

EFFECTS OF THERMAL ALTERATION ON THE NEAR-INFRARED AND MID-INFRARED SPECTRA OF PHYLLOSILICATES: IMPLICATIONS FOR MARS. 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 planet's earliest history [1, 2]. Nontronite, montmorillonite, saponite, kaolinite, chlorite, serpentine, and prehnite have all been detected on the martian surface [2-5]. These minerals were deposited when Mars was volcanically active and experiencing a high impact flux. Consequently, martian phyllosilicates experienced thermal alteration as a result of contact metamorphism, shock metamorphism, and impact-induced hydrothermal processes [6]. Understanding how phyllosilicates respond to thermal alteration constrains these minerals' formation and alteration and thus provides insight into early surface conditions on Mars. This study examines the effects of thermal alteration on the spectral properties of phyllosilicates and their 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 were allowed to cool in the oven before being removed and analyzed.

NIR Spectra: Prior to NIR spectral measurements, samples were placed on a 150°C hotplate under N₂ flow for two hours. A Nicolet 6700 FTIR spectrometer with a fiber optic probe, CaF₂ 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: NIR bands disappear at high temperatures, causing spectra to become featureless. New MIR bands appear at high temperatures because of 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 Fe-OH, Mg-OH, and Al-OH bonds [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. New MIR bands begin to appear at 600°C, with a significant change at 1100°C (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 , caused by a combination of 2Al-OH vibrations [4], becomes a single band at 500°C. Its depth decreases until 1000°C and then increases at 1100°C. Signifi-

cant 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 and 2.34 μm features decrease with increasing temperature before disappearing at 1000°C and 900°C, respectively. These absorption bands also shift to shorter wavelengths at high temperatures (Figs. 2, 3) due to the preferential destruction of bonds that are less heat resistant [4, 6]. The chlorite MIR spectra 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 [7] decreases in depth with increasing temperature but persists to 1000°C. This is the only mineral for which this feature is still present at 1000°C. 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 [7] decreases in depth before disappearing at 800°C. Significant changes in the MIR are seen at 600°C and 1000°C.

Prehnite: This mineral is unique because nearly all of its spectral features disappear at 800°C. This includes the characteristic 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. The prehnite sample heated to 1100°C for 24 hours melted and was unrecoverable. However, when heated at 1100°C for only four hours, we were able to recover some sample for analysis.

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. At high temperatures, however, NIR spectra become featureless. MIR spectra can then be used to identify high temperature secondary phases [6]. Current 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' alteration history and thus provide additional insight into conditions during Mars' earliest history. 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. 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.

This deposit likely consists of a mixture of saponite heated to different temperatures. For example, it may be a mixture of saponite heated to ~500-600°C and saponite heated to ~800°C. (Fig. 4). This evidence of alteration suggests that the saponite deposit is older than the impact crater and thus was not formed in an impact-induced hydrothermal system.

Acknowledgements: A NSF-funded REU program at the Arkansas Center for Space and Planetary Science supported this work. Dan Ostrowski provided the heated serpentine samples.

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] Ehlmann, B. L. et al (2010) *Geophys. Res. Lett.*, 37, L06201.

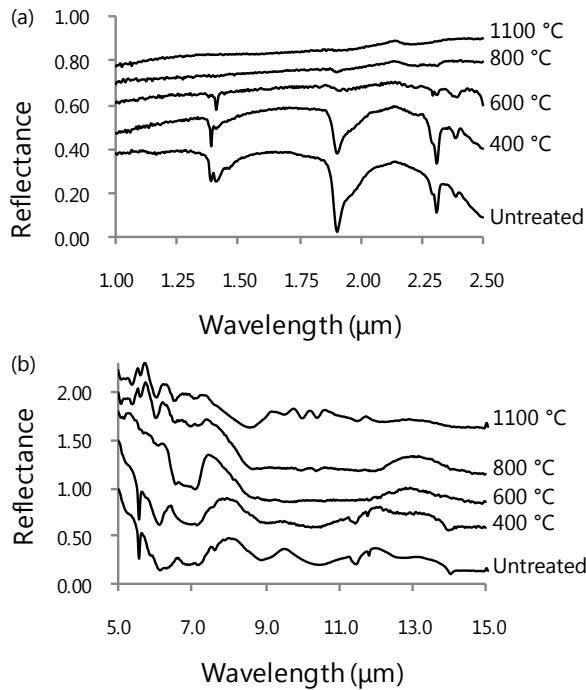


Figure 1. (a) NIR and (b) MIR spectra of saponite.

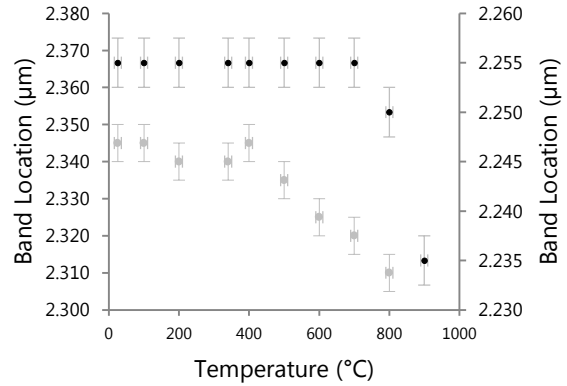


Figure 2. Changes in the location of the 2.26 and 2.34 μm bands in chlorite NIR spectra with temperature. The ordinate axis at right corresponds to the 2.34 μm feature (gray) and the ordinate axis at left is for the 2.26 μm feature (black).

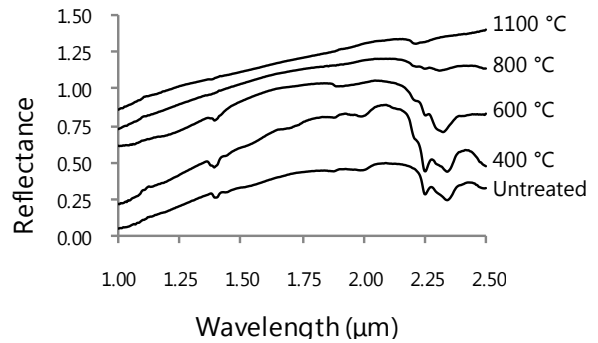


Figure 3. NIR spectra of chlorite.

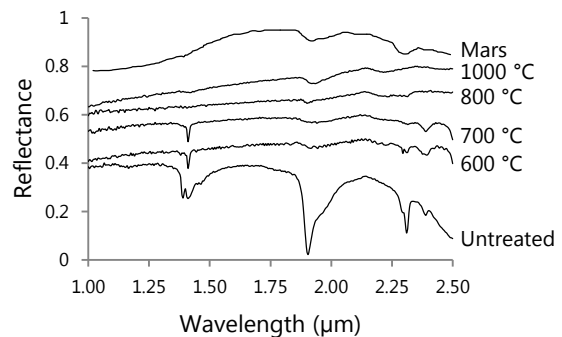


Figure 4. Comparisons of saponite in a crater in Mawrth Vallis [2] and experimental data.