Thermal alteration: A possible reason for the inconsistency between OMEGA/CRISM and TES detections of phyllosilicates on Mars?

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Abstract Previous laboratory analyses have shown that high temperatures can modify the crystal structures of some phyllosilicates in such a way that their spectroscopic signatures appear different from various wavelength perspectives. This may be the case in the Nili Fossae region of Mars, where our analyses indicate that thermally altered (~400°C) Fe-rich smectites might be possible mineral analogs to the phyllosilicate-bearing units in addition to mineral assemblages formed by Fe/Mg smectite and amorphous weathering products. We suggest that thermal alteration of phyllosilicates induced by impact shock or other heat sources might be a widespread process throughout Martian history. The mixing of altered and unaltered phyllosilicates might be partially responsible for the apparent disconnect between VNIR and TIR observations of Fe/Mg smectite-bearing surfaces on Mars.

1. Introduction

Previous studies using visible and near-infrared (VNIR) spectra from the Mars Express Observatoire pour la Minéralogie, l’Eau, les Glaces, et l’Activité (MEx/OMEGA) and the Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars (MRO/CRISM) have shown phyllosilicates to be present in the Martian crust and primarily associated with ancient, layered terrains, deep clay deposits exposed in canyon walls or exhumed by impact craters, or remobilized units in the highlands corresponding to intracrater fans and deltas [e.g., Poulet et al., 2005; Murchie et al., 2009]. The association of Martian phyllosilicates with ancient, heavily cratered terrains suggests that their post depositional history may be closely coupled to impact processes [e.g., Fairén et al., 2010; Ehlmann et al., 2011]. Models [Abramov and Kring, 2005] have shown that large impacts, forming basins >1000 km diameter can lead to long-term heating of the target rocks in dry systems and postimpact temperatures as high as 1200°C can last for tens of thousands of years. In the laboratory, most phyllosilicates start to lose H₂O at temperatures of ~100°C and exhibit significant degradations in their crystal structures between 400 and 800°C, mainly attributable to the dehydroxylation and recrystallization processes that occur as temperature increases [e.g., Milliken and Mustard, 2005; Fairén et al., 2010; Gavin and Chevrier, 2010; Che et al., 2011; Che and Glotch, 2012]. Therefore, we hypothesize that impact-induced dehydration and/or dehydroxylation of phyllosilicates was a widespread process on early Mars and that thermally altered phyllosilicates may be abundant on the Martian surface. In this study we show suggestive spectral evidence from the Nili Fossae region that impact-generated heating caused thermal metamorphosis of phyllosilicates while excavating these minerals from depth.

Nili Fossae is located west of the large Isidis Basin where Noachian crust is well exposed (Figure 1A). Interpretation of both OMEGA and CRISM spectra shows that Nili Fossae contains one of the most significant phyllosilicate exposures on Mars and that phyllosilicates detected in this region are predominantly Fe/Mg- rich smectite minerals [e.g., Poulet et al., 2005; Mangold et al., 2007; Ehlmann et al., 2009; Michalski et al., 2010]. Here we focus on the NE-SW striking graben shown in Figure 2A. The “on deposit” surface contains phyllosilicate signatures based on analysis of VNIR data [Ehlmann et al., 2009; Michalski et al., 2010]. The “off deposit” surface is located within the graben, eroded and flooded by Syrtis Major basaltic lavas; a mineralogical map based on OMEGA data shows that phyllosilicate minerals might be rare in this region [Michalski et al., 2010]. CRISM observations have been used to identify several phyllosilicate phases in the “on deposit” region, such as Al-rich phyllosilicates, serpentine, chlorite, and the most commonly detected Fe/Mg smectite mineral solid solution [Ehlmann et al., 2009]. The OMEGA VNIR spectrum [Michalski et al., 2010] of the “on deposit” area displays an Fe–OH feature at 2.28 μm and associated hydration bands (1.4 and 1.9 μm),

Key Points:
- We propose a post-impact thermal alteration hypothesis for clays on Mars.
- Thermally altered clays may be present on Mars and mixed with unaltered clays.
- The mixing may lead to disconnect between NIR and TIR detections of clay on Mars.

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suggesting the presence of Fe-rich smectite minerals. However, TIR spectra from the Thermal Emission Spectrometer (TES) consistently exhibit an absorption near 450 cm$^{-1}$, which does not match any particular Fe-rich smectite [Michalski et al., 2010]. Poorly crystalline aluminosilicates resulting from chemical weathering processes or shock metamorphism have been proposed as possible explanations for this spectral phenomenon [Michalski et al., 2010]. Our laboratory spectra [Che and Glotch, 2012] of ~400°C heated nontronite show that the triplet spectral feature in the Si–O bending region (~400–600 cm$^{-1}$) disappears at 400°C and is replaced by a single absorption at ~450 cm$^{-1}$ while displaying weak 1.9, 2.29, and 2.4 μm spectral bands in the NIR region (Figures S1 and S2). The objective of this study is to determine whether thermally altered Fe-rich smectites are a viable alternative to mineral phases or assemblages that might lead to the apparent disconnect between the NIR and TIR detections of Fe/Mg smectite minerals in the Nili Fossae region.

2. Data and Methods

We applied our laboratory spectra of 400°C heated nontronite on the Nili Fossae region by using a variety of spectroscopic methods, covering VNIR to TIR wavelengths. (1) We used the non-negative least squares (NNLS) linear deconvolution algorithm of Rogers and Aharonson [2008], with a spectral library (Table S1) that includes thermally altered (at 400°C) nontronite, to deconvolve an average TES spectrum of a surface in the Nili Fossae region that was determined to be Fe/Mg smectite bearing and nontronite bearing based on CRISM [Ehlmann et al., 2009] and OMEGA data [Michalski et al., 2010], respectively. For comparison, we also deconvolved an average TES spectrum of a nearby surface that appears spectrally neutral in OMEGA data. For this method, 30 and 23 high quality (low water ice opacity, low dust opacity, and high surface temperature) TES spectra from OCK 3245 were selected and averaged for the nontronite-bearing surface and the nearby

![Figure 1. Spectral characterization of thermally altered nontronite at Nili Fossae, Mars (part 1). (A) THEMIS daytime infrared gray scale mosaic of the Nili Fossae region. (B) Regional-scale map of the 450 cm$^{-1}$ index in the Nili Fossae region. Several smaller regions do indeed have high index values (white and black arrows). The black arrow in this index map points to a high 450 cm$^{-1}$ index region that corresponds to the study area outlined in Figure 2A. (C and D) FATT analysis of TES spectra gathered from the region of Nili Fossae depicted in Figure 1B. Figure 1C shows the FATT-derived spectra of thermally altered nontronite and pure nontronite. Neither FATT-derived spectrum is a perfect match to the laboratory target spectra, but the match to the thermally altered nontronite spectrum is clearly better. Figure 1D shows the linear deconvolution of our FATT-derived spectrum results in a good model fit using 46% altered nontronite.](https://example.com/figure1.png)
We used spectral ratios of TES data to help us determine the long-wavelength spectral character of the nontronite-bearing deposits. An average of 30 un-atmospherically corrected high quality TES spectra covering a deposit of interest was divided by a spectrum averaged from 23 un-atmospherically corrected TES spectra from an adjacent, relatively "spectrally neutral" surface. TES spectra from the same orbit were used to avoid errors brought by different atmospheric conditions between orbits [Rogers and Bandfield, 2009; Michalski et al., 2010]. We used local-scale spectral index mapping of thermally altered nontronite, based on the unique TIR spectral properties of this phase. This index was developed to map the ~450 cm\(^{-1}\) absorption feature of thermally altered nontronite [Che and Glotch, 2012]. This index was created according to the formula \(i = (\varepsilon_{508} + \varepsilon_{371})/(\varepsilon_{444} + \varepsilon_{466})\), where the subscripts represent the wavelengths of individual channels.

Figure 2. Spectral characterization of thermally altered nontronite at Nili Fossae, Mars (part 2). (A) Context image of the Nili Fossae region showing positions of TES and CRISM data shown in Figures 2B, 2C, and 3. (B) Measured surface and modeled TES spectra occurring on and off the nontronite deposit identified by OMEGA and CRISM. The gray box indicates a long-wavelength region where the spectra differ due to the possible presence of thermally altered nontronite in the deposit. (C) Ratios of TES spectra occurring on and off deposits identified in Nili Fossae as nontronite bearing by OMEGA. The long-wavelength (low wavenumber) portion of each ratio spectrum is a good match to a laboratory spectrum of nontronite heated to 400°C. It is a poor match to spectra of unaltered nontronite.
in the TES spectrum. (4) We used factor analysis and target transformation (FATT) [Malinowski, 1991] to determine the independently variable TIR spectral components in regions of interest. We gathered 5616 individual TES spectra from the Nili Fossae region and applied R-mode factor analysis and target transformation, using a linear deconvolution algorithm, with spectra of atmospheric components, basaltic TES Surface Type 1 (ST1), TES Surface Type 2 (ST2), Martian surface dust [Smith et al., 2000; Bandfield and Smith, 2003], thermally altered (at 400°C), and unheated nontronite as “targets.” (5) Using CRISM data, we performed local-scale index mapping of thermally altered nontronites using the ratio of band depths of the 1.4 and 1.9 μm spectral features. At 400°C, the 1.4 μm feature of nontronite disappears completely and irreparably while the 1.9 μm feature is still strong due to rehydration (Figure S2). Therefore, mapping the ratio of 1.4 and 1.9 μm may provide insight about whether the nontronite-bearing surfaces were dehydroxylated. To map this ratio, we created a 1.4 μm band depth index according to $i = (1 - R1430/(0.4*R1370 + 0.6*R1470))$ and a 1.9 μm band depth index according to $i = (1 - R1915/(0.77*R1857 + 0.23*R2112))$ [Pelkey et al., 2007].

3. Results

We recovered Martian atmospheric components and two surface components from TES data using the FATT algorithm [Malinowski, 1991]. Atmospheric dust, water ice, synthetic CO$_2$, and H$_2$O vapor are recovered and can account for the atmospheric variability in the data (Figure S3). The surface components include basalt (Figure S4) and a spectral shape (Figures 1C and 1D) that is modeled as 46% thermally altered nontronite, 20% other (unaltered) phyllosilicates and zeolites, and <10% of every other phase. The favored interpretation of the second surface component is that it is a mineral assemblage consisting primarily of thermally altered nontronite (400°C) that varies independently of the basaltic spectral shape.

Based on the results of our FATT spectral analysis, we performed additional detailed investigations of specific areas of interest. Figure 1B shows a TES band depth index map at ~450 cm$^{-1}$, which is the position of the main long-wavelength spectral feature of nontronite thermally altered at 400°C [Che and Glotch, 2012]. Several small (~100 km$^2$) regions have elevated index values (arrows), indicating the presence of a strong 450 cm$^{-1}$ band. The black arrow indicates a high index value region that corresponds to the elevation region cut by the graben (Figure 2A) with positive Fe/Mg smectite detections in CRISM and OMEGA data [Ehlmann et al., 2009; Michalski et al., 2010]. We investigated this region further using linear spectral mixture analysis [Rogers and Aharonson, 2008] of TES data and CRISM index mapping. The results of our spectral mixture analysis (Figure 2B) show that the average TES spectrum covering the “on deposit” surface is modeled with a substantial fraction (19 ± 8%) of thermally altered nontronite and a comparatively minor amount (8 ± 4%) of unaltered phyllosilicates and zeolites. By contrast, the “off deposit” spectrum is modeled with a smaller fraction (5 ± 6%) of altered nontronite and a larger fraction (13 ± 4%) of unaltered phyllosilicates. The mineralogical differences between these two deposits are also expressed in the measured and modeled spectra from these regions, which are shown in Figure 2B. In the spectral region highlighted in gray, the emissivity for the spectrum “on” the deposit has a lower overall emissivity and a shallower slope toward longer wavelengths as compared to the spectrum collected “off” the deposit. This can be explained by the long-wavelength spectral nature of the thermally altered nontronite and the contribution of this component to the TES spectrum on the deposit (Figure 2B).

The spectral ratio approach can help mitigate the errors due to atmospheric conditions and help us gain a better understanding of the spectral character of regions of interest [Rogers and Bandfield, 2009; Michalski et al., 2010]. Michalski et al. [2010] used this method to show that regions in Nili Fossae identified as nontronite-bearing by OMEGA display a unique long-wavelength spectral feature centered at ~450 cm$^{-1}$. Michalski et al. [2010] were not able to uniquely identify this feature at the time, but noted that it was a poor match to laboratory emissivity spectra of nontronite. In this work, we created ratio spectra from two TES orbits covering “nontronite” deposits identified by OMEGA and CRISM (on and off deposits shown in Figure 2A). These ratio spectra, shown in Figure 2C, are poor matches to the long-wavelength (~350–550 cm$^{-1}$) spectral features of nontronite, but compare favorably to the long-wavelength features of nontronite thermally altered at 400°C. The spectral band at shorter wavelength (~1050 cm$^{-1}$) is similar to basalt feature [Michalski et al., 2010]. The match between the laboratory and ratio spectra is relatively poor at longer wavelengths (200–280 cm$^{-1}$), but this is likely due to the strong influence of atmospheric dust in this region. Atmospheric dust is spectrally neutral at study wavelengths (~350–550 cm$^{-1}$), providing for a cleaner ratio in this region (Figure 3S).
Figures 3a and 3b show a 1.4 to 1.9 μm CRISM ratio index map and two characteristic CRISM ratio spectra of phyllosilicates from this region. Inspection of the index map reveals that the spectrum of spot A displays a relatively higher 1.4/1.9 μm index value than spot B (Figure 3a). The shape of spot A matches relatively well to a mixed spectrum of unaltered and thermally altered nontronite. The CRISM spectrum of spot B exhibits a weaker 1.4 μm feature. One possible interpretation of this observation is that spot B has more thermally altered nontronite than spot A. This result agrees well with the previous TES deconvolution result. However, the lack of a match with the CRISM data at 1.9 and 2.3 μm regions is also apparent in Figure 3b. The presence of various hydrated phases might account for the H₂O absorption bands. The observed absorption band with a minimum at 2.295 μm shows a mismatch with our mixing lab spectra of heated and unheated nontronite (2.285 μm). The cause of the 2.295 μm feature might be related to the presence of various compositions of smectite octahedral cations [e.g., Bishop et al., 2002; Bishop et al., 2008; Andrieux and Petit, 2010]; however, we favor the interpretation of its being due to Fe-rich smectite which could have a 2.295 micron feature. In earlier work that used NIR spectroscopy to study nontronite and ferruginous smectite, Frost et al. [2002] showed that the combination bands of the OH stretching frequencies of the FeFeOH units are observed in the range 4374–4351 cm⁻¹ (2.286–2.298 μm). Thus, the presence of different types of Fe-smectites would be consistent with our analysis results.

4. Discussion

Several issues related to the occurrence of thermally altered Fe-rich smectites in the Nili Fossae region still bear consideration, given that there are alternatives to “thermal alteration” as causes of the 450 cm⁻¹ feature in the Si–O bending region. At both ~2.3 μm and ~450 cm⁻¹ regions, absorption features of Fe/Mg smectite solid solution smoothly vary depending on its octahedral cations as well as the degree of order inside the mineral structure [e.g., Grauby et al., 1994; Andrieux and Petit, 2010]. The natural intermediate Fe/Mg smectite sample hvalfj054 in Ehlmann et al. [2012], for example, has a single feature at 450 cm⁻¹ and displays absorption band at ~2.3 μm. The 450 cm⁻¹ band may also be consistent with the products of weathering, hydrothermal alteration, or acid decomposition of phyllosilicates in addition to dehydroxylation at high temperatures [e.g., Madejová, 2003; Rampe, 2011]. Thus, mineral assemblages formed by Fe/Mg smectite and amorphous weathering products would be plausible alternatives to explain the IR data in the Nili Fossae region.

In this study, our remote sensing analysis of the Nili Fossae region suggests that thermally altered nontronite (at ~400°C) could be used as possible mineral analogs to the phyllosilicate-bearing units detected within the study region. Occurrences of dehydrated or dehydroxylated phyllosilicates on Mars likely require a specific set of conditions: (1) an ancient phyllosilicate-rich stratum, (2) source of heat, and (3) little or no liquid water availability. Phyllosilicates detected on Mars have been primarily dated as early-to-mid Noachian in age [e.g., Poulet et al., 2005; Bibring et al., 2006; Mangold et al., 2007; Michalski and Noe Dobrea, 2007]. Impacts, volcanic flows, and the cooling of Mars’ early crust can serve as heat sources [Ehlmann et al., 2011]. Given the widespread association of phyllosilicates with impact craters [e.g., Poulet et al., 2005; Bibring et al., 2006; Fairén
et al., 2010; Ehlmann et al., 2011), we propose two scenarios for phyllosilicate alteration: First, postimpact temperatures could be sufficiently high and long lasting to lead to thermal alteration of phyllosilicate deposits. Second, phyllosilicate-bearing rocks altered at depth due to other sources of heat might be exposed via cratering processes. However, it is important to point out that each scenario may have two possible consequences depending crucially on the water availability during formation of impact craters: the formation of hydrothermal systems, as is generally accepted [e.g., Fairén et al., 2010; Ehlmann et al., 2011; Tornabene et al., 2013], and anhydrous thermal alteration as we have proposed. If impact excavation occurred on ancient Mars, when the scale of groundwater aquifers was likely large enough to support and promote hydrothermal systems, then some phyllosilicates would likely be hydrothermally produced after the formation of impact craters [Fairén et al., 2010; Tornabene et al., 2013]. On the other hand, cratering or other heating during the Hesperian, with ceased hydrothermal activity and lower water availability, would provide favorable conditions for anhydrous thermal alteration. Additionally, the generally cold and dry surface conditions available at the time would enable the preservation of dehydrated or dehydroxylated phyllosilicates [Morris et al., 2010, 2011], either at the surface or in the subsurface.

It is also important to note that thermally altered phyllosilicates might not exist as a pure phase on Mars. For the Nili Fossae region, the co-existence of altered and unaltered nontronite is likely one of the possible reasons for the inconsistency between MIR and VNIR detections of nontronite. We suggest that the unaltered and thermally altered nontronite are mixed together such that the VNIR spectrum displays characteristic 1.4, 1.9, 2.29, and 2.4 μm features while the long-wavelength range is dominated by a strong 450 cm⁻¹ feature. This result is possible as mixing of VNIR spectra is highly nonlinear [Nash and Conel, 1974; Singer, 1981; Mustard and Pieters, 1989] and the spatial resolutions of TES and CRISM are very different (~3 x 8 km/pixel vs. 18 m/pixel).

5. Conclusions

Combining remote sensing analyses and laboratory investigations in this study has shown that it is reasonable to use thermally altered nontronite as mineral analogs for the phyllosilicate-bearing units in the Nili Fossae region of Mars in addition to mineral assemblages formed by Fe/Mg smectite and amorphous weathering products. Nontronite in the Nili Fossae region may not be present as a pure phase, suggesting that it was partially affected by postdepositional thermal alteration. The mixing of altered and unaltered phyllosilicates is likely one possible cause for the apparent disconnect between previous VNIR and TIR observations of nontronite-bearing surfaces in Nili Fossae. The possible presence of thermally altered phyllosilicates points to the potential effects of postdepositional thermal alteration of Martian sediments as a key component of understanding past Martian aqueous alteration history.

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