

The Effect of High Temperatures on the Emission and VNIR Reflectance Spectra of Phyllosilicates and Zeolites

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Introduction: This work is an important part of an ongoing project that includes infrared, NMR, and X-ray studies of the dehydration and dehydroxylation of phyllosilicates and zeolites. Because most phyllosilicates found on the surface of Mars are associated with ancient terrains [1-3], it is possible that the phyllosilicates were repeatedly subjected to high temperatures resulting from impact processes and continuous exposure to high temperatures is likely to lead to the dehydration and dehydroxylation of phyllosilicates. We hypothesize that the dehydration and dehydroxylation of phyllosilicates subjected to impact was a widespread process on early Mars, and that dehydrated and dehydroxylated phyllosilicates may be still abundant on the surface of Mars. Zeolites were also selected as a part of this study since zeolites may be another important class of minerals that are present on the surface of Mars in a hydrated state [4-6] and zeolites have similar chemical compositions to phyllosilicates, including a similar Si/O ratio.

In previous work we performed thermogravimetric analysis (TGA), X-ray diffraction (XRD), attenuated total reflectance (ATR), and mid-IR and far-IR reflectance measurements on fourteen phyllosilicates, two zeolites and their heating products [7]. Here we continue to report emissivity and visible and near-IR (VNIR) reflectance spectra for our samples in order to: (1) continue and improve the studies on how the IR spectra of phyllosilicates and zeolites change with exposure to increasingly higher temperatures; (2) provide emissivity and VNIR reflectance data to search for the existence of dehydrated or dehydroxylated phyllosilicates resulting from impact events on the surface of Mars.

Methodology: *Acquisition and preparation of samples* All of the samples were purchased from the Clay Minerals Society (CMS) repository except chlorite [Table 1]. To facilitate precise characterization of our samples, the phyllosilicates and zeolites used in this study were prepared to less than 2 μm prior to heating treatment. All of the samples were then heated for 24 hours to 100, 200, 300, 400, 500, 600, 700, 800, and 900 °C.

VNIR spectra The visible and near infrared reflectance (0.8-2.5 μm) spectra were acquired using a Nicolet diffuse reflectance accessory and ratioed

TABLE 1. Summary of phyllosilicates and zeolites for this study

Mineral	Sample Number	Source	Size Fraction
Montmorillonite ("Cheto")	SAz-1	CMS	<2 μm
Ca-Montmorillonite	STx-1	CMS	<2 μm
Na-Montmorillonite	SWy-2	CMS	<2 μm
Montmorillonite ("Otay")	SCa-3	CMS	<2 μm
Mica-montmorillonite	Syn-1	CMS	<2 μm
Beidellite	SBCa-1	CMS	<2 μm
Hectorite	SHCa-1	CMS	<2 μm
Saponite	SapCa-2	CMS	<2 μm
Nontronite	NAu-1	CMS	<2 μm
Nontronite	NAu-2	CMS	<2 μm
Kaolinite	KGa-1b	CMS	<2 μm
Sepiolite	SepSp-1	CMS	<2 μm
Palygorskite (Attapulgite)	PFI-1	CMS	<2 μm
Chlorite	BUR1340	BurminCO	<2 μm
Mordenite	27133	CMS	<2 μm
Clinoptilolite	27031	CMS	<2 μm

to a gold mirror standard. The Nicolet 6700 FTIR spectrometer was equipped with a CaF₂ beam splitter and an InGaAs detector. For each sample, 2048 scans in the VNIR spectral range were recorded with a resolution of 4 cm^{-1} .

Emissivity spectra Emissivity spectra in the mid-IR (400-2000 cm^{-1}) range were acquired by switching off the Glowbar IR source and detecting the radiation from samples directly. A blackbody heated to 70 °C and 100 °C was used to calibrate the emissivity spectra.

Mid-IR emissivity spectral results: Kaolinite-serpentine group Most spectral features belonging to the original kaolinite sample (KGa-1b) have disappeared at 400 °C. Characteristic Si-O stretching vibration absorptions around 1126, 1060, and 1008 cm^{-1} [8] no longer exist above 400 °C and a new spectral absorption feature forms at $\sim 1150 \text{cm}^{-1}$ [Figure 1].

Chlorite group Major spectral changes occur around 300 °C. The Si-O stretching band at $\sim 1003 \text{cm}^{-1}$ shifts to high frequencies after 300 °C.

Sepiolite-palygorskite group Significant changes are observed for palygorskite (PFI-1) in the Si-O stretching region around 1000cm^{-1} and Si-O bending region around $\sim 500 \text{cm}^{-1}$ at the temperature of 400 °C. For sepiolite (SepSp-1), spectral features change slightly at $\sim 300 \text{°C}$ and significant changes are observed between 700 °C and 800 °C spectra which may indicate the structure of sepiolite reaches a stable state again after heating to 800 °C. *smectite group* For montmorillonite samples (SAz-1, SCa-3, SWy-2, STx-1), a

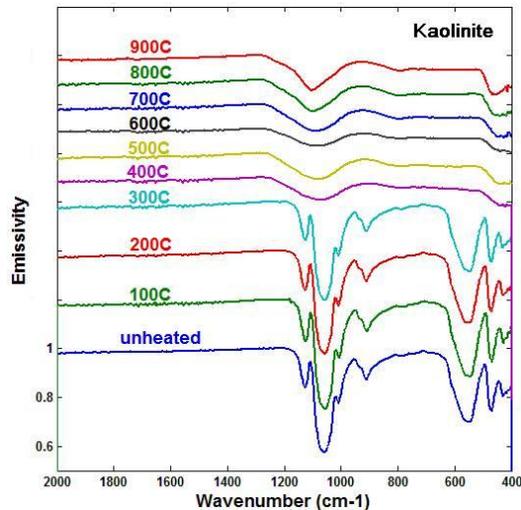


Figure 1: Emissivity spectra of kaolinite (KGa-1b) and its heating products in the range 400-2000 cm^{-1} . Spectra are offset for clarity.

new absorption feature forms in the Si-O stretching region at around 300 °C and disappears after heating to 800 °C. The doublet absorption features in the Si-O bending region are replaced by a single absorption feature at the temperatures higher than 400 °C. Compared to montmorillonites, saponite (SapCa-2) is relatively stable as temperature increases. The emissivity results do not show distinct changes until 800 °C. The single absorption feature at around 1000 cm^{-1} is replaced by multiple absorption features after heating to 800 °C. In the case of beidellite (SBCa-1, Syn-1), the doublet absorption features in the Si-O bending region are stable upon heating and are observed until heating to 900 °C. For hectorite (SHCa-1), spectral results show the structural changes due to heating take place between 400 and 500 °C [Figure 2] and emissivity spectra at temperatures higher than 700 °C are consistent with high-Ca pyroxene (confirmed by XRD measurements). For both of the two nontronite samples (NAu-1 and NAu-2), multiple Si-O bending spectral absorption features near 500 cm^{-1} disappear and turn into a single feature after heating to 400 °C. Si-O stretching features near 1050 cm^{-1} display similar changes at 400 °C.

Zeolite group For clinoptilolite (27031) and mordenite (27133), no distinct changes are observed for tetrahedron stretching feature at $\sim 1080\text{cm}^{-1}$ and bending feature around 470 cm^{-1} in the temperature range 100-900 °C.

VNIR reflectance spectral results: VNIR reflectance spectra of dehydrated and dehydroxy-

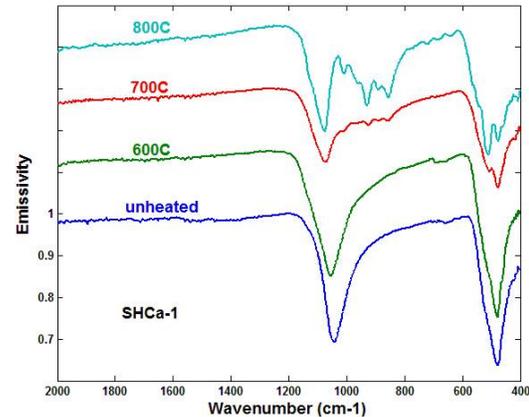


Figure 2: Emissivity spectra of hectorite (SHCa-1) and its heating products in the range 400-2000 cm^{-1} . Spectra are offset for clarity.

lated phyllosilicates have received much attention in past studies [9, 10] since the diagnostic hydration absorption features in this IR range can directly indicate whether or not water is still existing in mineral structure. In this study, VNIR spectra of heated phyllosilicates and zeolites do not only serve as indicators for water existence, they can also provide more insights about structural changes upon heating when spectral changes in VNIR range are compared with those in mid-IR and far-IR ranges. Spectra of some samples show similar changes upon heating in both VNIR and mid-IR ranges. For example, chlorite loses all the diagnostic spectral features at temperature of 300 °C, which is consistent with results from mid-IR emissivity of chlorite. However, there are significant differences for spectral changes in different IR ranges for some samples. The mid-IR emissivity spectrum of clinoptilolite (27031) does not exhibit distinct changes after heating to 900 °C while this sample loses all its spectral features in VNIR range at 800 °C. More detailed VNIR spectral results will be presented in the conference.

References: [1]Bibring, J.-P. et al. (2005) *Science* 307, 1576-1581. [2]Poulet, F. et al. (2005) *Nature* 438, 623-627. [3]Mustard, J.F. et al. (2007) *LPSC XXXIII*, Abstract 2071. [4]Bish, D. L. et al. (2003) *Icarus*, 164, 96-103. [5]Ruff, S. W. (2004) *Icarus*, 168, 131-143. [6]Ehlmann, B. L. et al. (2009) *JGR*, 114, E00D08. [7]Che, C. et al. (2009) manuscript in preparation. [8]Madejová, J. and P. Komadel (2001) *Clay and Clay Minerals*, 49, 410-432. [9]Milliken, R. E. and J. F. Mustard (2007a) *Icarus*, 189, 550-573. [10]Gavin, P. et al. (2008) *LPSC XXXIX*, Abstract 2033.