

SPECTROSCOPIC STUDY OF DEHYDRATED AND/OR DEHYDROXYLATED PHYLLOSILICATES AND NATURAL ZEOLITES: IMPLICATIONS FOR MARTIAN EXPLORATION. C. Che¹, T. D. Glotch¹,¹ Department of Geosciences, Stony Brook University, Stony Brook, NY 11794 (cche@ic.sunysb.edu)

Introduction and background: Phyllosilicates detected on the surface of Mars are primarily associated with heavily cratered Noachian terrains [1-4]. It has been suggested that at least some phyllosilicates on Mars were likely formed from long-lived hydrothermal systems initiated by impact processes (e.g. [5]), then pre-existing phyllosilicates were excavated by following repeated impact events [6]. Abramov and Kring [7] modeled an impact-induced hydrothermal system on Mars and the results indicated that temperatures as high as 1200 °C could last for thousands of years. Fairen et al. [6] calculated the temperature increases in a transient crater resulting from an impact, and their model showed that temperatures can reach close 1000 °C in a certain area around the point of impact. In the laboratory, 400-500 °C is efficient for phyllosilicates to lose their interlayer H₂O and most phyllosilicates can be completely dehydroxylated at 900 °C (e.g. [8]). These previous conclusions lead us to propose that phyllosilicates on Mars may have been affected by impact processes, with an emphasis on postshock heating and that dehydrated and/or dehydroxylated phyllosilicates may occur on the present-day Martian surface.

In order to (1) study how the infrared spectra of phyllosilicates change with exposure to increasingly higher temperatures and (2) provide a reference database for future searches for dehydrated and/or dehydroxylated phyllosilicates resulting from impact-induced high temperatures on Mars, we acquired attenuated total reflectance (ATR), mid-to-far-IR specular reflectance, mid-to-far-IR emissivity, near-IR diffuse reflectance spectra of incrementally heated phyllosilicate samples [8, 9]. Here we present the summary of spectroscopic study of dehydrated and/or dehydroxylated phyllosilicates and the implication for Martian exploration.

Methods: We would like to provide a comprehensive spectral library for thermally treated aluminosilicate minerals, so fourteen phyllosilicates from four structural groups (kaolinite, smectite, sepiolite-palygorskite, and chlorite) and two natural zeolites (mordenite and clinoptilolite) were selected for this study. Most of the minerals we have chosen to study have been identified or tentatively identified on Mars in OMEGA or CRISM data [1-4, 10]. All samples described in this study were prepared to <2 μm size fractions prior to heat treatments. The phyllosilicates and zeolites were then heated for 24 hours to 100, 200, 300, 400, 500, 600, 700, 800, and 900 °C. All heated

products were stored in a desiccator before spectral measurements.

Infrared spectra of thermally treated phyllosilicates and zeolites were acquired at Stony Brook University in the Vibrational Spectroscopy Laboratory (VSL) using a Nicolet 6700 FTIR spectrometer. Table 1 shows a summary of analysis techniques which were performed on dehydrated and/or dehydroxylated samples.

Table 1 Summary of measurements

Measurements	spectral range	Equipment description
Mid-IR specular reflectance	400-4000 cm ⁻¹	Baseline FT-30 accessory, KBr beamsplitter, TE-cooled deuterated L-alanine doped tryglycine sulfate (DLATGS) detector, KBr window
Far-IR specular reflectance	100-600 cm ⁻¹	Baseline FT-30 accessory, Thermo Fisher Solid Substrate beamsplitter, DLATGS detector, polyethylene window
NIR diffuse reflectance	1.2-2.5 μm	Nicolet diffuse reflectance accessory, CaF ₂ beamsplitter, InGaAs detector
Attenuated total reflectance	400-4000 cm ⁻¹	Smart Orbit single bounce ATR accessory with a type II A diamond ATR element
Mid-IR emissivity	400-2000 cm ⁻¹	KBr beamsplitter, DLATGS detector
Far-IR emissivity	100-600 cm ⁻¹	Thermo Fisher Solid Substrate beamsplitter, DLATGS detector

Summary of spectral results: (1) The OH stretching (~3600 cm⁻¹), OH bending (~590-950 cm⁻¹), and/or H₂O bending (~1630 cm⁻¹) bands all become very weak or completely disappear upon heating to temperatures >500 °C for phyllosilicates and zeolites; (2) The spectral changes associated with SiO₄ vibrations (~1000 cm⁻¹ and ~500 cm⁻¹) show large variations depending on the compositions and structures of phyllosilicates. Spectral features of kaolinite change significantly at ~400 °C and the new bands are relatively stable until 900 °C. Most smectite samples display two distinct spectral changes with increased temperature, which may be related to their dehydration and dehydroxylation processes respectively. Clinocllore also exhibited dual changes in spectral features on heating, likely due to the presence of two different types of hydroxyl groups. The modulated tetrahedral sheets of palygorskite/sepiolite minerals showed more complex spectral changes upon heating than other phyllosilicates included in this study. Compared to the phyllosilicates, the spectral features of two natural zeolites, clinoptilolite and mordenite, are less affected by thermal treatments. Even after heating to 900 °C, the IR spectral features do not show significant differences from those of un-

heated zeolites. These spectral results are consistent with the fact that the three-dimensionally rigid crystal structure of zeolite is more stable than the layer structure of phyllosilicates. (3) The composition of octahedral sites showed a great influence on spectral behaviors of phyllosilicates: IR spectra of Al^{3+} rich smectites are more stable than those of Fe^{3+} rich smectites; the stability of Al^{3+} rich smectites decreases as the Al^{3+} abundance decreases; spectral behaviors of Mg^{2+} rich phyllosilicates are distinctly affected by the formation of new crystal phases around 700 °C; phyllosilicates with a small amount of Mg^{2+} in their octahedral sites all showed new spectral bands at $\sim 920 \text{ cm}^{-1}$ upon heating to 700 °C or higher temperatures (Figure 1). (4) NIR spectral results showed that 14 of 16 samples analyzed in this study exhibited a new spectral band near $1.365 \mu\text{m}$ as temperature increased. The two exceptions are nontronites NAu-1 and NAu-2. This new feature varied between the different minerals. This new band disappeared simultaneously with the complete disappearance of other bands in near-IR region.

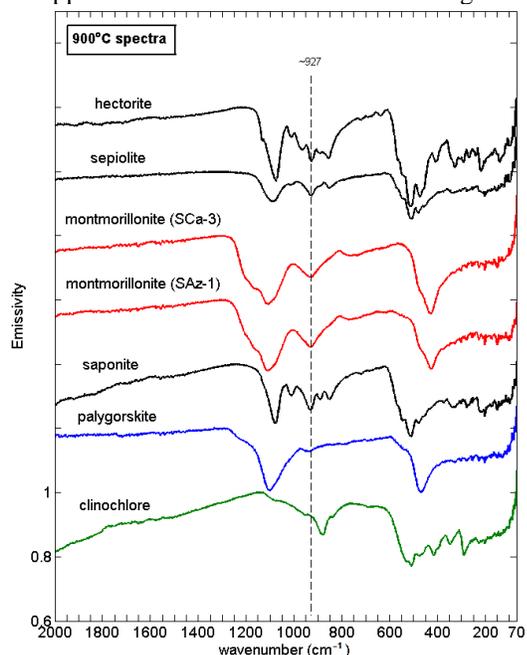


Figure 1. The 900 °C emissivity spectra of phyllosilicates containing Mg^{2+} cation. (hectorite: 19.77wt% MgO , sepiolite: 22.38 wt% MgO , saponite (24.49 wt% MgO , clinocllore: 25.36 wt% MgO , palygorskite: 9.52 wt% MgO , SCa-3 montmorillonite: 8.55 wt% MgO , SAz-1 montmorillonite: 5.8 wt% MgO)

Implications: Michalski et al. (2010) [11] analyzed the nontronite deposits in the Nili Fossae region using TES data. They did not detect the spectral features showing the occurrences of nontronite in long-wavelength region. Instead, TES data consistently exhibited a spectral absorption located near $\sim 450 \text{ cm}^{-1}$ on

the same surfaces where OMEGA and CRISM data identified the diagnostic NIR spectral bands ($1.9, 2.3,$ and $2.4 \mu\text{m}$) for nontronite. Spectra of nontronites heated to 400 °C (Figure 2) may help to explain the disconnect between the TIR and NIR observations of nontronite in Nili Fossae region. The doublet or triplet spectral feature in the Si-O bending region of nontronites of this study disappeared at 400 °C and was replaced by one single absorption centered at $\sim 450 \text{ cm}^{-1}$, while nontronite samples kept their weak $1.9, 2.3,$ and $2.4 \mu\text{m}$ spectral bands in NIR region. This leads to the possibility that the nontronite deposits in the Nili Fossae region may be partly composed with nontronite heated to temperatures around 400 °C.

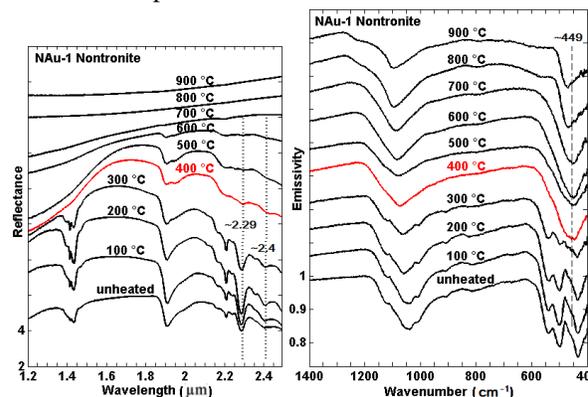


Figure 2. NIR reflectance and TIR emissivity spectral results of NAu-1 nontronite calcined at various temperatures.

Future work: Because previous studies [6, 12] and the spectral results of this project showed suggestive evidence of thermally affected phyllosilicates on Mars, we will work to identify and pursue opportunities to use spectral results from this work in conjunction with thermal IR and near IR data returned from the Martian surface.

References: [1] Poulet F. et al. (2005) *Nature*, 438, 623--627. [2] Bibring J. -P. et al. (2006) *Science*, 312, 400--404. [3] Mangold N. et al. (2007) *J. Geophys. Res.*, 112, E08S04, doi:10.1029/2006JE002835. [4] Michalski J. R. and Noe Dobrea E. Z. (2007) *Geology*, 35, 951-954. [5] Schwenzer S. P. et al. (2010), *LPSC XLI*, #1589. [6] Fair n A. G. et al. (2010), *Proceedings of the National Academy of Sciences*, 107, 12095-12100, doi:10.1073/pnas.1002889107. [7] Abramov O. and Kring D. A. (2005), *J. Geophys. Res.*, 110, E12S09, doi:10.1029/2005JE002453. [8] Che C. et al. (2010) *in preparation*. [9] Che C. et al (2010) *submitted*. [10] Ehlmann B. L et al. (2009), *J. Geophys. Res.*, 114, E00D08, doi:10.1029/2009JE003339. [11] Michalski J. R. et al. (2010) *Icarus*, doi:10.1016/j.icarus.2009.09.006. [12] Gavin P. et al. (2010) *Icarus*, 208, 721-734, doi:10.1016/j.icarus.2010.02.027.