

THE INFRARED SPECTRA STUDY OF DEHYDRATED AND DEHYDROXYLATED PHYLLOSILICATES. C. Che¹ and T. D. Glotch¹, ¹Department of Geosciences, 255 Earth and Space Sciences Building (ESS), Stony Brook University, Stony Brook, NY 11794-2100. checongcong@gmail.com

Introduction: The OMEGA visible and near infrared imaging spectrometer detected phyllosilicates in ancient Noachian terrains of Mars [1-3]—an observation later confirmed by the CRISM imaging spectrometer [4]. Detailed mapping has shown that the phyllosilicates, most of which are clay minerals, are found in ancient, heavily cratered terrains [1-3]. These clay-bearing deposits contain interbedded and buried craters, and it is possible the phyllosilicates were repeatedly subjected to high temperatures resulting from impact processes [5]. 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.

Here we report the results of changes in the infrared spectra of thirteen phyllosilicates with exposure to increasingly higher temperatures. By investigating the infrared spectral features of phyllosilicates when they are heated to different temperatures, we hope to establish a mid-IR spectral database for dehydrated and dehydroxylated phyllosilicates. This will increase the understanding of possible processes affecting phyllosilicate evolution on Mars and complement future emissivity measurements of phyllosilicates.

Sample description: Phyllosilicates with several different structures were selected for this study. A total of 13 phyllosilicate samples (Table 1) have been analyzed, most of which have been identified or tentatively identified on Mars based on OMEGA and CRISM data [1,4,6]. In order to remove impurities as much as possible from the original samples, the < 2 μm size fraction was isolated [7].

Methodology: Phyllosilicate samples were heated for 24 hours at temperatures from 100°C to 900°C, and infrared reflectance and ATR spectra were measured in the Laboratory for Infrared Spectroscopy (LIRS) at Stony Brook University, using Nicolet 6700 FTIR spectrometer. So far, we have acquired mid-infrared reflectance spectra (500-7000 cm^{-1}), far-infrared reflectance spectra (50-600 cm^{-1}) and ATR (attenuated total reflectance) (500-4000 cm^{-1}) spectra of 13 phyllosilicate samples at different temperatures (from 100°C to 900°C). In addition, we have collected TGA (thermogravimetric analysis) data for our samples to help us gain a more comprehensive understanding of these temperature-related processes.

Table 1. Phyllosilicate minerals to be examined in this work.

| Phyllosilicates | Source |
|----------------------------|--------|
| Kaolin KGa-1b | CMS |
| Sepiolite SepSp-1 | CMS |
| Attapulgite PFl-1 | CMS |
| Clinoptilolite 27031 | CMS |
| Mordenite 27133 | CMS |
| Beidellite SBcA-1 | CMS |
| Saponite SapCa-2 | CMS |
| Montmorillonite SCa-3 | CMS |
| Hectorite SHCa-1 | CMS |
| Montmorillonite SAz-1 | CMS |
| Mica-montmorillonite SYn-1 | CMS |
| Na-Montmorillonite SWy-2 | CMS |
| Ca-Montmorillonite STx-1 | CMS |

Results and Discussion: *OH-stretching vibrations:* The OH-stretching bands are observed in the range ~3500-3700 cm^{-1} [8]. Figure 1a shows the ATR spectra of kaolinite (KGa-1b) at different temperatures. Four distinct bands are observed at 3620, 3650, 3670, and 3680 cm^{-1} due to the OH-stretching vibrations [8]. These peaks disappear after 500°C, which indicates dehydroxylation of kaolinite may happen between 400 and 500°C.

Montmorillonite, from smectite group, is a typical clay mineral found on Mars. From the ATR spectra of chemically distinct montmorillonites (STx-1, SAz-1, SWy-2, SYn-1, SCa-3), we conclude that the dehydroxylation of montmorillonites may start at ~400°C, end near 700°C. We also analyzed three other clay minerals from smectite group that showed different behaviors when they were heated to lose OH: for hectorite (SHCa-1), the OH is likely to be removed from its structure after 700°C; for beidellite (SBcA-1), the dehydroxylation may happen after ~600°C; for saponite (SapCa-2), which is a thermally stable mineral, the OH is remains in its structure until 800°C.

The minerals from zeolite group (27031, 27133) don't exhibit OH-stretching bands near 3600 cm^{-1} , since there is no hydroxyl group in their structures.

For both the sepiolite (SepSp-1) and attapulgite (PFl-1), there are multiple bands for OH stretching vibrations and dehydroxylation may finish after 700°C.

H₂O-bending bands: As shown in Figure 1b, the montmorillonite (SCa-3) exhibit water bending bands near ~1620-1650 cm^{-1} [9]. The water bending bands disappear after 600°C. The complete removal of water may happen around 700°C for hectorite (SHCa-1).

Based on the IR spectra of beidellite (SBCa-1), the dehydration may finish near 600°C. Saponite (SapCa-2) is more stable than other minerals from smectite group, as evidenced by the fact that the water bending band still exists at 700°C.

The dehydration processes for the zeolite group (27031, 27133) end at higher temperatures than seen for the phyllosilicates--between 800 and 900°C.

Multiple bands for H₂O-bending modes are observed in both the sepiolite (SepSp-1) and attapulgite (PFL-1). The water is removed around 600°C for both samples.

There is no water bending band and dehydration process observed for kaolinite (KGa-1b) based on our spectra, since kaolinite (KGa-1b) has no water in its structure.

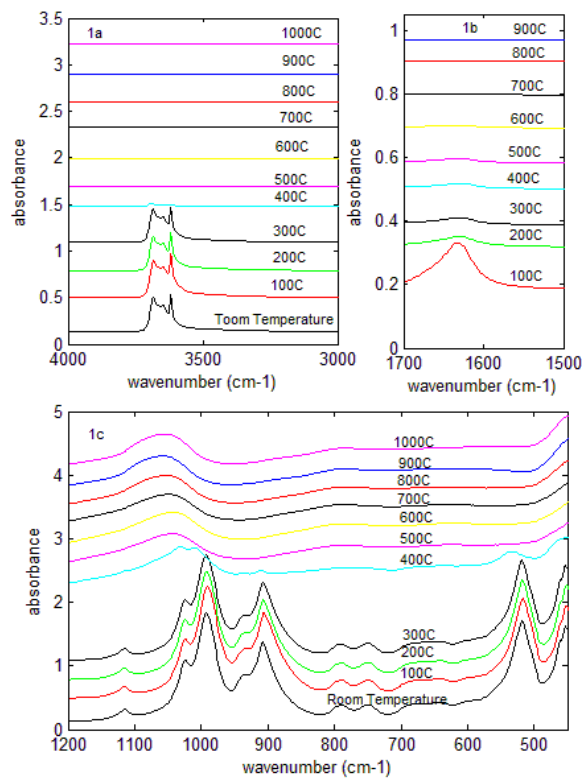


Figure 1: a) ATR spectra of kaolinite (KGa-1b) at different temperatures in the range $\sim 3500\text{--}3700\text{ cm}^{-1}$. b) ATR spectra of montmorillonite (SCa-3) at different temperatures in the range $\sim 1500\text{--}1700\text{ cm}^{-1}$. c) ATR spectra of kaolinite (KGa-1b) at different temperatures in the range $\sim 450\text{--}1200\text{ cm}^{-1}$.

SiO₄ structure: The SiO₄ stretching and bending vibrations are observed near $\sim 1000\text{--}1100\text{ cm}^{-1}$ and $\sim 500\text{ cm}^{-1}$ [8,9,10]. Substitutions of Al or Fe for Si in the tetrahedral sites may influence these vibration

bands [8,9]. Our spectra show that the SiO₄ structures change as the temperature increases, and as expected, these changes are consistent with the dehydration and dehydroxylation processes of each clay sample.

At 400°C, there are very weak peaks for OH in the spectrum of kaolinite (KGa-1b) (Fig. 1a) and the complete removal of hydroxyl may happen between 400°C and 500°C. Correspondingly, distinct change is observed in the SiO₄ stretching and bending vibration bands after 400°C (Fig. 1c).

The SiO₄ bending vibration bands of montmorillonites change more significantly than stretching vibration bands. In the spectra of hectorite and saponite, the SiO₄ stretching vibration bands split to multiple peaks at high temperatures, which may indicate there are new phases generated as temperature increases.

Minerals from zeolite group are more stable when they are heated. Distinct changes in the Si-O bands at high temperatures are not observed based on our spectra.

Both the IR spectra and TGA results show sepiolite and attapulgite may go through more than one step to lose water and OH, and the Si-O structure bands confirm this conclusion. Changes are observed in the SiO₄ stretching vibration bands at 400°C and 800°C.

Conclusion and Future work: Our results indicate that heating affects the structures of phyllosilicates by dehydration and dehydroxylation processes. There may be new phases generated when their structures are destroyed, which needs future work to identify. Different minerals show different behaviors when they are losing water and hydroxyl.

In our future work, we will continue to collect infrared spectra of additional phyllosilicates and collect additional data for our samples, including VNIR reflectance, X-ray Diffraction, NMR, and emissivity spectra, which can provide insights into the crystal structures and help us to answer the question: is it possible that dehydrated and dehydroxylated phyllosilicates are an explanation for poorly crystalline or amorphous materials on Mars?

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