

## THERMAL TRANSFORMATION OF PHYLLOSILICATES AND THEIR IMPLICATIONS FOR MARS.

A. Gillett<sup>1,2</sup>, P. Gavin<sup>2</sup>, V. Chevrier<sup>2</sup> and R. Ulrich<sup>2</sup>. <sup>1</sup>Arkansas Tech University, Russellville, AR 72801, <sup>2</sup>Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701, agillett@uark.edu.

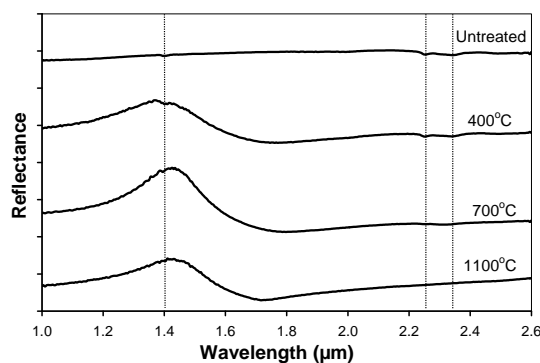
**Introduction:** OMEGA/Mars Express data was confirmed by CRISM/MRO data of the existence of phyllosilicate minerals on the surface of Mars [1, 2]. These phyllosilicates have been found in some of the oldest terrains of Mars and because of their Noachian age, they hold clues to the earliest history of the martian surface. Phyllosilicates have been detected in outcrops surrounded by lava flows and in the ejecta of small impact craters [3, 4]. Previous studies have suggested that phyllosilicates may form by impact-induced hydrothermal processes [5] while others imply that they formed much earlier and that thermally altered phyllosilicates may be responsible for the properties of the red dust that covers the martian surface [6, 7]. In this study, we investigate the effects of thermal treatment on the spectral properties of phyllosilicates, focusing on kaolinite, chlorite, serpentine and saponite, and their relation to the martian surface.

**Experimental and Analytical Methods:** One-gram samples of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), chlorite ( $\text{Na}_{0.5}(\text{Al,Mg})_6(\text{Si,Al})_8\text{O}_{18}(\text{OH})_{12}\cdot 5(\text{H}_2\text{O})$ ), serpentine ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) and half gram samples of saponite ( $\text{Ca}/2,\text{Na})_{0.3}(\text{Mg,Fe}^{2+})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2\cdot 4(\text{H}_2\text{O})$ ) were heated in a Lindberg tube furnace to temperatures ranging from 300°C to 1100°C for 24 hours. Samples were heated in air, allowed to cool, and weighed after heating. Samples were heated in air instead of  $\text{CO}_2$  because it has been shown that the composition of the atmosphere has little effect on the thermal transformation of phyllosilicates [2]. Here we show the results of our chlorite, saponite, and kaolinite samples.

Near infrared (NIR) and mid infrared (MIR) reflectance spectra were taken of each sample in the ranges of 1.0 – 2.6  $\mu\text{m}$  and 5 – 15  $\mu\text{m}$  using Fourier Transform Infrared Spectroscopy (FTIR). The NIR spectra used a range of 2000 to 12500  $\text{cm}^{-1}$ , a white light source, a DTGS detector and a  $\text{CaF}_2$  beamsplitter. The MIR spectra used a range of 350 to 7400  $\text{cm}^{-1}$ , an infrared source, a DTGS detector and a KBr beamsplitter.

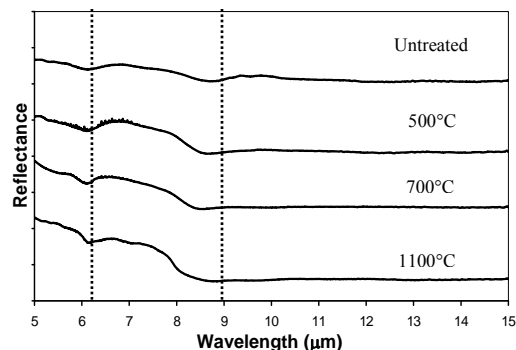
**Results and Discussion:** Weighing the heated samples showed there was an average mass decrease of about 25%, most likely due to loss of interlayer water, as it has been shown to be lost at lower temperatures than is structural water [6].

The NIR spectra of an untreated sample along with heated samples of chlorite are shown in Figure 1. At temperatures above 400°C, the 1.4 and 2.3  $\mu\text{m}$  bands corresponding to the phyllosilicate's structural hydroxyl and metal-hydroxyl bond, respectively, have essentially disappeared. This correlates with the fact that structural  $\text{OH}^-$  is lost in phyllosilicates at temperatures above  $\sim 300^\circ\text{C}$  [8].



**Figure 1:** NIR spectra of heated chlorite samples.

Figure 2 shows the MIR reflectance spectra of an untreated sample of chlorite compared to heated samples. The two characteristic bands are at 6.25 and 8.85  $\mu\text{m}$ . At temperatures above 500°C, the 6.25  $\mu\text{m}$  band shifts to higher wavelengths by 0.07  $\mu\text{m}$  and the 8.85  $\mu\text{m}$  band shifts to lower wavelengths by  $\sim 0.8$   $\mu\text{m}$ .



**Figure 2:** MIR spectra of heated chlorite samples.

The NIR spectra of heated saponite samples (Fig. 3) show that the 1.9 and 2.3  $\mu\text{m}$  bands are no longer visible above 700°C, although the 1.4  $\mu\text{m}$  band is still present, indicating the presence of some structural hydroxyls remaining in the mineral. At 400°C, a new band appears at 2.4  $\mu\text{m}$ . At temperatures above 700°C, the spectra become featureless in this range indicating

the structure of saponite has been completely destroyed.

Figure 4 shows the MIR spectra of heated samples of saponite. The characteristic bands are present at 5.59, 6.13, 7.24, 11.5, and 14.0  $\mu\text{m}$ . All these bands have disappeared at high temperatures ( $T > 1100^\circ\text{C}$ ) while new bands appear at 9.18, 9.62, 10.0, and 10.8  $\mu\text{m}$ . The presence of such new bands indicates the formation of secondary phases which could include sillimanite, hematite and possibly cristobalite [2].

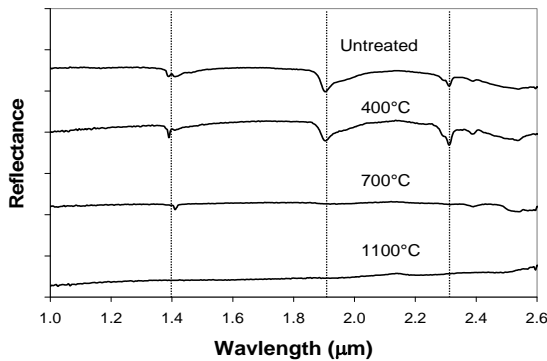


Figure 3: NIR spectra of heated saponite samples.

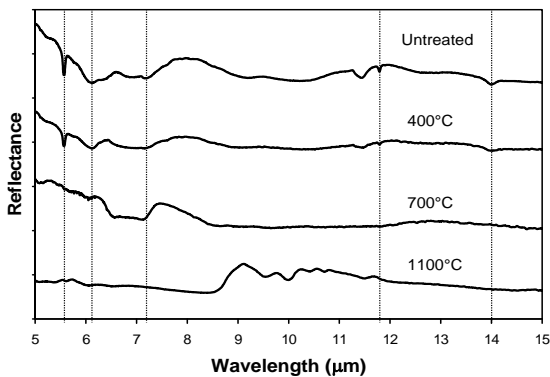


Figure 4: MIR spectra of heated saponite samples.

The NIR spectra of the heated kaolinite samples in Figure 5 shows that the 1.9, 2.16, and 2.20  $\mu\text{m}$  bands are no longer visible above 800 $^\circ\text{C}$ . Moreover, at temperatures as low as 400 $^\circ\text{C}$ , the overall shape of the spectra changes from a nearly flat continuum to a broad peak centered around 1.4  $\mu\text{m}$ .

**Implications for Mars:** The high temperatures from events such as volcanism would have easily transformed phyllosilicates into secondary phases. We have shown that high temperatures alters the spectra of phyllosilicates, allowing us to more accurately classify the spectra of martian phyllosilicates. Using NIR reflectance spectra of phyllosilicates, we will determine whether these phyllosilicates were thermally altered and to what extent. This will help better understand the age and formation process of martian phyllosilicates.

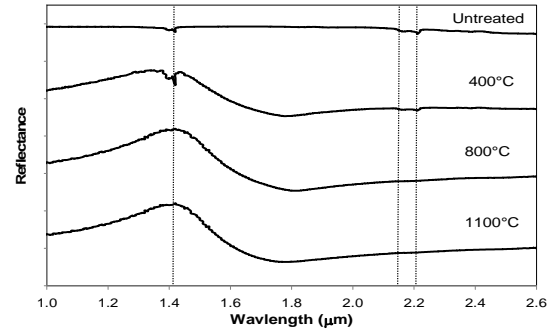


Figure 5: NIR spectra of heated kaolinite samples.

Figure 6 shows the MIR spectra of heated samples of kaolinite. The identifying bands are marked at 5.51, 6.16, and 7.76  $\mu\text{m}$ .

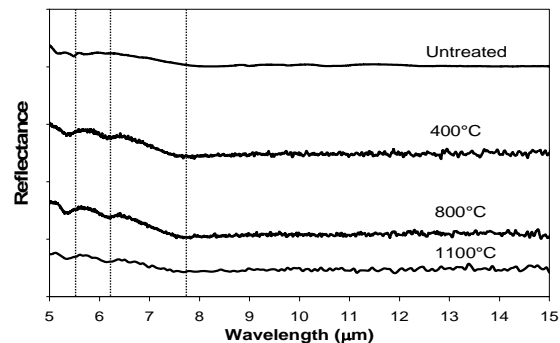


Figure 6: MIR spectra of heated kaolinite samples.

**Conclusions:** Heat is the substantial factor in the transformation of phyllosilicates, which are affected at temperatures as low as 350 $^\circ\text{C}$  through the loss of interlayer water. Phyllosilicates transform at high temperatures into secondary phases, which we identified from each minerals' MIR spectra. We found that chlorite, saponite and kaolinite transforms to sillimanite, albite, corundum, and anorthite.

**Future Work:** We will investigate the NIR/MIR spectra of other heated phyllosilicate minerals, including illite, biotite, phlogopite, muscovite, and clinocllore.

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**References:** [1] Chevrier, V. *et al.*, (2006) *Lunar Planet Sci.* XXXVII. [2] Gavin, P. and V. Chevrier, *Icarus* (2009) submitted. [3] Poulet, F., *et al.*, (2005) *Nature* 481, 623-627 [4] Mangold, N., *et al.*, (2007) *J. Geophys. Res.* 112. [5] Naumov, M., (2005) *Geofluids* 5, 165 - 184. [6] Weldon, R. J., *et al.*, (1982) *J. Geophys. Res.* 97, 10102-10114. [7] Boslough, M. B., *et al.*, (1986) *J. Geophys. Res.* 91, E207-E214. [8] MacKenzie, K. J. B. and D.E. Rogers, (1977) *Thermochemica Acta* 18, 177-196).