

SPECTROSCOPIC STUDIES OF NONTRONITE AFTER IMPACTS AT 3 PRESSURES. L. R. Friedlander¹, T. Glotch¹, J.R. Michalski², T.G. Sharp³, M.D. Dyar⁴, D.L. Bish⁵. lonia.friedlander@stonybrook.edu ¹Stony Brook University, ²Planetary Science Institute, ³Arizona State University, ⁴Mount Holyoke College, ⁵Indiana University.

Introduction: Phyllosilicates detected on the Martian surface by the Mars Express Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (MEx/OMEGA) [1,2] and Compact Reconnaissance Imaging Spectrometer for Mars (MRO/CRISM) [3,4] are seemingly early-to-mid Noachian deposits [1,5-6]. This suggests that phyllosilicates on Mars may have been exposed to a variety of alteration processes including shock heating and compression associated with meteor impacts. Impacts may be a particularly important process affecting phyllosilicates, especially in the excavation of altered material produced at depth [7].

In recent work [8], the effects of heating alone on the mid-IR spectra of many phyllosilicate minerals were explored. In contrast to our results, results in [9] showed minimal effects of pressure on the NIR and mid-IR spectra of phyllosilicates. Unlike in [9], we exposed our samples to very high pressures. We also attempt to quantify the effects of shock pressure on phyllosilicate mineral IR spectra by directly monitoring compression pressures. We used multiple spectroscopic techniques to understand the physical changes induced in clays by high-pressure impacts. An overview of the samples, shock technique, and other methods employed to analyze the samples is given in [10].

Methods and Materials: We gently ground samples of kaolinite (KGa-1b), nontronite (NAu-1), and chlorite, and separated the <2 μm size fraction using the techniques described in [8,10]. We sent the samples to the Flat Plate Accelerator facility at Johnson Space Center [11] where our samples were exposed to 10, 20 and 40 GPa impacts. The impact-shocked samples were then returned to the Vibrational Spectroscopy Laboratory [12] at Stony Brook University where we analyzed them using three spectroscopic techniques.

Spectroscopy. We used an ASD Fieldspec3 Max UV-visible-NIR reflectance spectrometer to collect reflectance data from 350-2500 μm for each sample. Spectra were referenced to a spectralon standard. In addition, we used a Nicolet 6700 FTIR Spectrometer to measure both attenuated total reflectance (ATR) ($4000\text{-}400\text{ cm}^{-1}$) and pressed-pellet emissivity spectra ($2000\text{-}200\text{ cm}^{-1}$) for each sample. ATR data were collected similarly to [8]. Emissivity spectra were referenced to blackbody calibration targets at 70 and 100 $^{\circ}\text{C}$ and calibrated in the manner of [13].

Results: We found distinct differences between pre-impact and post-impact samples for shock pres-

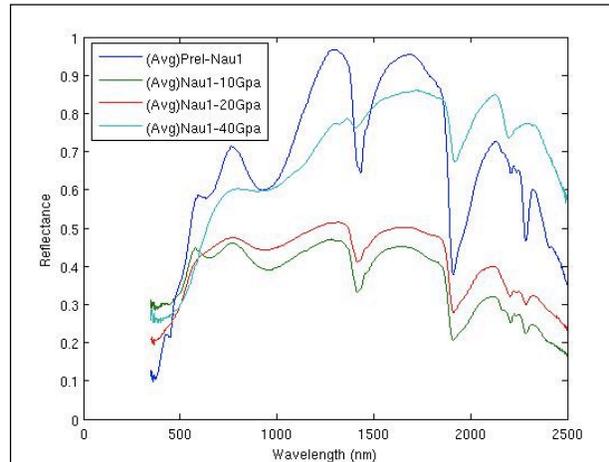


Figure 1. Reflectance spectra comparison of pre and post-impact nontronite samples at three pressures.

ures as low as 10 GPa, but the most dramatic structural changes occurred at pressures between 20 – 40 GPa. Currently, only the nontronite sample was exposed to shock pressures up to 40 GPa. As the nontronite series provides the greatest range of pressures and resulting spectral changes, we focus on it here.

Reflectance Spectroscopy. Figure 1 shows a comparison of the UV-visible-NIR reflectance spectra of the nontronite samples pre-impact, and after 10, 20 and 40 GPa shock compression. We observed gradual broadening and elimination of the feature at $\sim 0.6\ \mu\text{m}$, after exposure to 20 GPa pressure. This feature is attributed to octahedrally coordinated Fe^{3+} crystal field transitions [14]. We also observed visible color changes in the nontronite sample, reddening and darkening with increasing pressure. These observations can be explained by destruction of the Fe^{3+} coordination geometry within the octahedral sheet as a result of compression and partial dehydroxylation [14,15].

In [1], phyllosilicates on the Martian surface were identified using the OMEGA instrument by their $\sim 1.9\ \mu\text{m}$ absorptions, attributed to water of hydration. We observed broadening and shallowing of this feature, corresponding to dehydration of the nontronite sample, which is expected after pressure shock. We also observed the near-elimination of the $\sim 1.4\ \mu\text{m}$ feature, which corresponds to hydroxyl O-H vibrations, after exposure to 40 GPa shock-pressure. Elimination of this feature implies that exposure to shock-pressures

>40 GPa may result in fundamental structural reorganization as a result of dehydroxylation. This hypothesis is supported by observed changes in the absorptions between 2.2-2.4 μm , which correspond to metal-OH (Al-OH, in particular) vibrational overtones

ATR results: Attenuated total reflectance spectra in the mid-infrared wavelength region are given in Figure 2. These results also support alteration processes proceeding through dehydration/dehydroxylation.

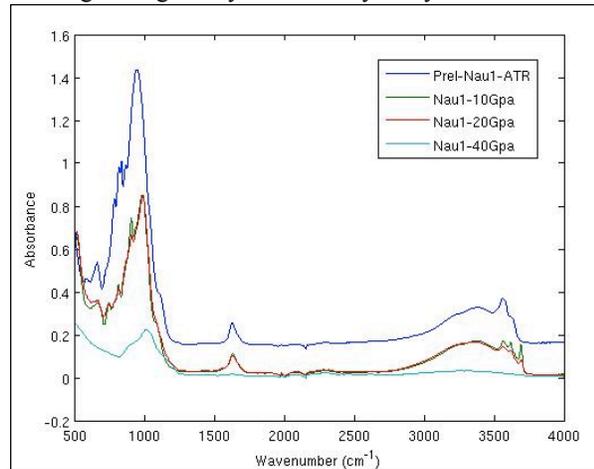


Figure 2. Comparison of ATR spectra of pre- and post-impact nontronite samples at three pressures.

Similarly to [8], we observed major changes among all the spectral features relating to OH groups, both metal-OH and structural H_2O . After 40 GPa shock pressure, the Fe-Fe-OH stretching band ($\sim 3560\text{ cm}^{-1}$), broad H_2O O-H stretching band ($\sim 3400\text{ cm}^{-1}$), and the H_2O bending band ($\sim 1630\text{ cm}^{-1}$) completely disappeared. The Al-Fe-OH, Fe-Fe-OH and Mg-Fe-OH deformation bands around 1000 cm^{-1} (approx. 908 , 808 and 742 cm^{-1}) also disappeared after 40 GPa shock-pressure and were replaced by one weaker, broader feature at $\sim 900\text{ cm}^{-1}$. In addition, the 1000 cm^{-1} Si-O stretching band was weaker, broader, and shifted slightly to higher wavenumbers.

Mid-infrared Emission Spectroscopy. The mid-IR, pressed-pellet emission spectroscopy results for nontronite are shown in Figure 3. Our emission results further suggest that the samples were dehydrated and dehydroxylated as a result of compression.

Phyllosilicate emission minima centered at $\sim 1100\text{ cm}^{-1}$ arise from Si-O stretching vibrations [16]. We observed almost complete elimination of these features in our nontronite samples after exposure to shock pressures of 20 GPa or higher. We also observed elimination of the complex phyllosilicate features observed in the $\sim 600\text{--}200\text{ cm}^{-1}$ range, associated with Si-O and metal-O bending modes [16].

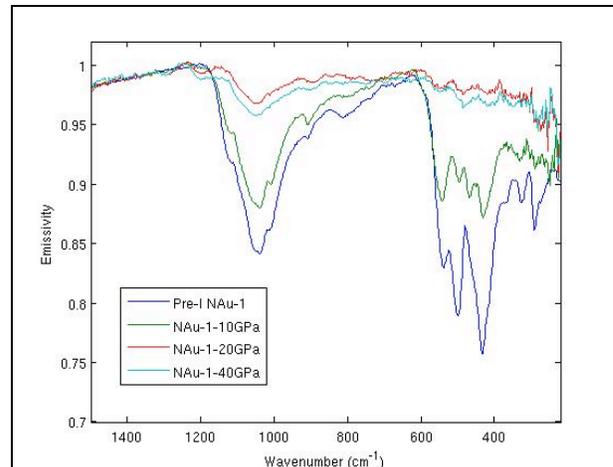


Figure 3. Comparison of emission spectra of nontronite samples, pre and post-impact at three pressures.

In contrast to our ATR and reflectance spectra, we observed few differences between the emissivity spectra of the 20 GPa and 40 GPa-shocked nontronites.

Discussion: Our results show that phyllosilicates can be expected to display characteristic spectral changes as a result of exposure to pressure. The total destruction of characteristic silicate features in mid-IR emissivity spectra, with retention of key hydration and M-OH bands in UV-vis-NIR range reflectance spectra, may help explain the apparent disconnect between NIR and mid-IR observations of phyllosilicate-bearing surfaces on Mars [e.g. 17]. Future work will involve spectroscopic studies including other phyllosilicate minerals and finer pressure gradations, as well as theoretical studies exploring structural degradation pathways and intermediate phases formed during this process.

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