

EFFECTS OF THERMAL ALTERATION ON THE NEAR-INFRARED AND MID-INFRARED SPECTRA OF MARTIAN PHYLLOSILICATES. T. Daly^{1,2}, P. Gavin¹, and V. Chevrier¹, ¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, ²Department of Geological Sciences, Brigham Young University, Provo, UT, terikdaly@byu.edu.

Introduction: Because of their Noachian age, martian phyllosilicates provide insight into the Mars' earliest history [1, 2]. Nontronite, montmorillonite, saponite, kaolinite, chlorite, serpentine, and prehnite have each been detected on Mars [2-5]. These minerals were deposited when Mars was volcanically active and experiencing a high meteoritic impact flux. Consequently, martian phyllosilicates probably experienced a high degree of thermal alteration from contact metasomatism, shock metamorphism, and impact-induced hydrothermalism. Understanding how phyllosilicates respond to thermal alteration constrains these minerals' formation and alteration, thereby providing insight into early surface conditions on Mars. This study examines the effects of thermal alteration on the spectral properties of phyllosilicates and these minerals' relationship to the martian surface.

Methods: Samples of saponite, kaolinite, chlorite, serpentine, and prehnite were ground and dry sieved to <63 μm . Next, samples were heated in a Lindberg tube furnace for 24 hours at temperatures between 300°C and 1100°C in 100°C increments. After heating, samples cooled in the oven before being removed and analyzed.

NIR Spectra: Prior to measuring NIR spectra, samples were placed on a 150°C hotplate under N_2 flow for two hours. A Nicolet 6700 FTIR spectrometer with a fiber optic probe, CaF_2 beamsplitter, and TEC detector was used to collect spectra from 1 to 2.5 μm .

MIR Spectra: MIR spectra (5-15 μm) were taken under ambient conditions using a diffuse reflectance accessory, KBr beamsplitter, and DTGS detector.

Results: For every mineral studied, NIR bands weaken with increasing temperature and finally disappear at high temperatures. New MIR bands appear at high temperatures due to the formation of secondary phases [6]. Bands in the 2.2 to 2.4 μm range may shift position due to the different thermal resistances of the cation-hydroxyl bond [4, 6].

Saponite: The 1.4 μm hydration feature disappears at 800°C. The 1.91 μm feature decreases in depth with increasing temperature. The 2.31 μm Mg-OH absorption band [2] disappears at 900°C. In the MIR, the 5.57 and 14.0 μm bands disappear at 600°C. New features at 5.08, 5.38, 5.56, 6.02, 9.92, and 10.39 μm appear at 800°C, a 6.96 μm feature appears at 1000°C, and new bands at 8.59, 9.50, and 11.47 μm appear at 1130° (Fig. 1).

Kaolinite: At 500°C the doublet near 1.4 μm becomes a single absorption feature, which decreases in depth before disappearing at 800°C. The doublet near

2.2 μm , a combination of 2Al-OH vibrations [4], becomes a single band at 500°C. Its depth decreases until 1000°C and then slightly increases at 1100°C. Significant changes in the MIR spectra occur at 500°C and 800°C.

Chlorite: The 1.4 μm hydration feature disappears at 800°C. The depths of the 2.26 μm feature (caused by AlFe-OH or AlMg-OH [7]) and 2.34 μm Mg-OH feature [7] decrease with increasing temperature before disappearing at 1000°C and 900°C, respectively. These absorption bands shift to shorter wavelengths at high temperatures (Fig. 2) due to the preferential destruction of bonds that with lower thermal resistances [4, 6]. The MIR spectra of chlorite show much less change than the spectra of the other minerals studied.

Serpentine: The slope of the 1 to 1.4 μm portion of the NIR spectra changes from negative to positive at 600°C. The OH stretch overtone at 1.4 μm [8] decreases in depth with increasing temperature but persists to 1000°C (Fig. 3). Since this is different from the other minerals in this study, the high temperature serpentine samples will be the subject of additional investigations. The Mg-OH combination band at 2.33 μm [8] decreases in depth before disappearing at 800°C. Significant changes in the MIR are seen at 600°C and 1000°C.

Prehnite: Nearly all of this mineral's spectral features disappear at 800°C, including the diagnostic 1.48 μm band [4], the shallow band near 1.9 μm , and all but one of the metal-OH bands. The most noticeable change in MIR spectra also occurs at 800°C, although some changes are seen at other temperatures.

Discussion and Conclusions: The NIR spectra of phyllosilicates evolve characteristically with temperature, allowing a mineral's NIR spectra to be used as a proxy thermometer for maximum alteration temperature. At high temperatures, however, NIR spectra become featureless. MIR spectra can then be used to identify high temperature secondary phases [6]. Future work includes studying additional minerals and identifying high temperature secondary phases using XRD and SEM.

Comparing spectra from Mars with those in this study may permit a better understanding of martian phyllosilicates' thermal alteration and in particular if the phyllosilicates found in craters result from post-impact hydrothermalism. For example, a CRISM spectrum of saponite in a Mawrth Vallis crater [2] lacks a 1.4 μm feature but has a 2.3 μm band. In addition, it has a shape that is clearly different from that of unheated saponite (Fig. 4). Our experiments show that saponite loses its 1.4 μm band at 800°C and that the

2.3 μm feature becomes weak beginning at 600°C, suggesting this saponite was heated during the impact event.

This deposit likely consists of a mixture of saponite heated to different temperatures by a temperature gradient caused by the impact. For example, it may be a mixture of saponite heated to ~500-600°C and saponite heated to ~800°C. This evidence for alteration suggests that the saponite deposit existed before the impact crater formed and thus was not formed in an impact-induced hydrothermal system.

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References: [1] Poulet, F. et al (2005) *Nature*, 438, 623-627. [2] McKeown, N. K. et al (2009) *JGR*, 114, E00D10. [3] Bibring, J-P. et al (2005) *Science*, 307, 1576-1581. [4] Ehlmann, B. L. et al (2009) *JGR*, 114, E00D08. [5] Mustard, J. F. et al (2008) *Nature*, 454, 305-309. [6] Gavin, P. and Chevrier, V. (2010) *Icarus*, 208, 721-734. [7] Bishop, J. L., et al (2008) *Clay Minerals*, 43, 35-54. [8] Ehlmann, B. L. et al (2010) *Geophys. Res. Lett.*, 37, L06201.

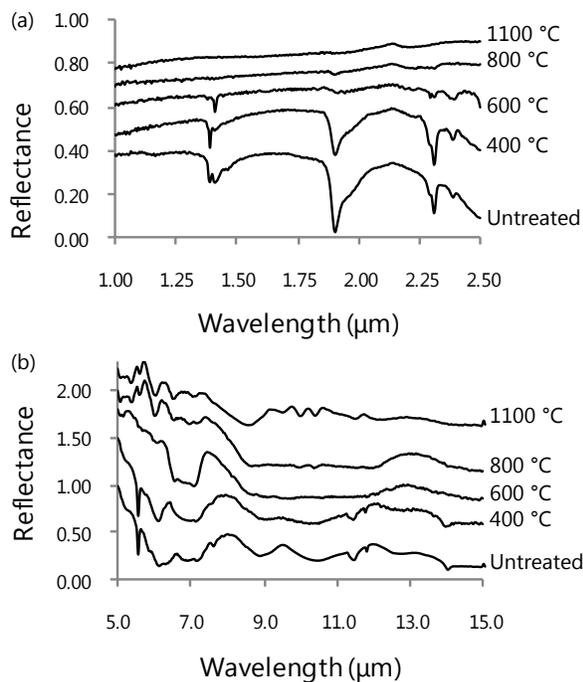


Figure 1. (a) NIR and (b) MIR spectra of saponite.

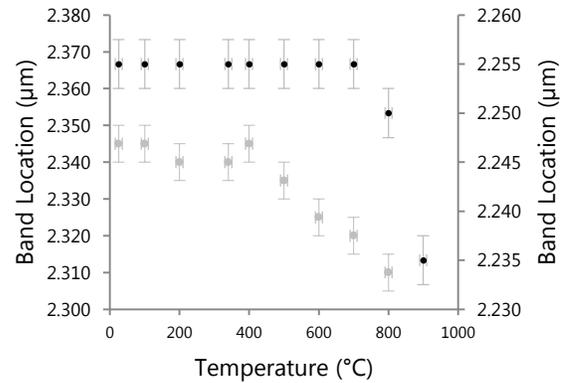


Figure 2. Changes in the location of the 2.26 and 2.34 μm bands in chlorite NIR spectra with temperature. The ordinate axis at right corresponds to the 2.34 μm feature (gray) and the ordinate axis at left is for the 2.26 μm feature (black).

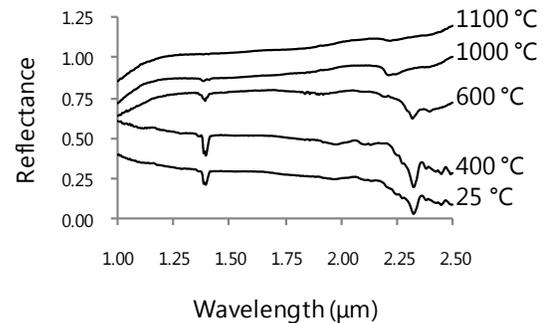


Figure 3. NIR spectra of serpentine.

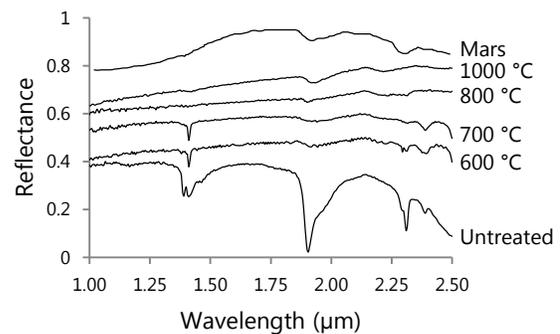


Figure 4. Comparisons of saponite in a crater in Mawrth Vallis [2] and experimental data.