

Variability of Hydration Across the Southern Hemisphere of the Moon as Observed by Deep Impact

K. L. Laferriere^{1,2} , J. M. Sunshine^{2,3} , and L. M. Feaga²

¹Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN, USA, ²Department of Astronomy, University of Maryland, College Park, MD, USA, ³Department of Geology, University of Maryland, College Park, MD, USA

Key Points:

- We provide evidence for compositional differences in hydration strength and loss rates between mare and highland deposits
- Variability in band shape, depth, and loss rates with temperature suggests that OH and H₂O are present, lost at different rates and temperatures
- Daytime variations over repeated observations reveal that the hydration feature is lost toward local noon and fully replenished by evening

Correspondence to:

K. L. Laferriere,
klaferri@purdue.edu

Citation:

Laferriere, K. L., Sunshine, J. M., & Feaga, L. M. (2022). Variability of hydration across the southern hemisphere of the Moon as observed by Deep Impact. *Journal of Geophysical Research: Planets*, 127, e2022JE007361. <https://doi.org/10.1029/2022JE007361>

Received 5 MAY 2022

Accepted 5 JUL 2022

Abstract Measurements of the 3 μm absorption feature, associated with the presence of hydroxyl and potentially molecular water, were first observed in 2009 by three separate spacecraft observations. Subsequent observations have revealed widespread but variable hydration over the sunlit regions of the Moon. The variability can help to disentangle the individual contributions of OH and H₂O to the 3 μm absorption feature and provide insight into the mechanism of production and loss of OH/H₂O on the lunar surface. We investigate the spatial and diurnal variations of hydration on the southern hemisphere of the Moon as observed by the Deep Impact spacecraft during the lunar flybys in 2009 at spatial scales of 30–70 km/pixel. For a subset of observations of across the lunar south polar region (~2% of the lunar surface), repeat coverage includes three different times spanning half a lunar day, allowing for exploration of diurnal variability. We determine that OH/H₂O is widespread but variable across the lunar south pole. At all but the lowest temperatures observed, highland regions have stronger hydration absorption features than the maria. Changes in band strength demonstrate variable loss rates controlled by surface temperatures with H₂O lost quicker at higher temperatures. Observed variability in the band shape strongly suggests higher H₂O abundance at low temperatures. These observations are strong evidence that the unique shape of the 3 μm band is due to both OH and H₂O. The rapid diurnal evolution of the absorption feature implies that migration of these constituents occurs locally over short distances driven by temperature changes.

Plain Language Summary We observed the Moon's surface over the south polar region at scales of 30–70 km/pix and detected the presence of OH/H₂O at 3 μm . This hydration feature was first found in 2009 in observations from three different spacecraft. In the time since, the origin of this feature and its variations has been explored and debated. Additional observations can help us understand the source of the OH/H₂O on the Moon and mechanisms driving the variability. In this paper, we investigate the distribution of the hydration on the southern hemisphere of the Moon, and how it changes from morning to evening. Consistent with previous work, we find that this feature is widespread across the lunar south polar region with variations in strength largely dependent on composition and temperature. We observe a trend of more water at lower temperatures. Highland regions tend to have stronger total absorption features, except at the lowest temperature regions observed. We also see systematic changes in the shape of the absorption feature, which suggest variations in the amount of H₂O as compared to OH. The rapid changes in hydration imply that the migration of these constituents occurs locally over short distances driven by daytime temperature changes.

1. Introduction

The ubiquitous presence of hydroxyl on the lunar surface has been established since 2009 through the discovery of a 3 μm absorption feature by the Moon Mineralogy Mapper (M³) onboard the Chandrayaan-1 mission (Pieters et al., 2009) and the subsequent verifications from data acquired by the Deep Impact (Sunshine et al., 2009) and Cassini (Clark, 2009) missions. The hydration feature, referred to as the 3 μm band, denotes an asymmetric absorption band that occurs in the near infrared between 2.7 and 4.0 μm . Associated with the O-H fundamental stretch transition band and the overtone of the H₂O vibration band, this absorption suggests the presence of hydroxyl and/or molecular water adsorbed to silicate minerals (Clark, 2009; Honniball, Lucey, Ferrari-Wong, et al., 2020; McCord et al., 2011). This feature was actually predicted to occur across the lunar surface due to production of OH by high-energy proton bombardment of the Moon as shown in experimental (Zeller et al., 1966) and theoretical work (Starukhina, 2001).

© 2022. The Authors.

This is an open access article under the terms of the [Creative Commons Attribution License](https://creativecommons.org/licenses/by/4.0/), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

En route to comet 103P/Hartley 2, the Deep Impact spacecraft observed the lunar surface for instrument calibration as part of its extended mission (EPOXI) using the High Resolution Instrument Infrared (HRI-IR) spectrometer. These observations were useful not only for calibration but allowed for confirmation of the presence of OH/H₂O on the surface of the Moon (Sunshine et al., 2009). Analysis of the June 2009 observations of the northern hemisphere revealed that the strength of the hydration feature is dependent on the instantaneous surface temperature and found that there is a diurnal variation in strength with the weakest feature occurring near local noon (Sunshine et al., 2009).

Diurnal variations were also reported in Pieters et al. (2009) using the M³ spectrometer; however, the spectral limitations of that instrument, which ended at 3 μm, prohibited a direct correction of thermal emission from the Moon. In the wavelength region of the 3 μm band, the underlying continuum spectral signal is composed of both reflected solar radiation and thermal emission. At the surface temperatures observed during the daytime on the lunar surface, the thermal emission contribution can exceed 50%. Without a method for accurately removing the thermal emission, the true strength and variability of the band can be misrepresented or even lost (Clark et al., 2011). The wavelength limitations of M³ have led to disagreements largely in band strength as different thermal corrections have produced results ranging from no diurnal variation to strong diurnal variations (Bandfield et al., 2018; Grumpe et al., 2019; Li & Milliken, 2017; Wöhler, Grumpe, Berezhnoy, & Shevchenko, 2017). The spectrometer aboard the Deep Impact spacecraft extends to 4.8 μm, allowing for a direct and more reliable removal of the thermal component (Klaasen et al., 2008).

Clark (2009), Pieters et al. (2009), and Sunshine et al. (2009) observed weaker hydration absorptions in the maria compared to highlands, a variation with latitude, and with temperature. Observations of lunar hydration revealed high spatial and temporal variability across the lunar surface. Recent works (Chauhan et al., 2021; Hendrix et al., 2019; Honniball, Lucey, Ferrari-Wong, et al., 2020; Kim et al., 2018; Klima & Petro, 2017; McCord et al., 2011; Poston et al., 2015; Wöhler, Grumpe, Berezhnoy, & Shevchenko, 2017) have observed a lower hydration content in the maria compared to highlands, while Li and Milliken (2017) detected no strong difference between the two distinct terrain types. The hydration band strength has been observed to vary with latitude (Honniball, Lucey, Ferrari-Wong, et al., 2020; Kim et al., 2018; McCord et al., 2011), suggesting a manifestation of temperature dependence (Li & Milliken, 2017). Hurley et al. (2015) and Williams et al. (2017) find that temperature is the major control in the variability of band strength. The diurnal variations have been shown to be strongest at the midlatitudes where temperature fluctuations are greatest (Honniball, Lucey, Ferrari-Wong, et al., 2020; Li & Milliken, 2017).

Despite extensive studies of the lunar hydration feature, the contribution to the 3 μm hydration feature from molecular water as compared to OH alone is unknown. The asymmetric shape of the 3 μm absorption feature may contain contributions from both OH and H₂O but the two compositions are difficult to separate from each other (Potin et al., 2020) particularly without data that extend beyond 3 μm. Honniball, Lucey, Li, et al. (2020) are the first to provide evidence for molecular water on the sunlit region of the lunar surface using the 6 μm H₂O absorption feature. Honniball et al. (2022) later detected surface abundance from the 6 μm feature that exceeds the amount measured for the lunar exosphere, suggesting that the feature is caused by molecular water trapped in an impact glass. In situ observations by the Chang'E-5 lander provide evidence for hydration, but cannot conclusively state whether the feature is provided by hydroxyl or molecular water (Lin et al., 2022). The exact source and transport processes are unknown with the current understandings and hypotheses presented in Schörghofer et al. (2021). Spectrally, the hydration feature has been suggested to result from OH/H₂O molecules that could range from ~70 (Lin et al., 2022) to 1,000 ppm (Pieters et al., 2009), potentially consisting of a fraction of a monolayer of molecules on the lunar regolith (Hendrix et al., 2019).

In this work, we use infrared spectroscopy of the southern hemisphere of the Moon from 1.05 to 4.8 μm acquired during the Deep Impact spacecraft lunar flyby in December 2009. The analyses discussed here make use of Deep Impact data taken after the publication of Sunshine et al. (2009) analysis of the northern terrains and include updated instrument calibrations (Klaasen et al., 2013). The spectral range constrains the thermal emission and characterizes the full 3 μm band. This data set enables the exploration of the majority of the southern hemisphere on kilometers scale, while providing observations of some regions at two or three separate local times of day. Variations in the strength and the shape of the hydration absorption feature with local terrain composition and temperature give insight into the mechanism for formation and replenishment of this feature. The observed

time-of-day dependencies provide evidence for changes of the abundance of OH and/or H₂O on short timescales, potentially tied to local migration of molecules.

2. Data

The spectra used in this work were obtained by the HRI-IR spectrometer aboard the Deep Impact spacecraft on 5, 12, and 18 December 2009 (DOY 339, 346, and 352, respectively) as part of the instrument's calibration measurements and are archived at the Planetary Data System Small Bodies Node (DIF-CAL-HRII-2-EPOXI-CALIBRATION S-V2.0, McLaughlin et al., 2011). These observations used the entire spectral range of the instrument spanning 1.05–4.87 μm across 512 channels. This included the 3 μm hydration feature that is due to the stretching mode of OH and H₂O and allowed constraints to be placed on the thermal emission from the Moon with the inclusion of the 4.0–4.5 μm region (Groussin et al., 2007).

For the HRI-IR, three binning modes were available. The observations presented here were taken with the fastest mode, a binned subframe (BINSF2), which had a minimum exposure time of 0.71 s (Klaasen et al., 2008). This binning mode only collected data along the central 64 spatial pixels of the slit so that the Moon was imaged through the anti-saturation filter situated in the center third of the slit. This filter limited the transmission of light at wavelengths longward of 2.7 μm such that the thermal contribution from warm objects was reduced (Klaasen et al., 2008, 2013).

As this instrument was designed to observe a comet, the combination of using the anti-saturation filter and shortest exposure time was necessary to prevent total saturation of the instrument when imaging the bright and warm Moon. However, saturation ($\sim 12,000$ DN) still occurred at wavelengths longward of 2.8 μm in some of the data. Saturated pixels are excluded from analyses as described in the following section as the thermal emission cannot be confidently determined and removed. The region of saturation in each observation is shown in Figure 1. The analysis is limited by this saturation to temperatures below 393 ± 1 K, latitudes poleward of 5° S, and local noon observations to incidence angles greater than 40° .

Scans of the lunar surface were taken using the HRI-IR as the spacecraft slewed perpendicular to the slit of the spectrometer at a rate of one slit width per integration, providing two-dimensional spatial maps of the lunar surface that contain spectral information in the third dimension. Each date of observation included a set of three scans composed of 100 frames. On December 18, the Moon was closest to the spacecraft and observations were extended by 35 frames per scan to incorporate the entire sunlit region of the Moon in the instrument's field of view. Each of these scans placed the sunlit region differently on the detector, such that the first scan (00) was centered on the limb, the middle scan (01) covered the majority of the lit surface, and the final scan (02) highlighted the terminator as shown in Figure 1. Each scan contained mostly but not entirely overlapping regions, which extends both the range of coverage and improves the SNR. Each day of observation is spaced 1 week apart providing a total of half a full lunar day of coverage. The total observed region covers just under half of the southern hemisphere. As the distance to the lunar surface changed, the spatial resolution varied among dates from 70 km/pixel to 49 km/pixel to 31 km/pixel. Having three scans per day with overlapping regions also facilitated validation of our thermal modeling.

Between the first and final observations, approximately half a lunar day passed (180° of rotation), which allowed a number of locations on the Moon to be observed at two different times of day and a select region to be observed at three separate times. The region of repeat observations is shown in Figure 1 for each observation. Notable features present in these observations are labeled in Figure 2 for the middle scans of each day (the most spatially extensive observations), which include craters Watson, Lippman, Fizeau, and Zeeman. South Pole Aitken Basin (SPA) is observed in the observations on 12 December 2009 and 18 December 2009 in the morning and evening, respectively.

3. Methods

After determining the proper dark images for these observations, the raw data (archived at the Planetary Data System Small Bodies Node; McLaughlin et al., 2011) were processed through the Deep Impact eXtended Investigation pipeline, which include corrections for the pixel-by-pixel nonlinearity response of the instrument, flat

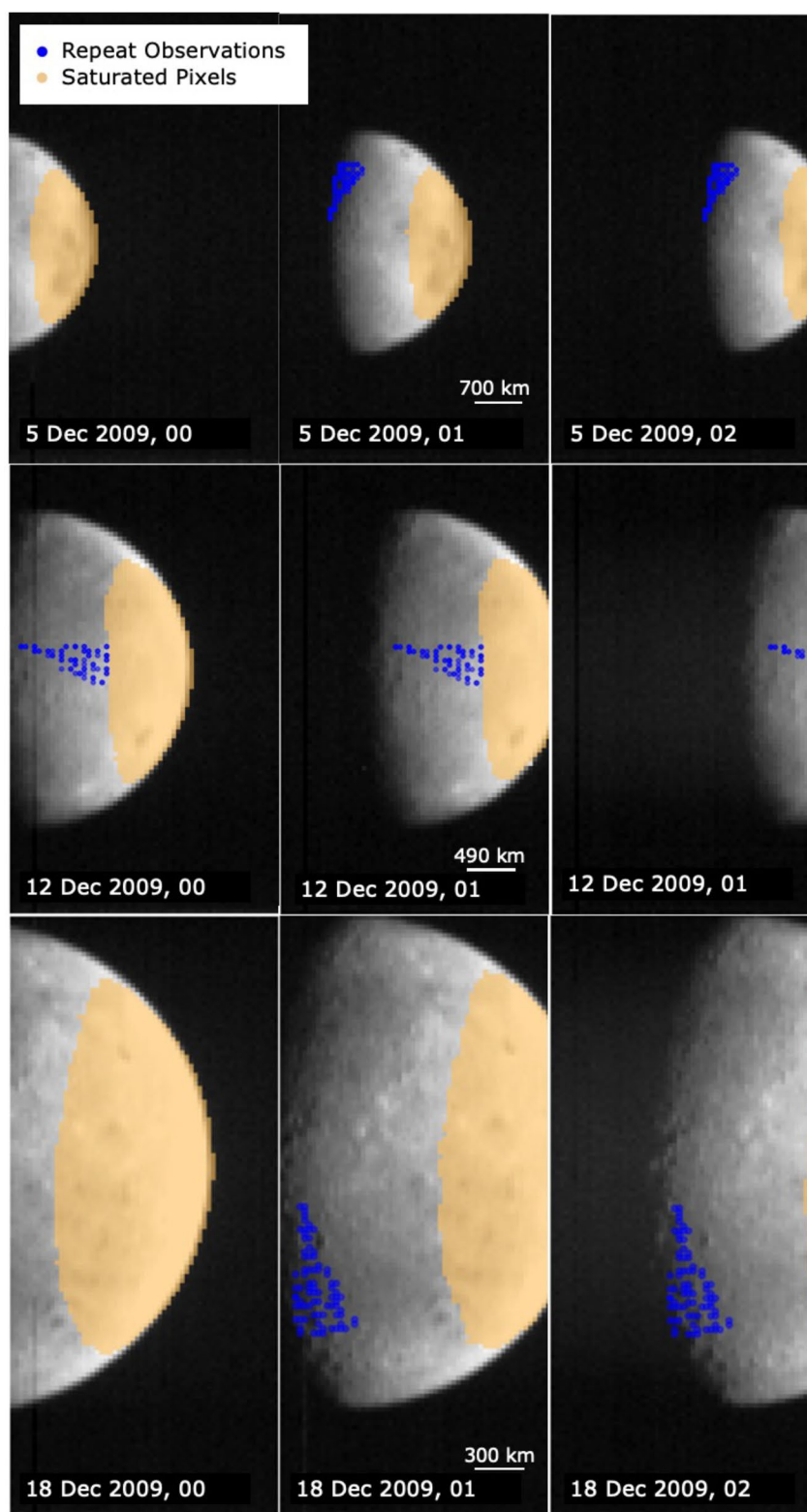


Figure 1. Images ($1.06 \mu\text{m}$) from all nine calibrated cubes for each of the three dates of observation. Three observations (scans 00, 01, and 02) were taken per day due to pointing uncertainty. The mask (beige) denotes where the data are saturated over $\frac{1}{4}$ of the wavelengths needed for thermal modeling, preventing their use in our analysis. Saturation occurs for surface temperatures $>393 \text{ K}$. The blue dots show the pixels with repeated observations over all 3 days, which span from morning (top) to evening (bottom) allowing for investigation of diurnal changes of a specific surface region. The spatial resolution increases from 70 km/pix (top) to 49 km/pix (middle) and to 30 km/pix (bottom).

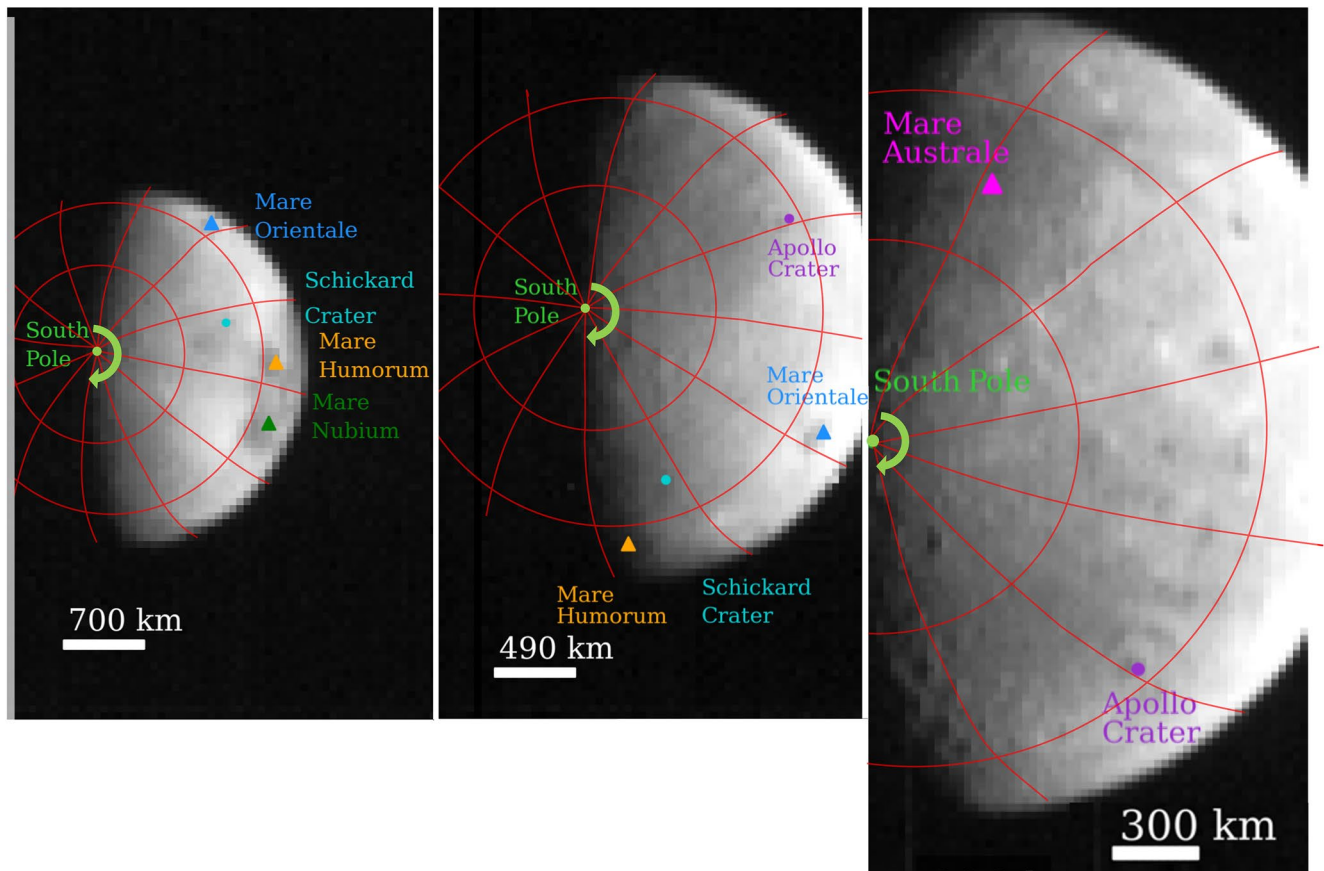


Figure 2. Center scan for each date (5, 12, and 18 December) with some notable surface features labeled for context. Maria are labeled with triangles and craters are labeled with circles. The rotation is also shown; it is important to note that the rotation direction is clockwise because we are observing from below the south pole. On the first and second days, Mare Orientale, Apollo Crater, and Mare Humorum are observed. On the second and third days, Schickard and a subset of the South Pole Aitken Basin (SPA) are observed. A small region, mostly of SPA between Mare Orientale and Schickard, is observed in all 3 days. Red lines denote latitude and longitude grids with a spacing of 30°.

field, known bad pixels, and absolute calibration using the IR spectrometer radiometric calibration curve (Klaasen et al., 2008, 2013). These steps are described in more detail below.

3.1. Calibration of the Data Set

Since the work of Sunshine et al. (2009), improvements have been made in the absolute calibration of the instrument (Klaasen et al., 2013). The steps in calibrating each frame of the HRI-IR data are: masking of known bad pixels, linearization, dark subtraction, division by the flat field, and multiplication by the absolute calibration coefficients. Calibrated scans were then compiled into total 3D (2D spatial and 1D spectral) cubes, which are used in our analysis. As described in Klaasen et al. (2013), these calibration improvements included an updated flatfield map using pixel-by-pixel processing with a new transmission function through the anti-saturation filter, improved pixel-by-pixel linearization coefficients, an updated bad pixel map derived with knowledge of the new pixel-by-pixel linearity behavior, an updated spectral calibration curve including the spectral smile model, and an improved pixel-by-pixel absolute calibration from several additional observations of Beta Hyi (a calibration star) (Klaasen et al., 2013). As the original purpose of this instrument was to observe a comet, the lunar observations are off-nominal particularly in the temperature with respect to the cometary observations. This largely affects the data by causing saturation and by limiting the use of darks.

In order to best understand the variation in the lunar hydration, it was necessary to include all observations in the study; however, there were no true equivalent sky darks associated with all nine observations of the southern hemisphere. Due to the configuration of the HRI-IR instrument, darks were acquired by observing a patch of dark

Table 1

The Scaling Factor Used to Adjust the Lunar Master Dark (From 5 December 2009) to Account for Variations Recorded in the Instruments' Optical Bench Temperatures (in Kelvin) During Observations

DOY	Date	Scale factor	Optical bench temperature (K)	Observation ID
339	5 December 2009	1	137.6	1000000, 1000001, 1000002
346	12 December 2009	1.03	137.8	1000000, 1000001, 1000002
352	18 December 2009	1.03	137.8	1000000, 1000001, 1000002

Note. Day of year (DOY) and observation ID are included for querying the PDS data set. All scans within these parameters were used.

sky such that the background signal is created by the thermal emission of the instrument surrounding the detector (Klaasen et al., 2013). Following the end of the primary mission (July 2005) until the extended mission cruise observations in December 2009, the IR dark background varied significantly, preventing a single master dark frame from being applicable to all observations (Klaasen et al., 2013). Klaasen et al. (2013) also determined that the background generation rates and inherent structure of the dark signal varied between the full-frame modes and subframe modes. The 5 and 12 December 2009 observations have associated sky darks, but they were taken using a different mode than the resolved lunar observations; thus, dedicated sky darks are not available for our data sets. We found that using an in-scene dark of the same mode (BINSF2) and applying a scaling factor to account for the instrument temperature were a better approach to optimizing the dark subtraction than using the full-frame darks. The 5 December 2009 observations ended well off the Moon (in the first scan 00, approximately 4,000 km off) and provide excellent darks that are free of scattered light and were acquired in the same instrument mode and at the same time as the lunar science observations. However, there were no regions of dark sky within the 12 or 18 December 2009 data due to the presence of $\sim 2\%$ – 5% scattered light in the infrared from the Moon even in the farthest reaches of the scans. This prevents the use of any frames from the scans on these two dates as dark frames. Due to the potential for the first frame issues caused by a background buildup in the instrument (Klaasen et al., 2013), we were unable to confidently use the first four frames of the 5 December 2009 scans for the creation of a master dark. In the end, we used the last 8 frames of the first science scan on the first day (5 December 2009), which were determined to be devoid of scattered light, to create our in-scene master dark in the proper BINSF2 mode. This lunar master dark was then applied with a scaling factor to each scan as described below.

The master dark was created by linearizing each of the 8 frames, normalized by the exposure time, and then combining them into a single image using a resistant mean with a cutoff of 2σ . Klaasen et al. (2013) showed that slight variations in the optical bench temperature caused differences in the background rate. To accurately apply this master dark as the temperature fluctuated between sets of scans, we applied a scaling factor as listed in Table 1. The scaling factor takes into account the optical bench temperature change from the original set of scans (5 December 2009) and is determined such that the spectra from the region farthest from the Moon is as close to zero as possible, indicating that there is no remaining light. Note that the scaling factor applied for the first day was 1, meaning no adjustment was made to the master dark as this was the origin of the values used to create it.

Following the work of Klaasen et al. (2013), we used a saturation cutoff for the raw data of 12,000 DN. Throughout the nine scans, there were various saturated pixels concentrated around the lit limb of the Moon. Saturation can occur at any wavelength, but most frequently occurred in the thermal region of the spectrometer. In our analysis, a wavelength is considered saturated and masked if the raw value was greater than 12,000 DN. In addition, if over a fourth of the data from 3.5 to 4.3 μm was greater than 12,000 DN, we could not obtain reliable thermal fits and that pixel was not analyzed. Pixels that saturated only beyond 4.3 μm do not affect our model and are considered valid. Noise from the anti-saturation filter was most prevalent beyond 4.5 μm so that region was not used for thermal modeling. If saturation occurred outside of the 3.5–4.3 μm region, that individual wavelength was ignored, but all unsaturated wavelengths of the pixel are used. As shown in Figure 1, saturation greatly limited our analysis of the entire observed surface, especially closest to the subsolar point. Due to this saturation, we are unable to make conclusions on the behavior of the 3 μm feature at the highest surface temperatures or at local noon for midlatitudes to the equator.

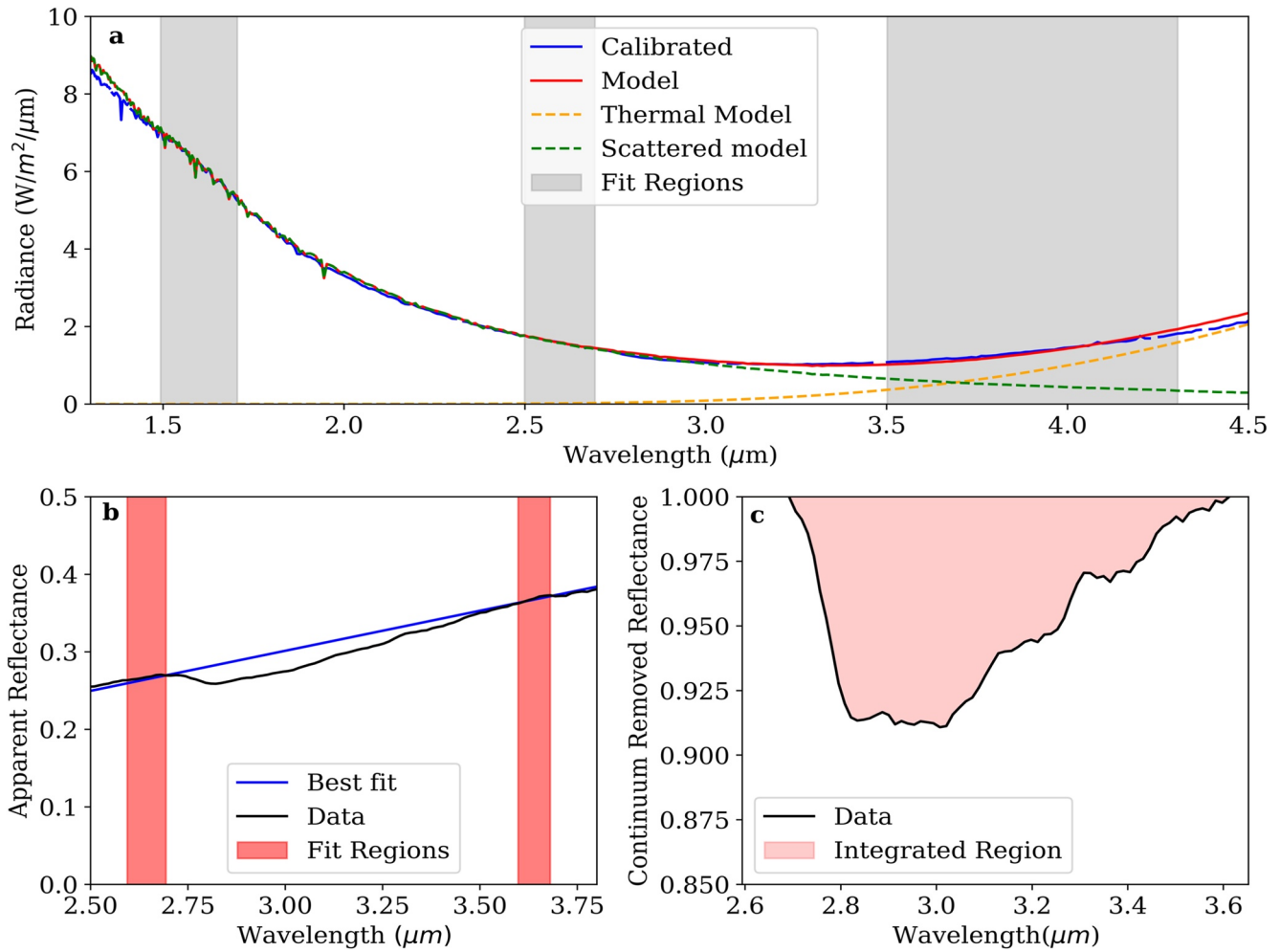


Figure 3. Example of model fitting to calibrated spectra. The thermal component is significant past $2.5 \mu\text{m}$ and must be removed to accurately assess the $3 \mu\text{m}$ hydration feature. This is uniquely enabled by the full wavelength coverage offered by the use of the Deep Impact HRI-IR spectrometer. (a) Calibrated spectrum from a single pixel in blue. The final fit of the full iterative model is in red with the individual thermal and scattered components shown as yellow and green dashed lines, respectively. The wavelength regions used to constrain the model are shaded. (b) The linear continuum (blue) across the $3 \mu\text{m}$ absorption band is determined from the shaded wavelength regions (red). The data (black) in apparent reflectance (which was thermally corrected based on the model in (a)). (c) Continuum removed reflectance of the full $3 \mu\text{m}$ band revealing both the depth and shape of the lunar hydration band.

3.2. Removal of Thermal Emission

For the unsaturated data analyzed here, the thermal component is significant longward of $\sim 2.5 \mu\text{m}$ and dominates longward of $\sim 3 \mu\text{m}$ as shown in Figure 3. An accurate thermal model is therefore necessary to correctly determine the strength of the $3 \mu\text{m}$ feature. Exploration of the entire shape of this $3 \mu\text{m}$ absorption feature is enabled by the full wavelength coverage specific to the Deep Impact spacecraft HRI-IR spectrometer that was not available for M^3 or Cassini. We iteratively modeled the total lunar radiance as the sum of two distinct components (Equation 1), scattered (reflected) light, $R_{\text{Reflected}}$, and thermal radiation, R_{Thermal} .

$$R_{\text{Model}} = R_{\text{Reflected}} + R_{\text{Thermal}} \quad (1)$$

The thermal contribution (R_{Thermal} , Equation 2) is modeled by a blackbody function of temperature T and wavelength λ , modulated by an emissivity ϵ that is also a wavelength-dependent function. Relevant parameters for our model are shown in Table 2. Kirchhoff's law is assumed in Equation 2 such that emissivity is not allowed to exceed 1.0.

Table 2

List of Parameters Used in the Removal of the Thermal Component With Units as Applicable

Variable	Parameter	Value
ϵ_0	Initial Emissivity	0.9
λ	Wavelength	μm
h	Planck's constant	$6.62607015 \times 10^{-34} \text{ J/Hz}$
c	Speed of light	$299,792,458 \text{ m/s}$
k_b	Boltzmann constant	$1.380649 \times 10^{-23} \text{ J/K}$
i	Incidence angle	$[0-90^\circ]$
F_{sun}	Solar continuum flux	$\text{W/m}^2/\mu\text{m}$
$m_{1,2,3}$	Slope of Reflectance	$1/\mu\text{m}$, Model output
$d_{1,2,3}$	Intercept of Reflectance	Unitless, Model output
T	Temperature	K, Model output
m_e	Slope of emissivity	$1/\mu\text{m}$, Model output
d_e	Intercept of emissivity	Unitless, Model output
$\epsilon(\lambda)$	Emissivity	$[0-1]$, Model output

Note. Outputs of the model are noted.

$$R_{\text{Thermal}} = (1 - \epsilon(\lambda)) \frac{2hc^2}{\lambda^5} \frac{1}{\frac{hc}{\lambda k_b T} - 1} \quad (2)$$

where h is Planck's constant, c is the speed of light, and k_b is the Boltzmann constant.

The reflected contribution ($R_{\text{Reflected}}$, Equation 3) is modeled as the amount of solar incident light, F_{Sun} , with a simple incidence angle, i , photometric correction of $\cos(i)/\pi$ such that the reflected component can be modeled as a linear function ($y = mx + d$) of wavelength (λ). We assumed that the difference in solar continuum between 1 AU and the true Moon-Sun distance at the time of observations was negligible and used the solar continuum as defined by MODTRAN at 1AU for all of our spectral modeling (Berk et al., 2003, 2014).

$$R_{\text{Reflected}} = \frac{\cos(i) F_{\text{Sun}}}{\pi} (m\lambda + d) \quad (3)$$

where i is the incidence angle, F_{Sun} is the solar continuum flux at 1 AU, m is the slope, d is the intercept, and λ is the wavelength.

A final equation was used in our iterative method to fit the continuum and solve for best-fit temperature. Equation 4 allows for us to transform quickly between the reflected light and thermal emission and defines the apparent reflectance.

$$\text{Apparent Reflectance} = \frac{\pi (R_{\text{Calibrated}} - R_{\text{Thermal}})}{F_{\text{Sun}} \cos(i)} \quad (4)$$

To remove the thermal radiance, we modeled both the reflected and thermal components as defined in Equations 2 and 3. We determined the best-fit parameters for each pixel in our set, finding both temperature and emissivity. As emissivity and temperature cannot be uniquely determined from the measured data, an iterative approach was necessary. To determine the best fit through our iterations, we fit spectral regions free of known absorption features (1.5–1.7, 2.5–2.7, 3.5–4.3 μm , shaded regions in Figure 3) and allowed for m , d , ϵ , and T to vary. For the analysis, only one temperature is assigned per pixel, which is a limiting factor on the model as the spatial resolution, and hence the surface covered in a single pixel, may incorporate many different temperatures. The procedure is as follows (shown in Figure 4):

Initial: We fit the calibrated radiance data, $R_{\text{Calibrated}}$, with a thermal component between 3.5 and 4.3 μm using Equation 2, assuming emissivity ϵ to be held at 0.9 at all wavelengths. This results in an initial estimate for temperature T_1 .

Step 1. The modeled thermal component is subtracted from $R_{\text{Calibrated}}$ and corrected for solar incidence by Equation 4.

Step 2. The slope and offset (m_1 , d_1) of $R_{\text{Reflected}}$ are determined by fitting Apparent Reflectance as a linear function of wavelength λ between 1.5–1.7 and 2.5–2.7 μm . These values (m_1 , d_1) are then plugged into $R_{\text{Reflected}}$.

Step 3. The new $R_{\text{Reflected}}$ is removed from $R_{\text{Calibrated}}$ to create an $R_{\text{Calibrated-Reflected}}$.

Step 4. $R_{\text{Calibrated-Reflected}}$ replaces $R_{\text{Calibrated}}$ in steps 1–3, running through instead with emissivity ϵ set as 1 - Apparent Reflectance in order to determine T_2 , m_2 , d_2 , and a new $R_{\text{Calibrated-Reflected}}$.

Step 5. Steps 1–3 are repeated for the new $R_{\text{Calibrated-Reflected}}$ with emissivity ϵ allowed to vary as a function of m_e and d_e with temperature held at T_2 in order to determine m_e , d_e , m_3 , d_3 , and $R_{\text{Calibrated-Reflected}}$.

Step 6. Step 1 is redone holding emissivity ϵ as a linear function of m_e and d_e and allowing T to vary. This allows for us to determine the best R_{Thermal} , which is then applied in Equation 4 to determine the final apparent reflectance.

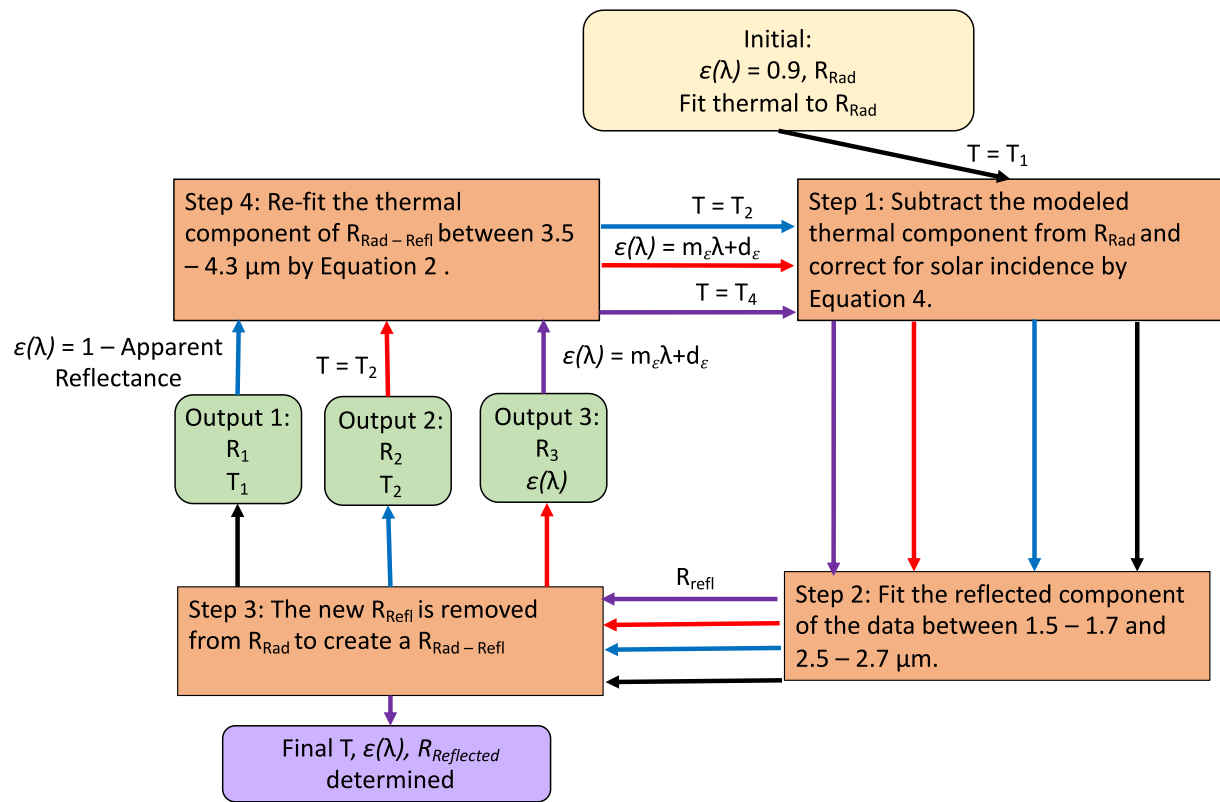


Figure 4. Flowchart describing the method (see Section 3.2) used to iteratively determine the temperature, emissivity, and reflected light in the Deep Impact spectra. Arrow colors signify each iteration, starting by determining the best-fit thermal for an assumed constant (0.9) emissivity, which results in an initial T estimate. Following the black arrows for the first iteration, we fit the reflected component and remove that from the original radiance data. Following the blue arrow through steps 1–4, the second iteration assumes a wavelength-dependent emissivity to better determine the thermal component, temperature, and reflected component. The third iteration assumes a temperature in order to fit emissivity as a wavelength-dependent function, following the red arrow through steps 1–4. For the final iteration, emissivity is held as the determined wavelength-dependent function such that the final best-fit temperature can be determined.

After iteration of the thermal modeling, the thermal contribution and the solar irradiance are removed from the calibrated data to determine the apparent reflectance. The robustness of this iterative method can be tested by exploring emissivity versus wavelength of the same region at different temperatures, enabled by the Deep Impact repeat observations of the same region of surfaces across different lunar times of day. The apparent reflectance, which is dependent on the emissivity value, is shown in Figure 5 below. The resulting variability in band depth is not a result of our thermal correction or observation geometry, but is instead a real effect occurring on the lunar surface.

3.3. Band Depth

To determine the band depth, a least squares straight line fit was made to the apparent reflectance between 2.6–2.7 μm and 3.6–3.7 μm . The band depth as a function of wavelength was then calculated by dividing this continuum from the apparent reflectance. This continuum removed and the wavelength-dependent absorption supports an evaluation of the band shape, including the wavelength location of the band minimum. To quantify the overall band strength, band depth was integrated over the absorption defined in Pommerol et al. (2009; Equation 2) and defined here as Equation 5 and shown in Figure 3c as the shaded region.

$$IBD = \sum_{i=\lambda_0}^{i=\lambda_1} C(i) - R(i) \quad (5)$$

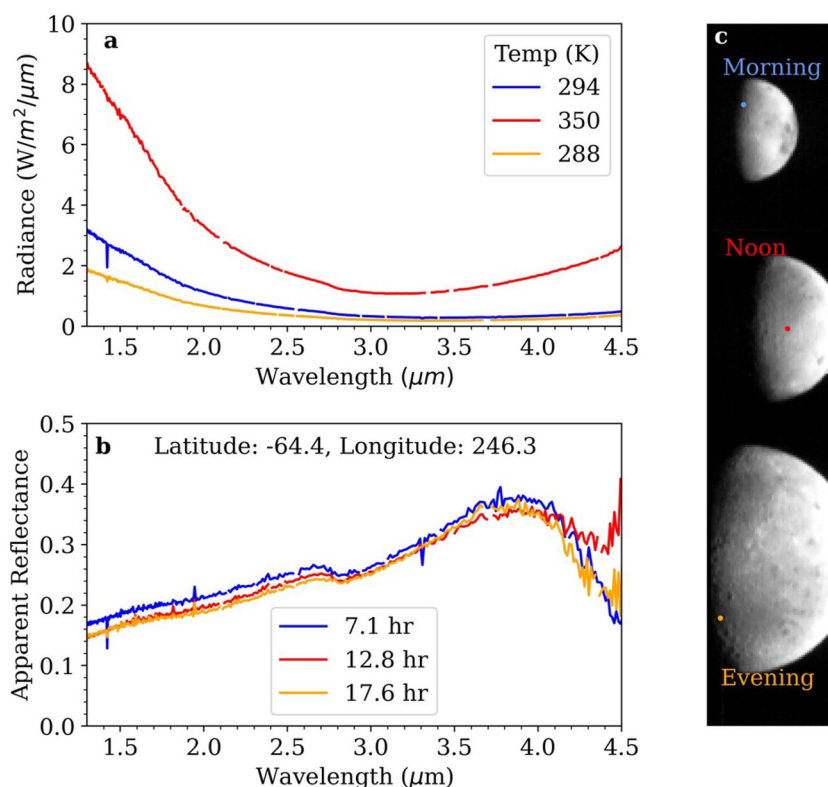


Figure 5. Thermal removal comparison for same location (lat, long) measured at three different times and temperatures. (a) Radiance versus wavelength for all three times. (b) Apparent reflectance versus wavelength for all three times. Note the difference in strengths of thermal contributions and hydration. (c) The location of the repeated point is identified on the Moon (color matched dot to (a) and (b)) with relative local time of day (Moon rotates clockwise in this geometry). Considering the changing spatial resolution, sub-spacecraft point, and time of day between the three dates of observation, we validated our model (e.g., tested that the emissivity for a given location on the Moon was indeed found to be approximately constant across the data) such that the resultant variations in the 3 μm band truly represent changes in hydration.

This integrated band depth (IBD) provides a measure of the strength of the hydration feature at all wavelengths. The shape is examined by tracing changes in the band minima as well as comparing the band shape from different regions.

Before calculating the IBD, we first smoothed the data in the spectral dimension by determining the running mean over every 3 wavelength steps with a 2σ cutoff in order to remove individual outliers from the spectra. This was done in order to combat bad pixels, which were neither originally caught and removed by the bad pixel maps nor saturated. Then, the value of the IBD was determined by integrating the region of [1-continuum], below unity and between 2.6 and 3.65 μm excluding any value greater than unity. This region of integration is shown in panel c of Figure 3. The uncertainty on the IBD values was determined by the covariance of our fits.

3.4. Distinguishing Maria and Highlands

Variations in the strength of the hydration features between mare and highland deposits were recognized in the first detections of the 3 μm features (Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009) and have been verified in many subsequent studies (Chauhan et al., 2021; Cheek et al., 2011; Kim et al., 2018; Klima & Petro, 2017; McCord et al., 2011; Poston et al., 2015; Wöhler, Grumpe, Berezhno, & Shevchenko, 2017). Kim et al. (2018) specifically related a decreased hydration strength to an increasing pyroxene content. McCord et al. (2011) compared the 2 μm band strength to that of the 3 μm band strength and found a linear relation. Given the large spatial scale provided by this data set, we investigate the compositional dependences by separating the data into two groups: mare and highland. Differences in the pyroxene abundance correspond to differences in the strength of the 2 μm absorption band (Adams, 1974). Determining mare/highlands boundaries within the pixel scale of

our observations allows for the classification of a pixel as a single terrain type, while previously defined boundaries occur on subpixel scales.

Using the same method used to calculate the IBD of the 3 μm band, we use the IBD of the 2 μm feature associated with pyroxene as our proxy for mare/highland compositional differences. After removing a continuum between 1.5–1.6 μm and 2.6–2.7 μm , we create a 2 μm band depth by integrating from 1.5 to 2.50 μm . Pixels are classified as mare or highland as $\geq 2.5\%$ or $< 2.5\%$ integrated 2 μm band depth, respectively. The inclusion of 2%–2.5% as highlands may be problematic, as this region is more intermediate than true highlands. For example, the center of Apollo crater is a mare-filled basin, and at our spatial resolution, has a 2 μm band depth of 2.3%. This pixel likely has contributions from the surrounding highland region and thus is truly intermediate but is designated as highlands. For the simplicity of exploring two populations, however, we include the intermediate values as highlands. At the scale of our data, this does not affect our findings significantly. However, note that using the 2 μm band depth to separate maria from highlands also places the South-Pole Aitken basin into the maria due to that region's relatively high pyroxene abundance (Moriarty & Pieters, 2018).

4. Results

Hydration is ubiquitous in the Deep Impact south polar data. In this work, the strength of the 3 μm hydration absorption feature is shown to vary with composition, latitude, solar incidence angle, time of day, and instantaneous temperature. The clearest dependencies of band strength are on mare-highland terrain type and temperature with band minima having a temperature-dependent shift. These observations provide an excellent opportunity to explore diurnal variability in the 3 μm band at the same surface location.

The results are limited by the saturation of the instrument such that the highest temperature observed is 393 ± 1 K and to a latitude of 5°S , which is also limited by the geometry of the flyby observations. These limitations prevent exploration of the variations in the 3 μm band at the highest temperatures achievable at the lunar surface, where the solar incidence angle approaches zero. Instead, the local noon observations are restricted to mid to high incidence angles with the lowest noon observation having an incidence angle of 40° .

Given the large spatial scales of the data set, on the order of tens of km per pixel, investigation of compositional differences between the maria and highlands is accessible only on a global scale. As shown by previous work (e.g., Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009), the strength of the hydration feature for the highlands is greater than maria. In this work, compositional differences are specifically defined by the abundance of pyroxene. Highland regions, identified here as when the 2 μm pyroxene absorption strength is below 2.5%, have higher IBD for the OH/H₂O band than their maria counterparts as shown in Figure 6. The entire data set for all nine observations is presented in Figure 6a, separated into the two compositional end-members. We find that there is a significant difference in the hydration strength across the temperature range between the two compositions with the highland regions having a stronger 3 μm absorption feature for all but the lowest temperatures. For both compositional groups, there is a general decreasing trend of 3 μm IBD with an increasing temperature.

The trend is more obvious when the data set is averaged to temperature bins of 5 K in order to increase the SNR as shown in Figure 6b, revealing how the rate of hydration loss changes with temperature. Only at the lowest temperature regimes, below 260 K, does the 3 μm IBD for highlands fall below that of the maria. This may be an artifact of our determination of composition, as SPA has been classified as maria due to the high pyroxene content and represents a large portion of the near-terminator and near-pole data from these observations. Regardless, Figure 6b clearly shows that this trend toward lower IBD is nonlinear over the observed temperature range. The maria are undergoing a significant loss of hydration from 240 to 290 K and a different, less-steep constant loss rate from 290 to 380 K, while the highlands undergo a similarly constant loss rate from 240 to 370 K. At 370 K, the highlands begin to undergo significant rate loss and fall to the low maria strength values. At this point, the two compositional groups both begin to drop in IBD significantly, until reaching similar IBD values at the highest temperature regions above 380 K. This work presents clear evidence for this compositional and temperature-dependent loss rates.

As the instantaneous temperature is related to the incidence angle, we expect to find a similar dependence on incidence angle as found for temperature. We find that the 3 μm IBD value increases with increasing incidence angle (Figure 7). The lack of data present below 50° is related to the saturation of the data set. The incidence

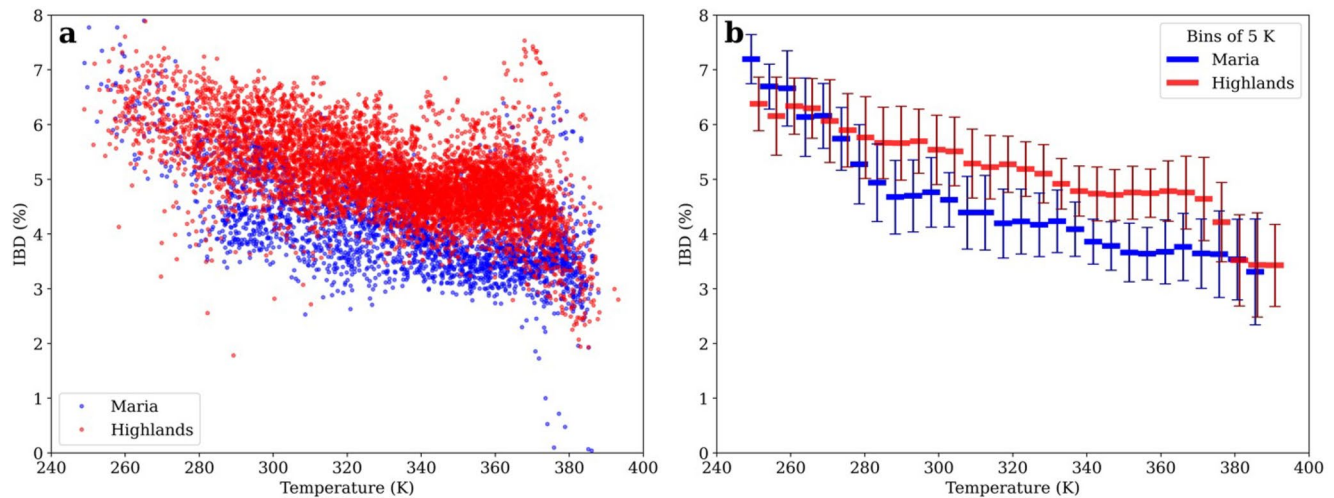


Figure 6. A clear temperature and compositional dependence of 3 μm band strength measured as integrated band depth (IBD). (a) The IBD of the 3 μm absorption feature versus temperature for individual pixels observed during the Deep Impact south polar flyby. As described in the text, the data are separated by composition into maria (blue) and highlands (red) based on the strength of their 2 μm pyroxene bands. A stark compositional dependence is revealed. (b) Blocks of 5 K are averaged and separated by composition. The relationship of the hydration strength with temperature is shown to be significantly nonlinear and to vary with composition.

angle is determined relative to a sphere such that it does not include effects of local topography. At the scale of our observations, variations in topography on sub-pixel scales and surface roughness are not able to be observed due to our average pixel size. The clearly defined composition separation shown in both Figure 7 with incidence angle and in Figure 6 with temperature indicates that the compositional separation is not a product solely of different temperature regimes in the two compositions but instead a real dependency based on the differences in composition between the highlands and maria and their ability to retain hydration.

The temperature and compositional dependence can also be explored through changes in the shape of the 3 μm band (shown in Figure 8). Changes in band depth and shape affect the IBD values, although the change in depth is more significant. Band depths are found to decrease with increasing temperature for both the maria and highlands (Figures 8a and 8b), resulting in the change with temperature as shown in Figure 6. Band shape is also observed to shift toward a shorter wavelength minimum with increasing temperature. The loss rate trend shown in Figure 6

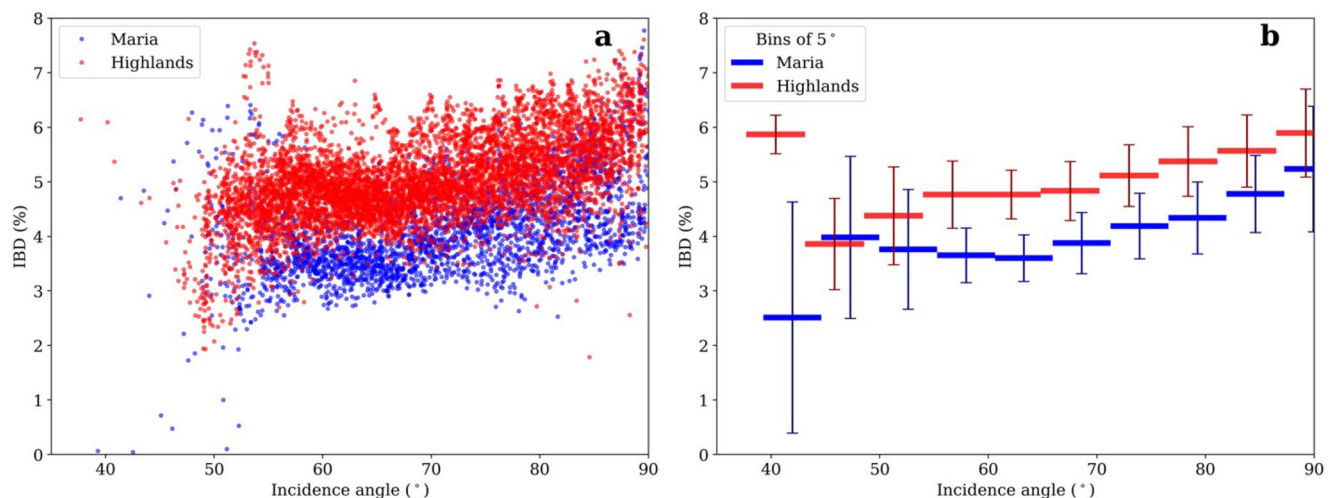


Figure 7. Incidence angle and compositional dependence of 3 μm integrated band depth (IBD). (a) The IBD of the 3 μm absorption feature versus incidence angle for individual pixels observed. As described in the text and Figure 6, the data are separated by composition into maria (blue) and highlands (red). A trend of increasing strength with increasing incidence angle is visible. The lack of data below 50° is due to saturation of the instrument. Compositional dependence is still evident as maria have lower IBD values across incidence angles. (b) Blocks of 5° are averaged and separated by composition. The relationship of the hydration strength with incidence is shown to be significantly nonlinear and to vary with composition.

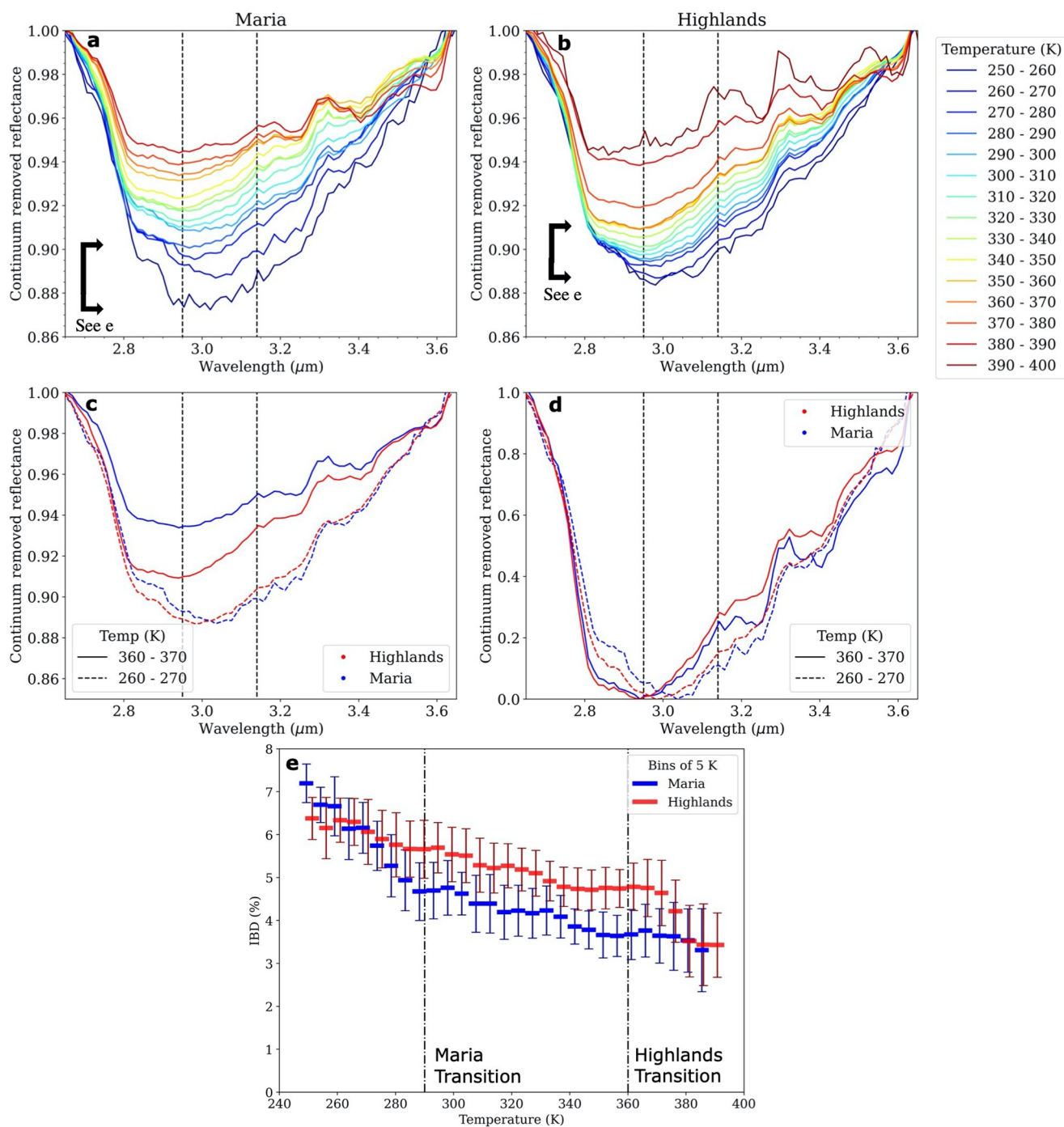


Figure 8. 3 μm absorption band shape as a function of wavelength for (a) maria and (b) highlands. Data for each composition are averaged into 10 K temperature bins for (a) and (b). The strength of the absorption band, shown by the depth of the absorption feature, increases as temperature decreases. This means that the band minima occur at a lower value of continuum removed reflectance for cooler temperatures. The location of the band minima shifts to shorter wavelengths with decreasing temperature for both. (c) Two bins of 10 K separated by 100 K reveal the differences in maria and highlands absorption band shape and band strength at both high and low temperatures. The band strength is more similar between the two terrain types at the low-temperature bin than at the high-temperature bin. (d) Same as (c), but the absorption bands are doubly normalized such that they appear to have the same strength, but differences in band shape and band minima are revealed. The highlands may have a band minima occurring at a shorter wavelength. Vertical dashed black lines in (a–d) are at 2.95 and 3.15 μm , the location of the symmetric and asymmetric stretching mode of an OH bond and the first overtone of the H_2O bending vibration, respectively. (e) Annotated version of Figure 6b with bins of 5 K, noting how the change in slope for integrated band depth versus temperature is a manifestation of the change in the spatial distribution of band depth bins of temperature shown in (a) and (b).

is visible in the band depth change of Figures 8a and 8b. Maria undergo a significant loss of hydration from 250 to 290 K, at which point the rate of change of IBD (shown in Figure 8e) and the band depth (Figure 8a) lessens. For temperatures between 290 and 390 K, maria undergo constant loss with temperature. The break in slope is linked to a change in behavior as the band minima shifts to shorter wavelengths. The significant jump to lower band depths from 360 to 380 K for highlands is manifested as a slope change in Figure 6/Figure 8d. The change in band depth distribution as shown in Figures 8a and 8b is manifested in Figure 8d as a break in slope.

Figure 8c shows the average highlands and maria band shapes and depth for the two end-member temperature bins. The band for the maria in the low-temperature range is similar in depth to the highlands band depth with a band minima shifted to slightly longer wavelength than the highland band. The band for the highlands and maria in the high-temperature range is not similar in depth as the highlands exhibit a stronger absorption feature at this temperature bin (360–370 K). The band shape at high temperature still varies between compositions but the band minima are the same.

There is a slight but noticeable movement for the band minima toward longer wavelengths at a lower temperature for both compositions. Figure 8c shows the greatest band center shift with the low-temperature maria having a longer wavelength band minima toward 3.15 μm . Normalizing these band depths more clearly reveals the shift to a longer wavelength band minima at temperatures 270–280 K (Figure 9). As shown in Figure 9, the normalized spectra for cold temperatures have a band minima just prior to 3.0 μm , while the medium- and high-temperature spectra have a band minima around 2.95 μm . This is true for both maria and highlands, suggesting that the shift is related to a temperature-controlled loss of a constituent. The temperature and the specific wavelength, which this occurs at, strongly suggest a loss of molecular water (Poston et al., 2015). The lack of major shape change despite a band minima shift suggests that the presence of molecular water is low compared to the hydroxyl, which dominates the 3 μm absorption feature.

While limited in scope, the three days of observations included in our data set provide a single geographical region that is observed each day covering 50–83°S and 212–252°E. Therefore, this region is repeatedly observed during local morning, noon, and evening. The spatial extent of these observations is limited by the saturation of points nearest the subsolar point and thus excludes the low latitudes, which would likely produce the most significant change in strength across a lunar day. These observations enable the exploration of the variability of the 3 μm band strength and band shape over the same surface. The hydration feature is observed to decrease in strength near local noon compared to observed morning values. The observed morning strength is found to recover in the evening, albeit with a temperature dependence such that lower temperatures result in higher IBD. Figure 10 shows the variation in strength of each point observed within the repeated region with local time of day. Figure 10c contains a subset (10° × 10°) of the repeat observations, selected to highlight the most extreme spaced time-of-day observations, which provides direct traces of individual pixels across all three observations. The evening data are the highest spatial resolution with each morning observation resulting in 1–2 pixels in the evening. The evening set of observations spans a wider range of temperatures and thus IBD values than the other two times of day observed. This is likely due to the change in the resolution, as the evening observations are almost twice the spatial resolution as the morning observations. Additionally, the evening observations are not perfectly symmetrical to the morning observations with the morning observations being closer to the terminator.

The observations shown in Figure 10 provide clear evidence of the same surface location undergoing a clear time of day-dependent variation in hydration strength. Generally, IBD is lost around local noon and recovered to morning values by evening (Figure 10a). However, there is an additional temperature dependence as evening values remain low due to higher surface temperatures. High latitudes experience loss of hydration strength toward local noon, but the trend is weaker, resulting in overall higher IBD values even near local noon. Figure 10b traces each pixel across the three times of day from a subset of the repeat region, revealing how IBD is lowest near local noon but recovers by the evening observations. Higher surface temperatures and lower latitudes would likely result in a more significant loss of hydration at local noon. The recovery in the evening is tied to the surface temperature. The lower IBD values are correlated with earlier evening times and higher temperatures. For the evening, the lowest values of near 3.5% IBD occur around 320 K with the highest IBD of 7.1% occurring right at the terminator at a surface temperature of 270 K. A similar pattern with temperature is seen in the morning and noon data, albeit less dramatic. Broadly, the observations of repeated regions across three times of day reveal how the variation of the hydration feature depends on a diurnal cycle. These observations reveal that the diurnal

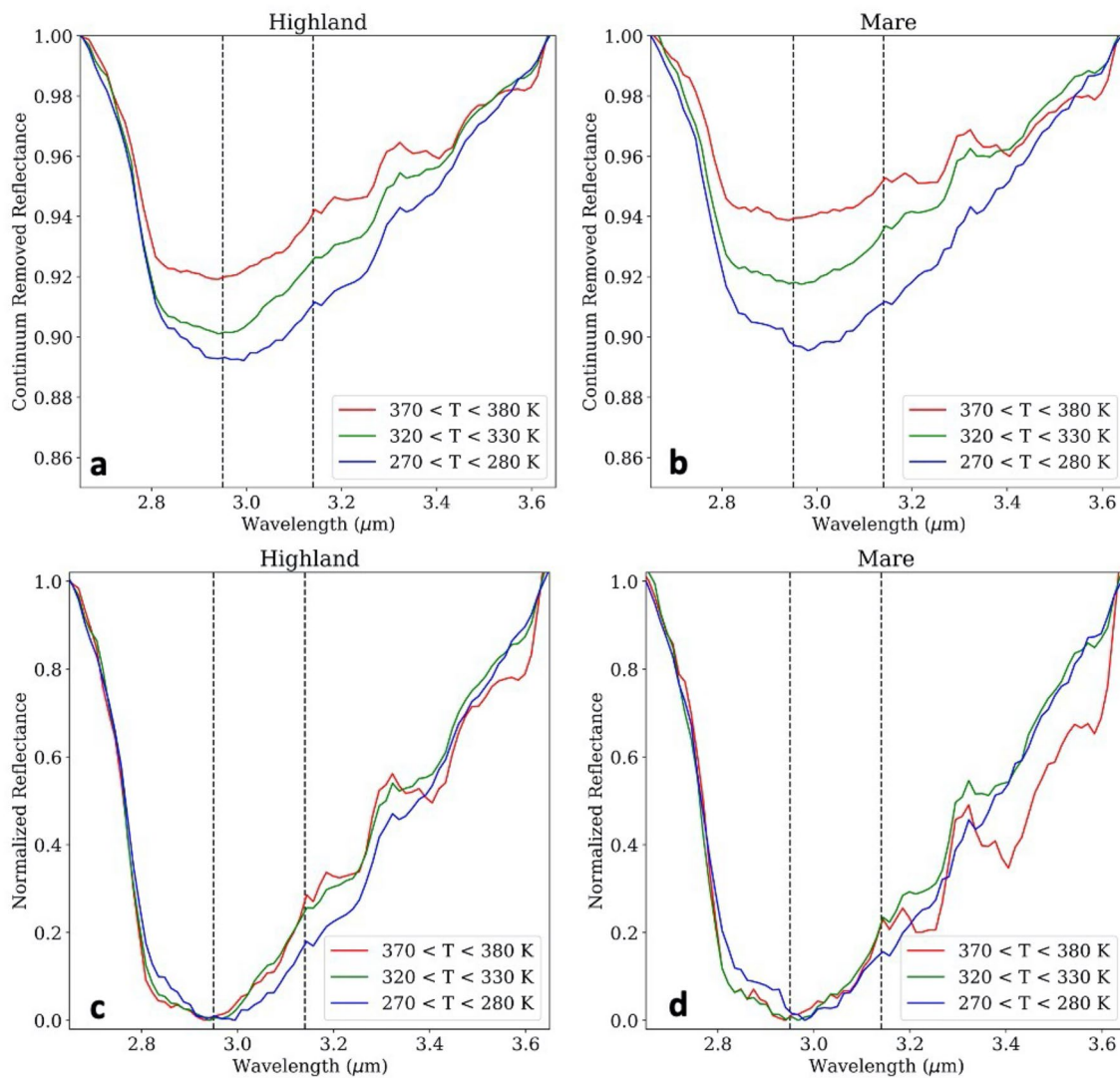


Figure 9. Spectra for three temperature ranges representing the highest, middle, and lowest 10 K of the temperature range. (a) Continuum removed reflectance for highlands and (b) maria both showing variability in band depth and shape. (c) Normalized reflectance for highlands and (d) maria showing the difference in band minima with a longward shift in wavelength for colder temperatures. Vertical dashed black lines are at 2.95 and 3.15 μm , the location of the symmetric and asymmetric stretching modes of an OH bond and the first overtone of the H₂O bending vibration, respectively. The band minima shift with temperature is most evident for the normalized reflectance at the lowest temperature range. The shift toward 3.15 μm is consistent with a higher presence of H₂O at lower temperatures.

variability is not the result of a nighttime recondensation process but rather a cycle that occurs during the lunar day (Sunshine et al., 2009).

5. Discussion

The Deep Impact south polar data set demonstrates, at a kilometers scale, the temporal and spatial variability of the widespread 3 μm hydration feature. While surface temperature has an inverse relationship to hydration absorption strength, it is clear that mare and highland compositions differ in the strength of their hydration and the rate of hydration loss with increasing temperatures. These variable loss rates with temperature provide evidence for the presence of both OH and H₂O, which is expressed as changes in band shape and a clear shift in band minima with temperature. The loss and recovery of the hydration are observed to occur entirely during the day. Such quick recovery times suggest either local migration of OH/H₂O or quick thermal loss and reconstitution from solar wind protons. Laboratory and experimental work can provide insight into the mechanisms that have resulted in these observations.

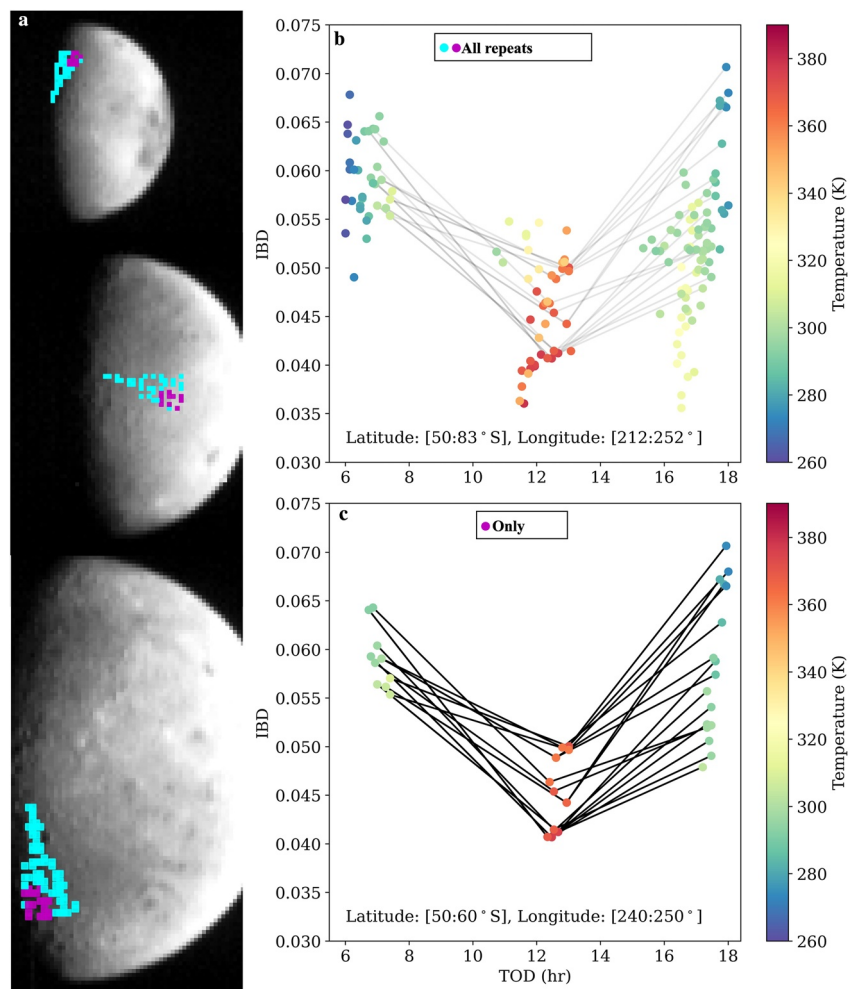


Figure 10. 3 μm integrated band depth (IBD) as a function of local time of day for a region observed in all 3 days. The decrease in strength toward local noon is regained by evening. The evening observations reveal increasing IBD with decreasing temperature related to time of day. Color bar (blue to red) indicates surface temperatures, showing the temperature dependence implicit in time-of-day results. The region presented is limited to a triangular shape of 33° by 40° (green points) as noted in the text. (a) The location of the subset (purple) and the full repeat coverage region (green). The repeat data are dominantly composed of highland pixels. The clear recovery of hydration strength without the need for emplacement at nighttime temperatures is evident. (b) The IBD for all of the pixels in the full repeat coverage region at each time of day. Gray lines show the same connections shown in the bottom panel. (c) A subset of the repeat region, chosen to show individual pixels evolving through the day, connected by the black lines.

Separate from the temperature dependence, we observe clear compositional differences in the strength of the 3 μm absorption with higher variability for the maria as previously noted in Sunshine et al. (2009) and in direct disagreement with Li and Milliken (2017). Only at temperatures below 270 K, do our observations show that the maria have a stronger hydration absorption feature. The observations reveal that the difference in hydration strength between highlands and maria cannot be solely attributed to a difference in temperature, as we present observations both across times of day and temperature. Additionally, the onset and rates of steep loss are observed to be different for the highlands compared to maria, indicating that these two compositions de-volatilize at different rates. These two compositions also have different loss rate–temperature dependences, such that the highlands are better able to retain hydration until 380 K. The difference in composition between maria and highlands plays an important role in the loss and formation of hydration.

Exploration of the compositional differences at better spatial resolutions and a more accurate definition of pyroxene dependence should be explored to understand the disparity in the production rate at the same temperatures between the two compositional end-members in future work. The compositional dependence on band strength is

likely related to the formation process of OH/H₂O on long timescales as shown in laboratory work through the formation of OH defects by proton bombardment of solar wind strength (Ichimura et al., 2012). However, the OH and H₂O loss rates are dependent on composition and temperature, so it is important that the observations in future work include maria and highlands at temperatures that span from dawn to dusk, including high temperatures around noon.

We observed a latitudinal and incidence angle dependence, which is best correlated as a temperature dependence, in agreement with Sunshine et al. (2009) for a strong dependency on instantaneous temperature. The unique temperature dependency of the hydration band strength in this work provides insight into the mechanism for the variations. Davidsson and Hossini (2021) determined that the meter-scale roughness of the lunar surface can influence the rate of adsorption and desorption, such that water can be retained on the sunlit hemisphere at any latitude and across all times of day for latitudes within 45° of each pole. Hayne et al. (2021) explored the importance of micro-cold traps and found that the contribution of small-scale (~cm sized) shadowing can lead to substantial volatile trapping on the lunar surface. These micro-shadowed regions could provide short-term thermal stability locations for migrating OH and H₂O. Our observations show that as soon as temperatures are observed to fall, the hydration feature is quickly replenished. This suggests that the molecules replenishing the absorption feature do not migrate far and may reside in thermally viable locations formed by shadowing from the roughness of the lunar surface. As we do not observe total loss of the 3 μm feature at the highest temperatures in these observations, a significant contribution to the observed hydration band strength could be from OH trapped within the glass of lunar agglutinates (Liu et al., 2012).

Poston et al. (2015) explored the desorption rate of adsorbed water for two Apollo samples representing a mare and a highland region across the range of lunar surface temperatures. They determined that the desorption rate varies nonlinearly across the temperature range and depends on the exposure value. The exposure value is defined as the controlled dosage of water provided prior to heating of the sample, equivalent to 1 L = 10¹⁵ molecules of water at the surface. The desorption rate for the mare sample peaks at 180 K, below the range of observable temperatures in our data set. However, they also observe a low but nonzero desorption rate occurring between 230 and 380 K for low exposures. For the lowest exposure of 1 L, they show a secondary peak around 250 K. This aligns well with our observation of the steeper slope of IBD change from 250 to 280 K for maria. From 280 to 380 K for this exposure of 1 L, the rate is relatively constant, again in agreement with our observations. However, there is not a good explanation provided by the Poston et al. (2015) work for the observed return to rapid loss above 380 K. As the work described is specifically focused on adsorbed water, this rapid loss observed in our work above 380 K is likely hydroxyl loss due to diffusive loss and photolysis (Grumpe et al., 2019). However, the diffusion rate to the surface for OH defects formed by the solar wind occurs on timescales from seconds to lunar hours dependent on temperature with higher temperatures resulting in faster diffusion rates (Jones et al., 2018). This temperature-dependent diffusion rate agrees with the observed trend of IBD at a high temperature. The highland observations from Poston et al. (2015) suggest a peak loss around 230 K with a decreasing desorption rate toward higher temperatures, which does not align with our observations of constant loss for highlands up to 380 K, nor the fast loss above 380 K. The variability in the rate of change in strength with temperature change is not well understood, especially for the highlands, and should be explored in future laboratory work.

The change in slope of the hydration band strength dependence on temperature suggests preferential loss of different constituents in different temperature regimes, likely representing loss of H₂O followed by OH as temperature increases. The two slopes for the hydration band strength dependence on temperature suggest up to 290 K; the feature is more quickly lost. In combination with the change in band shape, this effect is interpreted as a loss of molecular water followed by loss of OH at high temperatures. The change in band shape, specifically the movement of the band minima toward short wavelengths with increasing temperature, is not well understood but is interpreted as a change in the presence of adsorbed H₂O within the regolith. The band minima trends toward a shift toward 3.0 μm from 2.95 μm below temperatures of 270 K. This is suggestive of molecular water being responsible for the absorption at 3.1 μm due to the first overtone of the H₂O bending vibration (Sunshine et al., 2009). The desorption rate of adsorbed H₂O as described in Poston et al. (2015) is likely the controlling factor for the change in band minima. However, McLain et al. (2021) found that the 3 μm band of the Apollo sample 78,421 was shifted to longer wavelengths with increased proton irradiation fluence. The spectra from that work lack the 6.1 μm water feature. If these results are representative of the lunar surface, the band minima shift maybe unrelated to the production or loss of molecular water. Additionally, previous work has shown that

the wavelength of the band minima can be shifted due to OH bonding with different materials due to differences in bonding energy (e.g., Dyar et al., 2010). This variability in band minima would benefit from future studies to understand the presence and loss differences between of OH and H₂O.

Similar to Bandfield et al. (2018) and Simon et al. (2019), we find that hydration is widespread across the lunar surface. However, in contradiction to Bandfield et al. (2018), we find that there is a strong signature of diurnal variability. We find that daytime variation occurs with larger variations in strength for midlatitudes, similar to findings from Grumpe et al. (2019). Complementary to Wöhler, Grumpe, Berezhnoy, Feoktistova et al. (2017), Wöhler, Grumpe, Berezhnoy, & Shevchenko. (2017), a clear temperature dependence in the evening is observed, and both the morning and evening values denote a stronger absorption than midday. These diurnal observations, which have been shown to be depleted at local noon compared to initial morning values, demonstrate that the mechanism at work does not require emplacement over lunar night as the surface hydration features have begun to rebound, if not exceed, the morning values by the evening (similar to Wöhler, Grumpe, Berezhnoy, & Shevchenko. (2017)). The recovery of the IBD during daylight hours after a definite loss at local noon provides evidence that the recovery process is ongoing and occurs on the sunlit regions of the surface. Understanding how the hydration feature varies across time of day is important for understanding the process, which leads to recovery by evening. Additionally, this work would be greatly improved by observations around local noon between midlatitudes and the equator to understand the persistence of this feature.

The observations of the hydration strength time-of-day dependence shown here reveal that there is OH/H₂O that is readily removed and recovered. This cycle likely occurs through a combination of effects: the formation of OH from solar wind implantation (e.g., McCord et al., 2011), diffusion and thermal loss of OH and H₂O (e.g., Farrell et al., 2015; Reiss et al., 2021), photodissociation and photodesorption of OH and H₂O (e.g., Mitchell et al., 2013), reactions between H and O (e.g., Farrell et al., 2015), and surface migration (e.g., Hendrix et al., 2019). It is not yet known which process dominates and it is likely that a combination of these effects leads to the observed variable hydration across the lunar surface.

In the case of the diurnal variability that we observed in this work, we propose that the most likely mechanism is localized migration of OH. The localized migration is suggested based on the observed timescale of recovery of the strength of the 3 μ m band. Jones et al. (2018) noted that the timescale for recovery is not well fit for the solar wind alone to produce the necessary water content as the solar wind would have to contribute hundreds of ppm of water equivalent hydrogen over a lunar day. Additionally, modeling of OH formed by solar wind implantation reveals an excess of hydration observed at the morning terminator, which is not observed here (Jones et al., 2018).

Considering the effects of the Earth's magnetotail, it is important to note that the first date of observation, 05 December 2009 (DOY 339), was likely inside the magnetotail, while both the middle and final dates of observation (DOY 346 and DOY 352) were outside the magnetotail. The 3 μ m band recovers in the evening to similar strength values from the morning despite the difference in coverage from the Earth's magnetotail. This is consistent with the findings from Hendrix et al. (2019). Additionally, Hayne et al. (2021) provide evidence for small-scale topography creating micro cold traps near the lunar poles. Potentially, small scale topography results in the formation of locally cool spots, which could support the localized migration of OH/H₂O. The time-of-day dependence observed here would benefit from future work exploring the potential for the localized migration of OH and H₂O occurring along the lunar terminators and at midlatitudes to high latitudes, especially considering the effects of small-scale topography. These observations provide a unique opportunity to explore the variability of the lunar hydration feature, but additional observations of the 3 μ m band could greatly improve our understanding of the mechanism controlling this variability. Temperature-driven migration of OH/H₂O from a monolayer of molecules on the lunar surface is supported by the results of this analysis but is yet to be definitely proven.

6. Conclusions

We find that hydration is widespread and variable across the lunar surface. We observed significant differences in absorption band strength between maria and highlands, providing clear evidence that the highlands retain more hydration at daytime temperatures. At high temperatures, maria and highlands have similarly low-hydration band strength. Observations of the band shape are enabled by the extended spectral range available from the Deep Impact spectrometer that allows for more accurate thermal removal. The data provide strong evidence for loss of molecular water due to a shift to shorter wavelengths as the surface is heated above 270 K. Maria are

found to have stronger absorption features than highlands only at the lowest temperatures (<260 K) observed in this work. Repeat coverage enabled exploration of time-of-day dependence providing evidence for rehydration occurring prior to passage through the terminator. There is not a necessity for rebound across lunar night as the evening values just 12 lunar hours past the lunar morning observations show comparably strong values for the hydration feature. This rapid and temperature-dependent recovery suggests that the migration of both OH and H₂O molecules is occurring on the lunar surface on short spatial scales over diurnal timescales and likely over short distances.

Higher cadence observations will enable us to understand the critical temperatures and predict what times of day H₂O and OH are independently lost and returned. This work is limited by saturation-preventing exploration of the low latitudes and equatorial regions, especially at local noon. Future work should focus in these regions where more significant loss is occurring and higher surface temperatures are reached. The results of this work motivate the need for such higher cadence observations to explore the timescale of variability, potentially by a combination of observations by the upcoming Lunar Trailblazer mission, in-situ observations, and/or ground-based observations. Future data should explore the same geographic site over the full range of temperatures and times of day at a high temporal cadence and unsaturated at high temperatures near noon. Such data are critical for understanding the process of emplacement and destruction of hydration creating this spectral feature. The diurnal change investigation presented in this work was completed using a small strip of repeated data at spatial resolutions no better than 31 km/pixel; improvement (spectral or temporal) could greatly elevate our understanding. Observations taken on order of an Earth day would provide sub-hourly (lunar) observations of hydration variations. With topographic structures resolved in greater spatial resolution data and with rapid observational timescales, it will be possible to measure the sources, sinks, and rates of migration of hydration in the lunar surface.

Data Availability Statement

Observational data used in this study are available to the public in NASA's Planetary Data System Small Bodies Node (<http://pdssbn.astro.umd.edu>). The processed data are available through the Purdue University Research Repository (Laferrriere, 2022).

Acknowledgments

This work was partially funded by NASA's Solar System Exploration Research Virtual Institute (SSERVI) GEODES Grant #80NSSC19M0216 (to JMS) and by NASA's Lunar Data Analysis Program (to LMF and JMS) through a sub-contract (NNX15AP88G) from the Southwest Research Institute. The authors thank Tony L. Farnham for providing us with the latitude, longitude, and incidence angle data for the observations. The authors would like to thank Carlé Pieters and an anonymous reviewer for their careful and insightful reviews, which greatly improved our work.

References

- Adams, J. B. (1974). Visible and near infrared diffuse reflectance spectra of pyroxenes as applied to remote sensing of solid objects in the solar system. *Journal of Geophysical Research*, 79(32), 4829–4836. <https://doi.org/10.1029/JB079i032p04829>
- Bandfield, J. L., Poston, M. J., Klima, R. L., & Edwards, C. S. (2018). Widespread distribution of OH/H₂O on the lunar surface inferred from spectral data. *Nature Geoscience*, 11(3), 173–177. <https://doi.org/10.1038/s41561-018-0065-0>
- Berk, A., Anderson, G. P., Acharya, P. K., Hoke, M. L., Chetwynd, J. H., & Bernstein, L. S. (2003). *MODTRAN4 version 3 Revision 1 USERS' MANUAL*. Air Force Research Laboratory.
- Berk, A., Conforti, P., Kennett, R., Perkin, T., Hawes, F., & vanden Bosch, J. (2014). MODTRAN6: A major upgrade of the MODTRAN radiative transfer code. In *Proc. SPIE 9088, algorithms and technologies for multispectral, hyperspectral, and ultraspectral imagery XX*, 90880H. <https://doi.org/10.1117/12.2050433>
- Chauhan, P., Chauhan, M., Verma, P. A., Sharma, S., Bhattacharya, S., Kumar Dagar, A., et al. (2021). Unambiguous detection of OH & H₂O on the Moon from Chandrayaan-2 imaging infrared spectrometer (IIRS) reflectance data using 3.0 μm hydration feature. *Current Science*, 121(3), 391–401. <https://doi.org/10.18520/cs/v121/i3/391-401>
- Cheek, L. C., Pieters, C. M., Boardman, J. W., Clark, R. N., Combe, J. P., Head, J. W., et al. (2011). Goldschmidt crater and the Moon's North polar region: Results from the Moon Mineralogy Mapper (M³). *Journal of Geophysical Research*, 116, E00G02. <https://doi.org/10.1029/2010JE003702>
- Clark, R. N. (2009). Detection of adsorbed water and hydroxyl on the Moon. *Science*, 326(5952), 562–564. <https://doi.org/10.1126/science.1178105>
- Clark, R. N., Pieters, C. M., Green, R. O., Boardman, J., & Petro, N. E. (2011). Thermal removal from near-infrared imaging spectroscopy data of the Moon. *Journal of Geophysical Research*, 116, E00G16. <https://doi.org/10.1029/2010JE003751>
- Davidsson, B. J. R., & Hossini, S. (2021). Implications of surface roughness in models of water desorption on the Moon. *Monthly Notices of the Royal Astronomical Society*, 506(3), 3421–3429. <https://doi.org/10.1093/mnras/stab1360>
- Dyar, M., Hibbitts, C., & Orlando, T. (2010). Mechanisms for incorporation of hydrogen in and on terrestrial planetary surfaces. *Icarus*, 208(1), 425–437. <https://doi.org/10.1016/j.icarus.2010.02.014>
- Farrell, W. M., Hurley, D. M., & Zimmerman, M. I. (2015). Solar wind implantation into lunar regolith: Hydrogen retention in a surface with defects. *Icarus*, 255, 116–126. <https://doi.org/10.1016/j.icarus.2014.09.014>
- Groussin, O., A'Hearn, M. F., Li, J. Y., Thomas, P. C., Sunshine, J. M., Meech, K. J., et al. (2007). Surface temperature of the nucleus of comet 9P/Tempel 1. *Icarus*, 187, 16–25. <https://doi.org/10.1016/j.icarus.2006.08.030>
- Grumpe, A., Wöhler, C., Berezhnoy, A. A., & Shevchenko, V. V. (2019). Time-of-day-dependent behavior of surficial lunar hydroxyl/water: Observations and modeling. *Icarus*, 321, 486–507. <https://doi.org/10.1016/j.icarus.2018.11.025>
- Hayne, P. O., Aharonson, O., & Schörghofer, N. (2021). Micro cold traps on the Moon. *Nature Astronomy*, 5(2), 169–175. <https://doi.org/10.1038/s41550-020-1198-9>

- Hendrix, A. R., Hurley, D. M., Farrell, W. M., Greenhagen, B. T., Hayne, P. O., Retherford, K. D., et al. (2019). Diurnally migrating lunar water: Evidence from ultraviolet data. *Geophysical Research Letters*, 46(5), 2417–2424. <https://doi.org/10.1029/2018GL081821>
- Honniball, C. I., Lucey, P. G., Arredondo, A., Reach, W. T., & Malaret, E. R. (2022). Regional map of molecular water at high southern latitudes on the Moon using 6 μ m data from the Stratospheric Atmospheric Observatory for Infrared Astronomy. *Geophysical Research Letters*, 49(9), e2022GL097786. <https://doi.org/10.1029/2022GL097786>
- Honniball, C. I., Lucey, P. G., Ferrari-Wong, C. M., Florn, A., Li, S., Kaluna, H. M., & Takir, D. (2020). Telescopic observations of lunar hydration: Variations and abundance. *Journal of Geophysical Research (Planets)*, 125(9), e06484. <https://doi.org/10.1029/2020JE006484>
- Honniball, C. I., Lucey, P. G., Li, S., Shenoy, S., Orlando, T. M., Hibbits, C. A., et al. (2020). Molecular water detected on the sunlit Moon by SOFIA. *Nature Astronomy*, 5(2), 121–127. <https://doi.org/10.1038/s41550-020-01222-x>
- Hurley, D. M., Sarantos, M., Grava, C., Williams, J. P., Retherford, K. D., Siegler, M., et al. (2015). An analytic function of lunar surface temperature for exospheric modeling. *Icarus*, 255, 159–163. <https://doi.org/10.1016/j.icarus.2014.08.043>
- Ichimura, A. S., Zent, A. P., Quin, R. C., Sanchez, M. R., & Taylor, L. A. (2012). Hydroxyl (OH) production on airless planetary bodies: Evidence from H⁺/D⁺ ion-beam experiments. *Earth and Planetary Science Letters*, 345–348, 90–94. <https://doi.org/10.1016/j.epsl.2012.06.027>
- Jones, B. M., Aleksandrov, A., Hibbits, K., Dyar, M. D., & Orlando, T. M. (2018). Solar wind-induced water cycle on the Moon. *Geophysical Research Letters*, 45(20), 10959–10967. <https://doi.org/10.1029/2018GL080008>
- Kim, S., Yi, Y., Hong, I. S., & Sohn, J. (2018). Solar insolation effect on the local distribution of lunar hydroxyl. *Journal of Astronomy and Space Sciences*, 35, 47–54. <https://doi.org/10.5140/JASS.2017.35.1.47>
- Klaasen, K. P., A'Hearn, M., Besse, S., Bodewits, D., Carcich, B., Farnham, T., et al. (2013). EPOXI instrument calibration. *Icarus*, 225(1), 643–680. <https://doi.org/10.1016/j.icarus.2013.03.024>
- Klaasen, K. P., A'Hearn, M. F., Baca, M., Delamere, A., Desnoyer, M., Farnham, T., et al. (2008). Invited article: Deep impact instrument calibration. *Review of Scientific Instruments*, 79(9), 091301. <https://doi.org/10.1063/1.2972112>
- Klima, R. L., & Petro, N. E. (2017). Remotely distinguishing and mapping endogenic water on the Moon. *Philosophical Transactions of the Royal Society of London, Series A*, 375(2094), 20150391. <https://doi.org/10.1098/rsta.2015.0391>
- Laferriere, K. (2022). Lunar Hydration at the South Pole observed by Deep Impact [Dataset]. Purdue University Research Repository. <https://doi.org/10.4231/T3B9-QK78>
- Li, S., & Milliken, R. E. (2017). Water on the surface of the Moon as seen by the Moon Mineralogy Mapper: Distribution, abundance, and origins. *Science Advances*, 3(9), e1701471. <https://doi.org/10.1126/sciadv.1701471>
- Lin, H., Li, S., Xu, R., Liu, Y., Wu, X., Yang, W., et al. (2022). In situ detection of water on the Moon by the Chang'E-5 lander. *Science Advances*, 8, 1. <https://doi.org/10.1126/sciadv.abl9174>
- Liu, Y., Guan, Y., Zhang, Y., Rossman, G. R., Eiler, J. M., & Taylor, L. A. (2012). Direct measurement of hydroxyl in the lunar regolith and the origin of lunar surface water. *Nature Geoscience*, 5(11), 779–782. <https://doi.org/10.1038/NGEO1601>
- McCord, T. B., Taylor, L. A., Combe, J. P., Kramer, G., Pieters, C. M., Sunshine, J. M., & Clark, R. N. (2011). Sources and physical processes responsible for OH/H₂O in the lunar soil as revealed by the Moon Mineralogy Mapper (M³). *Journal of Geophysical Research*, 116(E6), E00G05. <https://doi.org/10.1029/2010JE003711>
- McLain, J. L., Loeffler, M. J., Farrell, W. M., Honniball, C. I., Keller, J. W., & Hudson, R. (2021). Hydroxylation of Apollo 17 soil sample 78421 by solar wind protons. *Journal of Geophysical Research (Planets)*, 126(5). <https://doi.org/10.1029/2021JE006845>
- McLaughlin, S. A., Carcich, B., Sackett, S. E., Klaasen, K. P., & Wellnitz, D. D. (2011). EPOXI inflight calibrations - HRII RAW SPECTRA V2.0, DIF-CAL-HRII-2-EPOXI-CALIBRATIONS-V2.0, NASA Planetary Data System.
- Mitchell, E. H., Raut, U., Fulvio, D., Schaible, M. J., Dukes, C. A., & Baragiola, R. A. (2013). Ultraviolet photodesorption as a driver of water migration on the lunar surface. *Planetary and Space Science*, 89, 42–46. <https://doi.org/10.1016/j.pss.2013.02.002>
- Moriarty, D. P., & Pieters, C. M. (2018). The character of south Pole-Aitken basin: Patterns of surface and subsurface composition. *Journal of Geophysical Research (Planets)*, 123(3), 729–747. <https://doi.org/10.1002/2017JE005364>
- Pieters, C. M., Goswami, J. N., Clark, R. N., Annadurai, M., Boardman, J., Buratti, B., et al. (2009). Character and spatial distribution of OH/H₂O on the surface of the Moon seen by M³ on Chandrayaan-1. *Science*, 326(5952), 568–572. <https://doi.org/10.1126/science.1178658>
- Pommerol, A., Schmitt, B., Beck, P., & Brissaud, O. (2009). Water sorption on martian regolith analogs: Thermodynamics and near-infrared reflectance spectroscopy. *Icarus*, 204(1), 144–136. <https://doi.org/10.1016/j.icarus.2009.06.013>
- Poston, M. J., Grieves, G. A., Aleksandrov, A. B., Hibbits, C. A., Dyar, M. D., & Orlando, T. M. (2015). Temperature programmed desorption studies of water interactions with Apollo lunar samples 12001 and 72501. *Icarus*, 255, 24–29. <https://doi.org/10.1016/j.icarus.2014.09.049>
- Potin, S., Manigand, S., Beck, P., Wolters, C., & Schmitt, B. (2020). A model of the 3- μ m hydration band with Exponentially Modified Gaussian (EMG) profiles: Application to hydrated chondrites and asteroids. *Icarus*, 343, 113686. <https://doi.org/10.1016/j.icarus.2020.113686>
- Reiss, P., Warren, T., Sefton-Nash, E., & Trautner, R. (2021). Dynamics of subsurface migration of water on the Moon. *Journal of Geophysical Research: Planets*, 126(5), e2020JE006742. <https://doi.org/10.1029/2020JE006742>
- Schörghofer, N., Benna, M., Berezhnoy, A. A., Greenhagen, B., Jones, B. M., Li, S., et al. (2021). Water group exospheres and surface interactions on the Moon, Mercury, and Ceres. *Space Science Reviews*, 217(6), 74. <https://doi.org/10.1007/s11214-021-00846-3>
- Simon, A. A., Donaldson Hanna, K. L., Drouet d'Aubigny, C. Y., Poggiali, G., Emergy, J. P., Brucato, J., et al. (2019). OSIRIS-Rex visible and near-infrared observations of the Moon. *Geophysical Research Letters*, 46(12), 6322–6326. <https://doi.org/10.1029/2019GL083341>
- Starukhina, L. V. (2001). Water detection of atmosphereless celestial bodies: Alternative explanations of the observations. *Journal of Geophysical Research*, 106(E7), 14701–14710. <https://doi.org/10.1029/2000JE001307>
- Sunshine, J. M., Farnham, T. L., Feaga, L. M., Groussin, O., Merlin, F., Milliken, R. E., & A'Hearn, M. F. (2009). Temporal and spatial variability of lunar hydration as observed by the Deep impact spacecraft. *Science*, 326(5952), 565–568. <https://doi.org/10.1126/science.1179788>
- Williams, J. P., Paige, D. A., Greenhagen, B. T., & Sefton-Nash, E. (2017). The global surface temperatures of the Moon as measured by the diviner lunar radiometer experiment. *Icarus*, 283, 300–325. <https://doi.org/10.1016/j.icarus.2016.08.012>
- Wöhler, C., Grumpe, A., Berezhnoy, A. A., Feoktistova, E. A., Evdokimova, N. A., Kapoor, K., et al. (2017). Temperature regime and water/hydroxyl behavior in the crater Boguslawsky on the Moon. *Icarus*, 285, 118–136. <https://doi.org/10.1016/j.icarus.2016.12.026>
- Wöhler, C., Grumpe, A., Berezhnoy, A. A., & Shevchenko, V. V. (2017). Time-of-day-dependent global distribution of lunar surficial water/hydroxyl. *Science Advances*, 3(9), e1701286. <https://doi.org/10.1126/sciadv.1701286>
- Zeller, E. J., Ronca, L. B., & Levy, P. W. (1966). Proton-Induced hydroxyl formation on the lunar surface. *Journal of Geophysical Research*, 71(20), 4855–4860. <https://doi.org/10.1029/JZ071i020p04855>