Infrared Spectra Analysis of Thermally Altered Iron Phyllosilicates and the Implications for Mars

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Infrared Spectra Analysis of Thermally Altered Iron Phyllosilicates and the Implications for Mars
Infrared Spectra Analysis of Thermally Altered Iron Phyllosilicates and the Implications for Mars

A thesis submitted in partial fulfillment of the requirements for the degree Master of Science in Space and Planetary Sciences

by

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Mississippi State University
Bachelor of Science in Geosciences, 2010

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This thesis is approved for recommendation to the Graduate Council.

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ABSTRACT

This study looks at two iron-rich phyllosilicates, which may be present on Mars. The minerals, greenalite and hisingerite, are rich in iron-II and iron-III, respectively. Small samples (~0.40 grams) of each mineral were crushed and heated in a Lindberg Tube Oven for approximately twenty-four hours at temperatures selected to mimic lava flows and impact events. Following heating, each sample was placed in a Fourier Transform Infrared (FT-IR) spectrometer to collect the near- and mid-infrared spectra. The spectra allowed for these terrestrial analogs to be analyzed with regards to how their structure breaks down with increasing temperature. The samples’ colors were also recorded and show varying degrees of oxidation following heating, which is expected in the oxygen-rich ambient atmosphere they were heated under. It is apparent from the spectra that for greenalite, heating at 765°C and higher breaks the mineral down into hematite and a high-temperature silica, such as cristobalite. Hisingerite exhibits the same behavior, but its basic spectra structure is retained in the 710°C sample. The near-infrared spectra were compared with spectra from different locations on Mars, collected by both Mars Express and the Mars Reconnaissance Orbiter. The spectra were also compared with each other to allow for analysis of how the iron-III polymorph of a mineral reacts differently from its iron-II counterpart. The multiple facets of the study aim to help understand the current state, history, and evolution of Mars, specifically if clay formation occurred deep in Mars’ past or as the result of impact-induced hydrothermal activity more recently in its history.
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DEDICATION

This thesis is dedicated to my parents, Tom and Linda Bryan, who have always stood by my side. They were always available to give advice, a swift kick in the pants, or just to listen. Their belief in me and their belief in the value of this project and degree are the biggest factors that led to the completion of this project and thesis. It simply would not have happened without them.
TABLE OF CONTENTS

I. INTRODUCTION 1
   A. MARS GEOLOGIC HISTORY 1
   B. EXPLORATION OF MARS 5

II. THESIS PROJECT 7
    A. PHYLLOSILICATE DISCOVERY AND PROJECT BACKGROUND 9
    B. MINERALS ANALYZED 12
        Greenalite 12
        Hisingerite 15
    C. METHODOLOGY 18
    D. RESULTS 20
        Color Change 20
        Weight Loss During Heating 21
        Band Depths 22
        Greenalite Near-Infrared Spectra 24
        Greenalite Mid-Infrared Spectra 26
        Hisingerite Near-Infrared Spectra 30
        Hisingerite Mid-Infrared Spectra 32
    E. DISCUSSION 34
        Spectra Comparison with Mars 34
        Greenalite Spectra Comparison with Hisingerite Spectra 37
    F. SUMMARY AND CONCLUSIONS 40

III. BIBLIOGRAPHY 43
I. INTRODUCTION

In 2005, phyllosilicates were discovered on the surface of Mars by the Mars Express spacecraft (Bibring et al., 2005). One year later, the Mars Reconnaissance Orbiter found their presence to be much diverse in both location and composition than previously believed (Ehlmann et al., 2011). The actual cause and timing of the clay formation is of great debate. Some researchers believe that the clays formed during the Noachian, a time in Mars’ past where the climate is believed to have been warmer and wetter (Fairén et al., 2010). Others, though, believe that the clays formed more recently in the planet’s history due to impact induced hydrothermal activity (Schwenzer and Kring, 2009).

Previous studies, including Gavin and Chevrier (2010) and Che and Glotch (2012), analyzed how clay minerals break down when heated to temperatures found in impact zones to understand both how the minerals break down with increasing temperature and to help determine if the clays were formed before or after the impact events. The study presented in this document, analyzed how two iron-rich clay minerals evolved with increasing temperatures, based off their near- and mid-infrared spectra. The spectral data can then be compared with Mars to help determine if the minerals formed before or after impact events. In order to complete the experiments, samples of greenalite and hisingerite were crushed to a fine powder, placed in a high-temperature tube oven and heated for approximately twenty-four hours. Following heating, the samples were allowed to cool to allow for handling. The near- and mid-infrared spectra were then taken.

A. MARS GEOLOGIC HISTORY

In order to begin to understand Mars, it is common to look for similarities it shares with Earth. When comparing the two planets, there appear to be many similarities. Both planets have
volcanoes, impact craters, fluvial features, and phyllosilicates. Both planets are differentiated and thus have a core, mantle, and crust. The planets, though, are two very different worlds.

Mars is approximately one-third of the size of Earth, orbits the Sun at 2.33 AU’s, has an atmosphere less than 1% that of Earth’s composed of primarily carbon dioxide. Mars also cooled much quicker. During the first few tens of millions of years, the planet differentiated, forming a thick crust relative to the planet’s size. Most geologic activity is confined to the first 1.5 billion years. The magnetic field that protects the Earth from harmful solar storms is believed to have only existed in the Pre-Noachian on Mars, leaving its atmosphere and surface open to attack for nearly 4 billion years. Mars, like the Earth, was subjected to large impacts during the Late Heavy Bombardment. The impacts formed basins on Mars, which are still found today, and are likely the cause of the great crustal thickness dichotomy, which formed during the Noachian.

The Noachian Era is the most important era for this thesis due to the formation of phyllosilicate minerals during the era. The time period, as seen in Figure 1, is characterized by minerals, notably phyllosilicates, formed by the weathering of the basaltic minerals, high rates of erosion and volcanism, and most of the accumulation of the Tharsis region. When the era ended 3.7 billion years ago, the Hesperian Era began, bringing with it a new set of conditions (Carr and Head, 2010).
The Hesperian on Mars was a time of dramatically reduced rates of impacts, valley formation, weathering, and erosion. It was also an era of increased volcanism, which resurfaced 30% of the planet, episodic large flood events, and canyon formation. The Valles Marineris is believed to have opened and formed during the Hesperian. As the planet cooled, any water still present likely became stable only below the surface and at the poles, thus forming the cryosphere.
Another distinguishing feature of the Hesperian is the presence of sulfate minerals, which indicate some water activity at the surface (Carr and Head, 2010).

The Hesperian era ended approximately 3 billion years ago, and the Amazonian era began. The Amazonian, which continues to present-day, is characterized by low rates of erosion, weathering, volcanism, and flooding. Gullies, along with glacier and ice formations became the primary geomorphologic features found in Amazonian terrains. At the poles, Mars’ obliquity patterns are preserved in fine-grained, small layers composed of ice and dust (Carr and Head, 2010). It is during the Amazonian era that humans are exploring the planet, trying to unravel the mysteries of what happened billions of years in the past, and understand, among other things, how clay minerals formed and evolved and what that means about the history of the planet.

![Diagram of Mars geologic timescale](image)

**Figure 2.** An alternate timescale for Mars based upon mineral assignments (Bibring et al., 2006).

An alternate geologic timescale for Mars was introduced by Bibring et al. (2006) after the discovery of clays on Mars. The timescale, see in Figure 2, is based on OMEGA mineral assignments. The first era, the phyllosian, is characterized by minerals formed by nonacidic aqueous alteration, i.e., phyllosilicates. The second era, the theiikian, follows a global climate change, likely caused by volcanic activity. The theiikian is a period where acidic conditions dominated the alteration of minerals, and sulfates were prominent. The final era is the siderikian.
The era began during the latter half of the Hesperian and is characteristic of aqueous-free alteration and is traced by ferric oxide minerals (Bibring et al., 2006).

**B. EXPLORATION OF MARS**

Since the advent of rocket propulsion and spacecraft in the 1950s, dozens of missions have been sent to Mars, but it was not until the early 2000s when the Mars Express mission began studying the planet that phyllosilicates were discovered (Bibring et al., 2006). Subsequent missions, including the Mars Reconnaissance Orbiter, expanded our knowledge of the minerals’ presence on Mars.

In 2003, the European Space Agency (ESA) got in the Mars exploration game with their spacecraft, Mars Express. The spacecraft carried a number of instruments, including OMEGA (Observatoire pour la Mine´ralogie, l’Eau, les Glaces et l’Activite), a visible and infrared spectrometer. OMEGA would prove to be one of the most important instruments ever sent to Mars when it discovered phyllosilicates on the surface (Bibring et al., 2005; ESA, 2013a, b).

While Mars Express was studying the planet, teams at NASA were preparing three spacecraft for an unprecedented study of the planet. The first two of these spacecraft were the Mars Exploration Rovers named Spirit and Opportunity. The twin rovers, each the size of a golf cart, launched in the summer of 2003 and landed on Mars in 2004 on opposite sides of the planet. The rovers both exceeded the expectations and planned mission timelines, during which Spirit discovered pure silica below the surface of the Columbia Hills which indicates previous hot spring activity in the area (Webster, 2011), and Opportunity found clay minerals in the wall of the Endurance crater along with basaltic breccias and gypsum rich veins (Bell III et al., 2013).
In 2006, NASA added another orbiter to study the planet and relay information to and from the surface-operating rovers. The orbiter is the Mars Reconnaissance Orbiter (MRO). Its suite of instruments led to detailed mapping of the martian surface; the distribution and diversity of phyllosilicate minerals was greatly expanded as a result (Bishop et al., 2008a; Ehlmann et al., 2009; Loizeau et al., 2007; Michalski and Noe Dobrea, 2007; Mustard et al., 2008; Wray et al., 2008).

On August 6, 2012, the car-sized Mars Science Laboratory (MSL) landed in Gale crater (Figure 3), which spans 154 kilometers in diameter and is dominated by the feature Mount Sharp, a feature that stands six kilometers high. Gale crater sits below the average elevation of Mars, making it a likely place where water would have flowed. Its walls contain layered strata, which

Figure 3. The map shows where NASA’s landers and rovers have touched on Mars. The Mars Science Laboratory touched down in Gale Crater, after this image was produced (Image credit: NASA/JPL-Caltech)
tell the history of the area. The six kilometer-high Mount Sharp is likewise composed of the layered strata. Imaging of Gale crater by MRO’s CRISM and HiRISE instruments, and Mars Express’ OMEGA instrument indicates that sulfates and clays are present in the crater, meaning that in its past, water once existed in abundance. Furthermore, some of Gale crater’s strata appears to be recently exposed, meaning if there are biosignatures in the geologic stacks, they stand a high chance of having not already been destroyed ultraviolet radiation (Brown et al., 2013). The rover has discovered conglomerate rocks, which indicate flowing water (Williams et al., 2013) and analysis of a clay-and sulfate-rich outcrop studied by the rover definitely found that Mars was suited for microbial life billions of years in its past (NASA, 2013).

II. THESIS PROJECT

In 2005, phyllosilicates were discovered on the surface of Mars by the Mars Express OMEGA instrument (Bibring et al., 2005). The discovery helped to confirm the theory that at one time in the martian past, water was a very active part of the planet. In 2006, when the Mars Reconnaissance Orbiter began studying the planet, the clay minerals were found to be much more abundant and diverse than originally indicated by the OMEGA instrument. The hydrated minerals are found in Noachian-aged terrain and are thus believed to be at least 3.7 billion years old (Carr and Head, 2010), although there is debate about whether the minerals truly formed then or if they are the result of impact-induced hydrothermal activity more recently in Mars’ past (Bibring et al., 2006; Fairén et al., 2010; Schwenzer and Kring, 2009).

Among the minerals detected were iron-rich clays (Poulet et al., 2005; Bibring et al., 2006). In 2010, a study done by Gavin and Chevrier looked at the thermal alteration of selected iron phyllosilicates. In their study, the minerals were crushed, heated to high temperatures simulating
lava flows and impact events, impacted at velocities comparable to meteor impacts, and analyzed via Fourier Transform Infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and environmental scanning electron microscopy (ESEM).

My study takes the procedures established by Gavin and Chevrier (2010) to analyze two more iron phyllosilicates: greenalite and hisingerite. Greenalite is an iron-II clay which forms primarily as an alteration mineral in hydrothermal environments (Rasmussen et al., 1998; Guggenheim and Eggleton, 1998). Hisingerite is the iron-III equivalent of greenalite which forms primarily as a weathering product but is also found to form in hydrothermal environments (Kohyama and Sudo, 1975). Each mineral was crushed and heated to temperatures which mimic lava flows and meteor impacts. Following heating, each sample was placed in an FT-IR spectrometer, and its near-infrared and mid-infrared spectrum were collected. The spectra allows for interpretation into how the minerals break down and evolve with increasing temperature. The spectra, once understood, were compared with previously published spectra from Mars to determine if either mineral is present on the Red Planet. It has been determined, albeit inconclusively, that both greenalite and hisingerite are likely to be present on Mars. Furthermore, comparison of the two minerals’ spectra with each other shows how the iron-II and iron-III minerals differ when heated.

It is the objective of this study to help expand the scientific database of the mineral characteristics and to determine the implications to Mars these characteristics have. Studying the clays allows us to look deep into the martian past and begin to understand what happened to the planet.
A. PHYLLOSILICATE DISCOVERY AND PROJECT BACKGROUND

In 2005, the OMEGA spectrometer onboard the Mars Express spacecraft detected the presence of phyllosilicates on the martian surface (Figure 4). The phyllosilicates were sparse but present nonetheless. Peaks at 1.4 and 1.9 µm were the key determining factors (Bibring et al., 2005). In 2006, when the Mars Reconnaissance Orbiter began its primary mission phase, its instrument, CRISM, confirmed the hydrous minerals’ presence (Bishop et al., 2008a; Mustard et al., 2008). The clays are found the walls of craters and valleys in three primary areas on Mars: Meridiani Planum (Wiseman et al., 2008), Mawrth Vallis (Bishop et al., 2008a; Michalski and Noe Dobrea, 2007), and Nili Fossae (Ehlmann et al., 2008; Mangold et al., 2007; Mustard et al., 2008). They have also been detected in impact craters in the southern hemisphere (Poulet et al., 2005) (Figure 5). The areas where the clays have been detected are all Noachian-aged terrain (>3.6 billion years) (Bibring et al., 2006). The clays detected are mostly smectites including magnesium-rich smectite, nontronite, an iron-III smectite, and montmorillonite, an aluminum-rich smectite (Poulet et al., 2005). Also detected, but much less abundantly are kaolinite, chlorite, micas, and serpentines (Bishop et al., 2008a; Ehlmann et al., 2009; Mustard et al., 2008). Iron-II-rich clays were also detected, although, their exact composition is unknown (Poulet et al., 2008).

The clay minerals were primarily detected in Noachian-aged terrain, which are typically heavily cratered (Bibring et al., 2006). One of the debates revolves around the exact origin of these clays. Some studies, including Schwenzer and Kring (2009), suggest that minerals formed as a result of impact-induced hydrothermal activity. The activity, as modeled by Abramov and Kring (2005), could contain temperatures as high as 1200°C for thousands of years, which would be sufficient for these minerals to form. Others, though, believe the clay minerals were formed by aqueous activity early in Mars’ past and were merely excavated due to the impacts (Fairén et al.,
If this is the case, then it can be expected that the energy from the impact altered the minerals. The degree of alteration caused by high temperatures and meteor impacts has been analyzed in multiple studies, including Gavin and Chevrier (2010), Fairén et al. (2010), and Che and Glotch (2012). It is also the focus of this thesis. Fairén et al. (2010) created a model after calculating the temperature increases in craters that result from impacts. Their model indicates that, depending on the size of the impactor and the dryness of the surface it impacts, temperatures can increase as much as 1300°C. Understanding how the minerals are affected by high temperatures is crucial to fully understanding how Mars evolved over the past 4.5 billion years.

**Figure 4.** Phyllosilicates are denoted by red in the above images. The top image is a global map of phyllosilicates from the OMEGA instrument. The bottom image is the same map overlain on an altitude reference map from the MOLA instrument onboard Mars Global Surveyor (Bibring et al., 2006). The presence of clays indicates a very different environment than what we see on Mars today.
Figure 5. When MRO reached Mars, it expanded the area and diversity of phyllosilicates believed to be present on the planet as evidenced by the above figure from Ehlmann et al. (2011). The open polygons on the map indicate MRO targets where phyllosilicates were not found. The graphic beside the map gives the “percentage frequency of detection of alteration phase(s) grouped by geologic setting”, while \( n \) is the total number of images where clay minerals were detected. Iron- and serpentine-phyllosilicates are found in abundance on Mars.

All phyllosilicates form in the presence of water. Many, such as smectite and kaolinite form primarily due the settling of small weathered particles in lakes and other water bodies (Michalski and Noe Dobrea, 2007). Other phyllosilicates, such as serpentinite, form from the hydrothermal alteration during impact events or volcanic activity of basaltic minerals, including olivine and pyroxene, both of which are abundant on Mars (Bibring et al., 2006; Guggenheim and Eggleton, 1998; Poulet et al., 2005; Rasmussen et al., 1998; Schwenzer and Kring, 2009). Clearly, water once played a critical role on Mars. How exactly the different minerals formed on Mars has not been definitively determined.

Each process holds different implications for the history of the planet. If the minerals formed from the settling of weathered particles as suggested by Michalski and Noe Dobrea (2007), then
water had to have once flowed across the planet in streams and rivers and had a site to settle. Information about the conditions of the Noachian can be gained from the clays if this was the formation pathway (Chevrier et al., 2007). Indeed, MRO images have indicated ancient stream channels, deltas, and possibly lakes. If the phyllosilicates form from the alteration of mafic minerals through hydrothermal activity, then the minerals may not be as old as currently believed (Fairén et al., 2009; Gavin and Chevrier, 2010). Understanding how the clay minerals and their spectral signatures evolve with through different alterations is crucial to determining their true age as well as re-creating the complex history of Mars.

B. MINERALS ANALYZED

Greenalite

Greenalite is an iron-II rich serpentine mineral. The serpentine mineral group, which also includes crysotile and antigorite, forms by low-grade metamorphism and from the hydrothermal alteration of ultra-mafic rocks (Guggenheim and Eggleton, 1998; Rasmussen et al., 1998). As water, which can be from an existing ground water source, precipitated and infiltrated from the atmosphere, or residual water during the cooling of a pluton, is heated and interacts with the rock, it alters the olivine and pyroxene minerals present and forms serpentine. The composition of the serpentine will largely depend on the composition of the parent rock. If the pluton it is altering is largely composed of forsterite or a magnesium-rich pyroxene, the serpentine mineral formed will most likely be either antigorite or chrysotile. If, however, the pluton is composed of fayalite or an iron-rich pyroxene, greenalite is likely form. Other factors that influence the type of serpentine formed are metamorphic environment, including temperature and pressure, and what other constituents the altering fluid already possesses. Greenalite forms in low- to medium-
grade metamorphic environments with temperatures estimated to be at a maximum of approximately 340°C (Rasmussen et al., 1998). The heat for the reactions can come from a variety of sources including igneous activity, a geothermal gradient, or meteorite impacts. The temperature and time period of heating depends on the initial temperature of the igneous body, the activity rate (slow rising pluton versus explosive volcano versus meteorite impact), and the properties of the surrounding bedrock.

Greenalite, a layered silicate, is composed of one octahedral sheet joined to one tetrahedral sheet. The arrangement is referred to as a 1:1 layer ratio or as TO. More complex phyllosilicates have 2:1 ratios, meaning there are two tetrahedral sheets to one octahedral sheet, and are often referred to as TOT type minerals.

The octahedral sheets in phyllosilicates consist of two closely packed planes of cations, iron-II in the case of greenalite, and hydroxide. The tetrahedral sheet is composed of units containing a silicon atom surrounded by four oxygen atoms. Three of the oxygen atoms surrounded the silicon at its base and are known as basal oxygens and are shared throughout the sheet’s structure. The fourth oxygen bonds to the top of the silicon. It is known as the apical oxygen. The two sheets are held together by weak forces, including van der Waals and hydrogen bonding.

Greenalite is considered trioctahedral because it possesses three iron-II atoms in each base unit of its octahedral layer. The three iron-II atoms are bonded with four hydroxide groups making up the layer. The result is a net charge of plus two, which is neutralized when the tetrahedral layer, unit composition being two silicon atoms and five oxygen atoms and a net negative two charge, is adjoined to it. The resultant base unit for greenalite is Fe₃Si₂O₅(OH)₄ (Gaines et al.,
1997a). It should be noted that while most the cations in greenalite are iron-II, there are typically trace amounts of iron-III in the structure as well (Guggenheim et al., 1982).

The sample of greenalite used in the study came from the San Valentin mine, Cartenga district outside of La Union, Murcia, Spain. The location was used as a lead, zinc, and iron mine. The greenalite formed in the late Tertiary in a hydrothermal environment one of the results of the replacement of limestone by fayalite, which was then replaced by greenalite and minnesotiate (Guggenheim et al., 1982). The sample used was procured from the Excalibur-Cureton Company.

Visual inspection of the mineral indicated a fairly pure sample with traces of galena. X-ray diffraction analysis by Guggenheim et al. (1982) indicated a fairly pure sample with an excess of silica in greenalite samples retrieved from the same mine. A lack of mid-infrared and near-infrared spectra of greenalite prevented a full confirmation via infrared spectra.

Further visual inspection of the mineral shows a dark green, microcrystalline sample. During crushing it was moderately difficult to break but was not overly difficult to crush to the proper size. The powder was lighter in color than the uncrushed sample. The sample did not exhibit any cleavage (Figure 6).
Greenalite in crystal form lacks definite cleavage (a) and is darker than its crushed powder form (b). Pictures taken by author on May 4, 2013 in the Old Museum Building at the University of Arkansas.

Some of the spectra from Mars taken by the CRISM instrument onboard the Mars Reconnaissance Orbiter spacecraft indicate the possible presence of this phyllosilicate on Mars, making its analysis important to understanding the planet (Chevrier et al., 2007; Elhmann et al., 2009). Furthermore, the mineral’s iron is in the reduced state, which is common when in banded iron formations. Banded iron formations occurred billions of years in the past on Earth during a time that free oxygen was not as abundant as it is now. The low abundances of free oxygen in Earth’s past correlate to early Mars when it is believed that free oxygen was also not very abundant, making greenalite an important mineral to analyze and compare with Mars (Jakosky and Phillips, 2001; Mel’ink, 1986, Blatt et al., 2006).

**Hisingerite**

Hisingerite is believed to be a poorly crystalline hydrated iron silicate. Since its initial investigation in 1810 by Hisinger, it has been attributed to a variety of different sources and associations, including that of the iron-III phyllosilicate mineral, nontronite, and halloysite, an aluminum serpentine mineral (Eggleton and Tilly, 1998; Hisinger, 1810; Manceau et al., 1995).
Kohyama and Sudo (1975) state that it is possible that ferrous iron exists in hisingerite, but X-ray diffraction studies, done by Eggleton and Tilly (1998) among others, of the original samples that led to the discovery and identification of hisingerite as a mineral, revealed a minimal to nonexistent presence of iron-II in the mineral.

Debate has raged in the literature as to the exact identifiers of the mineral. Ultimately, it is believed that the mineral is microcrystalline to amorphous, has resinous luster, and conchordial fracture patterns (Eggleton and Tilly, 1998). The mineral’s color ranges from brown to black. It is believed to primarily form from the weathering of iron-rich minerals such as olivine and pyroxene. It should be noted that it can also be deposited in hydrothermal environments (Kohyama and Sudo, 1975).

Eggleton and Tilly’s 1998 study using the original samples analyzed by Hisinger and others indicate the mineral is rich in water and easily absorbs it from the atmosphere. Their experiments show that, although the mineral will begin releasing its water at fairly low temperatures, it takes high temperatures to fully dehydrate the mineral. They state that after heating to 125°C for two hours, a weight loss between four and nine percent occurs. Residual water remains in the mineral until it has been heated to approximately 750°C. A more thorough analysis of the water loss data shows that there are two primary temperatures at which water loss occurs, 125°C and 330°C. Their analyses also confirm the hypothesis that the structure of hisingerite is a 1:1 tetrahedral-octahedral sheet ratio, which they relate to smectite and kaolinite. They note that in the samples they studied, the mineral is more abundant in silicon than the octahedral cations. The base formula for this fibrous, amorphous poorly crystalline mineral is written as: (Fe, Mn)SiO3, Fe2+Si2O7(OH)4 · 2H2O (Gaines et al., 1997b).
The hisingerite sample analyzed in my study was retrieved from the Agnew Nickel Deposit near Leinster, W.A., Australia. It was procured from the Excalibur-Cureton Company. It appears mostly as a brown mass with indistinguishable crystals. It has a metallic luster. Upon handling, the mineral felt very friable, and I felt as though the mineral could be broken and by hand without needing the use of excessive force. When placed in the mortar, it quickly crushed to a fine powder, its brown color lightening slightly. As was the case with greenalite, no cleavage was exhibited by hisingerite (Figure 7).

![Figure 7. Hisingerite in crystal form lacks definite cleavage (a) and is darker than its crushed powder form (b). Pictures taken by author on May 4, 2013 in the Old Museum Building at the University of Arkansas.](image)

Infrared spectra were unobtainable for this mineral, preventing confirmation. The infrared analysis I completed of hisingerite will aid determining the thermal alteration properties of the mineral, as well as aiding in understanding the present state of Mars as well as the reconstruction of the planet’s past.
C. METHODOLOGY

Experimental Protocol

The selected minerals were crushed and ground to a fine powder, sieved to remove any particles larger than 63 µm, and placed in a Lindberg high-temperature tube oven for heating prior to near- and mid-infrared spectra acquisition.

A rock hammer was initially used to break the minerals into pieces small enough to fit in a ceramic mortar. Approximately 1-3 grams of sample were put in the mortar at a time. Using a pestle, the mineral was further crushed and ground into a very fine powder.

Once the sample appeared to consist of mostly, if not entirely, fine powder, it was placed in a sieve and shaken for 10 minutes. Only the particles 63 µm and smaller passed through the filter. The filtered sample was weighed and placed in a labeled plastic storage tube to await heating.

The larger sample, which did not pass the size test, was weighed and either returned to the mortar and crushed again or placed in a labeled storage to tube to await further crushing. Weight measurements were taken before and after every sieve session.

Approximately 0.40 g of the sieved sample was placed in a high-temperature ceramic tube in a Lindberg high-temperature tube oven at predetermined temperatures for approximately 24 hours. In order to ensure proper temperature, the oven was turned on to specific settings, as denoted on the control dial, and allowed to warm for 2-4 hours without a mineral present in the tube. After sufficient warming time, a temperature probe was inserted into the tube, and the temperature was recorded. When the settings for approximately 500, 700, 900, and 1100 degrees Celsius were found, the heating portion of the experiment could begin. When the calibrated temperature was
lower or higher than my desired temperature by less than 30°C, adjustments of the setting, typically 0.10 of a setting were made without re-calibration.

Following heating, the oven and sample inside were allowed to cool for at least 12 hours before the sample were removed and weighed. It should be noted that it was not possible to remove all of the inserted samples from the tube. Mass loss of <0.01 g is estimated. The cooled samples were weighed and placed in small labeled plastic storage tubes.

**Spectra Acquisition Protocol**

Fourier transform infrared (FT-IR) reflectance spectra in the mid-infrared and near-infrared ranges were taken using a Nicolet 6700 Smart Diffuse spectrometer. Two sets of procedures were used; one for the near-infrared collection, the other for mid-infrared collection.

The Smart Diffuse Reflectance Accessory, DTGS detector, quartz-halogen (white light) source, and calcium fluoride (CaF$_2$) beam splitter were used to collect the near-infrared spectra. OMNIC was the computer program used. The experiment set up in the program was modified to use the parameters previously mentioned as well as the following: 400 scans at a resolution of 2 cm$^{-1}$ and a wavenumber range between 12500 and 2000 cm$^{-1}$. A spectralon background was taken before each sample. The collection was done under a flow of $N_2$ at ~30 psi.

The mid-infrared spectra collection used the same basic procedures as the near-infrared spectra collection. Modifications were needed to collect the proper part of the electromagnetic spectrum. These changes are: potassium bromide (KBr) use of a beam splitter, use of the Ever-Glo (infrared) source, a wavenumber range of 7400-350 cm$^{-1}$, and gold as the background.
Once the spectra were taken, they were converted from wavenumbers to µm using an automatic conversion in OMNIC. An automatic smoothing function in the program cleaned up noise that was present, enabling the proper identification of peaks. The peaks were identified using another tool in the program and by visual inspection. The source of the peaks is based upon the literature in combination with knowledge of the minerals’ compositions, formation, and associated minerals. Band depths were collected using a tool in the OMNIC software.

The peaks are the bonds inside the mineral, and their behavior, i.e. becoming shallower or deeper and shifting to higher or lower wavelengths, indicates how the mineral changes as it is subjected to progressively higher temperatures.

D. RESULTS

Color Change

The crushing and heating processes changed the color of both minerals. Greenalite prior to crushing was dark green. The apparent color of the mineral changed to olive gray (5Y/5/2) color (Munsell, 1954). When heated to 500°C, greenalite changed to a dark reddish brown color (5YR/3/4) (Table 1). All subsequent heated samples changed color to the red with varying degrees of intensity. The highest heated sample was heated to 1070°C and appears be deep red, almost brown, dark reddish brown (2.5YR/2/4) according to Munsell (1954).

Hisingerite prior to crushing was a brown, non-crystalline mass. The color of the crushed, unheated sample is light olive brown (2.5Y/5/4). Upon heating, the mineral oxidizes and becomes dark reddish brown (5YR/3/4) (Munsell, 1954). The color becomes more distinct at higher temperatures (Table 1). The highest temperature that a hisingerite sample was heated and removed from the ceramic tube is 920°C. The color is dark red (2.5YR/3/6) (Munsell, 1954).
<table>
<thead>
<tr>
<th>MINERAL</th>
<th>TEMP (°C)</th>
<th>HUE</th>
<th>VALUE</th>
<th>CHROMA</th>
<th>COLOR DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenalite</td>
<td>Unheated</td>
<td>5Y</td>
<td>5/</td>
<td>2</td>
<td>Olive gray</td>
</tr>
<tr>
<td>Greenalite</td>
<td>500</td>
<td>5YR</td>
<td>3/</td>
<td>4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>Greenalite</td>
<td>765</td>
<td>5YR</td>
<td>4/</td>
<td>6</td>
<td>Yellowish red</td>
</tr>
<tr>
<td>Greenalite</td>
<td>900</td>
<td>2.5YR</td>
<td>3/</td>
<td>6</td>
<td>Dark red</td>
</tr>
<tr>
<td>Greenalite</td>
<td>1070</td>
<td>2.5YR</td>
<td>2/</td>
<td>4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>Unheated</td>
<td>2.5Y</td>
<td>5/</td>
<td>4</td>
<td>Light olive brown</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>500</td>
<td>5YR</td>
<td>3/</td>
<td>4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>710</td>
<td>2.5YR</td>
<td>3/</td>
<td>4</td>
<td>Dark reddish brown</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>920</td>
<td>2.5YR</td>
<td>3/</td>
<td>6</td>
<td>Dark red</td>
</tr>
</tbody>
</table>

Table 1. Color change occurs as the minerals are heated to high temperatures. Hue, value, chroma, and color description are from Munsell (1954).

It should be noted that a sample of hisingerite was placed in the oven to be heated to approximately 1100°C, but a malfunction with the oven caused the sample to heat to 1190°C at the time of temperature acquisition. The sample was hot enough that it entirely melted and during the subsequent cooling, became adhered to the ceramic tube. Attempts to scrape out the sample, entirely or in part, were unsuccessful. Observation of the sample is limited due to the small diameter of the tube. What is apparent is a glassy texture with small circular pockets that are believed to be the signature of volatiles escaping the mineral. A light was used to illuminate the tube, which aided in observation. Using the flashlight, the sample appears to have oxidized, but the degree of oxidation cannot be confirmed or determined.

Weight Loss During Heating

A table of the weight loss incurred during heating can be seen in Table 2. The greenalite samples lost between 9 and 17.5% depending the temperature heated to. Until the 1070°C sample, a trend suggested that the higher the temperature the mineral was heated to, the greater the mass loss.
<table>
<thead>
<tr>
<th>MINERAL</th>
<th>TEMP (°C)</th>
<th>INITIAL MASS (g)</th>
<th>FINAL MASS (g)</th>
<th>MASS LOSS (g)</th>
<th>WEIGHT LOSS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenalite</td>
<td>500</td>
<td>0.41</td>
<td>0.37</td>
<td>0.04</td>
<td>9.76</td>
</tr>
<tr>
<td>Greenalite</td>
<td>650</td>
<td>0.39</td>
<td>0.34</td>
<td>0.05</td>
<td>12.82</td>
</tr>
<tr>
<td>Greenalite</td>
<td>765</td>
<td>0.40</td>
<td>0.34</td>
<td>0.06</td>
<td>15.00</td>
</tr>
<tr>
<td>Greenalite</td>
<td>900</td>
<td>0.40</td>
<td>0.33</td>
<td>0.07</td>
<td>17.50</td>
</tr>
<tr>
<td>Greenalite</td>
<td>1070</td>
<td>0.42</td>
<td>0.36</td>
<td>0.06</td>
<td>14.29</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>500</td>
<td>0.41</td>
<td>0.35</td>
<td>0.06</td>
<td>14.63</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>710</td>
<td>0.40</td>
<td>0.35</td>
<td>0.05</td>
<td>12.50</td>
</tr>
<tr>
<td>Hisingerite</td>
<td>920</td>
<td>0.41</td>
<td>0.33</td>
<td>0.08*</td>
<td>19.51</td>
</tr>
<tr>
<td>Hisingerite**</td>
<td>1190</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Mass loss occurs during the heating process. *A minor amount of mass loss occurred when the temperature probe was dropped in the sample while in the oven. **The oven was hotter than predicted. As a result, the sample melted itself to the tube and none of the sample was recovered.

Hisingerite has a weight loss between 12.50 and 14.63% weight loss. A small portion of the final sample was lost when the tool used to put the sample in the hot oven was dropped. Due to risk of contamination, the portion that fell off of the tube was discarded. An estimate of this weight loss is approximately 0.03 g.

**Band Depths**

When we look at band depths, we are seeing the amount of energy being absorbed by different bands in the minerals’ structures. High reflectance indicates a small amount of the incoming infrared radiation or white light, depending on the light source, is absorbed by the bands, thus the bands are not prominent. Low reflectance, however, indicates that the bond is absorbing a significant amount of the incoming energy, and thus the bonds are strong and prevalent at those wavelengths. A table of band depths for mineral and temperature can be seen in Tables 3-6.
<table>
<thead>
<tr>
<th>Greenalite-Unheated</th>
<th>Greenalite-500°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
<td>Band (µm)</td>
</tr>
<tr>
<td>1.400</td>
<td>0.169</td>
<td>1.930</td>
</tr>
<tr>
<td>1.920</td>
<td>0.209</td>
<td>2.320</td>
</tr>
<tr>
<td>2.345</td>
<td>0.580</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Greenalite-765°C</th>
<th>Greenalite-900°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
<td>Band (µm)</td>
</tr>
<tr>
<td>NO PEAKS DISCERNABLE</td>
<td>NO PEAKS DISCERNABLE</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Greenalite-1070°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
</tr>
<tr>
<td>NO PEAKS DISCERNABLE</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** Greenalite shows few peaks in the near-infrared segment of the spectrum.

<table>
<thead>
<tr>
<th>Greenalite-Unheated</th>
<th>Greenalite-500°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
<td>Band (µm)</td>
</tr>
<tr>
<td>2.785</td>
<td>1.375</td>
<td>2.935</td>
</tr>
<tr>
<td>6.095</td>
<td>0.496</td>
<td>4.265</td>
</tr>
<tr>
<td>8.745</td>
<td>0.241</td>
<td>6.050</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Greenalite-765°C</th>
<th>Greenalite-900°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
<td>Band (µm)</td>
</tr>
<tr>
<td>2.845</td>
<td>1.233</td>
<td>2.850</td>
</tr>
<tr>
<td>5.330</td>
<td>0.692</td>
<td>3.420</td>
</tr>
<tr>
<td>6.140</td>
<td>0.265</td>
<td>3.500</td>
</tr>
<tr>
<td>4.280</td>
<td>0.085</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Greenalite-1070°C</th>
<th>Depth (%) Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (µm)</td>
<td>Depth (%) Reflectance</td>
</tr>
<tr>
<td>4.385</td>
<td>0.141</td>
</tr>
</tbody>
</table>

**Table 4.** The band depths of greenalite’s mid-infrared spectra show the mineral’s evolution with increasing temperature.
### Table 5. Hisingerite’s near-infrared spectra provide more information than greenalite’s.

<table>
<thead>
<tr>
<th>Band (µm)</th>
<th>Depth (% Reflectance)</th>
<th>Band (µm)</th>
<th>Depth (% Reflectance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.415</td>
<td>0.640</td>
<td>1.915</td>
<td>2.102</td>
</tr>
<tr>
<td>1.920</td>
<td>2.261</td>
<td>2.310</td>
<td>1.866</td>
</tr>
<tr>
<td>2.310</td>
<td>1.133</td>
<td>2.400</td>
<td>0.545</td>
</tr>
<tr>
<td>2.400</td>
<td>0.321</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6. The mid-infrared spectra show hisingerite’s evolution with increasing temperature.

<table>
<thead>
<tr>
<th>Band (µm)</th>
<th>Depth (% Reflectance)</th>
<th>Band (µm)</th>
<th>Depth (% Reflectance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.905</td>
<td>1.818</td>
<td>NO PEAKS DISCERNABLE</td>
<td></td>
</tr>
<tr>
<td>2.205</td>
<td>1.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.305</td>
<td>2.554</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.390</td>
<td>0.945</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Greenalite Near-Infrared Spectra Description**

The steep slope at the front end of greenalite’s near infrared spectra is a key indicator that it is an iron phyllosilicate (Mustard et al., 2008) (Figure 6). The unheated sample has a shallow band at
1.4 µm, indicative of the presence of water. That band disappears in the subsequent samples. A doublet centered at approximately 2.3 µm is indicative of the presence of iron in the mineral (Bishop et al., 2002b, 2008b). Following the feature, the spectrum enters a negative slope.

**Figure 6.** The near-infrared spectra of the greenalite samples show both water and metal-OH bonds in the low temperatures before the mineral is transformed into an iron oxide, indicated by the featureless slope. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.

**Figure 7.** The near-infrared spectrum of hematite closely resembles the near-infrared spectra of heated greenalite (Clark et al., 2007).
The 500°C sample does not have a band at 1.4 µm or the doublet at 2.3 µm, but it does have a peak at 1.9 µm, likely from water reabsorbed following heating. The metal-OH doublet seen in the unheated sample is not present in this heated sample’s spectrum, but a small peak at 2.32 µm is present.

The 765°C, 920°C and 1070°C samples show no significant features, other than the steep slope. The steep, featureless slope is indicative of the mineral hematite, which is one of the minerals greenalite has decomposed into due to heating (Clark et al., 2007) (Figure 7). The clays studied in Fairén et al. (2010) all exhibited a similar absence of bands above 800°C, which the authors attribute to alteration into Fe-Mg-Al-rich silica glasses.

**Greenalite Mid-Infrared Spectra Description**

The mid-infrared portion of the electromagnetic spectrum covers from 2.5 µm out to 25 µm. The collection capabilities of the spectrometer enabled us to collect data from approximately 1.3 µm to approximately 25 µm. The collected spectra all flattened out and showed no information beyond approximately 9 µm. There was one exception to this, it being the 1070°C spectrum, which shows a new feature at 9.2 µm. Due to the flatness, lack of information, and to better view display the data, a cut was made in all spectra at 9 µm (Figure 8). Gavin and Chevrier (2010) made a similar cut. At the forward end of each spectrum, a cut at 2.5 µm was made, to avoid overlap with the near-infrared spectra of each sample.

At approximately 2.6 µm, the spectra, with the exception of the 1070°C spectrum, have an abrupt band appear. The slope is a straight drop. The band depth decreases significantly as the mineral was heated and disappears in the 1070°C sample. The center of the peak is at approximately 2.9
27 µm, which consistent with the location of the interlayer water band. The problem with assigning the band to interlayer in the case presented here is the continual appearance in the higher temperature samples. Greenalite being considered a hydrated mineral is expected display OH bands, which includes the 2.9 band. However, upon heating the signatures of the interlayer water should disappear. This leads to the hypothesis that there must be something else occurring at the wavelength. As seen in Figure 9, hematite and goethite have strong bands in the same location as interlayer water of phyllosilicates.

Figure 8. The mid-infrared spectra of greenalite show that with increasing temperature, the clay’s structure breaks down, forming an iron oxide and a high temperature quartz mineral. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.
Figure 9. The mid-infrared spectrum of hematite (A) and goethite (B) possess deep bands at approximately 3.0 μm, which matches well with the deep bands seen in the heated and thus oxidized minerals (Clark et al., 2007).
Figure 10. The mid-infrared spectra of the high-temperature samples of greenalite (A) indicate a strong presence of silica. One of the most apparent features is centered around 5.3 µm and is clearly seen in the silica spectra (B) from Salisbury et al. (1991). Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.

Beyond the 2.9 micron peak, the samples exhibit a negative slope. The unheated sample’s slope is not steep and ultimately culminates in a peak at approximately 6.2 µm, indicative of water in the sample. The 500°C sample remains relatively flat following the exit of the 2.9-micron peak. A band at appears at approximately 3.0 µm, which roughly corresponds with an upward feature in the unheated sample. The spectrum then enters into a deep peak at approximately 6.2 µm.
The 6.2 micron band is interesting because the depths do not consistently shallow or deepen with increasing temperature. The peak in the unheated sample is fairly shallow, at 500°C it is very deep, at 765°C it is once again very shallow, only to return to a deeper feature in the 900°C and 1070°C samples. Beyond the 6.2 micron band, the samples all show a negative slope of varying degrees. The reflectance of the samples nears zero percent at 9.0 μm.

The 765°C sample displays a new feature forming with a peak at 5.3 μm. The feature has “shoulders” and resembles a simple cosine feature graph. As the greenalite is further heated, the feature develops. At 900°C, shallow peaks form on either side of the main central peak; these peaks are centered at 4.9 and 5.6 μm. The sample of greenalite that was heated to 1070°C shows the accompanying peaks have deepened, the one at 4.9 μm more than 5.6 micron peak. The mineral formed is a high temperature form of silica, possibly cristobalite (Salisbury et al., 1991) (Figure 10).

The 900°C sample shows the start of a new feature between 4.2 and 4.5. The peaks are little more than dips along the negative slope of the spectra. When heated to 1070°C, though, the peak at 4.3 μm deepens. The feature is further evidence that silica is forming at the high temperature (Salisbury et al., 1991).

**Hisingerite Near-Infrared Spectra Description**

As with the greenalite near infrared spectra, a cut was made at 2.5 μm, eliminating everything beyond that point (Figure 11).

In the near-infrared, the unheated, 500°C, and 710°C samples start off with a sharp positive slope. The first peak for the unheated and 500°C samples appears at 1.4 μm and is due to the presence of water. The 1.4 micron peak does not appear in the 710°C or 920°C spectra.
At 1.9 µm, the unheated, 500°C and 710°C spectra display a peak, likely caused by reabsorbed water. The 920°C sample does not display this feature, which means the mineral’s structure has broken down to the point that water cannot reabsorb into the sample.

**Figure 11.** The near-infrared spectra of the hisingerite samples show both water and metal-OH bonds in the low temperatures before the mineral is transformed into an iron oxide. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.

A doublet centered at 2.3 µm indicates the presence of iron in the mineral (Bishop et al., 2002b, 2008b). At 710°C, the first half of the doublet, appears to be comprised of another doublet.
The 920°C sample displays few of the same features as the lower temperature samples. The steep slope is much shorter and transitions into a less steep almost concave upwards slope, indicating the presence of hematite (Figure 11B). At the high temperature, the mineral has most likely morphed into a high-temperature iron-rich glass (Fairén et al., 2010).

**Hisingerite Mid-Infrared Spectra Description**

As with greenalite, cuts at 2.5 µm and at 9 µm were made to preserve only the data between 2.5 and 9 µm (Figure 12). A broad band is seen in hisingerite-unheated, hisingerite-500°C, and hisingerite-710°C between 2.6 and 3.9 µm. This band is likely due to interlayer water in the unheated sample but is more likely indicative of goethite, an iron oxide, in the heated samples (Clark et al., 2007) (Figure 9). It is not present in the spectrum of hisingerite-920°C. The next prominent band in the spectra occurs at 6.2 µm. This band is attributed to reabsorbed water. While present in hisingerite-920°C, it is very shallow, which may indicate an incapacity of the mineral to reabsorb water in its structure. A new feature is seen forming at approximately 5.3 µm in hisingerite-920°C spectrum (Figure 13). This feature is believed to be silica forming, as seen in greenalite (Salisbury et al., 1991). Beyond the 6.2 micron band, the spectra display a negative slope that flattens out at approximately 8.0 µm.
Figure 12. The mid-infrared spectra of hisingerite show that with increasing temperature, the clay’s structure breaks down, forming an iron oxide and a high temperature silica mineral, possibly cristobalite. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.

Figure 13. The mid-infrared spectra of hisingerite heated to 920°C appears to have a feature forming at ~5.3 µm (in box of bottom image) indicative of quartz as seen in the silica mid-infrared spectra of quartz (Figure 10B).
E. DISCUSSION

**Spectra Comparison with Mars**

In 2005, Bibring et al., processed data from the Mars Express’ OMEGA instrument and found that data returned by the European Space Agency’s spacecraft had detected the spectral signature of phyllosilicates on the Red Planet. One year later, the Mars Reconnaissance Orbiter (MRO) entered orbit around Mars and cast its mechanical eyes on the surface of Mars. On the spacecraft’s list of mission objectives was to understand the presence and expanse of the hydrated, layered-silicate minerals. MRO discovered that the clay minerals are much more diverse and expansive than previously believed based off the OMEGA data (Bishop et al., 2008a; Mustard et al., 2008; Wiseman et al., 2008). Comparison of the near-infrared spectra returned from Mars with the near-infrared spectra collected in the lab allows for a direct correlation between the experimental data and the current state of Mars. Several spectra were compared with the laboratory gained spectra (Cuadros and Mickalski, 2013; Grindrod et al., 2012; Mickalski et al., 2013; Smith et al., 2013), while the spectra clearly indicate the presence of phyllosilicates, based primarily on the water bands at 1.4 and 1.9 µm, no spectra fit exactly with the laboratory gained spectra. A few did fit closely, though (Figures 14-15).
Figure 14. Spectrum 4 from Figure 6b (Mickalski et al., 2013) (a) can be correlated to hisingerite-unheated (Figure 11). Spectrum 1 from Figure 1 (Mustard et al., 2008) (b) can be correlated to hisingerite-710°C (Figure 11).
The CRISM 1 spectrum (Louizeau et al., 2012) (c) possesses similar features seen in both the low-temperature greenalite and hisingerite samples (Figures 6, 11) based upon the metal-OH bond’s location at approximately 2.3 µm. The spectrum on the bottom of the above figure from Davila et al. (2011) (d) resembles both the low-temperature greenalite and hisingerite samples (Figures 6, 11) based upon the metal-OH bond’s location at approximately 2.3 µm.

The other low-temperature spectra are similar to those returned from Mars, but have the metal-OH bond at a slightly higher wavelength. The laboratory gained spectra exhibited metal-OH bonds at approximately 2.3 µm, whereas the ones returned from Mars showed the bond at 2.2 µm.
While it cannot definitely said that hisingerite or greenalite are present on Mars, based upon the comparison between spectra returned from Mars and the spectra gained through experimentation, it is safe to safe that the possibility does exist for their presence on the planet. Ultimately, only direct observation, either through one of the rovers or human exploration, can confirm their existence on Mars.

**Greenalite Spectra Comparison with Hisingerite Spectra**

**Near-Infrared Spectra Comparison**

One of the objectives of this study was to understand how the minerals differ from one another. As previously stated, greenalite possesses few features in the near-infrared, and after heating to 500°C, the mineral becomes more or less featureless. Hisingerite, on the other hand, appears to be more resilient to heating when view in the near-infrared. When the two minerals’ spectra are compared with each other, we can determine the difference in evolution between an iron-II phyllosilicate such as greenalite and an iron-III phyllosilicate such as hisingerite.

![Figure 18. The unheated and 500°C near-infrared spectra of greenalite and hisingerite. Spectra are offset for clarity. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.](image-url)
The unheated near-infrared spectra of both possess a weak band at 1.4 µm. Hisingerite has a strong band at 1.9 µm; both bands are indicative of water. Greenalite has a band centered at approximately 2.35 µm, which is characteristic of the iron-OH bond. At the same wavelength, hisingerite has a positive feature, which is the center point between its iron-OH doublet (Figure 18).

When the samples are heated to 500°C, the 1.4 micron band mostly disappears, as does the iron-OH bond in greenalite. The 1.9 micron peak is still prominent in hisingerite and appears in greenalite; it is likely the result of reabsorbed water. The hisingerite spectrum still contains the strong iron-OH doublet at 2.35 µm (Figure 18).

When the samples are heated to over 700°C, greenalite becomes a featureless positive slope. Hisingerite, however, continues to maintain strong bands at 1.9 µm and the doublet at 2.3 µm (Figure 19). When heated to over 900°C, hisingerite’s peaks do not appear. Its spectrum becomes a general positive slope with a different morphology than greenalite’s (Figure 19).

Figure 19. The near-infrared spectra of greenalite and hisingerite heated at high temperatures. Spectra are offset for clarity. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.
**Mid-Infrared Spectra Comparison**

In the mid-infrared, the unheated minerals possess very similar spectra, the primary difference being greenalite slightly higher reflectance and uneven peak at approximately 2.9 µm. This feature is likely the result of contamination from another mineral present during the crushing of the sample (Figure 20).

**Figure 20.** The unheated and 500°C mid-infrared spectra of greenalite hisingerite-710°C. Spectra are offset for clarity. Wavelength (µm) is plotted on the x-axis and reflectance is along the y-axis.
The near-infrared spectra of greenalite and hisingerite heated at high temperatures. E: greenalite-765°C; F: greenalite-900°C; G: hisingerite-710°C; H: hisingerite-920°C. Spectra are offset for clarity.

The spectra of the two minerals continue to remain very similar after the minerals have been heated to 500°C (Figure 20). The spectra begin to differ significantly once they have been heated to temperatures above 700°C (Figure 21). At the high temperature, the spectrum of greenalite begins to show the formation of high-temperature silica based on the peaks around 5.3 µm. These differences are more apparent when the minerals are heated above 900°C (Figure 21). The silica feature dominates the greenalite spectrum, while it is just beginning to appear in hisingerite’s.

F. SUMMARY AND CONCLUSIONS

Two hundred and fifty million miles away in space, a dusty red planet one-third of the size of the Earth remains one of the most explored targets in our solar system. The planet has captured the attention of astronomers, scientists, and explorers for centuries. During the last decade, however, what we know about the planet has changed drastically. In 2003, the Mars Express orbiter began
studying the planet. One of its instruments, OMEGA, returned data that led to the discovery of phyllosilicates on Mars (Bibring et al., 2005). Phyllosilicates form in the presence of water, either due to mechanical weathering and deposition of sediment or by the hydrothermal alteration of parent rocks. Among the type of phyllosilicates discovered are iron-rich clays (Ehlmann et al., 2011).

Two of these iron-rich clays, greenalite and hisingerite, were heated to temperatures mimicking lava flows and impact events to understand how the minerals break down with increasing temperature and to aid in determining whether clay minerals formed during the Noachian or in impact-induced hydrothermal systems formed since. Following heating, the near-infrared and mid-infrared spectra were taken of each sample, along with an unheated sample of each mineral. The spectra reveal how the chemical bonds inside the minerals change with increasing temperature. It was found that both minerals break down into an iron oxide, likely hematite, and silica. A release of volatiles also occurs during heating.

After processing, the near-infrared spectra of each mineral were compared with spectra from Mars to understand if the minerals are present in either their unaltered or altered states. A definite determination cannot be made due to a lack of clarity with the MRO and Mars Express spectra; however, it is likely that unheated hisingerite and unheated greenalite, along with their altered forms at 500°C and 710°C (hisingerite) and 500°C (greenalite) are present on the surface. Hematite is also known to be present on the surface, as is pure silica (Webster, 2011).

The question still persists of the exact timing and mechanism of the clay formation, though. Did they form in the Noachian from the settling of particles from surface water and the hydrothermal systems during magmatic events or did they form later in the planet’s life, the result of impact-
induced hydrothermal activity? Studying the spectra of how the minerals change can help answer that question (Fairén et al., 2010; Schwenzer and Kring, 2009).

The implications for the timing and mechanism of formation are significant. If the clays formed during the Noachian, then Mars was likely once a warm wet planet for significant amounts of time (Fairén et al., 2010). If, however, the clays formed as the result of impact-induced hydrothermal activity, then it is possible that the planet cooled much quicker than previously believed (Schwenzer and Kring, 2009). The research presented, aims at helping answer the question by presenting data about the evolution of two clay minerals, greenalite and hisingerite, heated to temperatures seen in impact events.
III. BIBLIOGRAPHY


