The Case for Photothermal Spectroscopy in the Future of Planetary Science Missions

Christopher T. Cox

University of Central Florida
THE CASE FOR PHOTOTHERMAL SPECTROSCOPY IN THE FUTURE OF PLANETARY SCIENCE MISSIONS

by

CHRISTOPHER TYLER COX
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ABSTRACT

Optical PhotoThermal InfraRed (O-PTIR) is a relatively new spectroscopy method for studying materials. It produces transmission-like spectra using a remote reflectance technique that is rapid, requires little sample preparation, and is well-suited for the technique to be adapted for a space flight instrument. The method involves a tunable pulsed IR laser creating a photothermal effect on the surface of a material and measuring the distortion of a probing visible laser in the same region of the sample, which can be obtained at sub-micron spatial resolutions. A measurement campaign was performed utilizing Photothermal Spectroscopy Corporation’s O-PTIR instrument, mIRage®. In this campaign, individual minerals were analyzed using the O-PTIR technique, and their spectra were compared to existing transmission and reflectance spectra. Additionally, Space Resource Technologies (SRT) soil simulant mixtures were also analyzed to attempt to determine mineral contributions to the mixtures’ spectra. Samples were prepared using cylindrical sample holders adhered to glass slides which could easily and cleanly be mounted into the instrument. Hyperspectral maps of various sizes (dependent on grain size) were made, and their spectra were averaged to produce a single spectrum for each mineral and mixture. Constituent material spectra were compared to available spectra based on spectral features and corresponding peaks. Similarly, various SRT simulants representative of lunar (LHS-2, LMS-2, and LSP-2) and martian (JHZ-1 and MGS-1) surfaces were analyzed as well as their constituent materials in order to determine the contribution each mineral makes to the simulant mixture. It was found that data produced with the mIRage® instrument closely resembled transmission spectra in most cases and shared spectral shapes with reflectance spectra at mid-IR wavenumbers (980 - 1800 cm⁻¹). Further, the instrument’s performance was found to outperform commonly used techniques regarding speed, in some cases spatial resolution, and a reduced need for sample preparation. This work will support future prototyping of an instrument for in situ material analysis.
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CHAPTER 1: INTRODUCTION

Optical PhotoThermal InfraRed (O-PTIR) spectroscopy is a relatively new method of spectroscopy (Spadea et al., 2021). It is used in other fields (i.e. plastics and life sciences) but here I present the first case of its use in planetary science. In this chapter, I will present a science case for this thesis in Section 1.1, background on the technique in Section 1.2, and describe the instrument I used in Section 1.3. Additionally, I described other comparable forms of spectroscopy in Section 1.4 and existing data for minerals in the mid-IR in Section 1.5 which will be relevant later in this thesis.

1.1 Science Motivation

From previous analyses of meteorites and returned samples (Apollo program, stardust, Hayabusa, OSIRIS-REx, etc.), it is known that materials of planetary small bodies (i.e. asteroids and comets) are well mixed down to the micron level. This makes analysis of these bodies difficult. Ground-based observations have a natural limitation of low-spatial resolution. These limitations make disentangling of chemical and structural properties impossible in the spectra. Another method of obtaining these measurements is through remote sensing which includes fly-by missions and orbiter spacecraft. This method has a significantly better spatial resolution as it is not limited by the target’s distance from Earth. However, the complexity of the composition that produces the spectra measured makes inferences about chemical composition (e.g. Matteson & Herron, 1993; Ramer & Lendl, 2006) and surface structure (e.g. Martin et al., 2018; Rossman & Ehlmann, 2019) difficult. This leads to in-situ analysis. Previous in-situ studies have involved landers on Mars and asteroid sample return missions among others. These missions are equipped with instrument suites designed to accomplish the missions’ goals. Existing instruments that study chemical analysis for this purpose are plentiful and include imaging spectrometers (ex. CRISM) and mass spectrometers
(ex. SAM), but most current methods have limitations. The major limitations are spatial resolution, sample destruction, and hardware complexity. Further, sample return missions have complications specific to the mission type and the hardware it requires. Sample destruction and alteration are special issues here in that they can occur in the collection and transfer processes. The end goal of returning samples is to use state-of-the-art instrumentation for better analysis. These issues could be alleviated with a technique and instrument that could analyze planetary surface samples in situ, in a non-contact, non-destructive manner, with sub-micron resolution.

In addition to mineralogical studies, missions to distant bodies also have biological components (i.e. Viking Lander, Europa Clipper, etc.). Particularly, there is interest in studying prebiotic molecules and organics in the context of their environment. This combined with mineral study provides insight into the formation and evolution of these bodies and the Solar System. Organic involvement in particular will contribute to understanding the seeding and segregation of the building blocks of life throughout the Solar System’s history. Measurements with sub-micron resolution would allow the ability to distinguish differing evolutionary histories of in-situ materials (Ehrenfreund & Charnley, 2000; Tice et al., 2022). Cell sizes can range from sub-micron level to multiple microns so current existing limitations on spatial resolution make looking for cell structure difficult or impossible. Specifically, living cells on Earth are $\sim 1 \mu m^1$. This means that current spatial resolutions inhibit the search for life in the Solar System$^2$. Additionally, the issues of sample destruction discussed above also is an issue here. Destruction of the sample would destroy the prebiotic and organic materials in the sample also preventing detection and study.

Given the issues discussed here, it would be useful to have an in-situ method capable of performing non-contact chemical analysis at a sub-micron level and in a non-destructive manner. Additionally, the ability to scan areas versus individual measurement points with large gaps between has

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been highlighted as an advantage via the PIXL instrument on NASA’s Mars rover, Perseverance (Tice et al., 2022). ORIGINS (Organics and Regolith In-situ Grain Investigation using Near-range photothermal Spectroscopy) is a recently funded (NASA PICASSO) instrument concept that seeks to provide these capabilities. ORIGINS is currently using a commercially available instrument (mIRage®, described below) to collect data for later comparison of the new instrument concept. This thesis is focused on that data collection and analysis as it pertains to mineral identification and quantitative analysis of mixtures.

Figure 1.1: Interesting regions located in the wavenumber range 500 - 3600 cm$^{-1}$. The fingerprint region is highlighted in green. Functional groups are indicated as they appear in absorption features at a given wavenumber.

The wavenumber range that will be discussed here is 980 - 1800 cm$^{-1}$. This is due to the areas of interest within that range. The ”fingerprint region,” a region that contains many unique complex absorptions, lies in the 500 - 1500 cm$^{-1}$ (20.0-6.67 μm) range. This range is key to unambiguously identifying minerals and varying compounds. Several key mineralogical features lie specifically
in the 805 - 1300 cm$^{-1}$ (12.4-7.7 µm) range. Additionally, many functional groups (e.g., O-H stretches, C-H stretches, C=O stretches) lie in the region of 1500 - 3600 cm$^{-1}$ (6.67-2.78 µm) which is excellent for the detection of organic species. These ranges are depicted in Figure 1.1. Since, O-PTIR spectra are comparable to absorption spectra, identification and qualification of components should be possible. This is an improvement of the emission spectra typically measured on planetary surfaces. Further, I will classify the instrument’s capabilities and make a case for the use of O-PTIR (described below) in the future of planetary science by demonstrating the benefits of this method.

1.2 O-PTIR

The O-PTIR technique is based on the principles of thermal lens spectroscopy which is well described by Snook & Lowe (1995). O-PTIR is a pump-probe technique that utilizes the photothermal effect using two lasers: one in the IR (pumping laser) at the chosen frequency, and one in the visible (probing laser) to probe the thermal expansion of the sample (Bazin et al., 2022; Paulus et al., 2022). The IR absorption causes a photothermal effect on the target which consists of thermal expansion and a change in the index of refraction. The photothermal response that is measured is due to the changing intensity in the probe laser. O-PTIR spectroscopy is capable of producing FTIR absorption-like spectra at a sub-micron spatial resolution (Bazin et al., 2022). That is to say, the features and peaks of O-PTIR spectroscopy are commonly similar to FTIR absorption spectra. There have been many examples comparing this technique to FTIR absorbance and transmittance techniques to demonstrate its validity (i.e. Bazin et al., 2022; Zhang et al., 2016; Krafft, 2022) which have found strong correlations between the methods. O-PTIR spectroscopy utilizes the photothermal effect to push past the diffraction limit of traditional IR techniques and provides a significant increase in spatial resolution (Bazin et al., 2022; Paulus et al., 2022). O-PTIR is a
non-destructive method already in use by the life science community (Spadea et al., 2021, among others) and the microplastics community (Chen et al., 2022, among others). The spatial resolution and capability of this technique allow for the compositional study of materials on a cellular level. This allows for the specific study of individual grains within a mixture. This is important due to the ability to further study individual components of a larger mixture such as what would be measured by an orbiting remote sensing spacecraft. Additionally, the sub-micron resolution has advantages in astrobiology as it would allow for analysis into possible cell structures on foreign bodies.

1.3 mIRage® Instrument

Figure 1.2: Image of the mIRage® instrument. The optical camera, visible laser, microscope optics, and sample area are in the encasement imaged on the left. The tunable IR laser and IR optical path are in the encasement imaged on the right.
The mIRage® instrument (pictured in Figure 1.2) is an O-PTIR instrument that utilizes a probing visible laser (0.532 \( \mu m \)) and a tunable pulsing (pumping) IR laser (5.494 - 10.416 \( \mu m \); 1820 – 960 \( cm^{-1} \)). mIRage® produces a spectral measurement at each wavenumber the IR laser is tunable to, so it has a spectral resolution of 1 \( cm^{-1} \) and almost 900 spectral channels. A simplified version of the optical path is depicted in Figure 1.3. Both lasers are variable power lasers. The instrument is designed and produced by Photothermal Spectroscopy Corp.

![Simplified image of the optical path of the mIRage® instrument.](image)

**Figure 1.3:** Simplified image of the optical path of the mIRage® instrument. Infrared and visible lasers are directed to the same area of a surface for measurement using the O-PTIR technique. Image courtesy of Photothermal Spectroscopy Corps.

The sample is viewed using the instrument’s optical microscope and objective lenses. There are two objectives with varied magnification. The low objective has less magnification than the high objective and is used to find points of interest in a sample. When a point of interest is found, the microscope is switched to the high objective. The high objective has more magnification than the
low objective and is used to focus on the point of interest. The dual laser system passes through the high objective. The instrument produces measurements by emitting a visible laser into the distortion created by the IR laser. This photothermal effect is better described in Section 1.2. The visible laser reflects back into the detector and the difference of intensities is what produces the O-PTIR spectra that will be featured in Chapter 3. In the case of automated multiple measurements (i.e. a hyperspectral map), the instrument performs a quick and automated auto-focus prior to each individual measurement.

1.3.1 Instrument Power Settings

As described in Section 1.3, the measurements utilized varying power settings for both the visible laser and the IR laser. To make these measurements more comparable the power settings were characterized. Also, this characterization serves as a step to better the quantitative analysis that will be described in Section 3.3. The characterization was performed on the material anorthosite (results for anorthosite will be presented in Section 3.1.1). The characterization was performed by starting with the minimal power settings that produced signal then increasing the settings one at a time until the sample was damaged. For example, the probe power (power for the visible laser) was set to 3.5% and IR power was increased from 21% to 77% while taking a hyperspectral measurement at each setting. The probe power was increased and the process repeated. This repeated until probe power reached 37%. Settings past 77% IR power and/or 37% probe power caused damage to the sample.
Figure 1.4: Plotted data of the power analysis performed on the mIRage® Instrument. The plots labeled "Probe Power XX%" are plots of the max amplitude achieved with varying IR power. The plots labeled "IR Power XX%" are plots of the max amplitude achieved with varying probe power. The dotted lines shown are the lines of best fit for each plot. Equations for each line of best fit along with the corresponding $R^2$ value is shown on each plot.

Figure 1.4 shows plots of the data produced to analyze how the varying power of the instrument’s lasers affects the data produced by the instrument. The max amplitude achieved is plotted against given power settings. Cubic functions were applied for lines of best fit to achieve an $R^2$ value of 1. In the case of low power settings, the max amplitudes achieved were often tightly grouped. Higher power settings often produced increased signal and larger max amplitudes.
1.3.2 Instrument Repeatability

Figure 1.5: Mid-IR O-PTIR measurements of hydrated silica (left) and smectite. Both minerals have hyperspectral measurements presented in their respective subsections in Section 3.1. The measurements presented here are individual spectral measurements. For the hydrated silica, instrument settings were: 46% IR Power, 3.5% Probe Power, and 5x Detector Gain. For the smectite, instrument settings were: 21% IR Power, 2% Probe Power, and 10x Detector Gain. These measurements are not normalized to demonstrate the consistency in intensity in addition to spectral shapes and peaks. The hydrated silica measurements are offset by 8 and the smectite measurements are offset by 6 for ease of readability.

Figure 1.5 shows measurements of hydrated silica (left) and smectite (right) (both analyzed in their respective subsections in Section 3.1). Each set of measurements used the same power settings and location. These measurements were used to demonstrate the repeatability of the instrument. For each respective set of measurements, the spectra peak at the same locations, share spectral shapes, and almost every feature is present in each spectrum. This is a strong indicator that measurements
from the mIRage® instrument are consistent and repeatable. Even with extreme similarity, there are slight differences in the spectra shown. These differences could likely be attributed to the "turbulence" of the air between the emission of the laser to the top of the sample. This is also strong evidence of the non-destructive nature of the instrument and measurement technique.

1.4 Comparable Forms of Spectroscopy

In addition to O-PTIR, there are several other relevant forms of spectroscopy measurements. Among these are Fourier Transform InfraRed (FTIR) and Attenuated Total Reflection (ATR). FTIR are typically the most common in planetary sciences and are the most comparable to O-PTIR. FTIR instruments are typically divided into two categories, absorbance (the more comparable of the two) and reflectance. Absorbance is the measure of a material’s ability to absorb light and reflectance is the measure of the proportion of light that is reflected off the surface of a material. These measurements and their relationships will be discussed further below.

FTIR is a specific type of infrared spectroscopy and in some forms is capable of quantitative mineral analysis. The mineralogy of a mixture and the chemical structure of a single material can be extracted using FTIR (e.g. Matteson & Herron, 1993; Madejová, 2003; Chen et al., 2015). Additionally, it is a non-destructive form of chemical characterization of geological samples (e.g. Griffiths, 1983; Matteson & Herron, 1993; Chen et al., 2015). Sometimes the sample preparation can involve crushing and sieving materials, but the method itself is non-destructive (Farmer, 1974). In vibrational spectroscopy, FTIR works by measuring transitions of quantized vibrational energy states. This is particularly important in the mid-IR which is the range of focus for this thesis. Absorption of IR radiation when a molecule is excited to a higher energy state causes additional vibrations of molecular bonds which happens at varying wavelengths in the measuring region (Griffiths, 1983) (mid-IR in the case of this work). This method (FTIR Absorption) requires light
to pass through a sample. The optical properties of certain materials require this to be extremely thin ($< 50\mu m$). The thin material is typically accomplished using a pellet method which produces a "pellet" (also known as a "disc" or a "wafer") of material thin enough for some amount of light to pass through on the way to a detector (Farmer, 1974).

Photons must be conserved and are typically, transmitted, scattered (including reflection), or absorbed by a material. This means that at a given wavelength ($\lambda$), the total of these three features must equal 1 (absorbance$_\lambda$ + transmittance$_\lambda$ + reflectance$_\lambda$ = 1, or $A + T + R = 1$). For a black body, $A = 1$, $T = 0$, and $R = 1$. For a perfect window, $A = 0$, $T = 1$, and $R = 0$. For an opaque surface, $T = 0$ and $A + R = 1$. Additionally, absorbance and transmittance are always related by $A = -\log(T)$.

Beer’s Law, or Beer-Lambert Law, is a well-known relationship in spectroscopy. It describes a material’s absorbance of radiant energy. It can be represented as $A = \epsilon \cdot l \cdot c$. Here, $A$ is the absorbance, $\epsilon$ is the absorptivity, $l$ is the sample thickness (path length), and $c$ is the concentration of the sample. This relationship is what makes FTIR-A capable of quantitative analysis.

FTIR Reflectance (FTIR-R) techniques work similarly to FTIR Absorbance (FTIR-A) techniques (Chen et al., 2015). Unlike absorbance techniques, reflectance techniques do not require light to pass through the entirety of the sample. Exceptions exist, but in these cases, FTIR-R does not provide chemical information about an entire sample (Mustard & Glotch, 2019). However, this method (FTIR Reflectance) does still provide chemical information on functional groups distributed near the surface (Chen et al., 2015).
Figure 1.6: Concept of an ATR measurement. A crystal (black) is placed in contact with the sample (gold). An infrared source (red line) travels through the crystal and reflects back and forth through the crystal making multiple contacts with the sample before exiting the crystal. The evanescent wave (red triangle) is the electric component of the light propagating through the sample.

ATR (also known as ATR-FTIR) is a specific and common form of FTIR Reflectance. Figure 1.6 demonstrates the concept of an ATR measurement. There are several benefits of this technique including reduced required sample preparation and the ability to increase signal-to-noise ratios (SNR) (Ramer & Lendl, 2006). Particularly, SNR can be increased by increasing the signal’s interaction with the sample (i.e. the number of bounces/reflections off the sample). The number of bounces and the evanescent wave makes it difficult to quantize material with ATR.
1.5 Minerals in Mid-IR

In this work, I focus on the mid-IR range due to the features that exist within that range for organics and materials relevant to planetary science (i.e. anorthosite, basalt, and olivine). The minerals selected were chosen for their relevance to planetary sciences and their existence in the selected regolith simulants. In Section 1.1, I discuss the importance of features in the mid-IR. This thesis will focus on the wavenumber range 1800 – 980 $cm^{-1}$ (5.556 - 10.204 $\mu m$) due to limitations of the instrument discussed in Section 1.3.

These minerals are often well characterized in IR wavelengths and specifically in the wavelengths of interest for this thesis. Examples of this include multiple openly available databases. This work utilizes data from Infrared and Raman Users Group (IRUG)$^3$, SpectraBase$^4$, and U.S. Geological Survey (USGS)$^5$. These databases were selected for their open access and the availability of materials that overlapped with the materials analyzed in this thesis. Data from IRUG and SpectraBase are absorbance spectra and the data from USGS is reflectance data. Additionally, several minerals are discussed and described in *The Infrared Spectra of Minerals* (Farmer, 1974). The textbook and each above database include data that overlaps with the chosen wavelength.

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$^3$http://www.irug.org/search-spectral-database

$^4$https://spectrabase.com/

$^5$https://www.usgs.gov/
CHAPTER 2: METHODS AND SAMPLES

This work will demonstrate findings using technology (mIRage\textsuperscript{®} instrument) that is relatively new and utilizes the spectroscopy technique O-PTIR. This technique is not currently present in planetary science but has existed for a short time in other fields. This measurement campaign, using the aforementioned technology, produced mid-IR data for several minerals as well as mineral mixtures. In this chapter, I will describe the samples analyzed in this study (Section 2.1), how those samples were prepared for the purpose of analysis (Section 2.2), how the measurements were performed (Section 2.3), and how the data produced from those measurements were analyzed (Section 2.4). I will present the results in a later chapter.

2.1 Samples

Samples in this study are materials relevant to planetary sciences and mixtures that attempt to simulate foreign planetary surfaces. These samples include regolith simulants created and provided by Space Resource Technologies\textsuperscript{1} (SRT), the recent spin-off of the UCF Exolith Lab\textsuperscript{®} as well as constituent materials that make up these mixtures. The mixtures include lunar and martian regolith simulants. The constituent materials and mixtures will be discussed separately for ease of reading.

2.1.1 Constituent Materials

The simulant mixtures will serve as the primary focus of this thesis. Below, Table 2.1 lists each mineral that was characterized in this work. The most commonly accepted chemical formula is listed next to the material in the table. Some of these materials have entries in mid-IR

\footnote{\url{https://spaceresourcetech.com/}}
databases which are comparable to the data produced by the mIRage® instrument. The minerals with database entries (described above) used in this thesis are also denoted in the table.
Table 2.1: Chemical formulas of each constituent material used in the simulant mixtures analyzed in this thesis. Basalt’s chemical formula is left out since it is a rock and not a specific mineral. Anorthosite is also a rock but has a commonly accepted formula. Additionally, the materials with database entries are denoted with an ”x” in the respective database in which it has an entry. Database cells with hyphens indicate the mineral does not have an entry in that database.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
<th>IRUG</th>
<th>SpectraBase</th>
<th>USGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthosite</td>
<td>$CaAl_2Si_2O_8$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Basalt</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>x</td>
</tr>
<tr>
<td>Bronzite</td>
<td>$(Mg, Fe)_2Si_2O_6$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Fe-Carbonate (Siderite)</td>
<td>$FeCO_3$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>$Fe_{10}O_{14}(OH)_2$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$CaSO_4 \cdot 2H_2O$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Hematite</td>
<td>$Fe_2O_3$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Hydrated Silica</td>
<td>$H_{10}O_3Si$</td>
<td>–</td>
<td>x</td>
<td>–</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>$(Fe, Ti)_2O_3$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Magnetite</td>
<td>$Fe_3O_4$</td>
<td>–</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mg-Carbonate (Magnesite)</td>
<td>$MgCO_3$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mg-Sulfate (Epsomite)</td>
<td>$MgSO_4$</td>
<td>–</td>
<td>–</td>
<td>x</td>
</tr>
<tr>
<td>Olivine</td>
<td>$(Mg, Fe)_2SiO_4$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Smectite</td>
<td>$Al_2H_2O_6Si$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
2.1.2 *Simulant Mixtures*

In this section, I will discuss soil simulants by classification and then in alphabetical order. I will discuss what the constituent materials are for each simulant, their composition by weight, and the currently available work done for each simulant.

This laboratory experiment campaign utilized individual minerals as well as simulants produced by SRT Lab\(^2\). The individual simulants are described below.

\(^2\)https://spaceresourcetech.com/collections/all-simulants
Table 2.2: Compositions of each simulant mixture used in this thesis. Each component is given as a weight percentage. Cells with hyphens in them indicate the lack of presence of a given material in a simulant.

<table>
<thead>
<tr>
<th>Material</th>
<th>LHS-2</th>
<th>LMS-2</th>
<th>LSP-2</th>
<th>JHZ-1</th>
<th>MGS-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthosite</td>
<td>74.4</td>
<td>19.8</td>
<td>90.0</td>
<td>16.0</td>
<td>27.1</td>
</tr>
<tr>
<td>Basalt</td>
<td>24.7</td>
<td>32.0</td>
<td>10.0</td>
<td>13.5</td>
<td>22.9</td>
</tr>
<tr>
<td>Bronzite</td>
<td>0.3</td>
<td>32.8</td>
<td>–</td>
<td>12.0</td>
<td>20.3</td>
</tr>
<tr>
<td>Fe-Carbonate (Siderite)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Ferrhydrite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Gypsum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Hematite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrated Silica</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.4</td>
<td>4.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Magnetite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Mg-Carbonate (Magnesite)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>11.0</td>
<td>–</td>
</tr>
<tr>
<td>Mg-Sulfate (Epsomite)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Olivine</td>
<td>0.2</td>
<td>11.1</td>
<td>–</td>
<td>32.0</td>
<td>13.7</td>
</tr>
<tr>
<td>Smectite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>6.0</td>
<td>–</td>
</tr>
</tbody>
</table>
2.1.2.1 Lunar Regolith Simulants

Cannon & Britt (2019) created the Lunar Highland Simulant (LHS-1) and the Lunar Mare Simulant (LMS-1) using well characterized lunar samples as mineralogical references. These simulants were designed to replicate the geomechanical and geochemical properties of the regoliths they emulate. In this work, I present data on LHS-2 and LMS-2. According to the SRT’s website, the difference between LHS-1 and LHS-2 as well as LMS-1 and LMS-2 is a reduction of the mean particle size and an increase in the particle size distribution which was done to more closely match typical Apollo samples. In both cases, the simulants are identical mineralogically and chemically. Additionally, SRT created a simulant attempting to simulate the Lunar South Pole (LSP-2). This material was created using data presented in Lemelin et al. (2022) which reports individual components by potential percentages. The composition of LHS-2, LMS-2, and LSP-2 are presented in Table 2.2.

2.1.2.2 Martian Regolith Simulants

Similar to the lunar regolith simulants described above, the martian regolith simulants analyzed in this thesis (JHZ-1 and MGS-1) were created by SRT. These simulants were designed to replicate the geomechanical and geochemical properties of the regoliths they emulate. Mars Global Simulant (MGS-1) is intended to serve as a high-fidelity mineralogical analog to global basaltic regolith on Mars (Cannon et al., 2019). The mineralogy was determined using data from X-ray diffraction of the soil by the Mars Curiosity Rover. Jezero Crater Delta simulant (JEZ-1) was created to represent a more specific area on Mars, the Jezero Crater Delta (Yin et al., 2021). It was designed using data from the Mars Perseverance Rover and martian orbital remote sensing. JEZ-1 has a similar

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composition to MGS-1 but includes smectite, magnesite, and additional olivine (Yin et al., 2021). The composition of JEZ-1 and MGS-1 are presented in Table 2.2.

2.2 Sample Preparation

Though sample preparation is not required by the instrument, I prepared the samples for consistency in measurements and cleanliness of the instrument. To prepare the samples, cylindrical sample holders were 3D printed and adhered to glass slides that fit into the mIRage® instrument’s sample holder. This sample holder can be seen in Figure 2.1. The granular material was poured into a sample holder and flattened to reduce the height variation at the surface. The flattening process involved a light packing into the sample holder and then a straight edge was scraped over the surface of the sample holder. The packing was to prevent granules from shifting during transport and the straight edge was used to ensure a flat surface as well as allowing the container to be sealed.

2.3 Measurements

A measurement begins with the loading of a sample into the sample area (see Figure 2.1). The instrument is initialized and calibrated. The calibration process uses a known standard. A spectrum and heatmap are taken of the standard sample. The heatmap is a measure of intensity of the sample at a specific wavenumber. This baseline spectrum is used to show intensity of features and the level of noise in the system. The instrument software subtracts this background from each measurement. Humidity of the sample area, optimization of the alignment, and auto-focusing are also measured and calibrated as part of the calibration process. Background and calibration results are typically consistent but can change with varying humidity. Humidity is constantly monitored and if the humidity changed by more than 5%, the instrument was re-calibrated.
Figure 2.1: Image of the sample holder (left) and sample area of the mIRage® instrument (right). The sample holder is a 3D-printed cylinder adhered to a glass slide that fits into the sample area. The sample area is an optical stage designed to move the sample under the instrument’s microscope.

After calibration, the objectives are moved to be over the sample. To avoid damage and destruction of the sample, the power of the IR laser and visible laser are both adjusted per material. This information is recorded per spectrum. The power levels are adjusted until there is sufficient signal being returned to the sensors for both lasers. The higher the power in both lasers, the better the signal-to-noise ratio. Gain can also be used to increase the signal without increasing power and damaging the sample. Gain was also changed per material and was also recorded.

A single spectral measurement is taken of a single grain of a sample. A single grain is focused
on using the optical cameras and the high objective of the instrument. For the purposes of this thesis, a single spectral measurement will be a set of three spectra taken at a single point that are averaged together. The software for the instrument averages this set of spectra in real time into one spectrum. Multiple single spectral measurements are taken across an area of a sample to make sure no damage is being done to any part of a sample as this risk changes for different materials (for mixtures) within a sample. Once safety of the sample is ensured, a hyperspectral map is made of the sample. A hyperspectral map is, in this case, over 1000 individual hyperspectral measurements across the area of a sample. This is done to encapsulate multiple grains to account for issues from grain orientation, an issue demonstrated by Jaret et al. (2018); Martin et al. (2018); Pernet-Fisher et al. (2017), and to include multiple materials for mixtures.

2.3.1 Hyperspectral Maps

Figure 2.2 shows an example of a hyperspectral map used in this thesis. A hyperspectral map is a grid (in this case, evenly spaced) of hyperspectral measurements. For each point, a hyperspectral spectrum is produced and then the instrument moves the optical lens to the next location. The map that is produced from the grid of measurements is a sort of "heat map" where the map reflects intensity at a given signal. Since this is a hyperspectral map, the map can reflect intensity of the sample at multiple hundreds of wavenumbers.
Figure 2.2: Example image of a hyperspectral map used in this thesis. This map (78 x 78 µm, 2 µm spacing) is of bronzite (discussed in Section 3.1.3) and has a total of 1600 total hyperspectral points. The map took approximately 7 hours and 21 minutes to complete. The intensity of the signal is set to reflect the intensity of the various points in the map at 1017 cm$^{-1}$. The red areas are areas of most intense signal ranging down to purple being the least intense or no signal at the given wavenumber.
Figure 2.3: Mid-IR O-PTIR measurements of ilmenite. The solid black line is the measurement discussed in Section 3.1.9. The red line is a larger hyperspectral map of the same sample. "Larger" here means a larger measurement area with a similar spacing of measurements. For the smaller hyperspectral map (102 x 76 µm, 2 µm spacing, 2028 individual spectra), instrument settings were: 77% IR Power, 3.5% Probe Power, and 20x Detector Gain. The spectrum was normalized by a factor of 1.08 to be more visibly comparable to the larger map. For the larger hyperspectral map (635 x 475 µm, 5 µm spacing, 12288 individual spectra), instrument settings were: 60% IR Power, 3.5% Probe Power, and 20x Detector Gain. The spectrum was normalized by a factor of 100 to be more visibly comparable to the smaller hyperspectral map.
Figure 2.3 shows the mIRage® instrument measurements of two separate hyperspectral measurements of the same sample of ilmenite. The difference is a large difference in the number of points used to comprise the hyperspectral map. The larger map shows a peak at 1016 wavenumbers which is not seen in the spectrum of the smaller hyperspectral map. However, the peaks at 1033, 1448, 1468, and 1481 wavenumbers are all seen in both the spectrum produced by the small map and the spectrum produced by the large map. Additionally, the two measurements share very similar spectral shapes and the smaller map spectrum contains most features seen in the larger measurement. These similarities gave me the confidence to use fewer hyperspectral measurements to make hyperspectral maps for the purpose of this thesis. Additionally, the peak of the spectrum of the larger hyperspectral map was far more intense. This is likely due to the increased null space measured between grains.

2.4 Data Analysis

To analyze the data, I made hyperspectral maps (described in the previous section) and averaged the spectral points to produce a single spectrum. Again, this averaging is done within the software. These spectra were normalized to one to be more easily comparable to absorbance features from other forms of measurement. The normalization was done by finding the most intense peak and multiplying the entire spectrum by that value required to make the max intensity equal to one. A five-point-cubic Savitzky-Golay smoothing function was applied using system software (power of 3). Peaks were identified from this curve using the system’s software. Thresholds were set to distinguish peaks from noise in the measurement. Figure 2.4 shows a constituent material (anorthosite) plotted with the measurement and error bars. The error bars are the standard error of mean. With the error bars, the peaks are still visible and stand out against the noise. The measurement itself will be further discussed in Section 3.1.1. For constituent materials, this was the end
of the analysis unless there was a database entry I could utilize for comparison. If I could locate a database entry, I plotted the database data and overplotted the data produced by the mIRage®. This serves as a sort of demonstration that O-PTIR produces "transmission-like" spectra, as also demonstrated by Bazin et al. (2022).

![Hyperspectral Map Spectrum with Errorbars](image)

**Figure 2.4:** Plot of the hyperspectral map spectrum of anorthosite plotted with the standard error of mean error bars.

For simulant mixtures, I plotted mIRage® instrument measurements of the materials. I then correlated peaks and features from constituent materials of those simulant mixtures to the spectra they
produced.
CHAPTER 3: RESULTS

Using the measurement methods described in Chapter 2, I produced results for regolith simulants (lunar and martian) as well as the individual constituent materials that compose those simulant mixtures. In this chapter, I will present the mid-IR spectra for several materials (section 3.1) and regolith simulants (section 3.2). Spectra are presented as normalized spectra for an easier visual comparison. The "normalization factor" listed in each caption and in Table 3.1 indicates a spectrum was multiplied by that number to normalize the spectrum to one. Additionally, I will highlight the presence of constituent materials in the spectra of the regolith simulants. I will also identify the effects each material has on the simulant as the data suggests.
Table 3.1: Run information for each material analyzed in this thesis. Each subsection will have this information presented, but it is summarized in this table for ease of reference. "Peak Height" refers to the maximum unnormalized peak measured in the sample, "NF" (Normalization Factor) is what each spectrum value was multiplied by to normalize to one for visual comparison purposes, "IR Power" and "Probe Power" indicate the power setting of the respective laser, "HS Map Length" and "HS Map Width" refer to the size in microns of the hyperspectral map made of the sample, "Spacing" refers to the distance in microns between each measurement that composed the map, "THP" (Total Hyperspectral Points) is the total number of measurements in a given map. The hyphens in the Normalization Factor column indicate spectra that were not normalized due to not having a need for visual comparison. This would mean there was no database entry available for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak Height</th>
<th>NF</th>
<th>IR Power (%)</th>
<th>Probe Power (%)</th>
<th>Gain (x)</th>
<th>HS Map Length (µm)</th>
<th>HS Map Width (µm)</th>
<th>Spacing (µm)</th>
<th>THS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthosite</td>
<td>1.089</td>
<td>0.92</td>
<td>46</td>
<td>3.5</td>
<td>10</td>
<td>612</td>
<td>468</td>
<td>12</td>
<td>2080</td>
</tr>
<tr>
<td>Basalt</td>
<td>0.137</td>
<td>7.30</td>
<td>21</td>
<td>3.5</td>
<td>20</td>
<td>225</td>
<td>210</td>
<td>5</td>
<td>1978</td>
</tr>
<tr>
<td>Bronzite</td>
<td>13.178</td>
<td>0.08</td>
<td>5</td>
<td>3.5</td>
<td>10</td>
<td>78</td>
<td>78</td>
<td>2</td>
<td>1600</td>
</tr>
<tr>
<td>Fe-Carbonate (Siderite)</td>
<td>37.979</td>
<td>0.03</td>
<td>10</td>
<td>0.43</td>
<td>50</td>
<td>120</td>
<td>84</td>
<td>3</td>
<td>1189</td>
</tr>
<tr>
<td>Ferrhydrite</td>
<td>0.011</td>
<td>–</td>
<td>60</td>
<td>2</td>
<td>20</td>
<td>588</td>
<td>432</td>
<td>12</td>
<td>1850</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.033</td>
<td>30.30</td>
<td>60</td>
<td>2</td>
<td>10</td>
<td>576</td>
<td>408</td>
<td>12</td>
<td>1715</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.145</td>
<td>6.90</td>
<td>46</td>
<td>2</td>
<td>20</td>
<td>600</td>
<td>444</td>
<td>12</td>
<td>1938</td>
</tr>
<tr>
<td>Hydrated Silica</td>
<td>15.048</td>
<td>–</td>
<td>21</td>
<td>3.5</td>
<td>10</td>
<td>612</td>
<td>444</td>
<td>12</td>
<td>1976</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.924</td>
<td>1.08</td>
<td>77</td>
<td>3.5</td>
<td>20</td>
<td>102</td>
<td>76</td>
<td>2</td>
<td>2028</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.007</td>
<td>142.86</td>
<td>46</td>
<td>2</td>
<td>20</td>
<td>588</td>
<td>432</td>
<td>12</td>
<td>1850</td>
</tr>
<tr>
<td>Mg-Carbonate (Magnesite)</td>
<td>2.488</td>
<td>0.40</td>
<td>21</td>
<td>2</td>
<td>10</td>
<td>612</td>
<td>444</td>
<td>12</td>
<td>1976</td>
</tr>
<tr>
<td>Mg-Sulfate (Epsomite)</td>
<td>0.104</td>
<td>9.62</td>
<td>21</td>
<td>3.5</td>
<td>20</td>
<td>564</td>
<td>432</td>
<td>12</td>
<td>1776</td>
</tr>
<tr>
<td>Olivine</td>
<td>3.005</td>
<td>0.33</td>
<td>77</td>
<td>2</td>
<td>20</td>
<td>142</td>
<td>70</td>
<td>2</td>
<td>2592</td>
</tr>
<tr>
<td>Smectite</td>
<td>10.783</td>
<td>–</td>
<td>21</td>
<td>3.5</td>
<td>5</td>
<td>540</td>
<td>380</td>
<td>10</td>
<td>2145</td>
</tr>
<tr>
<td>LHS-2</td>
<td>0.162</td>
<td>6.17</td>
<td>46</td>
<td>3.5</td>
<td>10</td>
<td>520</td>
<td>290</td>
<td>10</td>
<td>1590</td>
</tr>
<tr>
<td>LMS-2</td>
<td>0.351</td>
<td>2.85</td>
<td>21</td>
<td>3.5</td>
<td>10</td>
<td>440</td>
<td>380</td>
<td>10</td>
<td>1755</td>
</tr>
<tr>
<td>LSP-2</td>
<td>0.226</td>
<td>4.42</td>
<td>10</td>
<td>3.5</td>
<td>10</td>
<td>420</td>
<td>380</td>
<td>10</td>
<td>1677</td>
</tr>
<tr>
<td>JEZ-1</td>
<td>9.74</td>
<td>0.10</td>
<td>21</td>
<td>3.5</td>
<td>10</td>
<td>220</td>
<td>155</td>
<td>5</td>
<td>1440</td>
</tr>
<tr>
<td>MGS-1</td>
<td>1.283</td>
<td>0.78</td>
<td>46</td>
<td>8</td>
<td>10</td>
<td>500</td>
<td>370</td>
<td>10</td>
<td>1938</td>
</tr>
</tbody>
</table>
Table 3.1 summarizes the run information for each measurement discussed in this thesis.

3.1 Constituent Materials

In this section, I discuss the results of each constituent material described above (again in alphabetical order). The findings are described and displayed in each subsection, but a summary is provided in Table 3.2. Each material with a database entry to compare will have IRUG data in blue, SpectraBase in red, and USGS in green. The database entry data will be dashed lines and the O-PTIR measurements will be solid black lines. O-PTIR data utilizes the left y-axis and the database entries utilize the right y-axis.
Table 3.2: Peak wavenumbers and wavelengths for each constituent material examined in this thesis. Dashes in a cell indicate the lack of a peak measured in this wavenumber range for that material.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Peak(s) (Wavenumber, cm$^{-1}$)</th>
<th>Peak(s) (Wavelength, µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthosite</td>
<td>986, 1027, 1150</td>
<td>10.1, 9.7, 8.7</td>
</tr>
<tr>
<td>Basalt</td>
<td>1004, 1447, 1465, 1483</td>
<td>10.0, 6.9, 6.8, 6.7</td>
</tr>
<tr>
<td>Bronzite</td>
<td>1023, 1465</td>
<td>9.8, 6.8</td>
</tr>
<tr>
<td>Fe-Carbonate (Siderite)</td>
<td>1039, 1444, 1465</td>
<td>9.6, 6.9, 6.8</td>
</tr>
<tr>
<td>Ferricydrite</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Gypsum</td>
<td>990, 1007, 1108, 1622</td>
<td>10.1, 9.9, 9.0, 6.2</td>
</tr>
<tr>
<td>Hematite</td>
<td>1013, 1020, 1087</td>
<td>9.9, 9.8, 9.2</td>
</tr>
<tr>
<td>Hydrated Silica</td>
<td>1082, 1632</td>
<td>9.2, 6.1</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>1033, 1448, 1468, 1481</td>
<td>9.7, 6.9, 6.8, 6.7</td>
</tr>
<tr>
<td>Magnetite</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg-Carbonate (Magnesite)</td>
<td>1021, 1468, 1482, 1514</td>
<td>9.8, 6.8, 6.7, 6.6</td>
</tr>
<tr>
<td>Mg-Sulfate (Epsomite)</td>
<td>1077, 1101, 1665</td>
<td>9.3, 9.1, 6.0</td>
</tr>
<tr>
<td>Olivine</td>
<td>1006, 1125</td>
<td>9.9, 8.9</td>
</tr>
<tr>
<td>Smectite</td>
<td>1028, 1447, 1466</td>
<td>9.7, 6.9, 6.8</td>
</tr>
</tbody>
</table>
3.1.1 Anorthosite

![Anorthosite O-PTIR](image)

Figure 3.1: Mid-IR measurements of the rock anorthosite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance and reflectance data are for anorthite (a plagioclase mineral). Absorbance data obtained from IRUG (blue) (Entries: IMP00197, IMP00270, IMP00284) and SpectraBase (red) (Spectrum ID: HGmXKwVLmf). Reflectance data obtained from USGS (green) (Sample ID: GDS28, HS201). For the O-PTIR measurement, instrument settings were: 46% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.92 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (612 x 468 μm, 12 μm spacing) which contained 2080 individual spectra.
Figure 3.1 shows the mIRage® instrument measurement compared to absorbance and reflectance database entries of anorthite (a similar mineral to the rock anorthosite). Anorthosite shows O-PTIR peaks at 998, 1019, and 1095 wavenumbers with intense peaks at all three wavenumbers. Anorthosite in O-PTIR peaks at a similar wavenumber to anorthite in absorbance. It also peaks at similar wavenumbers to anorthite in reflectance but the peaks in O-PTIR are significantly more intense. The spectral shape is similar between the O-PTIR measurement and most of the absorbance spectra.

Farmer (1974) lists peaks associated with anorthite in the IR. In the examined wavenumber range, anorthite peaks at 1020, 1085, and 1160. The peaks at 1020 and 1085 correspond closely with two of the measured O-PTIR peaks.
Figure 3.2: Mid-IR measurements of basalt. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Reflectance data obtained from USGS (green) (Sample ID: BHVO-2F). For the O-PTIR measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 7.30 to be more visibly comparable to reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (225 x 210 µm, 5 µm spacing) which contained 1978 individual spectra.

Figure 3.2 shows the mIRage® instrument measurement of the rock basalt compared to reflectance database entries of basalt. Basalt shows O-PTIR peaks at 1004, 1447, 1465, and 1483 wavenum-
bers with the most intense peak at 1004. Basalt O-PTIR does not match well with available reflectance data.
3.1.3 Bronzite

Figure 3.3: Mid-IR measurements of the mineral bronzite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entry: IMP00052) and SpectraBase (red) (Spectrum ID: 2USDscWsPeX). Reflectance data obtained from USGS (green) (Sample ID: HS9). In this case, the IRUG data is augite (a pyroxene mineral) and the SpectraBase and USGS data are bronzite. For the O-PTIR measurement, instrument settings were: 5% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.08 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (78 x 78 µm, 2 µm spacing) which contained 1600 individual spectra.
Figure 3.3 shows the mIRage® instrument measurement of the mineral bronzite compared to absorbance and reflectance database entries of augite and bronzite (which are both pyroxene minerals). Bronzite shows O-PTIR peaks at 1023 and 1465 wavenumbers with the more intense peak at 1023. Bronzite in O-PTIR peaks at a similar wavenumber to Bronzite in absorbance as well as augite (another pyroxene mineral) in absorbance. Additionally, the spectral shapes are similar in the entire wavenumber range.
Figure 3.4: Mid-IR measurements of the mineral siderite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entry: IMP00244) and SpectraBase (red) (Spectrum ID: AAprKgeisSl). Reflectance data obtained from USGS (green) (Sample ID: HS271). For the O-PTIR measurement, instrument settings were: 10% IR Power, .43% Probe Power, and 50x Detector Gain. The O-PTIR was normalized by a factor of 0.03 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (120 x 84 µm, 3 µm spacing) which contained 1189 individual spectra.
Figure 3.4 shows the mIRage® instrument measurement of the mineral siderite compared to absorbance and reflectance database entries of siderite. Siderite shows O-PTIR peaks at 1039, 1444, and 1465 wavenumbers with intense peaks at all three wavenumbers. Siderite in O-PTIR peaks at a similar wavenumber to siderite in absorbance and reflectance. The O-PTIR spectral shape closely resembles siderite in absorbance in the middle of this wavenumber range.

According to Farmer (1974), siderite has absorption features at 1071, 1415, and 1422. The siderite O-PTIR measured at 1039 cm$^{-1}$ could be attributed to the 1071 feature. It is 42 wavenumbers displaced, but the width of that feature is approximately 200 wavenumbers, so it could cover that band. Additionally, the peaks at 1444 and 1465 cm$^{-1}$ are part of a feature with a width of almost 300 wavenumbers. This puts this peak well within the range of values listed for $v_3$ for siderite.

Farmer (1974) also lists peaks associated with siderite in the IR. In the examined wavenumber range, siderite peaks at 1412. This peak is only 32 wavenumbers displaced from one of the measured peaks in the O-PTIR. Additionally, the feature around O-PTIR feature around the peak at 1039 is similarly in FTIR, but with differing intensities. This is potentially a polarization issue, but that is beyond the scope of this work.
Figure 3.5: Mid-IR measurements of the mineral ferrihydrite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. No database measurements were available in the wavelength range of this instrument from the used databases. For the O-PTIR measurement, instrument settings were: 60% IR Power, 2% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 90.91. The O-PTIR measurement is an average of a hyperspectral map (588 x 432 µm, 12 µm spacing) which contained 1850 individual spectra.

Figure 3.5 shows the mIRage® instrument measurement of the mineral ferrihydrite. Ferrihydrite does not show significant O-PTIR spectral features nor peaks in the chosen wavenumber range.
3.1.6 Gypsum

Figure 3.6: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entry: IMP00228) and SpectraBase (red) (Spectrum ID: BrGfyvDbcjU). Reflectance data obtained from USGS (green) (Sample ID: GDS42, HS333). One of the USGS entries on this plot is gypsum, but the IRUG, SpectraBase, and the other USGS entries are anhydrite (the "dry" version of gypsum). The USGS entries are labeled for clarity. For the O-PTIR measurement, instrument settings were: 60% IR Power, 2% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 30.30 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (576 x 408 µm, 12 µm spacing) which contained 1715 individual spectra.
Figure 3.6 shows the mIRage® instrument measurement of the mineral gypsum compared to absorbance and reflectance database entries of anhydrite and gypsum. Gypsum shows O-PTIR peaks at 990, 1007, 1108, and 1622 wavenumbers with the most intense peaks at 1108 and 1622. Gypsum in O-PTIR peaks at a similar wavenumber to anhydrite in absorbance. Gypsum and anhydrite are both calcium sulfates, but gypsum is a dihydrite. This could account for the difference in spectral shape as well as the difference of peaks at higher wavenumbers.

According to Farmer (1974), anhydrite has absorption features at 1013, 1095, 1126, and 1149 and gypsum has absorption features at 1000, 1006, 1117, 1118, 1131, 1138, 1142, and 1144. The gypsum O-PTIR measured at 1007 cm\(^{-1}\) could be attributed to the feature at 1006 as it is one wavenumber displaced. Additionally, the peak at 1108 cm\(^{-1}\) is part of a feature with a width of approximately 100 wavenumbers. This puts this peak well within the range of values listed for features for gypsum.

Farmer (1974) also lists peaks associated with anhydrite and gypsum in the IR. In this wavenumber range, anhydrite peaks at 1130 and 1159. Gypsum peaks at 1010, 1120, 1150, 1629, and 1690 in the examined wavenumber range. These peaks correspond closely with some of my measured peaks in the O-PTIR. Additionally, the feature around 1629 is seen in both O-PTIR and FTIR-A, but with differing intensities. This is potentially a polarization issue, but that is beyond the scope of this work.
3.1.7 Hematite

Figure 3.7: Mid-IR measurements of the mineral hematite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entries: IMP00330, IMP00364) and SpectraBase (red) (Spectrum ID: ANSPy-CpAy7E). Reflectance data obtained from USGS (green) (Sample ID: GDS69). For the O-PTIR measurement, instrument settings were: 46% IR Power, 2% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 6.90 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (600 x 444 µm, 12 µm spacing) which contained 1938 individual spectra.
Figure 3.7 shows the mIRage® instrument measurement of the mineral hematite compared to absorbance and reflectance database entries of hematite. Hematite shows O-PTIR peaks at 1013, 1020, and 1087 wavenumbers with intense peaks at all three wavenumbers. The available database data varies widely, but hematite in O-PTIR peaks at the same wavenumber as one of the IRUG entries and a similar wavenumber to the SpectraBase entry. The spectral shape is similar to those two entries in the lower wavenumber range.
3.1.8 Hydrated Silica

Figure 3.8: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from SpectraBase (red) (Spectrum ID: AISSo02TX8u). For the O-PTIR measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.07. The O-PTIR measurement is an average of a hyperspectral map (612 x 444 µm, 12 µm spacing) which contained 1976 individual spectra.

Figure 3.8 shows the mIRage® instrument measurement of the mineral hydrated silica. Hydrated Silica shows O-PTIR peaks at 1082 and 1632 wavenumbers with the more intense peak at 1082.
Figure 3.9: Mid-IR measurements of the mineral ilmenite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entry: IMP00176) and SpectraBase (red) (Spectrum ID: EQ4IPOeiyKO). Reflectance data obtained from USGS (green) (Sample ID: HS231). For the O-PTIR measurement, instrument settings were: 77% IR Power, 3.5% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 1.08 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (102 x 76 μm, 2 μm spacing) which contained 2028 individual spectra.
Figure 3.9 shows the mIRage® instrument measurement of the mineral ilmenite compared to absorbance and reflectance database entries of ilmenite. Ilmenite shows O-PTIR peaks at 1033, 1448, 1468, and 1481 wavenumbers with the most intense peak at 1033. Ilmenite in O-PTIR most closely matched the reflectance data in peak and spectral shape. The available absorbance data was largely varied.
3.1.10 Magnetite

Figure 3.10: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from SpectraBase (red) (Spectrum ID: IyJeymlJ1By). Reflectance data obtained from USGS (green) (Sample ID: HS195). For the O-PTIR measurement, instrument settings were: 46% IR Power, 2% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 142.86 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (588 x 432 µm, 12 µm spacing) which contained 1850 individual spectra.
Figure 3.10 shows the mIRage® instrument measurement of the mineral magnetite compared to absorbance and reflectance database entries of magnetite. Magnetite does not show significant spectral features in O-PTIR in the chosen wavenumber range. Given that there are no peaks, the spectrum cannot match either absorbance or reflectance peaks. However, the spectral shape is similar to the reflectance spectrum in that it was not reactive to O-PTIR in this wavenumber range.
3.1.11 Mg-Carbonate (Magnesite)

Figure 3.11: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entries: IMP00189, IMP00245, IMP00355) and SpectraBase (red) (Spectrum ID: KXHTd7Xjfe0). Reflectance data obtained from USGS (green) (Sample ID: HS47). For the O-PTIR measurement, instrument settings were: 21% IR Power, 2% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.40 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (612 x 444 µm, 12 µm spacing) which contained 1976 individual spectra.
Figure 3.11 shows the mIRage® instrument measurement of the mineral magnesite compared to absorbance and reflectance database entries of magnesite. Magnesite shows O-PITR peaks at 1021, 1468, 1482, and 1514 wavenumbers with the most intense peaks at 1021, 1468, and 1482. Magnesite in O-PTIR peaks at similar wavenumbers and in a similar wavenumber range as the available absorbance data. It also shares a similar spectral shape to most of the absorbance entries in the same wavenumber range.

According to Farmer (1974), magnesite has absorption features at 1436, 1450, and 1599. The magnesite O-PTIR measured at 1468 cm\(^{-1}\) could be attributed to the feature at 1450. It is less than 20 wavenumbers displaced, and the width of that feature is approximately 200 wavenumbers, so it could cover that band. The features located at 1436 and 1450 could help account for the concentration of absorbance peaks and the width of the O-PTIR feature at the wavenumber range. The O-PTIR feature around 1021 does not seem to have a corresponding absorbance peak.
3.1.12 Mg-Sulfate (Epsomite)

Figure 3.12: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Reflectance data obtained from USGS (green) (Sample ID: GDS149). For the O-PTIR measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 9.62 to be more visibly comparable to reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (564 x 432 μm, 12 μm spacing) which contained 1776 individual spectra.
Figure 3.12 shows the mIRage® instrument measurement of the mineral epsomite compared to a reflectance database entry of epsomite. Epsomite shows O-PTIR peaks at 1077, 1101, and 1665 wavenumbers with intense peaks at all three. Epsomite peaks at a similar wavenumber as epsomite in reflectance in the lower wavenumber range. It also shares a similar spectral shape until about 1200 cm\(^{-1}\).

According to Farmer (1974), epsomite has absorption features at 1020, 1085, 1110, 1155, 1175, and 1235. The epsomite O-PTIR measured at 1077 cm\(^{-1}\) could be attributed to the 1085 feature as it is less than 10 wavenumbers displaced. Additionally, the peak at 1101 cm\(^{-1}\) could be attributed to the 1110 feature as it is also less than 10 wavenumbers displaced. The feature those peaks are a part of is approximately 200 wavenumbers wide which could cover additional features.
Figure 3.13: Mid-IR measurements of the mineral gypsum. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. Absorbance data obtained from IRUG (blue) (Entry: IMP00206) and SpectraBase (red) (Spectrum ID: B8nrbi846V0). Reflectance data obtained from USGS (green) (Sample ID: GDS70). For the O-PTIR measurement, instrument settings were: 77% IR Power, 2% Probe Power, and 20x Detector Gain. The O-PTIR was normalized by a factor of 0.33 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (142 x 70 $\mu m$, 2 $\mu m$ spacing) which contained 2592 individual spectra.
Figure 3.13 shows the mIRage® instrument measurement of the mineral olivine compared to absorbance and reflectance database entries of olivine. Olivine shows O-PTIR peaks at 1006 and 1125 wavenumbers with intense peaks at both wavenumbers. Olivine in O-PTIR peaks at a similar wavenumber to olivine in absorbance, but not as much to olivine in reflectance. The O-PTIR spectral shape also resembles absorbance in this wavenumber range.

Farmer (1974) lists peaks associated with olivine in the IR. In the examined wavenumber range, olivine peaks at approximately 1000 cm$^{-1}$. This peak is only 6 wavenumbers displaced from one of the measured peaks in the O-PTIR.
3.1.14 Smectite

Figure 3.14: Mid-IR measurements of the mineral smectite. The solid black line is the measurement produced by the mIRage® instrument using the O-PTIR method. No database measurements were available in the chosen wavenumber range from the used databases. For the O-PTIR measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 5x Detector Gain. The O-PTIR was normalized by a factor of 0.09 to be more visibly comparable to absorbance and reflectance database entries. The O-PTIR measurement is an average of a hyperspectral map (540 x 380 µm, 10 µm spacing) which contained 2145 individual spectra.
Figure 3.14 shows the mIRage® instrument measurement of the mineral smectite. Smectite shows O-PTIR peaks at 1028, 1447, and 1466 wavenumbers with the most intense peak at 1028.

3.2 Simulant Mixtures

In this section, I discuss the results of each regolith simulant mixture described above in Section 2.1.2. Each constituent material has a specific color chosen for consistency. Figure 3.15 shows which color is associated with which constituent material. Each mixture plot also has a legend for convenience.

Figure 3.15: Caption
3.2.1 Lunar Regolith Simulants

3.2.1.1 LHS-2

Figure 3.16: Mid-IR O-PTIR measurements of the regolith simulant mixture LHS-2. The solid black line is the measurement of LHS-2 produced by the mIRage® instrument. The dashed lines (identified in the legend) are the various components that make up the mixture. For the LHS-2 measurement, instrument settings were: 46% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 6.17 to be more visibly comparable to the normalized constituent materials. The LHS-2 measurement is an average of a hyperspectral map (520 x 290 µm, 10 µm spacing) which contained 1590 individual spectra.
Figure 3.16 shows the mIRage® instrument measurement of the soil simulant mixture LHS-2. LHS-2 shows O-PTIR peaks at 1005, 1097, and 1445 wavenumbers with the most intense peaks at 1005 and 1097.

The O-PTIR spectrum of LHS-2 is clearly dominated by the anorthosite component. This is likely due to anorthosite making up over 70% of the lunar highlands soil simulant mixture. The spectrum also matches features in basalt’s and bronzite’s O-PTIR spectra which make up a combined 30% of the mixture. The full composition is shown in Table 2.2.
3.2.1.2 LMS-2

Figure 3.17: Mid-IR O-PTIR measurements of the regolith simulant mixture LMS-2. The solid black line is the measurement of LMS-2 produced by the mIRage® instrument. The dashed lines (identified in the legend) are the various components that make up the mixture. For the LMS-2 measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 2.85 to be more visibly comparable to the normalized constituent materials. The LMS-2 measurement is an average of a hyperspectral map (440 x 380 \( \mu m \), 10 \( \mu m \) spacing) which contained 1755 individual spectra.
Figure 3.17 shows the mIRage® instrument measurement of the soil simulant mixture LMS-2. LMS-2 shows O-PTIR peaks at 1028, 1074, and 1450 wavenumbers with the most intense peaks at 1028 and 1074.

The O-PTIR spectrum of LHS-2 is clearly dominated by the basalt component. This is likely due to basalt and bronzite making up over 60% of the lunar mare soil simulant mixture. Bronzite’s features are likely drowned out by the intense response of basalt, but the combined presence could explain the shifted peak at 1028 cm$^{-1}$ which does not perfectly match the basalt peak at a similar wavenumber. LMS-2 had a more intense response in the 1400-1550 wavenumbers range than LHS-2. The full composition is shown in Table 2.2.
3.2.1.3  LSP-2

Figure 3.18: Mid-IR O-PTIR measurements of the regolith simulant mixture LSP-2. The solid black line is the measurement of LSP-2 produced by the mIRage® instrument. The dashed lines (identified in the legend) are the various components that make up the mixture. For the LSP-2 measurement, instrument settings were: 10% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 4.42 to be more visibly comparable to the normalized constituent materials. The LSP-2 measurement is an average of a hyperspectral map (420 x 380 $\mu m$, 10 $\mu m$ spacing) which contained 1677 individual spectra.
Figure 3.18 shows the mIRage® instrument measurement of the regolith simulant mixture LSP-2. LSP-2 shows O-PTIR peaks at 1022, 1038, 1103, and 1471 wavenumbers with the most intense peaks at 1022 and 1103.

The O-PTIR spectrum of LSP-2 appears to be an anorthosite spectrum. This is likely due to LSP-2 being a simple mixture of anorthosite and basalt which is dominated but anorthosite at 90%.
3.2.2 Martian Regolith Simulants

3.2.2.1 JEZ-1

Figure 3.19: Mid-IR O-PTIR measurements of the regolith simulant mixture JEZ-1. The solid black line is the measurement of JEZ-1 produced by the mIRage® instrument. The dashed lines (identified in the legend) are the various components that make up the mixture. For the JEZ-1 measurement, instrument settings were: 21% IR Power, 3.5% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.10 to be more visibly comparable to the normalized constituent materials. The JEZ-1 measurement is an average of a hyperspectral map (220 x 155 \( \mu m \), 5 \( \mu m \) spacing) which contained 1440 individual spectra.
Figure 3.19 shows the mIRage® instrument measurement of the regolith simulant mixture JEZ-1. JEZ-1 shows O-PTIR peaks at 1031, 1051, 1468, and 1488 wavenumbers with the most intense peak at 1051.

The O-PTIR spectrum of JEZ-1 is not seemingly dominated by any one individual component. However, the regolith simulant mixture simulating the martian Jezero Crater does show similar features to several of its constituent materials. Particularly, JEZ-1’s spectrum has a similar peak to anorthosite, basalt, bronzite, epsomite, and hydrated silica in the lower wavenumber range. It also has a similar peak to magnesite, siderite, and smectite in the higher wavenumber range.
Figure 3.20: Mid-IR O-PTIR measurements of the regolith simulant mixture MGS-1. The solid black line is the measurement of MGS-1 produced by the mIRage® instrument. The dashed lines (identified in the legend) are the various components that make up the mixture. For the MGS-1 measurement, instrument settings were: 46% IR Power, 8% Probe Power, and 10x Detector Gain. The O-PTIR was normalized by a factor of 0.78 to be more visibly comparable to the normalized constituent materials. The MGS-1 measurement is an average of a hyperspectral map (500 x 370 μm, 10 μm spacing) which contained 1938 individual spectra.
Figure 3.20 shows the mIRage® instrument measurement of the regolith simulant mixture MGS-1. MGS-1 shows O-PTIR peaks at 1067 and 1446 wavenumbers with the more intense peak at 1067.

The O-PTIR spectrum of MGS-1 is not seemingly dominated by any one individual component (similar to JEZ-1). However, the soil simulant mixture simulating the martian global surface soil does show similar features to several of its constituent materials. Particularly, MGS-1’s spectrum has a similar peak to epsomite, gypsum, and hydrated silica in the lower wavenumber range. It also has a similar feature to anorthosite and basalt in the higher wavenumber range.

3.3 Quantitative Analysis Method

One of the goals of this thesis described in Section 1.1 was to demonstrate the quantitative analysis capabilities of the O-PTIR method and the mIRage® Instrument. Figure 3.21 is a plot of the O-PTIR measurement of LHS-2 (discussed in Sections 2.1.2.1 and 3.2.1.1) and a simulated spectrum of LHS-2 based off of its constituent materials.
The simulated spectrum is produced using O-PTIR measurements of the constituent materials. Each unnormalized intensity value that produces a constituent material’s spectrum was multiplied by the weight percentage it contributes to the regolith mixture being analyzed (in this case, LHS-2). The weighted values are then added together to produce the simulated spectrum (the dashed red line in Figure 3.21. The measurement and simulated spectrum were both normalized to make visual comparison easier. In this case, the values of the anorthosite measurement were multiplied
by .744, the values of the basalt measurement were multiplied by .247, and this was repeated for each material in the mixture. In this case, it was assumed that power settings were kept constant. However, in practice that was not the case. This will be further addressed in Section 4.3.

The simulated spectrum produced in this manner demonstrated the capability of the mIRage® Instrument to be used for quantitative analysis. Though the method could be improved, the constituent materials of the mixture were successfully used to produce a similar spectrum. The simulated spectrum shares all of the same spectral features as the LHS-2 measurement. Additionally, they share the same spectral peaks and have nearly identical spectral shapes.
CHAPTER 4: CONCLUSION

The measurement method presented in this thesis is unlike anything presented in the field of planetary science. In this chapter, I will discuss what makes this data unique and this methodology advantageous. Further, I will conclude with a summary of data and findings in Section 4.2.

4.1 Discussion

In this section, I will discuss the attributes that make this data unique. Additionally, I will go in depth on the benefits of the technology utilizing some of the discussion from Chapter 3.

4.1.1 High Resolution

As discussed above, the mIRage® instrument utilizes O-PTIR technology. One advantage of this IR method is the increased spatial and spectral resolution compared to other IR methods. The data presented in this thesis benefited by having single spectral measurements having a spatial resolution on the sub-micron scale (compared to a more traditional spatial resolution of 10-20 microns). This allowed me to more definitively say what I was measuring when using single spectral measurements. Additionally, as hyperspectral measurements were being taken, I was able to take more single spectral measurements within an area increasing the precision of the measurements.

The measurements also benefited from having increased spectral resolution.
4.1.2 Fast Measurements

The mIRage® instrument takes extraordinarily fast measurements. A single hyperspectral spectral measurement took approximately 15 s and a hyperspectral map with over 1000 points (three hyperspectral spectra averaged into one spectrum per point) could be completed in less than 10 hours, or more poignantly, approximately 4 single hyperspectral measurements per minute including time to average each set of individual spectra and the objective to move to the next point.

4.1.3 No Sample Preparation

Though I did prepare samples, as described above in section 2.2, the instrument and technology did not require it. I prepared samples to reduce dust contamination of the optics and sample area of the instrument.

4.1.4 Quantitative Analysis

Similar to FTIR Absorbance (FTIR-A) and FTIR Reflectance (FTIR-R) techniques (both described in Section 1.4) being capable of quantitative analysis, so too is O-PTIR (as described in Section 1.2). However, FTIR-A and FTIR-R face strict limitations in their analyses. FTIR-A requires a sample preparation method that requires the material to not be opaque at a certain thickness to produce the composition of a whole sample. FTIR-R does not require the same strict sample preparation but does not utilize light passing through the entire sample. Since the light reflects off of the sample, only a portion of the sample is analyzed. O-PTIR does not face either of the limitations and is the only technique currently available that can perform quantitative analysis on opaque materials.
In Section 3.3, I demonstrate the instrument’s, and therefore the technique’s, ability to perform such analysis. A mixture was well simulated using the measurements of its constituents. However, there are still limitations as many things affect a spectrum (i.e. packing density, granular orientation, etc.). Should O-PTIR be used in future in-situ measurements, the scans that it produces would be comparable to a database of materials. Models could be run to produce simulated spectra to determine the makeup of the newly measured regoliths. Due to O-PTIR’s ability to be compared to many forms of spectroscopy, it can also contribute to supporting remote sensing observations. The quick measurements and high resolution make O-PTIR a good candidate for ground truthing.

4.2 Summary

In this thesis, I presented O-PTIR spectra of various minerals and regolith simulant mixtures produced using the mIRage® instrument. I demonstrated the relevance of the method as it is comparable to existing data as well as its ability to analyze relevant minerals and materials to planetary science. I also make a case for the use of this technique in the planetary science community. The benefits of high spatial and spectral resolution, fast measurements, reduced need for sample preparation, and the ability to perform quantitative analysis on an opaque sample were demonstrated and discussed. O-PTIR is a useful technique for the future of planetary science and planetary science missions.

4.3 Future Works

This thesis was part of a larger project known as ORIGINS. This project will include a reduction of Size, Weight, and Power (SWaP). The work presented here serves as a foundation to support that future work. As parts are changed to SWAP, this data will serve to show changes in precision,
resolution, and overall function.

Another major change that is planned is the addition of the capability for Raman measurements to be obtained. The visible laser is incident on the sample and the reflected light is collected and analyzed. Because of this, this addition would only require a dichroic mirror in the beam path. This would allow the visible light to reflect to the detector and still allow the Raman signal to pass through for analysis. The addition of this complimentary technique offers additional advantages, especially in the identification of minerals and organics. This is offered by Photothermal Spectroscopy Corp. and is something that will hopefully be integrated into the planned benchtop model for the reduced SWaP.

Other scientific endeavors will include using the instrument in its current form. Plans are in place to better demonstrate the lack of need for sample preparation. I will better quantify how the surface roughness of a sample will affect the measurements produced via the mIRage® instrument. Also, this instrument will be used to analyze meteorite samples. There are currently carbonaceous chondrites, lunar samples, and martian samples ready to be analyzed. The regolith simulants analyzed here can readily be compared to corresponding samples as well as constituent materials may be identifiable within those meteorite samples. The instrument is capable of performing a quantitative analysis similar to that available to FTIR absorption techniques. Work will be done to better characterize the limitations mentioned in Section 4.1.4. With that characterization, the quantitative analysis methodology could likely be improved using the increased sample data. Additionally, the variations in the powers used will be applied to try and better capture certain spectral characteristics missing in the current simulated spectra. A database will be created so that this data is readily available for comparison purposes to future measurements outside of this research group.
LIST OF REFERENCES


Cannon, K., & Britt, D. 2019, Lunar ISRU 2019-Developing a New Space Economy Through Lunar Resources and Their Utilization, 2152, 5002


Griffiths, P. R. 1983, Science, 222, 297


Kraft, C. 2022, in Molecular and Laser Spectroscopy (Elsevier), 305–336


Madejová, J. 2003, Vibrational spectroscopy, 31, 1

Martin, P., Leiva, A., Bell, S., et al. 2018

Mustard, J. F., & Glotch, T. D. 2019, Remote compositional analysis: Techniques for understanding spectroscopy, mineralogy, and geochemistry of planetary surfaces, 21

Paulus, A., Yogarasa, S., Kansiz, M., et al. 2022, Nanomedicine: Nanotechnology, Biology and Medicine, 43, 102563


Ramer, G., & Lendl, B. 2006, Encyclopedia of analytical chemistry: applications, theory and instrumentation

Rossman, G. R., & Ehlmann, B. L. 2019, In Remote compositional analysis: Techniques for understanding spectroscopy, mineralogy, and geochemistry of planetary surfaces, 3

Snook, R. D., & Lowe, R. D. 1995, Analyst, 120, 2051

Spadea, A., Denbigh, J., Lawrence, M. J., Kansiz, M., & Gardner, P. 2021, Analytical chemistry, 93, 3938

