually present but not previously observed in non-atmospherically-corrected TES spectra.

2.1. The 465 Index (ST2 Index)

[7] The ST2 candidate phases (Figure 1) share a generally V-shaped feature centered near 1100 cm^{-1} and a second one

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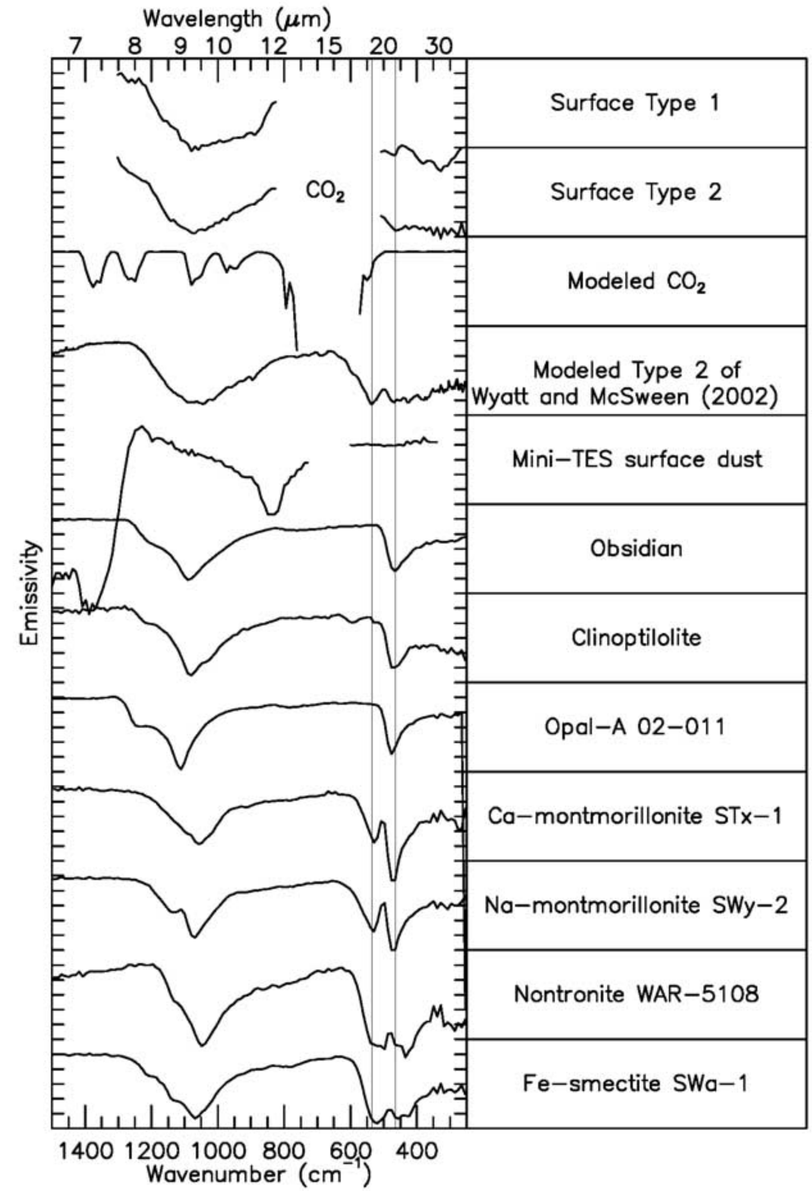

Figure 1. Spectra of TES surface types 1 and 2 vs. laboratory spectra of various candidate components of type 2. Vertical lines at 530 and 465 cm^{-1} highlight features described in the text. Modeled type 2 was produced using results of *Wyatt and McSween* [2002]. Surface dust from Gusev crater is shown at full spectral contrast [*Ruff et al.*, 2006]. Laboratory spectra were normalized to approximate contrast of the TES spectra.

near 465 cm^{-1} consistent with aluminosilicate stretching and bending modes, respectively [e.g., *Michalski et al.*, 2005]. The 465 index, as we will call it, is sensitive to the ~465 cm^{-1} feature. It uses a ratio of the average of TES channels 34 and 35 (~497 and 508 cm^{-1}) to the average of channels 31 and 32 (~466 and 476 cm^{-1}) and is applied to the global TES data set with the set of constraints shown in Table S1 of the auxiliary material.[1]

[8] We have established a threshold value for the 465 index that indicates whether an absorption feature is present or absent using the following rationale. Spectra from TES and the Miniature Thermal Emission Spectrometer (Mini-TES) instrument on each of the two Mars Exploration Rovers demonstrate that the globally homogenous dust on Mars is featureless (spectrally "gray") in the location of the 465 index [*Christensen et al.*, 2004a; *Christensen et al.*, 2004b] (Figure 1). Dust covered regions of Mars therefore provide spectrally neutral material for calibrating the index. The value of the 465 index from non-atmospherically-corrected spectra of dusty regions represents material that lacks an absorption feature at or near 465 cm^{-1} even though atmospheric absorptions may be present. To determine this value we used a total of 300 non-atmospherically-corrected spectra from five orbits over one of the dustiest parts of Arabia Terra based on the dust cover index of *Ruff and Christensen* [2002] (20°–23°N, 29° to 36°E). The value of the 465 index for these spectra is 1.003 with a standard deviation of 0.001. If this value represents surfaces with no absorption near 465 cm^{-1}, then a positive detection at a 3-sigma

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/gl/2007gl029602.

level of confidence requires a value ≥1.006. Therefore, locations on the planet with a 465 index value ≥1.006 are host to material with a spectral absorption at or near 465 cm^{-1}.

2.2. The 530 Index

[9] The ∼530 cm^{-1} feature of the smectite doublet occurs within the CO_2 exclusion region of atmospherically-corrected TES spectra and thus is not available for spectral deconvolution. Between 560 cm^{-1} and the typical lower limit of CO_2 exclusion at 508 cm^{-1}, the absorption by CO_2 is limited to a "hot band" at ∼545 cm^{-1} [e.g., *Maguire*, 1977] (Figure 1). The atmosphere becomes increasingly opaque at wavenumbers >560 cm^{-1}. Because of the relative transparency of the atmosphere between 508 and 560 cm^{-1}, spectral features of surface components are discernable. This has been demonstrated in the case of olivine, which has one of its compositionally diagnostic features near 520 cm^{-1} [*Hoefen et al.*, 2003].

[10] The 530 index, as we will call it, uses a ratio of TES channel 40 (∼561 cm^{-1}) to an average of channels 36 and 37 (∼518 cm^{-1} and ∼529 cm^{-1}). This set of channels avoids both the major absorption by CO_2 above 560 cm^{-1} and the minor CO_2 hot band at ∼545 cm^{-1}. Variations in atmospheric path length arising from topography do affect the strength of the absorption of the main CO_2 feature and hence the emissivity value in the 560 cm^{-1} region. However, according to modeling done for us by M. D. Smith that is analogous to that presented by *Smith et al.* [2000, 2004], the magnitude of this variation for all but the highest elevations on Mars (i.e., the Tharsis and Elysium volcanoes) is insufficient to confound the index. Atmospheric water-ice absorption does have this potential, so we have restricted the application of the index to TES spectra with a derived total ice value [*Smith et al.*, 2001] ≤0.05, the same constraint we used for the 465 index. All constraints on TES data selection are the same for the two indices (Table S1).

[11] Because surface dust also is spectrally gray in the region of the 530 index (Figure 1), we established a detection threshold value in the same manner as that for the 465 index (section 2.1) using non-atmospherically corrected TES spectra of Arabia Terra. The value of the 530 index for these spectra is 0.996 with a standard deviation of 0.003. If this value represents surfaces with no absorption near 530 cm^{-1}, then a positive detection at a 3-sigma level of confidence requires a value ≥1.005.

[12] The 530 index threshold value can be translated into a detection limit for smectites in cases where both indices occur above their respective thresholds. We added laboratory spectra of candidate smectites in fractional abundances to the Arabia Terra spectra to simulate fractional contributions of smectites to non-atmospherically-corrected TES spectra. This approach is highly dependent on the spectral contrast of the laboratory samples, which in turn is dependent on the physical state of the sample material. The best-case detection limit arises through the use of spectra from particulate samples that have been packed to reduce their porosity, thus increasing their spectral contrast. This is true of the smectite spectra we used from the Arizona State University spectral library [*Christensen et al.*, 2000]. With this approach we found that ∼15% of montmorillonite (STx-1) added to the Arabia Terra spectra yielded a 530 index value of 1.005. Similarly, ∼20% of nontronite (WAR-5108) and ∼10% of Fe-smectite (SWa-1) was needed to reach the threshold value. These values represent a lower limit of detectability for these smectites that will increase if the same ones on Mars have lower spectral contrast.

[13] A final note about the indices concerns their non-uniqueness. Any surface material with a strong enough absorption feature at or near 465 and 530 cm^{-1} will be detected. This can lead to errors of commission in which non-smectite phases are detected.

3. Results

[14] Global maps of the index values were binned at 16 pixels per degree (ppd) and gores and gaps were filled via a nearest neighbor interpolation technique. The map of the 465 index (Figure 2) clearly highlights Acidalia Planitia and other locations in the northern lowlands including parts of Vastitas Borealis where ST2 material was identified previously. Note that surfaces at high latitudes shown in gray had temperatures <250 K and their spectra were excluded. The 530 index map (Figure 2) shows spatially coherent distributions with elevated index values but none in the northern lowlands. In fact, the northern lowlands are indistinguishable from Arabia Terra and the other high albedo dusty places on the planet with respect to this index. We interpret this as an absence of a detectable smectite doublet but the clear presence of a single absorption feature at or near 465 cm^{-1}. Note that the Tharsis Montes and Elysium Mons display elevated 530 index values that are an artifact of their extreme topography, as expected from CO_2 modeling (section 2.2).

[15] The combination of 465 and 530 index maps shows no evidence for dioctahedral smectites in the northern lowlands, but isolated locations across the planet warrant additional scrutiny. For example, parts of Syrtis Major, Nili Fossae, Meridiani Planum (outside of the hematite-bearing region) and the outflow channels in the Lunae Planum region display intermediate to high values of both indices. Mawrth Vallis, where smectites were identified with OMEGA data [*Poulet et al.*, 2005], is another example. The spectra from these locations and many others must be isolated and examined in detail to establish whether clay minerals have been detected with TES spectra.

[16] The 465 index map is very similar to the combined maps of Northern and Southern Acidalia endmembers identified by *Rogers et al.* [2007] collectively representing ST2 surfaces that show a reduced distribution compared with the original map of *Bandfield et al.* [2000b]. Obvious mismatches are the hematite-rich locations of Meridiani Planum and Aram Chaos. This is an error of commission due to the overlap of a hematite spectral feature in the same region as the index.

[17] Because the 465 index uses only the low wavenumber portion of TES spectra, which has the highest signal-to-noise ratio (SNR) and is least sensitive to spacecraft-induced spectral artifacts [*Bandfield*, 2002] and atmospheric dust, we were able to use a temperature limit of 250 K, the full orbit range up to orbit (OCK) 26183, and a dust opacity up to 0.29 to produce the map. Consequently, this map serves as a high resolution (16 ppd), high SNR proxy for ST2, revealing a remarkable level of detail that is

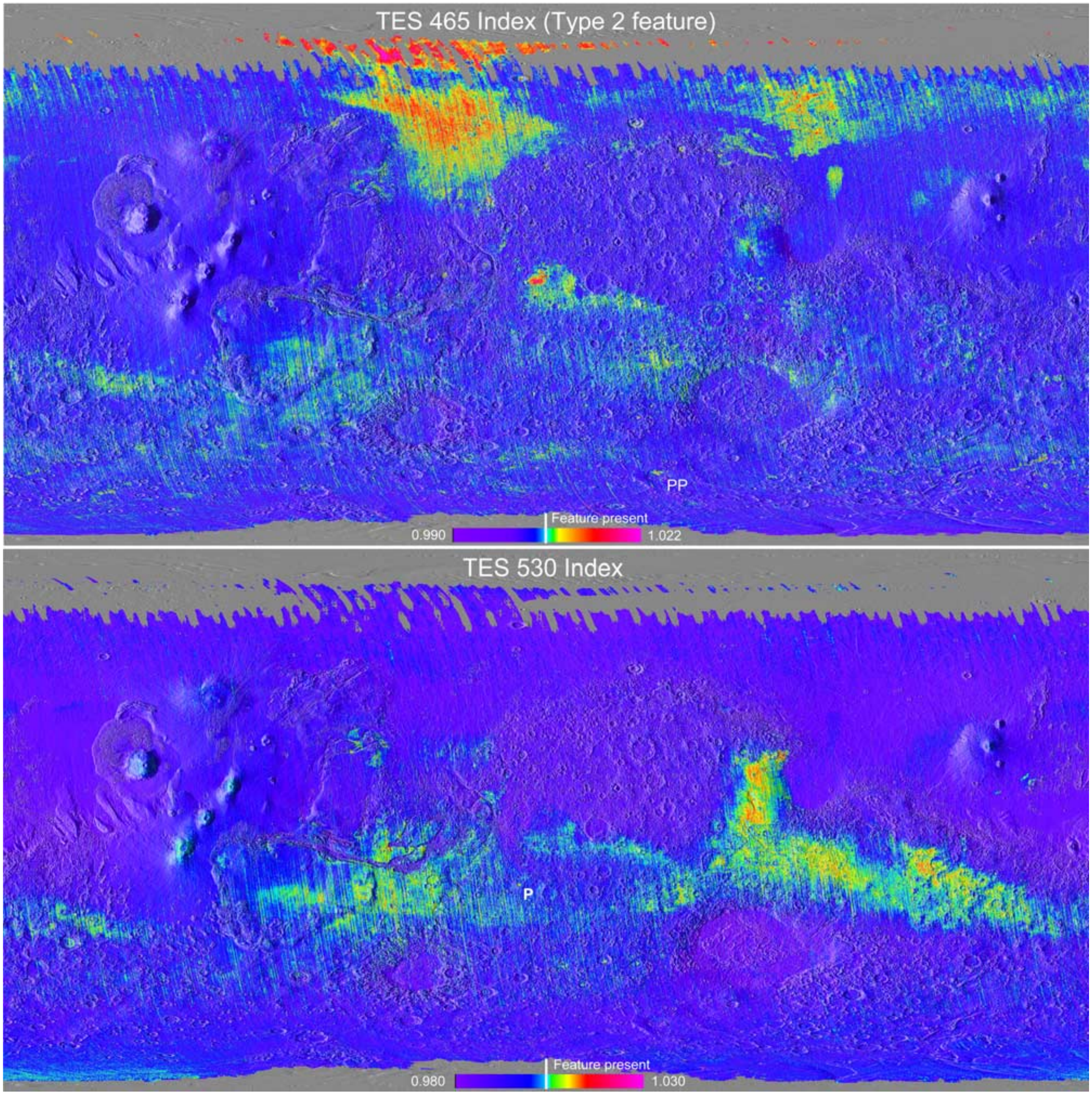

Figure 2. Maps of two indices (overlaid on MOLA shaded-relief) developed to search for dioctahedral smectites on Mars using TES spectra. Locations where both indices are elevated may host smectites. Lettered locations are described in the text and Figure 3.

not evident in the original [*Bandfield et al.*, 2000b] or more recent [*Rogers et al.*, 2007] 1 ppd global TES maps. For example, there are 10 s of isolated locations in the southern high latitudes (>50°) that have intermediate to high values of the 465 index but low 530 index values, suggestive of ST2 material. Some of these are large enough to show up as single pixels in the 1 ppd maps of *Rogers et al.* [2007] but might be dismissed because they are so isolated. We have examined many of these occurrences and found them to be associated with dune fields and sand sheets within and between craters in most cases. For example, Pityusa Patera southwest of the Hellas basin (PP in Figure 2) contains dunes whose spectra have a 465 index comparable to northern Acidalia. An averaged spectrum from this location clearly displays ST2 characteristics following atmospheric correction (Figure 3a), demonstrating that not only is a feature near 465 cm^{-1} common to both locations, but the full ST2 spectral character is as well.

[18] A clear correlation exists between the 530 index and the low albedo surfaces of the southern highlands where *Bandfield et al.* [2000b] mapped the strongest signatures of the global ST1 basaltic unit. Many of the primary igneous silicate phases of basalt, especially olivine, display absorptions in the region of the 530 index. Some of the strongest index values are located in Syrtis Major and Nili Fossae, places previously recognized as having identifiable exposures of olivine [*Hoefen et al.*, 2003; *Hamilton and Christensen*, 2005; *Mustard et al.*, 2005]. The 530 index therefore serves

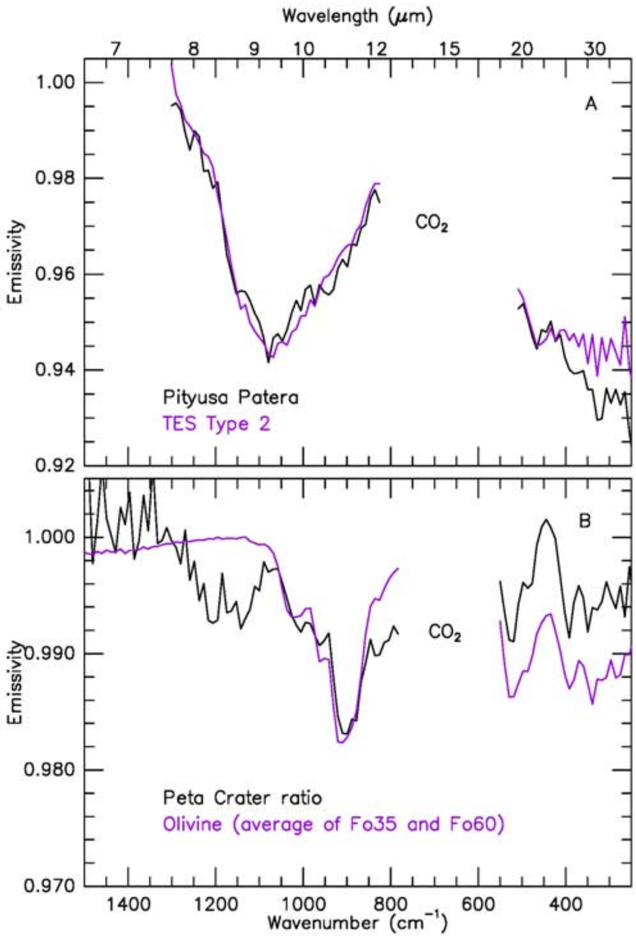

Figure 3. Example results obtained from maps in Figure 2. (a) Pityusa Patera (PP on the 465 index map in Figure 2) displays elevated 465 index values but low 530 index values. Deconvolution of an averaged TES spectrum from this location using the 7 endmembers of *Bandfield et al.* [2000a] produces an atmospherically-corrected spectrum similar to TES surface type 2. The misfit at low wavenumbers (<400) may be due to incomplete removal of atmospheric water vapor (the sawtooth features) in the original type 2 spectrum. (b) Peta Crater (P on the 530 index map in Figure 2) displays elevated 530 index values but low 465 index values. A ratio of TES spectra averaged from within the crater and an outside surface to the north matches the spectrum of two olivine compositions averaged together.

to highlight olivine-rich surfaces on the planet. For example, a small crater (~75 km diameter) southwest of Meridiani Planum called Peta (P in Figure 2) shows elevated 530 index values (average = 1.008) but low 465 index values (average = 1.003). A ratio of averaged TES spectra from inside and outside the crater to remove atmospheric contributions [e.g., *Ruff and Christensen*, 2002] reveals the clear signature of olivine (Figure 3b).

4. Discussion

[19] The absence of an absorption feature near 530 cm^{-1} throughout the northern lowlands severely constrains the possible mineral phases that can be present there because very few silicate phases lack an absorption feature in this spectral region. Combined with OMEGA results [e.g., *Poulet et al.*, 2005], the presence of clay minerals in ST2 material is increasingly unlikely. Among the candidate components for ST2, high-silica volcanic glass such as obsidian and aluminous or opaline silica show no absorption in the region of the 530 index (Figure 1). Many zeolites display only minor absorptions in this region but because they have a ~1.9 μm feature that has not been observed by OMEGA or any other near infrared spectrometer observing the northern lowlands, they are less likely candidate phases. High silica amorphous phases thus remain as the best candidate components of ST2 material, although we cannot distinguish between primary and secondary forms using our methodology.

[20] The apparent association of elevated 465-index values with high southern latitude dunes is notable given the fact that the highest values of the 465 index in the northern hemisphere occur in the dunes of the north polar erg (Vastitas Borealis). It is these dunes that display the most intense ST2 signature in the original map of *Bandfield et al.* [2000b]. Perhaps the association of high latitude dunes with ST2 signature in the northern and southern hemispheres implies a link to polar processes. Such speculation is consistent with the geographically constrained distribution of ST2 material suggested by *Wyatt and McSween* [2002] and *Wyatt et al.* [2004]. The association with dunes also could simply reflect the fact that the dunes in these cases are locally the darkest and least dusty surfaces, yielding the best spectra. Careful examination of the apparent southern hemisphere ST2 occurrences may provide new details on the origin of the still enigmatic nature of this material.

5. Conclusions

[21] (1) Dioctahedral smectites are not detected in abundances >10–20% in Acidalia Planitia or other northern lowlands. The absence of an absorption feature near 530 cm^{-1} combined with the presence of a strong feature near 465 cm^{-1} is most consistent with an amorphous high silica component in ST2 material, either as a primary or secondary phase.

[22] (2) The 465 index is a good proxy for ST2 material, highlighting locations that have been overlooked because they are below the spatial resolution of previous maps. Tens of locations in the southern high latitudes (>50°) display elevated values of the index and typically are associated with dunes. One such example is Pityusa Patera southwest of the Hellas Basin.

[23] (3) The 530 index is sensitive to olivine and serves as a reconnaissance tool for locating undiscovered occurrences, one of which is in Peta Crater south of Meridiani Planum. ST2 terrains appear devoid of olivine.

[24] **Acknowledgments.** The authors wish to thank Mike Smith for providing modeling of atmospheric CO_2 for this work. We also thank Deanne Rogers and Joe Michalski for their thoughtful reviews. This work was funded in part through NASA's Mars Global Surveyor Science Program.

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