Telescopic Observations of Lunar Hydration: Variations and Abundance

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Abstract Prior to 2009, the surface of the Moon was believed to be anhydrous. However, observations by three spacecraft revealed a hydrated surface by reporting a 3 μm absorption band attributed to hydroxyl and possibly molecular water. The Moon Mineralogy Mapper (M3) spectrometer on board the Chandrayaan-1 spacecraft has been used to study the lunar 3 μm band, but its spectral range ends at 3 μm. The limited wavelength range of M3 has allowed observed variations in the strength of the 3 μm band to be called into question due to uncertainties in thermal corrections. To investigate the validity of variations in the lunar 3 μm band, we used the SpeX infrared spectograph at the NASA InfraRed Telescope Facility at Maunakea Observatory in Hawai‘i. With SpeX, we are able to obtain lunar data over a wavelength range of 1.67 to 4.2 μm at 1–2 km spatial resolution. The long wavelengths provide strong constraints on separating thermal emission from solar reflectance. We confirm that the 3 μm band varies with lunar time of day as well as with latitude and composition. Pole-to-pole observation chords reveal strong variations in abundances of hydroxyl and possibly molecular water. The data reveal a decrease in abundance as lunar noon is approached, an asymmetric trend about the equator that favors the southern latitudes, and higher concentrations in highland regions. The longer wavelengths provided by SpeX have allowed us to examine variations in the 3 μm band and provide definitive evidence that the variations are due to changes in hydration.

Plain Language Summary Until recently, the Moon was thought to be dry. However, this view drastically shifted in 2009 when three spacecraft observed a hydration absorption feature in spectra of the lunar surface. The spacecraft observed the hydration feature varying with temperature on the Moon. However, due to uncertainties in correcting the data for emissions from the high temperature of the Moon, the variation of the hydration feature was called into question. To verify the variation of the hydration feature, we obtained new observations of the Moon that provide strong constraints on thermal corrections using the NASA InfraRed Telescope Facility at Maunakea Observatory in Hawai‘i. With this new data we find that the hydration feature on the Moon varies with temperature, latitude, and composition. The presence of variation shows that there are temperature-driven processes occurring on the surface of the Moon.

1. Introduction

In 2009 a major discovery in lunar science was the report of a widespread hydration feature on the surface of the Moon. The hydration was observed by spectrometers on three different spacecraft, Chandrayaan-1, Deep Impact, and Cassini (Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009). This hydration feature is in the 2.8 to 3.5 μm region (referred to as the “3 μm band”) and is due to the presence of hydroxyl (OH) attached to a metal cation or molecular water (H₂O) or a combination of the two. The 3 μm band on the surface of the Moon was suggested by several laboratory studies that observed OH in experiments simulating solar wind interactions with oxygen-rich materials (Hapke, 1965; Zeller et al., 1966; Zeller & Ronca, 1967). These studies showed that bombarding silicate glass materials (analogous to lunar regolith) with high-energy protons (analogous to solar wind) produces OH on the surface of grains and exhibits a 3 μm band (Zeller et al., 1966; Zeller & Ronca, 1967). Several studies confirmed hydroxyl formation (Bradley et al., 2014; Mattern et al., 1976), and some also report the formation of a 3 μm band (Gruen et al., 1975; Guermazi et al., 1987; Ichimura et al., 2012; Siskind et al., 1977).
Variations of the 3 μm band intensity with temperature were reported using global spectral imaging of the Moon by the infrared High Resolution Imaging spectrometer on Deep Impact (Sunshine et al., 2009). From the spacecraft’s distant vantage point during one of its two lunar flybys, the spectrometer captured global snapshots of the Moon in the 3 μm region. These data revealed a strong correlation between lunar surface temperature and the strength of the 3 μm band. Interpretaion of radiance spectra of the Moon in the 3 μm region is complicated by the fact that they are a combination of solar reflected radiance and thermally emitted radiance (e.g., McCord et al., 2011). However, data from Deep Impact, despite the relatively low spatial resolution and limited time of day coverage, has the distinct advantage of including data near and beyond 4 μm where the spectrum is dominated by thermal emission, enabling confident removal of this component. The thermally corrected Deep Impact spectra are highly likely to have detected strong variations in lunar hydration with lunar surface temperature. However, the data do not contain repeat coverage to definitively confirm diurnal variations.

Diurnal variations in the 3 μm band were also observed in data from the Chandrayaan-1 Moon Mineralogy Mapper (M3) spectrometer that collected high spatial resolution data from lunar polar orbit. Pieters et al. (2009) using M3 data (which has better temporal and spatial coverage than Deep Impact) report diurnal variations in the 3 μm band depth in repeat observations of the same locations at different lunar times of day. However, data from M3 terminate at 3 μm, leaving little spectral range to derive accurate corrections for thermal emission. Three groups have analyzed M3 data applying subtly different thermal corrections, and each arrive at strikingly different conclusions ranging from strong diurnal variation to no variation in 3 μm band intensity at all (Bandfield et al., 2018; Grumpe et al., 2019; Li & Milliken, 2017; Wöhler et al., 2017). However, McCord et al. (2011) pointed out that observations of the lunar surface at wavelengths beyond 3 μm greatly improve the removal of thermal emission due to the sharply increasing thermal emission with wavelength and are strongly recommended to address the validity of variation in the 3 μm band.

In this paper we use ground-based infrared spectroscopy of the Moon from 1.67 to 4.2 μm to characterize the lunar 3 μm band and constrain our thermal correction. This new data set allows us to determine the degree of diurnal variation in 3 μm band with repeat observations of the same lunar locations. We quantify the lunar surface hydration (the sum of molecular water and hydroxyl, known as “total water” in the Fourier transform infrared [FTIR] literature; Stolper, 1982; Starukhina, 2001; King et al., 2004; McIntosh et al., 2017) reflected in our spectra and compare these new estimates to previous spacecraft estimates. Observations were conducted at the NASA Infrared Telescope Facility (IRTF) at Mauna Kea Observatory, obtaining spatially resolved data (~1 to 2 km at the lunar center of disk) covering many lunar times of day over 180° of latitude from pole to pole near the zero longitude meridian.

2. Data

We collected 3,395 spatially resolved spectra of the lunar surface with the IRTF SpeX spectrograph on six nights between 17 January 2019 and 15 May 2019. Data were acquired in the long-wavelength cross-dispersed mode called “LXD Short” that produces spectra from 1.67 to 4.2 μm with a spectral resolution of R ~ 2,500 (Rayner et al., 2003). We use the narrowest slit available, 0.3 × 15 arcseconds (about 0.6 × 30 km at the lunar center of disk), to limit saturation using integration times ranging from 0.5 to 2 seconds depending on the lunar illumination conditions. Occasional saturation is observed at wavelengths near 4 μm when the lunar surface is the warmest; for the few spectra where saturation occurs, this region is avoided in processing and interpretation. We conservatively set our saturation threshold at ~70% of saturation as defined in the SpeXtool manual. When saturation is observed, data out to 3.6 μm still provide strong thermal constraints.

The observing goal was to acquire data for the same locations over a range of lunar times of day by taking advantage of the evolving lunar phase between observing nights. To maximize diurnal and latitude coverage, we scanned the spectrometer slit across the Moon while reading out the SpeX detector. We conducted these scans with the slit oriented either perpendicular (in a push broom fashion) or parallel (as a chord across the Moon) to the lunar meridian. After each detector readout, the slit is offset by 2 arcseconds per frame in the perpendicular mode or 7 arcseconds per frame (about half the slit length) in the parallel mode. The parallel orientation allows us to scan from one lunar pole to the other to create a spectral profile at 1 arcsecond intervals across the Moon. The offset rates of the scans is in both right ascension and declination to produce tracks
near the zero longitude meridian. The parallel orientation maximizes latitude and temperature coverage, producing data with near-constant lunar time of day for a given observation. Table 1 summarizes the observations, and Figure 1 shows the location of each scan on the Moon.

### 3. Methods

Data reduction includes flat-field correction, wavelength calibration, correction for stray light within the SpeX instrument, sky subtraction, telluric correction using solar analog stars, merging of the several orders into single spectra, thermal emission correction, and conversion of reflectance data to water abundance.

#### 3.1. SpeX Data Calibration

Standard flat-field and wavelength calibrations were conducted using the Spextool (V4.0) data reduction package (Cushing et al., 2004; Vacca et al., 2003) employing the internal flat-field and Ar lamp data obtained at the beginning and end of each night. Our SpeX data exhibit stray light from internal scattering within the spectrometer. When uncorrected, the stray light causes zero signal regions (due to atmospheric opacity) to have artificially elevated signals above 0. Typical observations of stars and other point sources remove this stray light background through beam switching, but this cannot be used for extended objects such as our lunar observations. Instead, the stray light is measured and removed during calibration of the data using Spextool (see supporting information for details on the removal of stray light).

Due to the Moon’s large spatial extent on the sky, chopping and nodding of the IRTF telescope to remove sky and telescope emissions are not possible. Removal of sky and telescope emissions requires sole observations of the sky near the Moon to capture thermal background and sky emission. Observations of the sky are taken just off the limb of the Moon for each lunar observations conducted and are subtracted from the lunar spectra.

The spectra are corrected for atmospheric transmission by normalizing the sky-subtracted lunar data to observations of solar analog stars. Stars are selected from solar analog stars used for asteroid observations with the IRTF (Takir & Emery, 2012). The solar analog spectrum is divided out from the sky corrected lunar data to remove atmospheric absorption lines and to correct for the solar spectral shape inherent to reflectance observations of planetary bodies. Figure 2 is an example of the fully calibrated lunar spectrum. While we chose calibration stars from Takir and Emery (2012) that are close in proximity to the Moon with a similar airmass, some atmospheric absorptions are not fully removed due to differences in atmospheric conditions between the lunar observations and star observations. The solar analogs used for each observation are listed in Table 1.

### Table 1

| Date UTC (2019) | Lunar local time | Longitude at equator | # of frames | Phase angle | Integration time (s) | Solar analog star | Slit orientation |
|----------------|------------------|----------------------|-------------|-------------|---------------------|------------------|------------------|
| 01-18          | 09:11–09:33      | −5.6°                | 990         | 40.3°       | 0.5                 | HD25680          | Perpendicular    |
| 01-20          | 10:23–11:29      | −3.5°                | 1,026       | 11.5°       | 0.5                 | HD25680          | Perpendicular    |
| 03-27          | 16:32–17:34      | 5.5°                 | 582         | −84.1°      | 1                   | HD162255         | Parallel         |
| 05-13          | 07:04–07:49      | 0.2°                 | 275         | 74.0°       | 2                   | HD89010          | Parallel         |
| 05-14          | 07:57–08:37      | 1.2°                 | 268         | 60.7°       | 2                   | HD106423         | Parallel         |
| 05-15          | 08:47–08:54      | 2.2°                 | 254         | 47.1°       | 1                   | HD106423         | Parallel         |

Note: Dates are formatted as mm-dd.

*Negative phase angle indicates lunar afternoon hours.

Figure 1. Image of the Moon with the location of lunar chord observations for this project.
3.2. Removal of Thermal Emission

Lunar spectra longward of 2.5 μm and below ~70° latitude are heavily affected by an additional component of thermally emitted radiance. As pointed out above, accurate removal of thermal emission is vital for investigation of the 3 μm feature and its variation. Ground-based observations of total water on asteroids has been conducted for over 40 years (Lebofsky, 1978). Asteroid spectra, like lunar spectra, are also affected by thermal emission, and methods are available for its correction. We follow the methodology used for asteroid thermal emission removal defined by Rivkin et al. (2005), Reddy et al. (2009), and Takir and Emery (2012) to remove thermal emission from our lunar spectra. We do this in part because they also used SpeX for their asteroid observations, and so this method is well established for that spectrometer.

Planetary astronomers observing in the visible and near infrared typically normalize their data to solar analog stars that have a spectral shape similar to the sun. This normalization produces astronomical spectra that are similar to spectra of samples with the same composition measured in the laboratory. However, at longer wavelengths such as used here, the thermal emission results in a rapid nonlinear increase in apparent reflectance that is inconsistent with the known spectral properties of the Moon (Figure 2). Rivkin et al. (2005) called this turn-up in spectra of asteroids the “thermal excess.” Thermal excess (γ) is defined as

\[ \gamma = \frac{R + T}{R} - 1, \]

where \( R \) is the reflected spectral component and \( T \) is the thermal spectral component of the target. Rivkin et al. (2005) uses the observed data to determine a measured thermal excess. For asteroids, the excess is fit using the Standard Thermal Model developed by Lebofsky et al. (1986), and the fit is subtracted from the asteroid data to remove the thermal emission. We follow the same procedure for the lunar data described below. All terms are wavelength-dependent vectors, and so we drop the \( \lambda \) subscript. Any constants are clearly called out in the text.

To find the measured lunar thermal excess (\( \gamma_{\text{measured}} \)), the numerator in the first term of Equation 1 (\( R + T \)) is the measured lunar radiance normalized to the solar standard star at a wavelength of 1.75 μm; this term is now apparent lunar reflectance (\( R_{\text{app}} \)) and contains both the reflected and thermal components. We chose the wavelength 1.75 μm because it is the closest wavelength to the Multiband Imager (MI; constant) reflectance data that are used as a reference in Equation 4. The \( R \) in the denominator of the first term in Equation 1, for the lunar case, is the lunar continuum (\( R_{\text{con}} \)) found by fitting the apparent lunar reflectance data with a straight line between 1.7 and 2.5 μm, avoiding the 2 μm lunar pyroxene band, and extrapolating to the longer wavelengths. For the lunar case, Equation 1 turns into the measured thermal excess:

\[ \gamma_{\text{measured}} = \frac{R_{\text{app}}}{R_{\text{con}}} - 1. \]

To obtain a purely reflectance spectrum of the Moon (\( R_{\text{Moon}} \)), we subtract a thermal excess model (\( \gamma_{\text{model}} \)) from the apparent lunar reflectance (\( R_{\text{app}} \)):

\[ R_{\text{Moon}} = R_{\text{app}} - \gamma_{\text{model}}. \]

3.2.1. Thermal Excess Model

To model the thermal excess (\( \gamma_{\text{model}} \)), we model both the expected lunar reflected radiance (including solar radiance) and expected lunar thermal radiance. The lunar reflected radiance (\( I_{\text{model}} \)) is given in Equation 4:
\[ I_{\text{model}} = \frac{I_{\text{solar}}}{\pi} \cdot \text{MI}_{30, 0, 30} \cdot R_{\text{con}} \text{ W/m}^2/\mu\text{m}/\text{sr} \] (4)

where \( I_{\text{solar}} \) is the solar irradiance [ASTM E490-00a, 2014] divided by \( \pi \) to convert it to units of irradiance. \( \text{MI}_{30, 0, 30} \) is a constant and is the reflectance of the Moon at 1.55 \( \mu\text{m} \) at our location extracted from data collected by the MI on the Kaguya spacecraft (Ohtake et al., 2008). The MI data are corrected from the standard photometric geometry of the data set (incidence \([i] = 30^\circ\), emission \([e] = 0^\circ\), phase angle \(= 30^\circ\)) to our observing geometry. The data are converted from the standard geometry to that of our observations using the methods of Hapke (2012). The retrieval of the MI reflectance value uses the latitude and longitude at which each spectrum was acquired and is resampled to our spatial resolution. We choose the longest wavelength available in the MI data, 1.55 \( \mu\text{m} \), because it is closest to our lunar data at 1.75 \( \mu\text{m} \) and the reflectance between these two wavelengths is close in value within \( \pm 0.1 \).

Asteroid thermal corrections typically use an asteroid standard thermal model (Harris, 1998). However, to speed up the calculations necessary for our large data set, we use a simplified thermal model that assumes the lunar surface to be composed of two components (to account for surface roughness): a single temperature for the hot illuminated component in radiative equilibrium and a single temperature for the cold shadowed component. Detailed thermal models show the shaded component to be very cold, typically less than 150 K (Bandfield et al., 2015). The two-component thermal model is defined as

\[ L = A\varepsilon_1 B(T_1) + (1 - A)\varepsilon_2 B(T_2), \] (5)

where \( L \) is the thermal model radiance, \( A \) is the proportion of area of the hot component (accounting for surface roughness), \( \varepsilon_1 \) is the emissivity of the hot component and \( T_1 \) is its temperature, and \( T_2 \) is the temperature of the cold component and \( \varepsilon_2 \) is its emissivity. In the spectral region less than 4 \( \mu\text{m} \), emission from surfaces at cold temperatures (\( T_2 \)) can be neglected, so the two-component thermal model simplifies to

\[ L_{\text{thermal}} = A\varepsilon B(T_1). \] (6)

For the purposes of this model we assume an emissivity of 0.9 (Takir & Emery, 2012). Rather than iteratively fit \( f_{\text{measured}} \), we compute a large lookup table for \( L_{\text{thermal}} \) varying \( A \) and \( T_1 \) with increments of 0.5\% in \( A \) and 0.5 K for \( T_1 \).

The final modeled thermal excess is given by

\[ \gamma_{\text{model}} = \frac{\left( \frac{L_{\text{model}} + L_{\text{thermal}}}{L_{\text{model}}} \right)}{R_{\text{model, con}}} - 1, \] (7)

where \( R_{\text{model, con}} \) is a model of the reflectance continuum and is found by fitting the numerator term in Equation 7 with a straight line between 1.7 and 2.5 \( \mu\text{m} \) and extrapolating to the longer wavelengths. Because lunar data are affected by thermal radiance at wavelengths shorter than 3 \( \mu\text{m} \), the lunar continuum (\( R_{\text{con}} \)) includes some of the thermal component in the measured thermal excess near 2.4 \( \mu\text{m} \). Due to this, the modeled thermal excess must be normalized at the same wavelengths as the data before the correct thermal excess model can be found.

With both the \( f_{\text{measured}} \) and the library of \( \gamma_{\text{model}} \) we then subtract all thermal excess models from each the lunar \( f_{\text{measured}} \) and use the mean of the absolute value of the difference between 3.4 and 4 \( \mu\text{m} \) to determine the best fit (if saturation is present the fit is found between 3.4 and 3.6 \( \mu\text{m} \)). The model that provides the minimum value is chosen as the best fit \( \gamma_{\text{model}} \). If saturation occurs at the longest wavelengths in the data then the best fit thermal excess model is defined out to 3.6 \( \mu\text{m} \) which still allows for strong thermal constraints beyond 3 \( \mu\text{m} \). If no saturation is observed, the best fit thermal model is defined out to 4 \( \mu\text{m} \). Figure 3 shows an example of a low-latitude spectrum and the thermal excess model that best fits the data shown in green. Applying thermal excess models that are a few kelvins off has noticeably large effects at longer wavelengths, causing either an upturn or downturn of wavelengths longer than \( \sim 3.5 \mu\text{m} \). Figure 4 (right) shows the reflectance using different thermal models, with an optimum model at 330 K and models that are \( \pm 5 \) and 10 K.
Once the appropriate thermal excess model has been found, we remove the optimum \( \gamma_{\text{model}} \) from our normalized continuum-removed lunar spectra. We then scale the data to MI reflectance at the standard viewing geometry (\( i, e, 30^\circ, 0^\circ, 30^\circ \)) and introduce the continuum back into the reflectance spectrum resulting in bidirectional reflectance at the photometric geometry of \( i = 30^\circ, e = 0^\circ, 30^\circ \) (Figure 4, left):

\[
R_{\text{Moon}} = MI_{30,0,30} \times \left( \frac{R_{\text{app}}}{R_{\text{con}}} - \gamma_{\text{model}} \right) \times R_{\text{con}}.
\] (8)

### 3.3. Estimating the Abundance of Total Water

The abundance of water and hydroxyl in geologic samples has been estimated for decades using the infrared absorption near 3 \( \mu m \) where the thickness of the sample is carefully measured, and use established absorption data for water and hydroxyland Beer’s Law to derive abundances. Milliken and Mustard (2005) developed a relationship for estimating the abundance of H\(_2\)O in remote sensing data. Later, Li and Milliken (2017) applied this approach to the Moon using empirical measurements of water-bearing glasses to calibrate M3 data to water concentration. To estimate the abundance of total water, we use the methods of Li and Milliken (2017) that employ the spectral parameter effective single-particle absorption thickness (ESPAT), which is linearly proportional to the abundance of total water.

ESPAT is a function of the single scattering albedo \( w \), which is the probability that a photon will survive an encounter with a grain. To calculate ESPAT from our reflectance data, we convert the reflectance spectra to \( w \) using work by Hapke (1981, 1993) (Li, 2017). We remove a continuum spectrum from the \( w \) spectra by fitting a straight line similar to the thermal excess process, but in \( w \) units. This differs from Li (2017), who used the \( w \) value at single wavelength (2.5 \( \mu m \)) and normalized the \( w \) spectrum to this value. The Li (2017) method does not take into account the inherently red lunar continuum, so with a single value as the continuum point it is possible to underestimate the continuum on the long-wavelength shoulder of the 3 \( \mu m \) band causing negative abundances at low total water abundances. Fitting the SpeX data between 1.7 and 2.5 \( \mu m \) with care to avoid fitting the 2 \( \mu m \) pyroxene band provides a red continuum more appropriate for the Moon. This method reduces the occurrence of negative values when low abundances of total water are present providing a mean of 0. The continuum-removed \( w \) is then used to calculate ESPAT:

Figure 3. Example lunar thermal excess and the thermal excess model to be removed. Longer wavelengths constrain which thermal model is selected. Spectrum taken at latitude 10°S and longitude 2°E on 15 May 2019.

Figure 4. On left is the spectrum from Figure 3 with a linear continuum removed and after the thermal emission has been corrected showing the lunar reflectance spectrum. On right is multiple thermal excess models removed that are \( \pm 5 \) and 10 K from the optimum thermal model.
Li and Milliken (2017) derived an empirical relationship to convert ESPAT to absolute total water content using a particle size of 70 to 80 μm. This particle range gives a conversion factor from ESPAT to wt.% of 0.5. However, Li and Milliken (2017) calculated this relationship at 2.86 μm, the maximum absorption of hydroxyl and the standard wavelength for laboratory measurement of total water using FTIR data. This wavelength is within the opaque region of atmospheric transmission, and therefore observations at this wavelength with the IRTF are not possible. For this reason we use the average value between 2.9 and 3 μm for the estimate of ESPAT of the 3 μm region. Instead of using 2.86 μm for the conversion of ESPAT to wt.%, we derive the empirical relationship at 2.95 μm providing a conversion factor of 0.8 (Figure 5). After the calculation of ESPAT, we convert to total water abundance in ppm H₂O via:

\[
H₂O \text{ ppm} = 0.8 \times ESPAT_{2.95} \times 10,000
\]

When the abundance of total water is low or 0, the ESPAT calculation sometimes results in negative numbers which is expected in the presence of noise.

4. Results

The presence of total water in our spectra is indicated by a clear discontinuity between 2.5 and 2.9 μm, similar to the “sharp 3 μm group” of Takir and Emery (2012) observed in some asteroid spectra. Figure 6 shows examples of “wet” spectra and “dry” lunar spectra. In addition to the total water feature, a pyroxene band is also observed at 2 μm in most spectra. Strong variations in depth of the 3 μm absorption are observed and range from no absorption (Figure 6 right) to a strong 3 μm absorption (Figure 6, left). Most of the “wet” spectra are found at higher latitudes, while most of the “dry” spectra are found at midlatitudes and near the equator. The “dry” spectra also show more noise at longer wavelengths compared to the “wet” spectra. This is due to the large thermal emission component near the equator compared to the reflectance component. When removing the thermal excess model from the equatorial spectra we are removing a majority of the observed signal and looking at the lower reflectance signal which introduces noise at the thermally dominated longer wavelengths enhancing small systematic and residual errors.

4.1. Diurnal Variation

We calculated the total water abundance from all data collected and plot it as a function of lunar latitude and lunar time of day in Figure 7. The data are interpolated to have one spectrum per degree of latitude. Although small spatial differences occur between these nearby chords (Figure 1), all cover similar terrain types. The size of the points represents the abundance of total water; larger points indicate more total water, while the smallest points have approximately 0 ppm H₂O. For the sake of viewing diurnal effects, the abundances are limited to a maximum of 500 ppm (maximum abundances do not exceed 700 ppm H₂O). Along each observed chord there are strong variations in total water concentrations as a function of latitude. The minimum water observed occurs at low northern latitudes at midmorning to noon hours. Maxima for each chord occur at high latitudes with larger abundances in the south compared to the north. Diurnal variations are seen across constant latitude in Figure 7. With increasing time of day the abundances decrease toward local noon. We lack data for the midafternoon, but the sunset data show the total water values have recovered. There is an asymmetric trend about the equator that favors the southern latitudes with higher total water abundances.

Figure 8a plots the total water abundance versus latitude where each color represents a single pole-to-pole observation and its time from local noon. The two pole-to-pole observations that were acquired at the furthest time from local noon (near 07:00 (blue) and 17:00 (purple) hours) show the highest abundances across all latitudes with a weak latitude dependence. The four other pole-to-pole observations show a strong latitude dependence. A sharp drop from morning, 4.8 hr before local noon to 3.1 hr before local noon, is also seen in...
this plot. In Figure 8b, we plot the abundance of total water versus time of day where the color is proportional to proximity to the equator with brighter colors being closer to the equator and therefore hotter than the darker colors that are farther from the equator and colder. The latitudes were binned into 10° increments from 90°S to 90°N, and the abundance within each 10° wide bin was averaged and plotted at their average time of day for each pole-to-pole observation. A sharp drop is observed at all latitudes from 07:00 to 08:00. After that, the abundance stays relatively constant at each latitude, except for an anomalous point for 80–90°N at ~09:00. At some point between local noon and late afternoon total water recovers close to the dawn values.

These plots show a strong diurnal variation at midsouthern latitudes and a weaker but still present diurnal variation at low latitudes and midnorthern latitudes. The high latitudes also show a weak diurnal variation but at later local times than at low latitudes and midlatitudes.

There is an asymmetry in abundance of total water with the northern latitudes having less total water than the southern latitudes (Figures 7 and 9). The asymmetry may be influenced by mare versus highland materials (McCord et al., 2011). Figure 9 shows the diurnal plot from Figure 7 with the highland material colored black and the mare material colored red. Mare is only observed at northern latitudes possibly explaining the

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Figure 6. “Wet” and “dry” spectra from 18 January 2019 observing run. The spectra show variations in strength and shape of the 3 μm band along with variations in the 2 μm pyroxene band.
asymmetry in total water between the north and south. However, the effects of composition are expected to be small compared to the effects of latitude and lunar time of day. This is expected because where mare was observed, the highland material observed nearby has similar abundances of total water.

5. Discussion

In our lunar spectra, corrected using the strong constraint of thermal wavelengths, we observe variations in the 3 μm hydration band depth and derived water content with latitude, time of day, and composition. This result is in agreement with a number of studies (Grumpe et al., 2019; Li & Milliken, 2017; Sunshine et al., 2009; Wöhler et al., 2017) that also observe variations in the 3 μm band in spacecraft data. The variation indicates that the species responsible for the 3 μm band are undergoing temperature-driven processes.

The observed diurnal variations are largely in agreement with Li and Milliken (2017), but with some differences. First, the total water abundances we measure are lower than those of Li and Milliken (2017) by a factor of about 1.5. This difference could be due to the uncertainty in removing thermal emission from M3 data unconstrained by thermally dominated wavelengths near 4 μm.

The second difference is our observed asymmetry between the northern and southern hemispheres. Li and Milliken (2017) observe higher abundances in the northern hemisphere, while we observe higher abundances in the southern hemisphere. One possible explanation for this is the lunar time of day at which the M3 observations were acquired. The M3 southern observations were taken slightly closer to lunar noon than the northern observations, possibly creating the asymmetry seen in M3 data. The asymmetry in our data cannot be explained by a difference in acquisition times. Another possible source for the observed asymmetry is composition. Across our pole-to-pole scan we traverse through mare and highland regions with most of our northern observations in mare regions and our southern observation in highland regions. Our results agree with Wöhler et al. (2017) and McCord et al. (2011) that highland material retains more total water than mare material.

Figure 7. Estimated total water abundance of the observed pole-to-pole chords plotted as lunar time of day versus latitude. Symbol size is proportional to the abundance of total water.

Figure 8.Variations of total water abundance in ppm H2O plotted against latitude (a) and time of day (b) for the pole-to-pole observations. In b the north and south latitudes are distinguished with solid and dashed lines, respectively.
Due to the lack of data in the lunar midafternoon, we cannot comment on the symmetry of abundance between dawn and dusk terminators, but we do note that abundances at 07:00 and 17:00 are similar. This is in contrast to Li and Milliken (2017) who report more total water in the morning than in the afternoon. Again, this could be due to the time of day the data were acquired with M3, with the afternoon observations beginning closer to noon than the morning observations. We are, however, in agreement with Wöhler et al. (2017) and Grumpe et al. (2019) who see similar abundances between morning and afternoon using their version of thermally corrected M3 data. Wöhler et al. (2017) and Grumpe et al. (2019) did not provide estimates of total water in absolute concentrations, and so we cannot directly compare our abundances to their results.

There are two models that have sought to explain previously reported diurnal variations. The first is that the variation is due to molecular water migrating along temperature gradients (Hendrix et al., 2012, 2019; Sunshine et al., 2009), and the second is that it is due to metastable OH forming during the process of solar wind H diffusing through the regolith (Farrell et al., 2017; Starukhina, 2006; Tucker et al., 2019). Hendrix et al. (2019) observed a diurnal variation in the far ultraviolet (FUV) water ice band ratio using Lyman Alpha Mapping Project (LAMP) data. They show a sudden drop in the FUV ratio intensity near lunar noon that they attribute to a release of molecular water that is bound to the surface with relatively high activation energy. This stands in contrast with our data that show a sudden spectral change in the early morning. If our observed signal is due to molecular water, then the activation energy that binds the water to the surface would be low. The FUV and infrared do sample the surface differently; at FUV wavelengths lunar surface particles are highly opaque, and spectral changes must be confined to effects on the grain surfaces. In contrast, at 3 μm particles are relatively transparent, and the reflectance signal can arise from the volume of the particle and several grains deep within the surface. However, it is difficult to envision how water could exchange with the grain interior over diurnal timescales, so in effect the infrared signal must be a surface phenomenon if due to water. If migrating water is the source of the spectral variations in the FUV and infrared, the two data sets are inconsistent in their timing during the diurnal cycle.

An additional issue with the hypothesis that molecular water can account for the diurnal variations is that it implies large amounts of water supplied to the lunar exosphere on a diurnal basis, something not measured by the Lunar Atmosphere Dust and Environment Explorer (LADEE). Hendrix et al. (2019) noted that their analysis suggested a few hundred particles per cubic centimeter at the altitude of the LADEE spacecraft. LADEE, however, measured water in the exosphere on the order of tens of particles per cubic cm or less (Benna et al., 2019).

Both our data and the FUV data are ambiguous with respect to whether signal is due to H2O versus OH. Tucker et al. (2019) investigated the alternate process that the infrared signal was due to temperature-dependent formation and destruction of metastable hydroxyl as solar wind hydrogen migrates through the optical surface. They found that the model abundances of hydroxyl could roughly account for the infrared signal published by Li and Milliken (2017) which are roughly consistent with our study. This hypothesis does not resolve the inconsistencies between the FUV and our infrared results, but metastable temperature-dependent hydroxyl is more consistent with the exospheric constraints than migrating H2O.

Finally, our observation of a latitude dependent hydration signal that persists even at local noon is consistent with the presence of stable total water. Water equivalent hydrogen at the ~100 ppm level that has been found in lunar impact glasses sampled at the equator by Apollo (Liu et al., 2012). When averaged over the lunar soil, which contains about 70% nominally anhydrous minerals (McKay et al., 1991), would be equivalent to about 30 ppm H2O, roughly consistent with our results. The increase with latitude is consistent with the model of Jones et al. (2018) that showed that equatorial hydroxyl would tend to be depleted by associative desorption of water and that hydroxyl would steadily increase with latitude but not exhibit a diurnal signal.

Figure 9. Mare versus Highland pole-to-pole chords plotted as lunar time of day versus latitude. Red points indicate mare compositions while black indicates highland compositions. Symbol size is proportional to the abundance of total water.
Our observations are best explained by a combination of metastable hydroxyl or molecular water that accounts for the diurnal signal and stable hydroxyl or water stored in impact glasses that accounts for the latitude dependence.

6. Conclusions

Using data constrained by thermally dominated wavelengths, we have applied published methods for processing spectra of asteroids to produce thermally corrected spectra of the lunar surface in the 3 μm region. Using pole-to-pole data scans near the zero longitude meridian obtained at several lunar times of day, we find that a 3 μm hydration absorption feature is widespread on the lunar surface, and its intensity shows strong variations with latitude, lunar time of day, and composition. The observed diurnal variations are most consistent with a model of diurnally evolving metastable hydroxyl. Attributing the signal to molecular water implies much more water in the exosphere than has been measured in lunar orbit by the LADEE spacecraft. Latitude variations superimposed on the diurnal signal are consistent with the presence of stable total water that has been found in lunar impact glasses. The latitude dependence is explained by a temperature-depended depletion of hydroxyl by associative desorption of water over much longer timescales than the lunar diurnal cycle.

Data Availability Statement

All raw data are available on the NASA/IPC Infrared Science Archive (https://irsa.ipac.caltech.edu/applications/irtf/). 18 months after the date listed in Table 1, and the file names of data used in this project are provided in the supporting information in Table S1. Prior to this we will make the data available on a temporary site at the University of Hawaii at Manoa.

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