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Stability of Phyllosilicates on Mars

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STABILITY OF PHYLLOSILICATES ON MARS
STABILITY OF PHYLLOSILICATES ON MARS

A dissertation submitted in partial fulfillment
of the requirements for the degree
Doctor of Philosophy in Space and Planetary Sciences

By

Patricia Gavin
Florida Institute of Technology
Bachelor of Science in Space Sciences, 2008

August 2012
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ABSTRACT

This study investigates the stability of phyllosilicates on the surface of Mars through laboratory experiments and analysis of terrestrial analogs. Phyllosilicates are mostly found in the oldest Noachian terrains on Mars and hence hold clues to the planet’s earliest aqueous and geologic history. Phyllosilicates relevant to Mars were heated up to ~1100°C for up to 24 hours and impacted with projectile velocities up to ~4.5 km/s. Heated samples were analyzed using x-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy in the near- (NIR, 1.0-2.5 µm) and mid-infrared (MIR, 5.0-15.0 µm) ranges. Impacted samples were also analyzed using Raman spectroscopy and cathodoluminescence (CL). Because of the precise evolution with temperature, NIR spectra can be used to estimate the temperature to which a sample was heated. At higher temperatures (> 700°C), MIR spectra are better for identifying secondary phase formation. All shocked samples, except prehnite, showed evidence of destruction of their mineralogical structure. NIR spectra of shocked clays were not strongly affected but their MIR spectra changed significantly. This could explain some discrepancies between NIR and thermal IR spectra of some phyllosilicates found in association with impact craters on Mars. The IR spectra can help determine formation processes by enabling a distinction between clays that were pre-existing and altered by impacts and those that were formed by impact-induced hydrothermal processes. Shocked serpentine partially transformed into magnesite, indicating shock-induced carbonation of serpentine which has never been shown before. These processes could explain the close association between serpentine and magnesite around impact craters on Mars. To better understand phyllosilicate formation and alteration on Mars, terrestrial analogs were also investigated. Samples from the intrabasaltic bole beds from the Deccan Volcanic Province, India, were analyzed. Red layers contained hematite and montmorillonite; yellow layers contained
vermiculite and montmorillonite; green layers contained celadonite and nontronite. While the
Deccan samples are all mineralogically different, they are chemically similar to each other and to
the underlying original basalt, suggesting transformation from one mineral to the next without
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intermediate step. This may help explain the stratigraphy of Mawrth Vallis, suggesting an
evolution of the alteration process from deuteric alteration to low-temperature weathering in a
closed system.
This dissertation is approved for recommendation to the Graduate Council.

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DEDICATION

I dedicate this doctoral dissertation to each and every person who gave me an encouraging word to show their support and interest in my path to excellence, and also to those who expressed their discouraging opinions of my efforts for they provided me the inspiration and motivation to prove them wrong.
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1 Introduction and Background

1.1 Phyllosilicates on Mars

Phyllosilicates are hydrated minerals consisting of parallel layered silicate sheets that form in the presence of liquid water. They were first discovered on Mars by the Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activite (OMEGA) spectrometer on Mars Express (Poulet et al., 2005) in some of the oldest Noachian terrains. This discovery further supported the hypothesis that Mars was once warm and wet in its early history. Phyllosilicates were initially identified in the Nili Fossae, Syrtis Major and Mawrth Vallis regions on Mars (Poulet et al., 2005) which was later confirmed using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars Reconnaissance Orbiter (Bishop et al., 2008; Mustard et al., 2008). They have since been extensively studied in Mawrth Vallis (Loizeau et al., 2007; Michalski and Noe Dobrea, 2007, Wray et al., 2008; Bishop et al., 2008) and Nili Fossae (Mangold et al., 2007; Mustard et al., 2007; Ehlmann et al., 2008) and have been identified in several other locations on Mars, including Sinus Meridiani (Wiseman et al., 2010), Isidis Basin (Mustard et al., 2009), and Valles Marineris (Roach et al., 2010) (Fig. 1-1), as well as in the central peaks and ejecta of small impact craters (Bibring et al., 2005; Mangold et al., 2007; Milliken et al., 2010; Wray et al., 2011) in the southern highlands (Fig.1-2). The majority of phyllosilicates found so far have been Fe/Mg- and Al-smectites (Bibring et al., 2005; Poulet et al., 2008; Carter et al., 2011) such as nontronite and montmorillonite, respectively, with minor kaolinites, chlorites, serpentines and micas (Ehlmann et al., 2009; Bishop et al., 2008; Mustard et al., 2008).
Figure 1-1 - Global map of Mars showing the locations that phyllosilicates have been identified on the surface (red dots). *From Carter et al., 2011.*
Figure 1-2 - Phyllosilicate deposits in (A) Mawrth Vallis (Bishop et al., 2008) and (B) Nili Fossae (Mustard et al., 2007).
The exact formation processes of phyllosilicates on Mars remain unclear. Some suggest they formed on the surface as a weathering product of basalts (Michalski and Noe Dobrea, 2007) due to the activity of water (Chevrier et al., 2007). Others hypothesize they formed from hydrothermal systems resulting from meteorite impacts (Fairen et al., 2010; Naumov, 2005) or volcanic activity on the surface (Poulet et al., 2005) or subsurface (Ehlmann et al., 2011). No matter which of these scenarios is correct, there is no doubt that the presence of water is imperative for the formation of phyllosilicates. Since these minerals are found in the oldest Noachian terrains, they hold clues to Mars’ earliest geologic and hydrologic history.

This study is a compilation of three major studies: heating experiments, impact experiments and a terrestrial analog. In the first (Chapter 2), nontronite and montmorillonite were heated to up to 1100°C to study the effects of high temperatures resulting from contact with lava flows. We found clear and precise evolution of the near- and mid-infrared spectra. The NIR spectra can be used as a thermometer to estimate the temperature to which a sample has been heated but only up to ~700°C. At higher temperatures, the MIR spectra are better for identifying secondary phases that formed as a result of the thermal alteration.

The second study (Chapter 3) investigated the effects of the shock pressure and temperature of meteoritic impacts on phyllosilicates. We observed deconstruction of most of the phyllosilicates’ mineralogical structure as a result of the shock treatment. The NIR spectra of the impacted samples did not change much from the original spectra but the MIR spectra showed significant changes. These results could possibly explain some discrepancies between NIR and thermal IR observations of phyllosilicates on Mars. Also, we found that shocked chlorite partially transforms into quartz and that magnesite is formed from shocked serpentine. The latter case shows impact-induced carbonation of serpentine which has not been demonstrated before.
Finally, in Chapter 4, we used the Deccan intrabasaltic bole beds in western India as an analog for phyllosilicate formation on Mars because of their similar stratigraphy to phyllosilicates in Mawrth Vallis – Al-smectite and iron oxide atop Fe\(^{3+}\)-phyllosilicate with a Fe\(^{2+}\)-phase between them. From our results, we suggest that the minerals transformed from one to the next without significant ion loss. This indicates an evolution in the formation process from deuteritic alteration to low-temperature weathering in low water-rock ratios rather than a change in the oxidation state of the surface.

Phyllosilicates are thought to have formed mostly during Mars’ earliest history when liquid water was stable on the surface. By investigating what processes occurred to alter these minerals, we can better understand the role of water on the early history of Mars’ geology. This also can give us clues to the environmental conditions present on the surface during this time and hence about Mars’ early climate. It is during this time in Mars’ history that is was most possible for the planet to have sustained life, or at least the right conditions for life to develop and thrive.

1.2 Background of analytical techniques

1.2.1 X-ray diffraction

X-ray diffraction analysis gives the crystallographic structure of a material. It uses the constructive and destructive interference of x-rays being reflected from all adjacent planes. The main adjacent planes in our case are the evenly spaced, parallel silicate sheets that make up the phyllosilicate. Since the x-rays are being reflected specularly (mirror-like), the angle of incidence equals the angle of reflection. Using Bragg’s Law (2dsin\(\theta\) = n\(\lambda\)) we can relate the angle of reflection \(\theta\), the interlayer spacing \(d\), and the incident wavelength \(\lambda\) (Fig. 1-3). Each unique crystalline structure produces a unique diffraction pattern.
Figure 1-3 - Diagram illustrating the constructive and destructive properties of x-rays reflected from a sample. *Image from USGS.*
A basic x-ray diffractometer consists of three components: the x-ray source (x-ray tube), the sample and the detector. These three components are arranged on a circle with the source and detector on the edge of the circle and the sample in the center (Fig. 1-4). The source remains stationary while the sample rotates through degrees $\theta$ and the detector revolves around the sample through degrees $2\theta$. This orientation allows the detector to remain aligned with the x-rays being reflected from the sample (Fig. 1-4). Two slit apertures are also used: a divergence slit and a receiving slit. The divergence slit is placed between the source and the sample and controls the area of the sample that is exposed to the incoming x-rays (Moore and Reynolds, 1997). The receiving slit is placed between the sample and the detector to block x-rays that are not in focus in the plane of the detector (Moore and Reynolds, 1997).
Figure 1-4 - Schematic of the circular arrangement of the x-ray source, sample, and detector, and positions of the divergence and receiving slits. Image from USGS.
The hardware: In the x-ray source, a voltage is maintained between the filament (usually tungsten) and a metal target (usually copper or cobalt) (Fig. 1-5), drawing electrons toward the target (USGS). A higher current flowing through the filament means more electrons are available to hit the target. The bombarding electrons excite electrons in the target and when these target electrons de-excite, and an x-ray is emitted. These x-rays leave the source through windows, usually beryllium, and head toward the sample. After reflecting from the sample, the x-rays enter the detector. These incoming x-rays hit and ionize gas, usually argon, in the tube into positively charged ions and electrons (Fig. 1-6) (USGS). The positively charged ions are attracted to the negatively charged cathode that is the exterior shell of the detector and the electrons move towards the positively charged anode (wire) in the center (Moore and Reynolds, 1997). When the electrons hit the wire, a voltage pulse is created that travels out of the detector and is processed by electronic circuitry.
Figure 1-5 - Cross section view of the x-ray source, or x-ray tube. *Image from USGS.*
Figure 1-6 - Cross section view of the detector in an x-ray diffractometer. Image from USGS.
1.2.2 Fourier Transform Infrared reflectance spectroscopy

Using infrared (IR) spectroscopy, one can detect which wavelengths or frequencies of light are absorbed by an atom or molecule. Different characteristics of a molecule can be determined by what frequencies of light it absorbs. Typically, infrared spectroscopy detects the vibrational state of a molecule. Other properties include rotational modes detected in the microwave region and the electronic state detected in the visible/ultraviolet. When IR spectroscopy was first being developed, a light source would shine one frequency of light on the sample, detect how much of that light was absorbed, then change the frequency of the source light and repeat the process (Griffiths and de Haseth, 1986). In Fourier transform infrared (FT-IR) spectroscopy, however, absorption data is collected over a wide range of frequencies simultaneously then a Fourier transform (mathematical algorithm) is applied to convert the raw data to a spectrum. FTIR is preferred over traditional absorption spectroscopy because it looks at several frequencies at once and generally produces a higher signal-to-noise ratio by combining several scans (usually up to ~100) over those frequencies (Griffiths and de Haseth, 1986).

A typical spectrometer is composed of three main components: a light source, a beam splitter and a detector. These three components are arranged in a Michelson interferometer configuration (Fig. 1-7). Multi-wavelength light comes from the source and hits the beam splitter, often a half-silvered mirror, where half of the light passes through and the other half is reflected. This split creates a path difference between the two beams so that they interfere upon recombination (Griffiths and de Haseth, 1986). After each hitting a mirror, the two beams are recombined and go on to the sample and detector which measures how much light was absorbed by the sample – this is the first data point. Next, one of the mirrors in the interferometer moves to create another path difference and hence a different combination of light frequencies that hits
the sample – this is the second data point. When all desired combinations of light frequencies have been observed, the computer takes all the data and applies a Fourier transform to essentially work backwards to infer which specific frequencies were absorbed.
Figure 1-7 - Diagram of a simple Michelson interferometer. *Image from Wikipedia (used with permission).*
1.3 References


2 Thermal alteration of nontronite and montmorillonite: Implications for the martian surface

2.1 Abstract

To test the effects of meteorite impacts on martian phyllosilicate deposits, we heated two smectites (nontronite and montmorillonite) to temperatures ranging from 350°C to 1150°C for durations of 4 to 24 hours in two different atmospheres, under air and a steady flow of CO₂. Samples were analyzed using X-ray diffraction (XRD) and near-infrared (NIR) and mid-infrared (MIR) reflectance spectroscopy. Interlayer water is lost after heating to temperatures of ~400°C. Between 400 and 700°C, nontronite converted to an intermediary phase which conserved the XRD pattern of untreated nontronite with the exception of the 001 peak. Nanocrystalline high-temperature phases formed for both smectites at temperatures between 700°C and 1000°C. Finally, after being heated to temperatures above ~1100°C, the samples melted and recrystallized into secondary phases. Secondary high-temperature phases included sillimanite and cristobalite for both smectites plus hematite for nontronite. NIR and MIR reflectance spectra significantly evolved with increasing temperature. NIR spectra of smectites showed that 1.4 and 1.9 μm bands decrease in intensity and disappear above 700°C. Similarly, the 2.2-2.3 μm metal-OH band showed a decrease in intensity as well as an overall shift towards lower wavelengths (for nontronite) due to the thermal resistance of the Al-OH bond compared to the Fe-OH bond. NIR spectra of montmorillonite showed a gradual increase in band depth up to temperatures between 500 and 600°C, then decreased with increasing temperature. In the MIR spectra of samples heated to temperatures above ~1100°C, newly formed bands confirmed the secondary phases identified by XRD. Similarities between the NIR spectra of our heated samples and the phyllosilicates in some martian craters imply that these phyllosilicates were
altered by the impact-generated heat and thus were not formed post-impact. In addition, NIR reflectance spectra provide a proxy for shock temperatures of smectites up to 700°C while MIR is optimum for identification of high-temperature phases of smectites above 700°C.  

2.2 Introduction

Phyllosilicates were first discovered by the Mars Express Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activite (OMEGA; Poulet et al., 2005), and then confirmed by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard Mars Reconnaissance Orbiter (MRO; Bishop et al., 2008a; Mustard et al., 2008). Phyllosilicates have been detected in three major regions: Meridiani Planum (Wiseman et al., 2008), Mawrth Vallis (Bishop et al., 2008a; Loizeau et al., 2007; Michalski and Noe Dobrea, 2007; Wray et al., 2008) and Nili Fossae (Ehlmann et al., 2008; Mangold et al., 2007; Mustard et al., 2007), as well as in several impact craters in the southern hemisphere (Mangold et al., 2007, Poulet et al., 2005). All these regions are dated to the Noachian era, suggesting a specific environment potentially different from the present-day cold and dry Mars (Bibring et al., 2006). The most abundant phases observed so far are smectites: Mg-smectite, nontronite (Fe$^{3+}$-smectite), and montmorillonite (Al-smectite; Poulet et al., 2005). Much less abundant are kaolinite, chlorite, serpentine and mica phases such as muscovite or illite and eventually some Fe$^{2+}$-phyllosilicates (Bishop et al., 2008a; Ehlmann et al., 2009; Mustard et al., 2008; Poulet et al., 2008a). The origin and exact formation processes of the phyllosilicate minerals are still a topic of debate. Some have suggested sedimentary origins (Michalski and Noe Dobrea, 2007) as a result of weathering of basaltic materials and thus would hold clues to the conditions reigning during the Noachian era (Chevrier et al., 2007). However, other phyllosilicate minerals could have formed by hydrothermal processes related to volcanic
activity (Poulet et al., 2005) or to impact craters (Fairén et al., 2009; Naumov, 2005). Indeed, phyllosilicates have been found in regions surrounded by lava flows (Poulet et al., 2005) and also in the ejecta of small impact craters (Mangold et al., 2007). Alternatively, phyllosilicates in impact craters may simply be ejecta from pre-existing former layers covered by more recent deposits. If, however, hydrothermal processes caused by impacts formed the phyllosilicates detected on Mars, those phyllosilicates may not be as old as previously thought (Fairén et al., 2009). Although impacts were most frequent on Mars during the Noachian era, they have continued throughout Mars’ history and possibly have been forming and altering phyllosilicates more recently. Such results would have prime importance for the evolution of geochemical conditions, which could have remained locally neutral to alkaline for longer timescales than sulfate deposits and acidic conditions suggest (Bibring et al., 2006; Chevrier et al., 2007).

For these reasons, we investigated the effect of thermal treatment on the mineralogical properties of Mars-relevant phyllosilicates. High temperatures may have been generated by volcanism and/or meteoritic impact. Previous studies have indicated that heated and/or shocked nontronite may be a source for the red dust on the surface of Mars because of its magnetic properties and color (Boslough et al., 1986; Weldon et al., 1982). In this study, we focus on the infrared properties of phyllosilicates, considering their importance in the analysis of planetary surface evolution. Previous studies on the infrared properties of some heated smectites have been performed (Milliken and Mustard, 2007) where the H2O band depths were related to the water content of the martian soil.

Several studies have been conducted on thermal alteration of phyllosilicates’ structure. Mossbauer studies of heated nontronite showed that it dissociates into hematite at temperatures
above 600°C (Heller-Kallai and Rozenson, 1980; MacKenzie and Rogers, 1977), which agrees with our results. Spectral analysis of the 3.0 µm band, attributed to interlayer water, showed that this band has completely disappeared after being heated to 600°C, indicating a collapse of the nontronite’s layered structure (Karakassides, et al., 2000). Madejova et al. (2000) studied the MIR spectra of heated montmorillonites and found that the mineral’s structure persisted through temperatures of up to 400°C. Upon heating to 600-700°C, the appearance of a new band at 12.5 µm and the absence of the Al-O-Si absorption band were attributed to the partial destruction of the mineral’s structure (Madejova, et al, 2000). XRD and IR spectroscopy studies done by Murad, et al. (2002) show that montmorillonite’s structure breaks down between temperatures of 550 and 850°C and that all IR bands have disappeared by 900°C. Other works on heated montmorillonite showed that the Fe-OH-Al and Mg-OH-Al absorption bands disappeared completely at 600°C, and the Al-OH-Al absorption band disappeared at 700°C, indicating the destruction of the montmorillonite’s structure (Heller-Kallai and Rozenson, 1980). This study also showed that nontronite destabilizes at lower temperatures than montmorillonite.

In this study, we investigated the evolution of the NIR and MIR spectra of nontronite and montmorillonite with increasing temperature, in conjunction with XRD and microscopic analyses. This study focused on the water content (both bound and interlayer), structural changes, and transformations into high-temperature secondary phases. We also tested the effect of the atmospheric composition on the resulting paragenesis. We then applied this information to the spectra of clay minerals observed on Mars to determine whether those minerals are raw or have undergone thermal alteration.
2.3 Methods

Our experiments focused on two smectites: a Ca,Al-nontronite from Cheney, WA (Ward’s #49E5108) and montmorillonite from Panther Creek, CO (Ward’s #46E0438). From XRF analyses conducted by Altheide et al. (2010), we determined the formulae of our smectites – nontronite: (Ca$_{0.15}$Na$_{0.01}$K$_{0.01}$)(Fe$^{3+}_{1.3}$Al$_{0.63}$Mg$_{0.10}$)(Si$_{3.57}$Al$_{0.45}$)O$_{10}$,(OH)$_2$·nH$_2$O; montmorillonite: (Na$_{0.27}$K$_{0.04}$Ca$_{0.07}$)(Al$_{1.65}$Mg$_{0.26}$Fe$_{3+}^{0.17}$)(Si$_{3.84}$Al$_{0.06}$)O$_{10}$,(OH)$_2$·nH$_2$O. X-ray diffraction and ESEM-EDAX analyses of untreated samples showed that both contain traces of quartz and that the nontronite contained anatase TiO$_2$ (total Ti content usually around 2 wt%). The samples were ground and sieved until their grain size was under 63 µm, mostly to increase the overall surface area and thus the kinetics of the reactions.

2.3.1 Experimental Protocol

One-gram samples of each smectite were placed in the center of a ceramic heating tube and then in a Lindberg high-temperature tube oven. The oven was then turned on and took about an hour to reach the desired temperature. The samples were heated to temperatures ranging from ~350°C to 1150°C for durations from 4 to 24 hours (Tables 2-1 and 2-2) in air as well as under a steady flow of CO$_2$ to more closely simulate the early Martian atmosphere. The selected temperature range was used to simulate both the temperatures reached in a terrestrial lava flow (Flynn and Mouginis-Mark, 1994) and numerical modeling of impact-induced hydrothermal systems (Barnhart, et al., 2010; Abramov and Kring, 2005; Rathbun and Squyres, 2002). After heating, the ovens were allowed to cool overnight and the samples were removed and weighed. Samples that had been heated under CO$_2$ remained under the gas flow until they had completely cooled. After weighing, the samples were placed into small (~2 oz) plastic tubes until they were analyzed.
Table 2-1 - Conditions of heating experiments of nontronite samples.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Atmosphere</th>
<th>Mass loss (%)</th>
<th>Munsell Color Code</th>
<th>Color Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>395</td>
<td>24</td>
<td>CO₂</td>
<td>22</td>
<td>10YR 4/6</td>
<td>Dark yellowish brown</td>
</tr>
<tr>
<td>470</td>
<td>24</td>
<td>air</td>
<td>15</td>
<td>7.5 YR 4/6</td>
<td>Strong brown</td>
</tr>
<tr>
<td>475</td>
<td>20</td>
<td>CO₂</td>
<td>20</td>
<td>7.5 YR 4/4</td>
<td>Dark brown</td>
</tr>
<tr>
<td>630</td>
<td>24</td>
<td>Air</td>
<td>22</td>
<td>7.5 YR 3/4</td>
<td>Dark brown</td>
</tr>
<tr>
<td>725</td>
<td>6</td>
<td>CO₂</td>
<td>20</td>
<td>5YR 3/4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>730</td>
<td>24</td>
<td>Air</td>
<td>20</td>
<td>n.d.^</td>
<td>----</td>
</tr>
<tr>
<td>800</td>
<td>6</td>
<td>Air</td>
<td>22</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>810</td>
<td>6</td>
<td>CO₂</td>
<td>22</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>875</td>
<td>6</td>
<td>CO₂</td>
<td>25</td>
<td>10YR 3/2</td>
<td>Very dark gray brown</td>
</tr>
<tr>
<td>880</td>
<td>6</td>
<td>Air</td>
<td>21</td>
<td>5YR 4/6</td>
<td>Yellowish red</td>
</tr>
<tr>
<td>880</td>
<td>22</td>
<td>Air</td>
<td>23</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>880</td>
<td>24</td>
<td>Air</td>
<td>27</td>
<td>5YR 4/6</td>
<td>Yellowish red</td>
</tr>
<tr>
<td>900</td>
<td>6</td>
<td>Air</td>
<td>23</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>905</td>
<td>6</td>
<td>CO₂</td>
<td>21</td>
<td>5YR ¾</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>906</td>
<td>4</td>
<td>CO₂</td>
<td>22</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>975</td>
<td>4</td>
<td>CO₂</td>
<td>31</td>
<td>5YR 3/4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>980</td>
<td>24</td>
<td>Air</td>
<td>26</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>1130</td>
<td>4</td>
<td>Air</td>
<td>28</td>
<td>10R 3/3</td>
<td>Dusky red</td>
</tr>
<tr>
<td>1130</td>
<td>6</td>
<td>Air</td>
<td>22</td>
<td>10R 2.5/2</td>
<td>Very dusky red</td>
</tr>
</tbody>
</table>

^ n.d. = not determined.
Table 2-2 - Conditions of heating experiments of montmorillonite samples. Data for samples marked with (*) were used with permission from Dan Ostrowski, Arkansas Center for Space and Planetary Sciences (Ostrowski et al., 2010).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Atmosphere</th>
<th>Mass loss (%)</th>
<th>Munsell Color Code</th>
<th>Color Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>----</td>
<td>----</td>
<td>Untreated</td>
<td>----</td>
<td>GLEY1 7/N</td>
<td>Gray</td>
</tr>
<tr>
<td>300*</td>
<td>24</td>
<td>Air</td>
<td>n.d.^</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>400*</td>
<td>24</td>
<td>Air</td>
<td>n.d.</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>500*</td>
<td>24</td>
<td>Air</td>
<td>n.d.</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>600*</td>
<td>24</td>
<td>Air</td>
<td>n.d.</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>630</td>
<td>6</td>
<td>Air</td>
<td>16</td>
<td>10YR 8/3</td>
<td>Very pale brown</td>
</tr>
<tr>
<td>700*</td>
<td>24</td>
<td>Air</td>
<td>n.d.</td>
<td>n.d.</td>
<td>----</td>
</tr>
<tr>
<td>725</td>
<td>6</td>
<td>CO₂</td>
<td>18</td>
<td>10YR 8/3</td>
<td>Very pale brown</td>
</tr>
<tr>
<td>775</td>
<td>24</td>
<td>CO₂</td>
<td>22</td>
<td>10YR 8/3</td>
<td>Very pale brown</td>
</tr>
<tr>
<td>880</td>
<td>24</td>
<td>Air</td>
<td>16</td>
<td>7.5 YR 7/6</td>
<td>Reddish yellow</td>
</tr>
<tr>
<td>1130</td>
<td>6</td>
<td>Air</td>
<td>melted</td>
<td>2.5YR 6/2</td>
<td>Light brown gray</td>
</tr>
</tbody>
</table>

^ n.d. = not determined.
2.3.2 Analytical Techniques

After each experiment, the samples’ color changes were cataloged using Munsell soil color charts (Munsell, 1954), which are used to precisely describe the color of a soil sample, using the same common reference. The color index used by the charts uses three components: hue, value and chroma. The hue term describes the sample’s color on the color wheel (Y: yellow, R: red, G: green, B: blue, YR: yellow red, RY: red yellow). The value component represents the lightness/darkness of the color. Pure white has a value of 10 and pure black has a value of 0. Finally, the chroma component describes the intensity of a color. A low chroma number means the color is pale or washed out whereas a high chroma means the color is vivid or saturated. These three components are noted by the hue first, then value, then chroma, with the value and chroma separated by a slash (/, see Tables 2-1 and 2-2).

Sample mineralogy was analyzed by X-ray diffraction (XRD) using a Philips PW 1830 X-ray monochrometer diffractometer with a CuKα cathode, a voltage of 45 kV, an intensity of 40 mA and a 0.25° divergence slit. The 2θ range was 5 – 80° with a step size of 0.02° and the time per step was 13 seconds resulting in a total analytical time of 13 h 45 min per sample. The powdered samples were spread onto a piece of two-sided tape and placed on a glass slide for analysis.

ESEM observations were performed using a Philips XL 30 ESEM with a beam intensity of 10 kV and SUTW sapphire detector coupled with an EDAX-EDX analytical system for semi-quantitative chemical analysis.

Fourier transform infrared (FTIR) reflectance spectra were taken using a Nicolet 6700 Smart Diffuse spectrometer. Near-infrared (NIR) spectra were recorded with attached CeramOptec optical probe. N₂ purge gas was run through the spectrometer for about two hours.
before each spectrum was recorded to remove atmospheric gases (H₂O and CO₂). Samples were placed into a ceramic tube also under a flow of N₂ gas, and then placed on a hotplate at 150°C for two hours, prior to spectral acquisition. The optical probe was inserted into a small hole drilled into the top of the tube and the sample’s spectrum was obtained (Fig. 2-1). This allowed for the removal of any adsorbed water from the sample that may have accumulated during cooling in the oven and further storage and transfer to the FTIR. NIR spectra were recorded in reflectance mode in the range of 4000 – 10,000 cm⁻¹ (1.0 – 2.5 µm, optimum range for the optical probe) with a resolution of 2 cm⁻¹. This allowed comparison to OMEGA and CRISM data available in the literature. This range is also optimum for the equipment: source, beamsplitter and detector, and to have the best signal to noise ratio. The configuration used a quartz-halogen IR source, a CaF₂ beam splitter, and a TECP detector. A background spectrum was taken using KBr powder and the same measurement protocol (N₂ flow, 150°C) and used to correct our samples’ spectra. After each samples’ spectrum was taken, the background spectrum was subtracted. To observe any effects of readsorbed water, some samples’ NIR spectra were measured using the same configuration as stated above, but using a DTGS detector under ambient conditions. This setup resulted in the spectra being on very different reflectance scales because they were recorded using a different detector (TECP with optical probe vs. DTGS without optical probe).
Figure 2-1 - Schematic of NIR analysis setup. (1) N₂ tank; (2) plastic tubing; (3) ceramic tube containing the sample; (4) hotplate; (5) optical probe holder; (6) CeramOptec optical probe; (7) FT-IR spectrometer.
Mid-infrared (MIR) spectra were recorded using the spectrometer without the optical probe in the range of 350 – 7350 cm\(^{-1}\) (1.4 – 28.6 \(\mu\)m). In the MIR range we focused on the 5 – 15 \(\mu\)m range for comparison to TES and THEMIS data. For this wavelength range we used an IR source, a KBr beamsplitter and a DTGS detector. Background spectra using a gold coated emery tape were systematically taken before each sample’s spectra to remove instrumental signal.

2.4 Results

2.4.1 Mineralogical observations: color, XRD and ESEM

The first and most noticeable result of heating the samples were their extreme color change. The nontronite samples started off as yellowish-green with a Munsell color of 5Y 8/4 (Table 2-1). After heating to low temperatures (T < 700\(^{\circ}\)C), the samples’ color had changed to reddish brown with a Munsell color of 7.5YR 4/6. Intermediate temperatures (700\(^{\circ}\)C < T < 1000\(^{\circ}\)C) made the samples’ color change to a brick red 5YR 4/6 and after being heated to high temperatures (T > 1000\(^{\circ}\)C), the samples’ color was a very dark reddish brown 10R 3/3. One exception to this general color trend was a sample heated to 900\(^{\circ}\)C for 6 hours in CO\(_2\). It changed to 5YR 3/4, much darker than the other samples heated to that temperature.

Montmorillonite samples also experienced color change, but in a much less significant way (Table 2-2). Samples started as gray at GLEY1 7/N and changed to light shades of orange and pink with a color index of 10YR 8/3 after being heated to low temperatures. After being heated to intermediate temperatures, the samples’ color was 7.5YR 7/6, which is a slightly darker tint of orange and had continued to change to 2.5Y 6/2 after being heated to high temperatures (Table 2-2). In both cases the color changes indicate phase transformation, but
in the case of nontronite, this is clearly evidence of a change in the Fe$^{3+}$ ion configuration (Hviid et al., 1994; Weldon et al., 1982) related to the formation of ferric oxides.

In the XRD diffractograms of nontronite heated to low temperatures (T = 630°C), the large 001 peak (2θ = 6.59°) disappeared but all other peaks (at 2θ values of 22.8°, 29.4°, 33.8°, 40.2° and 72.2°) were still present and had not changed in intensity (Fig. 2-2B). The collapse of the 001 interlayer space indicated a rearrangement of the crystalline structure as a result of water loss (~20 wt%, Table 2-1). This is in agreement with previous dehydration studies that showed that the interlayer distance of the 001 planes and water content decreases with increasing temperature (Bish et al., 2003). ESEM observations showed that this secondary product retained the original morphology of nontronite (Fig. 2-3A).
Figure 2-2 - XRD diffractograms of heated nontronite. (A) Untreated sample. (B) Sample heated to 630°C in CO₂ for 20 hrs. (C) Sample heated to 975°C in CO₂ for 4 hrs. (D) Sample heated to 1130°C in air for 4 hrs. Abbreviations: an, anorthite; cor, corundum; cri, cristobalite; hem, hematite; non, nontronite; qtz, quartz; sap, saponite; sil, sillimanite; S2, spinel, S3, ilmenite, S4, heterosite. S1 corresponds to peaks identified in the untreated sample yet cannot be labeled as “nontronite” due to the absence of the 001 peak. S2, S3, and S4 correspond to structures identified but lack the appropriate chemistry.
Figure 2-3 - ESEM images and EDAX analysis of samples. (A) Nontronite heated to 630°C in CO₂ for 20 hrs.  (B-D) Nontronite heated to 1130°C in air for 4 hrs.  (E-F) Montmorillonite heated to 1130°C in air for 6 hrs.  Abbreviations: cri, cristobalite; gls, glass; hem, hematite; sil, sillimanite.
XRD diffractograms of samples heated at intermediate temperatures (T = 975°C) contained shallow, broad and poorly-defined peaks (Fig. 2-2C), indicating nanophases and/or poorly crystalline phases. ESEM observations showed no identifiable crystals (down to the detection limits) confirming XRD results. Identified phases included intermediate temperature phases such as anorthite (CaAl$_2$Si$_2$O$_8$) and corundum (Al$_2$O$_3$) mixed with high temperature phases (cristobalite SiO$_2$, hematite α-Fe$_2$O$_3$ and sillimanite Al$_2$SiO$_5$). We also observed some peaks structurally related to some known phases whose formulae do not fit the chemistry of the nontronite. These phases are labeled S2, S3 and S4, and correspond to spinel (X$^{2+}$Y$^{3+}$O$_4$), ilmenite (Fe$^{2+}$TiO$_3$) and heterosite (Fe$_3$PO$_4$), respectively. Ilmenite may result from the small amount of titanium present in the sample and some ferrous iron often present in natural nontronites (Hviid et al., 1994). Moreover, ferri-ilmenite (Fe,Ti)$_2$O$_3$ is also a possibility. The spinel phase could also be magnetite (Fe$^{2+}$Fe$^{3+}$O$_4$) or maghemite γ-Fe$_2$O$_3$ with possible Al$^{3+}$ substitution, as previously observed in heated nontronite (Hviid et al., 1994; Moskowitz and Hargraves, 1984). However, the low resolution of the diffractograms prevented definitive determination of peak positions and the complex mixture prevented the identification of smaller characteristic peaks, such as the quadratic superstructure peaks that allow distinction between maghemite and magnetite. Therefore, we suggest the presence of complex, probably non-stoichiometric iron oxide phases. A separate paper will investigate in detail the complementary magnetic and Mossbauer properties of our heated nontronite samples with special emphasis on these intermediate iron phases.

By contrast, XRD diffractograms of samples heated at high temperatures (above 1100°C) contained high-intensity, sharp, well-defined peaks indicating melting and recrystallization of secondary phases (Fig. 2-2D). The mixture was composed of cristobalite
(SiO₂, Fig. 2-3B), sillimanite (Al₂SiO₅, Fig. 2-3C) and hematite (Fe₂O₃, Fig. 2-3D) representing the dominant chemical elements of nontronite (Si, Al and Fe, respectively). This is in agreement with previous studies that nontronite decomposes into hematite (Heller-Kallai and Rosenson, 1980). We could not identify any Ca or Mg phases, but these elements are relatively minor (Mg+Ca < 4 wt%, below the usual detection limits of X-ray diffraction) and the samples contained abundant glass due to fast cooling of the sample. This glass phase probably contains the remaining elements (including traces of K).

Figure 2-4 shows the XRD diffractograms of heated montmorillonite compared to the diffractogram of an untreated sample. At relatively low temperature (630°C), the 001 peak was still visible, but had shifted by 1.86° compared to the original position of 2θ = 7.25° and had largely decreased in intensity. We interpret this again to be the result of the loss of interlayer water confirmed by the average mass loss of ~18 wt% (Table 2-2), although this did not result in the complete loss in the 001 peak as in nontronite (Fig. 2-2). A new peak is seen at 2θ ~18°. All other signature peaks of montmorillonite were still intact, although some had also decreased in intensity, while the two small peaks at 2θ = 12° and 14° completely disappeared. We observed also traces of quartz and albite (NaAlSi₂O₈), both probably from the initial sample. At temperatures above 800°C, the structure of montmorillonite was completely destroyed, which was also observed by Murad et al., (2002), and we observed a mixture of sillimanite, cristobalite with minor albite and quartz (Fig. 2-4C). At temperatures above 1100°C, albite and quartz were no longer detected in the XRD diffractogram, which was expected since they are not stable at such temperatures. The new paragenesis was composed of well-crystallized sillimanite (Fig. 2-2E) and cristobalite, with also evidence for cordierite (Mg₂Al₄Si₄O₁₈), which is a typical phase of thermally metamorphosed Mg-rich argillaceous deposits. There was also evidence for the
formation of abundant amorphous glass as indicated by the large “hump” feature centered at $2\theta \sim 20^\circ$ in the XRD diffractograms of samples heated above 800°C (Fig. 2-4D), as well as in ESEM observations (Fig. 2-3F).
Figure 2-4 - XRD diffractograms of heated montmorillonite. (A) Untreated sample. (B) Sample heated to 630°C in air for 6 hrs. (C) Sample heated to 880°C in air for 24 hrs. (D) Sample heated to 1130°C in air for 6 hrs. The diffractogram of the sample heated to the highest temperature (T = 1130°C) was stopped at 2θ = ~50° due to an equipment malfunction during the time of analysis, although we had enough information to identify secondary phases. Abbreviations: alb, albite; crd, cordierite; cri, cristobalite; mon, montmorillonite; qtz, quartz; sil, sillimanite. mon* labels indicate the shifted 001 peak and a new peak formed identified as montmorillonite.
XRD diffractograms of nontronite samples heated to 975°C in air were compared to those heated to the same temperature in CO₂ (Fig. 2-5A). We did not observe any difference between the two diffractograms, both showing similar secondary mineralogy. We then compared the reflectance spectra of nontronite samples, both in the NIR and MIR ranges, of samples heated to 475°C in air and in CO₂ (Fig. 2-5B). Again, there was no visible difference between the spectra. We observed similar results between air and CO₂ atmospheres at all temperatures and also for montmorillonite. Thus we consider that all observed transformations are related to temperature and not the nature of the atmosphere.
Figure 2-5 - Comparison between samples of nontronite heated in air and in CO₂. (A) XRD diffractograms of an untreated sample and two samples heated to 975°C in air and in CO₂. The diffractograms were placed on different y-axis scales to emphasize the shallow peaks in the low and intermediate temperature samples. Abbreviations: an, anorthite; cor, corundum; cri, cristobalite; qtz, quartz; sil, sillimanite; S2, spinel; S3, ilmenite; S4, heterosite (see section 2.4.1 for details about these structures). (B) Reflectance spectra of nontronite heated to 475°C in air and in CO₂. Top: near-infrared (NIR) reflectance spectra. Bottom: mid-infrared (MIR) reflectance spectra.
2.4.2 *Near-infrared reflectance spectroscopy*

As for mineralogical observations, reflectance spectra did not show any change with atmospheric composition (Fig. 2-5B), but a clear evolution with temperature was evident (Fig. 2-6). Nontronite was identified by three specific absorption bands at 1.4, 1.9, and 2.28 µm as seen in the untreated sample (Bishop, et al., 2002; Bishop, et al., 2008b). The band at 1.4 µm represents the OH stretching overtones of both structural OH and molecular H₂O; the band at 1.9 µm represents H-O-H stretching of molecular H₂O and is usually attributed to interlayer water; the 2.28 µm band represents the Fe-OH bond (Bishop, et al., 2002a; Bishop, et al., 2008b). We also identified a smaller 2.21 µm band which corresponds to Al₂-OH (Bishop et al., 2008b), thus confirming the chemical results of an Al-substituted nontronite. A major identifier of water in minerals is the 3 µm band and is included in many spectroscopic analyses of clay minerals (Russell and Farmer, 1964; Bishop, et al, 1994; Bishop, et al, 2002a; Milliken and Mustard, 2007). However, this feature was excluded from this study due to the fact that an optical probe was used in the NIR analysis whose range extends only to 2.5 µm.
Figure 2-6 - Near-infrared (1.0-2.5 µm) reflectance spectra of nontronite heated to various temperatures. Positive bands in the higher temperature samples are artifacts of subtraction of the KBr background spectrum. Spectra have been offset for clarity.
From 400°C to 725°C we observed a progressive disappearance of the 3 bands while the spectra were very similar between 725°C and 900°C, and featureless above 975°C (Fig. 2-6). The most affected were the 1.4 and 1.9 µm bands while the 2.21 and 2.28 µm bands were replaced by a 2.17-2.21 µm doublet at temperatures above 400°C, with the 2.2-2.3 µm region taking a characteristic “plateau” shape. The 2.28 µm Fe-OH band remained visible up to 475°C, while the new doublet was visible up to temperatures of about 725°C, above which only the 2.17 µm band remained up to 900°C. The 1.4 and 1.9 µm bands remained visible up to 630°C. A small antiband appeared at 1.4 µm in the range 725-900°C. A background spectrum taken under a steady flow of N2 was subtracted from each sample’s spectrum. These antibands are artifacts of that subtraction. At low temperatures (T = 475°C), the continuum began to take a positive slope between 1.0 and 2.2 µm and at temperatures of 725°C and above the continuum had a positive slope for the entire 1.0 – 2.5 µm range.

Montmorillonite was identified by absorption bands at 1.4, 1.9 and 2.2 µm (Fig. 2-7). The 1.4 µm band represents the OH stretching overtones from both structural OH and molecular H2O; the 1.9 µm band represents the bending and stretching combination of molecular H2O characteristic of interlayer water; the 2.2 µm band represents the stretching and bending combination of Al-OH (Cariati, et al, 1981; Bishop et al., 1994; Bishop, et al., 2002a). Due to equipment restraints, the 3 µm band was not studied here. As expected, the reflectance spectra of heated montmorillonite samples presented a clear, yet slightly different behavior than for nontronite (Fig. 2-7). At first, the bands deepened until a temperature of about 500°C, then they progressively disappeared. The 2.2 µm band took the characteristic plateau shape at T = 600°C, due to the appearance of the characteristic 2.17-2.21 µm doublet. This band was present only in the spectrum of the sample heated to 600°C. The overall spectral evolution of montmorillonite
occurred at higher temperatures than for nontronite. For example, the 2.17-2.21 \( \mu m \) doublet was observed on montmorillonite at 600\( ^{\circ} \)C, compared to 400\( ^{\circ} \)C for nontronite, i.e. a 200\( ^{\circ} \)C difference. Nevertheless, all three features completely disappeared at a similar temperature of 1130\( ^{\circ} \)C (Fig. 2 - 7), which was due to melting of the samples. Small antibands were seen at 1.4 \( \mu m \) and 2.2 \( \mu m \) in the spectra of samples heated to 880\( ^{\circ} \)C and 1130\( ^{\circ} \)C, which are artifacts of the subtraction of the background spectrum.
Figure 2-7 - Near-infrared (1.0-2.5 µm) reflectance spectra of montmorillonite heated to various temperatures. Positive bands in the higher temperature samples are artifacts of subtraction of the KBr background spectrum. Spectra have been offset for clarity.
The NIR spectra of the heated samples showed a clear evolution of band depth with increasing temperature in both smectites. Band depths were recorded by measuring the distance from the minimum of the band to the continuum between the two shoulders on either side of the band. Band depth evolution with temperature for both smectites is shown in Figure 2-8. Data points for missing bands or positive bands were not included in the figure. In the nontronite samples, the bands simply decreased with increasing temperatures (Fig. 2-8A). Montmorillonite, however, showed a more complicated trend. All three band depths (1.4, 1.9 and 2.2 µm) increased up to temperatures between 500 and 600°C, then decreased with higher temperatures (Fig. 2-8B).
Figure 2-8 - Band depth evolution as a function of temperature for (A) nontronite and (B) montmorillonite. The band depths were normalized to the corresponding value for the untreated sample. Data points for absent bands or positive bands were not included in the figure.
2.4.3 Mid-infrared reflectance spectroscopy

As with the NIR spectra, there was no distinction between samples heated in air and those heated in CO₂ in the MIR range (Fig. 2-5B). Nontronite was identified in the mid-infrared range by two major bands at 6.2 and 8.3 µm and three minor bands at 9.2, 11.4 and 12.2 µm (Fig. 2-9). The 6.2 µm band is due to H₂O bending (Farmer, 1974; Sposito et al., 1983; Bishop, et al., 1994), the 8.3 µm band is due to the SiO₂ in the sample (Bishop, et al., 2008b) the 9.2 µm band is from Si-O stretching and bending (Farmer and Russell, 1964; Grim, 1968; Bishop et al., 2008b), the 11.4 µm band is a result of the OH bending in the Al-Fe³⁺-OH bond (Farmer and Russell, 1964; Russell and Farmer, 1964; Grim, 1968; Bishop, et al., 2002b, Bishop et al., 2008b), and the 12.2 µm band is due to the Fe³⁺₂-OH bond (Farmer and Russell, 1964; Grim, 1968; Bishop, et al., 2002b; Bishop et al., 2008b). All bands evolved with increasing temperature. The 6.2 µm band was stable up to temperatures of about 725°C. At this temperature, the band shifted to 6.3 µm. The 8.3 µm band began to deepen after 475°C and shifted to lower wavelengths by up to 0.4 µm. The 9.2 and 11.4 µm bands disappeared at low temperatures (T < 400°C) while the 12.2 µm band broadened and became more shallow up to 800°C then became more visible above 800°C. A new band at 5.4 µm formed at 630°C and a 5.8 µm band formed at 1130°C (Fig. 2-9). The negative slope of the continuum between 5 and 8 µm increased above 800°C.
Figure 2-9 - Mid-infrared (5.0-15.0 µm) reflectance spectra of nontronite heated to various temperatures. Top right: zoomed in view of the 5-7 µm range of high-temperature samples (T > 700°C) to highlight spectral features. Bottom right: zoomed in view of the 10-15 µm range of low-temperature samples (T < 700°C) to highlight spectral features. Spectra have been offset for clarity.
Montmorillonite was identified in the mid-infrared range by major bands at 5.5, 6.2, 7.15, 8.07, 9.12, and 12.6 µm and minor bands at 10.8 and 11.3 µm, as shown in Fig. 2-10. The 6.2 µm band is due to H2O bending (Farmer, 1974; Sposito et al., 1983; Bishop, et al., 1994), the 9.12 µm band is a result of Si-O stretching (Farmer and Russell, 1964; Russell and Farmer, 1964; Grim, 1968; Bishop, et al., 2008b), the 10.8 µm band is due to Al2-OH vibrations (Farmer and Russell, 1964; Russell and Farmer, 1964; Grim, 1968; Farmer, 1974; Sposito et al., 1983; Bishop, et al., 1994), the 11.3 µm band is due to Al-Fe-OH vibrations (Farmer and Russell, 1964; Russell and Farmer, 1964; Grim, 1968; Farmer, 1974; Sposito et al., 1983; Bishop, et al., 1994; Bishop et al., 2002b) and the 12.6 µm band is from Mg-Fe3+-OH vibrations (Farmer and Russell, 1964; Grim, 1968; Bishop et al., 2008b), both resulting from minor Mg and Fe3+ in the structure (see formula). The 5.5, 7.15 and 8.07 µm bands were not identified in the literature. The 5.5 µm band’s position and intensity were not affected by increasing temperature (Fig. 2-10). The 6.2 µm band decreased in intensity and shifted by 0.12 µm to higher wavelengths above 700°C. The 7.15 µm band gradually decreased in intensity and eventually disappeared at 600°C. The 8.07 µm band shifted to lower wavelengths beginning at a temperature of 400°C and shifted by about 0.52 µm. The 9.12 µm band did not shift at all but rather abruptly disappeared after 700°C. Finally, the 12.6 µm band gradually decreased in depth and eventually disappeared at 760°C. The continuum of the spectra also changed with increasing temperature. Similar to the behavior of the MIR spectra of nontronite, the negative slope of the continuum of the MIR spectra of montmorillonite increased in the 5 – 8 µm range above 700°C.
Figure 2-10 - Mid-infrared (5.0-15.0 µm) reflectance spectra of montmorillonite heated to various temperatures. Top right: zoomed in view of the 5-7 µm range of high-temperature samples (T > 700°C) to highlight spectral features. Bottom right: zoomed in view of the 10-15 µm range of low-temperature samples (T < 760°C) to highlight spectral features. Spectra have been offset for clarity.
2.5 Discussion

2.5.1 Effect of atmospheric composition

There generally appeared to be no mineralogical or spectral differences between samples heated in air and samples heated in CO\(_2\), suggesting that temperature was the primary parameter influencing the evolution of the studied smectites. This is due to the fact that there is no chemical reaction between smectites and CO\(_2\). Montmorillonite is an Al phyllosilicate (with minor traces of Mg or Fe) and thus not reactive with CO\(_2\) gas. Nontronite contains oxidized iron (Fe\(^{3+}\)) which is chemically the most reactive ion since it is the only one that could change its oxidation state to Fe\(^{2+}\) in our experimental conditions. However, CO\(_2\) already has the highest carbon oxidation state (+4) and is therefore not available to reduce iron. In only one sample of heated nontronite (6 hours at 810°C in CO\(_2\), see Table 1) did we see formation of abundant spinel (magnetite / maghemite, using magnetic analysis) and a much darker color which may indicate the presence of Fe\(^{2+}\). A spinel-type structure was also identified on the XRD diffractograms of samples heated in the range 700-1000°C. This was the only occurrence where we saw a significant difference between air and CO\(_2\) samples heated at the same temperature (6 hours at ~810°C, Table 2-1). This could result from a thermodynamic transition at this temperature, a kinetic effect (metastable phase) or the potential decomposition of CO\(_2\) into CO, which occurs around 800°C (Jin et al., 2006), followed by reoxidation by Fe\(^{3+}\) which reduces to Fe\(^{2+}\). This dark material could also result from reactions between nontronite and organic material (Campbell et al., 1997; Schwertmann et al., 1999; Bishop et al., 2004), although there was no evidence for organic material in our initial samples. A more detailed analysis of this sample will be included in a future paper on the magnetic properties of thermally treated nontronite. As we mentioned before, we will soon submit a paper focusing entirely on the magnetic properties of
thermally altered phyllosilicates and how they help understand such a difference. We want however to emphasize that except for this single occurrence (800-810°C), all other samples appeared completely identical between both atmospheres. Moreover, all these magnetic phases are very minor in terms of abundance, and should not significantly affect the reflectance properties, except for the albedo (magnetite is often used to artificially decrease the albedo in mixing models). Nevertheless, in the rest of this discussion we will focus only on the effect of temperature as controlling the mineralogical and spectral properties.

2.5.2 Effects of adsorbed water

To study the effects of readsorbed water, we remeasured the NIR spectra of the same samples after storing them under ambient conditions for several days. Due to the use of a different detector (DTGS versus TECP in the previous “dry” measurements), spectra were normalized for comparison to each other. Each spectrum was normalized using values from a neutral part of the spectrum (values at 1.71 µm for nontronite and 1.50 µm for montmorillonite) then offset for clarity. Figure 2-11 compares spectra of samples heated to 400°C before and after rehydration. There was a significant decrease in intensity in all three bands of nontronite, especially of the hydration bands at 1.4 and 1.9 µm (Fig. 2-11, spectra A in air and B in N₂). This indicated a significant decrease in the water content of the samples due to the removal of readsorbed water. The same effect was seen in the montmorillonite spectra (Fig. 2-11, spectrum C in air and D in N₂). The most affected band in these spectra was the 1.9 µm band, again indicating a significant loss of adsorbed water. This effect was most pronounced in the samples heated to low temperatures (T < 700°C) because their layered structure had not been destroyed at these temperatures, allowing for a large amount of water to be readsorbed. The new analytical set up (Fig. 2-1) successfully removed this adsorbed water from our samples. These results show
how reabsorbed, non-structural water can affect the NIR spectra of phyllosilicates, possibly showing the mineral to be in a higher hydration state than it really is. This could possibly explain the relatively low intensities of the hydration bands in phyllosilicate spectra from Mars compared to commonly used reference spectra of terrestrial phyllosilicates, such as those from Clark et al. (2007).
**Figure 2-11** - NIR spectra of samples heated to 400°C, measured in air (dashed line) and in N₂ (solid line). (A) Nontronite measured in air. (B) Nontronite measured in N₂. (C) Montmorillonite measured in air. (D) Montmorillonite measured in N₂. Because of the use of different detectors between measurements in air (DTGS) and in N₂ (TECP), nontronite and montmorillonite were normalized to a standard value at a wavelength of 1.71 and 1.50 μm, respectively, then offset for clarity.
2.5.3 *Effects of temperature*

The XRD diffractograms of heated nontronite samples suggested that the smectite’s crystalline structure evolved at relatively low temperatures ($T \geq 400^\circ$C) due to the disappearance of the 001 peak at $2\theta = 6.59^\circ$, but most other peaks remained visible (Fig. 2-2). Similarly, NIR spectra showed that hydration bands significantly decreased in intensity at $T \geq 400^\circ$C and had completely disappeared by 725$^\circ$C (Fig. 2-6). The 2.28 µm Fe-OH band in the untreated sample disappeared at 400$^\circ$C while the small 2.21 µm Al-OH band became more visible and formed a doublet with a band at 2.17 µm. This doublet was evidence of the Al$_2$-OH bond and is most often seen in spectra of kaolinite (Bishop, et al., 2008b). This indicated that Fe had been lost from the layered structure while the Al remained. The doublet disappeared at 975$^\circ$C, indicating the Al-OH bond was still intact up to this temperature. NIR spectra are sensitive to the nature of the chemical bonds while XRD analysis reveals the crystalline structure. Thus our results show that nontronite’s layered crystalline structure was lost by temperatures of about 475$^\circ$C while the Al-OH bond remained to higher temperatures. This was evidence of the reorganization of the crystalline structure due to the loss of interlayer water, resulting in the formation of an intermediate “new” phase between 400$^\circ$C and 700$^\circ$C. The loss of water explained both the absence of the 001 peak in the XRD diffractogram and the observed ~25 wt% loss between the fresh and heated samples (Table 2-1).

The XRD diffractogram of a sample of montmorillonite heated to low temperatures ($T < 800^\circ$C) was very similar to that of the untreated sample (Fig. 2-4). Most of the identifying peaks of montmorillonite were still present at the same position. The new peak seen at $2\theta \sim 18^\circ$ in the sample heated to 630$^\circ$C may be a result of the reorganization of the phyllosilicate structure due to higher temperatures. The 001 peak was still visible in the low-temperature
diffractogram. The peak shifted to higher 2θ values and lower intensity, but not to the extent that the nontronite samples showed. This same result was seen in samples of beidellite heated to 500°C (Lantenois et al., 2008) and was attributed to an overall compaction of the structure due to water loss. This suggests that montmorillonite is more resistant to heating than nontronite is, and doesn’t form an intermediate “new” phase before decomposing into high-temperature nanocrystalline phases at T ~ 700°C. This was confirmed by NIR showing that the 1.4, 1.9 and 2.2 μm bands were visible up to about 800°C (Fig. 2-7). In contrast, the NIR bands of nontronite disappeared at lower temperatures (T ~ 700°C).

In nontronite and montmorillonite samples, the mineralogical transformation of the samples from 700°C and up to ~1000°C were solid-solid and the samples did not melt. This was indicated by the reorganization of the crystalline structure at low temperatures and the nanophases formed at intermediate temperatures. It was only after being heated to high temperatures (T ~ 1100°C) that the samples showed evidence of melting and recrystallization into secondary phases, including glass.

We showed that the metal-OH band in the NIR reflectance spectra of heated montmorillonite was visible to higher temperatures than it was in the heated nontronite spectra. Moreover, in heated nontronite only the Al2-OH doublet remained while the Fe-OH band disappeared. This is due to the fact that the Fe-OH band destabilizes at lower temperature than the Al-OH (Heller-Kallai and Rosenson, 1980), because the bond dissociation energy of Al-O is 501.6 kJ/mol (Reddy et al., 1999) while the dissociation energies for Fe-O and Mg-O are 354.7 and 407.0 kJ/mol, respectively (Reddy et al., 2000; Lide, D., 2008-2009). These bond energies confirm both our XRD and NIR measurements that montmorillonite can withstand higher temperatures than nontronite can. It also explains the doublet at 2.17-2.21 μm in nontronite.
which results from the resistance to heating of the Al-OH band identified at 2.21 µm in the untreated sample.

Zoomed-in views of the 5-7 µm range for high temperatures and 10-15 µm range for low temperatures were added to Figures 2-9 and 2-10 to highlight the evolution of the MIR spectra. The montmorillonite bands, especially in the 10-15 µm range, remained visible to T = 700°C whereas the nontronite bands in the same range destabilized at T = 625°C. This further demonstrates that montmorillonite is more resistant to heat than nontronite is. Band depth analysis in the NIR spectra also showed that nontronite’s bands disappear at lower temperatures than montmorillonite’s bands. These deeper bands may be a result of larger grain size due to the higher temperatures (Bell et al., 1997) or of the reorganization of the phyllosilicate layers at higher temperatures. This reorganization could have formed a polymorph of montmorillonite causing the NIR bands to deepen and the two “new” peaks seen in the XRD of montmorillonite heated to 630°C (Fig. 2-4).

2.5.4 Identification of secondary phases

Two major secondary phases were common to both nontronite and montmorillonite samples: sillimanite and cristobalite, shown by the well-defined, sharp peaks in the XRD diffractogram of samples heated to 1130°C (Fig. 2-2D and 2-4D). In addition, nontronite showed abundant hematite as the high temperature carrier of ferric iron. The presence of abundant amorphous glass was detected in the montmorillonite sample, identified by the “hump” feature centered at 2θ ~ 20°.

NIR and MIR reflectance spectra were used for reference to compare to spectra of our heated samples (Fig. 2-12 and 2-13). Because of the impurity and non-ideal conditions of the terrestrial analog reference samples, spectra from two different sources were used for a more
comprehensive comparison. The hematite and sillimanite samples were taken from the USGS spectral library (hematite – WS161 for NIR and GDS69 for MIR, sillimanite – HS186.3B from Clark et al., 2007). The USGS reference sillimanite NIR spectrum contained OH bands at 1.4, 1.9 and 2.2 µm (Fig. 2-12), which were most likely due to traces of weathering products in the sample since there is no OH in sillimanite (Al₂SiO₅). The NIR spectrum of cristobalite (Bishop, pers. comm.) also contains a small shallow band at 1.9 µm which is most likely due to water and OH molecules on the surface of the fine-grained particles since there is no OH in cristobalite (SiO₂).
Figure 2-12 - NIR (1.0-2.5 µm) reference spectra compared to samples heated to 1130°C. Hematite and sillimanite spectra were taken from the USGS spectral database: hematite – WS161; sillimanite – HS186.3B (Clark et al., 2007). Spectra have been offset for clarity. Positive bands result from a small amount of adsorbed water on our KBr background that did not get removed even in N₂ flow at 150°C.
Figure 2-13 - MIR (5.0-15.0 µm) reference spectra compared to samples heated to 1130°C. Hematite and sillimanite spectra were taken from the USGS spectra database: hematite – GDS69; sillimanite – HS186.3B (Clark et al., 2007). Spectra have been offset for clarity.
The NIR spectra of nontronite heated to temperatures above 700°C were almost featureless except for a slight positive slope that could be attributed to hematite. However, the absence of bands prevented definitive identification of any secondary phases. This is mostly due to the fact that the secondary phases are featureless in this spectral region, especially when compared to “primary” phyllosilicates which exhibit strong spectral features.

MIR spectra of hematite and sillimanite are shown in Fig. 2-13 for comparison with the spectra of the heated montmorillonite and nontronite samples. The hematite and sillimanite spectra show significant features in the MIR not observed in the spectra of the heated clays. MIR spectra of cristobalite (Bishop, pers. comm.) also exhibit additional features not present in our experimental spectra. The bands identified in the reference spectra matching those identified in nontronite and montmorillonite heated to 1130°C are summarized in Table 2-3. In heated nontronite, the 5.4 µm band was matched in sillimanite, the 5.8 and 12.6 µm bands were matched in cristobalite, the 6.3 µm band was matched in all three reference spectra, and the 7.9 µm band was matched in hematite and sillimanite. These similarities in the spectra confirm our XRD data of the formation of hematite, cristobalite and sillimanite as secondary phases of heated nontronite. In heated montmorillonite, the 5.3 and 8.6 µm bands were matched to cristobalite and the 6.1 µm band was matched to sillimanite and cristobalite. Again, this confirms our XRD data of the formation of sillimanite and cristobalite as secondary products of heated montmorillonite.
Table 2-3 - MIR bands (in µm) identified in reference spectra and in samples heated to 1130°C. Bands of cristobalite were obtained via personal communication with Janice Bishop.

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It is clear from the reflectance spectra that the MIR range is more appropriate for identifying secondary phases in conjunction with XRD data. MIR spectra clearly showed bands of high-temperature secondary phases, where NIR spectra were featureless. Alternatively, the NIR range showed clearer evolution with temperature and can be used to determine the approximate temperature to which smectites have been heated, particularly in the range 400 – 700°C.

2.6 Implications for Mars

Phyllosilicates have been detected in association with impact craters on Mars (Mangold et al., 2007; Marzo et al., 2008; Poulet et al., 2008b). We found that the spectra of the phyllosilicates identified in these martian craters had more characteristics in common with our samples of nontronite heated to 400°C rather than that of an unaltered sample (Fig. 2-14). More specifically, we found that our samples heated to 400°C, measured in air (rehydrated sample) and in N₂ (dehydrated sample) resembled some phyllosilicates detected in Toro Crater in Syrtis Major (Fig. 2-14; Marzo et al., 2008).
Figure 2-14 - Near-infrared reflectance spectra of phyllosilicates detected by CRISM/MRO in association with Toro Crater on Mars and compared to nontronite samples heated to 400°C, measured in air and in N$_2$. Spectra have been normalized and offset for clarity. Toro Crater spectrum from Marzo et al. (2010).
Figure 2-14 shows the spectrum of phyllosilicates in Toro Crater on Mars (Marzo et al., 2008) compared to our samples of nontronite heated to 400°C. The spectra have been normalized and offset. All three spectra have the same overall neutral slope. The 2.3 μm band in all three spectra has morphed into a plateau shape rather than a distinct band. Since this band is still present yet altered, the post-shock temperatures in these deposits must have been near 400°C. This is in strong agreement with previous works that have modeled a hydrothermal system inside an impact crater and concluded that the maximum temperature for a crater of similar size to Toro Crater is only about 400°C (Barnhart, et al., 2010; Abramov and Kring, 2005; Rathbun and Squyres, 2002). The intensities of the hydration bands in the Toro Crater spectrum are visibly deeper than those of the “dehydrated” sample (bottom spectrum). This suggests that the phyllosilicates in Toro Crater have readorsbed some water from the atmosphere after being heated by the impact. This supports our data that 400°C is not a high enough temperature to completely destroy the phyllosilicate structure, allowing for the readsorption of water by the sample.

As previously mentioned, the NIR spectra of the smectites found in the martian crater most closely resemble that of heated smectites. Since the smectites were heated, they must have been on the surface prior to the impact event and altered by post-impact temperatures, not formed by post-impact hydrothermalism. If the smectites were formed by impact-induced hydrothermal processes, their spectral signatures would be that of unaltered smectites. This is clearly not the case (Fig. 2-14). Additionally, Fe-smectites do not precipitate from solutions above ~200°C (Chevrier, 2009). Thus we can conclude that this particular deposit of smectites dates back to the Noachian and is not a younger product of later hydrothermal processes.
Secondary phases formed by altered nontronite and montmorillonite are also of importance to the martian surface. XRD analysis of samples heated above 900°C shows the formation of hematite, sillimanite and cristobalite. Hematite has been shown to form as the result of thermally decomposed nontronite and is thought to be responsible for the red dust layer on the martian surface (Hviid, et al., 1994). A Fe-substituted cristobalite has also been seen as the result of heated nontronite in a magnetic study done by Moskowitz and Hargraves (1984) and was suggested to be a significant component of the red dust on Mars as detected by the Viking spacecraft. High-temperature, shock-generated crystals in Haughton Crater, Canada, have been identified as sillimanite and cristobalite (Martinez, et al., 1993) and it is possible that these minerals may have formed in a similar fashion on Mars. Therefore they may be associated to nanophase iron oxides (Poulet et al., 2007) in the red dust layer, resulting at least partially from repeated impacts on martian phyllosilicates. Careful analysis in the MIR range may help identify those phases and confirm the origin of the red dust.

2.7 Conclusions

We have experimentally determined the effects of various temperatures on the transformation of phyllosilicates, specifically nontronite and montmorillonite. Phyllosilicates were heated in air and under a flow of CO₂ to more closely replicate the early martian atmosphere. We found that the transformation of both types of phyllosilicates was not affected by the composition of the atmosphere in which it was heated. Our experiments showed that when heated to temperatures above 700°C, nontronite transformed into hematite, sillimanite and cristobalite, and montmorillonite transformed into sillimanite and cristobalite. Between 400 and 700°C, nontronite formed an intermediary phase characterized by a red color, the absence of
the 001 peak in XRD diffractograms, reduced 1.4 and 1.9 µm bands in NIR spectra, disappearance of the Fe-OH 2.28 µm band and the appearance of a 2.17-2.21 µm Al-OH doublet.

Due to their precise spectral evolution, heated smectites can be used to determine post-shock temperatures between 400 and ~700°C. Above 700°C, the spectra of nontronite and montmorillonite are mostly featureless in the NIR range because of the formation of high-temperature anhydrous phases (hematite, sillimanite, cristobalite). On the other hand, these minerals exhibit strong signatures in the MIR range which is more effective in identifying secondary phases formed at temperatures above 700°C. However, it is often difficult to make definitive identifications due to the quantity of bands and their variability with crystalline state and composition.

The NIR spectra of the phyllosilicates identified in the ejecta of the studied crater in the literature are more similar to those of heated nontronite, with or without post-heating rehydration, rather than untreated nontronite, indicating that they existed before the impact and were altered by the post-shock temperatures resulting from the impact. Thus these phyllosilicates were formed prior to the impact event and were not formed by a hydrothermal system created by the impact. Therefore our work provides an experimental basis for future characterization of phyllosilicates in impact craters and their formation process.

2.8 Acknowledgements

The authors would like to thank Dan Ostrowski for providing some of the heated montmorillonite samples. We thank Travis Altheide for allowing us to use his XRF data. We are also grateful to Drs. F. Poulet and G. Marzo for allowing us to use their spectra for comparison to ours. Finally, we thank Dr. Janice Bishop and an anonymous reviewer whose comments strongly improved the quality of our manuscript.
2.9 References


Experimental investigation into the effects of meteoritic impacts on the spectral properties of phyllosilicates on Mars

3.1 Abstract

Phyllosilicates have been identified in some of the most highly-cratered Noachian terrains on Mars. To study the effects of such impacts on the properties of phyllosilicates, we experimentally shocked six phyllosilicate minerals relevant to the martian surface: montmorillonite, nontronite, kaolinite, prehnite, chlorite and serpentine. The shock-treated samples were analyzed with x-ray diffraction (XRD), near- and mid-infrared (NIR and MIR) spectroscopy, Raman spectroscopy, cathodoluminescence (CL) and some were modeled using Autodyne® modeling software. XRD data show that the structure of each mineral, except prehnite, underwent partial structural deformation or amorphization. We also found that while the NIR spectra of shocked samples were very similar to that of the original sample, the MIR spectra changed significantly. This may explain some of the discrepancies between CRISM/OMEGA data (NIR) and TES/THEMIS (MIR) observations of phyllosilicates on Mars. Quartz was identified as a secondary phase in the XRD of shocked chlorite. XRD of shocked serpentine showed the formation of magnesite \([\text{MgCO}_3]\) suggesting the shock-induced carbonation of serpentine. If these processes occurred on Mars, they would have resulted in the observed association between Mg-carbonates and serpentine in and/or around some impact craters.

3.2 Introduction

Phyllosilicates were first identified in the Nili Fossae, Syrtis Major, and Mawrth Vallis regions on Mars by the Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activite (OMEGA) spectrometer on Mars Express (Poulet et al., 2005) and were later confirmed by the
Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars Reconnaissance Orbiter (MRO) (Bishop et al., 2008a; Mustard et al., 2008). Since their initial discovery, they have been found mostly in the oldest Noachian terrains (Bibring et al., 2006; Loizeau et al., 2007; Wiseman et al., 2008; Ehlmann et al., 2008a) in association with lava flows (Poulet et al., 2005) and in the central peaks and ejecta of impact craters (Mangold et al., 2007). Thus far, the most abundant phyllosilicates on Mars are Fe/Mg-smectites (nontronite or saponite) and Al-smectites (montmorillonite or kaolinite) (Carter et al., 2011) with less abundant chlorite, serpentine and Fe$^{2+}$ phases (Bishop et al., 2008a; Mustard et al., 2008; Poulet et al., 2008; Ehlmann et al., 2009).

The presence of phyllosilicates suggests a warm, wet climate much different from the current cold, dry martian surface conditions. However, their exact formation processes remain unclear. Some studies suggest phyllosilicates formed early in Mars’ history due to the activity of water on the surface (Chevrier et al., 2007) as a result of the weathering of basaltic material (Michalski and Noe Dobrea, 2007) while others indicate they result from surface (Poulet et al., 2005) or subsurface (Ehlmann et al., 2011) hydrothermalism due to volcanic activity or meteorite impacts (Schwenzer and Kring, 2009; Fairen et al., 2010). The exact formation processes of such minerals on Mars have significant implications for their age and thus the role of hydrothermal activity on Mars today. More recent observations have shown a discrepancy between the near-infrared and mid-infrared (5-15 µm) spectra of some phyllosilicates, mainly those that were identified in Mawrth Vallis (Michalski and Fergason, 2009) and Nili Fossae regions (Michalski et al., 2010). This raises the question as to the effects of meteoritic impacts on the spectral properties of phyllosilicates and is the focus of this paper.
Previous studies have investigated the effects of shock pressure and temperature on clay minerals but most of these studies have focused on the Fe-rich smectite nontronite. Weldon et al. (1982) showed that shock pressure indeed has an effect on nontronite because samples that were only heated showed more of a color change than those that were impacted. Additionally, Boslough et al. (1986) showed that above 600°C, shocked and heated nontronites are very dissimilar in color and magnetic properties. While these studies concentrated on nontronite in their search for the origin of the red dust on Mars, their results still suggest that shock pressure plays a major role in the alteration of clay minerals.

Clay minerals have been found on Earth from different shock metamorphic environments such as Cretaceous/Tertiary Boundary layers (Pollastro and Bohor, 1993; Salge et al., 2000), terrestrial impact structures (Dypvik and Ferrell, 1998; Krisimäe et al., 2002; Dypvik et al., 2003; Horton et al., 2006) and meteorites (Scott and Krott, 1998). In a pioneering study, shocked clay samples from a Barents Sea borehole near the Mjølnir Impact Structure were used to investigate changes in the clay assemblage associated with the submarine impact (Dypvik and Ferrell, 1998). They found that a randomly interstratified smectite-illite with 85% smectite layers forms the basis for a two-layer oceanic impact clay model that differs from published terrestrial cases. The smectite is assumed to represent seawater-altered impact glass from the ejecta blanked material that was mixed with resuspended shelf sediments by the collision-generated waves. The smectite-rich interval is overlain by a coarser unit containing abundant smectite, shocked quartz grains, and anomalous Ir contents at its base. This interval may have originated as a density/turbidity current, generated by the impact and the collapse and erosion of the crater rim.
More recently, clay minerals were described from shocked granitoid basement rocks of the Woodleigh impact structure (Australia), which are mainly smectite-rich (>75%) mixed-layer illite-smectite with some discrete illite formed as an alteration (replacement) product of biotite (Uysal et al., 2000). They concluded that these clay minerals formed by post-shock hydrothermal alteration processes. It has been hypothesized that similar hydrothermal processes resulted in the formation of smectites and other phyllosilicates on Mars either in the Noachian era (Poulet et al., 2005) or possibly more recently (Fairen, et al., 2011; Ehlmann et al., 2011).

Laboratory simulations of meteorite impacts are essential because they can provide the values of fundamental parameters used in equations, thus allowing estimates of the physical characteristics of meteorite impacts by comparing microstructures observed in naturally and artificially shocked minerals. Classically, laboratory experiments are based on the production of planar or quasi-planar shock fronts, generated either by confinement of explosive materials in contact (direct or not) with the sample in a rigid vessel (i.e. shock recovery experiments) or by target-projectile gun techniques (Martinez et al., 1995; Martinez and Agrinier, 1998). Additionally, by comparing the IR spectra of untreated and shocked phyllosilicates, we can determine whether a natural phyllosilicate existed pre-impact and was altered by the impact event or if it formed post-impact by hydrothermal processes. In this study, we will use various analytical techniques to determine the effect of shock treatment on the properties of several phyllosilicates and relate our results to the surface of Mars.

3.3 Methods

3.3.1 Description of samples

Six phyllosilicates were used in this study – montmorillonite, nontronite, kaolinite, prehnite, chlorite and serpentine. X-ray fluorescence (XRF) analysis of Altheide et al., (2010)
provided the exact chemical formulae of our montmorillonite
\[[(Na_{0.27}K_{0.04}Ca_{0.07})(Al_{1.65}Mg_{0.26}Fe^{3+}_{0.17})(Si_{3.84}Al_{0.06})O_{10}(OH)_{2}nH_{2}O] \] and nontronite
\[[(Ca_{0.15}Na_{0.01}K_{0.01})(Fe^{3+}_{1.3}Al_{0.63}Mg_{0.10})(Si_{3.57}Al_{0.45})O_{10}(OH)_{2}nH_{2}O] \] samples. The other samples
can be described by their general formulae: kaolinite \[Al_{2}(Si_{2}O_{5})(OH)_{4}\]; prehnite
\[Ca_{2}Al_{2}Si_{3}O_{12}(OH)\]; chlorite \[(Mg,Fe^{2+})_{5}Al(Si_{3}Al)O_{10}(OH)_{8}\]; serpentine \[(Mg,Fe)_{3}Si_{2}O_{5}(OH)_{4}\].
Montmorillonite samples (Ward’s #46E0438) are from Panther Creek, CO; nontronite (Ward’s
#49E5108) is from Cheney, WA; kaolinite (Ward’s #46E0995) is from Edgar, FL; prehnite is
from Poona, India; chlorite (Ward’s #46E1923) is from Madison Co, NC; and serpentine
(Ward’s #46E7263) is from Eden Mills, VT.

3.3.2 Experimental methods

The shock recovery experiments were carried out using a two-stage light gas gun at the
Institute of Astronautical Science, Japan Aerospace Exploration Agency (JAXA) (Croizer and
Hume, 1957; Mieno and Hasegawa, 2008-and references therein). A schematic diagram of the
light-gas gun, which has a 500 mm diameter and 1000 mm long target chamber, is shown in
Figure 3-1A. The projectile collides to a sample holder in the target chamber under 40 Pa of
pressure at room temperature. This gas gun can accelerate a projectile, polycarbonate cylinder of
7 mm diameter and 4.5 mm height with stainless-steel head of 4 mm diameter and 1 mm height,
to about 4.5 km/s. Sample holders (height = 20 mm, diameter = 100 mm) made of stainless-steel
(SUS304) or brass were laid in the target chamber. A sample room of 6 mm diameter at 5 mm
height was set at 5 mm depth from the surface of the holder as shown in Figure 3-1B. From
hence forth, impacted samples will be referred to by their projectile velocity since it was the
most accurately measured parameter in the shock experiments (Table 3-1).
Figure 3-1 - Schematic of the setup of the impact experiments. Each section’s dimensions are given in diameter x length in mm. A) Light gas gun. B) Sample holder. The sample sits in a container measuring 6 mm x 5 mm, indicated by the gray box in the center. The large arrow shows the direction of the projectile.
Table 3-1 - Impact experiment parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Projectile velocity (km/s)</th>
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<tbody>
<tr>
<td>Montmorillonite</td>
<td>2.25, 2.56, 3.66, 4.49</td>
</tr>
<tr>
<td>Nontronite</td>
<td>2.07, 2.15, 2.47, 3.27</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.23, 3.49, 4.32, ----</td>
</tr>
<tr>
<td>Prehnite</td>
<td>2.32, 3.50, 4.30, ----</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.30, 3.59, 4.30, ----</td>
</tr>
<tr>
<td>Serpentine</td>
<td>2.30, 3.51, 4.30, ----</td>
</tr>
</tbody>
</table>
3.3.3 Analytical techniques

3.3.3.1 X-ray diffraction

Each sample’s mineralogy was characterized by X-ray diffraction (XRD) using a Philips PW 1830 X-ray monochromator diffractometer with a CuKα cathode, a voltage of 45 kV, an intensity of 40 mA, and a 0.25° divergence slit. The 2θ range was 5-80° with a step size of 0.02° and a time per step of 13 s, resulting in a total analytical time of 13 h, 45 min per sample. The powdered samples were dispersed onto a glass slide with a few drops of acetone for analysis in random orientation. All reference XRD patterns and corresponding reference codes can be found in the supplementary material of this chapter.

3.3.3.2 Infrared reflectance spectroscopy

Fourier transform infrared (FT-IR) reflectance spectra were obtained using a Nicolet 6700 Smart Diffuse spectrometer (Gavin and Chevrier, 2010; Gavin et al., 2012). Near-infrared (NIR) spectra were taken with an attached CeramOptec optical probe. Samples were placed in a ceramic tube on a hotplate at ~150°C and dry N₂ purge gas flowed over the sample and through the spectrometer for about 2 hrs prior to recording each spectrum to remove any atmospheric gases. The optical probe was then inserted into a small hole drilled into the top of the ceramic tube and the sample’s spectrum was recorded. NIR spectra were recorded in reflectance mode in the range of 1.0-2.5 µm (optimum range for the optical probe) with a resolution of 2 cm⁻¹, allowing comparison to OMEGA and CRISM data available in the literature. The configuration used a quartz-halogen IR source, a CaF₂ beamsplitter, and a TECP detector. A background spectrum of Al₂O₃ powder was taken under the same measurement protocol (N₂ flow, 150°C) and was subtracted from each sample’s spectrum.
Mid-infrared (MIR) spectra were recorded using the same spectrometer but without the optical probe and at ambient temperatures. MIR spectra were recorded in the range 1.4-28.6 µm but were focused on the 5-15 µm range for comparison to TES and THEMIS data. This configuration used an IR source, a KBr beamsplitter and a DTGS detector. Background spectra of gold coated emery tape were taken before each samples’ spectrum was recorded.

3.3.3.3 **Raman spectroscopy**

The mineral assemblages and textures were characterized with a Nikon Eclipse LV100POL optical microscope. Raman spectra were recorded with a Renishaw Rm-2000 Raman spectrometer attached to a Leica DM/LM microscope at the Research Institute for Physics (Budapest, Hungary). The 623 nm line from an Ar⁺ laser served as excitation source and the laser power on the sample was 8 mW. The microscope focused the excitation beam into a 1-µm diameter spot. Raman spectra were recorded in the 200-1100 cm⁻¹ region using a CCD camera, the acquisition time was 60 sec. Intensity variations due to polarization effects were not observed.

3.3.3.4 **Cathodoluminescence (CL)**

CL analysis uses the induced luminescence of a material to obtain information on the material’s internal structure. In mineralogical studies, CL analysis (often coupled with SEM) provides information on the mineralogical order and structure of the sample. In our study, CL spectroscopy was undertaken by a scanning electron microscope (SEM)-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The CL emitted from the samples was collected using a retractable parabolic mirror coated with aluminum (collecting efficiency of 75%). The CL signal was dispersed by a grating monochromator, which has the following characteristics: 1200 grooves/mm, a focal length of 0.3
m, F of 4.2, a resolution limit of 0.5 nm, and a slit width of 4 mm at the inlet and outlet. The dispersed CL was recorded by a photon counting method using a photomultiplier tube (Hamamatsu: R2228) and converted to digital data.

All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp (Eppley Laboratory: Quartz Halogen Lamp). This correction prevents errors in the peak position of emission bands and allows quantitative evaluation of CL intensity. The spectral response varies smoothly between 300 and 800 nm with a maximum at 550 nm and shows the steps at approximately 450 and 730 nm, which correspond to discontinuous artifacts of Wood’s anomaly attributed to a specific characteristic of the grating. A detailed description of the equipment and analytical procedures can be found in Kayama et al. (2010). The corrected CL spectra in energy units were deconvoluted into the Gaussian component corresponding to each emission center using a peak-fitting software (Peak Analyzer) in OriginPro 8J SR2.

CL color imaging was carried out using Luminoscope (ELM-3R) consisting of a cooled charge-coupled device (CCD) camera. The Luminoscope contains a cold cathode discharge tube and a vacuum chamber, in which the sample is placed. The Luminoscope was operated stably with electron beams generated by excitation voltage at 10 kV and beam current of 0.5 mA at vacuum condition under 100 Torr. The diameter of the electron beam spot was maintained at a few mm size on the sample’s surface by a magnetic field. The CL images were converted to digital data using the Nikon imaging system (DS-5Mc). CL scanning images at high magnification were recorded by a Mini-CL detector (Gatan) consisting of multi-alkali photomultiplier tube installed on a SEM (JEOL: JSM-5410LV). Color CL images are provided in the supplementary material of this chapter.
3.3.4 Modeling

Because obtaining direct in situ measurements of shock pressures and temperatures of an impact experiment is impossible, numerical simulations using the parameters of the experiment are often used to calculate these values. Shock pressure and temperature were estimated from the experimental conditions using the Autodyn (Century Dynamics, Inc.) modeling software. Configuration of projectile and sample was the same as in Figure 3-1B, except for the sample holder, which was set to $H = 20$ mm and diameter $= 16$ mm. Simulations were done only for montmorillonite and nontronite in this study and porosity of the clay was not considered in the simulation because the samples were pressed into pellets prior to the shock experiments. According to the density data, we estimated that $C_1$ and $C_2$ parameters of clay minerals range from $1.85-2.05$ km/sec ($C_1$) and $1.45-1.65$ km/sec ($C_2$) (Ahrens and Johnson, 1995).

In the simulations, we adopted $C_1 = 1.95$ km/s and $C_2 = 1.55$. Constant pressure specific heat, thermal conductivity, and Grüneisen Coefficient of nontronite were estimated to be $771$ [J kg$^{-1}$ K$^{-1}$] at $300$ K (Wilson et al., 2006), $1.6$ [J m$^{-1}$ K$^{-1}$ s$^{-1}$] (Clifford and Fanale, 1985), and $1.36$ (Butler and Frost, 2006), respectively. Twenty-four gauge points positioned uniformly in the samples. The pressure and temperature were averaged among the twenty-four gauge points from shock wave arrival time on the each gauge point to $\sim 3.5 \times 10^{-3}$ ms. However, since shock pressure and temperature were inhomogeneous and time variable, the maximum pressure and temperature were also estimated among the gauge points until $3.5 \times 10^{-3}$ ms (Table 3-2).
Table 3-2 - Maximum and average temperatures and pressure for montmorillonite and nontronite as determined from Autodyne simulations.

<table>
<thead>
<tr>
<th>Projectile velocity (km/s)</th>
<th>Average temperature (°C)</th>
<th>Peak temperature (°C)</th>
<th>Average pressure (GPa)</th>
<th>Peak pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
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</tr>
<tr>
<td>2.56</td>
<td>79</td>
<td>311</td>
<td>0.40</td>
<td>7.0</td>
</tr>
<tr>
<td>3.66</td>
<td>147</td>
<td>653</td>
<td>0.67</td>
<td>11.4</td>
</tr>
<tr>
<td>4.49</td>
<td>202</td>
<td>947</td>
<td>0.74</td>
<td>15.0</td>
</tr>
<tr>
<td>Nontronite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>80</td>
<td>220</td>
<td>1.0</td>
<td>5.4</td>
</tr>
<tr>
<td>2.15</td>
<td>72</td>
<td>220</td>
<td>1.1</td>
<td>6.4</td>
</tr>
<tr>
<td>2.47</td>
<td>149</td>
<td>322</td>
<td>0.9</td>
<td>4.5</td>
</tr>
<tr>
<td>3.27</td>
<td>137</td>
<td>524</td>
<td>1.6</td>
<td>17.5</td>
</tr>
</tbody>
</table>
Images of the simulations were taken at certain time intervals. Simulations of the montmorillonite samples were stopped after $6 \times 10^{-3}$ ms whereas simulations of the nontronite samples were stopped after $3.764 \times 10^{-3}$ ms (10000 cycles) for $v = 2.47$ km/s, $7.836 \times 10^{-3}$ (10000 cycles) or $v = 2.15$ km/s, and $9.439 \times 10^{-3}$ (10000 cycles) for $v = 2.07$ km/s. It is important to note that each cycle in the Autodyn calculation did not consist of the same amount of time. Images of each step in the simulation are shown in the supplementary material of this chapter.

### 3.4 Results

#### 3.4.1 X-ray diffraction

Generally, the impacted samples showed evidence of alteration by a decrease in peak intensity. Most peaks in the sample of montmorillonite shocked with projectile velocity 4.49 km/s are still intact but have decreased in intensity, except for the large 001 peak at $2\theta \sim 5^\circ$ (Fig. 3-2A) which has increased in intensity. Additionally, there is a large “hump” feature around $22^\circ$ probably indicating the presence of amorphous glass. All of nontronite’s signature peaks are also intact but decreased in intensity in the XRD of the sample shocked to 3.27 km/s (Fig. 3-2B). A few small new peaks have appeared at $2\theta = 47, 49,$ and $51^\circ$. Kaolinite shocked to 4.32 km/s shows strong alteration in that most peaks have disappeared and those that are still visible are significantly decreased in intensity (Fig. 3-2C). Only small peaks of the original ones are seen at $2\theta = 12, 25, 34-40, 55$ and $62^\circ$. By contrast, the shocked prehnite seems to show very minimal alteration (Fig. 3-2D). Most peaks are still intact and some have even increased in intensity (e.g., $2\theta = 9, 27$ and $52^\circ$). Our unshocked chlorite sample was identified by XRD as clinochlore $[(\text{Fe,Mg})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8]$ and shows almost complete alteration in that most of the original peaks have almost disappeared. Several new peaks appear at $2\theta = 21, 27, 39-41, 43, 46, 50, 55-$
56, 60, 64, 68-69, 74, 76 and 78° (Fig. 3-2E) and are identified as quartz (Supp. Mat. Fig. 3-5). To highlight these new peaks, chlorite is shown on a square root y-axis rather than a linear scale. Serpentine (identified as antigorite \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\) with minor chamosite \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\) showed evidence of slight alteration (Fig. 3-2F) since some peaks in the original sample disappeared after shock treatment to 4.3 km/s (2θ = 6, 19, 30-31, and 57°). However, in each shocked sample, magnesite \([\text{MgCO}_3]\) was identified by peaks at 2θ = 32, 43, 47, 54, 67, 69-70, and 76° (Fig. 3-2F; Supp. Mat. Fig. 3-6).
Figure 3-2 - X-ray diffraction of untreated samples and samples shocked to high projectile velocity. A) Montmorillonite. B) Nontronite. C) Kaolinite. D) Prehnite. E) Chlorite, shown on a square root y-axis to highlight the new peaks formed in the impacted sample. These peaks are identified as quartz and are marked with a vertical line. F) Serpentine. Peaks identified as magnesite [MgCO₃] are marked with a vertical line.
3.4.2  Near-infrared spectroscopy

Overall, there were no significant changes between the NIR spectra of the untreated samples and the sample impacted with the highest projectile velocity (Fig. 3-3). In the spectrum of untreated montmorillonite, hydration bands are visible at 1.4 and 1.9 µm as well as the Al-OH band at 2.21 µm. In the spectrum of montmorillonite impacted at 4.49 km/s projectile velocity, a new band formed at 1.71 µm and the slope of the spectrum became more positive below ~1.8 µm (Fig. 3-3A) but the three signature bands are still intact. Hydration bands are also observed in the untreated nontronite spectrum at 1.4 and 1.9 µm as well as the Fe$^{3+}$-OH band at 2.28 µm. In the spectrum of nontronite impacted with 3.27 km/s projectile velocity, the bands have slightly increased in depth and a new band formed at about 2.1 µm (Fig. 3-3B). The two signature doublets of kaolinite at 1.40-1.42 (OH) and 2.17-2.21 µm (Al$_2$-OH, Bishop et al., 2008) are visible and unchanged in both spectra of the untreated and shocked samples (Fig. 3-3C). Signature bands of prehnite at 1.48, 2.25, 2.29 µm and the triplet at 2.34-2.37-2.40 µm are all present in both the unshocked and shocked spectra (Fig. 3-3D). The spectrum of untreated chlorite shows the triplet at 2.26-2.31-2.35 µm due to Al(Fe,Mg)-OH and Mg$_3$-OH (Bishop et al., 2008b) which shifted to lower wavelengths in the spectrum of chlorite impacted to 4.3 km/s while the hydroxyl band at 1.4 µm remained unchanged (Fig. 3-3E). The spectrum of untreated serpentine showed the hydroxyl band at 1.4 µm and the Mg$_3$-OH band at 2.33 µm (Bishop et al., 2008b, Fig. 3-3F), while the spectrum of serpentine impacted to 4.3 km/s showed a new band at ~2.0 µm and a new doublet at 2.12-2.14 µm.
Figure 3-3 - Near-infrared (1.0 – 2.5 µm) reflectance spectra of untreated samples and samples shocked to highest projectile velocity. A) Montmorillonite. B) Nontronite. C) Kaolinite. D) Prehnite. E) Chlorite. F) Serpentine. Dashed vertical lines indicate the major bands for each sample.
3.4.3 *Mid-infrared spectroscopy*

While there were little to no changes between the NIR spectra of untreated and impacted samples, the mid-infrared (MIR) spectra of impacted samples show significant changes compared to the untreated sample (Fig. 3-4). Untreated montmorillonite shows bands at 5.5, 6.2 (H$_2$O), 7.15, 8.07, 9.12 (Si-O stretching and bending), 10.8 (Al$_2$-OH), 11.3 (Al-Fe-OH, Bishop et al., 2008b) and 12.6 µm (Fig. 3-4A). In the spectrum of montmorillonite impacted to 4.49 km/s, bands from 5-9 µm decrease in intensity and the bands above 10 µm disappear completely. The spectrum of untreated nontronite shows bands at 5.58, 6.2 (H$_2$O), 8.3 (SiO$_2$), 9.2 (Si-O stretching and bending), 11.4 (OH bending in Al-Fe$^{3+}$-OH) and 12.2 µm (Fe$^{3+}$-OH, Bishop et al. (2008b), Fig. 3-4B). In the spectrum of nontronite impacted to 3.27 km/s, new bands appear at 6.68 and 7.31 µm and the bands at 5.58 and 8.37 µm shift to 5.69 and 8.47 µm, respectively. Most bands in the untreated kaolinite spectrum remain unchanged while new bands form at 6.85, 7.31 and 7.65 µm in the spectrum of kaolinite impacted to 4.3 km/s (Fig. 3-4C). The spectrum of prehnite impacted to 4.3 km/s shows that bands below ~8 µm disappear while new bands form at 12.1 and 12.9 µm (Fig. 3-4D). The overall slope of the shocked chlorite spectrum (v = 4.3 km/s) changes from strongly negative to slightly positive (Fig. 3-4E). The bands at 5.35, 6.15 and 9.60 µm in the untreated spectrum disappear in the impacted spectrum, new bands form at 12.6, 12.9 and 14.5 µm in the impacted spectrum and the large band at 8.76 µm shifts to 9.22 µm. The spectrum of serpentine impacted to 4.3 km/s also shows a change in slope from negative to slightly positive from the original sample (Fig. 3-4F). Bands at 5.59, 6.16 and 8.36 µm in the spectrum of the untreated sample disappear and new bands form at 9.31, 11.3 and 13.4 µm in the impacted spectrum.
Figure 3-4 - Mid-infrared (5.0 – 15.0 µm) reflectance spectra of untreated samples and samples shocked to highest projectile velocity. A) Montmorillonite. B) Nontronite. C) Kaolinite. D) Prehnite. E) Chlorite. F) Serpentine. Dashed vertical lines indicate the major bands for each sample.
3.4.4 Raman spectroscopy

Among our six experimentally shock-deformed clay minerals, only montmorillonite shows any detectable changes due to the shock metamorphism. Raman spectra of the shocked montmorillonite sample display systematic changes as a function of the increasing shock pressure as the result of the breakup of the linked SiO$_4^{4-}$ (Fig. 3-5). These systematic changes are indicated by the peak broadening and decrease in peak intensity of a vibrational band centered at 705 cm$^{-1}$ (Si-O-Al stretching vibrational mode) as well as an appearance of a new vibrational mode at 517 cm$^{-1}$ (anti-symmetric SiO stretching mode, Butler and Frost (2006) – and references therein, Fig. 3-5). The increasing full width at half maximum (FWHM) values of the 705 cm$^{-1}$ Raman peak are also in good agreement with the increasing shock pressure and post-shock temperature effects on the crystalline background of the shocked sample (Table 3-3). This indicates a pressure- and temperature-induced phase transformation (i.e. occurrence of the shock-induced amorphization) in the shocked montmorillonite, which was also shown in the XRD (see Section 3.4.1.).
Figure 3-5 - Raman spectra of untreated and shocked montmorillonite.
Table 3-3 - Full width at half maximum (FWHM) values of the Raman peak at 705 cm\(^{-1}\) in unshocked and shocked montmorillonite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshocked</td>
<td>12.96</td>
</tr>
<tr>
<td>2.56 km/s</td>
<td>14.46</td>
</tr>
<tr>
<td>3.66 km/s</td>
<td>15.25</td>
</tr>
<tr>
<td>4.49 km/s</td>
<td>22.50</td>
</tr>
</tbody>
</table>
3.4.5 Cathodoluminescence

3.4.5.1 Montmorillonite

Cathodoluminescence spectral properties of the unshocked sample show three characteristic broad bands centered at 410, 585, and 705 nm (Fig. 3-6A). The broad emission band at 585 nm is assigned to the AlO$_4$/M$^+$ center and the 705 nm band is related to activators such as Mn$^{2+}$ and Fe$^{3+}$ (Götze et al., 2002, Fig. 3-6A). CL spectra of the shocked sample (2.25 km/s) exhibit a disappearance of the activator-related peaks. Only a defect center shows a weak broad band at 425 nm (Fig. 3-6B). Peak intensity continued to decrease with increasing shock pressure until the CL spectra are featureless for the montmorillonite sample shocked at 4.49 km/s (Fig. 3-6D). The Luminoscope CL image of the unshocked montmorillonite sample (powdered) shows a great variety of CL colors from blue to orange in the visible light range (Supp. Mat. Fig. 3-7). Compared to the unshocked sample, the montmorillonite sample shocked at 2.25 km/s exhibits a moderate level of the CL coloring in its CL micrograph with relatively strong appearance of the CL dark areas.
Figure 3-6 - Cathodoluminescence (CL) spectra of untreated and shocked montmorillonite samples. A) Untreated montmorillonite. B) Montmorillonite shocked to 2.25 km/s. C) Montmorillonite shocked to 3.66 km/s. D) Montmorillonite shocked to 4.49 km/s.
3.4.5.2  Nontronite

The CL spectrum of unshocked nontronite shows only one broad band around 580 nm with smaller peak intensity than in the shocked sample (Fig. 3-7A). The shocked sample consists of two dominant broad bands centered at 575 and 685 nm, which are associated with Fe$^{3+}$-activation (Lemons and McAtee, 1983; Sherman and Vergo, 1988), and two narrow bands at 390 and 400 nm (defect centers, Fig. 3-7A). CL images of both unshocked and shocked (2.47 km/s) nontronite samples show pale blue color (Supp. Mat. Fig. 3-8). In a comparison with the unshocked sample, the shocked samples contain a relatively high level of the CL-dark areas.
Figure 3-7 - Cathodoluminescence (CL) spectra of untreated and shocked samples. A) Nontronite. B) Kaolinite. C) Prehnite. D) Chlorite. E) Serpentine. The different curves in each graph show the spectra taken from different points in the sample.
3.4.5.3 **Kaolinite**

The high-intensity broad peak containing two centers at 385 and 405 nm can be related to relatively high concentration of electron-hole centers in these samples (Götze et al., 2002) (Fig. 3-7B). The peak intensity of this broad band decreases systematically in the shocked kaolinite sample. Additionally, a minor peak appears at 585 nm in the shocked sample which is related to Mn$^{2+}$ activation (Fig. 3-7B). Dehydration-induced luminescence (Lahav et al., 1985) of the kaolinite samples was not observed. There is no significant CL color (blue) change observed in both unshocked and shocked (4.32 km/s) kaolinite samples (Supp. Mat. Fig. 3-8).

3.4.5.4 **Prehnite**

All of the CL spectral features in both unshocked and shocked prehnite samples show only one broad band centered at 585 nm which is assigned to a Mn$^{2+}$-related emission band (Tulloch, 1979) (Fig. 3-7C). The greenish yellow CL color of the unshocked prehnite sample is changed into heterogeneous yellow in the shocked sample (4.3 km/s) (Supp. Mat. Fig. 3-8).

3.4.5.5 **Chlorite**

CL spectra of both samples are dominated by two broad bands centered at 450 (AlO$_4$/M$^{+}$-center) and 625 nm (Mn$^{2+}$, Malins et al., 2004), Fig. 3-7D). As a function of the increasing shock pressure, there is a significant and systematic shift of the Mn-related peak from 625 to 585 nm as well as an increase of peak intensity of the defect center at 450 nm (Fig. 3-7D). The unshocked chlorite sample shows a pale purple CL color in its CL images whereas the shocked one (at 4.3 km/s) represents a heterogeneous color distribution from purple to orange (Supp. Mat. Fig. 3-8).
3.4.5.6 Serpentine

The shocked serpentine sample exhibits a higher peak intensity of the 650 nm band, related to the Mn$^{2+}$-activation (Götze et al., 2002), than in the unshocked sample (Fig. 3-7E). Both unshocked and highly shocked (4.3 km/s) serpentine samples show homogeneous orange-red color (due to Mn$^{2+}$-activation) in their CL images (Supp. Mat. Fig. 3-8).

3.4.6 Modeling

Shock experiments with montmorillonite and nontronite were modeled using Autodyn modeling software to estimate the peak and average temperatures and pressures during the impact experiment. Average shock pressures reached 0.74 GPa for montmorillonite and 1.6 GPa for nontronite while peak pressures reached up to 15 GPa in montmorillonite and 17.5 GPa in nontronite (Table 3-2). Average temperatures were up to ~200°C for montmorillonite and ~140°C for nontronite while peak temperatures reached ~950°C in montmorillonite and ~525°C for nontronite (Table 3-2). With reasonable assumptions of similar physical properties, we can safely assume that these values should be quite similar for other phyllosilicates. Modeling images show the temperature and pressure waves propagating through the sample (Fig. 3-8; Supp. Mat. Fig. 3-9). In both shocked montmorillonite and nontronite simulations, the pressure wave propagated relatively uniformly through the entire sample. This allowed the entire sample to reach peak shock pressures. The temperature wave, however, was much more localized near the impactor-sample contact point (Fig. 3-8), creating a steep temperature gradient between one side of the sample and the opposite side. This means only part of the sample reached the maximum shock temperature. This may explain why montmorillonite and nontronite showed little evidence of thermal alteration in XRD and NIR spectra and why the peak and average temperatures are very different, sometimes by several hundred degrees.
Figure 3-8 - Images from the Autodyne software modeling the impact experiments of montmorillonite shocked with 3.66 km/s projectile velocity showing the A) temperature and B) pressure wave propagating through the sample (white box in t = 0 s image) and their respective scales. Total time elapsed in the simulation is 6.0 x 10^{-3} ms.
The calculated maximum and average temperatures and pressures reached in our shock experiments (Table 3-2) can be considered lower limits since the average projectile speed for Mars has been estimated at 9.3 km/s (Steel, 1998). Additionally, the main difference between shock recovery experiments and natural impacts is the duration of the passage of the shock wave through the rocks. In experiments, the shocked state typically lasts microseconds, or even nanoseconds when lasers are used. In nature, the shock duration depends on the impactor size and can reach a few seconds while temperatures remain elevated for much longer (on the order of years). Another difference between nature and experiments may come from shock and post-shock temperatures. Indeed, in natural impacts, the porosity of the material is usually higher than in shock experiments because of numerous fractures and pores existing at different scales. As a consequence, shock temperatures achieved for a given pressure are usually higher in natural impacts than in shock experiments (Martinez et al., 1995; Martinez and Agrinier, 1998) and last much longer.

3.5 Discussion

3.5.1 Structural deformation / amorphization and secondary phase formation

Each sample shocked to maximum projectile velocity showed evidence of structural deformation and/or partial amorphization as indicated by their XRD, CL or Raman data. The XRD of shocked montmorillonite showed a decrease in peak intensity and a large hump feature at 2θ ~22° indicating the presence of amorphous glass in the shocked sample. Prehnite seemed to show the most resistance to shock alteration while kaolinite and chlorite show the strongest evidence for structural deformation by the loss of most peaks in their respective XRD data. The significant decrease in peak intensity in all samples (except prehnite) indicates major deformation in each mineral’s structure. Though not enough to cause complete
melting/recrystallization as has been shown in other heating studies (Gavin and Chevrier, 2010; Che et al., 2012), partial melting and/or shock-induced phase change without melting/recrystallization is evidenced by the appearance of quartz in the shocked chlorite (new peaks at 2θ = 21, 27 and > 35°) and the formation of magnesite [MgCO₃] in shocked serpentine (new peaks at 2θ = 32, 43, 47, 54, and > 65°).

Wada and Kamitakahara (1991) investigated the pressure dependence of the OH stretching mode in muscovite and vermiculite layered silicates by using micro-Raman spectroscopy. Hotz et al. (1993) studied the hydrostatic pressure effects on the Raman spectral features of the layered aluminosilicates and found that there is a peak shift indicating that the vibration is affected by van der Waals forces between the bounding oxygens and the interlayer cation. Recently, there were several Raman studies which observed distinct changes in the crystallinity of clay minerals due to the increasing pressure (i.e., Duffy et al., 1995; Huang et al., 1996; Comodi and Zanazi, 1997; Johnson et al., 2002). They concluded that application of pressure indicates the bond shortening which results in an increase in the vibrational wavenumber in most of the clay minerals.

Further evidence for structural deformation comes from each sample’s CL spectra and images, especially in montmorillonite and chlorite (Figs. 3-6, 3-7D; Supp. Mat. Figs. 3-7, 3-8). In contrast to other clay minerals, the luminescence (especially thermoluminescence) properties of montmorillonite are highly affected by not only the capacity for a cation exchange due to substitution with elements at lower valence (Ferraresso, 1967), but also the type of exchangeable cation (Lemons and McAtee, 1982). The dehydration-induced cathodoluminescence was not observed in our shocked montmorillonite clay mineral sample. Additionally, the peak intensity
change due to shock metamorphism may be related to the effect of adsorbed iron (Coyne and Banin, 1986).

The CL changes in the shocked sample of chlorite indicate the distortion of the crystalline background due to the shock wave resulting in an amorphous phase. This shocked-induced CL behavior has been known, especially in the rock-forming minerals from different shock metamorphic environments such as meteorites, impactites and the Moon, for many decades. Sippel and Spencer (1970) observed that shock metamorphism caused peak shifts, peak broadening and decrease of luminescence intensity compared to the undamaged counterpart in the CL spectra of shock-metamorphosed lunar feldspars. They noted that the distortions or disorder in the crystal field results in crystal field perturbations and these local variations result in a broadened distribution of excited state energies. Recently, CL spectral measurements were performed on natural and experimentally shocked oligoclases (An19.7 single crystal shocked between 10.5 and 45 GPa) and plagioclases from the equilibrated ordinary chondrites (Dar al Gani and Tenham) (Kaus and Biscoff, 2000). They observed disappearance of the crystal field sensitive Mn$^{2+}$ and Fe$^{3+}$-related peaks resulting from breakdown of the crystal structure (i.e. occurrence of diaplectic glass) at around 35 GPa. Our impacted chlorite sample shows similar CL peak broadening at ~15 GPa and are in good agreement with previous observations on the changes of the CL properties on some shocked minerals due to the increasing shock pressure.

Weldon et al. (1982) described the color changes in nontronite impacted to 18 and 30 GPa due to the shock-induced heating that changed the coordination of the Fe$^{3+}$ in the octahedral layer to a mixture of 4- and 6-fold coordination. Our samples, however, did not display such a color change likely due to the lower shock pressure regimes of ~1.0 GPa average and ~17.0 GPa peak (Table 3-2). Weldon et al. (1982) also heated their nontronite samples to 350 and 500°C
and observed similar color changes. While the peak temperatures in our impacted samples reached much higher than this (~950°C for montmorillonite and ~525°C for nontronite, Table 3-2), these peak temperatures were very localized in the sample (see Section 3.4.6.; Fig. 3-8) whereas the maximum temperature would be throughout the entire sample in heating experiments. This would explain the differences in color change between previous impact and heating experiments and the results of this study.

Only two of the six shocked phyllosilicate samples showed evidence of secondary phase formation. Shocked chlorite partially transformed into quartz and shocked serpentine showed the formation of magnesite (Fig. 3-2E&F; Supp. Mat. Figs. 3-5, 3-6). While most clearly identified in the XRD, the secondary phases are also evident in the IR spectra of the shocked samples, except for quartz which is featureless in the NIR range. However, quartz may be responsible for the change in slope and the new bands at 12.6, 12.9 and 14.5 µm in the MIR spectrum of shocked chlorite (Fig. 3-9B) (Baldridge et al., 2009). The NIR spectrum of shocked serpentine shows a new band at ~2.0 µm which is similar to the large 2.0 µm band in magnesite (Fig. 3-9A) (Baldridge et al., 2009). The formation of magnesite may also be responsible for the change in slope and new bands at 11.3 and 13.4 µm in the MIR spectrum of shocked serpentine (Fig. 3-9B).
Figure 3-9 - IR spectral comparisons between our impacted samples of chlorite and serpentine and reference spectra of minerals identified from XRD. A) Impacted serpentine and magnesite (ASTER database, sample #C-6A). The impacted chlorite and quartz comparison was excluded here because quartz is featureless in the NIR range. B) Impacted chlorite compared to quartz (ASTER database, sample #quartz.2) and impacted serpentine compared to magnesite. Reference spectra from Baldridge et al. (2009).
The formation of magnesite from shocked serpentine in our experiments is very interesting because of the absence of data of serpentine carbonation via impact processes. In our experiments, there are two possible carbon sources – the polycarbonate part of the projectile (Fig. 3-1B) or contamination from organics in the original sample. If the projectile did indeed act as a carbon source, we would expect to find carbonates in the other shocked samples, which is not the case. Thus we can assume there was organic material present in the original serpentine sample, especially since serpentines are often closely associated with organic matter. Further analysis is needed to determine the amount of organic matter in our original sample and the amount of carbonate formed in each impact experiment. This will be the focus of a separate study and publication.

3.5.2 **Comparison to thermal alteration**

Our experiments investigated the combined effects of shock pressures and temperatures on the structure and spectral properties of phyllosilicates. Several previous works have studied the effects of only temperature on clay minerals (e.g. Moskowitz and Hargraves, 1984; Gavin and Chevrier, 2010; Daly et al., 2011; Che et al., 2011; Che and Glotch, 2012) and there are some notable differences. In recent thermal alteration studies, Gavin and Chevrier (2010) and Daly et al. (2011) showed that phyllosilicates are stable up to higher temperatures than those reached in our shock experiments. For example, montmorillonite is structurally stable up to \(\sim 700^\circ\text{C}\), nontronite up to \(\sim 650^\circ\text{C}\) (Gavin and Chevrier, 2010), and prehnite and serpentine degrade above \(\sim 600^\circ\text{C}\) and \(\sim 500^\circ\text{C}\), respectively (Daly et al., 2011). Using NIR and MIR spectra, Che et al. (2011) found that dehydration/dehydroxylation occurs at much lower temperatures, i.e. between 300-400\(^\circ\text{C}\) for montmorillonite, nontronite and kaolinite. The fact that our shocked samples show degradation at lower temperatures (average temperature <
~200°C, Table 3-2) suggests the pressure wave propagating through the sample plays a major role in the deformation of the minerals’ structure and that we are observing alteration due to the combination of temperature and shock pressure.

Another possible explanation of the difference in alteration results could be the localization of the temperature in the shocked samples (Fig. 3-8). Even though peak temperatures in our shocked samples reached ~950°C in montmorillonite and 525°C in nontronite, the average temperatures were less than ~200°C (Table 3-2). The temperature gradient was restrained to only part of the sample whereas the pressure wave affected the entire sample (Fig. 3-8). It is very likely that the small amount of sample that was recovered and analyzed from the shock experiments may be a mixture of thermally altered and unaltered material.

3.5.3 Alteration of IR signature

Each shocked sample showed little change in the NIR range (1.0 – 2.5 µm) but very significant change in their MIR spectra (5 – 15 µm, Figs. 3-3, 3-4). Near-infrared spectra have been used in previous studies to identify phyllosilicates on Mars (e.g. Poulet et al., 2005; Bibring, et al., 2006; Bishop et al., 2008; Mustard et al., 2008) and also as a potential proxy for determining the temperature to which a sample has been heated (Gavin and Chevrier, 2010; Fairen et al., 2010; Elsenousy et al., 2011; Daly et al., 2011) while the mid-infrared spectra can help identify secondary phase formation (e.g. Gavin and Chevrier, 2010). Indeed, NIR spectra are more sensitive to water and hydroxyl bonds while MIR spectra are sensitive to (Si,Al)-O bonds in tetrahedral sheets and Si-O-M (M = Fe²⁺, Fe³⁺, Mg²⁺, Al³⁺) in octahedral-tetrahedral sheet pairs (Michalski et al., 2006), which can give a more accurate sense of the state of the general mineralogical structure. Since the shocked samples’ average temperature was relatively
low (< ~200°C), the NIR spectra was not strongly affected, especially with respect to hydration/hydroxyl bands and even the heterogeneous higher peak temperatures prevented most of the samples from being altered. This is in good agreement with previous dehydration/dehydroxylation studies of phyllosilicates (e.g. Che et al., 2011). The significant changes in the MIR spectra, however, illustrate the change in mineralogical structure even with minimal loss of H₂O/OH⁻. Again, when compared to previous heating studies, these alterations occur at much lower temperatures. This is due to the fact that we are observing the effects of both temperature and shock pressure within the sample rather than from temperature alone.

3.6 Implications for Mars

3.6.1 Formation of magnesite

Magnesium carbonate [MgCO₃, magnesite] was identified in our shocked serpentine. Carbonates were first found on Mars in the Nili Fossae region in close proximity to Fe/Mg phyllosilicates (Ehlmann et al., 2008b) and later in the same region in association with olivine and serpentine (Ehlmann et al., 2009). Magnesite is commonly found in igneous and sedimentary rocks and has been known to form in hydrothermal systems as a weathering product of serpentine and peridotite but there has been no work done exploring the possibility of serpentine carbonation via impact processes. Depending on the exact conditions at the time of impact, complete carbonation may not have occurred, leaving some of the serpentine and olivine unaltered. Thus, of the magnesium carbonate deposits observed on Mars, those that are in close association with impact craters may be the result of shock-altered serpentine target rock.
3.6.2 Discrepancy between NIR and thermal IR observations

Phyllosilicates have been identified on Mars by their spectral signature in the near-infrared region (i.e. 1.0-2.5 μm) (Poulet et al., 2005). However, more recent studies of the martian surface, specifically in the Mawrth Vallis and Nili Fossae regions, show a discrepancy between the NIR and thermal IR observations of phyllosilicates. For example, thermal IR observations of Mawrth Vallis failed to identify nontronite (Fe-smectite) (Michalski and Fergason, 2009) while it was clearly identified using NIR spectrometers such as OMEGA and CRISM (e.g. Bishop et al., 2008).

Possible explanations for these discrepancies include (1) the effects of temperature or (2) surface texture, (3) the phyllosilicate deposits could be below the detection limit of Mars Global Surveyor’s Thermal Emission Spectrometer (TES) and Mars Odyssey’s Thermal Emission Imaging System (THEMIS), or (4) the phyllosilicates are poorly crystalline resulting in weak bands at higher wavelengths (Michalski and Fergason, 2009; Michalski et al., 2010). Poorly crystalline phyllosilicates would suggest (1) water-poor conditions at the time of their formation, (2) crystallinity changes due to chemical weathering (e.g. Altheide et al., 2010; Dehouck et al., 2012), or (3) the phyllosilicates experienced shock metamorphism after formation (Michalski et al., 2010). The latter of these scenarios is of particular interest since most phyllosilicates have been identified in highly cratered Noachian terrains. This suggests they were most likely the targets of meteoritic impacts during the Noachian and early Hesperian eras.

We have shown that while the NIR spectral signature of shock-treated phyllosilicates remains for the most part unchanged (Fig. 3-3), the spectra of these minerals changes dramatically at longer wavelengths (Fig. 3-4). If thermal IR spectrometers are indeed observing shocked phyllosilicates, this could explain why phyllosilicates are clearly identified by NIR
spectrometers but TES and THEMIS fail to see them. This discrepancy supports the hypothesis that phyllosilicates in these regions were formed early in Mars’ history and underwent shock metamorphism as a result of meteoritic impacts rather than being formed later by impact-induced hydrothermalism.

3.7 Conclusions

We observed the effects of shock pressure and temperature on the properties of phyllosilicates. The shock pressure wave moved homogeneously through the entire sample while the shock temperature gradient remained relatively localized at the point of contact between the projectile and the sample. Shocked montmorillonite and chlorite showed evidence of amorphization through their CL data; XRD of nontronite showed a decrease in peak intensity but no secondary phases; XRD of kaolinite showed its mineralogical structure was almost completely destroyed due to shock treatment though no secondary phases formed; prehnite seemed the most resistant to shock treatment; XRD data of serpentine showed partial transformation into magnesite.

The near-infrared spectra of each shocked sample did not change much from the original sample, however, the mid-infrared spectra changed significantly. The heterogeneous temperature of the samples during shock experiments implies little change in their hydration state which dominates their NIR spectra while the shock pressure affected the sample homogeneously, destroying or altering the crystalline structure, appearing as a large change in the MIR spectra (and also the CL and Raman spectra). This may explain some of the inconsistencies between NIR and thermal IR observation of phyllosilicates on Mars, especially in the Mawrth Vallis and Nili Fossae regions.
Quartz and magnesite were identified as secondary phases formed from shocked chlorite and serpentine, respectively. The formation of magnesite suggests the possible shock-induced carbonation of serpentine on which there is little to no experimental data. These processes may result in carbonates in association with serpentines that have been previously observed in impact craters on Mars, specifically in the Nili Fossae region.

3.8 Acknowledgements

This study was supported in part by the Space Plasma Laboratory, ISAS, JAXA. We also recognize Drs. Mourad Benamara and Mike Hawkridge of the University of Arkansas’ Nano-Bio Materials Characterization Lab for use of their facilities and technical assistance while obtaining our XRD data. Finally, we thank the reviewers of this manuscript for their constructive comments.

3.9 References


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### 3.10 Supplementary Material

#### SM1. Montmorillonite

![Supplementary Material 3-1](image)

**Supplementary Material 3-1** - XRD of montmorillonite with reference diffractogram code.
SM2. Nontronite

Supplementary Material 3-2 - XRD of nontronite with reference diffractogram code.
Supplementary Material 3-3 - XRD of kaolinite with reference diffractogram code.
Supplementary Material 3-4 - XRD of prehnite with reference diffractogram code.
Supplementary Material 3-5 - XRD of unshocked and shocked chlorite with reference diffractogram codes.
Supplementary Material 3-6 - XRD of unshocked and shocked serpentine with reference diffractogram codes.

$\nu = 4.3 \text{ km/s}$
Supplementary Material 3-7 - CL color images of unshocked and shocked montmorillonite.
Supplementary Material 3-8 - CL color images of unshocked and shocked nontronite, kaolinite, prehnite, chlorite, and serpentine.
Supplementary Material 3-9 - Images from each time step in the Autodyne simulation of shocked montmorillonite.
4 Spectral analysis of Deccan Intrabasaltic bole beds: Implications for Phyllosilicate formation on Mars

4.1 Abstract

To fully understand phyllosilicate formation on Mars, it’s beneficial to study analogs on Earth. One attractive candidate for martian phyllosilicates is the intrabasaltic bole beds (palaeosols) from the Deccan Volcanic Province of India. Eleven samples from the upper-layer red Deccan bole beds and underlying yellow and green Deccan bole beds were analyzed by X-ray diffraction (XRD), near-infrared (NIR; 1.0-2.5 µm) and mid-infrared (MIR; 5-15 µm) reflectance spectroscopy. Analysis of the bole beds indicated that the red boles are composed of a mixture of montmorillonite and hematite, yellow boles contain vermiculite and minor montmorillonite and green boles are composed mainly of nontronite (smectite) and celadonite (mica). While the red, yellow and green samples are all chemically similar to each other and to the underlying original basalt, they are mineralogically different. This suggests transformation from one mineral to the next without ion transfer or loss. In fact, celadonite can transform into smectites (such as montmorillonite), often with vermiculite as an intermediate step. This not only explains the stratigraphy and mineralogy of the Deccan bole beds but may also explain the layered phyllosilicates identified in Mawrth Vallis. The transition observed in the Deccan bole beds (and in Mawth Vallis) suggests an evolution of the alteration process from deuteritic alteration to low-temperature weathering, likely due to changes in temperature, in a closed system (no significant ion transfer) as evidenced by the minerals’ similar chemistry. Thus, the Deccan bole beds are a good analog for the phyllosilicates in Mawrth Vallis and by studying the chemistry, mineralogy and spectral properties of the Deccan bole beds, we can link their formation processes to that of martian phyllosilicates. This will provide a clearer understanding
of the environmental conditions on Mars at the time of the phyllosilicates’ formation and hence during Mars’ earliest history.

4.2 Introduction

Phyllosilicates were first identified on Mars by the Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activite (OMEGA) spectrometer on board Mars Express (Poulet et al., 2005) and later confirmed by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars Reconnaissance Orbiter (MRO) (Bishop et al., 2008a; Mustard et al., 2008). These minerals have been found in the oldest Noachian terrains, such as Meridiani Planum (Wiseman et al., 2008), Mawrth Vallis (Bishop et al., 2008a) and Nili Fossae (Ehlmann et al., 2008), in association with lava flows (Poulet et al., 2005) and in the central peaks and ejecta of impact craters (Mangold et al., 2007). The most abundant phyllosilicates observed so far are smectites such as nontronite (Fe$^{3+}$) or saponite (Mg) and montmorillonite (Al) and vermiculite (Fe$^{2+}$) (Carter et al., 2011), whose exact origins remain unclear. Some studies suggest these phyllosilicates are the result of weathering of basaltic material (Michalski and Noe Dobrea, 2007) while others believe they were formed from surface (Poulet et al., 2005) or subsurface (Ehlmann et al., 2011) hydrothermalism resulting from volcanic activity or meteoritic impacts (Fairen et al., 2010; Schwenzer and Kring, 2009).

In order to better understand phyllosilicate formation on Mars, it is beneficial to study analog materials on Earth. One potential candidate for Martian phyllosilicates is the Intrabasaltic bole beds from the Deccan Volcanic Province of India. These bole beds have been the primary focus of several studies investigating palaeoenvironments (Ghosh et al., 1995; Ghosh et al., 2001; Fürish et al., 2005; Sayyed and Hundekari, 2006; Ghosh et al., 2006; Sheldon and Tabor, 2009) and can give insight into the environmental conditions prevailing during their formation. The
boles’ geochemistry shows they are composed mainly of smectites (Greenberger et al., 2011; Ghosh et al., 2006; Roy et al., 2001) and were formed by the chemical weathering of basalts (Wilkins et al., 1994). While the mineralogy of each bole bed is different from each other and of the underlying basalt from which they formed, their chemistries are very similar. This implies the formation of the bole beds without significant ion transfer. This study investigates the mineralogy and spectral properties of the Deccan bole beds and compares them to those of the phyllosilicates identified in Mawrth Vallis, Mars, in an effort to link terrestrial formation processes with those that occurred on Mars.

4.3 Sample description and analytical techniques

4.3.1 Sample description

The Deccan Volcanic Province (popularly known as Deccan Traps) is one of the largest continental flood basalt plains in the world, covering about 500,000 km² of western and central India (e.g. Ghosh et al., 2006). These basaltic flows are generally tholeiitic in composition (containing plagioclase feldspar, clinopyroxene, iron ore and glass, but with little or no olivine) and exceed 2 km thickness in the western regions (Ghosh et al., 2006). The Deccan Traps are made up of several basaltic lava flows frequently showing the presence of bole beds sandwiched between two successive lava flows which range in thickness from 20-50 cm (Sayyed and Hundekari, 2006) and vary in color of different shades of red, green, brown, purple or grey.

While there is still debate on the origin of these soils, chemical and physical characteristics indicate they are the weathering product of the respective underlying basaltic flow (Ghosh et al., 2006; Roy et al., 2001; Sayyed and Hundekari, 2006; Wilkins et al., 1994). Further supporting this idea is the bole beds’ physical setting in association with the basaltic flows. The bole beds show sharp contact with overlying flows and intermixing with underlying
flows, suggesting they are the weathering product of the underlying basalts and were covered by subsequent flows (see Fig. 1 in Ghosh et al., 2006).

### 4.3.2 Analytical techniques

Samples in this study were taken from red and green bole beds of similar horizons between basaltic flows. Each sample’s color was precisely categorized using Munsell soil color charts (Munsell, 1954). Samples were crushed and sieved into < 63 μm grain size and their mineralogy was analyzed by X-ray diffraction (XRD) at the Wadia Institute of Himalayan Geology, India, with a CuKα anode, a voltage of 45 kV, an intensity of 40 mA and a 0.5° divergence slit. The 2θ range was 4 – 65° with a step size of 0.017° and the time per step was 16.24 seconds.

Fourier Transform Infrared (FT-IR) reflectance spectra were taken of each sample using a Nicolet 6700 Smart Diffuse Spectrometer with dry N₂ purge gas. Near-infrared (NIR) spectra were recorded with an attached CeramOptec optical probe (Gavin and Chevier, 2010) in reflectance mode in the 4,000 – 10,000 cm⁻¹ (1.0 – 2.5 μm range) with 2 cm⁻¹ resolution. Samples were placed in a ceramic tube under a flow of dry N₂ on a hot plate at 150°C for two hours before each spectrum was recorded. The optical probe was inserted into a small hole drilled into the top of the tube and sample’s spectrum was recorded. This ensured the removal of any atmospheric or adsorbed water on the sample. The configuration consisted of a quartz-halogen IR source, a CaF₂ beamsplitter, and a TECP detector. A background spectrum was taken using KBr powder under the same measurement protocol as the samples.

Mid-infrared (MIR) spectra were recorded using the spectrometer without the optical probe under ambient conditions in the range 670 – 2000 cm⁻¹ (5 – 15 μm). For this spectral range, we used an IR source, a KBr beamsplitter, and a DTGS detector. Background spectra
using a gold coated emery tape were taken before each sample’s spectrum was recorded. Each NIR and MIR spectrum was normalized to the maximum value for consistent comparison.

4.4 Results

4.4.1 Color and XRD

The samples were divided into three color categories: red, yellow and green. Each sample’s color was precisely categorized using Munsell soil color charts (Table 4-1) (Munsell, 1954). Red samples ranged from reddish brown 2.5YR 5/4 (e.g., Sample E) to various shades of red 10R 5/8 (e.g., Sample F). Yellow samples were either pale yellow 2.5Y 7/4 (Sample EG) or light olive brown 2.5Y 5/4 (Sample HG). Green samples were pale olive 5Y 6/3 (Sample B) and olive 5Y 5/3 (Sample D). Previous studies suggest that the red samples’ color is due to their iron oxide content and green samples’ color is due to their chlorite content (Ghosh et al., 2006).
Table 4-1 - Munsell soil colors for Deccan samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Munsell Color Index</th>
<th>Color Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.5 YR 4/6</td>
<td>Red</td>
</tr>
<tr>
<td>B</td>
<td>5Y 6/3</td>
<td>Pale olive</td>
</tr>
<tr>
<td>C</td>
<td>2.5 YR 5/6</td>
<td>Red</td>
</tr>
<tr>
<td>D</td>
<td>5Y 5/3</td>
<td>Olive</td>
</tr>
<tr>
<td>E</td>
<td>2.5 YR 5/4</td>
<td>Reddish brown</td>
</tr>
<tr>
<td>EG</td>
<td>2.5Y 7/4</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>F</td>
<td>10R 5/8</td>
<td>Red</td>
</tr>
<tr>
<td>G</td>
<td>10R 4/6</td>
<td>Red</td>
</tr>
<tr>
<td>HG</td>
<td>2.5Y 5/4</td>
<td>Light olive brown</td>
</tr>
<tr>
<td>HR</td>
<td>2.5YR 5/6</td>
<td>Red</td>
</tr>
<tr>
<td>I</td>
<td>2.5 YR 5/6</td>
<td>Red</td>
</tr>
</tbody>
</table>
XRD diffractograms of each sample contained a large peak at 2θ values ~5° (Fig. 4-1), as previously reported by Roy et al. (2001), similar to that of smectites. Red samples showed evidence for the smectite montmorillonite \([\text{Na}_0.3\text{Ca}_0.3\text{Al}_2\text{Mg}_2\text{Si}_4\text{O}_{10}\text{OH}_2\cdot n\text{H}_2\text{O}]\) by the large 001 peak at \(2\theta = 5.7^\circ\) and several others in addition to iron oxides, specifically hematite \([\text{Fe}_2\text{O}_3]\) (Fig. 4-1A). The Table given in Supplementary Materials lists each peak identified for each sample and the mineral associated with those peaks. XRD diffractograms of yellow samples also showed evidence of the presence of montmorillonite along with the \(\text{Fe}^{2+}\)-phyllosilicate vermiculite \([(\text{Mg,Fe}^{2+}_2\text{Al})_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}]\) whose 001 peak was identified at 6.1° (Fig. 4-1B). Vermiculite would explain the samples’ yellow color (Anthony et al., 2001). XRD of green samples suggested a mixture of the \(\text{Fe}^{3+}\)-smectite nontronite \([\text{Na}_0.3\text{Fe}^{3+}_2\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O}]\) and the \(\text{Fe}^{2+}/\text{Fe}^{3+}\) mica celadonite \([\text{K(Mg,Fe}^{2+}_2\text{Al})_3\text{Si}_4\text{O}_{10}(\text{OH})_2]\) and traces of quartz \([\text{SiO}_2]\) (Fig. 4-1C).
Figure 4-1 - X-ray diffraction of Deccan Palaeosols. A) Red Deccan sample; B) Yellow Deccan sample; C) Green Deccan sample. Abbreviations: mont: montmorillonite; hem: hematite; ver: vermiculite; non: nontronite; cld: celadonite; qtz: quartz.
4.4.2 Near-infrared spectroscopy

The NIR spectra were also categorized according to the sample’s general color (i.e., red, green or yellow). All spectra showed bands at 1.4 and 1.9 µm (Fig. 4-2) similar to those in phyllosilicate minerals which represent the OH stretching overtones of both structural OH and molecular H₂O, and the H-O-H stretching of molecular water most commonly observed as interlayer water, respectively (Bishop et al., 2008b; Bishop et al., 2002a; Bishop et al., 2002b). This supports previous studies that the bole beds are mainly composed of phyllosilicates (Ghosh et al., 2006; Roy et al., 2001). Every sample also showed bands in the 2.2 – 2.4 µm range, representing the cation-hydroxyl (OH) bond. Table 4-2 gives the exact positions of the bands identified in each sample’s NIR spectrum. All red samples showed a band at ~2.21 µm, representing the Al-OH bond, and some showed an additional weak band or shoulder at 2.25 µm or 2.29 µm indicating small amounts of Mg-OH or Fe³⁺-OH, respectively (Bishop et al., 2008b). Green and yellow samples showed a band at ~1.05 and ~2.37 µm, due to the presence of Fe²⁺-OH, while a band at 2.25 µm suggested (Al/Mg)Fe³⁺-OH, and a band at 2.30 µm suggested Fe³⁺Fe³⁺-OH (Bishop et al., 2008b).
Figure 4-2 - Near-infrared (1.0 – 2.5 µm) reflectance spectra of Deccan Palaeosols. Spectra have been normalized and offset for clarity.
Table 4-2 - Near-infrared band positions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band Position (microns)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Red</td>
</tr>
<tr>
<td>A</td>
<td>1.42 1.92 2.22 2.25*</td>
</tr>
<tr>
<td>C</td>
<td>1.42 1.92 2.24 ----</td>
</tr>
<tr>
<td>E</td>
<td>1.43 1.92 2.23 2.30*</td>
</tr>
<tr>
<td>F</td>
<td>1.43 1.92 2.23 2.29</td>
</tr>
<tr>
<td>G</td>
<td>1.42 1.93 2.21 ----</td>
</tr>
<tr>
<td>HR</td>
<td>1.42 1.92 2.24 2.29</td>
</tr>
<tr>
<td>I</td>
<td>1.42 1.92 2.21 ----</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
</tr>
<tr>
<td>EG</td>
<td>1.07 1.42 1.92 2.25* 2.30 2.37</td>
</tr>
<tr>
<td>HG</td>
<td>1.06 1.42 1.92 2.24 2.29 ----</td>
</tr>
<tr>
<td></td>
<td>Green</td>
</tr>
<tr>
<td>B</td>
<td>1.04 1.43 1.92 2.25 2.31 2.36</td>
</tr>
<tr>
<td>D</td>
<td>1.04 1.43 1.92 2.26 2.30 2.36</td>
</tr>
</tbody>
</table>

*shoulder
4.4.3 Mid-infrared spectroscopy

MIR spectra were also categorized according to the sample’s general color. All samples contained bands at 6.1 and ~8.5 µm (Fig. 4-3) representative of H₂O bending and SiO₂, respectively (Bishop et al., 2008b), and are similar to MIR spectra of minerals such as nontronite, montmorillonite, and celadonite (Bishop et al., 2008b; Gavin and Chevrier, 2010). Green samples contained additional bands at 5.4, 5.6, 7.9, 10.2 (OH bending), 12.5 (MgFe³⁺OH) and 14.5 µm (Mg₃OH) (Table 4-3) as well as a peak at ~9.5 µm indicating the Si(Al,Fe)O₄ vibrations (Bishop et al., 2008b).
Figure 4-3 - Mid-infrared (5 – 15 µm) reflectance spectra of Deccan Palaeosols. Spectra have been normalized and offset for clarity.
Table 4-3 - Mid-infrared band positions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band Position (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Red</em></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>5.53* 6.12 8.51</td>
</tr>
<tr>
<td>C</td>
<td>---- 6.11 8.48</td>
</tr>
<tr>
<td>E</td>
<td>---- 6.12 8.68</td>
</tr>
<tr>
<td>F</td>
<td>---- 6.13 8.38</td>
</tr>
<tr>
<td>G</td>
<td>---- 6.11 8.48</td>
</tr>
<tr>
<td>HR</td>
<td>---- 6.12 8.51</td>
</tr>
<tr>
<td>I</td>
<td>5.53* 6.12 8.52</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Yellow</em></td>
<td></td>
</tr>
<tr>
<td>EG</td>
<td>6.12 8.46</td>
</tr>
<tr>
<td>HG</td>
<td>6.12 8.49</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Green</em></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5.36 5.62 6.14 7.84 8.65 10.19 12.52 14.53</td>
</tr>
</tbody>
</table>

*shoulder
4.5 Discussion

4.5.1 Red bole samples

Our XRD results indicated the presence of phyllosilicates in the red bole samples by the large 001 peak at low 2θ values (Fig. 4-1). This confirmed previous studies (Ghosh et al, 2006; Roy et al., 2001) identifying the Al-smectite montmorillonite in the red boles. NIR spectra (Fig. 4-2) confirmed XRD data of the presence of montmorillonite by the absorbance bands at 1.4, 1.9 and 2.21 µm. Figure 4-4A shows the NIR spectrum of a red Deccan sample compared to that of montmorillonite. The 1.4 and 2.21 µm bands are clearly seen in both the red bole sample and the montmorillonite spectra. A band at ~2.30 µm in some of the red samples suggests the montmorillonite may have some Fe$^{3+}$ substitution for Al in its mineralogical structure (Bishop et al. 2002a,b). These Fe$^{3+}$ bands are not likely representative of the hematite indicated by XRD since hematite has no spectral signature in this range. Hematite, along with most other iron oxides, is more easily identified by its MIR spectrum (Gavin and Chevrier, 2010). Yet, hematite was not evident in the MIR spectrum of the red bole samples (Fig. 4-5A). This may be due to the fact that there may be enough hematite in the sample to give it the red color but not enough, relative to the montmorillonite, to show a strong signal in the MIR range.
Figure 4-4 - Near-infrared (1.0 – 2.5 µm) reflectance spectra of Deccan samples compared to reference spectra and spectra from Mawrth Vallis, Mars. A) Red Deccan sample compared to montmorillonite (Gavin and Chevrier, 2010), hematite (Clark et al., 2007) and the top Al-phyllosilicate layer in Mawrth Vallis (Bishop et al., 2008a); B) Yellow Deccan sample compared to vermiculite (Clark et al., 2007) and the middle Fe$^{2+}$-phyllosilicate layer in Mawrth Vallis (Bishop et al., 2008a); C) Green Deccan sample compared to celadonite (Bishop et al., 2008b), nontronite (Gavin and Chevrier, 2010) and the lower Fe$^{3+}$ phyllosilicate layer in Mawrth Vallis (Poulet and Carter, 2011).
Figure 4-5 - Mid-infrared (5 – 15 µm) reflectance spectra of Deccan samples compared to reference spectra.  A) Red Deccan sample compared to montmorillonite (Gavin and Chevrier, 2010) and hematite (Clark et al., 2007); B) Yellow Deccan sample compared to vermiculite (Clark et al., 2007); C) Green Deccan sample compared to celadonite (Bishop et al., 2008b), nontronite (Gavin and Chevrier, 2010).
4.5.2 Yellow bole samples

XRD of yellow bole samples identified the Fe$^{2+}$-phyllosilicate vermiculite, which explains the samples’ yellow color, as well as minor montmorillonite (Fig. 4-1B). The NIR spectra of the yellow samples confirmed the presence of Fe$^{2+}$-OH by the bands at ~1.07 and 2.37 µm (Fig. 4-2). We compared the NIR spectra of the yellow bole samples to that of vermiculite (Clark et al., 2007) (Fig. 4-4B). Both spectra clearly display hydration bands at 1.4 and 1.9 µm as well as Fe$^{2+}$-OH bands at ~1.07 and 2.37 µm. However, the Deccan sample’s spectrum had a more positive slope between 1.0 – 2.0 µm than the vermiculite spectrum and vermiculite’s spectrum had a band at 1.1 µm while the Deccan samples’ spectrum had a band closer to 1.0 µm. MIR spectra of yellow boles were also compared to that of vermiculite (Fig. 4-5B). The MIR spectra of the yellow Deccan samples and vermiculite contained large bands at 6.1 and 8.5 µm and their overall shape was very similar. However, those two bands are common to the MIR spectra of most smectites (e.g. Bishop et al., 2008b) and no other bands were identified in either spectrum to associate the two minerals. Nevertheless, XRD and NIR data present conclusive evidence of the presence of vermiculite in the yellow bole samples.

4.5.3 Green bole samples

The XRD of the green bole samples indicated the presence of the Fe$^{3+}$-smectite nontronite and the Fe$^{2+}$/Fe$^{3+}$ mica celadonite (Fig. 4-1C), both of which would explain the green color of the samples (Anthony et al., 2001). NIR spectra of the green boles supported this data by the presence of both Fe$^{2+}$-OH and Fe$^{3+}$-OH bands (Fig. 4-2). However, the NIR spectra of the green Deccan samples were more similar to celadonite (Bishop et al., 2008b) than to nontronite (Gavin and Chevrier, 2010) (Fig. 4-4C). The overall shape of the green bole’s spectrum was very similar to celadonite with a slight positive slope between 1.0 and ~2.2 µm and very shallow
hydration bands at 1.4 and 1.9 µm. Both spectra displayed Fe$^{2+}$-OH bands at ~1.0 and 2.36 µm, a Fe$^{3+}$-OH band at 2.31 µm, and a shallow Mg-OH band at 2.25 µm. Overall, the green bole sample’s spectrum more closely resembled that of celadonite, suggesting celadonite is the main component of the sample, but also contained evidence of nontronite.

We also compared the MIR spectra of the green bole samples to that of celadonite (Bishop et al., 2008b) and nontronite (Gavin and Chevrier, 2010) (Fig. 4-5C). The overall spectral shape more closely resembled nontronite but several features suggested the presence of celadonite as well. Bands at 5.4, 12.5 and 14.5 µm were common to both the green bole sample and celadonite spectra while the large band at 6.1 µm and the peak at 9.5 µm are similar to the nontronite spectrum. Also, bands at 5.6 and 7.8 µm in the green bole sample were matched to shoulders at these positions in the celadonite spectrum. This confirms NIR and XRD data that the green boles are mostly composed mostly of celadonite mixed with some nontronite. This would explain their green color and the presence of both Fe$^{2+}$ and Fe$^{3+}$ bands in the NIR spectra.

4.5.4 Mineralogy and possible formation processes

Previous studies have indicated that the bole beds are the weathering product of their respective underlying basalt (Ghosh et al., 2006; Roy et al., 2001; Wilkins et al., 1994). Although all three bole beds exhibit similar elemental compositions (Ghosh et al., 2006), they have very different mineralogy. While the yellow and green samples have been previously grouped together due to their common Fe$^{2+}$ content compared to higher Fe$^{3+}$ in the red bole beds (Ghosh et al., 2006), elemental analyses shows that the yellow samples are in fact more similar to the red samples than either is to the green samples (Fig. 4-6). Along with their stratigraphic positions relative to each other, this suggests a possible transformation of the basalt into the celadonite/nontronite green bole beds most likely via deuteric (low water-rock ratio) alteration.
and/or low-temperature hydrothermal alteration (Wise and Eugster, 1964; Scheidegger and Stakes, 1977; Seyfried et al., 1978), then further weathering of the green bole beds into the montmorillonite/hematite red bole beds. These transitions have been observed and studied both in nature and in the lab (Reid et al., 1988; Robert, 1973). In this pathway, the vermiculite-dominated yellow bole bed is a metastable intermediate phase during the transformation of celadonite into tetrahedral and octahedral smectites (Robert, 1973; Scott et al., 1960; Scott and Reed, 1962; Reid et al., 1988). These experimental studies have shown that celadonite transforms into vermiculite by the removal of interlayer K\(^+\) as indicated by chemical analysis (Ghosh et al., 2006). Since each Deccan sample’s Fe\(^{2+}\)/total Fe ratios are relatively similar, a change in oxidation state is probably not responsible for the minerals’ evolution. Moreover, the Deccan bole beds’ similar chemical composition (Fig. 4-6; Ghosh et al., 2006) but different mineralogy implies very limited ion transfer or loss. Most probably this mineralogical pathway results from the evolution of the alteration process from deuteric alteration to low-temperature weathering, possibly due to changes in the rock-water system temperature. In this case, complete mineral transformations occur without significant chemical changes.
Figure 4-6 - Ternary diagram comparing the chemical compositions of the red, yellow and green bole beds and their respective underlying basalts. Open circles: red bole beds; open triangles: yellow bole beds; open diamonds: green bole beds; solid squares: underlying basalts. Chemical analysis from Ghosh et al. (2006).
4.6 Implications for Mars

A very specific stratigraphic sequence of phyllosilicates has been found in the Mawrth Vallis region (Loizeau et al., 2007; Bishop et al., 2008a; Wray et al., 2008; McKeown et al., 2009; Loizeau et al., 2010). The topmost layer has been identified as an Al-bearing phyllosilicate, most likely montmorillonite and/or kaolinite, with evidence of iron oxides also present and the bottom layer has been identified as a Fe/Mg-phyllosilicate unit, most likely nontronite (Loizeau et al., 2007). More recent higher resolution spectra of the region have revealed a ferrous iron (Fe$^{2+}$) layer between the Al-bearing and the Fe/Mg-bearing units, characterized by a strong positive slope between 1.0 – 2.0 µm (Bishop et al., 2008a).

A similar stratigraphy of layers containing Al-phyllosilicates and iron oxides overlying layers with Fe$^{3+}$-phyllosilicates with a Fe$^{2+}$/Fe$^{3+}$ layer between them are observed in the Deccan bole beds (Ghosh et al., 2006). Indeed, comparison of the NIR spectra from Mawrth Vallis to the Deccan bole beds shows several similarities (Fig. 4-4). Our red Deccan sample contains the characteristic 2.21 µm band indicating the presence of Al-OH, which is similar to the spectrum of montmorillonite and the top layer in Mawrth Vallis (Fig. 4-4A). The ferrous iron-bearing middle layer in Mawrth Vallis is similar to both our spectrum of the yellow Deccan bole bed and vermiculite (Fig. 4-4B). All three spectra have hydration bands at 1.4 and 1.9 µm, as well as Fe$^{3+}$Fe$^{3+}$-OH and Fe$^{2+}$ bands at ~2.30 and 2.39 µm, respectively. Our yellow Deccan sample also shows a very strong positive slope between 1.0 – 2.1 µm similar to the spectrum from Mawrth Vallis. Several minerals have been proposed for the composition of this ferrous iron layer in Mawrth Vallis: olivine, ferrous chlorites such as chamosite, or ferrous micas such as celadonite or glauconite (McKeown et al., 2009; Bishop et al., 2008a). We suggest vermiculite possibly mixed with celadonite as another possible candidate for the Fe$^{2+}$ layer observed in
Mawrth Vallis. Finally, the Fe$^{3+}$-phyllosilicate bottom layer in Mawrth Vallis shares shallow hydration bands at 1.4 and 1.9 µm with our green Deccan bole sample and celadonite (Fig. 4-4C) although it is lacking the strong positive slope between 1.0 – 2.0 µm and has been identified as essentially nontronite (Bishop et al. 2008a). Alternatively, phyllosilicate mixing models have shown that the small band at 2.35 µm in the spectrum from Mawrth Vallis only appears in spectra that include celadonite (Poulet and Carter, 2011). Therefore, the difference between our green bole bed and the bottom layer in Mawrth Vallis might result from a difference in relative amounts of celadonite and nontronite possibly due to different chemistries of the original basalt.

Several pathways have been previously proposed for the formation of phyllosilicates on Mars, especially in Mawrth Vallis. The Fe/Mg-phyllosilicate layer, likely composed of nontronite (± celadonite), formed by aqueous alteration of basalt in a neutral to alkaline environment (Bishop et al., 2008a; Chevrier et al., 2007). In contrast, Al-bearing phyllosilicates such as kaolinite or montmorillonite can appear in more acidic conditions (Altheide et al., 2009). This mineralogical change has often been attributed to changes of the surface conditions possibly associated to the acidification of the surface of Mars (Bishop et al., 2008a). On the other hand, the transition from Fe$^{3+}$-bearing phyllosilicates in the lower stratigraphic layers to the Fe$^{2+}$-bearing minerals in the middle layers to the Fe$^{3+}$-rich minerals associated with montmorillonite in the upper layers also suggests a change in oxidation conditions. But our results on the bole bed palaeosols suggest an alternative pathway in which the transition of phyllosilicate chemistry is not necessarily due to changes in acidity or oxidation, but rather due to the evolution of the alteration conditions from deuteric alteration to low-temperature weathering. In the case of the Deccan bole beds, the very limited chemical changes suggest that this transition was mostly due to a decrease in temperature. Without detailed chemical compositions, we cannot definitively
conclude that a single process or mineralogical transformation is responsible for the observations in Mawrth Vallis. For example, the presence of kaolinite still suggests that weathering has been more extensive and resulted in some form of ion loss.

4.7 Conclusions

Eleven samples from the Intrabasaltic bole beds (palaeosols) from the Deccan Traps of India were analyzed using XRD and near- and mid-infrared spectroscopy. XRD analysis showed the red boles contained montmorillonite (smectite) and hematite (iron oxide). NIR and MIR spectra of red samples resembled that of montmorillonite. XRD of yellow boles showed the presence of the Fe$^{2+}$ phyllosilicate vermiculite. NIR spectra of yellow boles contained bands indicative of phyllosilicates with Fe$^{2+}$ being the prominent cation supporting the XRD data. XRD of the green bole samples showed the presence of the Fe$^{2+}$/Fe$^{3+}$ mica celadonite and the Fe$^{3+}$ smectite nontronite, both of which would explain the samples’ green color. NIR spectra of the green sample showed strongest similarities to that of celadonite while the MIR spectra showed similarities to celadonite and nontronite, suggesting a celadonite-dominated mixture of the two minerals. We interpret the evolution of the bole beds by the transformation of celadonite resulting from deuteric alteration of the basalt into vermiculite then into smectites. This complete mineralogical transformation occurs with very minor chemical changes (loss of potassium between the green and yellow/red bole beds).

The stratigraphy of the Deccan bole beds presents similarities to the phyllosilicates identified in Mawrth Vallis from Mg,Fe smectite to Al-dominated smectite with an intermediate Fe$^{2+}$ component. From our results we suggest that the evolution of the mineral paragenesis in Mawrth Vallis may be the result of a shift in the formation process from deuteric alteration to low-temperature weathering with limited ion loss. Therefore, important mineralogical changes
can occur without significant ionic fractionation, suggesting only limited amounts of water during the alteration process.

4.8 Acknowledgements

The authors would like to thank the Director of the WIHG for providing the XRD data of our samples. We also thank Janice Bishop and Francois Poulet for providing the spectra from Mawrth Vallis, Mars, for comparison with our spectra. We are also grateful to the reviewers for their constructive comments which greatly improved this manuscript.

4.9 References


4.10 Supplementary Material

Supplementary Material 4-1 - XRD peaks for Deccan samples.

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5 Conclusions and Future Work

We have experimentally determined the effects of high temperatures and shock pressures and temperatures on the properties of phyllosilicates relevant to the surface of Mars. Our heating experiments showed that phyllosilicates will completely transform into secondary phases upon heating to high temperatures (~1100°C) such as those reached upon contact with a lava flow. We determined that can use the NIR spectra of heated phyllosilicates as a thermometer to estimate the temperature to which phyllosilicates on Mars have been heated and thus determine the degree of alteration they have undergone. We demonstrated that phyllosilicates will succumb to structural deformation or even collapse due to shock pressure similar to those reached during a meteorite impact. However, secondary phases do not form at such low pressures except in shocked chlorite (in which quartz formed) and shocked serpentine (in which magnesite formed).

In investigating the effects of temperature and pressure on the properties of phyllosilicates, we provided a means of estimating the temperature to which phyllosilicates were heated and altered. We also provided a mechanism to determine whether phyllosilicates in association with impact craters existed pre-impact or were formed by post-impact hydrothermal processes. Our spectral analysis of impacted phyllosilicates provided a possible explanation for the discrepancies between near-infrared and mid-/thermal-infrared observations of phyllosilicates on Mars, especially those in and around impact craters. We demonstrated a possible explanation of the carbonate/serpentine observations in craters in Nili Fossae and showed evidence of the alteration history of Mawrth Vallis from mineral transformation.

Future work includes further analysis of other heating experiments which include kaolinite, prehnite, chlorite, serpentine and saponite (Mg-rich phyllosilicate). These samples’ were heated and their NIR and MIR spectra recorded following the same protocol as described in
Chapter 2. However, XRD and ESEM analysis is needed to determine which secondary phases were formed. We would also like to conduct more impact experiments in which the samples are impacted with higher projectile velocities. This will allow us to determine the effects of higher shock pressures and temperatures on the structure of the phyllosilicates and if secondary phases can result from such shock treatment. Additionally, we will further analyze the shocked serpentine to better understand the processes that took place to form carbonate in our shocked serpentine samples.

Finally, we will compare our experimental data to that returned by the Mars Science Laboratory (MSL) rover Curiosity which will be landing in Gale Crater in August of 2012. Not only will Curiosity be the first rover to investigate phyllosilicates on Mars, it will also be analyzing these minerals with its XRD/XRF instrument called ChemMin. This will be the first in situ XRD study of phyllosilicates on Mars allowing us to delve deeper into Mars’ past and better understand the environment during the time of phyllosilicate formation.

The presence of phyllosilicates on Mars suggests a time period in the planet’s history of warmer, wetter surface conditions that may have been suitable to the evolution of life. By studying the processes that occurred to alter phyllosilicates early in Mars’ history, we are investigating a time in which Mars may have harbored life. By understanding the surface conditions and mineralogical formation and evolution during this era, we move closer to understanding the kind of environment that dominated early Mars and thus the environment that may have cradled the development of life elsewhere in our universe. This consequently gives mankind a “second data point” in the quest for understanding the origins of life on Earth.
Thermal alteration of nontronite and montmorillonite: Implications for the martian surface
Patricia Gavin *, Vincent Chevrier

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Spectroscopy

A B S T R A C T
To test the effects of meteorite impacts on martian phyllosilicate deposits, we heated two smectites (nontronite and montmorillonite) to temperatures ranging from 350 °C to 1150 °C for durations of 6–24 h in two different atmospheres, under air and a steady flow of CO₂. Samples were analyzed using X-ray diffractometry (XRD) and near-infrared (NIR) and mid-infrared (MIR) reflectance spectrometry. Interlayer water was lost after heating to temperatures of ~400 °C. Between 400 °C and 700 °C, nontronite converted to an intermediary phase which preserved the XRD pattern of unretrogressed nontronite with the exception of the 0.672 peak. Nanocrystalline high-temperature phases formed for both smectites at temperatures between 700 °C and 1000 °C. Finally, after being heated to temperatures above ~1100 °C, the samples melted and recrystallized into secondary phases. Secondary high-temperature phases included stillimanite and cristobalite for both smectites plus hematite for nontronite. NIR and MIR reflectance spectra significantly evolved with increasing temperature. NIR spectra of smectites showed that 1.4 and 1.9 μm bands decrease in intensity and disappear above 700 °C. Similarly, the 2.2–2.3 μm metal–OH band showed a decrease in intensity as well as an overall shift towards lower wavelengths (for nontronite) due to the thermal resistance of the Al–OH bond compared to the Fe–OH bond. NIR spectra of montmorillonite showed a gradual increase in band depth up to temperatures between 500 °C and 600 °C, then decreased with increasing temperature. In the MIR spectra of samples heated to temperatures above ~1100 °C, newly formed bands confirmed the secondary phases identified by XRD. Similarities between the NIR spectra of our heated samples and the phyllosilicates in some martian craters imply that these phyllosilicates were altered by the impact-generated heat and thus were not formed post-impact. In addition, NIR reflectance spectra provide a proxy for shock temperatures of smectites up to 700 °C while MIR is optimum for identification of high-temperature phases of smectites above 700 °C.

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1. Introduction
Phyllosilicates were first discovered by the Mars Express Observeratoire pour la Mineralogie, l’Eau, les Glaces et l’Activité (OMEGA; Poulet et al., 2005), and then confirmed by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard Mars Reconnaissance Orbiter (MRO; Bishop et al., 2008a; Mustard et al., 2008). Phyllosilicates have been detected in three major regions: Meridiani Planum (Wiseman et al., 2008), Meridian Vallis (Bishop et al., 2008a; Laasouf et al., 2007); Michalski and Nee Dobrea, 2007; Wray et al., 2008) and Nil Fossae (Ehlmann et al., 2008; Mangold et al., 2007; Mustard et al., 2007), as well as in several impact craters in the southern hemisphere (Mangold et al., 2007; Poulet et al., 2005). All these regions are dated to the Noachian era, suggesting a specific environment potentially different from the present-day cold and dry Mars (Bibring et al., 2006). The most abundant phases observed so far are smectites: Mg–smectite, nontronite (Fe²⁺–smectite), and montmorillonite (Al–smectite; Poulet et al., 2005). Much less abundant are kaolinite, chlorite, serpentine and mica phases such as muscovite or illite and eventually some Fe³⁺–phyllosilicates (Bishop et al., 2008a; Ehlmann et al., 2009; Mustard et al., 2008; Poulet et al., 2008a). The origin and exact formation processes of the phyllosilicate minerals are still a topic of debate. Some have suggested sedimentary origins (Michalski and Nee Dobrea, 2007) as a result of weathering of basaltic materials and thus would hold clues to the conditions reigning during the Noachian era (Chevrier et al., 2007). However, other phyllosilicate minerals could have formed by hydrothermal systems related to volcanic activity (Poulet et al., 2005) or to impact craters (Talan et al., 2009; Schoniger and Kling, 2009). Indeed, phyllosilicates have been found in regions surrounded by lava flows (Poulet et al., 2005) and also in the ejecta of small impact craters (Mangold et al., 2007). Alternatively, phyllosilicates in impact craters may be simple ejects of former layers covered by more recent deposits. If, however, hydrothermal processes caused by impacts formed the
phyllosilicates detected on Mars, those phyllosilicates may not be as old as previously thought (Faïnèn et al., 2009). Although impacts were most frequent on Mars during the Noachian era, they have continued throughout Mars’ history and possibly have been forming and altering phyllosilicates more recently. Such results would have prime importance for the evolution of geochemical conditions, which could have remained locally neutral to alkaline for longer timescales than sulfate deposits and acidic conditions suggest (Bibring et al., 2006; Chevrier et al., 2007).

For these reasons, we investigated the effect of thermal treatment on the mineralogical properties of Mars-relevant phyllosilicates. High temperatures may have been generated by volcanism and/or meteoritic impact. Previous studies have indicated that heated and/or shocked nontronite may be a source for the red dust on the surface of Mars because of its magnetic properties and color (Boslough et al., 1986; Weldon et al., 1982). In this study, we focus on the infrared properties of phyllosilicates, considering their importance in planetary surface analyses. Previous studies on the infrared properties of some heated smectites have been performed (Milliken and Mustard, 2007) where the H2O band depths were related to the water content of the martian soil.

Several studies have been done on thermal alteration of phyllosilicates’ structure. Mosbauer studies of heated nontronite showed that it dissociates into hematite at temperatures above 600 °C (Heller-Kallai and Rozenson, 1980; MacKenzie and Rogers, 1977). Spectral analysis of the 3.0 μm band, attributed to interlayer water, showed that this band has completely disappeared after being heated to 600 °C, indicating a collapse of the nontronite’s layered structure (Karaksisidès et al., 2000). Madejová et al. (2000) studied the MIR spectra of heated montmorillonites and found that the mineral’s structure persisted through temperatures of up to 400 °C. Upon heating to 600–700 °C, the formation of a new band at 12.5 μm and the absence of the Al-O-Si absorption band were attributed to the partial destruction of the mineral’s structure (Madejová et al., 2000). XRD and IR spectroscopy studies done by Murad et al. (2002) show that montmorillonite’s structure breaks down between temperatures of 530 and 850 °C and that all IR bands have disappeared by 900 °C. Other works on heated montmorillonite showed that the Fe-OH-Al and Mg-OH-Al absorption bands disappeared completely at 600 °C, and the Al-OH–Al absorption band disappeared at 700 °C, indicating the destruction of the montmorillonite’s structure (Heller-Kallai and Rozenson, 1980). This study also showed that nontronite destabilizes at lower temperatures than montmorillonite.

In this study, we investigated the evolution of the NIR and MIR spectra of nontronite and montmorillonite with increasing temperature, in conjunction with XRD and microscopical analyses. This study focused on the water content (both bound and interlayer), structural changes, and transformations into high-temperature secondary phases. We also tested the effect of the atmospheric composition on the resulting paragenesis. We then applied our results to the spectra of clay minerals observed on Mars to determine whether those minerals have undergone thermal alteration.

2. Methods

Our experiments focused on two smectites: a Ca2Al–nontronite from Cheney, WA (Ward’s #4605108) and a montmorillonite from Panther Creek, CO (Ward’s #4606438). From XRF analysis (Altheide and Chevrier, personal communication), we determined the formulae of our smectites – nontronite: (Ca2.05Na0.0,0K0.05)[Fe2+3Al5O2(OH)2]-H2O; montmorillonite: (Na2.25K0.84Ca0.05)[Al3.5Si2.5O10(OH)2]-H2O. X-ray diffraction and ESEM-EDAX analyses of untreated samples showed that both contain traces of quartz and that the nontronite contained anal.

tase TiO2 (total Ti content usually around 2 wt.%). The samples were ground and sieved until their grain size was under 63 μm, mostly to increase the overall surface area and thus the kinetics of the reactions.

2.1. Experimental protocol

One-gram samples of each smectite were placed in the center of a ceramic heating tube and then in a Lindberg high-temperature tube oven. The oven was then turned on and took about an hour to reach the desired temperature. The samples were heated to temperatures ranging from ~350 °C to 1150 °C for durations from 4 to 24 h (Table 1 and 2) in air as well as under a steady flow of CO2 to more closely simulate the early martian atmosphere. The selected temperature range was used to simulate both the temperatures reached in a terrestrial lava flow (Flynn and Mouginis-Mark, 1994) and numerical modeling of impact-induced hydrothermal systems (Barnhart et al., 2010; Abramov and Kring, 2005; Rathburn and Squyres, 2002). After heating, the ovens were allowed to cool overnight and the samples were removed and weighed. Samples that had been heated under CO2 remained under the gas flow until they had completely cooled. After weighing, the samples were placed into small (~2 oz) plastic tubes until they were analyzed.

2.2. Analytical techniques

After each experiment, the samples’ color changes were cataloged using Munsell soil color charts (Munsell, 1954), which are used to precisely describe the color of a soil sample, using the same common reference. The color index used by the charts uses three components: hue, value and chroma. The hue term describes the sample’s color on the color wheel: Y: yellow, R: red, G: green, B: blue, YR: yellow red, RY: red yellow). The value component represents the lightness/darkness of the color. Pure white has a value of 10 and pure black has a value of 0. Finally, the chroma component describes the intensity of a color. A low chroma number means the color is pale or washed out whereas a high chroma means the color is vivid or saturated. These three components are noted by the hue first, then value, then chroma, with the value and chroma separated by a slash (/; see Tables 1 and 2).

Samples’ mineralogy was analyzed by X-ray diffraction (XRD) using a Philips PW 1830 X-ray powder diffractometer with a Cu Ka cathode, a voltage of 45 kV, an intensity of 40 mA and a 0.25° divergence slit. The 2θ range was 5–80° with a step size of 0.02° and the time per step was 13 s resulting in a total analytical time of 13 h 45 min per sample. The powdered samples were spread onto a piece of two-sided tape and placed on a glass slide for analysis.

ESEM observations were performed using a Philips XL 30 ESEM with a beam intensity of 10 kV and SUTW sapphire detector coupled with an EDAX-EDX analytical system for semi-quantitative chemical analysis.

Fourier transform infrared (FT-IR) reflectance spectra were taken using a Nicolet 6700 Smart Diffuse spectrometer. Near-infrared (NIR) spectra were recorded with attached CeramOptec optical probe. N2 purge gas was run through the spectrometer for about 2 h before each spectrum was recorded to remove atmospheric gases (H2O and CO2). Samples were placed into a ceramic tube also under a flow of N2 gas, and then placed on a hotplate at 150 °C for 2 h, prior to spectral acquisition. The optical probe was inserted into a small hole drilled into the top of the tube and the sample’s spectrum was recorded (Fig. 1). This allowed for the removal of any adsorbed water from the sample that may have accumulated during cooling in the oven and further storage and transfer to the FT-IR. NIR spectra were recorded in reflectance mode in the range of 4000–10,000 cm−1 (1.0–2.5 μm, optimum
Table 1

Conditions of heating experiments of nontronite samples.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Atmosphere</th>
<th>Mass loss (%)</th>
<th>Munsell color</th>
<th>Color description</th>
</tr>
</thead>
<tbody>
<tr>
<td>395</td>
<td>24</td>
<td>CO₂</td>
<td>22</td>
<td>7.5YR 4/6</td>
<td>Dark yellowish brown</td>
</tr>
<tr>
<td>400</td>
<td>24</td>
<td>CO₂</td>
<td>25</td>
<td>7.5YR 3/4</td>
<td>Dark brown</td>
</tr>
<tr>
<td>405</td>
<td>24</td>
<td>CO₂</td>
<td>22</td>
<td>2.5YR 3/6</td>
<td>Light brown</td>
</tr>
<tr>
<td>409</td>
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<td>CO₂</td>
<td>22</td>
<td>7.5YR 4/6</td>
<td>Dark yellowish brown</td>
</tr>
<tr>
<td>475</td>
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<td>CO₂</td>
<td>20</td>
<td>7.5YR 4/4</td>
<td>Dark brown</td>
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<td>478</td>
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<td>Dark red brown</td>
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<tr>
<td>600</td>
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<td>22</td>
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<tr>
<td>630</td>
<td>24</td>
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<td>2.5YR 3/6</td>
<td>Light brown</td>
</tr>
<tr>
<td>690</td>
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<td>CO₂</td>
<td>22</td>
<td>7.5YR 4/6</td>
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<tr>
<td>725</td>
<td>24</td>
<td>Air</td>
<td>22</td>
<td>7.5YR 3/4</td>
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</tr>
<tr>
<td>730</td>
<td>24</td>
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<tr>
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<tr>
<td>805</td>
<td>6</td>
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<tr>
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<tr>
<td>875</td>
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<td>CO₂</td>
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</tr>
<tr>
<td>880</td>
<td>6</td>
<td>Air</td>
<td>21</td>
<td>7.5YR 4/6</td>
<td>Yellowish red</td>
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<td>Air</td>
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<td>n.d.</td>
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<tr>
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<td>24</td>
<td>Air</td>
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<tr>
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<td>Air</td>
<td>26</td>
<td>n.d.</td>
<td>–</td>
</tr>
<tr>
<td>1130</td>
<td>4</td>
<td>Air</td>
<td>28</td>
<td>10R 3/3</td>
<td>Dark red</td>
</tr>
<tr>
<td>1130</td>
<td>6</td>
<td>Air</td>
<td>22</td>
<td>10R 2.5/2</td>
<td>Very dark red</td>
</tr>
</tbody>
</table>

* Not determined.

Table 2

Conditions of heated experiments of montmorillonite samples. Data for samples marked with (−) were used with permission from Dan Ostrowski, Arkansas Center for Space and Planetary Sciences (Ostrowski et al., 2010).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Atmosphere</th>
<th>Mass loss (%)</th>
<th>Munsell color</th>
<th>Color description</th>
</tr>
</thead>
<tbody>
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<td>300</td>
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<td>n.d.*</td>
<td>n.d.</td>
<td>GLEY1 7/N</td>
<td>Gray</td>
</tr>
<tr>
<td>400</td>
<td>24</td>
<td>n.d.*</td>
<td>n.d.</td>
<td>GLEY1 7/N</td>
<td>Gray</td>
</tr>
<tr>
<td>500</td>
<td>24</td>
<td>n.d.*</td>
<td>n.d.</td>
<td>GLEY1 7/N</td>
<td>Gray</td>
</tr>
<tr>
<td>600</td>
<td>24</td>
<td>n.d.*</td>
<td>n.d.</td>
<td>GLEY1 7/N</td>
<td>Gray</td>
</tr>
<tr>
<td>630</td>
<td>16</td>
<td>10YR 8/3</td>
<td>n.d.</td>
<td>Very pale brown</td>
<td></td>
</tr>
<tr>
<td>725</td>
<td>6</td>
<td>CO₂</td>
<td>18</td>
<td>10YR 8/3</td>
<td>Very pale brown</td>
</tr>
<tr>
<td>775</td>
<td>24</td>
<td>CO₂</td>
<td>22</td>
<td>10YR 8/4</td>
<td>Very pale brown</td>
</tr>
<tr>
<td>880</td>
<td>24</td>
<td>Air</td>
<td>16</td>
<td>7.5YR 7/6</td>
<td>Reddish yellow</td>
</tr>
<tr>
<td>1130</td>
<td>6</td>
<td>Air</td>
<td>20</td>
<td>Melted</td>
<td>2.5Y 6/2</td>
</tr>
</tbody>
</table>

* Not determined.

3. Results

3.1. Mineralogical observations: color, XRD and ESEM

The first and most noticeable result of heating the samples was their extreme color change. The nontronite samples started off as yellowish-green with a color index of 7Y 8/4, as determined by Munsell soil color charts (Table 1). After heating to low temperatures (7 < 700 °C), the samples’ color had changed to reddish brown with a color index of 7.5YR 4/6. Intermediate temperatures (700 °C < 7 < 1000 °C) made the samples’ color change to a brick red 5YR 4/6 and after being heated to high temperatures (7 > 1000 °C), the samples’ color was a very dark reddish brown 10R 3/3. One exception to this general color trend was a sample heated to 875 °C for 6 h in CO₂. It changed to a much darker 10YR 3/2 color index.

Montmorillonite samples also experienced color change, but in a much less significant way (Table 2). Samples started as gray at GLEY1 7/N and changed to light shades of orange and pink with a color index of 10YR 8/3 after being heated to low temperatures. After being heated to intermediate temperatures, the samples’ color was 7.5YR 7/6, which is a slightly darker tint of orange and had continued to change to 2.5Y 6/2 after being heated to high temper-
In both cases the color changes indicate phase transformation, but in the case of nontronite, this is clearly evidence of a change in the Fe\(^{3+}\) ion configuration (Hvid et al., 1994; Weldon et al., 1982) related to the formation of ferric oxides.

In the XRD diffractograms of nontronite heated to low temperatures (T = 630 °C), the large 0 0 1 peak (2θ = 6.59°) disappeared but all other peaks (at 2θ values of 22.8°, 29.4°, 33.8°, 40.2° and 72.2°) were still present and had not changed in intensity (Fig. 2B). The collapse of the 0 0 1 interlayer space indicated a rearrangement of the crystalline structure as a result of water loss (~20 wt%, Table 1). This is in agreement with previous dehydration studies that showed that the interlayer distance of the 0 0 1 planes and water content decreases with increasing temperature (Bish et al., 2003). ESEM observations showed that this secondary product retained the original morphology of nontronite (Fig. 3A).

XRD diffractograms of samples heated at intermediate temperatures (T = 975 °C) contained shallow, broad and not well-defined peaks (Fig. 2C), indicating nanophases and/or poorly crystalline phases. ESEM observations showed no identifiable crystals (down to the detection limits) confirming XRD results. Identified phases included intermediate temperature phases such as anorthite (CaAl\(_2\)Si\(_2\)O\(_8\)) and corundum (Al\(_2\)O\(_3\)) mixed with high-temperature phases (cristobalite Si\(_2\)O\(_2\), hematite \(\alpha\)-Fe\(_2\)O\(_3\) and sillimanite Al\(_2\)Si\(_3\)O\(_9\)). We also observed some peaks structurally related to some known phases whose formulas do not fit the chemistry of the nontronite. These phases are labeled S2, S3 and S4, and correspond to

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**Fig. 2.** XRD diffractograms of heated nontronite. (A) Untreated sample. (B) Sample heated to 630 °C in CO\(_2\) for 20 h. (C) Sample heated to 975 °C in CO\(_2\) for 4 h. (D) Sample heated to 1 1 30 °C in air for 4 h. Abbreviations: an, anorthite; cor, corundum; cri, cristobalite; non, nontronite; qtz, quartz; ssp, saponite; ail, sillimanite; S2, spinel; S3, ilmenite; S4, hesitesite. S1 corresponds to peaks identified in the untreated sample yet cannot be labeled as “nontronite” due to the absence of the 0 0 1 peak. S2, S3 and S4 correspond to structures identified but lack the appropriate chemistry.
spinel ($X^2\cdot Y^2\cdot Z^2\cdot O_4$), ilmenite ($Fe^2TiO_3$) and heterosite ($Fe^2TiO_4$), respectively. Ilmenite may result from the small amount of tita-
nium present in the sample and some ferrous iron often present in
atural nontronites (Hvid et al., 1994). Moreover, ferri-ilmenite
($Fe\cdot Ti\cdot O_3$) is also a possibility. The spinel phase could also be mag-
netite ($Fe^3\cdot Fe^2\cdot O_4$) or maghemite ($gamma-Fe_2O_3$), with possible $Al^3+$
substitution, as previously observed in heated nontronite (Hvid et
al., 1994; Moskowitz and Hargraves, 1984). However, the low
resolution of the diffractograms prevented definitive determina-
tion of peak positions and the complex mixture prevented the
identification of smaller characteristic peaks, such as the quadratic
superstructure peaks that allow distinction between magnetite and
magnetite. Therefore, we suggest the presence of complex,
probably non-stoichiometric iron oxide phases. A separate paper
will investigate in detail the complementary magnetic and Moss-
bauer properties of our heated nontronite samples with special
emphasis on these intermediate iron phases.

By contrast, XRD diffractograms of samples heated at high tem-
peratures (above 1100 °C) contained high-intensity, sharp, well-
defined peaks indicating melting and recrystallization of secondary
phases (Fig. 2D). The mixture was composed of cristobalite ($SiO_2$,
Fig. 3B), sillimanite ($Al_2SiO_5$, Fig. 3C) and hematite ($Fe_2O_3$
Fig. 3D) representing the dominant chemical elements of nontron-
ite ($Si, Al$ and $Fe$, respectively). This is in agreement with previous
studies that nontronite decomposes into hematite (Heller-Kallai
and Rozenson, 1980). We could not identify any $Ca$ or $Mg$ phases,
but these elements are relatively minor ($Mg + Ca < 4$ wt.%, below
the usual detection limits of X-ray diffraction) and the samples
contained abundant glass due to fast cooling of the sample. This
glass phase probably contains the remaining elements (including
traces of $K$).

Fig. 4 shows the XRD diffractograms of heated montmorillonite
compared to the diffractogram of an untreated sample. At rela-
tively low temperature (630 °C), the 0 0 1 peak was still visible,
but had shifted by 1.8° compared to the original position at $2\theta = 7.25^\circ$ and had largely decreased in intensity. We interpret this
again as the loss of interlayer water confirmed by the average mass
loss of ~18 wt.% (Table 2), although this did not result in the com-
plete loss in the 0 0 1 peak as in nontronite (Fig. 2). A new peak is
seen at $2\theta = 18^\circ$. All other signature peaks of montmorillonite were
still intact, although some had also decreased in intensity, and the
two small peaks at $2\theta = 12^\circ$ and $14^\circ$ had completely disappeared.
We observed also traces of quartz and albite ($NaAlSi_3O_8$), both
probably from the initial sample. At temperatures above 800 °C,
the structure of montmorillonite was completely destroyed, which
agreed with results from Murad et al. (2002), and we observed a
mixture of sillimanite, cristobalite with minor albite and quartz
(Fig. 4C). At temperatures above 1100 °C, albite and quartz were
no longer detected in the XRD diffractogram, which was expected
since they are not stable at such temperatures. The new paragene-
sis was composed of well-crystallized sillimanite (Fig. 2E) and cris-
tobalite, with also evidence for cordierite ($Mg_2Al_2Si_3O_9$), which is
a typical phase of thermally metamorphosed Mg-rich argilaceous deposits. There was also evidence for the formation of abundant amorphous glass as indicated by the large “hump” feature centered at 2θ ~ 20° in the XRD diffractograms of samples heated above 800 °C (Fig. 4D), as well as in ESEM observations (Fig. 3F).

XRD diffractograms of nontronite samples heated to 975 °C in air were compared to those heated to the same temperature in CO₂ (Fig. 5A). We did not observe any difference between the two diffractograms, both showing similar secondary mineralogy. We then compared the reflectance spectra of nontronite samples, both in the NIR and MIR ranges, of samples heated to 475 °C in air and in CO₂ (Fig. 5B). Again, there was no visible difference between the spectra. We observed similar results between air and CO₂ atmospheres at all temperatures and also for montmorillonite. Thus we consider that all observed transformations are related to temperature and not the nature of the atmosphere.

3.2. Near-infrared reflectance spectroscopy between 1.0 and 2.5 μm

As for mineralogical observations, reflectance spectra did not show any change with atmospheric composition (Fig. 5B), but a clear evolution with temperature was evident (Fig. 6). Montmorillonite was identified by three specific absorption bands at 1.4, 1.9, and 2.28 μm as seen in the untreated sample (Bishop et al., 2002a). The band at 1.4 μm represents the OH stretching overtones of both structural OH and molecular H₂O; the band at 1.9 μm represents H–O–H stretching of molecular H₂O and is usually attributed to interlayer water; the 2.28 μm band represents the Fe–OH bond (Bishop et al., 2002a, 2008b). We also identified a smaller 2.21 μm band which corresponds to Al₂–OH (Bishop et al., 2008b), thus confirming the chemical results of an Al-substituted nontronite. A major identifier of water in minerals is the 3 μm band and is included in many spectroscopic analyses of clay minerals (Russell and Farmer, 1964; Bishop et al., 1994, 2002a; Milliken and Mustard, 2007). However, this feature was excluded from this study due to the fact that an optical probe was used in the NIR analysis whose range extends only to 2.5 μm.

From 400 °C to 725 °C we observed a progressive disappearance of the three bands while the spectra were very similar between 725 °C and 900 °C, and featureless above 975 °C (Fig. 6). The most affected were the 1.4 and 1.9 μm bands while the 2.21 and 2.28 μm bands were replaced by a 2.17–2.21 μm doublet at temperatures above 400 °C, with the 2.2–2.3 μm region taking a characteristic “plateau” shape. The 2.28 μm Fe–OH band remained visible up to 475 °C, while the new doublet was visible up to temperatures of about 725 °C, above which only the 2.17 μm band remained up to 900 °C. The 1.4 and 1.9 μm bands remained visible up to 630 °C. A small antiband appeared at 1.4 μm in the range 725–900 °C. Each sample’s spectrum was divided by a KBr background spectrum taken under a steady flow of N₂. These antibands are artifacts of that division. At low temperatures (T = 475 °C), the continuum began to take a positive slope between 1.0 and 2.2 μm and at
Fig. 5. Comparison between samples of nontronite heated in air and in CO₂. (A) XRD diffractograms of an untreated sample and two samples heated to 975 °C in air and in CO₂. The diffractograms were placed on different y-axis scales to emphasize the shallow peaks in the low and intermediate temperature samples. Abbreviations: an, anorthite; co, cordierite; cr, cristobalite; qz, quartz; il, illite; sm, smectite; s2, spilitic; s3, illite; s4, hetselite. (B) Reflectance spectra of nontronite heated to 475 °C in air and in CO₂. Top: near-infrared (NIR) reflectance spectra. Bottom: mid-infrared (MIR) reflectance spectra.

Fig. 6. Near-infrared (1.0–2.5 μm) reflectance spectra of nontronite heated to various temperatures. Positive bands in the higher temperature samples are artifacts of division by the KBr background spectrum. Spectra have been offset for clarity.

Fig. 7. Near-infrared (1.0–2.5 μm) reflectance spectra of montmorillonite heated to various temperatures. Positive bands in the higher temperature samples are artifacts of division by the KBr background spectrum. Spectra have been offset for clarity.

temperatures of 725 °C and above the continuum had a positive slope for the entire 1.0–2.5 μm range. Montmorillonite was identified by absorption bands at 1.4, 1.9 and 2.2 μm (Fig. 7). The 1.4 μm band represents the OH stretching overtones from both structural OH and molecular H₂O; the 1.9 μm
band represents the bending and stretching combination of molecular H$_2$O characteristic of interlayer water; the 2.2 μm band represents the stretching and bending combination of Al–OH (Cariati et al., 1981; Bishop et al., 1994, 2002a). Due to equipment restraints, the 3 μm band was not studied here. As expected, the reflectance spectra of heated montmorillonite samples presented a clear, yet slightly different behavior than for nontronite (Fig. 7). At first, the bands deepened until a temperature of about 500 °C, then they progressively disappeared. The 2.2 μm band took the characteristic plateau shape at T = 600 °C, due to the appearance of the characteristic 2.17–2.21 μm doublet. This band was present only in the spectrum of the sample heated to 600 °C. The overall spectral evolution of montmorillonite occurred at higher temperatures than for nontronite. For example, the 2.17–2.21 μm doublet was observed on montmorillonite at 600 °C, compared to 400 °C for nontronite, i.e., a 200 °C difference. Nevertheless, all three features completely disappeared at a similar temperature of 1130 °C (Fig. 7), which was due to melting of the samples. Small antibands were seen at 1.4 μm and 2.2 μm in the spectra of samples heated to 880 °C and 1130 °C, which are artifacts of the division by the background spectrum.

The NIR spectra of the heated samples showed a clear evolution of band depth with increasing temperature in both smectites. Band depths were recorded by measuring the distance from the minimum of the band to the continuum between the two shoulders on either side of the band. Band depth evolution with temperature for both smectites is shown in Fig. 8. Data points for missing bands or positive bands were not included in the figure. In the nontronite samples, the bands simply decreased with increasing temperatures (Fig. 8A). Montmorillonite, however, showed a more complicated trend. All three band depths (1.4, 1.9 and 2.2 μm) increased up to temperatures between 500 and 600 °C, then decreased with higher temperatures (Fig. 8B).

3.3. Mid-infrared reflectance spectroscopy between 5.0 and 15.0 μm

As with the NIR spectra, there was no distinction between samples heated in air and those heated in CO$_2$ in the MIR range (Fig. 8B). Nontronite was identified in the mid-infrared range by two major bands at 6.2 and 8.3 μm and three minor bands at 9.2, 11.4 and 12.2 μm (Fig. 9). The 6.2 μm band is due to H$_2$O bending (Farmer, 1974; Sposito et al., 1983; Bishop et al., 1994), the 8.3 μm band is due to the Si–O stretching and bending (Farmer and Russell, 1964; Grimm, 1968; Bishop et al., 2002b), the 11.4 μm band is a result of the OH bending in the Al–Fe$^{2+}$–OH bond (Farmer and Russell, 1964; Russell and Farmer, 1964; Grimm, 1968; Bishop et al., 2002b, 2008b), and the 12.2 μm band is due to the Fe$^{3+}$–OH bond (Farmer and Russell, 1964; Grimm, 1968; Bishop et al., 2002b, 2008b). All bands evolved with increasing temperature. The 6.2 μm band was stable up to temperatures of about 725 °C. At this temperature, the band shifted to 6.3 μm. The 8.3 μm band began to deepen after 475 °C and shifted to lower wavelengths by up to 0.4 μm. The 9.2 and 11.4 μm bands disappeared at lower temperatures (7 < 400 °C) while the 12.2 μm band broadened and became more shallow up to 600 °C then became more visible above 800 °C. A new band at 5.4 μm formed at 630 °C and a 5.8 μm band formed at 1130 °C (Fig. 9). The negative slope of the continuum between 5 and 8 μm increased above 800 °C.

Montmorillonite was identified in the mid-infrared range by major bands at 5.5, 6.2, 7.15, 8.07, 9.12, and 12.6 μm and minor bands at 10.8 and 11.3 μm, as shown in Fig. 10. The 6.2 μm band is due to H$_2$O bending (Farmer, 1974; Sposito et al., 1983; Bishop et al., 1994), the 9.12 μm band is a result of Si–O stretching (Farmer and Russell, 1964; Russell and Farmer, 1964; Grimm, 1968; Bishop et al., 2008b), the 10.8 μm band is due to Al–OH vibrations (Farmer and Russell, 1964; Russell and Farmer, 1964; Grimm, 1968; Farmer, 1974; Sposito et al., 1983; Bishop et al., 1994), the 11.3 μm band is due to Al–Fe–OH vibrations (Farmer and Russell, 1964; Russell and Farmer, 1964; Grimm, 1968; Farmer, 1974; Sposito et al., 1983; Bishop et al., 1994, 2002b) and the 12.6 μm band is from Mg–Fe$^{2+}$–OH vibrations (Farmer and Russell, 1964; Grimm, 1968; Bishop et al., 2008b), both resulting from minor Mg and Fe$^{2+}$ in the structure (see formula in Section 2). The 5.5, 7.15 and 8.07 μm bands were not identified in the literature. The 5.5 μm band’s position and intensity were not affected by increasing temperature (Fig. 10). The 6.2 μm band decreased in intensity and shifted by 0.12 μm to higher wavelengths above 700 °C. The 7.15 μm band gradually decreased in intensity and eventually disappeared at 600 °C. The 8.07 μm band shifted to lower wavelengths beginning at a temperature of 400 °C and shifted by about 0.52 μm. The 9.12 μm band did not shift at all but rather abruptly disappeared after 700 °C. Finally, the 12.6 μm band gradually decreased in depth and eventually disappeared at 760 °C. The continuum of the spectra also changed with increasing temperature. Similar to the behavior of the MIR spectra of nontronite, the negative slope of the continuum of the MIR spectra of montmorillonite increased in the 5–8 μm range above 700 °C.

4. Discussion

4.1. Effect of the atmospheric composition

There generally appeared to be no mineralogical or spectral differences between samples heated in air and samples heated in CO$_2$, suggesting that temperature was the primary parameter influenc-
Fig. 9. Mid-infrared (5.0–15.0 μm) reflectance spectra of nontronite heated to various temperatures. Top right: zoomed-in view of the 5–7 μm range of high-temperature samples (T > 700 °C) to highlight spectral features. Bottom right: zoomed-in view of the 10–15 μm range of low-temperature samples (T < 700 °C) to highlight spectral features. Spectra have been offset for clarity.

Fig. 10. Mid-infrared (5.0–15.0 μm) reflectance spectra of montmorillonite heated to various temperatures. Top right: zoomed-in view of the 5–7 μm range of high-temperature samples (T > 700 °C) to highlight spectral features. Bottom right: zoomed-in view of the 10–15 μm range of low-temperature samples (T < 700 °C) to highlight spectral features. Spectra have been offset for clarity.

The evolution of the studied smectites. This is due to the fact that there is no chemical reaction between smectites and CO₂. Montmorillonite is an Al phyllosilicate (with minor traces of Mg or Fe) and thus not reactive with CO₂ gas. Nontronite contains oxidized iron (Fe³⁺) which is chemically the most reactive ion since it is the only one that could change its oxidation state to Fe⁴⁺ in our experimental conditions. However, CO₂ already has the highest carbon oxidation state (+4) and is therefore not available to reduce iron. In only one sample of heated nontronite (6 h at 875 °C in CO₂, see Table 1), we saw formation of abundant spinel (magnetite).
magnetite, using magnetic analysis) and a much darker color which may indicate the presence of Fe$^{3+}$. A spinel-type structure was also identified on the XRD diffractograms of samples heated in the range 700–1000 °C. This was the only occurrence where we saw a significant difference between air and CO$_2$ samples heated at the same temperature (6 h at $\sim$875 °C, Table 1). This could result from a thermodynamic transition at this temperature, a kinetic effect (metastable phase) or the potential decomposition of CO$_2$ into CO, which occurs around 800 °C (Jin et al., 2006), followed by reoxidation by Fe$^{2+}$ which reduces to Fe$^{3+}$. This dark material could also result from reactions between nontronite and organic material (Campbell et al., 1997; Schwertmann et al., 1999; Bishop et al., 2004), although there was no evidence for organic material in our initial samples. As we mentioned before, we will soon submit a paper focusing on the magnetic properties of thermally altered nontronite and how they help understand such a difference. We want however to emphasize that except for this single occurrence (875 °C), all other samples appeared completely identical between both atmospheres. Moreover, all these magnetic phases are very minor in terms of abundance, and should not significantly affect the reflectance properties, except for the albedo (magnetite is often used to artificially decrease the albedo in mixing models). Nevertheless, in the rest of this discussion we will focus only on the effect of temperature as controlling the mineralogical and spectral properties.

4.2. Effects of adsorbed water

To study the effects of adsorbed water, we remeasured the NIR spectra of the same samples after storing them under ambient conditions for several days. Due to the use of a different detector (DTGS vs. TECP in the previous “dry” measurements), spectra were normalized for comparison to each other. Each spectrum was normalized using values from a neutral part of the spectrum (values at 1.71 μm for nontronite and 1.50 μm for montmorillonite) then offset for clarity. Fig. 11 compares spectra of samples heated to 400 °C before and after rehydration. There was a significant decrease in intensity in all three bands of nontronite, especially of the hydration bands at 1.4 and 1.9 μm (Fig. 11, spectra A in air and B in N$_2$). This indicated a significant decrease in the water content of the samples due to the removal of adsorbed water. The same effect was seen in the montmorillonite spectra (Fig. 11, spectrum C in air and D in N$_2$). The most affected band in these spectra was the 1.9 μm band, again indicating a significant loss of adsorbed water. This effect was most pronounced in the samples heated to low temperatures (T < 700 °C) because their layered structure had not been destroyed at these temperatures, allowing for a large amount of water to be adsorbed. The analytical setup (Fig. 1) successfully removed this adsorbed water from our samples.

4.3. Effects of temperature

The XRD diffractograms of heated nontronite samples suggested that the smectite’s crystalline structure evolved at relatively low temperatures (T > 400 °C) due to the disappearance of the 0.01 peak at 2θ = 6.59°, but most other peaks remained visible (Fig. 2). Similarly, NIR spectra showed that hydration bands significantly decreased in intensity at T > 400 °C and had completely disappeared by 725 °C (Fig. 6). The 2.28 μm Fe–OH band in the untreated sample disappeared at 400 °C while the small 2.21 μm Al–OH band became more visible and formed a doublet with a band at 2.17 μm. This doublet was evidence of the Al$_2$–OH bond and is most often seen in spectra of kaolinite (Bishop et al., 2008b). This indicated that Fe had been lost from the layered structure while the Al remained. The doublet disappeared at 975 °C, indicating the Al–OH bond was still intact up to this temperature. NIR spectra are sensitive to the nature of the chemical bonds while XRD analysis reveals the crystalline structure. Thus our results show that nontronite’s layered crystalline structure was lost by temperatures of about 475 °C while the Al–OH bond remained at higher temperatures. This was evidence of the reorganization of the crystalline structure due to the loss of interlayer water, resulting in the formation of an intermediate “new” phase between 400 °C and 700 °C. The loss of water explained both the absence of the 0.01 peak in the XRD diffractogram and the observed ~25 wt.% loss between the fresh and heated samples (Table 1).

The XRD diffractogram of a sample of montmorillonite heated to low temperatures (T < 800 °C) was very similar to that of the untreated sample (Fig. 4). Most of the identifying peaks of montmorillonite were still present at the same position. The new peak seen at 2θ ~ 18° in the sample heated to 630 °C may be a result of the reorganization of the phyllosilicate structure due to higher temperatures. The 0.01 peak was still visible in the low-temperature diffractogram. The peak shifted to higher 2θ values and lower intensity, but not to the extent that the nontronite samples showed. This same result was seen in samples of beidellite heated to 500 °C (Lantenois et al., 2008) and was attributed to an overall compaction of the structure due to water loss. This suggests that montmorillonite is more resistant to heating than nontronite is, and does not form an intermediate “new” phase before decomposing into high-temperature nanocrystalline phases at T ~ 700 °C. This was confirmed by NIR showing that the 1.4, 1.9 and 2.2 μm bands were visible up to about 800 °C (Fig. 7). In contrast, the NIR bands of montmorillonite disappeared at lower temperatures (T < 700 °C).

In nontronite and montmorillonite samples, the mineralogical transformation of the samples from 700 °C and up to ~1000 °C were solid–solid and the samples did not melt. This was indicated by the reorganization of the crystalline structure at low temperatures and the nanophases formed at intermediate temperatures. It was only after being heated to high temperatures (T ~ 1100 °C) that the samples showed evidence of melting and recrystallization into secondary phases, including glass.

We showed that the metal–OH band in the NIR reflectance spectra of heated montmorillonite was visible to higher temperatures than it was in the heated nontronite spectra. Moreover, in heated nontronite only the Al$_2$–OH doublet remained while the
Fe–OH band disappeared. This is due to the fact that the Fe–OH band destabilizes at lower temperature than the Al–OH (Heller-Kallai and Rozen, 1980), because the bond dissociation energy of Al–O is 501.6 kJ/mol (Reddy et al., 1999) while the dissociation energies for Fe–O and Mg–O are 407.0 and 354.7 kJ/mol, respectively (Reddy et al., 2000; Lide, 2010). These bond energies confirm both our XRD and NIR measurements that montmorillonite can withstand higher temperatures than nontronite can. It also explains the doublet at 2.17–2.21 μm in nontronite which results from the resistance to heating of the Al–OH band identified at 2.21 μm in the untreated sample.

Zoomed-in views of the 5–7 μm range for high temperatures and 10–15 μm range for low temperatures were added to Figs. 9 and 10 to highlight the evolution of the MIR spectra. The montmorillonite bands, especially in the 10–15 μm range, remained visible to T = 700 °C whereas the nontronite bands in the same range destabilized at T = 625 °C. This further demonstrates that montmorillonite is more resistant to heat than nontronite is. Band depth analysis in the NIR spectra also showed that nontronite’s bands disappear at lower temperatures while montmorillonite’s bands deepen (Fig. 8). These deeper bands may be a result of larger grain size (Bell et al., 1997) or of the reorganization of the phyllosilicate layers at higher temperatures. This reorganization could have formed a polymorph of montmorillonite causing the NIR bands to deepen and the two “new” peaks (20 = 9.1 and 18°) seen in the XRD of montmorillonite heated to 630 °C (Fig. 4).

4.4. Identification of secondary phases

Two major secondary phases were common to both nontronite and montmorillonite samples: sillimanite and cristobalite, shown by the well-defined, sharp peaks in the XRD diffractogram of samples heated to 1130 °C (Figs. 2D and 4D). In addition, nontronite showed abundant hematite as the high temperature carrier of ferroic iron. The presence of abundant amorphous glass was detected in the montmorillonite sample, identified by the “hump” feature centered at 2θ = 20°.

NIR and MIR reflectance spectra of our heated samples were compared to reference spectra from the USGS database (Figs. 12 and 13). Because of the impurity and non-ideal conditions of the terrestrial analog reference samples, spectra from two different sources were used for a more comprehensive comparison. The hematite and sillimanite samples were taken from the USGS spectral library (hematite – WS161 for NIR and GD569 for MIR, sillimanite – HS186.3B from Clark et al. (2007)). The USGS reference sillimanite NIR spectrum contained OH bands at 1.4, 1.9 and 2.2 μm (Fig. 12), which were most likely due to traces of weathering products (smectites) in the sample since there is no OH in sillimanite (Al₂SiO₅).

The NIR spectra of nontronite heated to temperatures above 700 °C were almost featureless except for a slight positive slope that could be attributed to hematite. However, the absence of bands prevented definitive identification of any secondary phases. This is mostly due to the fact that the secondary phases are featureless in this spectral region, especially when compared to “primary” phyllosilicates which exhibit strong spectral features.

MIR spectra of hematite and sillimanite are shown in Fig. 13 for comparison with the spectra of the heated montmorillonite and nontronite samples. The hematite and sillimanite spectra show significant features in the MIR not observed in the spectra of the heated clays. MIR spectra of cristobalite (Bishop, personal communication) also exhibit additional features not present in our experimental spectra. The bands identified in the reference spectra matching those identified in nontronite and montmorillonite heated to 1130 °C are summarized in Table 3. In heated nontronite, the 5.4 μm band was matched in sillimanite, the 5.8 and 12.6 μm bands were matched in cristobalite, the 6.3 μm band was matched in all three reference spectra, and the 7.9 μm band was matched in hematite and sillimanite. These similarities in the spectra confirm our XRD data of the formation of hematite, cristobalite and sillimanite as secondary phases of heated nontronite. In heated montmorillonite, the 5.3 and 8.6 μm bands were matched to cristobalite and the 6.1 μm band was matched to sillimanite and cristobalite. Again, this confirms our XRD data of the formation of sillimanite and cristobalite as secondary products of heated montmorillonite.

It is clear from the reflectance spectra that the MIR range is more appropriate for identifying secondary phases in conjunction with XRD data. MIR spectra clearly showed bands of high-temperature secondary phases, whereas NIR spectra were featureless. Alternatively, the NIR range showed clearer evolution with temperature and can be used to determine the approximate temperature to which smectites have been heated, particularly in the range 400–700 °C.

4.5. Implications for Mars

Phyllosilicates have been detected in association with impact craters on Mars (Mangold et al., 2007; Marzo et al., 2010; Poulet et al., 2008b). We found that the spectra of the phyllosilicates identified in these martian craters had more characteristics in common with our samples of nontronite heated to 400 °C rather than that of an unaltered sample (Fig. 14). More specifically, we found that our samples heated to 400 °C, measured in air (rehydrated sample) and
heated to 400 °C. The spectra have been normalized and offset. All three spectra have the same overall neutral slope. The 2.3 μm band in all three spectra has morphed into a plateau shape rather than a distinct band. Since this band is still present yet altered, the post-shock temperatures in these deposits must have been near 400 °C. This is in strong agreement with previous works that have modeled a hydrothermal system inside an impact crater and concluded that the maximum temperature for a crater of similar size to Toro Crater is about 400 °C (Barnhart et al., 2010; Abramov and Kriss, 2005; Ratibun and Squyres, 2002). The intensities of the hydration bands in the Toro Crater spectrum are visibly deeper than those of the “dehydrated” sample (bottom spectrum). This suggests that the phyllosilicates in Toro Crater have readsorbed some water from the atmosphere after being heated by the impact. This supports our data that 400 °C is not a high enough temperature to completely destroy the phyllosilicate structure, allowing for the readsorption of water by the sample.

As previously mentioned, the NIR spectra of the smectites found in Toro Crater most closely resemble that of heated smectites. Since the smectites were heated, they must have been on the surface prior to the impact event and altered by post-impact temperatures, not formed by post-impact hydrothermalism. If the smectites were formed by impact-induced hydrothermal processes, their spectral signatures would be that of unaltered smectites. This is clearly not the case (Fig. 14). Additionally, Fe–smectite do not precipitate from solutions above ~200 °C (Chevrier, 2009). Thus, we can conclude that this particular deposit of smectites dates back to the Noachian and is not a younger product of later hydrothermal processes.

Secondary phases formed by altered nontronite and montmorillonite are also of importance to the martian surface. XRD analysis of samples heated above 900 °C shows the formation of hematite, sillimanite, and cristobalite. Hematite has been shown to form as the result of thermally decomposed nontronite and is thought to be responsible for the red dust layer on the martian surface (Hvid et al., 1994). Fe-substituted cristobalite has also been seen as the result of heated nontronite in a magnetic study done by Morozowitz and Hargraves (1984) and was suggested to be a significant component of the red dust on Mars as detected by the Viking spacecraft. High-temperature, shock-generated crystals in Haughton Crater, Canada, have been identified as sillimanite and cristobalite (Martinez et al., 1993) and it is possible that these minerals may have formed in a similar fashion on Mars. Therefore they may be associated to nanophas iron oxides (Poulet et al., 2007) in the

in N₂ (dehydrated sample) resembled some phyllosilicates detected in Toro Crater in Syrtis Major (Fig. 14; Marzo et al., 2010). Fig. 14 shows the spectrum of phyllosilicates in Toro Crater on Mars (Marzo et al., 2010) compared to our samples of nontronite

| MIR bands (in μm) identified in reference spectra and in samples heated to 1130 °C. Bands of cristobalite were obtained via personal communication with Janice Bishop. |
|---|---|---|---|---|
| Nontronite | Montmorillonite | Hematite | Sillimanite | Cristobalite |
| 5.4 | 5.3 | 6.3 | 5.4 | 5.3 |
| 5.8 | 6.1 | 6.8 | 5.6 | 5.6 |
| 6.3 | 7.6 | 7.9 | 6.1 | 5.6 |
| 7.9 | 8.6 | 9.1 | 6.3 | 6.1 |
| 8.5 | 9.7 | 7.9 | 7.3 |
| 12.6 | 11.2 | 8.7 | 8.3 |
| 14.7 | 9.6 | 8.6 |
| 10.7 | 9.7 |
| 11.3 | 12.3 |
| 12.4 | 12.6 |
| 12.8 | 14.3 |
| 13.2 | 14.5 |

Fig. 13. MIR (5.0–15.0 μm) reference spectra compared to samples heated to 1130 °C. Hematite and sillimanite spectra were taken from the USGS spectral database: hematite – G069; sillimanite – HS18638 (Clark et al., 2007). Spectra have been offset for clarity.

Fig. 14. Near-infrared reflectance spectra of phyllosilicates detected by CRISM/MARO in association with Toro Crater on Mars and compared to nontronite samples heated to 400 °C, measured in air and in N₂, Spectra have been normalized and offset for clarity. Toro Crater spectrum from Marzo et al. (2010).
red dust layer, resulting at least partially from repeated impacts on martian phyllosilicates. Careful analysis in the MIR range may help identify those phases and confirm the origin of the red dust.

5. Conclusions

We have experimentally determined the effects of various temperatures on the transformation of phyllosilicates, specifically nontronite and montmorillonite. Phyllosilicates were heated in air and under a flow of CO₂ to more closely replicate the early martian atmosphere. We found that the transformation of both types of phyllosilicates was not affected by the composition of the atmosphere in which it was heated. Our experiments showed that when heated to temperatures above 700°C, nontronite transformed into hematiite, illite-mica, and stilpnomelane; and montmorillonite transformed into stilpnomelane and stilpnomelane. Between 400 and 700°C, nontronite formed an intermediate phase characterized by a red color, the absence of the 0.01 1 peak in XRD diagraphs, reduced 1.4 and 1.9 µm bands in NIR spectra, disappearance of the Fe–OH 2.2 μm band and the appearance of a 2.17–2.21 μm Al–OH doublet.

Due to their precise spectral evolution, heated smectites can be used to determine post-shock temperatures between 400 and ~700°C. Above 700°C, the spectra of nontronite and montmorillonite are mostly featureless in the MIR range because of the formation of high-temperature anhydrous phases (hematite, illite-mica, and stilpnomelane). On the other hand, these minerals exhibit strong signatures in the MIR range which is more effective in identifying secondary phases formed at temperatures above 700°C. However, it is often difficult to make definitive identifications due to the number of bands and their variability with crystalline state and composition.

The IR spectra of the phyllosilicates identified in the ejecta of the studied crater in the literature are more similar to those of heated nontronite, with or without post-heating rehydration, rather than untreated nontronite, indicating that they existed before the impact and were altered by the post-shock temperatures resulting from the impact. Thus these phyllosilicates were formed prior to the impact event and were not formed by a hydrothermal system created by the impact. Therefore our work provides an experimental basis for future characterization of phyllosilicates in impact craters and their formation process.

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References


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Appendix B First-Author Conference Presentations


**THERMALLY TRANSFORMED NONTRONITE AS A COMPONENT OF THE RED DUST LAYER ON MARS**

P. Gavin, V. Chevrier, P. Rochette

JVM Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, USA.

**INTRODUCTION**

A very thin layer of red dust covers the surface of Mars; this dust has specific properties in terms of mineralogy and chemical properties. But its precise origin remains controversial. Several works, conducted after the Viking missions, suggested that impacted and heated nontronite Ca_{16}Fe_{3}Mg_{14}Al_{6}(OH)_{20}O(OH)_{2} could contribute to the mineralogical properties of the martian regolith [1,2]. Alternatively, phyllosilicate outcrops containing nontronite have been recently identified on Mars by the Mars Express OMEGA visible-near (VIS-NIR) infrared spectrometer [3,4]. Since these outcrops have been found on the oldest, intensively craterized crust (Fig. 1), they mostly have been metamorphosed and further incorporated into the regolith. We present here our first results on thermally treated nontronite in Air (oxidant atmosphere), and CO_{2} (closer to present day past atmosphere on Mars).

**PROTOCOL**

One-gram samples were placed in the middle of a ceramic heating tube, where heating was optimal. The oven was then turned on to the desired temperature. Experiments of several different durations and temperatures were performed (Table 1). Trials were also performed in air and under a CO_{2} flow, isolating the inside of the furnace from the outside environment. Resulting products were studied using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and magnetic susceptibility.

**RESULTS and DISCUSSION**

**Mineralogical results:**

- Transformation starts at temperature around 750°C. At 500°C, nontronite loses significant weight, about 20-25 % (Table 1), becomes ilmorrich red (Figure 3), and the interlayer 001 peak disappears on XRD (Figure 2a). However, no significant metasomatic phase appears (Figure 2b).
- At higher temperatures nontronite is mostly the same between the CO_{2} and air atmospheres (Figure 2c), including quartz, cristobalite, anorthite, hematite (Figure 3b), silicates, cristobalite, and so on as several phases that fill the unidentifiable peaks but without the corresponding chemistry. These peaks are labelled S1 (ferrous spinel FeAl_{2}O_{4}), S2 (hematite Fe_{2}O_{3}), and S3 (hematite Fe_{2}O_{3}).
- At 1000°C, the mineralogy is simpler and composed of high temperature phases: cristobalite (Figure 3b) and hematite (Figure 3b) and silicate (Figure 3c).

**Magnetic (hysteresis and thermomagnetic) results:**

- Magnetic mineralogy dominated by a mixture of 2 strongly magnetic phases, in variable relative concentrations depending on the atmosphere and the temperature:
  - A phase with a high coercivity (Figure 5b), saturating at around 5 T and with a low Curie temperature, around 200°C and probably corresponds to the phase previously identified. These properties suggest a particular type of hematite.
  - A second phase with a hysteresis signal similar to spinel (Figure 5b), but no spinel-type Curie temperature has been identified. The K_{15} decreases linearly in the range 200-700°C.

The unusual magnetic properties of both phases suggest substituted hematite and magnetite, eventually with Si or Al. These "acicular" phases could describe the undetermined peaks in the XRD results.

**CONCLUSIONS**

The present study confirms the validity of the Ingalls equation, providing a theoretical basis for modeling of liquid CO_{2} evaporation on Mars. In addition, changes in water activity due to solute ion interactions have to be considered when building a stability model of Martian brines. In the future, we will explore the effect of a variety of conditions, including the possible effect of solute ions (Table 6).

**REFERENCES**


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Methods
- 2 different relevant clays
  - Montmorillonite (Ca, Al clay)
  - Nontronite (Fe⁺ clay)
- Thermal treatment
  - $350^\circ C < T < 1150^\circ C$
  - $4\text{hrs} < t < 24\text{hrs}$
  - Air and CO₂ atmospheres
- Impacted with light gas gun
  - Projectile speed ~2.5 km/s

Color Changes
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<th>Time (hrs)</th>
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XRD Results
- $T > 500^\circ C$: collapse of structure
- $T > 800^\circ C$: complex mixture of secondary phases
- $T > 1000^\circ C$: melting + crystallization of high temperature phases

ESEM Observations
- Sillimanite
- Cristobalite
- Hematite
Conclusions

- Diagnostic features of metamorphosed clays:
  - High temperature phases (cristobalite)
    - Potential source for red dust
  - Unidentified peaks in NIR reflectance spectra of impacted samples
  - New (?) magnetic phase detected
Nontronite: Intermediate temperature
- $800 < T < 1000^\circ C$
- complex mixture of secondary phases
- Large peak at $T = 900^\circ C$
- Solid-solid transformation
- No melting

NIR Reflectance
Nontronite: Intermediate temperature

Nontronite: High temperature
- $T > 1100^\circ C$
- melting and crystallization of high temperature phases
- sillimanite
- hematite
- cristobalite
- glass

NIR Reflectance
Nontronite: High temperature

NIR Reflectance
Montmorillonite heated in Air
- $T = 800^\circ C$
- $T = 600^\circ C$
- $T = 1100^\circ C$

Methods
- Same clays
  - Montmorillonite (Ca, Al clay)
  - Nontronite (Fe$^2+$ clay)
- Impact with light gas gun
  - Velocity 2 - 3.3 km s$^{-1}$
  - Pressure 10 - 50 GPa
  - SUS projectile
- Analysis
  - XRD
  - Reflectance spectra
Impacted nontronite

- No real change
- All peaks still present
- Interlayer peak intact

NIR Reflectance

NIR Reflectance

Impact affects smectites
- Decrease in band depth (impact glass?)

Conclusions

- No distinctive effect of CO₂ on spectral properties
  - Mostly effect of temperature rather than composition
- Heating: intense effect on clays
  - Loss of water at relatively low temperatures
  - Melting and recrystallization at high temperatures
  - Disappearance of bands in FTIR
- Impact affects smectites

Implications for Mars

- Confirms that clays detected in small crater ejecta were pre-existing
- Large impacts may generate enough heat to induce transformations
- Contact with lava flows should strongly affect clays

Hematite vs. Nontronite

**Effects of Impact and Heating on the Properties of Clays on Mars**

**Patricia Gavin**

- 2 relevant clays
  - Montmorillonite (Ca-Al clay)
  - Nontronite (Fe**²⁺** clay)
- Thermal treatment in tube oven
  - $350°C < T < 1150°C$
  - 4 hr < t < 24 hr
  - Air and CO₂ atmosphere
- Analysis
  - XRD
  - ESEM
  - Reflectance spectra

**Color Changes**

**Nontronite**

<table>
<thead>
<tr>
<th>Untreated</th>
<th>Heated</th>
</tr>
</thead>
</table>

**Nontronite: Low temperature**

- $T < 750°C$:
  - Loss of interlayer peak
  - Collapse of structure
  - Loss of water
  - ~25% mass

**Nontronite: Low Temperature**

<table>
<thead>
<tr>
<th>Untreated</th>
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</thead>
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<td>Water band</td>
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<tr>
<td>Metal-OH band</td>
<td></td>
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- Clays surrounded by lava flows and in crater ejecta
- Heat and shock effects
- Possible effects on clays
- Loss of water
- Structural change
- New phases formed
- Experiments
  - Heat in oven
  - Impact in light gas gun
Nontronite: Intermediate Temperature
- $800 < T < 1000^\circ$C: complex mixture of secondary phases
- Large peaks of nanocrystalline phases
- Solid-solid transformation
- No melting

Nontronite: High Temperature
- $T > 1100^\circ$C: melting and crystallization of high temperature phases
  - sillimanite
  - hematite
  - cristobalite
  - glass

Montmorillonite: Low Temperature
- $T < 750^\circ$C: most peaks still intact
- More resistant to thermal alteration
  - Quartz
  - Albite

Montmorillonite: High Temperature
- $T > 1100^\circ$C: formation of high temperature phases
  - sillimanite
  - cristobalite
  - mica
  - amorphous glass

Montmorillonite heated in Air
- $T = 800^\circ$C
- $T = 600^\circ$C
- $T = 1130^\circ$C
Impact Experiments
- Same clays
  - Montmorillonite (Ca-Al clay)
  - Nontronite (Fe²⁺-clay)
- Impact with light gas gun
  - Velocity 2 - 3.5 km/s
  - SUS projectile
- Analysis
  - XRD
  - Reflectance spectra
  - Autodyne software
  - Max pressure and temperature

Impacted nontronite
- No real change
- All peaks still visible
- Interlayer peak intact
- Peak intensity decrease

Impacted Nontronite

Shock Wave Propagation Modeling

Impacted Montmorillonite

Clays in Craters on Mars
Clays in Craters on Mars

Magnetic Properties

- $T < 600^\circ$C; paramagnetic Fe$^{2+}$
- $T > 1000^\circ$C:
  - Low saturation magnetization
  - High remnant magnetization
  - High coercive field
  - Similar to hematite

Magnetic Properties

- $800^\circ$C < $T$ < $1000^\circ$C: Wasp-waisted
  - Two or more components present
  - Multiphasic and paramagnetic particles
  - Maghemite

Conclusions

- No distinctive effect of CO$_2$ on clay transformations
- Heating: intense effect on clays
  - Loss of water at relatively low temperature
  - Melting and dehydration at high temperatures
  - Disappearance of bands in FTIR
- Impact affects smectites
  - Decrease in band depth (impact glass?)
- Magnetic properties
  - Possible new phase at intermediate temperatures
  - Non-stoichiometric phase

Implications for Mars

- Clays detected in small crater ejecta were pre-existing
  - Different spectral features from untreated samples
  - Large impacts may generate enough heat to induce transformations
  - Contact with lava flows should strongly affect clays
- Heated nontronite may explain origin and magnetic properties of red dust
  - Hematite (superparamagnetic phase)
  - Maghemite

**Thermal Alteration of Nontronite and Montmorillonite: Implications for the Martian Surface**

*Patricia Gavin, Vincent Chevrier*

**Introduction**
- Clays surrounded by lava flows and in crater ejecta
- Possible effects on clays
  - Loss of water
  - Structural change
  - New phases formed
- Experimental simulation of volcanic activity

**Experimental Procedure**
- 2 relevant clays
  - Montmorillonite (Ca, Al smectite)
  - Nontronite (Fe(II) smectite)
- Thermal treatment in tube oven
  - 500 K < T < 1400 K
  - 4 hr < t < 24 hr
  - Air and CO₂ atmosphere
- Analysis
  - XRD
  - ESEM
  - Reflectance spectra

**Color Changes**

<table>
<thead>
<tr>
<th>Untreated</th>
<th>Heated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nontronite</td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td></td>
</tr>
</tbody>
</table>

**CO₂ vs. Air**
- No distinctive difference
- No effect of atmosphere on transformation

**XRD: Nontronite**
- T < 1000 K
  - Collapse of structure
- 1000 < T < 1300 K
  - Nanocrystalline phases
- T > 1300 K
  - Crystallization of secondary phases
Near-infrared Reflectance: Nontronite
- 1.4 µm band
- OH band
- Disappears first
- 1.9 µm band
- Hydration band
- Up to ~1100 K
- 2.3 µm band
- Metal-OH band
- Plateau shape

Mid-infrared Reflectance: Nontronite
- 6.2 µm band
- Gradually decreases
- Shifts to higher wavelengths
- 8.3 µm band
- Shifts to lower wavelengths
- New: 5.4 µm band
- Forms after 900 K

XRD: Montmorillonite
- T < 1000 K
  - 001 peak still intact
- 1000 < T < 1300 K
  - Albite forms
  - Amorphous glass
- T > 1400 K
  - Silimanite
  - Cristobalite

Near-infrared Reflectance: Montmorillonite
- 1.4 µm band
  - Deepens
  - Disappears first
- 1.9 µm band
  - Up to ~1150 K
- 2.2 µm band
  - Deepens
  - Plateau shape
- Double band at 875 and 975 K
- 2.18 and 2.32 µm
Mid-infrared Reflectance: Montmorillonite
- In general, bands decrease
- 8.07 µm band shifts to lower wavelength

Clays in Impact Crater on Mars
- 2.3 µm band
- Plateau
- \( T_{\text{impact}} \leq 900 \text{ K} \)
- \( T > 900 \text{ K} \) = band disappears
- Clays existed pre-impact

Clays in Toro Crater
- Similar to heated montmorillonite

Conclusions
- No distinctive effect of CO₂ on clay transformations
- Heating: most intense effect on clays
  - Loss of water at relatively low temperatures
  - Melting and recrystallization at high temperatures
  - Shape change then disappearance of bands in FTIR

Implications for Mars
- Clays detected in small craters were pre-existing
  - Spectra more similar to thermally altered smectites than untreated smectites
  - Larger impacts may generate enough heat to induce complete transformations
  - Contact with lava flows should significantly alter clays
- NIR spectra of heated smectites used as thermometer in impact craters
Experimental Investigation of the Effect of Meteoritic Impacts on Clays on Mars

Patricia Gavin¹ Vincent Chevrier¹ Kiyotaka Ninagawa² Arnold Gucsik² Sunao Hasegawa³

¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, USA ²Dept. of Applied Physics, Okayama University of Science, Okayama, Japan ³Max Planck Institute for Chemistry, Germany

Introduction

• Clays have been found in some of the oldest Martian terrains [1 – 3].
• Clays found in central peaks and ejecta of impact craters on Mars (blue area) [4].

Methods

• Samples were impacted using a light gas gun.
• Projectile velocities: 2.07, 2.15, 2.47, and 3.27 km/s.
• SUSI projectile with known equations of state.
• Shock pressures and temperatures could be determined from the projectiles’ velocities.
• AUTO-DYN software used to simulate shock pressure and temperature propagation through the sample during impact [9, 10].

Experimental Results

• Shock pressure from impact seemed to have little, if any, effect on the clays (Fig. 2).
• 001 peak is still visible in XRD spectrum of impacted nontronite.
• Temperatures during impact did not get high enough to significantly alter the clays (Fig. 3).
• NIR spectra all still contain the three identifying bands of nontronite at 1.4, 1.9 and 2.3 μm.

Table 1: Summary of the experimental results for each impacted sample.

<table>
<thead>
<tr>
<th>Projectile velocity (km/s)</th>
<th>Average Pressure (GPa)</th>
<th>Peak Pressure (GPa)</th>
<th>Average Temperature (K)</th>
<th>Peak Temperature (K)</th>
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<td>3.27</td>
<td>1.6</td>
<td>17.5</td>
<td>412</td>
<td>799</td>
</tr>
</tbody>
</table>

Figure 2: XRD spectrum of a untreated sample of nontronite (blue) with that of a sample impacted with a projectile velocity of 3.27 km/s (red). The major change seen was seen indicating the impact did not significantly alter the clay. Even the 001 peak (arrow) is still visible.

Figure 3: Near-infrared (NIR) reflectance spectra of the impacted samples compared to that of an untreated sample of nontronite. All three signature bands are still visible even at the highest velocity impact indicating the shock pressures near the shock temperatures significantly altered the clay.

Simulations

Figure 6: Simulations of the A) pressure and B) temperature gradients propagating through the sample during impact. Projectile velocity was 2.47 km/s. Maximum pressure reached 4.5 GPa and maximum temperature reached 600 K.

Conclusions and Implications for Mars

• Slight alteration effects are visible.
• Decrease in NIR band intensity.
• Increase in 001 peak in XRD spectrum.
• All three signature bands visible in NIR spectra.

References


**Experimental Investigation of the Effect of Meteoritic Impacts on the Spectral Properties of Phyllosilicates on Mars**

**Patricia Gavin¹ Vincent Chevrier¹ Kiyotaka Ninagawa² Arnold Gucsik³ Sunao Hasegawa³**

¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, USA ²Dept. of Applied Physics, Okayama University of Science, Okayama, Japan ³Max Planck Institute for Chemistry, Germany

**Introduction**

- Phyllosilicates have been found in the oldest Martian terrains [1-3].
- Phyllosilicate found in central peaks and ejecta of impact craters on Mars [4,5].
- Formation processes are unclear:
  - Formed during the Nectarian due to surface water activity [6].
  - Formed later by impact-induced hydrothermal processes [7,8].
- Experimental simulations of meteoric impacts will determine several facts about phyllosilicates:
  - The effects of shock pressures and temperatures.
  - Whether phyllosilicates found in association with impact craters were formed by the impact or existed prior to impact and were altered by it [9].

**Methods**

- Samples were impacted using a light gas gun:
  - Nontronite, montmorillonite, kaolinite, serpentine, chlorite and phyllosilicate.
  - Projectile velocities: 2 – 5 km/s.
  - Steel projectile with known equations of state.
- Shock pressures and temperatures can be modeled from the projectile velocities using AUTOCOLL software [10,11].
- Analytical techniques: FT-IR (near and mid-infrared), X-ray diffraction, cathodoluminescence, Raman spectrometry.

**Modeling Results**

<table>
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<th>Projectile Velocity (km/s)</th>
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<td>0.7</td>
<td>11.4</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>4.48</td>
<td>0.7</td>
<td>15.0</td>
<td>475</td>
</tr>
</tbody>
</table>

Table 1: Maximum and average pressures and temperatures for nontronite and montmorillonite samples calculated from simulations.

**Experimental Results**

**Simulations**

- Figure 1: NMR spectra of impacted samples A: chlorite; B: kaolinite; C: phyllosilicate; D: serpentine; E: montmorillonite; F: nontronite.

- Figure 2: Simulations of A: pressure and B: temperature gradients going through a sample of nontronite impacted to 2.47 km/s. Time range: 0 – 1.1x10⁶ ms.

- Figure 3: Simulations of A: pressure and B: temperature gradients going through a sample of montmorillonite impacted to 3.56 km/s. Time range: 0 – 6.0x10⁶ ms.

**Conclusions and Implications for Mars**

- Slight alteration effects are visible.
- Decrease in NMR band intensity.
- Shock pressures and temperatures from small impacts do not significantly alter clays.
- All three signatures visible in NMR spectra.
- Low maximum temperatures reached during the impact.
- Sample was only heated for times on the order of milliseconds in a very localized space.

**References**

Spectral Analysis of Deccan Paleosols, India: Analog for Phyllosilicates on Mars

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² Department of Geology, Poona College, Camp, Pune 411 001, India
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Introduction
• Phyllosilicates detected on the oldest terrains on Mars by CRISM and OMEGA [1-3]
• Formation processes unclear
• Formed during the Noachian from activity of liquid water on surface [4]
• Formed later due to hydrothermal systems resulting from meteorite impacts [4-5]
• Use Deccan Paleosols in western India as analog for martian phyllosilicates
• Result of basaltic or volcanic ash weathering [6,7]
• Pyroclastic origin [8]
• This study will:
  • Focus on the spectral features of the Deccan Paleosols
  • Compare them to known mineral phases
  • Attempt to link their origin with the origin of smectites on the martian surface

Samples and Analytical Methods
• Eleven (11) samples from Deccan Traps, India
• Colors range from red to yellow to green
• Samples analyzed using:
  • X-ray diffraction (XRD)
  • Fourier Transform Infrared (FT-IR) reflectance in near- and mid-infrared ranges

Results
• Nontronite was identified by the large 001 peak in XRD analysis (Fig. 1)
• Some secondary phases were identified by XRD (e.g., hematite) suggesting the samples had undergone some sort of alteration, most likely thermal
• Reflectance spectra in the NIR (Fig. 2) and MIR (Fig. 3) closely resemble nontronite
  • Varying band depths suggest thermal alteration [9]
• NIR spectra show strong similarities to both untreated and thermally altered nontronite (Fig. 4)

Conclusions
• Deccan paleosols closely resemble nontronite
• Spectral analyses show alteration to various extents
• Deccan paleosols are a mixture of phyllosilicates and thermal alteration products
• Phyllosilicates on Mars may have formed and been altered in similar processes to that Deccan paleosols

References
Experimental Investigation into the Effects of Meteoritic Impacts on Martian Phyllosilicates

**Experimental Setup**
- Impacted phyllosilicates
  - Montmorillonite
- Nontronite
- Kaolinite
- Pyrophyllite
- Chlorite
- Serpentine
- Unvented sample holder
- Projectile velocity up to ~5 km/s
- Stainless steel (US304)

**Analytical Techniques**
- Experiments simulated by Autodyn software
- Peak and average pressure and temperature
- X-ray diffraction (XRD)
- Near-infrared reflectance (NIR)
- ~10.2.5 μm
- Mid-infrared reflectance (MIR)
- Raman spectroscopy
- Cathodoluminescence (CL)

**Autodyn Simulations**

**Montmorillonite**

<table>
<thead>
<tr>
<th>Projectile velocity (km/s)</th>
<th>Average Temperature (K)</th>
<th>Peak Temperature (K)</th>
<th>Average Pressure (GPa)</th>
<th>Peak Pressure (GPa)</th>
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</thead>
<tbody>
<tr>
<td>3.66</td>
<td>420</td>
<td>505</td>
<td>0.47</td>
<td>11.4</td>
</tr>
<tr>
<td>4.49</td>
<td>475</td>
<td>720</td>
<td>0.74</td>
<td>15.0</td>
</tr>
</tbody>
</table>

*Our study represents the lower limit of shock effects
*Average projectile velocity for Mars: 9.3 km/s (Steele, 1998)*

**X-ray Diffraction**
- No new peaks formed
- Amorphization observed in shocked montmorillonite

**Reflectance Spectra - Montmorillonite**

**Nontronite**

**Montmorillonite**

- **NIR:**
  - New band at 1.71 μm
  - Change of slope below ~1.8 μm
- **MIR:**
  - 5-9 μm bands decrease in intensity
  - Bands >10 μm disappear
Reflectance Spectra - Nontronite

- **NIR:**
  - Bands increase in depth
  - New band at 2.1 μm

- **MIR:**
  - New bands at 6.68 and 7.33 μm
  - 5.58 μm → 5.69 μm
  - 8.37 μm → 8.47 μm

Reflectance Spectra - Kaolinite

- **NIR:** No significant change

- **MIR:**
  - 5.2, 5.5, 9.02 and 10.6 μm bands are unchanged
  - New bands at 6.85, 7.31, and 7.65 μm

Reflectance Spectra - Prehnite

- **NIR:** No significant change

- **MIR:**
  - Bands from 9-8 μm disappeared
  - New bands at 12.1 and 12.3 μm

Reflectance Spectra - Chlorite

- **NIR:**
  - 3.26-3.31-3.35 μm epmilt shifts to lower wavelengths

- **MIR:**
  - 5.05, 6.17, 3.59 μm bands disappeared
  - New bands at 12.6, 12.9 and 14.4 μm
  - 8.47 μm → 9.90 μm
  - Change in slope

Reflectance Spectra - Serpentine

- **NIR:**
  - New band at ~2.0 μm
  - New doublet at 2.12-2.14 μm

- **MIR:**
  - Bands at 5.6, 6.15, and 8.36 μm disappear
  - New bands at 9.28, 11.3, and 13.4 μm
  - Change in slope

Raman Spectroscopy - Montmorillonite

- **705 cm⁻¹ peak**
  - Si-O-Al stretching vibrational mode
  - Broadens and decreases intensity

- **New peak forms at 517 cm⁻¹ (g) in shocked samples**
  - Anti-symmetric SiO stretching vibrational mode
Summary

- NIR spectra not significantly affected by impacts
- XRD spectra slightly affected
- MIR, Raman and CL strongly affected
- Strong evidence for shock-induced amorphization
  - XRD broad feature (hump)
  - Anti-symmetric band in Raman (short-range ordering)
  - Decrease in CL peak intensity (disordering of recombination centers)
  - Shifts in CL peak positions to lower wavelength
- Spectral properties more significantly affected by temperature than shock pressure (Gavin and Chevrier, 2010, Icarus)

Implications for Mars

- NIR identified phyllosilicates in crater ejecta
- Some MIR observations not consistent with NIR identifications
  - MIR spectra of impacted phyllosilicates are different from spectra of unaltered sample
- MIR spectra can help determine formation processes
  - Pre-existing OR formed from impact-induced hydrothermalism
- Compare MIR spectra with phyllosilicates in/near martian impact craters
Spectral Properties of the Deccan Palaeosols, India: Implications for Thermally Altered Phyllosilicates on Mars

Introduction
- Origin of martian phyllosilicates [1-3] is uncertain
- Possibly formed from surface liquid water activity during the Neochor [4] or from impact-induced hydrothermal systems [5]
- Use Deccan Palaeosols as an analog
- Formed from weathered volcanic material [6]
- Original material was heated by subsequent lava flows [7]

This study
- Investigated the spectral properties of the Deccan Palaeosols
- Compared them with known minerals
- Linked terrestrial alteration processes with those that occurred on Mars

Samples and Analytical Methods
- Eleven samples from Deccan Traps, India (Fig. 1)
- Seven colored red, two colored yellow, two colored green
- Samples analyzed using:
  - X-ray diffraction (XRD)
  - FTIR reflectance in near- and mid-infrared

Results
- Phyllosilicate minerals were identified in XRD by the large 001 peak (Fig. 2), along with iron oxides
  - Red samples: montmorillonite
  - Yellow samples: vermiculite, montmorillonite
  - Green samples: nontronite, celadonite
- NIR spectra showed smectite signatures (Fig. 3)
  - 1.4 and 1.9 µm hydration band
  - 2.2-2.4 µm metal-OH bands
- Green and yellow samples showed evidence of Fe3+
  - 1.0-1.2 µm band
  - 2.35-2.37 µm band
  - Consistent with the presence of celadonite (green) and vermiculite (yellow)
- MIR spectra also resembled smectites (Fig. 4)
  - All spectra contain 6.1 and 8.5 µm bands
  - Green samples also contain 5.4, 5.6, and 12.6 µm bands

Discussion and Conclusions
- Red samples contain Al3+ and Fe3+ [9]
  - Al3+ confirmed by NIR spectra
  - Lack of Fe3+ bands in NIR suggest presence of iron oxides (Hematite?)
- NIR spectra of yellow and green samples indicate Fe2+/Fe3+ smectites
- NIR and MIR spectra compared to that of known minerals [10] (Figs. 5, 6)
  - 5.4, 5.6 and 12.6 µm bands in MIR spectra similar to heated nontronite (Fig. 6)
- Deccan samples appear to be mixture of several minerals, as well as unaltered and thermally altered material
- Deccan samples are good terrestrial analogs for studying phyllosilicates on Mars

References
Introduction

- Origin of martian phyllosilicates [1-3] is uncertain
- Possibly formed from surface liquid water activity during the Noachian [4] or from impact-induced hydrothermal systems [5]
- Use Deccan bolide beds as an analog
- Formed from weathered volcanic material [6]
- This study
- Investigates the mineralogy and spectral properties of the Deccan bolide beds
- Links terrestrial formation and alteration processes with those that occurred on Mars

Samples and Analytical Methods

- Eleven samples from Deccan Traps, India (Fig. 1)
- Seven red samples
- Two yellow samples
- Two green samples
- Samples analyzed using:
  - X-ray diffraction (XRD)
  - FTIR reflectance in near- and mid-infrared

Results

- Munsell soil colors (Fig. 2):
  - Red: 5YR 4/6
  - Yellow: 2.5 Y 7/4
  - Green: 5Y 6.3
- Phyllosilicate minerals identified in XRD by the large 001 peak at low 2θ values (Fig. 3), along with iron oxides
- Red samples: montmorillonite, hematite
- Yellow samples: vermiculite, montmorillonite
- Green samples: nontronite, celadonite
- NIR spectra showed smectite signatures (Fig. 4)
  - 9.4 and 10.5 μm hydration bands
  - 2.2-2.4 μm metal-OH bands
- Green and yellow samples showed evidence of Fe2+
  - Bands at 2.0-1.2 μm and 2.3-2.57 μm
  - Consistent with the presence of vermiculite (yellow) and celadonite (green)
- MIR spectra also resembled smectites (Fig. 5)
  - All spectra contain bands at 6.3 μm (Mg0) and 8.5 μm (SO3) and a peak at 9.5 μm (Al2O3)
  - Green samples also contained bands at 5.4, 5.6, 7.9, 10.2 (OH), 12.5 (MgFe2O3) and 14.5 μm (MgOH)

Discussion

- Green bolide beds on bottom layer – celadonite and nontronite (Fig. 6A)
- Yellow bolide beds in middle layer – vermiculite and minor montmorillonite (Fig. 6B)
- Red bolide beds in top layer – montmorillonite and hematite (Fig. 6C)
- Different mineralogy but similar chemistry [7]
- Celadonite transforms into smectite with vermiculite intermediate step [8], by the removal of interlayer K+
- Evolution of the alteration process from deuterated alteration to low-temperature weathering [9]

Results

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ImPLICATIONS FOR MARS

- Stratigraphy of phyllosilicates in Wadham Falls similar to Deccan bolide beds
  - Al-phyllosilicate layer overlying Fe2+-phyllosilicate layer with Fe2+-layer between (2)
- Similar spectral features (Fig. 6)
- Previously thought to result from changes in pH or oxidation
- Possibly due to evolution of formation process from deuterated alteration to low-temperature weathering
- Provides clues to the aqueous history of the region

References

**Experimental Investigation into the Effects of Heating and Impacts on the Spectral Properties of Phyllosilicates on Mars**

**Patricia Gavin¹, Terik Daly², Vincent Chevrier¹, Kiyotaka Ninagawa¹, Arnold Guescix², Sunao Hasegawa³**

¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701, ²Dept. of Geological Sciences, Brigham Young University, Provo, UT, ³Dept. of Applied Physics, Okayama University of Science, Okayama, Japan; 4Max Planck Institute for Chemistry, Germany; 5Institute of Space and Astronautical Science, Japan Exploration Agency

**Introduction**

- Phyllosilicates found on oldest Noachian terrain on Mars [1,2].
- Outcrops surrounded by lava flows [1].
- An exposure and control groups of impact craters [3].
- Formation processes unclear.
- Via weathering of basaltic material [4] through the activity of water on the surface [5].
- Via surface [1] or subsurface [6] hydrothermalism due to volcanic activity or meteorite impacts [8,9].
- Possibly altered by the heat and/or pressure of contact with lava flows and meteoritic impacts.

**Purpose of this study**

Determine alteration processes of phyllosilicates on Mars by studying their spectral signatures.

**Experimental and Analytical Methods**

- Phyllosilicates identified on Mars [9].
- Montmorillonite, nontronite, kaolinite, prehnite, chlorite, serpentine.
- 300°C < T < 1100°C.
- No h < c < 24 h.
- Heated in air and under CO₂ flow.
- Impacted with 505 projectile using light gas gun.
- Projectile speeds up to ~4.5 km/s.
- Samples analyzed using:
  - X-ray diffraction (XRD).
  - Near- and mid-infrared (NIR and MIR) reflectance spectroscopy.

**Results – Heating**

- X-ray diffraction (XRD) and montmorillonite (label), which both completely transformed into secondary phases at T > 1100°C. Also, montmorillonite nontronite secondary phases are more quartz at high temperatures, whereas kaolinite remains kaolinite at intermediate temperatures.

**Results - Impacting**

- Decrease in XRD peak intensity (Fig. 9), except in prehnite.
- Effects of shock pressure and low shock temperature on meteorite structural [Ware 3,10].
- NIR of shocked samples not significantly affected.
- MIR of shocked samples showed strong alteration (Fig. 7).
- Possible evidence of shock-induced secondary phases.

**Table 1. Average peak temperatures and pressures in impact experiments.**

- **Table 2.** NIR and MIR spectra of heated nontronite.

**Implications for Mars**

- Thermally altered nontronite may be origin of red dust on Mars.
- Formations of hematite.
- MIR spectra can determine pre-or post-impact formation.
- Some spectra of martian phyllosilicates more similar to heated sample (Fig. 9).
- Phyllosilicates at T < 700°C.
- Discrepancy between NIR and MIR observations of some phyllosilicates rich locations on Mars [11,12].
- Possibly caused by observation of shock altered phyllosilicates as a result of the impact.
- Indicates phyllosilicates pre-date impact event.

**References**
