

Water on the Lunar Surface as Seen by the Moon Mineralogy Mapper: Distribution,
Abundance, and Origins

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3. Vesta's surface compositional studies: DAWN VIR and FC.
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After my defense, the first thing I want to tell the world is that my student status is permanently over finally! I spent nine years in graduate schools, two years in China for my first master's degree, two years at Indiana University for my second master's degree, one year at University of Notre Dame and four years at Brown University for my PhD degree. I think I experienced more than typical PhD students. So, I have more stories to tell and more people to thank.

First, I would like to thank my parents, especially my father who helped me to build up my career goal. Without this goal, I cannot insist nine years in graduate schools for a PhD degree. When I was little, like other kids, I always asked my parents for stories. My father told me tons of stories about famous people in old societies of China who started from scratch but worked hard and finally received great accomplishments in their careers. I think my career goal becoming a great scientist was planted at that time although it was very vague. While the first step to become a great scientist is to receive high quality education and training. That is one of the most important reasons I applied graduate school programs in US after I got my first master's degree in China.

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application of the graduate program of Brown University was extremely competitive and I did not get approved! But this is not the end of my story.

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Introduction

Water is one of the most volatile species in our solar system and cannot condense to solid phase at locations close to the Sun (i.e., $< \sim 3$ AU, known as the ‘snow’ line) due to its low condensation temperature [Hayashi, 1981; Podolak and Zucker, 2004; Martin and Livio, 2014]. Yet the water content and distribution on planetary bodies within the ‘snow’ line can provide important constraints on modeling solar system formation and evolution [e.g., Martin and Livio, 2014]. Water on the surface can be assessed with orbital observations, but there is no such technology to assess the hydration state of the interior of a planetary body directly. Alternatively, water associated with internal activities (i.e., magmatism) may provide probes to planetary interiors [Saal *et al.*, 2008]. Our Moon is an ideal place to examine the hydration state both on the surface and in its interior because returned samples and multiple orbital observations are available, although most observations are limited to the surface. The bulk of my research focuses on identifying and quantifying the water ($\text{H}_2\text{O}/\text{OH}$) on the lunar surface and deciphering endogenous and exogenous sources using reflectance spectroscopy and laboratory experiments. Results of this work can provide critical constraints on modeling the formation and evolution of the Earth-Moon system. Additionally, the framework developed in this research can be applied to explore the hydration state at other planetary bodies within the ‘snow’ line of our solar system when similar datasets are available in future, which can provide more data points for improving our understanding on the solar system formation and evolution.

Lunar surface water has been continuously investigated both remotely and with Apollo returned samples for several decades. Lunar samples have been studied to evaluate the extent of water and possible sources. Four different water sources identified

with indirect (pyrolysis) measurements are (1) terrestrial contamination, (2) solar wind, (3) impact delivery (e.g., carbonaceous chondrite meteorites and comets [Watson *et al.*, 1961]), and (4) lunar indigenous water [Epstein and Taylor Jr, 1970; Friedman *et al.*, 1970; Friedman *et al.*, 1971; Epstein and Taylor Jr, 1972; 1973; DesMarais *et al.*, 1974; Epstein and Taylor Jr, 1974; Friedman *et al.*, 1974; Merlivat *et al.*, 1974]. Hydrogen isotopes (δD) of lunar samples measured by pyrolysis are very close to terrestrial values, initially interpreted to suggest that most of the measured water in lunar samples is from terrestrial contamination and that the Moon has almost no indigenous water (less than a few ppm) [Epstein and Taylor Jr, 1970; Friedman *et al.*, 1970; Friedman *et al.*, 1971; Epstein and Taylor Jr, 1972; 1973; DesMarais *et al.*, 1974; Epstein and Taylor Jr, 1974; Friedman *et al.*, 1974; Merlivat *et al.*, 1974]. Water sources (2) – (4) were also proposed based on *in situ* measurements (SIMS: Secondary Ion Mass Spectrometer and FTIR: Fourier-transform infrared spectrometer) [Saal *et al.*, 2008; McCubbin *et al.*, 2010; Greenwood *et al.*, 2011; Hauri *et al.*, 2011; Liu *et al.*, 2012; Hui *et al.*, 2013; Saal *et al.*, 2013]. Pyrolysis measurements showed that solar wind implanted water in lunar samples might reach >100 ppm [Epstein and Taylor Jr, 1970; Friedman *et al.*, 1970]. Similarly, up to ~140 ppm water recently measured with SIMS in Apollo 11 agglutinates was attributed to solar wind implantation [Liu *et al.*, 2012]. Solar wind implanted water is mostly concentrated in the upper 200 nm of grains, whereas surficially bonded and grain interior water are significantly lower [Leich and Tombrello, 1973]. Large amounts of water (100s – 1000s ppm) was detected with SIMS in apatite of lunar samples and hydrogen isotopes suggest that a significant portion was delivered by comets shortly after lunar formation [Greenwood *et al.*, 2011] or that fractionation due to degassing has

occurred during emplacement of these materials [e.g., *Saal et al.*, 2013]. In addition, water-enriched exotic grains delivered by impacts are rare in lunar samples and only found in Apollo 16 samples [*El Goresy et al.*, 1973]. However, impact delivered and solar wind implanted water at optical depth (i.e., $< \sim 100\text{s } \mu\text{m}$) might not be stable under the lunar surface environment (strong photodissociation and kinetic diffusion) and accumulation of massive water might only occur in permanently shaded regions (PSR) and high latitude (i.e., $>60^\circ$) [*Watson et al.*, 1961; *Arnold*, 1979]. The most controversial observation between indirect (pyrolysis) and *in situ* (SIMS) measurements is how much water in the lunar samples is indigenous. *In situ* measurements indicated that the Moon is not totally dry as suggested with indirect measurements [*Saal et al.*, 2008; *McCubbin et al.*, 2010; *Greenwood et al.*, 2011; *Hauri et al.*, 2011; *Hui et al.*, 2013]. Up to ~ 70 ppm and ~ 1400 ppm water were detected in lunar pristine volcanic glass beads and olivine-hosted melt inclusions within those glasses, respectively, which were all interpreted as lunar indigenous water [*Saal et al.*, 2008; *Hauri et al.*, 2011; *Saal et al.*, 2013]. Additionally, up to 2.7 ppm water was detected in pristine plagioclase in lunar ferroan anorthosite (FAN, primary products of lunar magma ocean) with FTIR methods, suggesting the lunar magma ocean may have contained 320 ppm water [*Hui et al.*, 2013]. The lunar surface water reservoirs in Apollo samples and their sources, speciation, abundances, and likelihood of existence at proposed locations are summarized in table 1. In summary, twenty six indirect [*Epstein and Taylor Jr*, 1970; *Friedman et al.*, 1970; *Friedman et al.*, 1971; *Epstein and Taylor Jr*, 1972; 1973; *Friedman et al.*, 1974; *Merlivat et al.*, 1974] and seventy six *in situ* [*Saal et al.*, 2008; *Greenwood et al.*, 2011; *Liu et al.*, 2012; *Saal et al.*, 2013] measurements from major constituents of lunar

samples show that the water content in bulk Apollo samples is 44.3 ppm (only *in situ* measurements) and 63.0 ppm (all measurements, indirect measurements might have terrestrial contaminations) (see chapter 2 for details).

Lunar surface and shallow sub-surface water has also been explored remotely. Lunar polar water was detected with the Moon Mineralogy Mapper (M^3) onboard Chandrayaan-1 mission and mostly was attributed to solar wind implantation [Pieters *et al.*, 2009]. The variation of lunar surface hydration with local time and surface composition (mare vs. highlands) has been observed by EPOXI (>10 km/pixel), suggesting a solar wind origin [Sunshine *et al.*, 2009]. While the higher spatial resolution of M^3 data (i.e., ~ 280 m/pixel for M^3 vs. > 10 km/pixel for EPOXI) was beneficial for observing variations in hydration at high latitudes [Pieters *et al.*, 2009], detection of water at low latitude was constrained by thermal emissions [McCord *et al.*, 2011]. Lunar surface water was also quantitatively assessed with images acquired by the Visual and Infrared Mapping Spectrometer (VIMS) onboard Cassini [Clark, 2009]. It was determined that high latitude regions could contain ~ 1000 ppm water accumulating from impact delivery and solar wind implantation [Clark, 2009]. However, the spatial resolution of images acquired by VIMS is too low (~ 175 km/pixel) to observe localized water-enriched regions (e.g., volcanic glass enriched areas) to probe the lunar interior. Up to 1.5 ± 0.8 wt.% buried water near lunar poles (~ 1 m depth) was detected with neutron data acquired by Lunar Prospector [Feldman *et al.*, 1998; Feldman *et al.*, 2001]. However, neutrons can be complicated by compositional variations and rare earth elements [Hodges, 2002; Maurice *et al.*, 2004] and examining localized water-enriched regions is constrained by low spatial resolution of the data (> 13 km/pixel [Feldman *et al.*,

1998]). High spatial resolution Earth-based radar data did not observe massive water accumulation near the lunar south pole [*Campbell et al.*, 2006], which contradicts the neutron observations. Therefore, although it is clear that there are several distinct water reservoirs on the Moon, the distribution and water content of those reservoirs remains poorly constrained.

In summary, my thesis mainly focuses on assessing the following unsolved or partially unsolved questions. (1) How to quantitatively estimate water content on the lunar surface with the high spatial and spectral M^3 dataset, especially at low latitudes complicated by severe thermal issues? (2) How does the lunar surface water vary with local time, latitude, exposure time, and different lunar units/terrains? Can the temporal and spatial variation or coherence with compositions of lunar surface water inform its sources? (3) Is it possible to resolve the lunar interior water exposed on the surface with M^3 observations? How much water may exist in the lunar interior, and what is its distribution? (4) Can we correlate our knowledge of lunar sample water to orbital observations?

Reflectance spectra of M^3 data have severe thermal contributions at wavelengths longer than $\sim 2 \mu\text{m}$, which mutes the OH fundamental stretching absorption centered near $\sim 2.7 - 3 \mu\text{m}$. Previously, thermal effects of M^3 level 2 (reflectance) data were removed with a conservative algorithm [*Clark et al.*, 2011; *McCord et al.*, 2011], and water absorptions were only observed at high latitudes due to this insufficient thermal removal [*Pieters et al.*, 2009]. My research in chapter 1 focuses on solving the thermal issue of M^3 data. Ideally, independent measurements of lunar surface temperature acquired at the same locations and local times as M^3 spectra could be used to estimate and then separate

thermal emission from surface reflectance. However, such data were not simultaneously acquired when radiance spectra were measured with M^3 . Fortunately, the Diviner radiometer onboard the *Lunar Reconnaissance Orbiter* (LRO) is capable of measuring and mapping lunar surface temperature and was launched shortly after *Chandrayann-1* [Paige *et al.*, 2010]. Diviner-based temperatures acquired at the same location and local time can be applied to remove thermal effects for M^3 data. However, not every M^3 pixel has an overlapping Diviner-based temperature acquired at the same local lunar time, we examined empirical relationships in visible-near infrared laboratory reflectance spectra of Apollo soil and glass samples for which thermal emission is not present. These data were used to develop an empirical model for estimating thermal contribution in M^3 data, and we demonstrate that this model is validated by reflectance properties observed in M^3 data that were independently corrected using Diviner-based surface temperatures. These results provide the foundation for development of a new thermal correction model for M^3 data that 1) should be valid for the majority of typical lunar surface compositions and that 2) does not require independent knowledge of surface temperature at the same local time as M^3 data were acquired.

The new thermally corrected M^3 data enable us to examine the water content across the global lunar surface. In chapter 2, I used the new thermally-corrected M^3 dataset to estimate the absolute water content of the lunar surface with M^3 data and supporting laboratory experiments. Water mapped at the Apollo sampling latitude zone (i.e., $\pm 30^\circ$) was compared with that measured from Apollo samples to evaluate our mapping results. Variation in lunar surface water as a function of latitude and longitude was investigated to understand its spatial distribution. Whether or not the water content

differs between different compositional units (mare vs. highland; high vs. low crystallinity areas) was also examined to examine whether the water variation trends observed in laboratory or predicted from theoretical modeling show on the lunar surface. The diurnal variation of lunar surface water is assessed and compared with that observed by *Sunshine et al.* [2009] to see whether more details about this diurnal variation can be resolved with much higher spatial resolution dataset (i.e., ~280m/pixel for M³ vs. > 10km/pixel for EPOXI). One of the most striking findings of chapter 2 is that the lunar surface water is dominantly controlled by the latitude, suggesting solar wind origin and the major water loss mechanism - temperature dependent diffusion. However, exceptions include large pyroclastic deposits, which exhibit increased water signatures relative to surrounding terrains regardless of latitude or time of day, suggesting additional water inventories associated with magmatism. These localized water anomalies were examined in chapter 3.

Research in chapter 3 focuses on investigating the localized water anomalies associated with magmatism found in chapter 2 to constrain the distribution and abundance of water (H₂O and/or OH) derived from the lunar interior. Knowing water from the lunar interior is critical for addressing important questions associated with the formation and evolution of the Moon. A ‘wet’ or ‘dry’ lunar interior has been debated for decades. Hundreds parts per million (ppm) of water has been identified as of endogenous lunar origin in Apollo 15 and 17 volcanic glasses [*Saal et al.*, 2008; *Hauri et al.*, 2011]. However, other lines of evidence suggest that the lunar interior may not have such high values of water [*Epstein and Taylor*, 1970; *Sharp et al.*, 2010; *Elkins-Tanton and Grove*, 2011], and assessing water variations in the lunar interior is constrained by limited

sampling locations. Orbital detection of lunar surface water provides an alternative way to test these hypotheses. If any ‘excess’ water signature is observed after subtracting the maximum contribution from the solar wind (i.e., 100 ppm [*Li and Milliken*, in prep.]), it must be either associated with impacts or the internal processes (i.e., pyroclastic deposits and silicic domes), where the former case can be ruled out if there are no impact features associated with the water anomalies. The correlation between water content and volcanic glass abundance at pyroclastic deposits can be applied to further validate whether it is sourced from the lunar interior. A positive correlation between the water content and respective pyroclastic range at each deposit predicted by magma ascent modeling [*Wilson and Head*, 1981] was also examined to offer additional evidence supporting the lunar interior water hypothesis. Previously reported silicic domes at the lunar surface may also host interior water and were examined in this work. These domes may be formed through fractional crystallization of magmas or ascent of silica-rich melts due to their immiscibility and low density [*Glotch et al.*, 2010; *Jolliff et al.*, 2011]. If there were any water in the source regions then it could have been concentrated in such melts and brought to the surface. If preserved, this excess inventory of water should be identifiable at silicic domes compared with surrounding terrains. Almost all examined pyroclastic deposits in chapter 3 exhibited significant ‘excess’ water signatures. There is only one exception - Sinus Aestuum - one of the largest pyroclastic deposits that exhibits no water from the lunar interior. Strikingly, Sinus Aestuum is the only pyroclastic deposit associated with exposures of spinel and spectral features of spinel at this area suggest that it is Cr/Fe-rich, not Mg-rich as is observed elsewhere on the Moon. Questions including the connection between the lack of indigenous water and the presence of spinel at Sinus

Aestuum, and implications for the magma source difference between Sinus Aestuum and other pyroclastic deposits, are proposed and addressed in chapter 4.

The geologic mapping and integration with spectral data that is outlined in chapter 4 is essential to understand the connection between the lack of indigenous water and the presence of spinel at Sinus Aestuum. I examine whether the absence of lunar interior water at Sinus Aestuum is associated with specific geologic settings, compositions, or dilution due to lateral/vertical mixing. Detailed geomorphological mapping at both Sinus Aestuum and Rima Bode (for comparison) was performed using Multiband Imager (MI) 750 nm reflectance data to derive the geological settings for presence/absence of water and spinel. Empirical band parameters and band ratios derived from Clementine data were employed on MI data to understand whether the presence/absence of water and spinel was associated with specific compositional units. Nonlinear spectral unmixing analyses using radiative transfer modeling and in-scene endmembers in conjunction with MI and M^3 data were applied to quantitatively investigate the lateral/vertical mixing. The spectral features of pixels with highest abundance of spinel (i.e., > 90%) were examined to understand their speciation (e.g., Cr or Al spinel), which informed the magma sources and formation processes.

In summary, this work provides a detailed study on the lunar surface water distribution, abundances, and origins using orbitally-acquired reflectance data and supported laboratory experiments. This work broadens our knowledge on the distribution, variation, and origin of the lunar surface water and allows us to understand rates of hydroxyl formation and destruction at the lunar surface and to assess water sourced from the lunar interior. More localized water anomalies associated with specific geological

features remain to be explored in future studies to better understand the role of water in the geological history of the Moon. The framework developed in this thesis is ready to be applied to other airless bodies in our solar system to explore the effects of water during solar system formation and evolution.

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Table Captions

Table 1. Summary of lunar surface water reservoirs and respective sources, speciation, abundances, and likelihood of existence at proposed locations. Light to dark brown color corresponds low to high water abundance. Blue color means high likelihood, while light blue indicates low likelihood (see text for details). Speciation of water on the Moon cannot be distinguished with M^3 data due to lack of infrared bands covering the full OH fundamental stretching absorptions (from $\sim 2.7\mu\text{m}$ to $\sim 4\mu\text{m}$) and the H_2O fundamental bending absorptions (at $\sim 6\mu\text{m}$). Moreover, water abundance on the Moon is too low that any overtones and combinations of OH and H_2O fundamental absorption bands at shorter wavelengths are too weak to be measurable.

Tables

Reservoirs	Sources	Speciation	Abundances	Low	Existence	Possibility	High
				High latitude	*Pyro. low lat.	*Non-pyro. low lat.	
Surficially bonded 'water' on grains	Solar wind	Mostly OH	Very low				
	Impact delivery	OH/H ₂ O	Very low				
	Indigenous 'water'	OH/H ₂ O	Might not be stable				
Sub-surficially coated 'water' in grains <i>(0 < depth in grains < ~200 nm)</i>	Solar wind	Mostly OH	0-100s ppm				
	Impact delivery	OH/H ₂ O	Very low				
	Indigenous 'water'	OH/H ₂ O	Very low				
'Water' inside grains <i>(Depth in grains from ~200 nm to cores)</i>	Solar wind	Solar wind implantation < ~200 nm in depth					
	Impact delivery	OH/H ₂ O	Exotic grains, very rare				
	Indigenous 'water'	OH/H ₂ O	0-1000s ppm?				
Massive 'water' accumulations	Solar wind	OH/H ₂ O	Generally ~1000 ppm?				
	Impact delivery	OH/H ₂ O					
	Indigenous 'water'	OH/H ₂ O	PSR could be ~1 wt. %?				

Chapter 1: An empirical thermal correction model for Moon Mineralogy Mapper data
constrained by laboratory spectra and Diviner temperatures

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Abstract

Radiance measured by the Moon Mineralogy Mapper (M³) at wavelengths beyond ~2 μm commonly includes both solar reflected and thermally emitted contributions from the lunar surface. Insufficient correction (removal) of the thermal contribution can modify and even mask absorptions at these wavelengths in derived surface reflectance spectra, an effect that precludes accurate identification and analysis of OH and/or H₂O absorptions. This study characterized thermal effects in M³ data by evaluating surface temperatures measured independently by the Lunar Reconnaissance Orbiter Diviner radiometer, and results confirm that M³ data (Level 2) currently available in the Planetary Data System (PDS) often contain significant thermal contributions. It is impractical to use independent Diviner measurements to correct all M³ images for the Moon because not every M³ pixel has a corresponding Diviner measurement acquired at the same local time of lunar day. Therefore, a new empirical model, constrained by Diviner data, has been developed based on the correlation of reflectance at 1.55 μm and at 2.54 μm observed in laboratory reflectance spectra of Apollo and Luna soil and glass-rich samples. Reflectance values at these wavelengths follow a clear power law,

$R_{2.54\mu\text{m}} = 1.124R_{1.55\mu\text{m}}^{0.8793}$, for a wide range of lunar sample compositions and maturity. A nearly identical power law is observed in M³ reflectance data that have been independently corrected using Diviner-based temperatures, confirming this is a general reflectance property of materials that typify the lunar surface. These results demonstrate that reflectance at a thermally-affected wavelength (2.54 μm) can be predicted within 2% (absolute) based on reflectance values at shorter wavelengths where thermal contributions are negligible and reflectance is dominant. Radiance at 2.54 μm that is in excess of the

expected amount is assumed to be due to thermal emission and is removed during conversion of at-sensor radiance to reflectance or I/F. Removal of this thermal contribution using this empirically-based model provides a more accurate view of surface reflectance properties at wavelengths $>2\ \mu\text{m}$, with the benefit that it does not require independent measurements or modeling of surface temperatures at the same local time as M³ data were acquired. It is demonstrated that this model is appropriate for common lunar surface compositions (e.g., mare and highlands soils, pyroclastic deposits), but surface compositions with reflectance properties that deviate strongly from these cases (e.g., pyroxene-, olivine-, or spinel-rich locations with minimal space weathering) may require the use of more sophisticated thermal correction models or overlapping Diviner temperature estimates.

1. Introduction

The Moon Mineralogy Mapper (M^3) imaging spectrometer onboard the *Chandrayaan-1* mission measured radiance from the lunar surface at wavelengths between $\sim 0.5 \mu\text{m}$ and $\sim 3 \mu\text{m}$, and these data have been used to derive reflectance spectra for much of the Moon [Green *et al.*, 2011]. Understanding the spatial distribution and relative (if not absolute) abundance of minerals, impact products, and pyroclastic deposits in the lunar crust is critical for revealing the history of lunar evolution [e.g., Cahill *et al.*, 2009; Dhingra *et al.*, 2011; Klima *et al.*, 2011; Mustard *et al.*, 2011; Pieters *et al.*, 2011a; Cheek *et al.*, 2013; Moriarty *et al.*, 2013; Hanna *et al.*, 2014]. In this context, the data acquired by M^3 provide important spectral information for discriminating between mineral components that dominate the lunar surface, including pyroxene, plagioclase, olivine, and spinel by their unique Fe^{2+} absorption features centered near $1 \mu\text{m}$ and $2 \mu\text{m}$, $1.25 \mu\text{m}$, $1 \mu\text{m}$, and $2 \mu\text{m}$, respectively [Adams, 1975; Pieters *et al.*, 2011b]. In addition, vibrational absorptions due to OH/H₂O occur at $\sim 2.7 - 4 \mu\text{m}$, a wavelength range that is partly covered by M^3 and that can enable detection of water at the lunar surface that may record information about solar wind processes, volatile-rich impacts, or volatiles sourced from the lunar interior (here we define ‘water’ or ‘hydration’ as H₂O and/or OH) [Epstein and Taylor, 1970; Saal *et al.*, 2008; Clark, 2009; Pieters *et al.*, 2009; Sunshine *et al.*, 2009; McCubbin *et al.*, 2010; Greenwood *et al.*, 2011; Hauri *et al.*, 2011; Liu *et al.*, 2012; Saal *et al.*, 2013]

However, thermal emission from the lunar surface can have a significant influence on remotely sensed radiance and surface reflectance spectra derived from such data at wavelengths beyond $2 \mu\text{m}$ [Clark, 1979; Singer and Roush, 1985; Vasavada *et al.*,

1999; *Hinrichs and Lucey*, 2002; *Clark et al.*, 2011]. Indeed, mineral or hydration absorptions at wavelengths $>2\text{ }\mu\text{m}$ can be modified or even masked by thermal emission contributions due to high daytime temperatures (e.g., $>400\text{K}$ near the lunar equator) [*Singer and Roush*, 1985; *Clark*, 2009; *Combe et al.*, 2011; *McCord et al.*, 2011]. Such thermal effects can alter the shape (e.g., apparent band center) of the $2\text{ }\mu\text{m}$ absorption caused by Fe^{2+} in pyroxene M2 sites or tetrahedral Fe^{2+} in spinel, features that are important for identifying the chemistry of these minerals [e.g., *Burns*, 1993]. As such, an accurate understanding of lunar surface composition and hydration state from M^3 data will be limited without first correcting for the contribution of thermal emission.

The importance of the thermal contribution in M^3 data has been previously recognized, but the initial estimates of these effects were only examined empirically due to the lack of independent measurements of lunar surface temperature acquired at the same local time as M^3 data were acquired [*Green et al.*, 2010; *Clark et al.*, 2011]. Indeed, other studies have recognized that early thermal correction models for M^3 data are insufficient for detailed analysis of the distribution of lunar surface water [*Combe et al.*, 2011; *McCord et al.*, 2011]. In addition, current thermal correction models, such as the one that has been used to generate the M^3 Level 2 data in the Planetary Data System (PDS), may not be adequate for spectra with strong absorption bands at $\sim 2\text{ }\mu\text{m}$ [*Clark et al.*, 2011; *Lundeen et al.*, 2011].

Ideally, independent measurements of lunar surface temperature acquired at the same locations and local times as M^3 spectra could be used to estimate and then separate thermal emission from surface reflectance. However, such data were not simultaneously acquired when radiance spectra were measured with M^3 . Fortunately, the Diviner

radiometer onboard the *Lunar Reconnaissance Orbiter* (LRO) is capable of measuring and mapping lunar surface temperature and was launched shortly after *Chandrayaan-1* [Paige et al., 2010a]. It has been suggested that lunar surface temperatures have no or negligible seasonal and annual variations due to the lack of atmosphere and the 1.5 degree obliquity of the Moon [e.g., Vasavada et al., 1999], which implies that variations in lunar surface temperature are dominated by differences in lunar local time. Thus, an alternative approach is to employ Diviner temperature products acquired at the same local time as M^3 data but not necessarily in the same season and/or year. However, it should be noted that the temperature at local noon near the equator may vary by several degrees due to variations in solar distance.

In this study we examine potential thermal contributions in a subset of M^3 data by evaluating Diviner-based temperatures acquired at the same location and local time. Two different types of lunar surface temperature products are available from the Diviner data, including lunar surface brightness temperature derived from individual Diviner channels and surface bolometric temperature calculated from Diviner channels 3-9, where the latter may be closer to the average surface temperature [Paige et al., 2010b]. The temperatures derived from shorter wavelengths is more sensitive to the hotter surface components compared with temperatures derived from longer wavelengths due to surface roughness, especially at high incidence angles [Bandfield et al., 2015]. Thus, thermal contributions to M^3 data (2-3 μm) could still be underestimated when applying temperatures derived from the longer wavelength Diviner data (7.55-200 μm). Both types of temperature products were examined in this study and are discussed below. It has been noted that surface roughness on the Moon may cause brightness temperatures derived

from shorter wavelengths (i.e., Diviner channel 3, 7.55-8.05 μm) to differ significantly from those derived from longer wavelengths (i.e., Diviner channel 9, 100-200 μm) when the solar incidence angle is greater than $40^\circ - 50^\circ$ [Bandfield *et al.*, 2015]. Consequently, the derived bolometric temperature from the Diviner channel 3-9 data (7.55-200 μm) may deviate from (underestimate) the ‘true’ surface temperature that affects M^3 data in the 2-3 μm region at high solar incidence angles (i.e., $> 40^\circ - 50^\circ$). This potential effect was also evaluated in the present study.

Because not every M^3 pixel has an overlapping Diviner-based temperature acquired at the same local lunar time, we examined spectral properties and empirical relationships in visible-near infrared laboratory reflectance spectra of Apollo soil, rock, mineral and glass samples for which thermal emission is not present. These data were used to develop an empirical model for estimating thermal contribution in M^3 data, and we demonstrate below that this model is validated by reflectance properties observed in M^3 data that were independently corrected using Diviner-based surface temperatures. These results provide the foundation for development of a new thermal correction model for M^3 data that 1) should be valid for the majority of typical lunar soil compositions and that 2) does not require independent knowledge of surface temperature at the same local time as M^3 data were acquired.

2. Methods

2.1. Laboratory Visible-Near Infrared Reflectance Spectra

Visible-near infrared reflectance spectra for a wide range of Apollo soil and glass samples were used to examine the relationship between reflectance at wavelengths

unaffected by thermal emission and those likely to be affected by thermal emission in M^3 data. The goal was to use spectra of actual lunar materials to determine if reflectance values at longer wavelengths could be accurately predicted based on observed reflectance values at shorter wavelengths. As discussed in detail by *Clark et al.* [2011], reflectance values of lunar soils are strongly correlated at near-infrared wavelengths, and this is in part due to the effects of space weathering in the lunar surface environment [*Pieters et al.*, 2000]. The result is that the reflectance value at one wavelength is often highly correlated to (or readily predicted from) the reflectance value at a different wavelength.

For this study we chose to examine a ‘short’ wavelength at $\sim 1.55 \mu\text{m}$ because this wavelength lies outside of major iron absorptions and potential thermal effects in M^3 data are negligible at this wavelength even at maximum lunar surface temperatures. A ‘long’ wavelength of $\sim 2.54 \mu\text{m}$ was chosen for comparison because this wavelength position will contain a component of thermally emitted radiance for a relatively wide range of lunar surface temperatures. Because the Planck function shifts to shorter wavelengths with increasing temperature, adopting a ‘long’ wavelength at a shorter position ($< 2.54 \mu\text{m}$) would result in excess thermal radiance being identified for only a smaller subset of potential surface temperatures (skewed toward the warmest surfaces). An even longer wavelength could also be used, but $2.54 \mu\text{m}$ has the advantage that it lies outside of the fundamental OH/H₂O absorptions (which typically start at $\geq 2.65 \mu\text{m}$) and thus will not be affected by the presence of these absorbing species.

Spectra of Apollo soil and glass samples were included in the analysis to cover the dominant compositional and particle size variations expected at the lunar surface. We did not focus on spectra of Apollo rock and mineral samples in this study because it has

been demonstrated that the lunar surface is dominated by regolith, the optical properties of which are controlled primarily by particles 10-20 μm in diameter [[Pieters et al., 1993](#)], and the abundance of rock exposed on the lunar surface is generally estimated to be <5% [[Bandfield et al., 2011](#)]. However, lab spectra of lunar rocks and minerals at M^3 wavelengths were also examined to understand general spectral properties of these materials and are discussed below. All available reflectance spectra (0.3 - 2.6 μm , spectral resolution of 5 nm) for Apollo samples were obtained from the NASA Reflectance Experiment LABoratory (RELAB) facility database at Brown University [[Pieters, 1983](#)]. This produced a total of 559 soil and 28 glass-rich sample spectra in total, all measured with the RELAB bi-directional (BDR) spectrometer, and reflectance values at 1.55 and 2.54 μm were extracted from each spectrum and plotted against each other (Figure 1). Longer wavelength FTIR data for each sample, as well as for lunar mineral separates and rocks, were also obtained from the RELAB database to assess spectral properties from $\sim 2 - 5 \mu\text{m}$. RELAB sample and spectrum identifications are listed in Table S1.

2.2. Analysis of Overlapping M^3 and LRO Diviner Data

Eight regions of interest on the Moon were identified for co-analysis of M^3 and Diviner data, with an emphasis on selecting areas that would span a range in optical maturity, albedo, solar incidence angle, latitude, and composition. The selection of these regions was limited in part to whether or not Diviner data acquired at the same lunar local time as overlapping M^3 data were publicly available at the time of the study. Our final study regions included two mare regions (Orientale and Moscoviense), three highland

regions (Apollo 16 landing site, an optically fresh highland, and an optically mature highland), and three pyroclastic deposits (Sinus Aestuum, Humorum, and Rima Bode) (Figure 2).

The three types of regions of interest span the dominant compositional terrains on the lunar surface as well as a range in space weathering/maturity (as determined from the optical maturity, OMAT, parameter [Lucey *et al.*, 2000]; see Figure 3). Pyroclastic deposits are very dark at visible-near infrared wavelengths [e.g., Gaddis *et al.*, 2003], and Sinus Aestuum is of particular interest because this region exhibits the presence of spinel [Sunshine *et al.*, 2010; Yamamoto *et al.*, 2013]. Reflectance spectra of spinel show a much broader 2 μm absorption feature than is observed for pyroxene, which can result in lower reflectance values at 2.54 μm and may make the reflectance trends for spinel-rich regions deviate from those observed for more common lunar compositions.

2.2.1. Selection of M^3 Data

M^3 Level 1 radiance data were downloaded from the PDS and utilized in this study. M^3 data from all different optical periods were considered for this study, but we avoided those images acquired when the sensor was marked as ‘hot’ [Lundeen *et al.*, 2011]. For each research region, only a subset of one image cube is used to make the maximum variation of the solar incidence angle in this area no more than 1° , which is critical to obtain the best matched Diviner data at the same local time of a lunar day (see the section 2.2.2).

All M³ images were registered to the planetocentric coordinate system as that used for Diviner data [[PDS Geosciences Node, 2012](#)] in order to be georeferenced with the corresponding Diviner bolometric temperature images.

2.2.2. Selection of Diviner Data

We used solar azimuth angles, incidence angles, and the geographic coordinates of the M³ images in our regions of interest as criteria for searching Diviner radiance data with the DIVINER RDR QUERY tool [[PDS Geosciences Node, 2012](#)]. Because the solar azimuth angle is defined in different ways for the Diviner radiometer and M³ datasets, we used solar azimuth angles in M³ data to determine whether the data were acquired in the morning or afternoon. If the M³ data were acquired in the morning then we used 6-12 hours past midnight in the search box ‘Filter by local time of Day’ of the DIVINER RDR QUERY tool. Otherwise, we used 12-18 hours after midnight as the search parameter.

The minimum and maximum solar incidence angles in the M³ data were used as inputs for the search box ‘Filter by emission, Solar Incidence, and Solar Azimuth Angles’ in the query tool and we did not specify the emission angle and the solar azimuth angle inputs. The reason we do not use the emission angle as a criterion is that the observation geometry of M³ and many Diviner data is primarily nadir [[Paige et al., 2010a](#); [Green et al., 2011](#)], and at low incidence angles the emission angle will have minimal effect on lunar surface temperature. The Diviner dataset was searched by area (as opposed to pixel-by-pixel) to improve the search efficiency. The search area was set small enough such that the difference between the maximum and minimum solar incidence angle of M³ data was within 1°, which means that the maximum difference between the solar incidence

angle of M^3 and the matching Diviner data does not exceed 1° . Uncertainties that may be introduced by this maximum 1° difference are discussed below. Finally, shadow features observed in overlapping M^3 and Diviner images were also compared to visually confirm that the data were acquired at the same lunar local time.

For Diviner data that met these search criteria, radiance data for channels 3 – 9 were downloaded and used to calculate the bolometric temperature based on the procedures described in the supplementary materials of [Paige et al. \[2010b\]](#). Brightness temperature data for Diviner channel 3 were also downloaded to investigate effects due to potential non-isothermal behavior (i.e., wavelength-dependent surface temperatures), which may be due in part to small-scale roughness effects at the lunar surface [[Vasavada et al., 2012](#); [Bandfield et al., 2014](#); [Bandfield et al., 2015](#)].

2.3. Empirically-based Thermal Correction Model Using Kirchoff's Law

The radiance, L , at each wavelength channel (band) measured by a satellite instrument such as M^3 can be expressed as:

$$L_{Sat} = L_r + L_T \quad (1)$$

where $L_r = J/\pi * R$ is the reflected radiance in which R is the bidirectional reflectance without thermal effects, J is the solar irradiance spectrum, $L_T = L_{bb}(T) * E$ is the thermally emitted radiance, E is the emissivity, and $L_{bb}(T)$ is the Planck function for a blackbody at temperature, T . Assuming Kirchhoff's law, $E = 1 - R$, Equation 1 can be rewritten as:

$$L_{Sat} = J/\pi * R + L_{bb}(T)(1 - R) \quad (2)$$

In Equation 2, only R and T are unknown. If the reflectance is known for a given band, then the temperature can be solved from Equation 2, and vice versa. As mentioned above, we examined the correlation between laboratory reflectance spectra of Apollo samples at two wavelengths (equivalent to two M^3 bands) that do not coincide with major absorption features. The short wavelength band should be free of thermal effects whereas the long wavelength band might contain thermal contributions depending on the specific lunar surface conditions. Any observed empirical correlation (e.g., Figure 1) can be applied to M^3 data to predict the reflectance of a ‘long’ wavelength band that might be affected by thermal emission, and this predicted reflectance value can be inserted into Equation 2 in order to estimate the surface temperature (and its associated radiance contribution) at this wavelength. If the observed reflectance value is identical to or lower than the predicted value then it can be assumed there is no thermal contribution to that spectrum.

The derived temperature can then be reinserted in Equation 2 to solve for the reflectance values at all other wavelengths. The result is a thermally-corrected reflectance spectrum for the wavelength region of interest. A primary assumption of this simple model is that the portion of a surface that is actually sensed within an M^3 pixel is effectively isothermal at these wavelengths, an effect that is discussed below. An alternative approach would be to solve Equation 2 using independent Diviner-based estimates of surface temperature. Trends in reflectance values between short and long wavelength M^3 data that are thermally-corrected based on this approach could then be compared with the trends observed in the laboratory spectra of lunar samples. Both approaches were evaluated as part of this study and results are presented in Section 3.

2.4. Radiative Transfer-based Thermal Correction Model

Radiative transfer models can also be used to estimate and then remove thermal contributions, but these differ from the empirical approach described above in terms of how the L_T term is treated in Equation 1. In radiative transfer models such as those of Hapke [2005], multiple scattering effects of the upwelling thermal emission are accommodated, which may be a more accurate representation of potential thermal effects compared with models based solely on Kirchhoff's law (e.g., section 2.3) [Hapke, 2005]. For a radiative transfer-based approach we adopt the expression $L_T = \sqrt{1-\omega} * H(\omega, \mu) * L_{bb}(T)$ (Equation 13.21 in Hapke [2005]) for the thermal emission, where ω is the single scattering albedo, $H(\omega, \mu)$ is the multiple scattering function for the upwelling energy, μ is cosine of the emergence angle, and T is the Diviner-based surface temperature. Thus, Equation 1 can be rewritten as:

$$L_{Sat} = J/\pi * R + \sqrt{1-\omega} * H(\omega, \mu) * L_{bb}(T) \quad (3)$$

To compare our results with publicly released M^3 reflectance data [Lundeen *et al.*, 2011] it was necessary to have the output be the radiance factor, R_f , which can be expressed by Equation 36 in Hapke [1981]:

$$R_f = R * \pi = \frac{\omega}{4} \frac{\mu_0}{\mu + \mu_0} [(1 + B(g)P(g) + H(\omega, \mu_0)H(\omega, \mu) - 1)] \quad (4)$$

where μ_0 is the cosine of incidence angle, $B(g)$ is the back scattering function, $P(g)$ is the phase function, g is the phase angle. The parameterization of $B(g)$, $P(g)$, $H(\omega, \mu)$ and $H(\omega, \mu_0)$ used in this study is the same as that of Li and Li [2011].

Substituting into Equation 3, L_{Sat} can then be written as

$$L_{Sat} = J * \frac{\omega}{4} \frac{\mu_0}{\mu + \mu_0} [(1 + B(g)P(g) + H(\omega, \mu_0)H(\omega, \mu) - 1) + \sqrt{1 - \omega} * H(\omega, \mu) * L_{bb}(T)] \quad (5)$$

Viewing geometry (i , e , g) for each pixel is stored in the M³ observation files, thus it is straightforward to solve for the only unknown parameter, ω , in Equation 5 if T is known. Once ω is known it is then possible to use Equation 4 to calculate the radiance factor without the contribution of thermal emission. It should be noted that we do not use the statistical ‘polishing’ step when processing the M³ radiance data in this study as has been done by the M³ team because this may alter absorption features at 1000 nm and 2000 nm [Lundeen *et al.*, 2011]. Small differences between our reflectance spectra and Level 2 M³ spectra can be attributed to this difference.

2.5. Photometric and Topographic Corrections for M³ Data

It is necessary to apply several photometric and topographic corrections to the reflectance values produced by our models in order for direct comparison to M³ Level 2 data available in the PDS, and the methods used in this study were the same as those used by the M³ team [Lundeen *et al.*, 2011]. To account for topographic effects, the solar incidence (i) and emergence (e) angles need to be recalculated by incorporating the solar azimuth angle (sa), M³ sensor azimuth (ma), pixel facet slope (s), and facet aspect (p) [Lundeen *et al.*, 2011]:

$$i' = \cos^{-1}(\cos(i) * \cos(s) + \sin(i) * \sin(s) * \cos(sa - p)) \quad (6)$$

$$e' = \cos^{-1}(\cos(e) * \cos(s) + \sin(e) * \sin(s) * \cos(ma - p)) \quad (7)$$

where i' and e' are the topographically corrected solar incidence and emergence angle, respectively. The values for i , e , sa , ma , s , and p can be found in the M³

observation files associated with each spectral data file. When deriving the single scattering albedo, ω , with equation 4, the values for i' and e' are used to account for the topographic effects.

The Lommel-Seeliger model has been used for M^3 photometric correction following the same approach that was done for Clementine spectral data [Hillier *et al.*, 1999; Buratti *et al.*, 2011; Lundeen *et al.*, 2011]. M^3 reflectance (radiance factor) data after topographic correction are normalized to a ‘standard’ viewing geometry at $i = 30^\circ$, $e = 0^\circ$, and $g = 30^\circ$ with the photometric correction model

$$R_{f-corrected} = R_f \frac{\cos 30^\circ / (\cos 30^\circ + \cos 0^\circ)}{\cos i' / (\cos i' + \cos e')} \frac{f(30^\circ)}{f(g)} \quad (8)$$

where $R_{f-corrected}$ is the reflectance after topographic and photometric correction, R_f is the reflectance after topographic correction, and f is the phase function whose values are derived from M^3 radiance data with the Lommel-Seeliger model [Buratti *et al.*, 2011; Lundeen *et al.*, 2011]. The f values can be found in the PDS M^3 Level 2 release. Applying these corrections to our calculated reflectance spectra allows for direct comparison with the publicly available Level 2 M^3 reflectance spectra, with the exception that we have not used the statistical polish, as discussed above.

3. Results

3.1. Laboratory Reflectance Spectra of Lunar Samples

Reflectance values at $1.55 \mu\text{m}$ and $2.54 \mu\text{m}$ as observed in laboratory reflectance spectra for the 587 lunar soil and glass samples are presented in Figure 1. It is clear that there is a strong and slightly nonlinear correlation between reflectance values at these two

wavelengths. The relationship is best fit by the power law $R_{2.54} = 1.124R_{1.55}^{0.8793}$. This demonstrates that the reflectance at a wavelength potentially affected by thermal emission in M^3 data can be predicted based upon the observed reflectance at a shorter wavelength where thermal emission is negligible. We demonstrate below that a similar power law trend is observed in the M^3 data that were independently corrected using Diviner-based temperatures. Therefore, we explore below how this power law can be used to predict the reflectance at 2.54 μm and used in conjunction with the empirical thermal correction model described in section 2.3 to remove thermal contributions from M^3 data. The temperatures associated with this empirical correction can also be compared to surface temperatures estimated from Diviner data.

Although the power law trend is based on a finite number of lab spectra (and thus a finite number of compositions), it is important to note that this dataset includes a wide range of lunar compositions. This includes highland soils, mare soils, soils that range in maturity/degree of space weathering, and pyroclastic glasses; individual phases within these samples include pyroxene, olivine, plagioclase, metal, glass, agglutinates, submicroscopic iron, and Fe/Ti-oxides, to name a few. Such materials, and Apollo highland and mare soils in particular, are expected to be volumetrically dominant at the optical surface of the Moon, thus we hypothesize a similar power-law trend may exist in most thermally corrected M^3 reflectance spectra. However, M^3 pixels that are extremely pyroxene-, olivine-, or spinel-rich and that have minimal space weathering may deviate from this trend.

3.2. Thermal Correction of M³ Data Using Diviner-Based Temperatures

We applied the radiative transfer thermal model described above to M³ data for the eight different regions of interest shown in Figure 2, using the Diviner-based bolometric temperatures (BOT) as the estimates for surface temperature for each corresponding M³ pixel. We also compared the Diviner BOT values with temperatures estimated from the M³ Level 2 reflectance data to determine whether or not M³-derived temperatures were over- or underestimated relative to Diviner estimates. The maximum wavelength range of M³ ($\sim 3 \mu\text{m}$) restricts the range of M³-derived surface temperatures to relatively high values, thus M³ temperatures with very low reported values (e.g., 0.1K) represent pixels for which no thermal contribution was detected using the thermal model of *Clark et al.* [2011].

The results for the three different surface types (highland, mare, pyroclastic) are discussed below. Temperature ‘maps’ from Diviner data were overlain on grayscale images of band 85 from overlapping M³ images, which were visually examined to qualitatively check that solar incidence was similar between the two datasets (M³ band 85 is typically dominated by thermal radiance when such effects are present in the data). We confirmed that in all cases the shadowed regions observed in M³ data were regions of low temperature in Diviner data and regions of high illumination in M³ corresponded to higher Diviner temperatures.

For each region of interest we also present example reflectance spectra to show how the reflectance features differ between M³ spectra that have been thermally corrected with Diviner BOT values, the publicly available M³ Level 2 reflectance data, and M³ I/F data (with no thermal correction). The reflectance at band 49 ($1.55 \mu\text{m}$) was also plotted

against reflectance at band 74 (2.54 μm) for M³ data that were thermally corrected with the Diviner BOT values. This was done to see if the thermally-corrected lunar surface spectra exhibited a similar trend as observed in the Apollo sample spectra presented in Figure 1.

3.2.1. Thermal Correction Results for Mare Regions

The two selected mare regions, Mare Moscoviense and Orientale, are presented in Figure 5. Comparison of illumination, shadows, Diviner BOT values, and M³ radiance data shows that the two datasets were collected at the same local time (the maximum difference between their solar incidence angle is less than 1° according to our searching criteria, as described above). A plot of Diviner BOT and channel 3 brightness temperature versus temperature estimates from the thermal correction used to generate M³ level 2 data (Figure 4) demonstrates that the latter are typically underestimated by ≤ 30 K and ≤ 15 K for Orientale and Moscoviense, respectively. In contrast, the temperature derived from our empirical model matches well (mostly < 5 K) with the Diviner BOT and channel 3 brightness temperatures (Figure 4). This indicates that surface temperatures associated with the thermal correction used for M³ Level 2 reflectance data are highly conservative compared with Diviner-based temperatures and generally underestimate the radiance due to thermal emission in mare regions under these illumination conditions.

To compare uncorrected (I/F) M³ reflectance spectra with thermally corrected Level 2 reflectance data (PDS) and spectra corrected using our BOT-based model, we randomly selected two pixels from each region. One pixel was selected to correspond to a

‘bright’ region (higher reflectance value at 750 nm) and one pixel was selected from a ‘dark’ region (lower reflectance value at 750 nm). These locations are highlighted by arrows in Figure 5a and the corresponding reflectance spectra are presented in Figure 5b. The Diviner BOT for the bright pixel in Orientale is 319 K, whereas the thermal correction model for M³ Level 2 data predicts a surface temperature of 0.1K, indicating there is no thermal contribution for this pixel at these wavelengths. However, when the Diviner BOT is used in the radiative transfer thermal model the resulting reflectance spectrum exhibits a downturn at wavelengths >2.7 μm , indicating an OH stretching absorption may be present in this region.

The Diviner BOT for the dark pixel in Orientale is 309 K, whereas the value predicted from the M³ Level 2 thermal correction is 292 K (Figure 5b). The spectrum that was thermally corrected with the Diviner BOT (dashed blue spectrum) deviates downward beyond $\sim 2.7 \mu\text{m}$ relative to the M³ Level 2 spectrum due to this 17 K difference in temperature, though no evidence for a distinct absorption is present in either thermally-corrected spectrum. The bright and dark pixel spectra for Moscoviense also exhibit a stronger downturn at long wavelengths when corrected using the Diviner BOT values.

The I/F spectrum for the dark pixel in Moscoviense exhibits a strong positive slope starting at $\sim 2 \mu\text{m}$ that is due to strong contributions of thermal emission (Figure 5b, dashed red line). After thermal correction, both the M³ Level 2 spectrum and the BOT-corrected spectrum show an absorption starting at $\sim 2.7 \mu\text{m}$. The temperature difference between Diviner BOT and M³ Level 2 is only 1K for this example, yet using the former yields a clear increase in absorption strength. This may be a result of the fact that our

radiative transfer thermal correction model uses a multiple scattering term in the component of thermal emission, which was not considered in the empirical model of *Clark et al.* [2011] that was used to produce the M³ Level 2 data. In other words, even using the same temperature, the radiative transfer model might remove more thermal contribution than the previously used empirical model. Alternatively, the difference in the spectra could indicate that when lunar surface temperature is high even a one degree difference in temperature can cause a large difference in thermal emission, which is not unexpected given that these wavelengths are on the short wavelength edge of the Planck function for common lunar surface temperatures.

Figure 6 presents results from an example M³ pixel in Mare Moscoviense to demonstrate differences in thermally corrected spectra due to different models (simple Kirchoff's Law versus radiative transfer approach) and a temperature difference of 1K. As described above, even the same input temperature will yield different (lower) reflectance values at long wavelengths if a Hapke-based radiative transfer model is used (compare solid blue line with solid green line in Figure 6). Because the radiative transfer model associates more of the observed radiance with thermal emission (due to scattering effects), the empirical model based solely on Kirchoff's Law may be considered a more 'conservative' approach in the sense that it will tend to yield weaker OH/H₂O absorptions at the longest wavelengths. It is also clear from Figure 6 that a temperature difference of 1K has a strong effect on reflectance values at the longest wavelengths for this particular temperature range (378-379K) regardless of which model is used. This is because these temperatures correspond to the steep, short wavelength edge of the Planck function at these wavelengths. Higher or lower temperatures that are not associated with the steepest

part of the Planck function would have weaker effects on reflectance values at these wavelengths for a similar 1K difference.

Reflectance values at 1.55 μm and 2.54 μm from the M^3 spectra that were thermally corrected using the radiative transfer model based on the independently measured Diviner BOT values are presented in Figure 5c. The empirical power-law regressed from lab reflectance spectra for lunar samples (Figure 1) is also shown for comparison, along with dashed lines that represent an offset of $\pm 2\%$ absolute reflectance. This comparison demonstrates that reflectance values for nearly all M^3 pixels corrected using Diviner BOT values fall within $\pm 2\%$ of what would be predicted based on the power law shown in Figure 1. The average incidence angle (i) for the M^3 data is also listed for each region (Figure 4), which is roughly similar to the phase angle (Figure 5c).

3.2.2. Thermal Correction Results for Highland Regions

Three highland regions were selected to include an optically fresh highland region (based on OMAT [Lucey *et al.*, 2000]), an optically mature highland region, and the highland region near the Apollo 16 landing site. Results are presented in Figure 7, following the same format as the results for mare regions discussed above (i.e., Figure 5). As with the mare examples, the temperatures estimated from the M^3 Level 2 thermal correction are significantly underestimated compared to the Diviner BOT and channel 3 brightness temperatures (Figure 4). This effect is stronger for the optically mature highland region compared with the Apollo 16 highland region, though in both cases it appears likely that nearly every M^3 Level 2 spectrum has not accounted for enough thermal emission. In contrast, the temperatures derived from our empirical model (which

uses the power law described above in conjunction with the model described in section 2.3) are much closer to the Diviner BOT and channel 3 brightness temperatures, although values for some pixels are lower by 5-10 K (Figure 4).

Importantly, M³ Level 2 spectra within the ‘fresh’ (optically immature) highland region have not accounted for any thermal contribution, as evidenced by the temperature values of 0.1K (Figure 4), yet many of the Diviner BOT values are well within the temperature range for which thermal effects should be present at wavelengths >2 μm . The effect that this strong difference in temperature has on the derived reflectance spectra is evident in Figure 7b, particularly for the ‘bright’ pixel in the optically immature highland region. For this example, there is effectively no difference between the M³ I/F spectrum and the Level 2 spectrum (red versus black spectrum in Figure 7b; small differences are due to our exclusion of the ‘polishing’ step in M³ processing). However, when the Diviner BOT is used in the radiative transfer thermal correction it is clear that there is a downturn (absorption) at wavelengths >2.7 μm .

The comparison of M³ band 49 (1.55 μm) with band 74 (2.54 μm) in Figure 7c demonstrates that the thermally corrected M³ spectra based on the Diviner BOT values exhibit similar reflectance properties as the lab spectra of Apollo and Luna samples. Spectra from the Apollo 16 and optically mature highland region span a relatively narrow range in reflectance values for these two wavelengths, whereas reflectance values for the optically immature region span an extremely large range. In all cases the vast majority of values are within $\pm 2\%$ absolute reflectance of what would be predicted based on the power law derived from the laboratory spectra. Also shown are results for the optically mature highland region in which the surface brightness temperature derived from Diviner

channel 3 (C3) were used in the radiative transfer thermal model instead of the BOT values. The results from these two temperature estimates are effectively indistinguishable for this region. The reason for this test of different Diviner temperatures (BOT versus C3) and the significance of these results are described below.

3.2.3. Thermal Correction Results for Pyroclastic Deposit Regions

Pyroclastic deposits near Humorum, Aestuum, and Aristarchus were selected as regions of interest to represent lunar surfaces with low albedo and likely high volcanic glass content [Gaddis *et al.*, 2003]. Results for these regions are presented in Figure 8 and are qualitatively similar to results for mare and highland regions. Temperatures derived from the M³ Level 2 thermal correction are commonly underestimated compared with Diviner BOT and channel 3 brightness temperatures (Figure 4). Most pixels in the three pyroclastic deposits were underestimated by 10 - 20 K in current M³ Level 2 data, whereas the empirical model presented here yields temperatures that are closer to (mostly within <5 K) Diviner BOT and C3 values (Figure 4).

As with the mare and highland examples, using the Diviner BOT values in the radiative transfer thermal correction model results in removal of more radiance that is attributed to thermal emission, which then results in lower reflectance values at wavelengths >2 μm (Figure 8b), compared with current M3 Level 2 spectra. Thermal emission effects are particularly noticeable in the M³ I/F examples (red spectra) for Aestuum, where Diviner BOT values approach ~390-400K. Even though the temperatures derived during the M³ Level 2 thermal correction are also high (380-391K), the resulting reflectance spectra still exhibit a slight upturn at the longest wavelengths.

Though not definitive, this spectral shape suggests thermal contributions may still be present in those data. A similar effect is observed in the examples for Aristarchus, where the M³ Level 2 spectra retain a noticeable curvature (increase in spectral slope with increasing wavelength) at the longest wavelengths, an effect that is not observed in lab spectra of lunar soils or rocks (Figure 12). This effect (spectral curvature) is reduced even further when the Diviner BOT values are used in the thermal correction (red spectra).

A plot of reflectance at 1.55 μm versus 2.54 μm for the thermally corrected M³ spectra (based on the Diviner temperatures) shows similar results as was observed for the mare and highland examples (Figure 8c). When using the Diviner BOT values, the resulting thermally corrected reflectance spectra in the pyroclastic regions exhibit similar trends as those observed in lab reflectance spectra. This is perhaps not unexpected given that our analysis of laboratory spectra indicated lunar soils and pyroclastic glass-bearing samples exhibited similar spectral trends at these wavelengths (Figure 1). Similar to the highland example, the results for Aestuum were effectively indistinguishable when brightness temperatures derived from Diviner channel 3 were used instead of BOT values (bright and dark green crosses in Figure 8c), which is not unexpected given that the lunar surface is largely isothermal at small incidence angles [*Bandfield et al.*, 2015]. The reflectance value at 2.54 μm for nearly all thermally corrected M³ spectra in these regions is within $\pm 2\%$ of the value that would be predicted based on the lab-derived power law, and most values are within $\pm 1\%$. Though this general statement is true for Aestuum, we note that the reflectance values at 2.54 μm for this region are systematically lower than what would be predicted based on the power law. This means that the thermal

contribution for most M^3 data at Aestuum would be underestimated if using the empirical best-fit power law trend.

4. Discussion and Significance

4.1. Uncertainties in Temperature Due to Mismatch in Solar Incidence Angle

As mentioned above, we did not search Diviner data to match M^3 data at the lunar local time pixel by pixel, but rather by small areas, which leads to a potential 1° maximum mismatch in solar incidence angle between the two datasets. A one-dimensional thermal model was used to evaluate the potential uncertainty in surface temperature that this may cause. Specifically, the two-layer thermal model constructed by *Mitchell and De Pater* [1994] and further extended to the lunar case by *Vasavada et al.* [1999] was applied in this study, and a finite difference algorithm was used to derive the solutions [Crank, 1975]. Surface temperatures were modeled for several different latitudes, including the equator, tropics, and polar regions.

The lunar surface daytime temperature profile as a function of solar incidence angle is plotted in Figure 9a for several different latitudes. A derivative of the temperature profiles along the solar incidence angle provides the temperature gradient per degree of solar incidence angle and is presented in Figure 9b. The temperature shown in Figure 9a is based on the integrated radiance over a wide wavelength range and is thus most similar to Diviner BOT values. The derivatives for the temperature profile curves show that the maximum temperature difference caused by a 1° offset in incidence angle will be $\sim 2.5\text{K}$. This value occurs at high incidence angles (60°) at equatorial and tropical

latitudes. In contrast, high incidence angles at high latitudes result in a potential temperature difference of $\sim 1.3\text{K}$.

These results demonstrate that the largest temperature differences induced by uncertainties in incidence angle will occur at low latitudes and high incidence angle. In the case of M^3 , which was pointed nadir, this would be similar to data acquired at high phase angles at low latitudes. However, the vast majority of M^3 data for low and mid-latitudes were acquired under low phase (low incidence) angles (Figure 10). Although this is a relatively simple thermal model and we do not take into account local effects of topography (which can lead to locally high incidence angles), the net result is that potential temperature differences between Diviner BOT values and surface temperatures at the exact time of M^3 data acquisition are likely on the order of 1-2K (Table 1), with the higher values applying to regions of high local incidence angle at low latitudes. Indeed, some of the scatter in the reflectance trend plots (Figures 5c, 7c, 8c) may result from this type of temperature discrepancy, though this cannot be definitively proven without independent surface reflectance or temperature measurements.

4.2. Assessing Potential Under/Overcorrection of M^3 Data

4.2.1 Checks on Spectral Properties of Corrected M^3 Data

A check that can be performed on M^3 data to determine if too much thermal contribution has been removed (which would give rise to false absorption features) is to examine the shape of the resulting reflectance spectrum from $\sim 2.5 - 2.9 \mu\text{m}$. Structural or adsorbed OH/H₂O gives rise to absorptions with a short wavelength edge that commonly begins near $\sim 2.65\text{-}2.7 \mu\text{m}$, where this edge is represented as a rapid decrease in

reflectance (i.e., it often has a sharp edge, particularly for OH and/or materials with low water contents). This is observed in laboratory spectra of hydrated glasses, clay minerals, zeolites, sulfate salts, and other hydrated materials [e.g., *Milliken*, 2006 and references therein]. Similarly, hydration absorptions observed in the RELAB FTIR spectra for lunar glasses and soils, some of which is likely due to surface-adsorbed OH/H₂O, also begin near ~2.6 - 2.7 μm . Therefore, if corrected M³ reflectance spectra exhibit a downturn in reflectance at wavelengths <2.65 μm , then it is likely that too much thermal contribution has been removed from the data.

This spectral property can be observed in the RELAB FTIR spectra of Apollo and Luna samples, which consists of 45 mineral separates, 84 rock samples, and 149 soil samples. The downturn (decrease in reflectance) for the ‘water’ band in these samples all begins near 2.68 μm ($2\sigma=0.055$) (Figure 11a, Table S2). If the downturn of a thermally corrected M³ spectrum begins at a wavelength shorter than ~2.65 μm then it is likely that too much thermal contribution has been removed. To avoid this potential over-correction when implementing our empirical model, if the initially corrected M³ spectrum exhibits a downturn at a wavelength <2.65 μm then we allow the trend line $R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793}$ to increase incrementally by 0.001 ($R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} + n * 0.001$, where n is the iteration number) until any potential downturn occurs beyond ~2.65 μm . If no downturn or absorption is present in the initially corrected spectrum then this step is skipped. This check is designed to account for M³ pixels whose actual 1.5 vs. 2.54 μm reflectance trend may lie above the best-fit power law described above, in which case they may be susceptible to over-correction.

We also apply a second threshold in an attempt to prevent the underestimation of thermal effects in our empirical model. The slope of the spectral continuum between $\sim 2.7\text{-}2.9\ \mu\text{m}$ is typically smaller than the slope of the spectral continuum from $1.5\text{-}2.9\ \mu\text{m}$ for Apollo and Luna samples, regardless of whether they are anhydrous or ‘wet’ (Figure 11b). In other words, the spectral slope does not tend to increase strongly with increasing wavelength for lunar samples, which means that the difference of the $2.7\text{-}2.9\ \mu\text{m}$ and $1.5\text{-}2.9\ \mu\text{m}$ slopes is commonly a negative value (Figure 11b). If thermally corrected M^3 spectra exhibit a difference in slopes that is greater than zero it is possible that there is still thermal contribution to the spectrum. We implement this check in our model such that if the difference in slope after the initial correction (based on the best-fit power law) is greater than 0.2 (note that all lab data are <0.15 in Figure 11b), then the trend line $R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793}$ will be allowed to decrease incrementally by 0.001 ($R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} - n * 0.001$, where n is the iteration number) until the difference between the two continuum slopes is less than this value. This check is designed to account for M^3 pixels whose actual 1.5 vs. $2.54\ \mu\text{m}$ reflectance trend may lie below the best-fit power law, in which case they may be susceptible to under-correction.

4.2.2 Effects of Anisothermality

Previous Diviner-based studies that have examined lunar surface temperatures, such as those of *Vasavada et al.* [2012] and *Bandfield et al.* [2015] have noted that surfaces on the Moon are likely to be represented by a distribution of temperatures rather than a single, uniform temperature. Such anisothermality will be strongly influenced by small-scale topography and incidence angle [*Bandfield et al.*, 2014; *Bandfield et al.*,

2015]. As an example, a rough surface that is illuminated at high incidence angles will have a larger fraction of shadowed (and thus colder) or partly illuminated components compared to a similar surface illuminated at low incidence angles. Because the lunar regolith is highly insulating, these illumination effects can lead to very strong gradients in temperature over short length scales. An outcome of this effect is that a surface temperature derived from radiance observed at a longer wavelength is likely to be lower than the surface temperature that would be derived based on radiance at a shorter wavelength [*Bandfield et al.*, 2015].

In practical terms this means that our use of Diviner BOT values may be underestimating the true thermal emission contribution at the shorter wavelengths that we are correcting in the M³ dataset. This effect was discussed by *Bandfield et al.* [2015], where it was shown that surface brightness temperatures estimated from Diviner data are likely to vary depending on which channel is used, and the shorter wavelength channels will tend to yield higher estimates of surface temperature. However, such temperature differences are primarily a function of incidence angle for a given surface roughness, with the effect being stronger as incidence angle increases. Anisothermality is relatively weak for incidence angles $<40^\circ$ and expected wavelength dependency of brightness temperature due to surface roughness is likely negligible at $i \leq 30^\circ$ [*Bandfield et al.*, 2015].

Therefore, the conditions under which anisothermality is likely to be most manifest in M³ radiance is for data acquired at high incidence angles, which will occur in the early morning, late afternoon, and at high latitudes (i.e., $> \sim 40^\circ$). However, the vast majority of M³ data are acquired under conditions for which anisothermality is likely not

a major factor. Data at equatorial and mid-latitudes was typically acquired during late morning or early afternoon, when incidence angles were $\leq 30^\circ$ (Figure 10) and wavelength-dependency of brightness temperature is minimal. Incidence angles for M^3 data are progressively higher at higher latitudes, but surface temperatures are lower for these regions and thermal contribution to M^3 data is typically absent or very weak [Clark *et al.*, 2011].

Anisothermality is certainly important for lunar surfaces, but for the reasons stated above it is not expected to be a major issue for the wavelength range of the M^3 data for the particular conditions under which most of those data were acquired. However, in order to test this hypothesis we evaluated the radiative transfer thermal model using the Diviner channel 3 surface brightness temperatures for the optically mature highland region and the Sinus Aestuum pyroclastic region. As shown in Figures 7c and 8c, and as noted above, the reflectance trends in the thermally corrected spectra are extremely similar regardless of whether channel 3 or BOT values are used, which is in accordance with the small differences (typically <5 K) between Diviner channel 3 brightness temperature and BOT values at these locations (Figure 4). The Diviner channel 3 temperatures are typically slightly higher than the BOT values, as expected for a slightly anisothermal surface. The result of using the C3 temperatures in the radiative transfer model would thus be a slight increase in the thermal removal, but the differences that this yields in the corrected reflectance spectra are extremely small and well within the $\pm 2\%$ scatter in absolute reflectance that characterizes the dataset as a whole. This is observed for both test regions, which vary substantially in incidence angle ($i=8^\circ$ for Aestuum and $i=53^\circ$ for the optically mature highlands).

In summary, lunar surfaces are expected to be anisothermal under a range of illumination (and roughness) conditions, but the illumination conditions under which these effects are strong are not typical for the M³ dataset. This is confirmed based on the minor differences between the Diviner channel 3 brightness temperature and BOT values, and consequently in our results when channel 3 temperatures are used instead of BOT values. Wavelength-dependent temperature effects are expected to be much stronger at low latitudes for data acquired in the early morning or late afternoon when incidence angle is higher, but such cases are relatively rare in the global M³ dataset (e.g., Figure 10). Regardless, even if such effects are still present in our thermally corrected reflectance spectra, the implication is that our model has not removed enough thermal contribution at the shorter M³ wavelengths and is therefore a conservative approach with respect to estimates of surface temperature.

We also note that additional thermal removal would lower the reflectance values at wavelengths $>2\ \mu\text{m}$ even further, which would cause the M³ surface reflectance spectra to deviate strongly from reflectance trends that typify the actual reflectance properties of returned lunar samples (thus violating the constraints described in section 4.2.1). In other words, although it may be fortuitous that the 1.55 versus 2.54 μm reflectance trends observed in our thermally corrected (Diviner based) data are the same as the lunar samples, we consider this unlikely given that the Apollo soils are generally regarded as being representative of materials that typify the lunar surface in terms of particle size and composition. However, we stress again that pixels which represent compositions that differ strongly from typical lunar soils, such as very pyroxene-, spinel-, or olivine-rich pixels or pixels that lack effects of space weathering, may require a more detailed thermal

correction model to retrieve accurate surface reflectance properties at the longest M³ wavelengths.

4.2.3 Effects of +/-0.02 Offset on Thermally Corrected M³ Spectra

As discussed above, the majority of M³ pixels within our 8 study regions that were corrected using independent Diviner temperatures lie within +/-0.02 absolute reflectance of values at 2.54 μm predicted by the best-fit power law. The spectral checks discussed in section 2.4.1 are designed in part to account for these potential deviations, but it is also worth evaluating the effects that these offsets can have on the resulting spectra. Figure 12 presents spectra for two example pixels for each study region. For each case a spectrum is shown for the original M³ I/F values, the current M³ Level 2 spectra, the corrected spectrum that results from our best-fit power law as used in the empirical model, and cases where we use a +0.02 and -0.02 offset to the best fit power law (corresponding to potential under- and over-correction, respectively). Temperatures associated with each case are listed, as are Diviner BOT and C3 temperatures. Examples in the left column of panels correspond to cases where temperatures associated with the nominal (best-fit power law) empirical model are lower than Diviner BOT and/or C3 values, whereas examples in the right column of panels correspond to cases where empirical model temperatures are at, between, or slightly above Diviner BOT and C3 values.

Overall, the shape of spectra that were thermally corrected with the trend $R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} - 0.02$ (blue lines in Figure 12a-c) commonly exhibit evidence for overestimation of thermal effects (the hydration absorptions begin at wavelengths shorter

than $\sim 2.65 \mu\text{m}$), as expected for this offset. In contrast, the shape of spectra that were thermally corrected with $R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} + 0.02$ (brown lines in Figure 11a-c) exhibit characteristics indicating underestimation of thermal effects, as suggested by both the lower temperatures compared with Diviner measurements and the strong increase in spectral slope at wavelengths greater than $\sim 2.7 \mu\text{m}$ when compared with spectra of Apollo samples at the same wavelength region (Figure 13).

We note that in nearly all cases the nominal empirical model (including the spectral checks described above) yields temperatures that are largely consistent with Diviner BOT and/or C3 values (Figure 4), as well as spectra whose shapes and general properties are in accordance with lab spectra of lunar materials (Figure 13). As with any model there remain uncertainties with the empirical model presented here, and it is likely that some M^3 pixels will remain over or under-corrected with this approach, particularly those pixels corresponding to surfaces whose spectral properties deviate strongly from the best-fit power law trend in Figure 1. However, the thermal correction model and results presented here for the M^3 dataset suggest the empirical model is likely sufficient for evaluating regional and global trends in surface reflectance properties, where small-scale topographic variations are averaged out and for which major compositional units (e.g., highland, mare, and pyroclastic soils) are represented in the lunar sample collection.

It should be noted that reflectance studies concerned with smaller scale topography, where local incidence angles may be high and thus anisothermality may be more important, may require a more sophisticated model that accounts for these issues. Apparent differences in composition (or hydration features) between a sunlit and partially shadowed wall of a crater, for example, should be interpreted with care. We note, though,

that it is not entirely clear that small-scale roughness and the anisothermality that it introduces will necessarily always have a significant effect at M^3 wavelengths. Areas in shadow within a given pixel will not contribute directly reflected solar radiation to the sensor (only scattered photons), and because they are in shadow these areas would also likely be at low temperatures that do not contribute thermally emitted radiance in the 2-3 μm wavelength region. Therefore, the presence of shadows may simply reduce the overall radiance signal observed by the M^3 sensor (perhaps proportional to the fraction of surface within a pixel that is shadowed), but it may not always introduce a wavelength-dependent thermal emission effect.

4.3. Significance of Thermal Correction Results

The results presented above demonstrate that 1) temperatures associated with current M^3 Level 2 data available in the PDS are significantly lower than Diviner-based temperatures and thus are too conservative with respect to thermal correction, as indicated in *McCord et al.* [2011] and *Combe et al.* [2011], 2) laboratory reflectance spectra of lunar samples exhibit a strong relationship in reflectance values at 1.55 and 2.54 μm , and 3) M^3 reflectance spectra exhibit similar reflectance trends when corrected using a radiative transfer approach with independently estimated surface temperatures from Diviner. The significance of these findings is that the reflectance trend observed for lab spectra of lunar samples appears to be a fundamental characteristic of lunar surface reflectance spectra for materials that dominate the lunar optical surface at regional and global scales (e.g., highland, mare and pyroclastic soils). As such, the observed power-law trend can be used to apply an empirical thermal correction model to the M^3 dataset,

as described in section 2.3, without the need for overlapping Diviner data acquired at the same local lunar time of day.

However, we note that an empirical thermal correction based on the predictive power law trend has only been demonstrated in this study for a finite range of compositions (i.e., compositions represented by the lunar samples used in this study and compositions within the overlapping M³ and Diviner data for the eight study regions). Although these compositions are likely dominant for much of the Moon, the reflectance trends presented in Figure 1 and Figures 5c, 7c, and 8c may not apply to M³ pixels for surfaces dominated by significantly different compositions than found in returned lunar samples, different forms of space weathering, or high abundances of non-particulate materials (i.e., high rock abundances). Such regions would of course be of high scientific interest, but they are likely to be rare and volumetrically small within the M³ dataset at regional and global scales. Therefore, the empirical power-law thermal correction model presented here is expected to be valid for a wide range of space-weathered lunar soils and thus the majority of M³ spectra. However, apparent reflectance variations that are strongly correlated with small-scale topography, changes in phase angle, or regions of unusual mineralogy (e.g., spinel-rich regions) should be interpreted with care if this type of thermal model is applied.

Insufficient thermal removal in currently available M³ Level 2 reflectance spectra may also lead to an apparent increase in strength or center wavelength shift of absorption features. As an example, an absorption feature is apparent near $\sim 2 \mu\text{m}$ for the two M³ Level 2 spectra at Sinus Aestuum (black spectra, middle plot of Figure 8c). The absorption is apparent in part because of an increase in reflectance at the long

wavelengths, giving the appearance of a local minimum near $\sim 2 \mu\text{m}$. In standard band depth (absorption strength) calculations it is necessary to define an absorption by choosing a local reflectance maximum on both the short and long wavelength side of a feature (that is, the user defines the spectral continuum) [Clark and Roush, 1984]. In the spectra for Aestuum there appears to be a local maximum near $\sim 2.85 \mu\text{m}$, which could be chosen as the long wavelength end of the spectral continuum and thus yield a positive band depth value for what appears to be a $\sim 2 \mu\text{m}$ absorption. However, the same spectra that were thermally corrected with the Diviner BOT values exhibit a continuous increase in reflectance with wavelength (blue lines, middle plot in Figure 8c). Thus, a $\sim 2 \mu\text{m}$ absorption feature is not readily apparent in these spectra corrected with Diviner BOT, which yields reflectance spectra that are more typical of mature lunar regolith [e.g., Pieters *et al.*, 1993].

The same conclusion can also be drawn regarding the $2 \mu\text{m}$ absorptions seen in M³ Level 2 reflectance spectra for the two pixels at Aristarchus: the apparent presence or strength of a $\sim 2 \mu\text{m}$ Fe absorption feature may be greater compared with the spectra that were thermally corrected using independent (Diviner) surface temperature estimates. As mentioned above, the $2 \mu\text{m}$ absorption feature is critical for identifying pyroxene, spinel, and to quantitatively estimate mineralogical information of the Moon. Because insufficient thermal correction will affect how a spectral continuum is defined, residual thermal contribution may affect the apparent center wavelength position of Fe-related absorptions, which can in turn affect interpretations of pyroxene chemistry. These results indicate that caution must be exercised in studies that rely on the strength and center wavelength position of absorptions near $2 \mu\text{m}$ when using M³ Level 2 data. These issues

are expected to be minimized when using the thermal correction procedures discussed here.

The thermal correction model presented here also shows potential to provide new information on the distribution and strength of OH/H₂O related absorptions near $\sim 3 \mu\text{m}$. Lunar surface water has previously been investigated with M³ data [*Pieters et al.*, 2009; *Kramer et al.*, 2011; *McCord et al.*, 2011], but the details on its spatial distribution, relative abundance between mare and highland materials, and variation as a function of local lunar time [e.g., *Sunshine et al.*, 2009] have been constrained by the presence of thermal effects, especially at low latitudes. M³ data that have been thermally corrected with the empirical model presented here (or by using the radiative transfer model where/when appropriate Diviner data are available) will enable a more accurate assessment of lunar surface hydration at regional and global scales. In turn, this will provide new insight into how lunar surface water is distributed spatially and temporally on the Moon and how it is connected to solar wind, volatile-rich impacts, and interior sources such as volatile-bearing magmas.

4.4. Advantages and Constraints of a Diviner-Validated Empirical Model

A new empirical thermal correction model has been developed for M³ spectra based on the $R_{1.55\mu\text{m}} - R_{2.54\mu\text{m}}$ trend of Apollo soil and glass reflectance spectra, a trend that is independently observed in M³ data corrected using Diviner-based temperatures (Figure 14). An empirically-based thermal correction, based on the observed power law relationship, can be applied to the entire M³ data to produce reflectance spectra that are

expected to have less residual thermal contribution compared with currently available M³ Level 2 data.

As shown in Figure 13, nearly all of the data discussed here fall within $\pm 2\%$ absolute reflectance relative to the power line $R_{2.54\mu m} = 1.124 R_{1.55\mu m}^{0.8793}$. This relationship can be used to thermally correct the M³ data using the following steps for each M³ pixel:

Step 1: By inserting the observed reflectance at 1.55 μm (M³ band 49) into $R_{2.54\mu m} = 1.124 R_{1.55\mu m}^{0.8793}$, the surface reflectance at 2.54 μm (band 74) can be predicted.

Step 2: The predicted reflectance at 2.54 μm can be used in Equation 2 to predict the expected thermal radiance at 2.54 μm and the associated surface temperature (L_{Sat} and R are known). This step assumes that Kirchoff's Law is generally valid for lunar surfaces.

Step 3: The estimated surface temperature can then be inserted into Equation 2 and the reflectance is then solved for each wavelength based on the observed total radiance value; the modeled reflectance at 2.54 μm will be equivalent to the predicted reflectance value based on the power law in Step 1.

Step4: The photometric and topographic corrections for the thermally corrected reflectance spectra can be applied using Equations 6 – 8.

Step5: Finally, the criteria derived from laboratory measured reflectance spectra of Apollo and Luna samples described in section 4.2.2 are applied to the thermally corrected M³ spectra to examine whether thermal effects may be under- or over-estimated. If thermal effects for a pixel are underestimated (the difference between the 2.7-2.9 μm continuum slope is 0.2 greater than the 1.5-2.9 μm continuum slope, see section 4.2.1 for details), step 1 through 5 are re-executed on this pixel by replacing

$R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793}$ in step 1 with $R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793} - n * 0.001$ incrementally and iteratively (n is the iteration number) until the difference between the two continuum slopes is less than 0.2 or reaching $R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793} - 0.1$ (Figure 1). If thermal effects for a pixel were overestimated (the downturn of hydration absorptions begins shorter than 2.65 μm), step 1 through 5 are re-executed on this pixel by replacing $R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793}$ in step 1 with $R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793} + n * 0.001$ incrementally and iteratively (n is the iteration number) until the downturn position of hydration bands begins at a wavelength greater than 2.65 μm or reaching $R_{2.54\mu m} = 1.124 * R_{1.55\mu m}^{0.8793} + 0.05$ (Figure 1).

The power law $R_{2.54\mu m} = 1.124 R_{1.55\mu m}^{0.8793}$ represents the best approximation for lunar samples and M³ data as a whole, but because nearly all data fall within a $\pm 2\%$ absolute reflectance range of this trend it is also possible to consider likely upper and lower bounds. Adopting the equation $R_{2.54\mu m} = 1.124 R_{1.55\mu m}^{0.8793} + 0.02$ will provide an upper estimate of reflectance values, which provides a minimum estimate of the thermal contribution (i.e., a more conservative thermal correction, the lower limit of derived temperature). Conversely, adopting the equation $R_{2.54\mu m} = 1.124 R_{1.55\mu m}^{0.8793} - 0.02$ provides a lower estimate on reflectance values and will attribute more of the radiance observed at the sensor to thermal emission (i.e., a stronger thermal removal, the upper limit of derived temperature). The lower and upper limits of the temperature derived by assuming a $\pm 2\%$ offset of the empirical trend at our eight studying areas are shown in Figure 15. It suggests that the Diviner BOT and channel 3 temperature are within the lower (black)

and upper (green) limits of our derived temperature for most pixels. We consider the best-fit power law to be the most reasonable approach for large scale or global studies because it represents the middle ground between over- and underestimating thermal effects, but for detailed studies of specific regions that are known to deviate from this best-fit power law (e.g., Sinus Aestuum in Figure 8d) it may be better to use a slightly modified power law.

The cause(s) of the $\pm 2\%$ variation in the $R_{1.55\mu m} - R_{2.54\mu m}$ trend is not entirely clear, but it may result in part by variations in optical maturity. Reflectance spectra of samples with higher maturity will be ‘redder’ than those with lower maturity [Pieters *et al.*, 1993; Pieters *et al.*, 2000; Hapke, 2001]. The resultant reflectance at 2.54 μm will thus be higher for more mature samples, though the 1.55 μm reflectance varies less significantly as a function of optical maturity. Our mare regions of interest and the pyroclastic deposits at Aristarchus and Humorum have moderate optical maturities (Figure 3 and Table 2, where lower OMAT represents increased optical maturity) [Lucey *et al.*, 2000]. The best-fit power law regressed from the lunar samples lies very close to the values for all pixels in these three areas (Figure 5d and 8d). In contrast, many reflectance values at 2.54 μm for the mature highland region fall slightly above the power line (Figure 7d), whereas those for the optically immature highland region tend to fall below the power line (Figure 7d). When the 2.54 μm reflectance of the optically immature (‘fresh’) highland pixels exceeds ~ 0.3 , however, it falls slightly above of the power line (Figure 7d), which indicates that these spectra are brighter ($R_{2.54\mu m} > 0.3$) but also ‘redder’ compared with darker spectra at this area.

This contradicts the coupled reddening and darkening effects of space weathering and is uncommon in Apollo samples. It may represent a coupled effect of higher maturity (redder and darker) and finer particle size (brighter), but the exact cause is unclear. The $R_{1.55\mu\text{m}} - R_{2.54\mu\text{m}}$ trends for the Apollo 16 highland and Aestuum pyroclastic deposit region also deviate slightly from the best-fit power law, with pixels from both regions plotting below the trend observed for the lunar samples. The former has the lowest mean OMAT value of our regions of interest (Figure 3 and Table 2), whereas deviations in the Aestuum spectra may be associated with the presence of spinel in this region [Yamamoto *et al.*, 2013]. The latter is possible because tetrahedral iron in spinel generates a broad $\sim 2\mu\text{m}$ absorption that depresses the reflectance at $2.54\mu\text{m}$.

In summary, though all of our test data (M^3 and Apollo sample spectra) fall along a common trend line, local heterogeneity is observed (within 2% of absolute reflectance). If the best-fit power law is used in the empirical thermal model then thermal effects may be slightly overestimated for mature highlands (and fresh highlands with $R_{2.54\mu\text{m}} > 0.3$), whereas thermal effects may be slightly underestimated for fresh highlands with $R_{2.54\mu\text{m}} < 0.3$ and pyroclastic deposits at Sinus Aestuum. Some of these variations may be due to uncertainties in estimates of surface temperature from the Diviner data, as discussed above, but this may be unlikely given that the offsets are rather systematic for all pixels within certain regions regardless of variations in local topography, surface roughness, and/or incidence angle.

We conclude that for small-scale, local studies or analyses that seek to examine differences in reflectance between areas that differ strongly in surface roughness or local incidence angle, the best approach is to use a more sophisticated thermal model that

accounts for these effects or to use independent Diviner temperature estimates acquired at the same local lunar time. However, for large-scale (i.e., regional or global) studies that span a wide range in albedo, optical maturity, and composition (including typical highland, mare and pyroclastic regions), the empirical thermal model presented here provides a time efficient way to assess and at least bracket effects due to thermal emission at M^3 wavelengths.

5. Conclusions

A new empirical thermal correction model for M^3 data has been developed that does not require independent information on lunar surface temperature information. This empirical model is based on a power law relationship between reflectance values at 1.55 μm and at 2.54 μm observed in a wide variety of Apollo soil and glass sample reflectance spectra. A radiative transfer-based thermal model was used in conjunction with the Diviner-based estimates of lunar surface temperature to independently remove thermal emission effects from M^3 data in eight regions of interest. These regions included mare, highland, and pyroclastic deposits that span a range in optical maturity, thus encompassing materials that typify the optical surface of the Moon. M^3 reflectance spectra corrected with the radiative transfer thermal model exhibited a similar power law trends as was observed for the laboratory spectra, indicating this relationship is a fundamental reflectance characteristic of typical lunar materials.

Nearly all laboratory and M^3 spectra evaluated in this study are within $\pm 2\%$ of absolute reflectance of this trend, and most spectra are within $\pm 1\%$ (Figure 8). These results demonstrate that the power law $R_{2.54\mu\text{m}} = 1.124 R_{1.55\mu\text{m}}^{0.8793}$ can be used in an empirical

thermal correction model to provide the best approximation for the thermal effects in M^3 data for regional or global studies, whereas the equations $R_{2.54\mu m} = 1.124R_{1.55\mu m}^{0.8793} + 0.02$ and $R_{2.54\mu m} = 1.124R_{1.55\mu m}^{0.8793} - 0.02$ can be used to bracket the lower and upper limits of the thermally emitted radiance, respectively.

The results presented here also confirm that there are significant residual thermal effects in the current M^3 Level 2 data available in the PDS. Insufficient thermal correction of M^3 data can modify (i.e., strengthen, broaden) or even create the appearance of absorptions at wavelengths $>2 \mu m$, including masking the presence of OH/H₂O absorptions near $\sim 3 \mu m$. The new empirical model presented here is capable of minimizing and largely eliminating these effects, though more sophisticated thermal models may be better suited for spectra acquired under conditions in which strong anisothermality is expected to be present at M^3 wavelengths (e.g., high incidence angle at low latitudes for rough surfaces).

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Table Captions

Table 1. The approximate maximum temperature offset for our research area due to 1° mismatch in the solar incidence angle between Diviner and M³ data

Table 2. OMAT values and their standard deviations at our research areas

Table S1. RELAB sample and spectrum identifications for Apollo and Luna samples used in this study

Table S2. FTIR spectra scaled with BDR spectra of Apollo and Luna samples in the RELAB database

Figure Captions

Figure 1. Correlation between reflectance at 1.55 μm (equivalent to band 49 in M³ data) and at 2.54 μm (equivalent to band 74 in M³ data) for Apollo and Luna soil and glass-rich sample spectra obtained from the RELAB database. The solid line is a regression line and the dashed lines are $\pm 2\%$ offset lines.

Figure 2. Locations of research areas (red rectangles) overlain on a Clementine 750 nm global mosaic. Diviner data that overlap M³ data and were acquired at similar lunar local time were used in this study.

Figure 3. The optical maturity (OMAT) ranges for the regions shown in Figure 2 (also see Table 2) overlain on the histogram of OMAT values for the entire Moon. All OMAT values are derived from Clementine images. The regions used in this study span a wide range in OMAT that is characteristic of much of the lunar surface.

Figure 4. Comparison of Diviner bolometric temperature (BOT) with other temperature products, including those associated with thermally-corrected M³ Level 2 (L2) data from the Planetary Data System (black), temperatures derived from the empirical model presented here ($R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793}$, green), and Diviner channel 3 (C3) brightness temperatures (red). Values are shown for (a) mare, (b) highland, and (c) pyroclastic deposit study regions. Solid blue lines are 1:1 lines and dashed blue lines are 10K offset lines for comparison.

Figure 5. Overlapping Diviner and M³ data for mare study regions. (a) Diviner bolometric temperature data overlain on band 85 radiance image from M³ at mare Moscoviense (left, M³ image ID: M3G20081229T022350_V03_RDN) and Orientale (right, M³ image ID: M3G20090712T220912_V03_RDN); white and black arrows point at bright (at 750 nm) and dark (at 750 nm) pixels, respectively, where the example spectra were collected. (b) Comparison between M³ IoF, Level 2 reflectance spectra, and M³ spectra thermally corrected with the Diviner bolometric temperature and the radiative transfer model for the mare regions. Examples are shown for ‘bright’ and ‘dark’ pixels, corresponding to white and black arrows in panel (a). (c) The reflectance at band 74 (2.54 μm) and 49 (1.55 μm) of M³ data that were thermally corrected using Diviner bolometric temperatures at the two mare regions. The best-fit power law observed for spectra of the Apollo and Luna samples (see Figure 1) is shown as a solid gray line for comparison. Dashed gray lines represent $\pm 2\%$ offset lines. Note that M³ data corrected with independent Diviner temperatures exhibit a trend similar to lab spectra of returned samples.

Figure 6. Potential effects of a 1 K temperature difference on thermally corrected spectra for an example M³ pixel in Mare Moscoviense. At these temperatures a 1 K difference can have a noticeable effect on reflectance values at the longest M³ wavelengths, regardless of which model (simple Kirchoff’s law or radiative transfer) is used. Colder or warmer surfaces for which the steep, short wavelength part of the Planck function is not at these wavelengths may exhibit weaker spectral differences for a similar 1 K temperature difference. See main text for details.

Figure 7. Overlapping Diviner and M³ data for highland study regions. (a) Diviner bolometric temperature data overlain on band 85 radiance image from M³ at Apollo 16 highland region (left, M³ image ID: M3G20090108T044645_V03_RDN), an optically mature highland region (middle, M³ image ID: M3G20081225T074420_V03_RDN), and an optically fresh highland region (right, M³ image ID: M3G20090601T193005_V03_RDN); white and black arrows point at bright (at 750 nm) and dark (at 750 nm) pixels, respectively, where the example spectra were collected. (b) Comparison between M³ IoF, Level 2 reflectance spectra, and M³ spectra thermally corrected with the Diviner bolometric temperature and the radiative transfer model for the highland regions. Examples are shown for ‘bright’ and ‘dark’ pixels, corresponding to white and black arrows in panel (b). (c) The reflectance at band 74 (2.54 μm) and 49 (1.55 μm) of M³ data that were thermally corrected using Diviner bolometric temperatures at the three highland regions. The best-fit power law observed for spectra of the Apollo and Luna samples (see Figure 1) is shown as a solid gray line for comparison. Dashed gray lines represent $\pm 2\%$ offset lines. Note that M³ data corrected with independent Diviner temperatures exhibit a trend similar to lab spectra of returned samples.

Figure 8. Overlapping Diviner and M³ data for pyroclastic study regions. (a) Diviner bolometric temperature data overlain on band 85 radiance image from M³ at three pyroclastic deposits near Aristarchus (left, M³ image ID: M3G20090419T013221_V03_RDN), Humorum (middle, M³ image ID: M3G20081119T021733_V03_RDN), and Aestuum (right, M³ image ID: M3G20090609T183254_V03_RDN); white and black arrows point at bright (at 750 nm) and dark (at 750 nm) pixels, respectively, where the example spectra were collected. (b) Comparison between M³ IoF, Level 2 reflectance spectra, and M³ spectra thermally corrected with the Diviner bolometric temperature and the radiative transfer model for the pyroclastic regions. Examples are shown for ‘bright’ and ‘dark’ pixels, corresponding to white and black arrows in panel (b). (c) The reflectance at band 74 (2.54 μm) and 49 (1.55 μm) of M³ data that were thermally corrected using Diviner bolometric temperatures at the three pyroclastic regions. The best-fit power law observed for spectra of the Apollo and Luna samples (see Figure 1) is shown as a solid gray line for comparison. Dashed gray lines represent $\pm 2\%$ offset lines. Note that M³ data corrected with independent Diviner temperatures exhibit a trend similar to lab spectra of returned samples.

Figure 9. Lunar surface daytime temperature profiles at different latitudes (top plot) were modeled from a two-layer thermal model (see text for details). The derivatives of the temperature profiles at different latitudes indicate the temperature gradient per incidence angle variation (bottom plot).

Figure 10. (a) The phase angle of M³ OP2C data at $\pm 45^\circ$ latitude. If more than one measurements was available for a pixel (i.e., overlapping observations) then the minimum phase angle was chosen. (b) A histogram of the phase angle values mapped in (a). (c) Cumulative percentage curve of the phase angles in (a).

Figure 11. Spectral properties of Apollo and Luna samples used to constrain the empirical thermal model. (a) The wavelength position of the downturn (decrease in reflectance) for ‘water’ bands observed in lunar samples. Nearly all water absorptions begin at a wavelength $>2.65 \mu\text{m}$. (b) The difference between the spectral continuum slope from $2.7\text{--}2.9 \mu\text{m}$ and the slope from $1.5\text{--}2.9 \mu\text{m}$ for lunar samples. The continuum endpoint at $1.5 \mu\text{m}$ is determined as the maximum reflectance point between 1.4 and $1.6 \mu\text{m}$. The RELAB identifications for the spectra corresponding to the points in these plots are listed in Table S2.

Figure 12. Effects on thermally-corrected M^3 spectra when considering a $\pm 2\%$ offset to the best-fit empirical power law shown in Figure 1. Two example spectra are plotted for each of the eight study regions. Panels in the left column generally correspond to temperatures similar to or lower than Diviner values when using the baseline empirical thermal correction, panels in the right column generally correspond to temperatures at or slightly above Diviner values when using the baseline empirical model. Red: IoF spectra showing radiance measured by M^3 divided by the solar spectrum. Cyan: M^3 Level 2 spectra (and associated temperature) from the PDS. Green: spectra and associated temperature based on the empirical model and best-fit power law. Dark red: Spectra and associated temperature assuming a $+0.02$ offset to the best-fit power law. Blue: Spectra and associated temperature assuming a -0.02 offset to the best-fit power law. See Figure 15 for additional effects on temperatures of M^3 pixels when considering the $\pm 2\%$ offset. Differences between some M^3 Level 2 spectra and all other spectra in a given plot are due to the use of a statistical polisher in processing of the former (see text for details); this effect is more pronounced at higher reflectance values because it is multiplicative.

Figure 13. Example reflectance spectra for (a) ‘dry’ Apollo rock samples, (b) ‘dry’ Apollo mineral separates, and (c) Apollo bulk soils with water bands of different strengths. All spectra were obtained from the RELAB database.

Figure 14. The reflectance trend between band 74 ($2.54 \mu\text{m}$) and band 49 ($1.55 \mu\text{m}$) for all M^3 data thermally corrected with the Diviner bolometric temperature at the eight study regions compared with the trend observed in Apollo and Luna samples (e.g., data from Figure 1). The solid gray line is the best-fit power law shown in Figure 1 for the laboratory spectra of returned lunar samples, and nearly all thermally-corrected M^3 data are within a $\pm 2\%$ offset (dashed lines) when Diviner bolometric temperatures are used in a radiative transfer model. The similarity between lab spectra independently corrected M^3 data suggests this power-law trend is typical of common lunar highland, mare, and pyroclastic soils.

Figure 15. Temperatures associated with the lower ($R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} + 0.02$) and upper ($R_{2.54\mu\text{m}} = 1.124 * R_{1.55\mu\text{m}}^{0.8793} - 0.02$) offsets to the best-fit power law shown in Figure 1 and Figure 14 compared with Diviner bolometric (BOT) and channel 3 (C3) temperature values. For the eight study regions examined here, the lower offset largely underestimates temperature and the upper offset largely overestimates temperature compared with

Diviner values. Temperatures associated with the best-fit power law used in the empirical model are shown in Figure 4 and are in better agreement with Diviner-based values.

Tables

Table 1.

	Mare		Highland			Pyroclastic deposit		
	Orientale	Moscoviense	Fresh	Mature	Apollo 16	Humorum	Aristarchus	Aestuum
Solar incidence angle	~59	~31	~48	~55	~22	~37	~52	~8
Latitude	~21	~27	~63	~52	~9	~27	~25	~4
Diviner BOT range (K)	207-356	335-392	174-354	274-368	361-391	339-384	267-364	386-398
Maximum temperature offset (K)	~2.5	~1.5	~1.8	~1.8	~1.5	~1.8	~2	~0.5

Table 2

	Orientale	Moscoviense	Immature HL	Mature HL	A16	Aristarchus	Aestuum	Humorum
OMAT	0.134	0.132	0.186	0.123	0.116	0.155	0.131	0.135
std.	0.016	0.020	0.031	0.020	0.012	0.014	0.030	0.022

Table S1

Glass-rich samples (N = 28)			Soils (N = 559)		
Sample Name	Spectrum ID	Sample ID	Sample Name	Spectrum ID	Sample ID
76015 Xt05+Gl95	C1LX02	LX-CMP-002	1637	CBLR05	LR-CMP-005-B
76015 Xt05+Gl95	LALX02	LX-CMP-002	1637	CCLR05	LR-CMP-005-C
76015 Xt90+Gl10	C1LX03	LX-CMP-003	1637	LALR05C	LR-CMP-005-C
76015 Xt90+Gl10	C2LX03	LX-CMP-003	1637	CDLR05	LR-CMP-005-D
76015 Xt90+Gl10	C3LX03	LX-CMP-003	1637	CELR05	LR-CMP-005-E
76015 Xt90+Gl10	CMLX03	LX-CMP-003	1637	CALR06	LR-CMP-006
76015 Xt90+Gl10	LALX03	LX-CMP-003	1637	CALR07	LR-CMP-007
76015 Xt90+Gl10	LBLX03	LX-CMP-003	1637	CALR08	LR-CMP-008
76015 Xt10+Gl90	C1LX04	LX-CMP-004	1637	CALR09	LR-CMP-009
76015 Xt10+Gl90	C2LX04	LX-CMP-004	2014	C1LR10	LR-CMP-010
76015 Xt10+Gl90	C3LX04	LX-CMP-004	2014	LALR10	LR-CMP-010
76015 Xt10+Gl90	CMLX04	LX-CMP-004	2014	C1LR11	LR-CMP-011
76015 Xt10+Gl90	LALX04	LX-CMP-004	2014	LALR11	LR-CMP-011
76015 Xt10+Gl90	LBLX04	LX-CMP-004	2014	BKR2LR012	LR-CMP-012
76015 Xt80+Gl20	C1LX05	LX-CMP-005	2014	C1LR12	LR-CMP-012
76015 Xt80+Gl20	LALX05	LX-CMP-005	2014	C2LR12	LR-CMP-012
76015 Xt20+Gl80	C1LX06	LX-CMP-006	12003	C3LR12	LR-CMP-012
76015 Xt20+Gl80	LALX06	LX-CMP-006	24085	LALR12	LR-CMP-012
76015 Xt70+Gl30	C1LX07	LX-CMP-007	24085	C1LR14	LR-CMP-014
76015 Xt70+Gl30	LALX07	LX-CMP-007	24085	C2LR14	LR-CMP-014
76015 Xt30+Gl70	C1LX08	LX-CMP-008	24085	LALR14	LR-CMP-014
76015 Xt30+Gl70	LALX08	LX-CMP-008	24085	C1LR15	LR-CMP-015
76015 Xt60+Gl40	C1LX09	LX-CMP-009	61161	C3LR15	LR-CMP-015
76015 Xt60+Gl40	LALX09	LX-CMP-009	61241	LALR15	LR-CMP-015
76015	C1LX10	LX-CMP-	72321	C1LR16	LR-CMP-

Xt40+Gl60		010			016
76015 Xt40+Gl60	LALX10	LX-CMP-010	715015	C2LR16	LR-CMP-016
76015 Xt50+Gl50	C1LX11	LX-CMP-011	715015	C3LR16	LR-CMP-016
76015 Xt50+Gl50	LALX11	LX-CMP-011	715015	LALR16	LR-CMP-016
			1202459	C1LR17	LR-CMP-017
			1202459	C2LR17	LR-CMP-017
			1203055	C3LR17	LR-CMP-017
			1203056	LALR17	LR-CMP-017
			1203057	C1LR18	LR-CMP-018
			1203057	C2LR18	LR-CMP-018
			1203058	C3LR18	LR-CMP-018
			1425915	LALR18	LR-CMP-018
			1425915	C1LR19	LR-CMP-019
			1425915	LALR19	LR-CMP-019
			1425915	C1LR20	LR-CMP-020
			1425915	LALR20	LR-CMP-020
			1425915	C1LR21	LR-CMP-021
			1425915	LALR21	LR-CMP-021
			1425915	C1LR22	LR-CMP-022
			1425915	LALR22	LR-CMP-022
			1425915	C1LR23	LR-CMP-023
			1425915	LALR23	LR-CMP-023
			1425915	C1LR24	LR-CMP-024
			1425915	LALR24	LR-CMP-024
			1425915	LBLR24	LR-CMP-024
			1425915	LCLR24	LR-CMP-024
			1425915	C1LR25	LR-CMP-025
			1425915	LALR25	LR-CMP-

					025
			1425915	C1LR26	LR-CMP-026
			1425915	LALR26	LR-CMP-026
			1425915	C1LR27	LR-CMP-027
			1425915	LALR27	LR-CMP-027
			1425915	C1LR28	LR-CMP-028
			1425915	LALR28	LR-CMP-028
			1425915	C1LR29	LR-CMP-029
			1426068	LALR29	LR-CMP-029
			1426072	C1LR30	LR-CMP-030
			1426077	LALR30	LR-CMP-030
			1426082	C1LR31	LR-CMP-031
			6114171	LALR31	LR-CMP-031
			6114171	C1LR32	LR-CMP-032
			6114175	LALR32	LR-CMP-032
			6114175	BKR1LR038	LR-CMP-038
			6114179	C1LR38	LR-CMP-038
			6114179	C1LR39	LR-CMP-039
			6114184	C2LR39	LR-CMP-039
			6114184	C3LR39	LR-CMP-039
			6114189	C4LR39	LR-CMP-039
			6114189	CALR39	LR-CMP-039
			6223114	CBLR39	LR-CMP-039
			6223114	C1LR40	LR-CMP-040
			6223114	C2LR40	LR-CMP-040
			6223114	C3LR40	LR-CMP-040
			6223114	C1LR41	LR-CMP-041
			6223114	C2LR41	LR-CMP-

					041
			6223114	C1LR42	LR-CMP-042
			6223114	C1LR43	LR-CMP-043
			6223114	C1LR44	LR-CMP-044
			6223114	C1LR45	LR-CMP-045
			6223114	C2LR45	LR-CMP-045
			6223114	C1LR46	LR-CMP-046
			6223114	C2LR46	LR-CMP-046
			6223114	C1LR47	LR-CMP-047
			6223114	C2LR47	LR-CMP-047
			6223114	C1LR48	LR-CMP-048
			6223114	C2LR48	LR-CMP-048
			6223114	C1LR49	LR-CMP-049
			6223114	C1LR50	LR-CMP-050
			6223114	C1LR51	LR-CMP-051
			6223114	BKR3LR052	LR-CMP-052
			6223114	C1LR52	LR-CMP-052
			6223114	C2LR52	LR-CMP-052
			6223114	C3LR52	LR-CMP-052
			6223114	C1LR53	LR-CMP-053
			6223114	C1LR54	LR-CMP-054
			6223114	C1LR55	LR-CMP-055
			6223114	C1LR56	LR-CMP-056
			6223114	C1LR57	LR-CMP-057
			6223114	C2LR57	LR-CMP-057
			6223114	C3LR57	LR-CMP-057
			6223114	CALR57	LR-CMP-057
			6223114	LALR57	LR-CMP-

					057
			6223114	LBLR57	LR-CMP-057
			6223114	C1LR58	LR-CMP-058
			6223114	LALR58	LR-CMP-058
			6223114	LBLR58	LR-CMP-058
			6223114	C1LR59	LR-CMP-059
			6223114	LALR59	LR-CMP-059
			6223114	LBLR59	LR-CMP-059
			6223114	C1LR60	LR-CMP-060
			6223114	LALR60	LR-CMP-060
			6223114	LBLR60	LR-CMP-060
			6223121	C1LR61	LR-CMP-061
			6223125	C1LR62	LR-CMP-062
			6223125	C1LR63	LR-CMP-063
			6223130	C1LR64	LR-CMP-064
			6223130	C1LR65	LR-CMP-065
			6223135	LALR65	LR-CMP-065
			6223142	LBLR65	LR-CMP-065
			6223142	C1LR66	LR-CMP-066
			6223142	C1LR67	LR-CMP-067
			6748170	C1LR68	LR-CMP-068
			6748170	BKR1LR069	LR-CMP-069
			6748174	C1LR69	LR-CMP-069
			6748174	LALR69	LR-CMP-069
			6748179	LBLR69	LR-CMP-069
			6748179	BKR1LR070	LR-CMP-070
			6748184	C1LR70	LR-CMP-070
			6748184	LALR70	LR-CMP-

					070
			6760187	LBLR70	LR-CMP-070
			6760187	BKR1LR071	LR-CMP-071
			6760187	C1LR71	LR-CMP-071
			6794169	LALR71	LR-CMP-071
			6794169	LBLR71	LR-CMP-071
			7106115	C1LR72	LR-CMP-072
			7106115	BKR1LR073	LR-CMP-073
			7106115	BKR2LR073	LR-CMP-073
			7324182	C1LR73	LR-CMP-073
			7326169	C2LR73	LR-CMP-073
			7328169	CALR73	LR-CMP-073
			7508043	LALR73	LR-CMP-073
			7922191	LBLR73	LR-CMP-073
			7922191	BKR1LR074	LR-CMP-074
			7922191	C1LR74	LR-CMP-074
			10084255	C2LR74	LR-CMP-074
			10084255	BKR1LR075	LR-CMP-075
			10084255	C1LR75	LR-CMP-075
			10084255	C2LR75	LR-CMP-075
			10084255	C1LR76	LR-CMP-076
			10084255	C1LR77	LR-CMP-077
			10084255	LALR77	LR-CMP-077
			10084255	LBLR77	LR-CMP-077
			10084255	C1LR78	LR-CMP-078
			10084255	LALR78	LR-CMP-078
			10084255	LBLR78	LR-CMP-078
			10084255	C1LR79	LR-CMP-

					079
			10084255	BKR1LR080	LR-CMP-080
			10084255	C1LR80	LR-CMP-080
			10084255	C2LR80	LR-CMP-080
			10084255	CALR80	LR-CMP-080
			10084255	C1LR81	LR-CMP-081
			10084255	C1LR82	LR-CMP-082
			10084255	C1LR83	LR-CMP-083
			10084255	C1LR84	LR-CMP-084
			10084255	C1LR85	LR-CMP-085
			10084255	C1LR86	LR-CMP-086
			12001853	C1LR87	LR-CMP-087
			12001853	C1LR88	LR-CMP-088
			12001854	C1LR89	LR-CMP-089
			12001854	C1LR90	LR-CMP-090
			12001873	C1LR91	LR-CMP-091
			12023136	C1LR92	LR-CMP-092
			12023136	C1LR93	LR-CMP-093
			12030132	BKR1LR094	LR-CMP-094
			12030132	C1LR94	LR-CMP-094
			12030144	C1LR95	LR-CMP-095
			12030144	BKR1LR096	LR-CMP-096
			12030145	C1LR96	LR-CMP-096
			12030145	C1LR97	LR-CMP-097
			12030146	BKR1LR098	LR-CMP-098
			12030146	C1LR98	LR-CMP-098
			12030156	BKR1LR099	LR-CMP-099
			12030157	C1LR99	LR-CMP-

					099
			12030157	BKR1LR100	LR-CMP-100
			12030157	C1LR100	LR-CMP-100
			12030158	C1LR101	LR-CMP-101
			12030159	C1LR102	LR-CMP-102
			12037189	C1LR103	LR-CMP-103
			12070853	C1LR104	LR-CMP-104
			12070853	BKR1LR105	LR-CMP-105
			12070853	C1LR105	LR-CMP-105
			12070853	BKR1LR106	LR-CMP-106
			12070853	C1LR106	LR-CMP-106
			12070853	BKR1LR107	LR-CMP-107
			12070853	C1LR107	LR-CMP-107
			12070853	BKR1LR108	LR-CMP-108
			12070853	C1LR108	LR-CMP-108
			12070853	BKR1LR109	LR-CMP-109
			12070853	C1LR109	LR-CMP-109
			12070853	BKR1LR110	LR-CMP-110
			12070853	C1LR110	LR-CMP-110
			12070853	BKR1LR111	LR-CMP-111
			12070853	C1LR111	LR-CMP-111
			12070853	BKR1LR112	LR-CMP-112
			12070853	C1LR112	LR-CMP-112
			12070853	BKR1LR113	LR-CMP-113
			12070853	C1LR113	LR-CMP-113
			12070853	BKR1LR114	LR-CMP-114
			12070853	BKR2LR114	LR-CMP-114
			12070853	BKR3LR114	LR-CMP-

					114
			12070853	C1LR114	LR-CMP-114
			14141141	C2LR114	LR-CMP-114
			14141156	BKR1LR115	LR-CMP-115
			14141160	C1LR115	LR-CMP-115
			14141160	BKR1LR116	LR-CMP-116
			14141165	C1LR116	LR-CMP-116
			14141170	BKR1LR117	LR-CMP-117
			14141170	C1LR117	LR-CMP-117
			14148178	BKR1LR118	LR-CMP-118
			14149182	C1LR118	LR-CMP-118
			14163888	BKR1LR119	LR-CMP-119
			14163892	C1LR119	LR-CMP-119
			14163897	BKR1LR120	LR-CMP-120
			14163902	C1LR120	LR-CMP-120
			14240110	BKR1LR121	LR-CMP-121
			14259628	C1LR121	LR-CMP-121
			14259632	BKR1LR122	LR-CMP-122
			14259637	C1LR122	LR-CMP-122
			14259642	BKR1LR123	LR-CMP-123
			15041210	C1LR123	LR-CMP-123
			15041210	BKR1LR124	LR-CMP-124
			15041210	C1LR124	LR-CMP-124
			15041210	BKR1LR125	LR-CMP-125
			15041210	C1LR125	LR-CMP-125
			15041211	BKR1LR126	LR-CMP-126
			15041211	C1LR126	LR-CMP-126
			15041211	BKR1LR127	LR-CMP-

					127
			15041221	C1LR127	LR-CMP-127
			15041222	BKR1LR128	LR-CMP-128
			15041222	C1LR128	LR-CMP-128
			15041222	BKR1LR129	LR-CMP-129
			15041223	C1LR129	LR-CMP-129
			15041224	BKR1LR130	LR-CMP-130
			15041224	C1LR130	LR-CMP-130
			15041224	BKR1LR131	LR-CMP-131
			15071156	C1LR131	LR-CMP-131
			15071156	BKR1LR132	LR-CMP-132
			15071157	C1LR132	LR-CMP-132
			15071157	BKR1LR133	LR-CMP-133
			15071167	C1LR133	LR-CMP-133
			15071168	BKR1LR134	LR-CMP-134
			15071168	C1LR134	LR-CMP-134
			15071168	BKR1LR135	LR-CMP-135
			15071168	C1LR135	LR-CMP-135
			15071169	BKR1LR230	LR-DSM-230
			15071170	BKR1LR231	LR-DSM-231
			15261208	BKR1LR232	LR-DSM-232
			15301329	BKR1LR233	LR-DSM-233
			15401136	BKR1LR234	LR-DSM-234
			15401136	BKR1LR136	LR-SKN-136
			15401136	C1LR136	LR-SKN-136
			15401136	BKR2LR137	LR-SKN-137
			15601340	C1LR137	LR-SKN-137
			60051133	C2LR137	LR-SKN-

					137
			60501120	BKR1LR138 A	LR-SKN- 138-A
			60501120	C1LR138A	LR-SKN- 138-A
			60501120	BKR1LR138 B	LR-SKN- 138-B
			61221156	C1LR138B	LR-SKN- 138-B
			61221156	BKR1LR138 C	LR-SKN- 138-C
			61221160	C1LR138C	LR-SKN- 138-C
			61221160	BKR1LR138 D	LR-SKN- 138-D
			61221165	C1LR138D	LR-SKN- 138-D
			61221165	BKR1LR138 E	LR-SKN- 138-E
			61221170	C1LR138E	LR-SKN- 138-E
			61221170	BKR1LR139 A	LR-SKN- 139-A
			63501148	C1LR139A	LR-SKN- 139-A
			63501148	BKR1LR139 B	LR-SKN- 139-B
			63501148	C1LR139B	LR-SKN- 139-B
			64801151	BKR1LR139 C	LR-SKN- 139-C
			64801151	C1LR139C	LR-SKN- 139-C
			64801155	BKR1LR139 D	LR-SKN- 139-D
			64801160	C1LR139D	LR-SKN- 139-D
			64801165	BKR1LR139 E	LR-SKN- 139-E
			66041128	C1LR139E	LR-SKN- 139-E
			66041128	C2LS30	LS-CMP- 030
			66041128	CALS30	LS-CMP- 030
			67461142	CBLS30	LS-CMP- 030
			67461142	CCLS30	LS-CMP- 030
			67461151	CDLS30	LS-CMP- 030
			67461151	CELS30	LS-CMP- 030
			67461155	CFLS30	LS-CMP-

					030
			67461155	CGLS30	LS-CMP-030
			68501601	CILS30	LS-CMP-030
			68501601	CKLS30	LS-CMP-030
			68501601	CLS30A	LS-CMP-030
			69961144	CLS30B	LS-CMP-030
			70181136	CLS30C	LS-CMP-030
			70181136	CLS30D	LS-CMP-030
			70181137	CLS30E	LS-CMP-030
			70181137	CLS30F	LS-CMP-030
			70181137	CLS30G	LS-CMP-030
			70181137	CLS30H	LS-CMP-030
			70181138	CLS30I	LS-CMP-030
			70181138	CLS30K	LS-CMP-030
			70181147	CLS30U	LS-CMP-030
			70181147	CLS30V	LS-CMP-030
			70181155	CLS30W	LS-CMP-030
			70181155	CLS30X	LS-CMP-030
			70181160	CLS30Y	LS-CMP-030
			70181160	CLS30Z	LS-CMP-030
			70181165	CNLS30	LS-CMP-030
			70181165	COLS30	LS-CMP-030
			71061139	CPLS30	LS-CMP-030
			71061139	CQLS30	LS-CMP-030
			71061140	CRLS30	LS-CMP-030
			71061140	CSLS30	LS-CMP-030
			71061158	CTLS30	LS-CMP-030
			71061158	CULS30	LS-CMP-

					030
			71061158	CVLS30	LS-CMP-030
			71061158	CWLS30	LS-CMP-030
			71061158	CXLS30	LS-CMP-030
			71061158	CYLS30	LS-CMP-030
			71061163	CZLS30	LS-CMP-030
			71061163	LOG	LS-CMP-030
			71061163	NCLS30	LS-CMP-030
			71061168	NDLS30	LS-CMP-030
			71061168	SVLS30	LS-CMP-030
			71061168	CALS31	LS-CMP-031
			71501226	CBLS31	LS-CMP-031
			71501226	CCLS31	LS-CMP-031
			71501227	CDLS31	LS-CMP-031
			71501227	CELS31	LS-CMP-031
			71501239	CFLS31	LS-CMP-031
			71501247	CGLS31	LS-CMP-031
			71501252	CKLS31	LS-CMP-031
			71501257	CLS31G	LS-CMP-031
			72701150	CLS31K	LS-CMP-031
			74001439	CNLS31	LS-CMP-031
			74002339	COLS31	LS-CMP-031
			74002339	CPLS31	LS-CMP-031
			74220806	CQLS31	LS-CMP-031
			79221103	CRLS31	LS-CMP-031
			79221103	CSLS31	LS-CMP-031
			79221103	CTLS31	LS-CMP-031
			79221103	CULS31	LS-CMP-

					031
			79221104	CVLS31	LS-CMP-031
			79221104	CWLS31	LS-CMP-031
			79221104	CXLS31	LS-CMP-031
			79221104	NCLS31	LS-CMP-031
			79221105	CALS32	LS-CMP-032
			79221105	CBLS32	LS-CMP-032
			79221118	CCLS32	LS-CMP-032
			79221118	CDLS32	LS-CMP-032
			79221118	CELS32	LS-CMP-032
			79221118	CFLS32	LS-CMP-032
			79221118	CGLS32	LS-CMP-032
			79221118	CKLS32	LS-CMP-032
			79221126	CLS32G	LS-CMP-032
			79221131	CLS32K	LS-CMP-032
			79221131	CNLS32	LS-CMP-032
			79221131	COLS32	LS-CMP-032
			79221136	CPLS32	LS-CMP-032
			79221136	CQLS32	LS-CMP-032
			100841776	CRLS32	LS-CMP-032
			100841776	CSLS32	LS-CMP-032
			100841776	CTLS32	LS-CMP-032
			100841777	CULS32	LS-CMP-032
			100841778	CVLS32	LS-CMP-032
			100841778	CWLS32	LS-CMP-032
			100841778	CXLS32	LS-CMP-032
			100841779	NCLS32	LS-CMP-032
			100841779	SVLS32	LS-CMP-

					032
			100841779	CALS33	LS-CMP-033
			100841780	CBLS33	LS-CMP-033
			100841946	CCLS33	LS-CMP-033
			100841946	CDLS33	LS-CMP-033
			100841946	CELS33	LS-CMP-033
			100841947	CFLS33	LS-CMP-033
			100841947	CGLS33	LS-CMP-033
			100841947	CJLS33	LS-CMP-033
			100841947	CKLS33	LS-CMP-033
			100841948	CLS33G	LS-CMP-033
			100841948	CLS33K	LS-CMP-033
			100841960	CMLS33	LS-CMP-033
			740022216	CNLS33	LS-CMP-033
			740022216	COLS33	LS-CMP-033
			740022217	CPLS33	LS-CMP-033
			740022217	CQLS33	LS-CMP-033
			740022218	CRLS33	LS-CMP-033
			740022218	CSLS33	LS-CMP-033
			740022219	CTLS33	LS-CMP-033
			740022219	CULS33	LS-CMP-033
			100841780 <25 um	CVLS33	LS-CMP-033
			100841780 <25 um	CWLS33	LS-CMP-033
			100841780 <25 um	CXLS33	LS-CMP-033
			100841780 <25 um	NCLS33	LS-CMP-033
			100841780 <45 um	C1LS45	LS-CMP-045
			100841780 <45 um	C2LS45	LS-CMP-045
			100841780	C3LS45	LS-CMP-

			<45 um		045
			100841780 <45 um	C1LS46	LS-CMP-046
			100841780 45-75 um	C1LS47	LS-CMP-047
			100841780 45-75 um	NBLS47	LS-CMP-047
			100841780 45-75 um	NCLS47	LS-CMP-047
			100841780 75-125 um	C1LS48	LS-CMP-048
			100841780 75-125 um	NBLS48	LS-CMP-048
			100841780 75-125 um	NCLS48	LS-CMP-048
			100841961 20-45 um	C1LS49	LS-CMP-049
			100841961 20-45 um	CALS49	LS-CMP-049-A
			100841961 20-45 um	CLS49A	LS-CMP-049-A
			100841961 20-45 um	NBLS49A	LS-CMP-049-A
			100841962 10-20 um	NCLS49A	LS-CMP-049-A
			100841962 10-20 um	CELS49	LS-CMP-049-E
			100841962 10-20 um	CLS49E	LS-CMP-049-E
			100841962 10-20 um	NBLS49E	LS-CMP-049-E
			100841963 <10 um	NCLS49E	LS-CMP-049-E
			100841963 <10 um	CGLS49	LS-CMP-049-G
			100841963 <10 um	NBLS49G	LS-CMP-049-G
			100841963 <10 um	NCLS49G	LS-CMP-049-G
			12001874 20-45 um	CHLS49	LS-CMP-049-H
			12001874 20-45 um	NBLS49H	LS-CMP-049-H
			12001874 20-45 um	NCLS49H	LS-CMP-049-H
			12001874 20-45 um	C1LS50	LS-CMP-050
			12001874 20-45 um	C1LS51	LS-CMP-051
			12001874 20-45 um	C2LS51	LS-CMP-051
			12001874 20-45 um	LALS51	LS-CMP-051
			12001875 10-	C1LS53	LS-CMP-

			20 um		053
			12001875 10-20 um	C2LS53	LS-CMP-053
			12001875 10-20 um	LALS53	LS-CMP-053
			12001876 <10 um	C1LS54	LS-CMP-054
			12001876 <10 um	C1LS55	LS-CMP-055
			12001876 <10 um	C1LS56	LS-CMP-056
			1400396 Median size 1.7 um	BKR1LS057	LS-CMP-057
			1400396 Median size 16.7 um	C1LS57	LS-CMP-057
			1400396 Median size 2.7 um	C2LS57	LS-CMP-057
			1400396 Median size 6.7 um	C1LS58	LS-CMP-058
			1400396 Respirable	C1LS59	LS-CMP-059
			2014 Luna 20 soil 100-250 um	C1LS60	LS-CMP-060
			2014 Luna 20 soil 250-1000 um	C1LS61	LS-CMP-061
			2014 Luna 20 soil agglutinate separate 100-1000 um	C1LS62	LS-CMP-062
			2014 Luna 20 soil residual after agglutinate separation 100-1000 um	C2LS62	LS-CMP-062
			61221114 Fractions	CALS65	LS-CMP-065-A
			61221114 Fractions	CBLS65	LS-CMP-065-B
			61221114 Fractions	CCLS65	LS-CMP-065-C
			61221114 Fractions	CDLS65	LS-CMP-065-D
			61221114 Fractions	CELS65	LS-CMP-065-E
			61221114 Fractions	CFLS65	LS-CMP-065-F

			61221114 Fractions	NFLS65	LS-CMP- 065-F
			61221114 Fractions	CGLS65	LS-CMP- 065-G
			61221114 Fractions	CHLS65	LS-CMP- 065-H
			61221114 Fractions	NHLS65	LS-CMP- 065-H
			61221114 Fractions	CILS65	LS-CMP- 065-I
			61221114 Fractions	CJLS65	LS-CMP- 065-J
			61221114 Fractions	CLS65J	LS-CMP- 065-J
			61221114 Fractions	CSLS65	LS-CMP- 065-J
			64801116 Fractions	CALS66	LS-CMP- 066-A
			64801116 Fractions	CBLS66	LS-CMP- 066-B
			64801116 Fractions	CCLS66	LS-CMP- 066-C
			64801116 Fractions	CDLS66	LS-CMP- 066-D
			64801116 Fractions	CELS66	LS-CMP- 066-E
			64801116 Fractions	CFLS66	LS-CMP- 066-F
			64801116 Fractions	NFLS66	LS-CMP- 066-F
			64801116 Fractions	CGLS66	LS-CMP- 066-G
			64801116 Fractions	CHLS66	LS-CMP- 066-H
			64801116 Fractions	NHLS66	LS-CMP- 066-H
			64801116 Fractions	CILS66	LS-CMP- 066-I
			64801116 Fractions	CJLS66	LS-CMP- 066-J
			64801116 Fractions	CLS66J	LS-CMP- 066-J
			64801116 Fractions	CLS66Z	LS-CMP- 066-J
			64801116 Fractions	CZLS66	LS-CMP- 066-J
			67461111 500-1000 um	CALS67	LS-CMP- 067-A
			67461112 250-500 um	N1LS67A	LS-CMP- 067-A
			67461113 150-250 um	N2LS67A	LS-CMP- 067-A
			67461114 90- 150 um	NALS67A	LS-CMP- 067-A

			67461115 45-90 um	CBLS67	LS-CMP-067-B
			67461116 20-45 um	CCLS67	LS-CMP-067-C
			67461118 (from 67461110) bulk	CDLS67	LS-CMP-067-D
			67461123 <20 um	CELS67	LS-CMP-067-E
			67461124 10-20 um	NALS67E	LS-CMP-067-E
			67461127 <10 um	CFLS67	LS-CMP-067-F
			67461146 20-45 um	NALS67F	LS-CMP-067-F
			67461146 20-45 um	CGLS67	LS-CMP-067-G
			67461146 20-45 um	CHLS67	LS-CMP-067-H
			67461146 20-45 um	NALS67H	LS-CMP-067-H
			67461146 20-45 um	CILS67	LS-CMP-067-I
			67701181 500-1000 um	CJLS67	LS-CMP-067-J
			67701182 250-500 um	CALS68	LS-CMP-068-A
			67701183 150-250 um	CBLS68	LS-CMP-068-B
			67701184 90-150 um	CCLS68	LS-CMP-068-C
			67701184 90-150 um	CDLS68	LS-CMP-068-D
			67701185 45-90 um	CELS68	LS-CMP-068-E
			67701185 45-90 um	CFLS68	LS-CMP-068-F
			67701186 20-45 um	CGLS68	LS-CMP-068-G
			67701188 (from 67701180) bulk	CHLS68	LS-CMP-068-H
			67701188 (from 67701180) bulk	CILS68	LS-CMP-068-I
			67701188 (from 67701180) bulk	CJLS68	LS-CMP-068-J
			67701188 (from 67701180)	CALS69	LS-CMP-069

			bulk		
			67701199 <20 um	CALS70	LS-CMP-070
			67701199 <20 um	CALS71	LS-CMP-071
			67701200 10-20 um	CALS72	LS-CMP-072
			67701202 <10 um	CALS73	LS-CMP-073
			68501601 <10 um	CALS74	LS-CMP-074
			68501601 <10 um	CALS75	LS-CMP-075
			68501601 bulk	C2LS76	LS-CMP-076
			68501601 bulk	CALS76	LS-CMP-076
			68501601 bulk	C2LS78	LS-CMP-078
			690039 bulk	CALS78	LS-CMP-078
			690039 bulk	CALS80	LS-CMP-080
			6900444 <250 um	C2LS81	LS-CMP-081
			6900444 <250 um	CALS81	LS-CMP-081
			6900444 <250 um	C2LS83	LS-CMP-083
			6992133 <10 um	CALS83	LS-CMP-083
			6992133 <10 um	BKR1LS100	LS-M1O-100
			6992133 <250 um	CALS100	LS-M1O-100
			6992133 <250 um	CBLS100	LS-M1O-100
			6992133 <45 um	BKR1LS101	LS-M1O-101
			6992133 <45 um	CALS101	LS-M1O-101
			6992133 10-20 um	CBLS101	LS-M1O-101
			6992133 10-20 um	BKR1LS102	LS-M1O-102
			6992133 20-45 um	CALS102	LS-M1O-102
			6992133 20-45 um	CBLS102	LS-M1O-102
			6994141 <10 um	BKR1LS103	LS-M1O-103
			6994141 <10 um	CALS103	LS-M1O-103
			6994141 <250	CBLS103	LS-M1O-

			um		103
			6994141 <250 um	BKR1LS104	LS-M10-104
			6994141 <45 um	CALS104	LS-M10-104
			6994141 <45 um	CBLS104	LS-M10-104
			6994141 10-20 um	CALU01	LU-CMP-001-A
			6994141 10-20 um	CBLU01	LU-CMP-001-B
			6994141 20-45 um	CDLU01	LU-CMP-001-D
			6994141 20-45 um	CELU01	LU-CMP-001-E
			70181138 Freon Extend Exp.	CFLU01	LU-CMP-001-F
			70181138 Freon Extend Exp.	CALU02	LU-CMP-002-A
			70181138 Freon Limit Exp.	CBLU02	LU-CMP-002-B
			70181138 Freon Limit Exp.	CCLU02	LU-CMP-002-C
			Luna 16 <10 um	CLU02C	LU-CMP-002-C
			Luna 16 <10 um	CXLU02	LU-CMP-002-C
			Luna 16 10-20 um	CDLU02	LU-CMP-002-D
			Luna 16 10-20 um	CELU02	LU-CMP-002-E
			Luna 16 20-45 um	CALU03	LU-CMP-003-A
			Luna 16 20-45 um	CLU03A	LU-CMP-003-A
			Luna 20 <10 um	CBLU03	LU-CMP-003-B
			Luna 20 <10 um	CLU03B	LU-CMP-003-B
			Luna 20 10-20 um	CCLU03	LU-CMP-003-C
			Luna 20 10-20 um	CLU03C	LU-CMP-003-C
			Luna 20 20-45 um	CDLU03	LU-CMP-003-D
			Luna 20 20-45 um	CELU03	LU-CMP-003-E
			Luna 24 <10 um	CLU03E	LU-CMP-003-E
			Luna 24 <10 um	C1LU07	LU-CMP-

			um		007-1
			Luna 24 10-20 um	C2LU07	LU-CMP- 007-2
			Luna 24 10-20 um	C3LU07	LU-CMP- 007-3
			Luna 24 20-45 um	C4LU07	LU-CMP- 007-4
			Luna 24 20-45 um	C1SN05	SN-CMP- 005
			Luna 24 24160	LASN05	SN-CMP- 005
			Luna 24 24160	C1SN06	SN-CMP- 006
			MIXLS1	LASN06	SN-CMP- 006

Table S2

Mineral Separates (N = 45)			Soils (N = 149)			Roks (N = 84)		
Sample Name	Sample ID	Spectrum ID	Sample Name	Sample ID	Spectrum ID	Sample Name	Sample ID	Spectrum ID
72415	LR-CMP-014	LALR14	62241	LR-CMP-183	BKR1LR 183	76015 Xt95+G105	LX-CMP-001	LALX01
15555	LR-CMP-168	BKR2LR 168	62241	LR-CMP-223	BKR1LR 223	76015 Xt05+G195	LX-CMP-002	LALX02
15555	LR-CMP-168	BKR3LR 168	12030	LR-CMP-005-C	LALR05C	76015 Xt90+G110	LX-CMP-003	LALX03
15555	LR-CMP-169	BKR2LR 169	12001	LR-CMP-010	LALR10	76015 Xt90+G110	LX-CMP-003	LBLX03
15555	LR-CMP-169	BKR3LR 169	12001	LR-CMP-011	LALR11	76015 Xt10+G190	LX-CMP-004	LALX04
15555	LR-CMP-170	BKR2LR 170	15041	LR-CMP-012	BKR2LR 012	76015 Xt10+G190	LX-CMP-004	LBLX04
15555	LR-CMP-170	BKR3LR 170	15041	LR-CMP-012	LALR12	76015 Xt80+G120	LX-CMP-005	LALX05
15555	LR-CMP-171	BKR1LR 171	15041	LR-CMP-013	LALR13	76015 Xt20+G180	LX-CMP-006	LALX06
15058	LR-CMP-172	BKR1LR 172	10084	LR-CMP-015	LALR15	76015 Xt70+G130	LX-CMP-007	LALX07
15058	LR-CMP-172	BKR2LR 172	10084	LR-CMP-016	LALR16	76015 Xt30+G170	LX-CMP-008	LALX08
15058	LR-CMP-173	BKR1LR 173	79221	LR-CMP-017	LALR17	76015 Xt60+G140	LX-CMP-009	LALX09
15058	LR-CMP-173	BKR2LR 173	79221	LR-CMP-018	LALR18	76015 Xt40+G160	LX-CMP-010	LALX10
15058	LR-CMP-174	BKR1LR 174	15071	LR-CMP-019	LALR19	76015 Xt50+G150	LX-CMP-011	LALX11
70017	LR-CMP-175	BKR1LR 175	15071	LR-CMP-020	LALR20	12063	LS-CMP-009	LALS09
70017	LR-CMP-176	BKR1LR 176	10084	LR-CMP-021	LALR21	12021	DD-BKR1DD	035
70017	LR-CMP-177	BKR1LR 177	79221	LR-CMP-022	LALR22	12021	MDD-035 DD-BKR1DD	036
70017	LR-CMP-178	BKR1LR 178	70181	LR-CMP-023	LALR23	67627	MDD-036 LR-CMP-001-A	LALR01 A
70035	LR-CMP-179	BKR1LR 179	70181	LR-CMP-024	LALR24	67627	LR-CMP-002-A	LALR02 A
70035	LR-CMP-180	BKR1LR 180	70181	LR-CMP-024	LBLR24	67627	LR-CMP-002-B	LALR02B
70035	LR-CMP-181	BKR1LR 181	70181	LR-CMP-024	LCLR24	67627	LR-CMP-002-C	LALR02C
70035	LR-CMP-182	BKR1LR 182	70181	LR-CMP-025	LALR25	67627	LR-CMP-002-D	LALR02 D
62241	LR-CMP-183	BKR1LR 183	71061	LR-CMP-026	LALR26	67627	LR-CMP-002-E	LALR02E
15058	LR-CMP-208	BKR1LR 208	71061	LR-CMP-027	LALR27	69935	LR-CMP-003-A	LALR03 A
15058	LR-CMP-209	BKR1LR 209	71501	LR-CMP-028	LALR28	69935	LR-CMP-003-B	LALR03B
15058	LR-CMP-210	BKR1LR 210	71501	LR-CMP-029	LALR29	69935	LR-CMP-003-C	LALR03C
15555	LR-CMP-211	BKR1LR 211	12030	LR-CMP-030	LALR30	69935	LR-CMP-003-D	LALR03 D
15555	LR-CMP-212	BKR1LR 212	12030	LR-CMP-031	LALR31	69935	LR-CMP-003-E	LALR03E
15555	LR-CMP-213	BKR1LR 213	12030	LR-CMP-032	LALR32	69935	LR-CMP-004-A	L1LR04A
15555	LR-CMP-	BKR1LR	68501	LR-CMP-	BKR1LR	10068	LR-CMP-	LALR36

	214	214		038	038		036	
70017	LR-CMP-215	BKR1LR 215	15401	LR-CMP-052	BKR3LR 052	10068	LR-CMP-037	LALR37
70017	LR-CMP-216	BKR1LR 216	71061	LR-CMP-057	LALR57	15058	LR-CMP-152	BKR1LR 152
70017	LR-CMP-217	BKR1LR 217	71061	LR-CMP-057	LBLR57	15058	LR-CMP-153	BKR2LR 153
70017	LR-CMP-218	BKR1LR 218	71061	LR-CMP-058	LALR58	15555	LR-CMP-154	BKR1LR 154
70035	LR-CMP-219	BKR1LR 219	71061	LR-CMP-058	LBLR58	70017	LR-CMP-156	BKR1LR 156
70035	LR-CMP-220	BKR1LR 220	71061	LR-CMP-059	LALR59	70035	LR-CMP-158	BKR1LR 158
70035	LR-CMP-221	BKR1LR 221	71061	LR-CMP-059	LBLR59	15058	LR-CMP-204	BKR1LR 204
70035	LR-CMP-222	BKR1LR 222	71061	LR-CMP-060	LALR60	15555	LR-CMP-205	BKR1LR 205
62241	LR-CMP-223	BKR1LR 223	71061	LR-CMP-060	LBLR60	70017	LR-CMP-206	BKR1LR 206
15415	LR-CMP-224	BKR1LR 224	12030	LR-CMP-065	LALR65	70035	LR-CMP-207	BKR1LR 207
60015 plagioclase 75-150 um	LR-LEN-229	BKR1LR 229	12030	LR-CMP-065	LBLR65	15058	LR-CMP-228	BKR1LR 228
76535	LS-CMP-004	NCLS04	10084	LR-CMP-069	BKR1LR 069	15555	LS-CMP-001	N2LS01
12063	LS-CMP-009	LALS09	10084	LR-CMP-069	LALR69	15555	LS-CMP-002	N2LS02
15415	LS-CMP-011	NCLS11	10084	LR-CMP-069	LBLR69	60019	LS-CMP-017	NCLS17
78235	LS-CMP-012	LALS12	10084	LR-CMP-070	BKR1LR 070	73217	LS-CMP-018	NCLS18
78235	LS-CMP-091	LALS91	10084	LR-CMP-070	LALR70	76015	LS-CMP-028	LALS28
			10084	LR-CMP-070	LBLR70	76015	LS-CMP-028	LALS28X
			10084	LR-CMP-071	BKR1LR 071	76015	LS-CMP-028	LBLS28X
			10084	LR-CMP-071	LALR71	76015	LS-CMP-028	NCLS28
			10084	LR-CMP-071	LBLR71	73155	LS-CMP-029	NCLS29
			12001	LR-CMP-073	BKR1LR 073	77075	LS-CMP-035	NCLS35
			12001	LR-CMP-073	BKR2LR 073	72435	LS-CMP-039	NCLS39
			12001	LR-CMP-073	LALR73	76215	LS-CMP-077	NCLS77
			12001	LR-CMP-073	LBLR73	76295	LS-CMP-079	NCLS79
			12001	LR-CMP-074	BKR1LR 074	67729	LS-CMP-087-A	L2LS87A
			12001	LR-CMP-075	BKR1LR 075	67729	LS-CMP-087-B	LALS87B
			15041	LR-CMP-077	LALR77	67729	LS-CMP-087-C	LALS87C
			15041	LR-CMP-077	LBLR77	67729	LS-CMP-087-D	LALS87D
			15041	LR-CMP-078	LALR78	67729	LS-CMP-087-E	LALS87E

15041	LR-CMP-078	LBLR78	12032	LS-CMP-088-A	L1LS88A
15071	LR-CMP-080	BKR1LR080	67095	LS-CMP-089-A	L1LS89A
14141	LR-CMP-094	BKR1LR094	67095	LS-CMP-089-B	LALS89B
14141	LR-CMP-096	BKR1LR096	67095	LS-CMP-089-C	LALS89C
62231	LR-CMP-098	BKR1LR098	67095	LS-CMP-089-D	LALS89D
62231	LR-CMP-099	BKR1LR099	67095	LS-CMP-089-E	LALS89E
64801	LR-CMP-100	BKR1LR100	67936	LS-CMP-090-A	L2LS90A
61221	LR-CMP-105	BKR1LR105	76055	LS-CMP-092-A	L2LS92A
61221	LR-CMP-106	BKR1LR106	12033	LS-CMP-093-A	L2LS93A
61221	LR-CMP-107	BKR1LR107	68815	LS-CMP-094-A	L1LS94A
61221	LR-CMP-108	BKR1LR108	67475	LS-CMP-095-A	L2LS95A
61141	LR-CMP-109	BKR1LR109	15445	LS-CMP-096-A	L2LS96A
61141	LR-CMP-110	BKR1LR110	15445	LS-CMP-096-B	LALS96B
61141	LR-CMP-111	BKR1LR111	15445	LS-CMP-096-C	LALS96C
61141	LR-CMP-112	BKR1LR112	15445	LS-CMP-096-D	LALS96D
67461	LR-CMP-113	BKR1LR113	15445	LS-CMP-096-E	LALS96E
67461	LR-CMP-114	BKR1LR114	64455	LS-CMP-097-A	L1LS97A
67461	LR-CMP-114	BKR2LR114	64455	LS-CMP-097-B	LALS97B
67461	LR-CMP-114	BKR3LR114	64455	LS-CMP-097-C	LALS97C
67461	LR-CMP-115	BKR1LR115	64455	LS-CMP-097-D	LALS97D
67461	LR-CMP-116	BKR1LR116	64455	LS-CMP-097-E	LALS97E
67481	LR-CMP-117	BKR1LR117	72255	LS-CMP-099-A	L1LS99A
67481	LR-CMP-118	BKR1LR118	72255	LS-CMP-099-B	LALS99B
67481	LR-CMP-119	BKR1LR119	72255	LS-CMP-099-C	LALS99C
67481	LR-CMP-120	BKR1LR120	72255	LS-CMP-099-D	LALS99D
Luna 24 20- 45 um	LR-CMP-121	BKR1LR121	72255	LS-CMP-099-E	LALS99E
Luna 24 10- 20 um	LR-CMP-122	BKR1LR122			
Luna 20 20- 45 um	LR-CMP-124	BKR1LR124			
Luna 20 10- 20 um	LR-CMP-125	BKR1LR125			

Luna 16 20- 45 um	LR-CMP- 127	BKR1LR 127
Luna 16 10- 20 um	LR-CMP- 129	BKR1LR 129
74002	LR-CMP- 130	BKR1LR 130
74002	LR-CMP- 131	BKR1LR 131
74002	LR-CMP- 132	BKR1LR 132
74002	LR-CMP- 133	BKR1LR 133
74002	LR-CMP- 134	BKR1LR 134
Luna 24	LR-CMP- 135	BKR1LR 135
14003	LR-DSM- 230	BKR1LR 230
14003	LR-DSM- 231	BKR1LR 231
14003	LR-DSM- 232	BKR1LR 232
14003	LR-DSM- 233	BKR1LR 233
14003	LR-DSM- 234	BKR1LR 234
69003	LR-SKN- 136	BKR1LR 136
69004	LR-SKN- 137	BKR2LR 137
69921	LR-SKN- 138-A	BKR1LR 138A
69921	LR-SKN- 138-B	BKR1LR 138B
69921	LR-SKN- 138-C	BKR1LR 138C
69921	LR-SKN- 138-D	BKR1LR 138D
69921	LR-SKN- 138-E	BKR1LR 138E
69941	LR-SKN- 139-A	BKR1LR 139A
69941	LR-SKN- 139-B	BKR1LR 139B
69941	LR-SKN- 139-C	BKR1LR 139C
69941	LR-SKN- 139-D	BKR1LR 139D
69941	LR-SKN- 139-E	BKR1LR 139E
62231	LS-CMP- 030	NCLS30
62231	LS-CMP- 030	NDLS30
10084	LS-CMP- 031	NCLS31
12070	LS-CMP- 032	NCLS32
14259	LS-CMP- 033	NCLS33

10084	LS-CMP-047	NBLS47
10084	LS-CMP-047	NCLS47
10084	LS-CMP-048	NBLS48
10084	LS-CMP-048	NCLS48
10084	LS-CMP-049-A	NBLS49A
10084	LS-CMP-049-A	NCLS49A
10084	LS-CMP-049-E	NBLS49E
10084	LS-CMP-049-E	NCLS49E
10084	LS-CMP-049-G	NBLS49G
10084	LS-CMP-049-G	NCLS49G
10084	LS-CMP-049-H	NBLS49H
10084	LS-CMP-049-H	NCLS49H
79221	LS-CMP-051	LALS51
71501	LS-CMP-053	LALS53
68501	LS-CMP-057	BKR1LS057
61221	LS-CMP-065-F	NFLS65
61221	LS-CMP-065-H	NHLS65
64801	LS-CMP-066-F	NFLS66
64801	LS-CMP-066-H	NHLS66
67701	LS-CMP-067-A	N1LS67A
67701	LS-CMP-067-A	N2LS67A
67701	LS-CMP-067-A	NALS67A
67701	LS-CMP-067-E	NALS67E
67701	LS-CMP-067-F	NALS67F
67701	LS-CMP-067-H	NALS67H
60501	LS-M1O-100	BKR1LS100
62231	LS-M1O-101	BKR1LS101
63501	LS-M1O-102	BKR1LS102
66041	LS-M1O-103	BKR1LS103
67601	LS-M1O-104	BKR1LS104
70181	SN-CMP-005	LASN05

70181		SN-CMP-		LASN06	
		006			

Figures

Figure 1

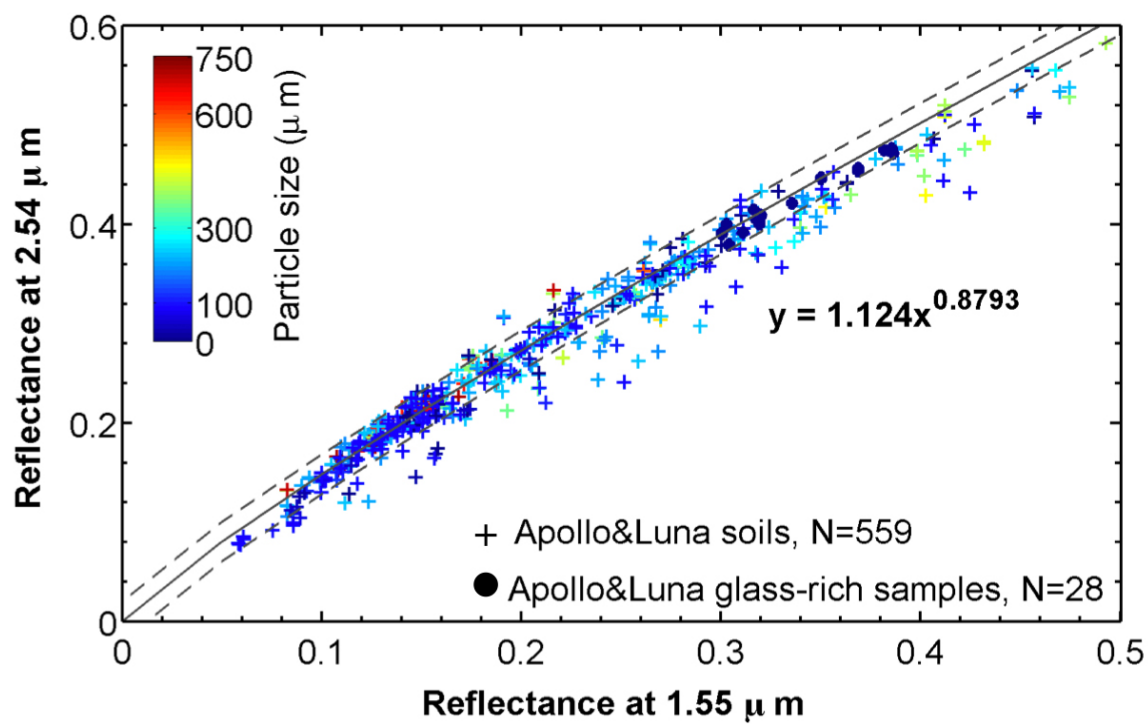


Figure 2

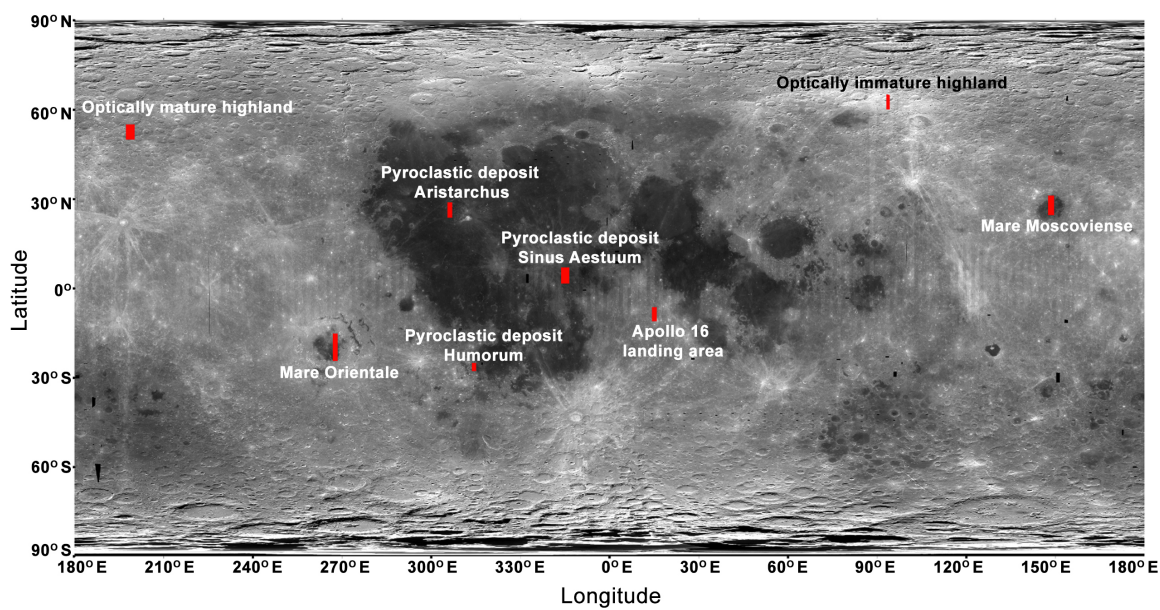


Figure 3

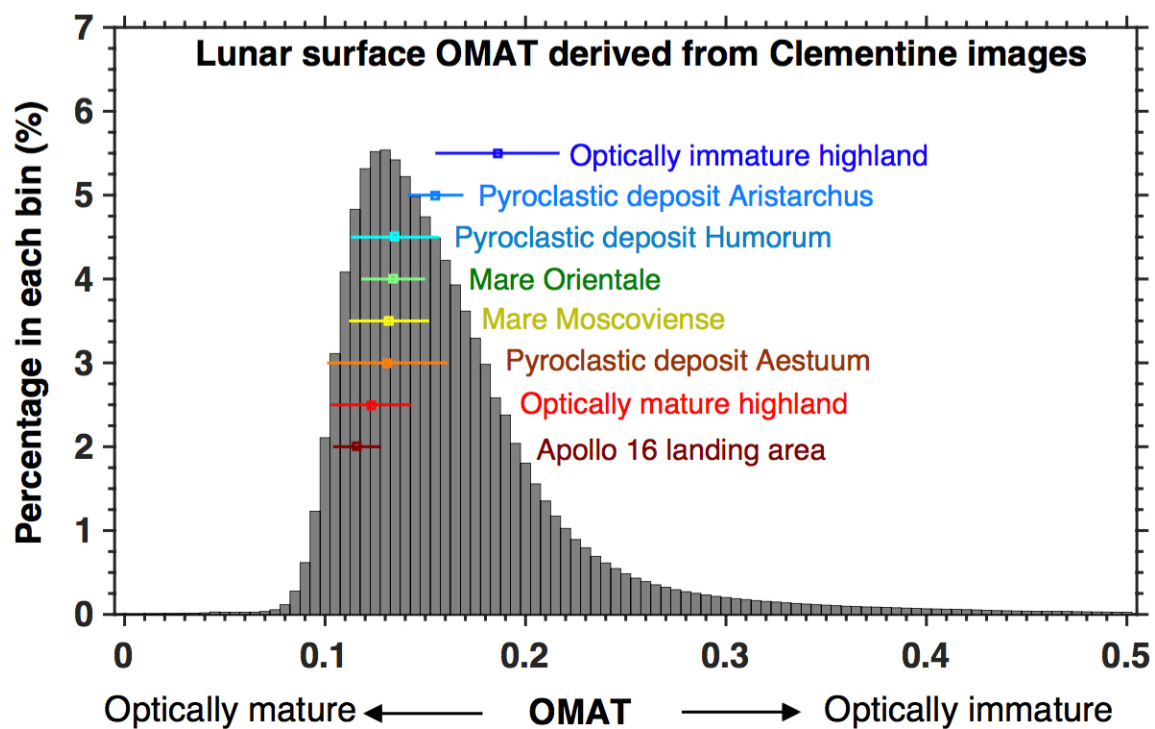


Figure 4

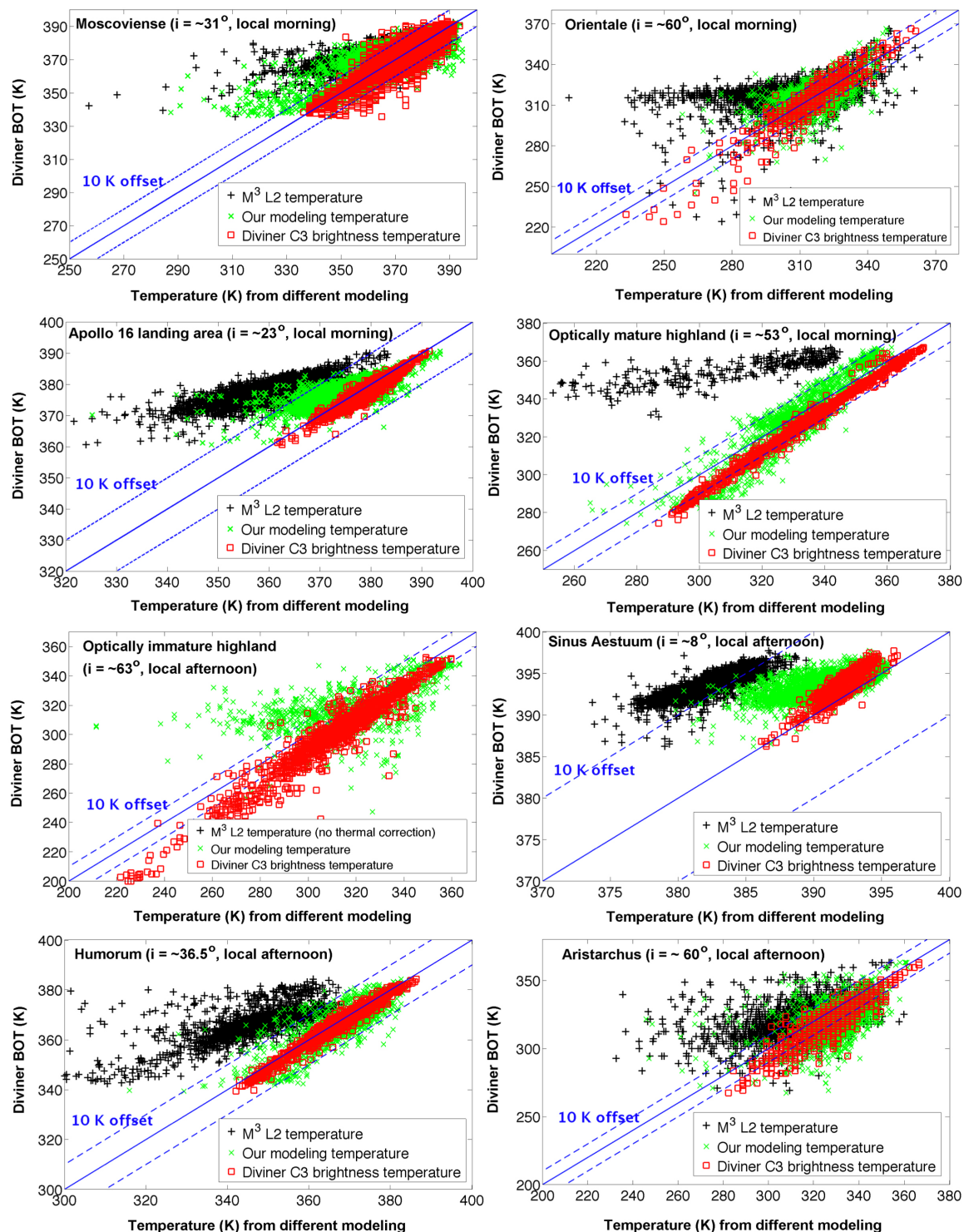


Figure 5

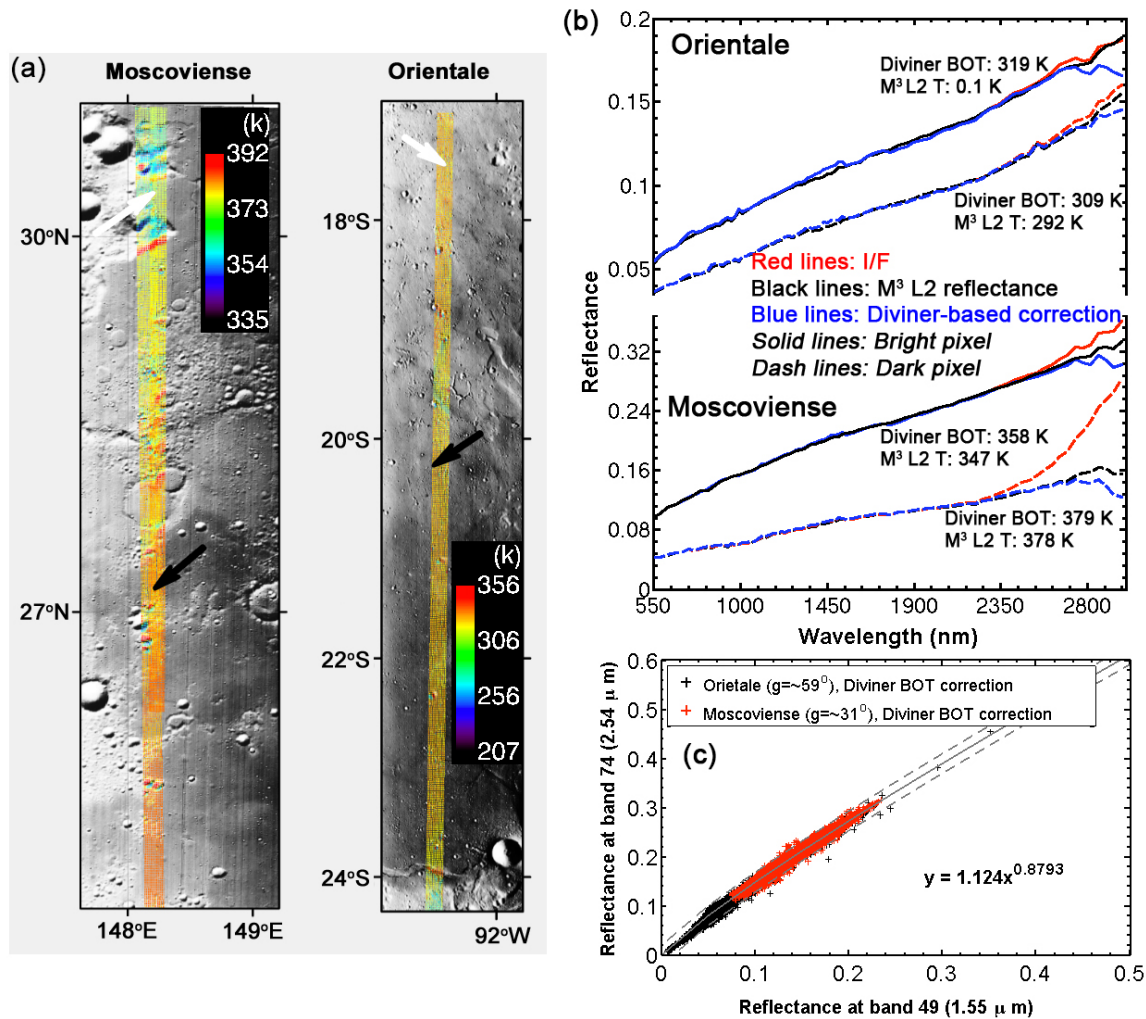


Figure 6

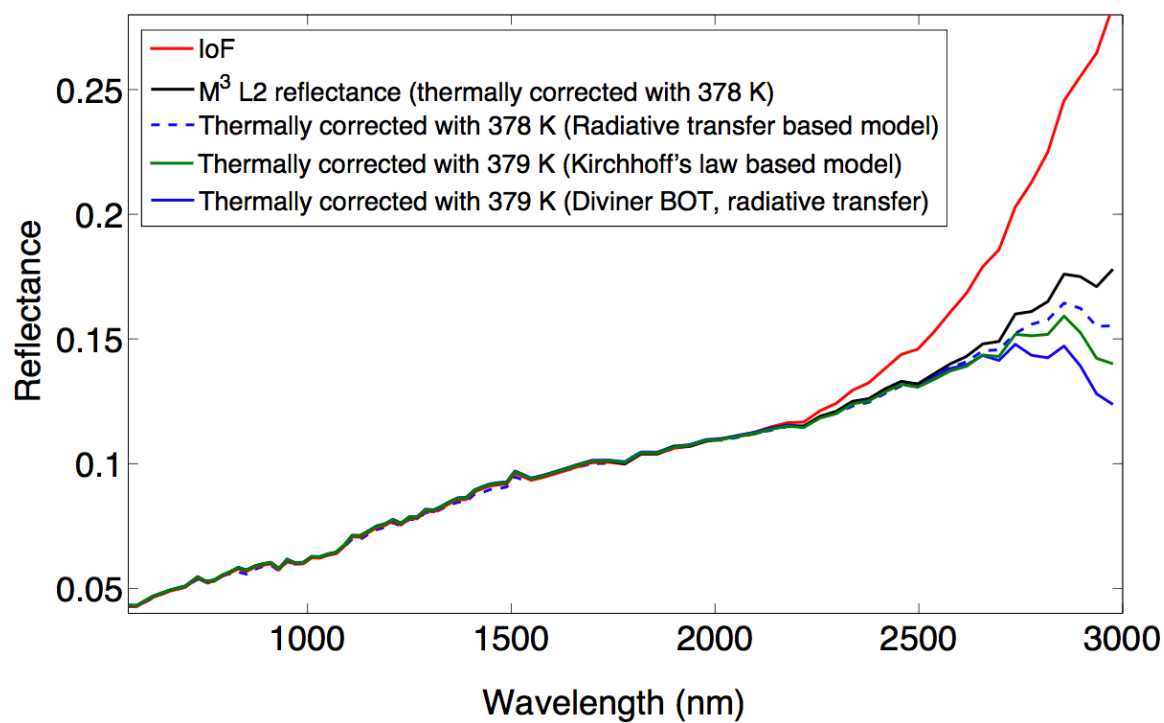


Figure 7

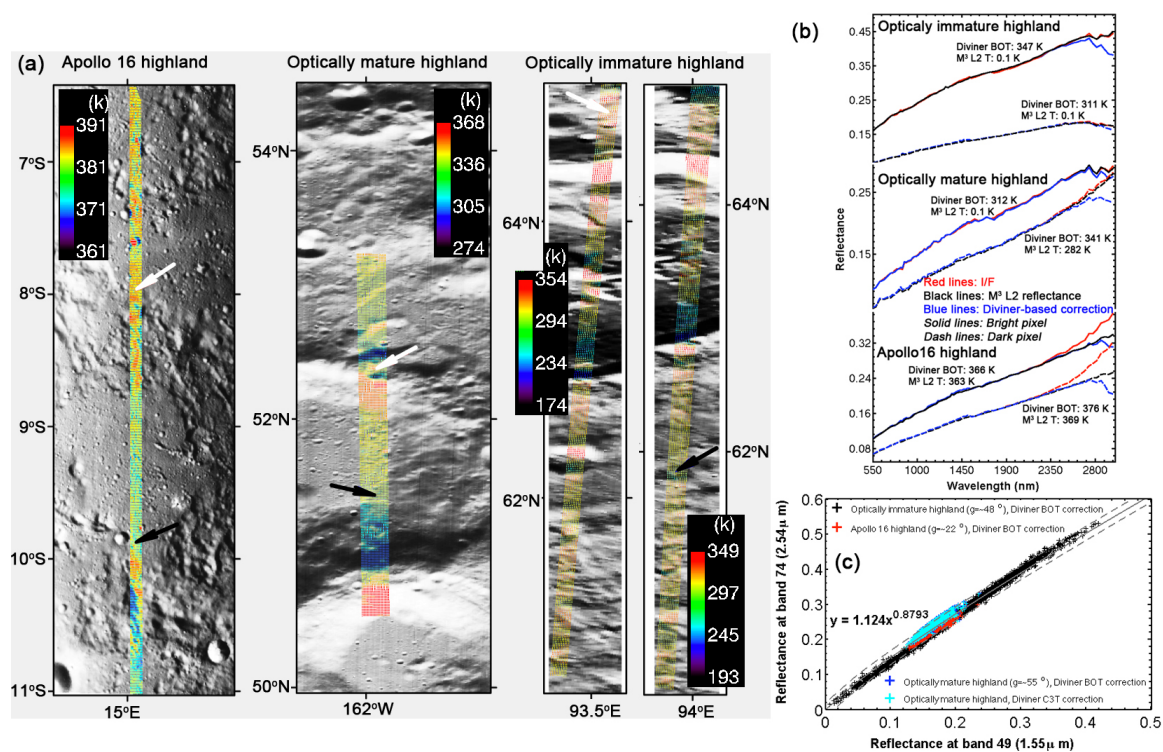


Figure 8

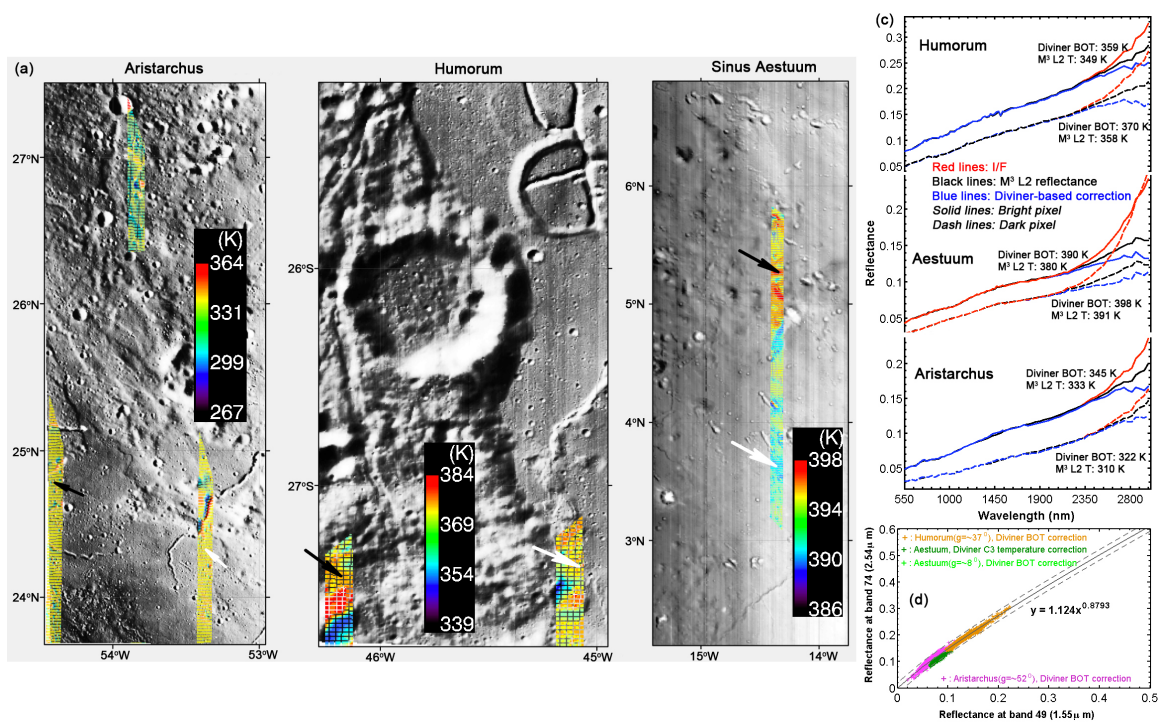


Figure 9

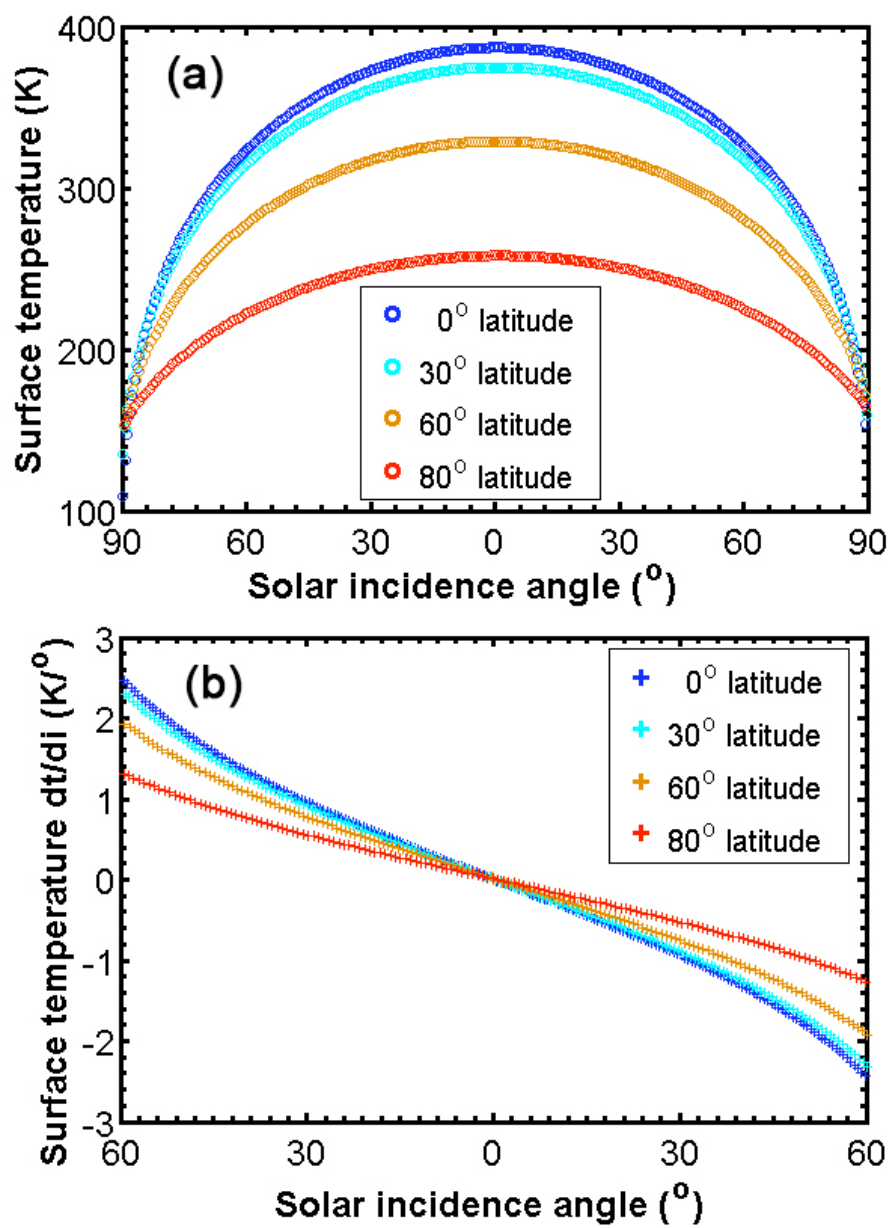


Figure 10

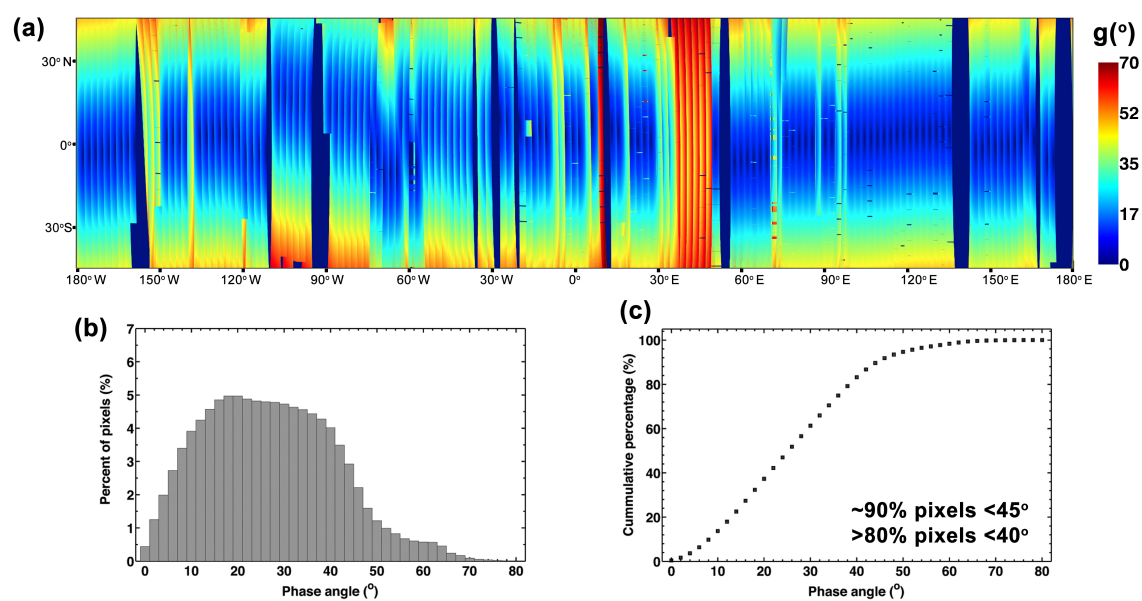


Figure 11

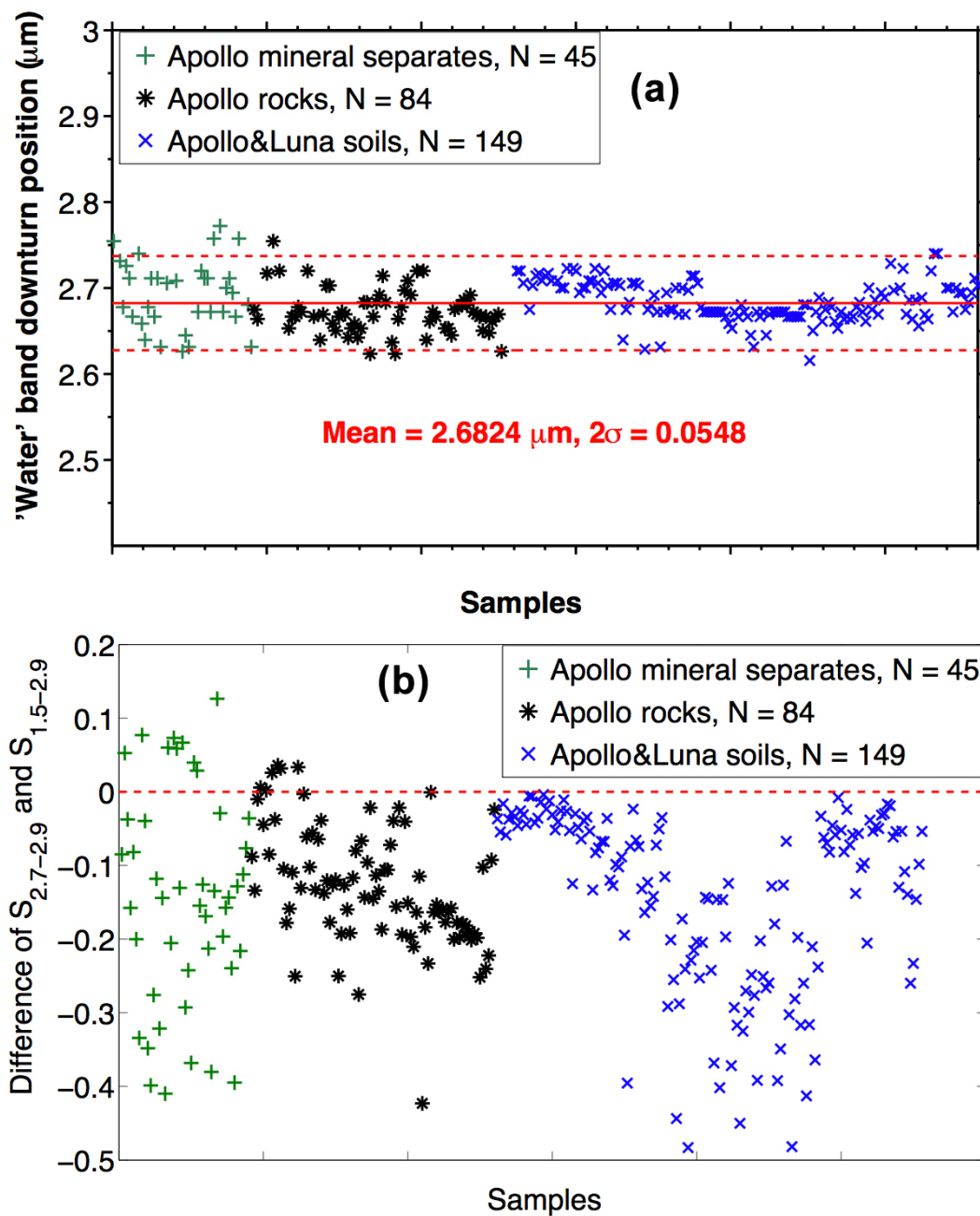


Figure 12a

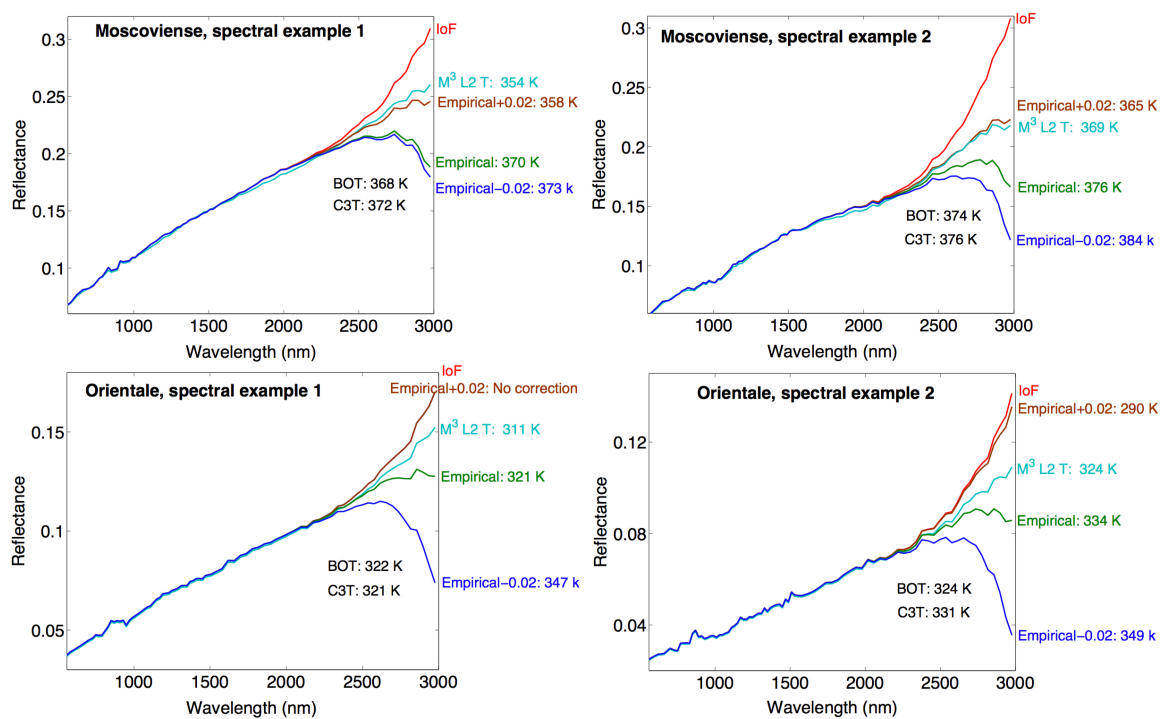


Figure 12b

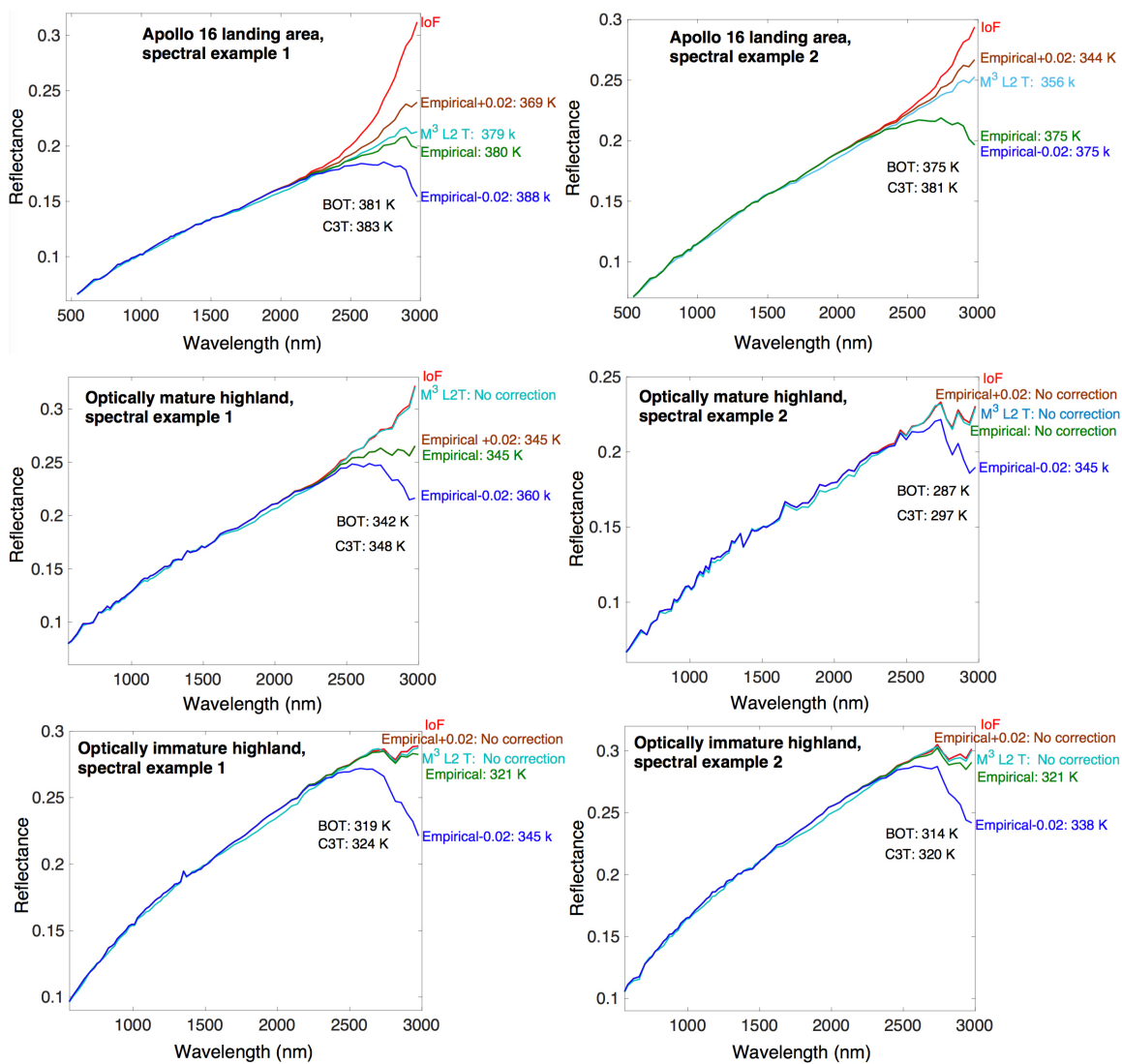


Figure 12c

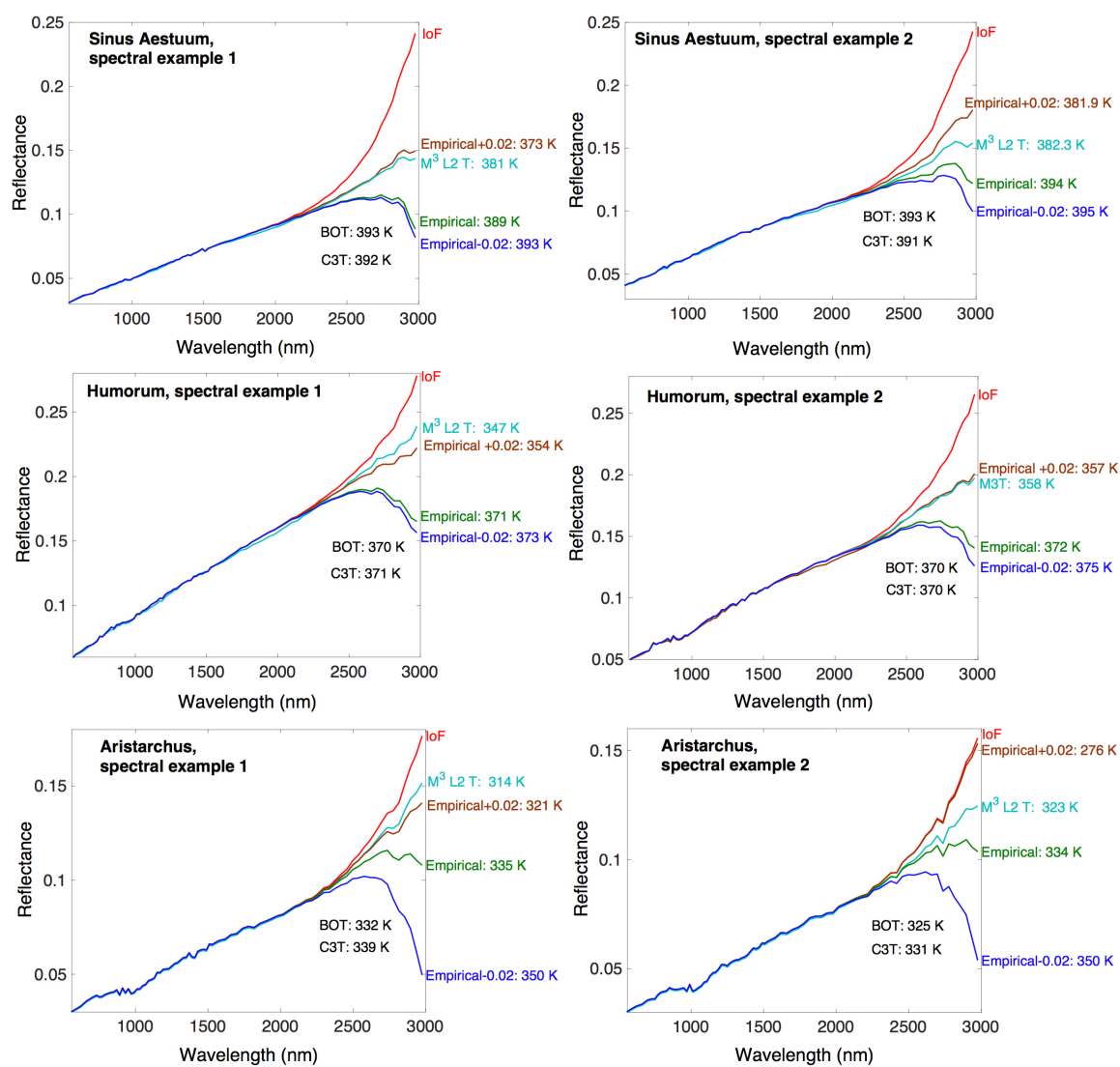


Figure 13

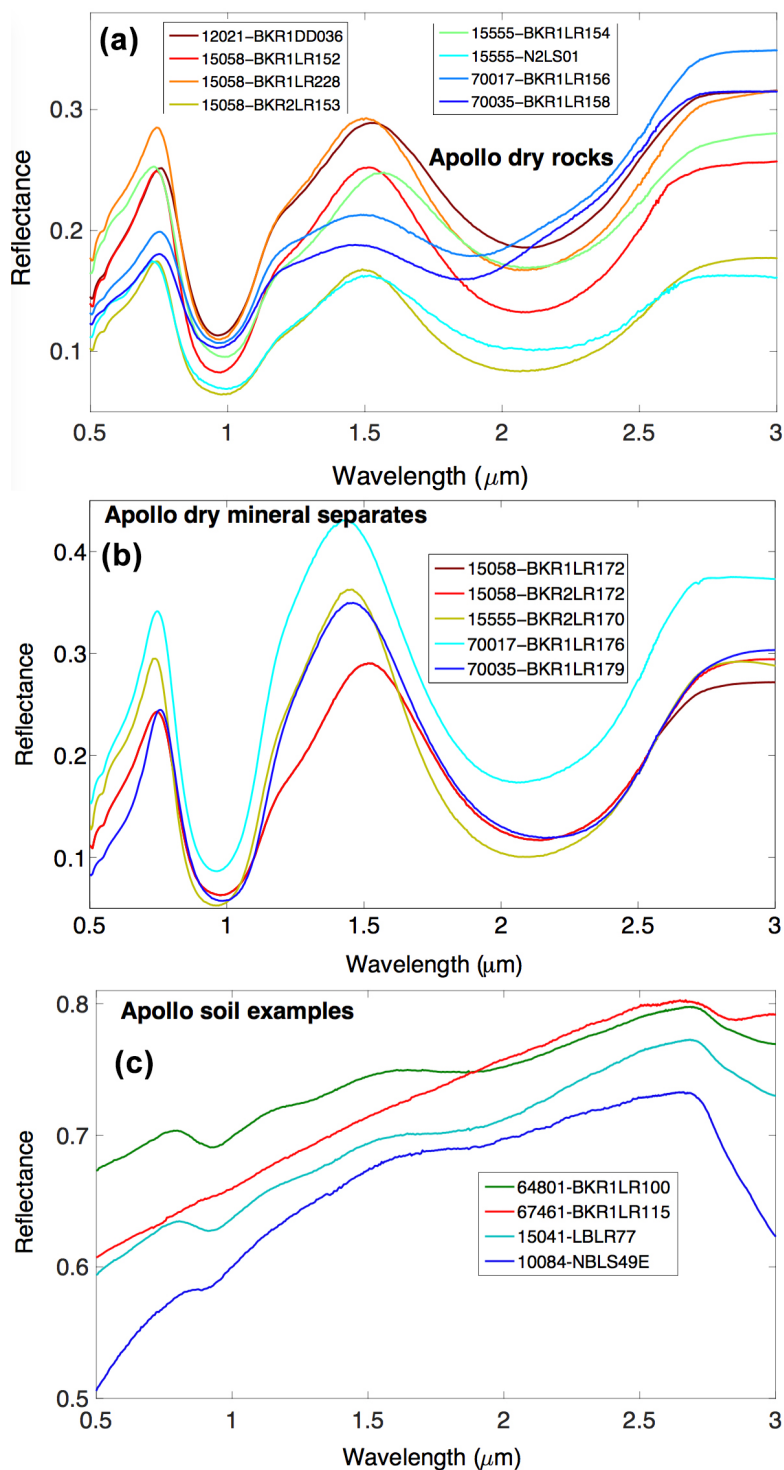


Figure 14

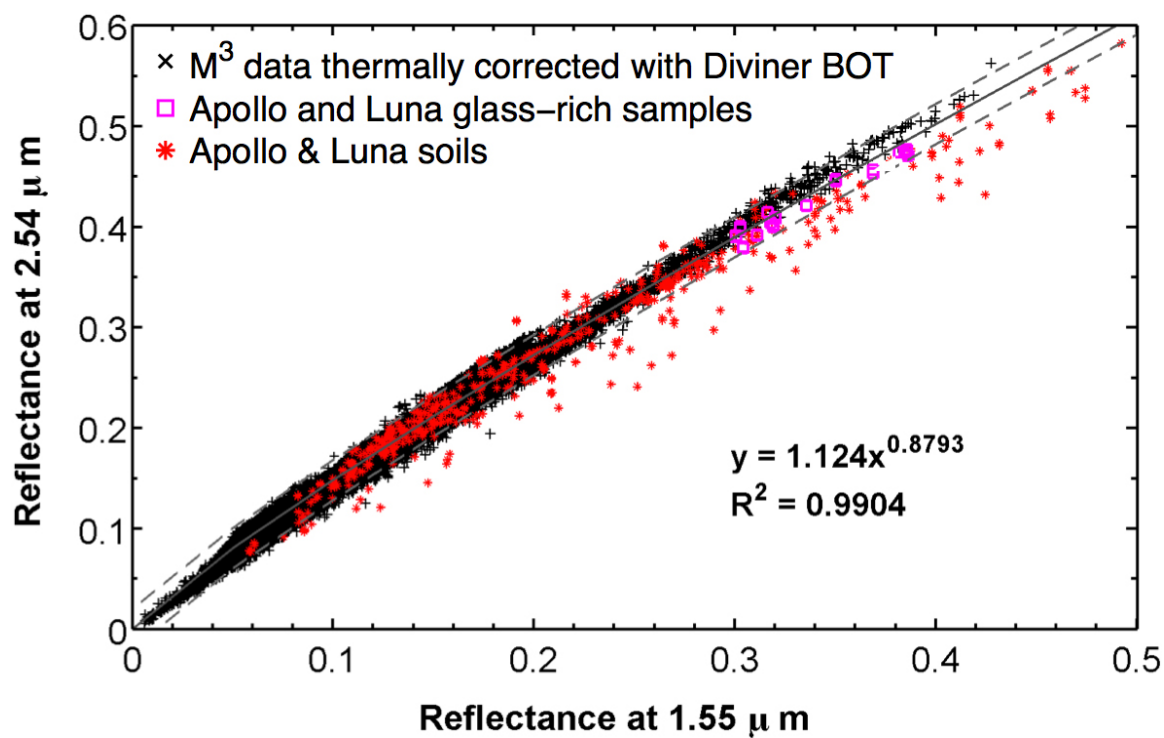
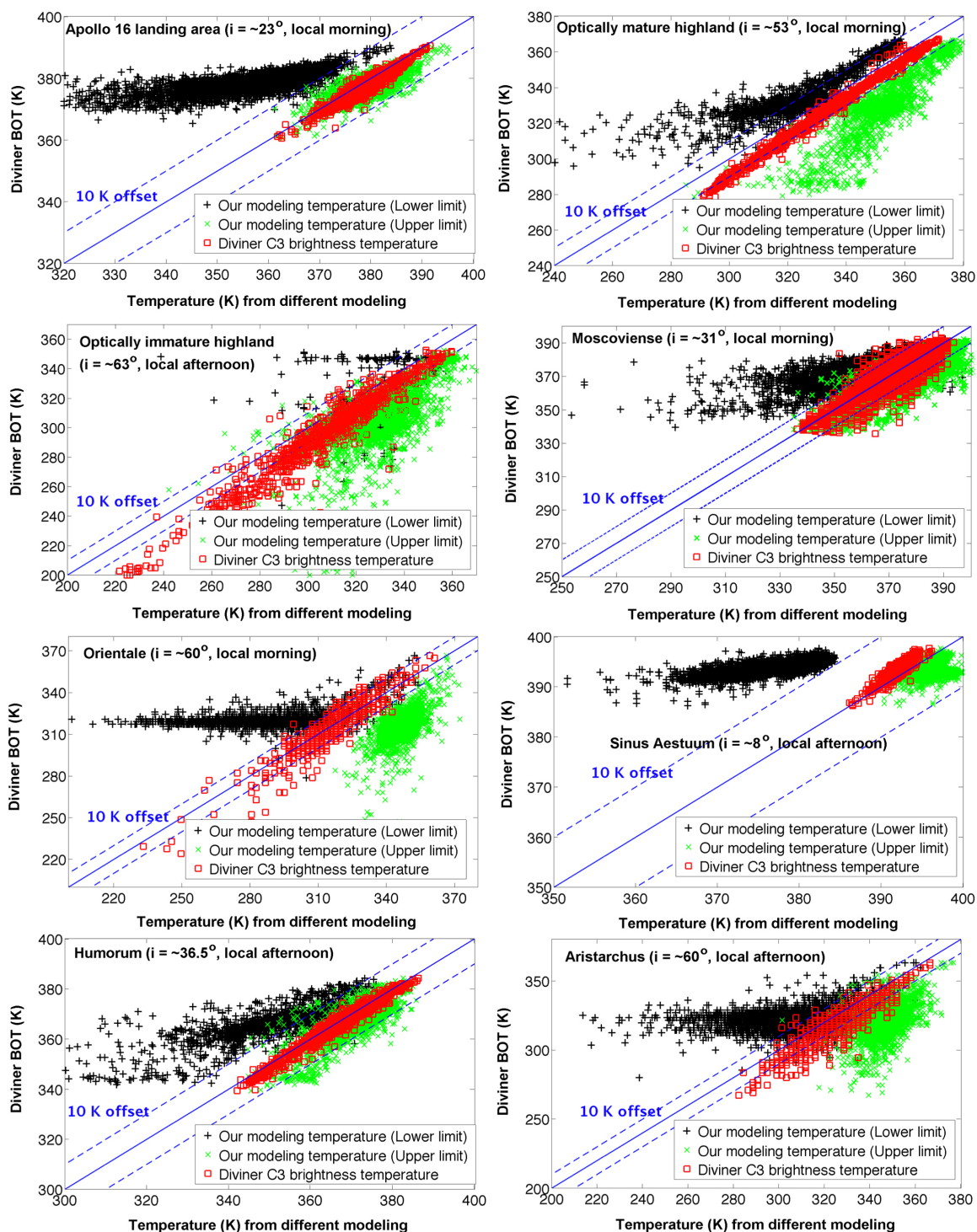


Figure 15



Chapter 2: Water on the Surface of the Moon as Seen by the Moon Mineralogy

Mapper Instrument: Distribution, Variation, and Origin

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and

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Abstract

Measurements of the lunar optical surface indicate that ‘water’ (e.g., OH and/or H₂O) is widespread and may be sourced from solar wind, water-enriched impactors, and/or volatile-rich magmas [Watson *et al.*, 1961; Epstein and Taylor Jr, 1970; Ducati *et al.*, 1973; Arnold, 1979]. To assess the role of these potential sources it is first necessary to quantify the amount of water at the lunar surface in the spatial and temporal domains. Previous efforts in this regard have been constrained by the low spatial resolution (> 10 km/pixel) of orbital data [Clark, 2009; Sunshine *et al.*, 2009] or by thermal emission effects at near-infrared (NIR) wavelengths that obfuscate detections of key OH/H₂O vibrational absorptions [Pieters *et al.*, 2009; Combe *et al.*, 2011; McCord *et al.*, 2011]. We account for the latter by applying a new thermal correction model to Moon Mineralogy Mapper (M³) near-infrared (NIR) reflectance spectra and evaluate the results using a radiative transfer model and laboratory experiments to provide estimates on absolute water content of the lunar surface. The distribution and abundance of lunar surface water increases with latitude, approaching values of 1000 ppm at the lunar poles, and is largely similar for anorthositic and basaltic surface compositions. Exceptions include large pyroclastic deposits (>1000 km²), which exhibit increased water signatures relative to surrounding terrains regardless of latitude or time of day. Diurnal variation in surface hydration is confirmed, but the variation is most manifest at low latitudes where diurnal temperature variations are strongest and water abundance is low, commonly <100 ppm. These results are consistent with lunar surface hydration originating primarily from solar wind implantation and subsequently migrating due to temperature-controlled diffusion processes.

1. Introduction

The presence of H-bearing species such as OH and H₂O, hereafter referred to simply as ‘water’, in lunar materials and at the lunar surface can record important information about solar wind implantation, impact delivery of volatiles, and the incorporation and retention of volatiles during accretion [Watson *et al.*, 1961; Epstein and Taylor Jr, 1970; Ducati *et al.*, 1973; Arnold, 1979]. A variety of studies over the past decade have presented new evidence for water in the lunar interior as well as water at the lunar surface, demonstrating that multiple reservoirs are present and leading to speculation that surficial water may migrate on diurnal timescales. Lines of evidence for interior water have the advantage that they are based on *in situ* measurements of returned lunar samples, with the drawback that only a small fraction of the Moon has been sampled. By contrast, remote sensing data can provide a global view of water at the lunar surface but are limited in that commonly used methods yield only indirect measurements of lunar water and/or are model-dependent.

In the latter category, absorptions consistent with the presence of OH/H₂O at the optical surface of the Moon have been observed in near-infrared (NIR) reflectance spectra acquired by multiple spacecraft, with data acquired by the Moon Mineralogy Mapper (M³) instrument on the Chandrayaan-1 spacecraft providing global coverage. It has been hypothesized that these spectral signatures are primarily the result of solar wind (H⁺) implantation in the uppermost fraction of the lunar regolith. This is in broad agreement with laboratory experiments and theoretical models [Watson *et al.*, 1961; Arnold, 1979] that also suggest retention of water on the lunar surface may depend on surface temperature [Ducati *et al.*, 1973], composition [Ducati *et al.*, 1973], crystallinity

[*Hibbitts et al.*, 2011], and degree of space weathering [*Ichimura et al.*, 2012]. However, in order to evaluate potential sources and sinks of lunar water it is important to first be able to quantify the various reservoirs that currently exist, which is the primary focus of this study.

This work builds upon initial qualitative M³ observations of water at the optical surface of the Moon by providing the first global quantitative estimates of this reservoir. This is accomplished by applying a newly developed thermal correction model to M³ data that yields improved estimates of surface reflectance properties at wavelengths $\geq 2 \mu\text{m}$ [*Li and Milliken*, in review], a region that includes fundamental vibrations of OH/H₂O. The corrected spectra are also evaluated using a radiative transfer model and compared with laboratory experiments in order to relate absorption strength to absolute water content. Uncertainties and ranges in estimated water content are discussed, as are apparent relationships between water content and location (latitude), surface composition, optical maturity of the lunar regolith, and local lunar time of day. The results presented here provide a new and improved view of the distribution of water at the optical surface of the Moon and provide a quantitative foundation that can be compared directly with independent theoretical and laboratory studies related to water delivery and retention at the lunar surface.

2. Background

2.1. Overview of Water Measured in Lunar Samples

The results and interpretations of recent studies related to lunar ‘water’ can be divided into measurements inferred to represent volatiles sourced from the lunar interior

(e.g., volatiles in magma source regions) and those resulting from post-accretion external sources (e.g., solar wind and volatile-rich impactors). In theory, there is potential for any lunar sample to contain either or both components. Volcanic glasses, for instance, are likely to have solar wind implanted hydrogen in their rims, whereas even non-pyroclastic regolith components may accumulate volatiles from the lunar interior that have migrated along the lunar surface during or after eruption from a volcanic source region (e.g., pyroclastic vent). Therefore, determination of likely water sources for a given lunar sample is non-trivial. Here we present a brief overview of measurements that have been conducted on lunar samples to provide context for the distribution and abundance of water that may be expected at the lunar surface. This overview is by no means comprehensive, and for more detailed information we refer the reader to the individual papers as well as a recent review article by *Robinson and Taylor* [2014] and references therein.

The two commonly applied techniques to measure water content in lunar samples are pyrolysis experiments [*Epstein and Taylor Jr*, 1972] and Secondary Ion Mass-Spectrometry (SIMS) measurements [*Saal et al.*, 2008], though other methods such as Fourier Transform Infrared Spectroscopy (FTIR) have also been used [*Saal et al.*, 2008; *Liu et al.*, 2012; *Hui et al.*, 2013]. SIMS measurements may be considered advantageous in that they have much higher detection limits compared with pyrolysis experiments and can avoid cross-contamination of hydrogen of different origins without heating the sample during measurement. On the other hand, water observed in pyrolysis experiments of bulk lunar materials may be more directly relevant to the hundreds of meters to kilometers per pixel scales observed by orbital instruments such as M³.

Results from select pyrolysis measurements that were performed on lunar regolith, mineral separates, agglutinates, and rocks sampled from the Apollo 11, 12, 14, 15, 16, and 17 landing sites are presented in Table 1. Only water amounts measured from temperatures above 300°C are listed in order to minimize potential effects of terrestrial water. However, it must be considered that all data may suffer from some degree of terrestrial contamination that could introduce large uncertainties in the δD values (where $\delta D = [(D/H)_{\text{sample}} / (D/H)_{\text{standard}} - 1] \times 1000$), which is one of the most important indices used to determine the origin of lunar water [Epstein and Taylor Jr, 1970; Friedman et al., 1970; Friedman et al., 1971; Epstein and Taylor Jr, 1972; 1973; Friedman et al., 1974; Merlivat et al., 1974; Greenwood et al., 2011; Liu et al., 2012; Saal et al., 2013; Robinson and Taylor, 2014]. Indeed, the large range in δD values from the pyrolysis approach, some of which overlap terrestrial values, have been considered an indication of likely terrestrial contamination [Epstein and Taylor Jr, 1970; Friedman et al., 1970; Epstein and Taylor Jr, 1972; 1973; Friedman et al., 1974; Merlivat et al., 1974]. It can be seen that the average water content of examined Apollo samples is 63.0 ppm and their δD values are within the range of Earth and Sun (Table 1 and Figure 1).

For comparison with pyrolysis measurements, SIMS results for Apollo 11 agglutinate, Apollo 15 volcanic glasses, Apollo 16 agglutinate, and Apollo 17 agglutinate and volcanic glasses are presented in Table 2. It has been argued that water observed in these agglutinates are largely the product of solar wind processes [Liu et al., 2012], whereas water observed in the volcanic glasses are indicative of water in magma source regions [Saal et al., 2008; Saal et al., 2013]. This can be evaluated by examining the δD values for these materials, where it can be seen that Apollo agglutinate, rock, regolith

samples are very similar to the Sun (low δD) and thus consistent with a solar wind origin (Figure 1) [Epstein and Taylor Jr, 1970; Friedman et al., 1970; Friedman et al., 1971; Epstein and Taylor Jr, 1972; 1973; Friedman et al., 1974; Leich et al., 1974; Merlivat et al., 1974; Liu et al., 2012]. A similar conclusion was reached by Stephant and Robert [2014] based on D/H ratios measured in rims (<150 nm) and ‘interiors’ (<3 μ m) for a range of agglutinate, plagioclase, and volcanic glass grains. In contrast, higher δD values found in apatite in lunar basalts and in olivine-hosted melt inclusions in lunar pyroclastic glass indicate some lunar water may be sourced from carbonaceous chondrites and comets [Greenwood et al., 2011; Tartèse and Anand, 2013; Saal et al., 2013; Füri et al., 2014]. Therefore, although SIMS measurements of water in the interior of volcanic glass beads exhibit classic diffusion profiles and a wide range in δD that may be consistent with magma degassing and eruption (indicating water originating from the lunar interior), volcanic glass beads also likely contain solar wind implanted hydrogen in their outer ~100-200 nm rims.

It is not possible to measure δD values with reflectance spectra such as M³, and because the range in water contents measured in lunar volcanic glass beads overlaps the range associated with solar wind implantation in agglutinates and other regolith components (Figure 1) it is also unlikely that water content alone can be a useful discriminator between endogenous and exogenous sources. However, as is discussed below, accumulation, migration, and retention processes may differ for these potential sources, which in turn can be used to construct hypotheses about how each type of water may be manifest at the optical surface sensed by the M³ instrument.

2.2. Potential Sources and Retention of Water at the Lunar Surface

2.2.1. Water Sourced from the Solar Wind and Its Retention on the Lunar Surface

Water measured in bulk lunar samples, most commonly via pyrolysis, has an average abundance of 40-60 ppm and is widely interpreted to result from solar wind implantation based on isotopic signatures and correlations between volatile content and surface area (i.e., volatiles are observed to be surface-correlated in lunar soils). The concentrations of hydrogen as well as other volatile elements Ni, Zn, Ga, Ge, Cd, In, Ir, and Au in Apollo samples all exhibit strong correlation with size fractions of respective samples, which strongly indicates that they are sourced from solar wind implantation [DesMarais *et al.*, 1974; Boynton *et al.*, 1975].

Water of solar wind origin can be formed by several different mechanisms. First, solar wind can penetrate through the upper ~ 200 nm ($D_{PenetrationDepth}$) of lunar regolith grains and hydroxyl (OH⁻) can be formed if any solar wind hydrogen is bonded with oxygen [Zeller *et al.*, 1966; Epstein and Taylor Jr, 1970; Ducati *et al.*, 1973; Leich and Tombrello, 1973; Leich *et al.*, 1974; Tombrello, 1980]. Second, oxides (i.e., FeO) in lunar regolith grains can be reduced by solar wind hydrogen to form water ($\text{FeO} + 2\text{H} + e^- \rightarrow \text{Fe}^0 + \text{H}_2\text{O}$) with energy provided by micrometeorite bombardment [Arnold, 1979]. Taking the hydrogen flux of solar wind (4×10^{15} H/cm²/yr) measured by the Apollo 11, 12, 14, 15, and 16 Solar Wind Composition (SWC) experiments [Geiss *et al.*, 1970; Geiss *et al.*, 2004] and laboratory radiation experiments [Ducati *et al.*, 1973], one can reasonably assume that lunar regolith grains at the optical surface are initially saturated with hydrogen ($\rho_H^{SurfaceDensity} = \sim 10^{17}$ H/cm²) [Ducati *et al.*, 1973]. It has been shown that a fraction, p , of around 20% - 50% of the hydrogen is bonded with oxygen to form

hydroxyl or molecular water [Epstein and Taylor Jr, 1972]. Assuming a lunar surface regolith density ($\rho_{bulk} = \sim 1.8 \text{ g/cm}^3$) [Mitchell et al., 1972], we can estimate the water content in the bulk lunar soils that is sourced from the solar wind as:

$$H_2O = \left(\frac{1}{2} \frac{p^* \rho_H^{SurfaceDensity}}{D_{PenetrationDepth}} \right) / Na * 18 / \rho_{bulk}, \text{ where } Na \text{ is Avogadro's constant } (6.022 * 10^{23}).$$

Plugging all parameters into the above equation, the total solar wind contribution is estimated to range from approximately 0.83 wt.% (8300 ppm) to 2.1 wt.% (21000 ppm) H₂O in the bulk lunar regolith.

However, much of the water formed in this manner is not stable under the harsh lunar environment, and it is estimated that only ~0.2% may be retained after a series of destructive processes that occur at the lunar surface and that are particularly effective at equatorial latitudes [Ducati et al., 1973; Leich and Tombrello, 1973; Leich et al., 1974; Tombrello, 1980]. The major destructive mechanisms include: 1) photodissociation of surficial water through radiation [Watson et al., 1961; Arnold, 1979]; 2) 20-50% loss by vaporization that is induced by micrometeorite bombardment [Arnold, 1979]; 3) sputtering by solar wind and cosmic rays, which is latitude-dependent and may be 10x more effective at low latitudes compared with high latitudes [Arnold, 1979]; 4) hydrogen diffusion along radiation damaged lattices (damage diffusion) [Ducati et al., 1973]; 5) volume diffusion, driven by kinetic energy, that is dependent on lunar surface temperature; 6) annealing, a self-diffusion process that can release trapped water [Ducati et al., 1973]. In contrast, the major mechanism for water retention may be formation of radiation damage traps (surface defects) that inhibit hydrogen diffusion through the crystal lattice [Ducati et al., 1973].

The bulk water content of the lunar regolith at equatorial regions that is expected to be sourced from solar wind can thus be estimated to be on the order of $21000 \times 0.2\% = 42$ ppm, roughly in line with value observed for bulk lunar soils as mentioned above. In addition, because volume diffusion will be affected by surface temperature, it is possible that surficial water content may vary as a function of local lunar time of day, particularly for low latitudes where surface temperatures can approach values in excess of 400K. Furthermore, laboratory irradiation experiments have shown that crystalline (mineral) phases and more mature grains more readily accept hydrogen to form hydroxyl than glassy, immature regolith grains [Hibbitts *et al.*, 2011; Ichimura *et al.*, 2012]. Therefore, higher concentrations of water originating from solar wind processes may be expected for terranes with higher proportions of crystalline phases, higher maturity, and/or at higher latitudes (lower temperatures), all of which can be tested with M^3 data.

Water that is of solar wind origin might also be preferentially retained and concentrated in polar regions where surface temperatures are lower and consequently diffusion is slower. The amount of solar wind water retained at these regions would depend on the rate of hydrogen supply from the solar wind and availability of oxygen bonding sites within the regolith. Indeed, it is possible that massive water (i.e. ~1 - 10%) might be accumulated and retained by hydrogen migration and cold trapping in permanently shadowed regions at the lunar poles [Arnold, 1979; Feldman *et al.*, 1998; Feldman *et al.*, 2001; Crider and Vondrak, 2002], though the presence, distribution, and amount of water in such regions is an area of active debate [Hodges, 2002; Campbell *et al.*, 2006]. Though water deposits in these shadowed regions may be of interest for *in situ*

resource utilization, they are not examined in this study because there are no appropriate M^3 reflectance spectra at such locations.

2.2.2. Water Sourced from the Impacts and Its Retention on the Lunar Surface

In contrast to water of solar wind origin, water in bulk lunar soils that might originate from volatile-rich impactors is likely to be a relatively minor component. Water sourced from impacts (mainly carbonaceous chondrites and comets) can be estimated based on the present meteoritic influx rate ($\sim 20 \text{ g/cm}^2$) [Brown, 1960; Watson *et al.*, 1961]. However, only 3% of these meteorites contain water ranging from 0.02% to 20% [Watson *et al.*, 1961]. Assuming this exogenous materials are distributed homogeneously in the upper 1 m of the lunar surface [Arnold, 1979], we can estimate the water content in the bulk lunar regolith to be: $(20 \times 3\% \times [0.02\%, 20\%]) \text{ g/cm}^2 / 100 \text{ cm} / 1.8 \text{ g/cm}^3 = [0.7 \text{ ppm}, 666.7 \text{ ppm}]$, where the bulk density of lunar regolith 1.8 g/cm^3 is determined from Apollo samples [Mitchell *et al.*, 1972].

This type of water can be retained in two different ways. The first is based on the assumption that impact-delivered water is subject to the same mechanisms as the solar wind water, for which up to 0.2% may be retained ($[0.7 \text{ ppm}, 666.7 \text{ ppm}] \times 0.2\% = [0.001 \text{ ppm}, 1.3 \text{ ppm}]$). It is also possible that water-bearing impactor fragments may not be subject to the same destruction processes as solar wind implanted hydrogen, or that impact delivered water could be quenched in lunar regolith melt (e.g., agglutinate) that might inhibit diffusion [Ducati *et al.*, 1973; Liu *et al.*, 2012]. However, meteoritic remnants found in Apollo samples are less than 2% by volume [Heiken *et al.*, 1991].

Therefore, even if all of this water were to be retained, it may only account for $(20 \times 3\% \times [0.02\%, 20\%] \times 2\%) \text{ g/cm}^2 / 100 \text{ cm} / 1.8 \text{ g/cm}^3 = [0.01 \text{ ppm}, 13.3 \text{ ppm}]$.

Given these expected low concentrations and homogenization due to regolith gardening, it is perhaps impractical to distinguish water associated with impactor material from solar wind implantation in typical lunar soils using remote sensing data alone. However, water signatures associated with craters or crater ejecta that are anomalously high compared to surrounding terrains may indicate the presence of impact-delivered volatiles, as has recently been suggested for Dawn observations of the asteroid 4 Vesta [De Sanctis *et al.*, 2015].

In addition to water that is present in volatile-rich impactor fragments, we note that water vapor released during an impact may also be retained on the Moon if it is able to migrate towards cold traps at the lunar poles where it can be stabilized over geologic timescales. In general, it is currently poorly understood how to quantify the amount of water from an impactor that might be retained during the impact process on an airless body and how such water might be partitioned between unmelted impactor material, impact melt products, and vapor-deposited species. Hypervelocity impact experiments (up to 5 km/s) using serpentine (~18 – 24% H₂O by weight) as projectiles suggests that 2% - 10% of projectile's OH can be retained during impact depending on target properties and impact angles, and additional OH might be captured by impact produced breccias [Daly and Schultz, 2016]. This supports our assumption that 2% of all available OH from impactors may be retained in lunar regolith, although the retention efficiency may be lower on the Moon due to higher impact velocity (generally > 10 km/s [Heiken *et*

al., 1991]) and drier projectiles [*Watson et al.*, 1961]. Therefore, the maximum contribution of water from impacts to the lunar surface may be on the order of 10 ppm.

2.2.3. Water Sourced from the Lunar Interior

Prior to the return of lunar samples it was not known how much water might be present in the lunar interior [*Watson et al.*, 1961; *Arnold*, 1979], and even early measurements of water in bulk Apollo samples suggested the water content may be less than 1 ppm [*Epstein and Taylor Jr*, 1970]. However, any endogenous water could be concentrated in certain materials, including volcanic glasses such as those discussed above [*Saal et al.*, 2008; *Saal et al.*, 2013], mineral phases such as apatite in lunar basalts [*Boyce et al.*, 2010; *McCubbin et al.*, 2010; *Greenwood et al.*, 2011], and late-stage products of magma ocean crystallization such as KREEP materials [*Robinson and Taylor*, 2014; *Tartèse et al.*, 2014]. Measurements of several ppm of water in lunar anorthosite have also been used to indicate the presence of significant water in the lunar magma ocean, possibly up to 320 ppm [*Hui et al.*, 2013].

Direct measurements of water in lunar materials that are likely linked to interior reservoirs can perhaps best be summarized as diverse and somewhat contradictory. Lower values in KREEP apatites compared with mare apatites suggest a somewhat drier lunar magma ocean [*Robinson and Taylor*, 2014], in contrast to a “wetter” scenario implied by water contents of ferroan anorthosites [*Hui et al.*, 2013]. In contrast, water in mare apatites and volcanic glasses are both consistent with volatile-rich magmas, though the source of these volatiles may have been impact delivery after most of the magma ocean had crystallized.

Not all minerals and phases within lunar samples are expected to be enriched in water due to the presence of volatiles in their source region, and indeed most measurements over the past decade have appropriately focused on small samples using high-resolution analytical techniques. Therefore, the lines of evidence for interior water that are based on direct measurements of lunar samples may be impractical to distinguish at a global scale using orbital spectroscopy, particularly for low water abundances. However, indicators of interior water that have some potential to be expressed at the optical surface include enhanced spectral absorptions in KREEP-rich terrains, large pyroclastic deposits, or strong variation within or between mare deposits.

2.3. Near-Infrared Reflectance Spectra of Lunar Surface Water

Water at the lunar surface has been identified using space-based reflectance spectra acquired by Deep Impact/EPOXI [*Sunshine et al.*, 2009], the Visible and Infrared Mapping Spectrometer (VIMS) on the Cassini spacecraft [*Clark*, 2009], and the M³ instrument on Chandrayaan-1 [*Pieters et al.*, 2009]. These investigations relied on the detection of fundamental vibration absorptions of OH/H₂O that occur in the ~2.7-4 μm wavelength region, sometimes referred to simply as the “3 μm region”. Though EPOXI and VIMS data were constrained by their low spatial resolution (>10 km/pixel) and M³ data only extend to ~2.9 μm , several major characteristics of lunar surface water were observed.

Appreciable amounts of water (estimated to be ~1000 ppm) were inferred from both VIMS and M³ data, particularly at high latitudes, and were attributed to the accumulation of water sourced from the solar wind and volatile-rich impacts [*Clark*, 2009;

Pieters et al., 2009]. Intriguingly, EPOXI observed diurnal changes in absorption strength that were interpreted to represent accumulation and subsequent loss/migration of lunar water as a function of local lunar time of day [*Sunshine et al.*, 2009], though effects due to viewing geometry and surface temperature may be responsible for some of the observed changes.

Lunar surface water has been assessed using current M³ level 2 reflectance data that have significant thermal residuals at low latitudes. Two absorption bands centered at 2.8 μm and 2.97 μm (the last band of M³ data) were characterized to discriminate the water speciation (OH or H²O) [*McCord et al.*, 2011], which could be deceptive owing to the artifacts in the last spectral band of M³ data. Although the absorption strength at 2.8 μm and 3 μm seems to be correlated with composition (i.e., highland shows stronger absorptions than mare), a more quantitative analysis is required to discriminate whether this correlation suggests a compositionally dependent hydration formation process or is just due to observation bias [*Starukhina and Shkuratov*, 2000; *McCord et al.*, 2011]. Localized hydration anomalies are also discussed in previous studies. Hydration features associated with eleven swirls on the global lunar surface have been examined [*Kramer et al.*, 2011]. It showed that the absorption at 2.8 μm is always stronger at off-swirls than on-swirls, suggesting that localized magnetic anomalies protect swirls from solar wind [*Kramer et al.*, 2011]. Hydration anomalies are observed at a high latitude volcanic complex at Compton-Belkovich [*Petro et al.*, 2013]. However, due to the known thermal issue with current M³ level 3 dataset, observations at low latitudes (e.g., $< \sim 60^\circ$) could be biased [*McCord et al.*, 2011].

Potential variations in water content between regions of different surface composition (e.g., mare versus highlands), degree of space weathering, and purported diurnal effects can be explored in more detail at a global scale with M^3 data, which provide global coverage at ~ 280 m/pixel and for some locations include repeat observations at different local times of day. However, qualitative and quantitative assessments of water at low latitudes using M^3 spectra are hindered by the presence of thermally emitted radiance that can weaken and fully mask water absorptions in the $3\ \mu\text{m}$ region [Combe *et al.*, 2011; McCord *et al.*, 2011; Li and Milliken, in review]. Unless properly accounted for, these thermal effects can produce a strong bias in the apparent surface distribution and strength of water absorptions at NIR wavelengths, which in turn can lead to large uncertainties when attempting to quantify the amount of water that is present.

In this study we examine the global distribution of lunar surface water using new thermally-corrected M^3 data based on methods presented in Li and Milliken [in review] that provide a significant improvement over previous M^3 thermal corrections [Li and Milliken, in review]. The thermally corrected spectra are then used in a radiative transfer model and compared with empirically derived relationships between water content and absorption strength based on laboratory experiments. The integration of these steps allows us to place quantitative constraints on the spatial and temporal distribution of water at the optical surface of the Moon. The resulting quantitative maps of surficial water are used to evaluate its potential origins based on the predicted characteristics of solar wind, impact, and interior-derived sources as outlined in the preceding discussion.

3. Methods

3.1. Thermal Correction Model for M³ Data

The thermal correction model for M³ data used in this study is described in detail in *Li and Milliken* [in review], but here we provide a brief overview. It has been suggested that thermal removal for the publicly available M³ Level 2 data (reflectance spectra) is insufficient for evaluating lunar surface water in regions where radiance-at-sensor includes a thermal contribution from the lunar surface [*Combe et al.*, 2011; *McCord et al.*, 2011]. A new semi-empirical thermal correction model for M³ data has been developed based on laboratory reflectance spectra of Apollo samples, and this model has been independently validated with a radiative transfer model in conjunction with lunar surface temperatures measured by the Diviner instrument on the Lunar Reconnaissance Orbiter [*Li and Milliken*, in review]. Laboratory reflectance spectra of Apollo samples measured under ambient conditions were collated, and *Li and Milliken* [in review] proposed an empirical model based on the correlation between reflectance values at 1.55 μm (band 49 of M³ images) and at 2.54 μm (band 74 of M³ images).

A short wavelength of 1.55 μm was selected because there are no major absorptions near this region for lunar materials and it is not affected by thermal emission even at maximum lunar surface temperatures. A long wavelength of 2.54 μm was selected because it is far enough beyond pyroxene absorption centered at ~ 2 μm , lies outside of the OH stretching band centered at ~ 2.9 μm , and can be affected by thermal emission under a wide range of lunar surface temperatures. The reflectance at 1.55 μm is highly correlated to the reflectance at 2.54 μm in lab reflectance spectra of Apollo and

Luna samples (where there are no thermal emission effects), thus the former can be used to predict the latter within $\sim 2\%$ absolute reflectance for a wide range of lunar materials.

Diviner-based surface temperature data for several regions of interest (covering a wide variety of optical maturity, albedo, solar incidence angle, latitude, and composition) were used to estimate and remove thermal contributions from M^3 data acquired at the same locations at the same lunar local time. A Hapke-based radiative transfer model [Hapke, 1993] was applied to the M^3 data using the matched Diviner surface temperatures, which yielded thermally-corrected reflectance spectra for each M^3 pixel within the regions of interest. The correlation between reflectance at 1.55 and 2.54 μm in these thermally-corrected M^3 data was effectively the same as the trend observed in lab spectra of the Apollo samples, indicating it is an inherent property in reflectance spectra of materials that typify the lunar surface.

Based on these results, [Li and Milliken, in review] concluded that reflectance values observed at 1.55 μm in M^3 data could be used to predict the reflectance values at 2.54 μm , and any excess reflectance at the longer wavelength can be assumed to result from thermal emission. Any excess thermal emission can then be estimated and removed from the original radiance data prior to conversion to surface reflectance. A key benefit of this model is that M^3 data can be thermally corrected without the need for independently measured surface temperatures acquired at the same local lunar time of day. The thermally corrected spectra have an uncertainty of $\pm 2\%$ or better absolute reflectance at wavelengths affected by thermal emission.

3.2. Laboratory Experiments and Numerical Simulations to Quantify Water Content Based on Reflectance Spectra

Identification and quantification of water from reflectance spectra is commonly based on fundamental OH and H₂O stretching absorptions observed near $\sim 2.65 - 2.9 \mu\text{m}$. However, the strength of water absorptions is complicated by effects of multiple scattering, albedo variation, viewing geometry, particle size, and possibly composition [Hapke, 1993; Milliken and Mustard, 2005; 2007b]. Previous studies have demonstrated that Hapke's Effective Single Particle Absorption Thickness (ESPAT) [Hapke, 1993], calculated at a wavelength of $\sim 2.9 \mu\text{m}$ from single scattering albedo spectra [Hapke, 1993], exhibits a particle size-dependent linear correlation with water content for a wide variety of hydrous materials [Milliken and Mustard, 2005; 2007b]. Building on this previous work, we carried out new laboratory experiments to determine specific wt.% H₂O - ESPAT trends for compositions directly relevant to the Moon and for particle sizes that typify lunar soils.

3.2.1. Determination of ESPAT-%H₂O Trends

The ESPAT values for water absorptions observed in spectra of the samples studied here were determined based on the methodology outlined in Milliken and Mustard [2005; 2007a; 2007b]. First, single scattering albedo (ω) is calculated from the measured reflectance (R) at $\sim 2.9 \mu\text{m}$ based on Hapke theory [Hapke, 1993]:

$$R = \frac{\omega}{4\pi} \frac{\mu_0}{\mu_0 + \mu} \left\{ [1 + B(g)] P(g) + H(\mu_0, \omega_{ave}) H(\mu, \omega_{ave}) - 1 \right\} \quad (1)$$

where μ_0 is the cosine of the incidence angle (i), μ is the cosine of the emergence angle (e), g is the phase angle, $B(g)$ is the back scattering function, $P(g)$ is the phase function, and the H functions account for multiple scattering processes. The ESPAT value at $\sim 2.9 \mu\text{m}$, which commonly corresponds to the maximum absorption point for water-bearing materials, is then determined by:

$$ESPAT = \frac{\omega}{1 - \omega} \quad (2)$$

The calculated ESPAT value for each sample can then be plotted against the known or estimated water content (Figure 2).

The $\text{H}_2\text{O}\%$ -ESPAT trend can also be numerically simulated using Equations 1 and 2 if the optical constants (real (n) and imaginary (k) components of the complex index of refraction) are known. This is because the single scattering albedo is a function of n , k , and the optical path length, $\langle D \rangle$ (which can be related to particle size, d). Using Hapke theory, the optical constants can be used to forward calculate ω , and thus ESPAT, for a given particle size. *Stolper* [1982] derived a relationship between water concentration (c) and absorbance (A) at $\sim 2.9 \mu\text{m}$ for a variety of silicate glasses, where these properties were related by

$$c = \frac{18.02 * A}{d * \rho * \varepsilon} \quad (3)$$

where d , ρ , and ε are the thickness, density, and extinction coefficient of silicate glasses, respectively. In this work we adopted the average value of $\varepsilon = 67 \text{ L/mol}\cdot\text{cm}$ reported by *Stolper* [1982] for a variety of glass compositions (both silicic and basaltic). In radiative transfer theory,

$$A = \alpha \langle D \rangle \quad (4)$$

where α is the absorption, defined as

$$\alpha = \frac{4\pi k}{\lambda} \quad (5)$$

and $\langle D \rangle$ is the optical path length. The optical path length can be related to particle diameter, d , by $\langle D \rangle = 0.2d$ for irregular shaped particles [Hapke, 1981; Shkuratov *et al.*, 1999; Shkuratov *et al.*, 2005]. If we assume the density (ρ) of silicate glass to be 3g/cm^3 , and substitute A with $\alpha\langle D \rangle$, equation 5 can be rewritten as:

$$\alpha = (558.66 \pm 10\%)c \quad (6)$$

ESPAT values are calculated from ω spectra (equation 2), where ω can be calculated as:

$$\omega = s_e + (1 - s_e) \frac{(1 - s_i)\Theta}{1 - s_i\Theta} \quad (7)$$

where s_e is the external scattering coefficient and s_i is the internal scattering coefficient, defined by

$$s_e = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} + 0.05, \quad s_i = 1 - \frac{4}{n(n+1)^2} \quad (8)$$

and a simple form of the internal transmission factor can be defined as

$$\Theta = e^{-\alpha\langle D \rangle} \quad (9)$$

We assume $n = 1.5$ (an average between values for water (1.33) and silicate glasses (~ 1.7)); the term k in s_e is negligible because of its significantly smaller value compared with n for silicate minerals (k varies from 10^{-4} to 5×10^{-3} for silicate minerals) [Li and Li, 2011]. Particle size (d) is left as a free parameter, thus ω (and by extension, ESPAT) is only a function of α and d . Based on the above equations, ESPAT values can be modeled as a function of water content ($\text{H}_2\text{O}\%$, c) and particle size (d) at a given

wavelength (λ). Following these steps, ESPAT-%H₂O trends were numerically simulated for water-bearing glass (assuming the extinction coefficient of *Stolper* [1982]) for <45 μm , 32-53 μm , 63-75 μm , and 106-125 μm diameter particles. The results are presented in Figure 2, where dashed lines are calculated using the mean particle size for each of the four scenarios. Though our samples (glasses and otherwise) are compositionally distinct from the ones measured in that study, this modeling step provides a first-order independent assessment of potential %H₂O-ESPAT trends as a function of particle size for comparison with the experimental results.

3.2.2. Acquisition and Analysis of Laboratory Reflectance Spectra

Reflectance spectra were measured for a series of synthetic hydrated basaltic glasses (lunar compositions), terrestrial volcanic glasses, and terrestrial anorthites (Table 4&5). Different particle size ranges and water contents were examined to determine relevant H₂O%- ESPAT trends and to examine how these factors affect these trends. Specifically, the average particle size for typical lunar regolith is ~60 - 80 μm [*Heiken et al.*, 1991], but the optical properties of the lunar surface are dominated by particles 10-20 μm in diameter [*Pieters et al.*, 1993]. Therefore, experiments were carried out for four groups of fine powders corresponding to these particle size ranges.

Reflectance spectra for each sample were measured in the NASA Reflectance Experiment LABoratory (RELAB) facility at Brown University using a Nicolet FTIR over a wavelength range of ~1-25 μm . All reflectance spectra were converted to single scattering albedo spectra using equation 1, and the resulting SSA spectra were then used in equation 2 to determine ESPAT values for the water absorptions at a wavelength of

~2.9 μm . Samples were ground and dry-sieved to various particle sizes, as discussed below, and measured under continuous flow of dry air (scrubbed for CO_2 , dewpoint of ~203 K). Information for these samples is listed in Table 4&5.

3.2.2.1. Anorthositic Materials

A sample of terrestrial anorthosite from Timmons, Ontario, provided by Dr. Ralph Milliken (Brown University), was ground and sieved to $<45 \mu\text{m}$. Sample weight and reflectance spectra (~1 μm – 25 μm) were recorded at ambient temperature, after 20 minutes of purging in dry air, and after heating from 100-600°C in 50 °C increments for 30 minutes at each step. Sample weight and spectra were measured immediately after each heating step to avoid contamination from atmospheric water (Table 3; Figure 3).

The sample was contaminated by organic matter showing an absorption at ~3.4 μm (Figure 3, black arrow) due to C-H vibrations, which can affect the apparent strength of water absorptions in the 3 μm region as well as measured weight losses. To account for the contribution of organics we assume that ESPAT values for organic bands at ~3.4 μm are, like water, linearly correlated to abundance. ESPAT values for the organic contribution, E_o , can thus be related to organic content, W_o , by $W_o\% = a_o E_o$, where a_o is the slope. Similarly, ESPAT of the water contribution, E_w , can be related to water content, W_w , by $W_w\% = a_w E_w$ [Milliken and Mustard, 2005; Milliken, 2006; Milliken and Mustard, 2007a; 2007b]. The total weight loss after each step of heating is defined as

$W_{loss} \% = W_o \% + W_w \%$, which can be rewritten as $a_o E_o + a_w E_w = W_{loss} \%$. In matrix form,

$$EA_{ow} = W, \text{ where } E = \begin{bmatrix} E_{o1} & E_{w1} \\ E_{o2} & E_{w2} \\ \bullet & \bullet \\ E_{on} & E_{wn} \end{bmatrix}, \quad A_{ow} = \begin{bmatrix} a_o \\ a_w \end{bmatrix}, \quad W = \begin{bmatrix} W_1 \\ W_2 \\ \bullet \\ W_n \end{bmatrix}.$$

The values for E_o and E_w are calculated from SSA spectra at ~ 3.4 and $\sim 2.9 \mu\text{m}$, respectively, corresponding to each step of the heating experiments. The two unknowns, a_o and a_w , are then estimated using a least-squares approach: $A_{ow} = (E'E)^{-1}E'W$. This yields a value of $a_w = 1.8$ that can be used to predict water content based on ESPAT values for this sample (Figure 2).

3.2.2.2. Synthetic Glasses of Lunar Composition

Reflectance spectra of a green and orange glass with the same bulk chemical composition as the Apollo green and orange glasses were measured to examine their $\text{H}_2\text{O}\%$ -ESPAT trend. These samples were synthesized under lunar-like conditions and characterized, including water contents via SIMS measurements, by *Wetzel et al.* [2015]. Samples were ground and dry-sieved to $<45 \mu\text{m}$ diameter. Reflectance spectra for these samples are presented in Figure 4.

3.2.2.3. Terrestrial Volcanic Glasses

A suite of Middle Ocean Ridge Basalt (MORB) glasses were provided by Dr. Alberto Saal (Brown University) to assess ESPAT- $\text{H}_2\text{O}\%$ trends to explore volcanic samples with a wider range in water content than present in the synthetic lunar glasses.

Two criteria were used for selection of these samples. First, the water content should be less than 2000 ppm (0.2 wt.%), which is an appropriate range for lunar materials. Second, the samples should be as visually homogeneous and free of alteration as possible. Four samples in total were examined, and absolute water content of these glasses were previously measured with SIMS [Shimizu *et al.*, 2015]. The sample information and their water contents are listed in Table 5. These samples were sieved into four particle size ranges (<45 μm , 32-53 μm , 63-75 μm , and 106-125 μm) to determine how H₂O%-ESPAT trends may be affected by particle size and for comparison to the numerical ESPAT simulations described above. Stepwise heating experiments similar to what was done for the anorthosite were carried out, but no correction for organic contaminants was necessary. Their spectra are shown in Figure 5. The H₂O%-ESPAT trends for MORB glasses within the different particle size groups are plotted in Figure 2.

3.3. Mapping of Lunar Surface Water with M³ Data

As discussed above and as will be demonstrated below, ESPAT values are linearly correlated to water content, thus maps of lunar surface water can be calculated directly from global maps of ESPAT values calculated from M³ spectra. This is done by first converting the thermally corrected M³ reflectance spectra to single scattering albedo (SSA) spectra, which is accomplished using the procedures described in *Li and Milliken* [in review]. Reflectance spectra are converted to SSA using the model of *Hapke* [1993] (e.g., Equation 1) and adopting the parameterization of *Li and Li* [2011]. The resulting SSA spectra can then be used to calculate the ESPAT values for each spectrum (M³ pixel) at a specified wavelength using Equation 2. For this study, we used M³ band 82

($\sim 2.85\mu\text{m}$) to avoid the edge of the detector (band 85) and because it is close to the typical absorption maximum ($\sim 2.9\mu\text{m}$) for water-bearing materials. These procedures are carried out for each M^3 spectral image cube.

Individual image cubes are then map-projected using the associated geometrical information, where we adopt a simple cylindrical map projection. The individual images are then mosaicked to produce a global map of M^3 ESPAT values at $\sim 2.85\mu\text{m}$. M^3 image cubes from all optical periods are employed to create the best coverage global map. The mean ESPAT value is applied for overlapping pixels.

The resulting map is further improved by filtering the data to minimize the effects of several complicating factors due to spectral artifacts and low signal-to-noise ratios (SNR) for some M^3 data (e.g., spectra acquired under poor solar illumination). The $1.55\mu\text{m}$ wavelength (band 47 of M^3 data) is utilized to remove the thermal effects as mentioned above. However, in some pixels an anomalous decrease in reflectance is observed at band 47 as shown in the schematic plot in Figure 6. Because the exact reflectance value of band 47 for these pixels is unknown, we mask all pixels if they have this type of artifact (Figure 7). Pixels exhibiting this type of artifact are concentrated at polar regions, suggesting the effect may be due to the low signal to noise ratio of M^3 data at these areas where solar illumination is weak.

To remove pixels associated with low signal, which may lead to false positive detections of absorptions, we calculate a signal to noise ratio index (SNRI) based on the difference between measured spectra and versions that have been smoothed with a cubic spline algorithm [De Boor, 1978]:

$$SNRI = \frac{\left(\sum_{i=2}^{73} abs((r_i' - r_i)/r_i') \right)}{72} \quad (5)$$

where r_i' and r_i are the reflectance values from the smoothed and measured spectra at band i , respectively. Wavelengths $>2.5 \mu\text{m}$ are not included in the index calculation due to the potential propagation of artifacts at band 47 to ‘water’ absorption bands centered at $\sim 2.9 \mu\text{m}$ during thermal removal of M^3 data, as discussed in the preceding paragraph. Example spectra showing different SNRI values are presented in Figure 8. An empirical limit of $SNRI > 0.1$ was chosen to mask pixels with low signal. Pixels that were above this threshold and thus masked from the final M^3 maps are shown in Figure 9; nearly all are concentrated near the poles, as expected given low illumination conditions and thus lower signal in these regions.

Uncertainties in ESPAT values resulting from the potential 2% uncertainty associated with the thermal correction were also evaluated. ESPAT values for each pixel in the regions of interest studied by *Li and Milliken* [in review] were calculated based on M^3 spectra that were thermally corrected using the Diviner surface temperatures. These values were then compared with ESPAT values derived from M^3 data that were thermally corrected using the empirical approach described in section 3.1, which may lead to $\pm 2\%$ uncertainty in reflectance. Results of this comparison show that ESPAT values calculated from thermally corrected spectra based on the empirical method may differ by 20% (relative) compared with ESPAT values determined from spectra corrected using actual Diviner-based temperatures. Because conversion of ESPAT to $\%H_2O$ is a simple scalar (the value of which is particle-size dependent), the relative uncertainty in estimated water

content that is associated with potential uncertainty in ESPAT values propagated from uncertainty in the thermal correction is also 20%.

4. Results

4.1. ESPAT-%H₂O Trends from Laboratory Data and Simulations

Based on the results of *Milliken and Mustard* [2007a; 2007b], it is expected that ESPAT values will be linearly correlated to water content but that the slope of the line will vary as a function of particle size. Our experimental results confirm this; wt.% H₂O is linearly correlated with ESPAT for each type of material but the slope of the %H₂O-ESPAT trend differs for different particle size groups (Figure 2). Observed changes in slope as a function of particle size are in agreement with results of *Milliken and Mustard* [2007b]: smaller particles exhibit steeper %H₂O-ESPAT trends. In addition, the three sample types (anorthosite, synthetic glasses, MORB glasses) all follow a similar %H₂O-ESPAT trend for the <45 μm particle size (Figure 2).

The numerically simulated %H₂O-ESPAT trends are shown as dashed lines on Figure 2 for comparison with measured values. Though there are some deviations between measured values and predicted trends, the agreement is generally quite good between the different MORB particle size groups and predicted slopes. Together, these observations suggest %H₂O-ESPAT trends are 1) linear for the examined range of water content, 2) linear for lunar-relevant compositions, and 3) similar in slope for different compositions. These results are in agreement with those of *Milliken* [2006] and *Milliken and Mustard* [2005; 2007a,b] where similar trends were observed for a wide variety of

other hydrated phases. Based on these results, ESPAT values derived from M^3 data are expected to be an appropriate linear proxy for water content.

4.2. Results from Mapping of M^3 Data

Based on the preceding section, it is clear that in order to convert ESPAT values derived from M^3 data to estimates of water content it is first necessary to make an assumption about particle size of the lunar regolith at the optical surface. Such values are not known for each M^3 pixel, but the likely range of particle sizes of lunar regolith can be constrained based on Apollo soil samples. It has been shown that the lunar surface is dominated by fine-grained regolith (>99.5% areal fraction [Bandfield *et al.*, 2011]), and the particle size for typical lunar regolith has an average value of 60 - 80 μm [Heiken *et al.*, 1991]. However, the optical (reflectance) properties of lunar soils are largely controlled by smaller particles with diameters of 10 – 20 μm [Pieters *et al.*, 1993].

As shown in Figure 2, the $\text{H}_2\text{O}\%$ -ESPAT trends for <45 μm and ~63-75 μm particle sizes are both linear but the slope is higher for the smaller particle size range. Though it is contrary to the demonstrated role of the finest fraction in reflectance spectra of lunar soils, adopting the $\text{H}_2\text{O}\%$ -ESPAT trend for the larger (63-75 μm) particle size provides a conservative, minimum estimate of water content when applied to the M^3 data. Under this assumption, water content for each pixel can be estimated as being equivalent to ~59% or roughly half of the corresponding ESPAT value. The original ESPAT values and associated water contents that result from this assumption are presented in Figure 10. Water contents at Apollo sampling latitudes ($\sim\pm 30^\circ$) are estimated from the derived ESPAT map by assuming a 60 – 80 μm particle size and results are compared with

measurements from bulk Apollo samples (Figure 11). Our estimation of lunar surface water at these latitudes exhibits broad agreement with values measured from those samples.

4.2.1. Comparison between Water Content and Latitude and Longitude

The strongest variation in ESPAT (and thus water content) seen in our water map (Figure 10) is as a function of latitude. Equatorial latitudes ($< \pm 30^\circ$) typically lack evidence for widespread water absorptions, similar to the findings of *Pieters et al.* [2009], but enhanced water signatures are observed at higher latitudes starting from $\sim 30^\circ$ in both the northern and southern hemispheres (Figure 10). The water content increases from ~ 100 ppm at 30° N/S to ~ 500 ppm at 60° N/S and to ~ 1000 ppm near the poles (Figure 10). The water content of all pixels at each is averaged along their longitude and plotted in Figure 14a. A strong correlation between water content and latitude is apparent from the equator to poles. There is no clear correlation between water content and longitude at a global scale.

4.2.2. Comparison Between Water Content and Optical Maturity

We compared optical maturity (OMAT) values calculated from the Clementine dataset (resampled from 100 m/pixel Clementine resolution to match the 280 m/pixel resolution of our M^3 maps) as an index for surface exposure age [*Lucey et al.*, 2000]. OMAT is a parameter derived from the visible optical properties of lunar materials and has been used as a proxy for degree of space weathering, where higher OMAT values indicate less space weathering (i.e., ‘fresh’ or ‘immature’ soils). Though OMAT values

cannot indicate exposure ages older than Copernican (~ 1.2 Ga), they are roughly indicative of maturity for typical lunar particles with mean sizes of 60-80 μm [Heiken *et al.*, 1991].

A plot of OMAT versus ESPAT for all longitudes in the $\pm 30^\circ$ latitude zone (Figure 12) suggests that water content (ESPAT) does not vary strongly as a function of optical maturity. This may be because ESPAT values at these latitudes are largely close to zero, but OMAT values less than ~ 0.14 (increased optical maturity) exhibit a weak increase in ESPAT values. This may be a weak indicator that more mature materials accept solar wind implantation more efficiently, as is observed in laboratory experiments [Ichimura *et al.*, 2012], but not all pixels with low OMAT values exhibit this trend. A weak positive correlation between optical maturity and ESPAT is observed at latitudes between 30° and 60° in both southern and northern hemisphere (Figure 12), and this correlation becomes even strong at higher latitudes of 60° - 70° . It is not possible to accurately determine trends at latitudes above 70° because of lower signal to noise ratio of M^3 data in polar regions. These results indicate that OMAT and ESPAT are linearly correlated but that this correlation is strongly latitude-dependent.

4.2.3. Comparison Between Water Content and Surface Composition

There are no strong differences in water content (ESPAT values) between mare and highland regions for a given latitude (Figure 10). As noted above, most variations in hydration at the optical surface can be described as a function of latitude or optical maturity. Interestingly, KREEP-like lithologies within Procellarum basin do not show enhanced water content, nor do Ti-rich regions such as Tranquilitatis. However, some

(but not all) regions where crystalline plagioclase exposures have been identified [*Hanna et al.*, 2014] show enhanced hydration features (Figure 13). Major exceptions to the apparent composition-independent nature of surface hydration are the lunar pyroclastic deposits. Nearly all deposits previously mapped as large pyroclastic deposits [*Gaddis et al.*, 2003] exhibit water contents that are anomalously high compared to surrounding terrains, regardless of latitude and optical maturity (Figure 10).

4.2.4. Water Content Variations as A Function of Local Time of Day

Reflectance data for approximately one million pixels located at latitude $\sim 14^\circ\text{N}$ to 58°N and longitude $\sim 200^\circ\text{E}$ to 278°E were sampled by M^3 at three different local time periods: morning (6:00-10:00 am), noon (10:00 am – 2:00 pm), and afternoon (2:00 – 6:00 pm). These pixels were grouped based on their acquisition time (morning, noon, and afternoon) and mosaicked to assess water content as a function of local lunar time. Water content of all pixels at each latitude ($\sim 0.0098^\circ$ bins) was averaged separately for the three acquisition time periods along their longitudes (0.0098° bins) and is presented in Figure 14b. It shows that pixels acquired in the morning have the highest water content among the three time periods (Blue cross in Figure 14b), whereas pixels acquired at local afternoon show slightly lower water content than those at morning but higher than those at noon (red circles, Figure 14b). It shows not very promising crossover between pixels acquired at noon and afternoon at latitudes beyond $\sim 50^\circ$, which may be due to topographical effects. When the latitude is greater than $\sim 55^\circ$, the diurnal variation in water content is no longer apparent (Figure 14b).

5. Discussion

The presence of water on the Moon at a global scale is highly suggestive that most of this water is sourced from the solar wind. This can be further validated by comparing our mapping results at equatorial regions with theoretically predicted values (section 2.2.1) and measurements from Apollo soil samples, for which the water is attributed mostly to solar wind [Liu *et al.*, 2012; Stephant and Robert, 2014].

We do not observe any hydration anomalies associated with impacts. However, at equatorial regions, in contrast to most highland and mare that exhibit no hydration features, almost all very large pyroclastic deposit (areal expansion $>1000 \text{ km}^2$), such as Aristarchus, Montes Harbinger, South West of Mare Humorum, Rima Bode, Sulpicius Gallus, mare Vaporum, and south of Mare Moscoviense [Gaddis *et al.*, 2003], exhibit persistent hydration anomalies (Figure 10), suggesting additional sources of water. Their ESPAT values are over ten times greater than the average ESPAT at the same latitudes. The particle size of volcanic glasses measured from Apollo samples is $\sim 30 - 40 \text{ }\mu\text{m}$, which can only accommodate a factor of two difference in ESPAT values (and thus water content) compared with lunar regolith with $60 - 80 \text{ }\mu\text{m}$ size particles (Figure 2).

There is no obvious water contribution from impacts because of a lack of correlation between water content and impact craters or ejecta at these locations. These enhanced water signatures are also not likely to be contributed by solar wind because laboratory experiments show that glasses are the least efficient at accepting solar wind to form hydroxyl [Hibbitts *et al.*, 2011]. Water sourced from the lunar interior has been identified from Apollo volcanic glasses sampled from pyroclastic deposits at Apollo 15 and 17 landing sites [Saal *et al.*, 2008; Hauri *et al.*, 2011]. The enhanced water features

at these pyroclastic deposits may thus be indicative of volatiles sourced from the lunar interior, and this idea will be explored in more detail in a separate study.

The lunar surface water distribution and variation are primarily correlated to latitude, which is a spatial manifestation of control by temperature. The latitudinal variation of lunar surface water (Figure 10 and 14a) may be associated with the lower temperatures at polar latitudes and consequently slower rates of diffusion in these regions. However, we cannot determine how the average ESPAT/water content varies for latitudes higher than $\sim \pm 80^\circ$ due to low signal to noise ratios of M^3 data and large areas of shadowed regions (no reflectance data available). Regardless, it is clear that the diurnal variation in lunar surface water content (ESPAT) gets weaker towards the poles (Figure 14b), which is entirely consistent with increased water retention and accumulation due to lower temperatures (slower diffusion of hydrogen). Thus, more water is expected to accumulate in lunar regolith with increasing exposure time at polar latitudes where it is thermally more stable. This is in accordance with the observation that only high latitudes (i.e., $> 60^\circ$) exhibit a strong linear correlation between OMAT and water content (Figure 12).

Some locations with exposed crystalline plagioclase at higher latitudes also show promise for enhanced water features, including areas near Lorentz crater, southern Orientale, and southern Humorum (Figure 13). In this thermal regime we observe that materials with higher crystallinity (e.g., ‘crystalline’ plagioclase) may be more efficient at accepting solar wind to form hydroxyl, as suggested by laboratory experiments [Hibbitts *et al.*, 2011], and water content increases with surface exposure as estimated via OMAT. Together, these results indicate that temperature is the primary control on the distribution

and retention of water linked to solar wind processes, and such water is transient at the optical surface for equatorial and tropical latitudes. However, at higher latitudes the surface temperatures are low enough over the course of a lunar day to maintain water produced by the solar wind.

6. Conclusions

Water (OH and/or H₂O) at the optical surface of the Moon has been quantitatively mapped using spectral images acquired by the Moon Mineralogy Mapper instrument. Laboratory measurements of lunar-relevant materials and numerical simulations that relate water absorption strength to water content confirm that Hapke's effective particle absorption thickness (ESPAT) parameter is linearly correlated to water content. As such, this parameter can be used as a proxy for water content at the lunar surface, and absolute water contents can be estimated if particle size for lunar regolith is known or assumed. A conservative estimate of lunar regolith being optically dominated by particles ~60-80 μm in diameter yields similarly conservative estimates of water content, and assuming smaller particle sizes would yield higher estimates.

Estimated water contents at equatorial and tropical latitudes, including the Apollo sampling sites, are commonly <100 ppm, in broad agreement with values measured for the Apollo soils. Water content is lowest at these latitudes during local noon and higher in afternoon and morning. In contrast, water contents at high latitudes approaches values of ~1000 ppm and appears to be stable throughout the course of a lunar day. These observations are consistent with most water at the optical surface being produced by interaction of the solar wind with the regolith, where temperature-dependent diffusion

controls diurnal migration of water. Because of this temperature control, water content varies primarily as a function of latitude, with optical maturity (surface exposure) playing a subordinate role.

There are no strong differences in water content between mare and highland regions, though such trends cannot be ruled out if they are within the uncertainties of the methods presented here or if any expected differences are smaller than the detection capabilities of M^3 . In contrast, nearly all large lunar pyroclastic deposits exhibit a distinct increase in hydration relative to surrounding terrains, and this distinction persists even at local noon when surface temperature (and thus loss of solar wind H^+) is highest. This indicates that some water observed within lunar pyroclastics may represent endogenous sources, such as volatiles in magma source regions, and further study of this possibility is warranted.

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Table Captions

Table 1. Pyrolysis measurements of water and δD for bulk Apollo samples.

Table 2. SIMS measurements of water and δD for bulk Apollo samples.

Table 3. Sample weights and weight loss at each step of heating experiments for anorthosites.

Table 4. Water contents of synthesized lunar green and orange glasses

Table 5. Sample information and references for MORB glasses

Table 6. Sample weights and weight loss at each step of heating experiments for MORB glasses

Figure Captions

Figure 1. Water contents of bulk Apollo samples measured via pyrolysis and SIMS techniques are plotted with their δD values, the δD ranges of carbonaceous chondrites (CC), interstellar materials, and comets are from [Robert *et al.*, 2000], the δD range of the Earth is from [Lecuyer *et al.*, 1998], and the δD range of the Sun is from [Hashizume *et al.*, 2000; Robert *et al.*, 2000].

Figure 2. The $H_2O\%$ -ESPAT trends derived from laboratory experiments and simulations for a wide variety of compositions and particle sizes.

Figure 3. Single scattering albedo (SSA) after continuum removal at 2.5 μm to 3.8 μm for anorthosite of our stepwise heating experiment results; the blue solid arrow indicating the hydration absorption band centered $\sim 3 \mu m$, whereas, the black dash arrow pointing organic matter absorption bands.

Figure 4. Reflectance spectra of lunar orange and yellow glasses synthesized under the lunar condition.

Figure 5. Reflectance spectra of four particle size groups of MORB glasses after continuum removal; Sample D38A is applied to do stepwise heating experiments.

Figure 6. A schematic plot shows the artifacts at band 47 of M^3 data.

Figure 7. Pixels shown in white are masked due to artifacts at band 47.

Figure 8. Examples of spectra have different SNRI values from low to high, note that pixels with $SNRI > 0.1$ are masked.

Figure 9. The pixels in white are masked due to their low signal to noise ratio.

Figure 10. The global map of ESPAT at $\sim 2.9 \mu m$ calculated from the band 82 of M^3 data overlain on the Lunar Orbiter Laser Altimeter (LOLA) shaded relief, the $H_2O\%$ is calculated from the $H_2O\%$ -ESPAT trend derived from laboratory experiments and simulations (Figure 2), assuming the particle size of 60-80 μm , Apollo landing sites are labeled on this map.

Figure 11. Comparison between mapped water content (assuming 60 - 80 μm particle size) at Apollo sampling latitudes (between $\pm 30^\circ$) and that measured from bulk Apollo samples.

Figure 12. The comparison between the water content (ESPAT) and optical maturity (OMAT) of lunar surface regolith.

Figure 13. The crystalline plagioclase exposure locations [Hanna *et al.*, 2014] overlain on our mapped lunar surface water.

Figure 14. (a) The latitudinal variation of ESPAT ($\sim 0.0098^\circ$ bin); (b) the diurnal variation of lunar surface water ($\sim 0.0098^\circ$ bin).

Tables

Table 1

Reference	Sample Name	H ₂ O (ppm)	δD (‰)	Temperature
Merlivat et al., 1974	15600 regolith	46.8	-59	>600°
	15600 regolith	68.4	-95	
	68501 regolith	93.6	-115	
	72501 regolith	90	-88	
	72501 regolith	82.8	-82	
	78501 regolith	104.4	-72	
	15229 agglutinate	228.6	-52	
	15229 agglutinate	7.2	-242	
	70215 basalt	48.6	-165	
	75035 basalt	44.6	-92	
	75035 basalt	50.4	-252	
Epstein and Taylor, 1973	15021.4 regolith	48.6	-252	630°-melting
	64421.21 regolith	109.8	-280	500°-melting
	65513.1 regolith	268.2	-173	500°-melting
	62221.8 regolith	199.8	-88	500°-melting
	74220.22 regolith	46.8	-154	500°-melting
Friedman et al., 1971	12030.30 regolith	7	-300	430°-1025°
Friedman et al., 1970	10046.21 agglutinate	455	-756	300°-950°
	10046.22 agglutinate	372	-576	300°-950°
	10060.11 agglutinate	152	-865	300°-950°
Epstein and Taylor, 1970	10084.2 rock and minerals	90.4	-380	500°-1400°
	10084.1 rock and minerals	208.4	-268	500°-1400°
	10061 rock and minerals	160.2	-409	500°-1400°
Epstein and Taylor, 1972	14422 regolith	48.6	-419	550°-600°
Friedman et al., 1974	66095.62 rock	9	-194	690°-1350°
	66095.31 rock	13.5	-153	690°-1350°

Table 2

Sample Name	H ₂ O (ppm)	δD (‰)	Reference
10084 Agglutinate	470	4555	Liu et al., 2012
	27	5413	
	225	-562	
	282	-789	
	246	-843	
	161	-731	
	188	191	
	207	267	
70051 Agglutinate	200	-711	
	209	-844	
	203	-781	
64501 Agglutinate	79	-558	Saal et al., 2013
74220 Glass	5.0	446	
	3.5	194	
	4.6	283	
	5.5	412	
	4.6	453	
	4.9	291	
	4.4	235	
	3.8	416	
	3.2	269	
	8.7	392	
	6.7	299	
	5.7	330	
	3.7	406	
	3.1	396	
15426 Low Ti glass	3.5	307	
	69.3	474	
	51.9	347	
	40.7	349	
	39.2	459	
	34.8	804	
	32.7	2199	
	30.8	2258	
	28.1	843	
	27.9	545	
	27.8	2244	
	25.1	502	
	22.8	469	
	22.0	1210	
15427 Very Low Ti glass	16.8	2160	
	16.3	580	
	33.8	578	
	28.6	1802	
	14.4	4045	
	12.1	1043	
	11.4	830	
	10.8	209	
	9.4	761	
	9.1	1028	
	8.7	616	
	7.4	80	
	6.9	371	
	6.4	-378	
	6.2	487	
	6.1	626	
	6.1	2	
	5.7	-616	
	5.6	-93	

	5.5	-119	
	5.5	-213	
	5.5	-139	
	5.3	318	
	5.3	837	
	5.3	50	
	5.1	523	
	4.9	273	
	4.4	-338	
	4.4	-165	
	4.2	2209	
	4.1	-733	
	3.6	-651	

Table 3

Temperature (°C)	Weight (g)	Weight loss (g)
Ambient	3.2526	0.0000
20-min Dry	3.2526	0.0000
100	3.2522	0.0004
150	3.2521	0.0001
200	3.2519	0.0002
250	3.2517	0.0002
300	3.2516	0.0001
350	3.2513	0.0003
400	3.2510	0.0003
450	3.2507	0.0003
500	3.2505	0.0002
550	3.2503	0.0002
600	3.2503	0.0000
600 - 1.5h	3.2503	0.0000
600 - 16h	3.2499	0.0004
Sample cup weight (g)	2.8945	

Table 4

Sample Name	Water Content (ppm)	Reference
Orange glass (OGV-5)	390	[Wetzel <i>et al.</i> , 2015]
Yellow glass (YG-5)	305	

Table 5

Sample Name	Initial Water Content (ppm)	Reference
D9A	976.49	
D38A	16227.00	[<i>Shimizu et al.</i> , 2015]
D44A	815.44	
D44B	888.00	

Table 6

	D38A 106-125 μm	D38A 63-75 μm	D38A 32-53 μm	D38A <45 μm
Dish weight (g)	2.8935	2.8248	2.9928	2.8940
Temperature ($^{\circ}\text{C}$)	Sample Weight (g)			
0	3.2021	3.1209	3.2468	3.1702
350	3.2018	3.1197	3.2455	3.1667
400	3.2013	3.1196	3.2454	3.1665
450	3.1990	3.1194	3.2449	3.1664
500	3.1971	3.1186	3.2440	3.1663
550	3.1966	3.1184	3.2436	3.1657
600	3.1960	3.1175	3.2436	3.1657
650	3.1958	3.1169	3.2436	3.1657
700	3.1950	3.1164	3.2436	3.1657
750	3.1943	3.1161	3.2436	3.1657
800	3.1942	3.1158	3.2436	3.1657

Figures

Figure 1

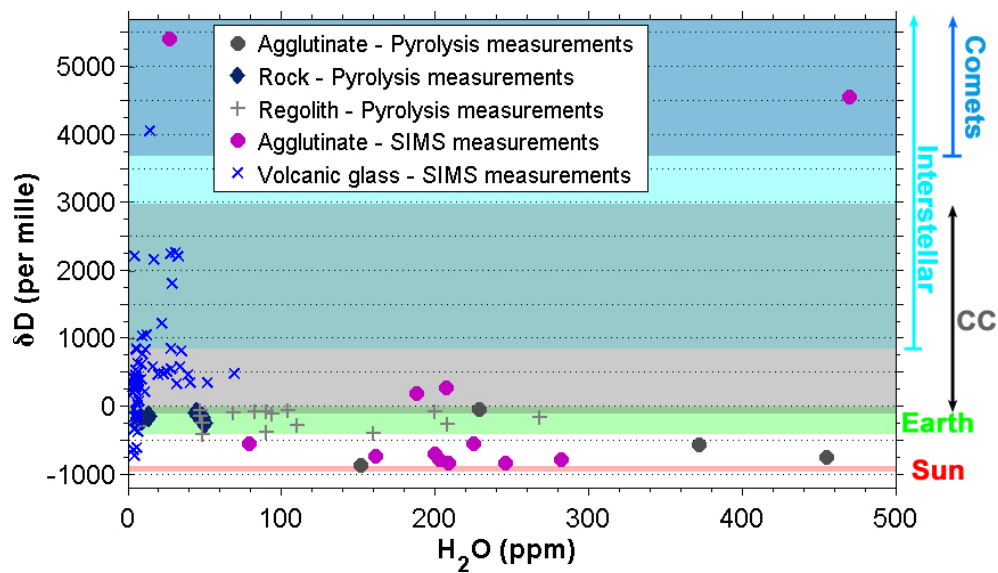


Figure 2

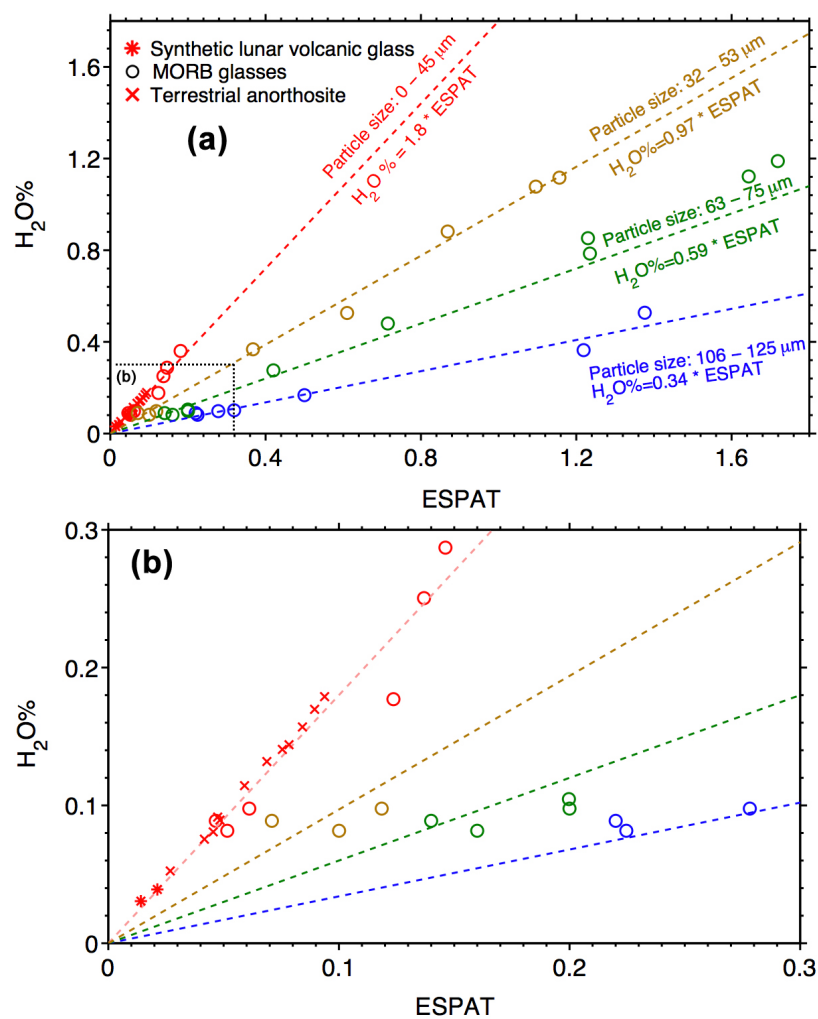


Figure 3

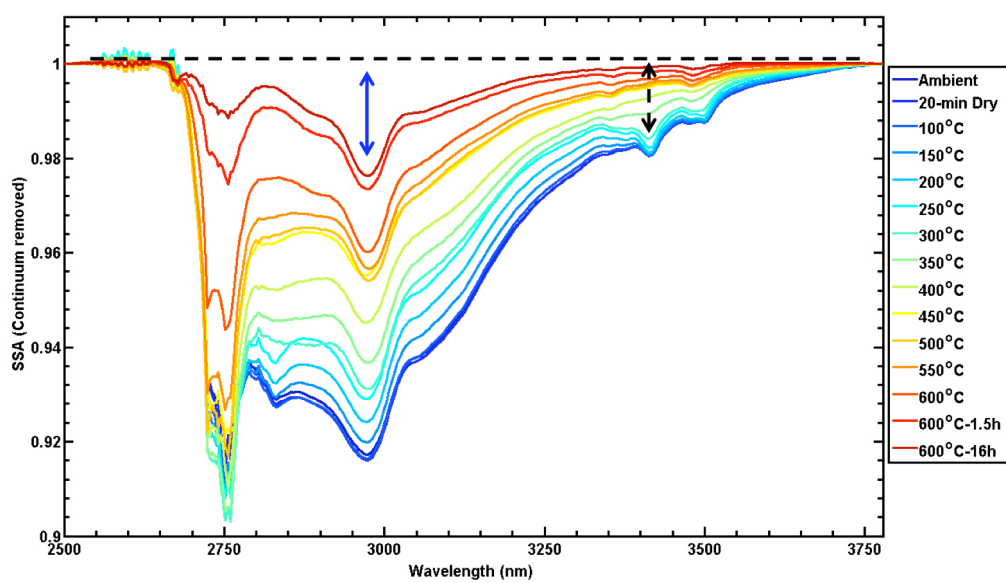


Figure 4

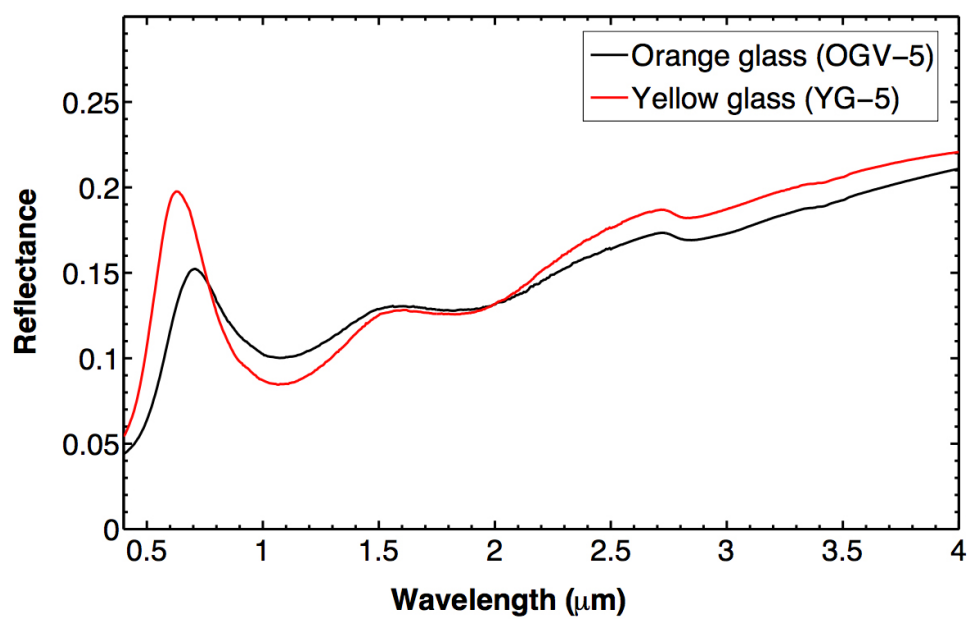


Figure 5

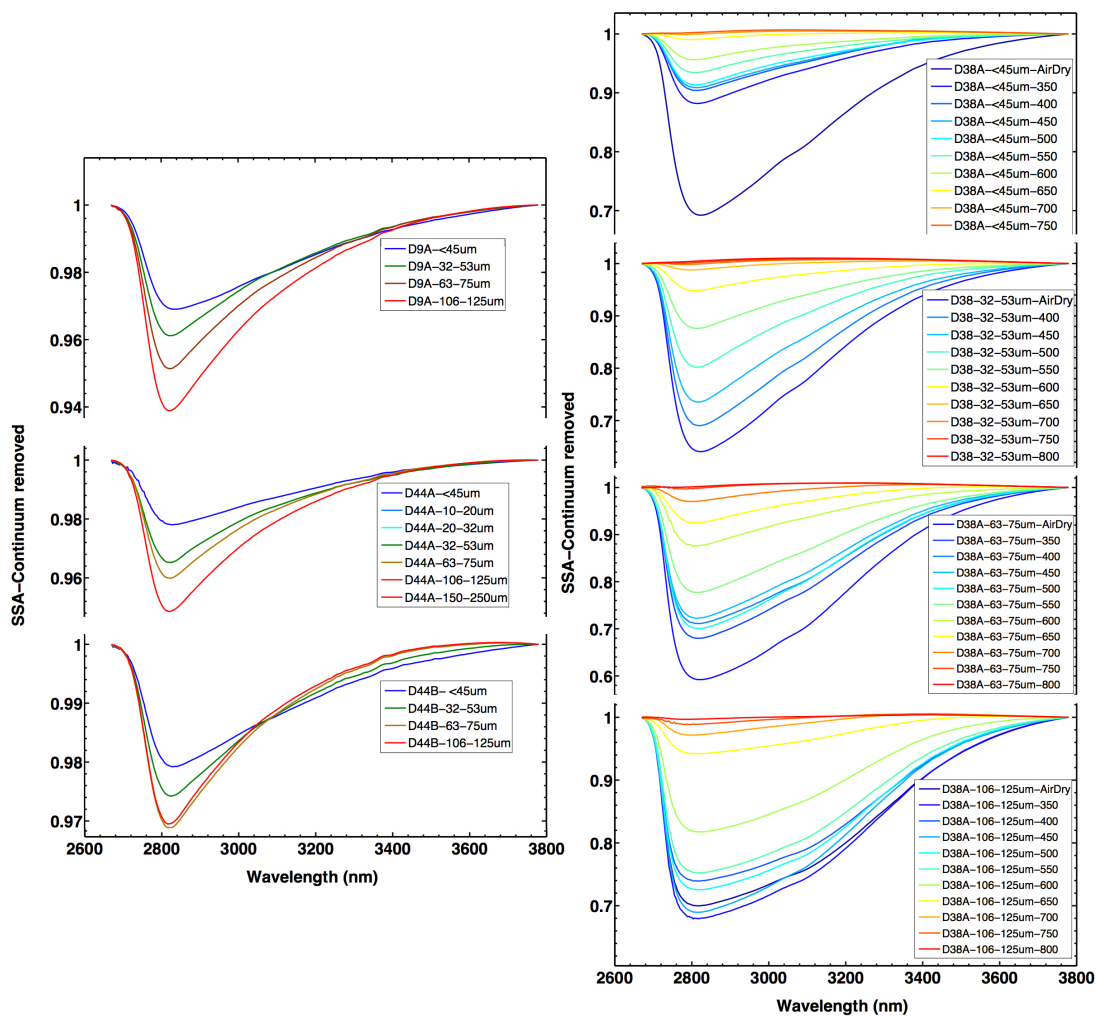


Figure 6

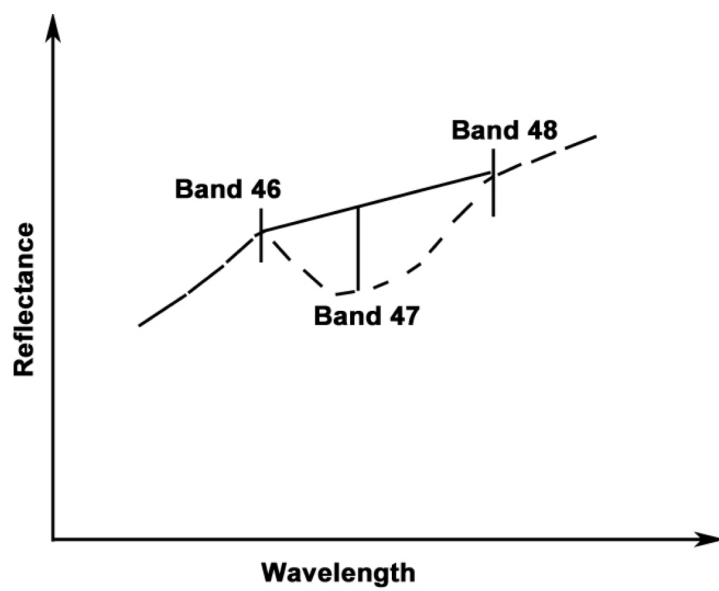


Figure 7

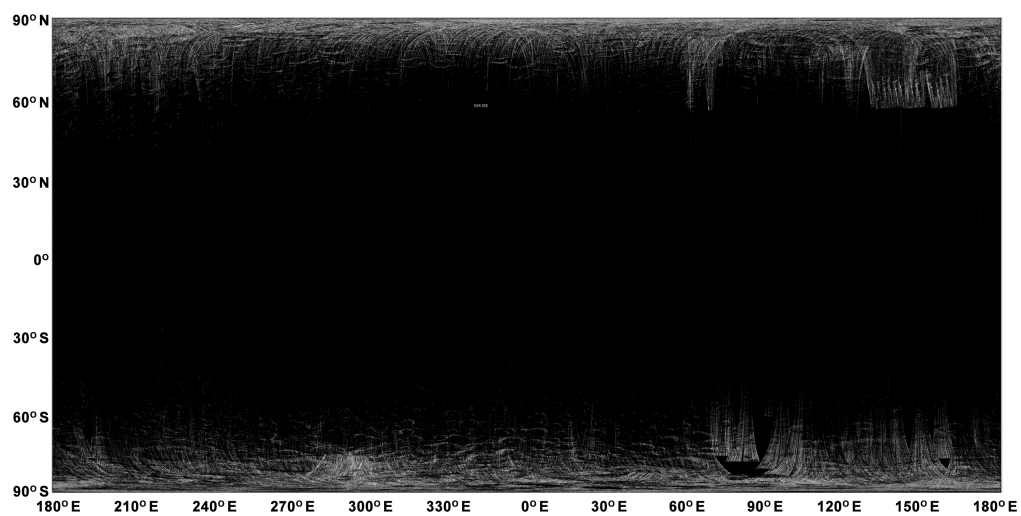


Figure 8

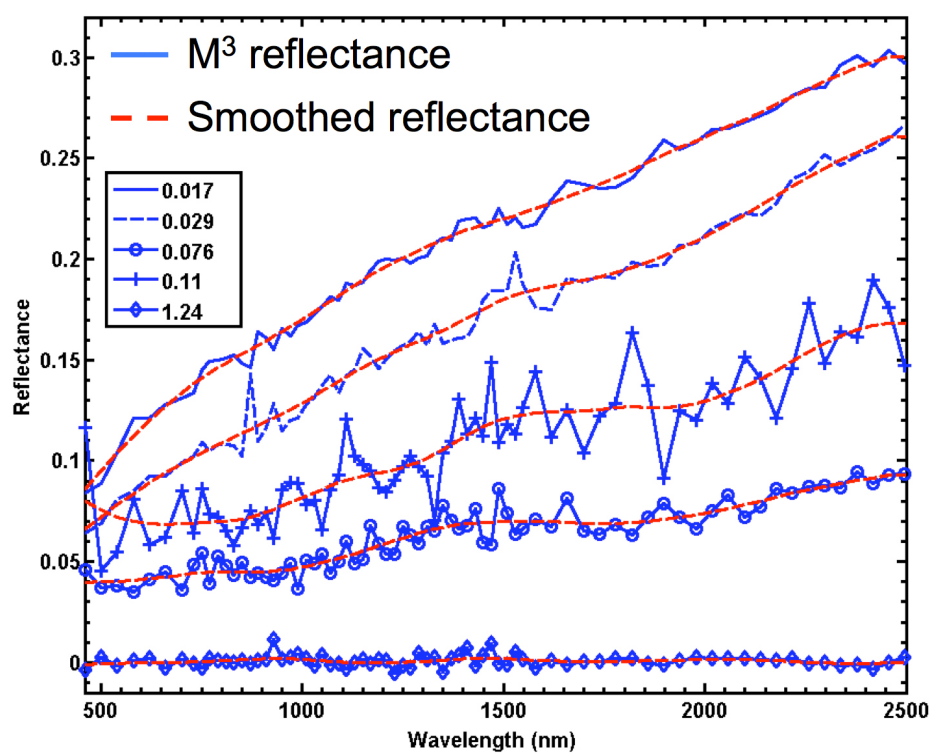


Figure 9

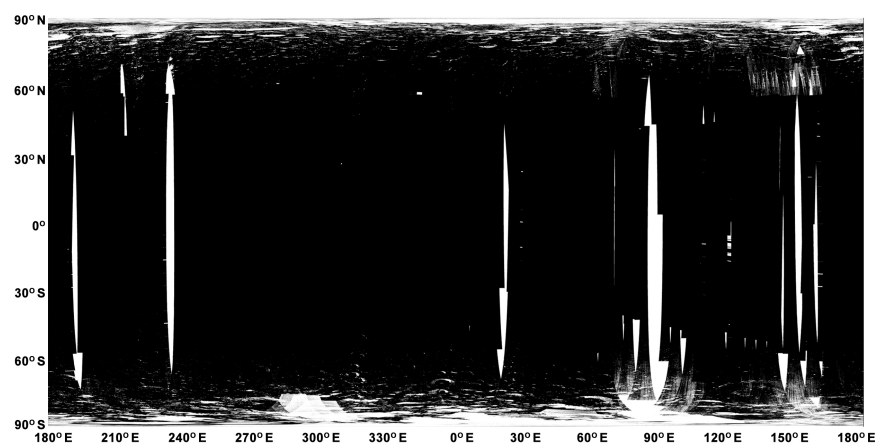


Figure 10

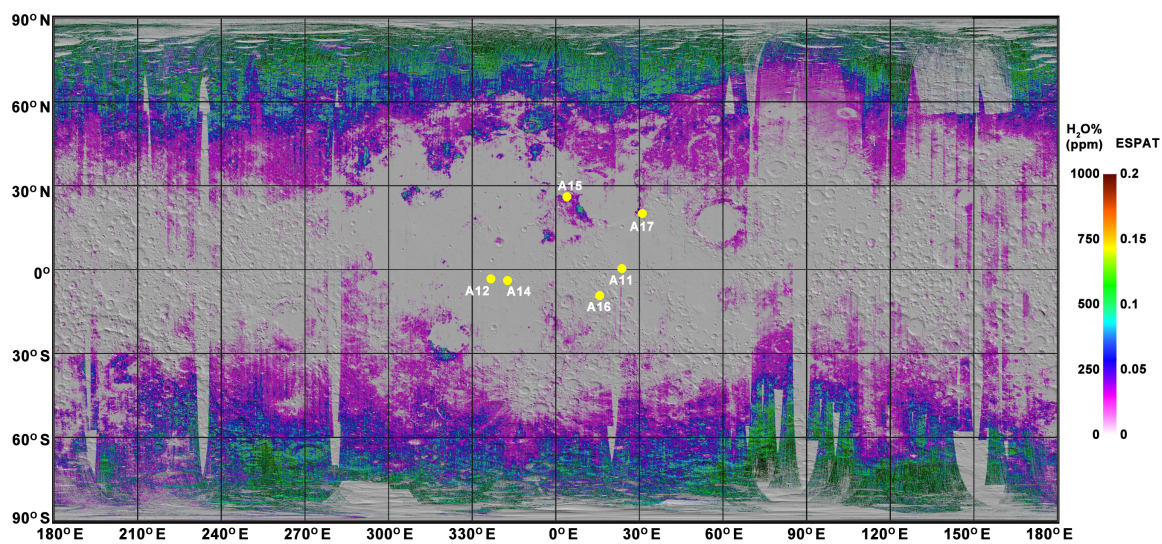


Figure 11

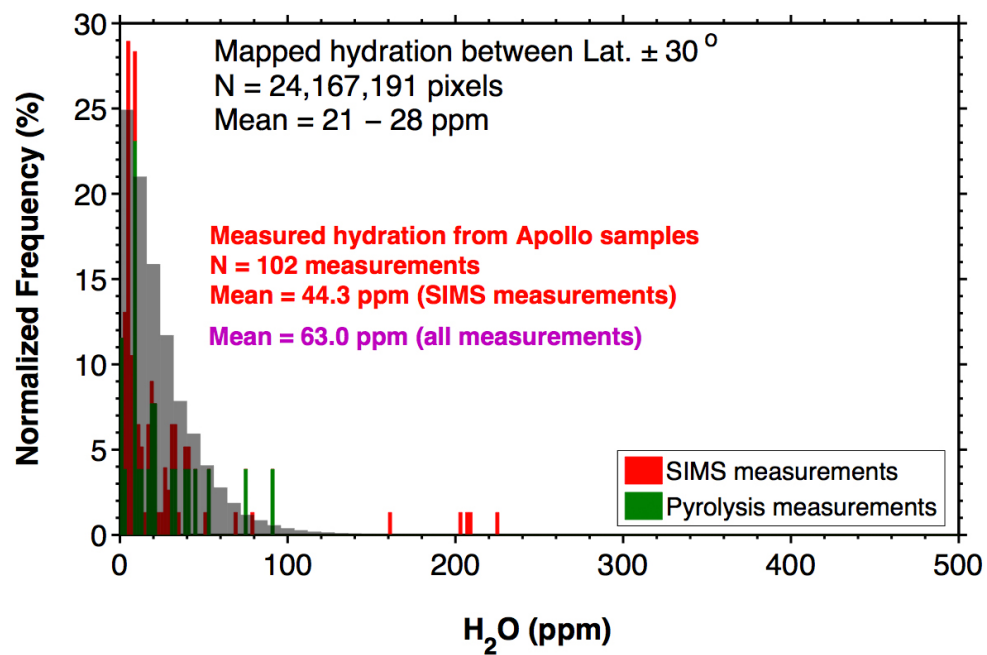


Figure 12

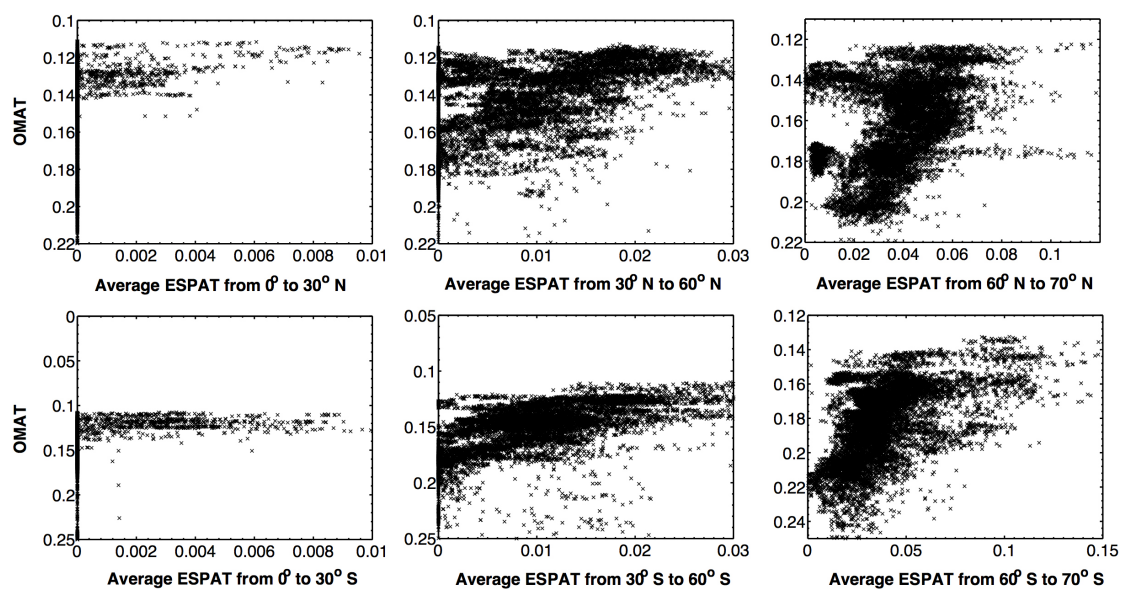


Figure 13

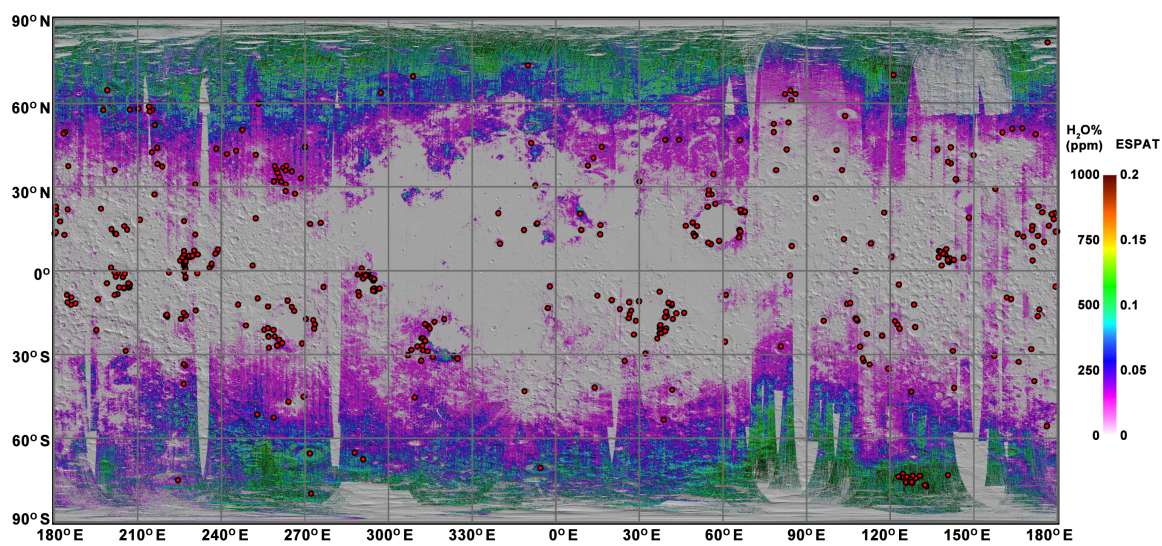
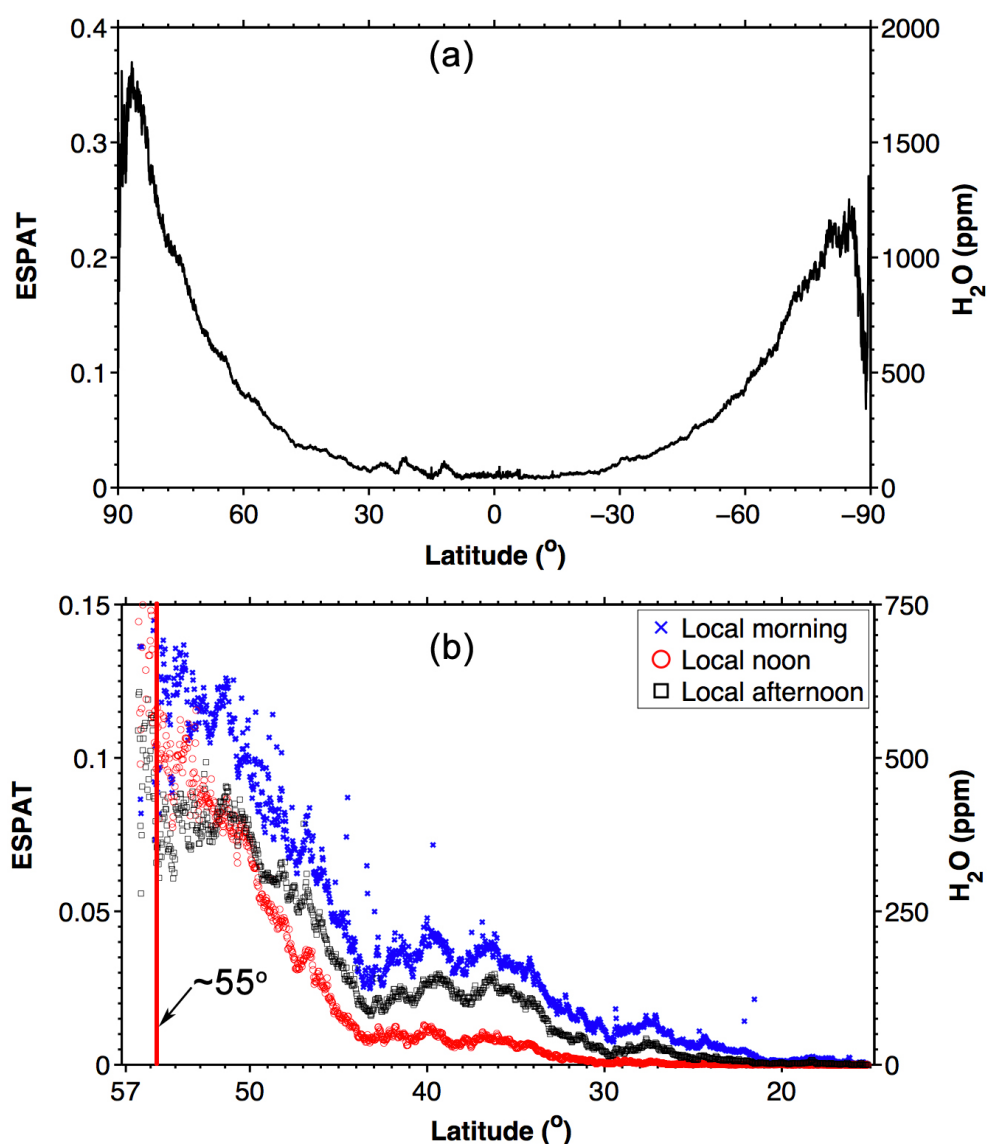


Figure 14



Chapter 3: Orbital Evidence for Water in Lunar Pyroclastic Deposits and
Implications for Volatiles in the Lunar Interior

Shuai Li

and

Ralph E. Milliken

Abstract

Constraining the distribution and abundance of volatiles such as water (H_2O and/or OH) in the lunar interior is crucial for assessing the formation, source(s), and retention of volatiles during lunar accretion and crystallization of the lunar magma ocean. Hundreds of parts per million (ppm) of water of endogenous origin has been measured in Apollo 15 and 17 volcanic glasses [Saal *et al.*, 2008; Hauri *et al.*, 2011] and even higher concentrations in lunar apatite [Boyce *et al.*, 2010; McCubbin *et al.*, 2010; Greenwood *et al.*, 2011]. However, whether or not such samples reflect the volatile inventory of the bulk Moon or instead represent unusually volatile-rich magma source regions is not clear, and contrary views hold that the lunar mantle may be relatively dry [Epstein and Taylor, 1970; Sharp *et al.*, 2010; Elkins-Tanton and Grove, 2011]. Measurements of lunar samples provide critical insight to this question but are inherently biased towards the limited number of locations that have been sampled. In contrast, near-infrared reflectance spectra acquired by the Moon Mineralogy Mapper (M^3) provide the means to characterize water at a global scale. Here we demonstrate that enhanced water signatures in M^3 spectra of lunar pyroclastic deposits and silicic-rich domes are consistent with volatiles sourced from the lunar interior. Nearly all large pyroclastic deposits exhibit these signatures, equivalent to several hundreds of ppm H_2O , and estimated abundances of water differ between inferred low- and high-Ti deposits. These results suggest water is likely present throughout the lunar mantle and that variations in abundances observed at the optical surface reflect variations in source region volatile content or magma degassing history. Water observed from orbital data can thus provide an important link between sample-scale measurements and global-scale processes.

1. Introduction

Constraining the distribution and abundance of water (hereafter the term ‘water’ is used to include H₂O and/or OH) in the lunar interior is critical for addressing important questions associated with the formation and subsequent evolution of the Moon. Is water distributed hetero- or homogeneously in the lunar interior? What would this imply about the origin and retention of lunar water over geologic timescales? Was water retained during the Moon-forming impact, was it present in the earliest history of lunar magma ocean (LMO) crystallization, or was it delivered by volatile-rich impactors after initial accretion? How did the presence of water affect the petrologic evolution of the Moon?

This study examines these questions through a study of lunar surface deposits previously identified as being associated with magmatic activity, including pyroclastic deposits and silicic domes. Near-infrared (NIR) reflectance spectra acquired from lunar orbit by the Moon Mineralogy Mapper (M³) instrument on the Chandrayaan-1 mission are used to map, quantify, and evaluate water in these deposits. We demonstrate that spectral signatures of water in pyroclastic deposits are indicative of volatiles in magma source regions, not solely products of solar wind interaction, and thus record important information about interior volatile distribution and magma degassing during lunar evolution.

2. Background

Water brought to the lunar surface environment that is sourced from the lunar interior, such as water released during volatile-driven pyroclastic eruptions, has the potential to be been emplaced and preserved in surface materials [*Watson et al.*, 1961;

Epstein and Taylor, 1970; *Arnold*, 1979; *Saal et al.*, 2008]. Hundreds of parts per million (ppm) of water has been identified in Apollo 15 and 17 volcanic glasses, providing direct evidence for water in magma source regions in the lunar interior [*Saal et al.*, 2008; *Hauri et al.*, 2011]. Higher amounts of water have been measured in apatite from lunar basalts [*Boyce et al.*, 2010; *McCubbin et al.*, 2010; *Greenwood et al.*, 2011] also indicating possible MORB-like water contents in the lunar mantle. Perhaps most intriguing, the detection of water in plagioclase from ferroan anorthosites [*Hui et al.*, 2013] suggests not only that the Moon contains appreciable water but also that this water may have been present very early during crystallization of the lunar magma ocean.

However, other lines of evidence, including petrologic models of lunar magma ocean crystallization, suggest that the bulk interior may not have such high concentrations of water [*Epstein and Taylor*, 1970; *Sharp et al.*, 2010; *Elkins-Tanton and Grove*, 2011]. Indeed, it is not clear to what extent volatile contents deduced from Apollo samples are indicative of values for the bulk Moon or whether they instead may represent anomalous, volatile-enriched magma source regions. Existing lunar samples are not likely to resolve this question given that there are limited sampling locations for Apollo and Luna samples and that specific source regions for lunar meteorites are unknown. However, remote sensing data acquired from lunar orbit provide an alternative way to assess the global distribution of water in surface materials, including those associated with magmatic processes.

Vibrational absorption features indicative of OH and/or H₂O have been observed in NIR reflectance spectra of the lunar surface acquired by the EPOXI [*Sunshine et al.*, 2009], Cassini VIMS [*Clark*, 2009], and Chandrayan-1 Moon Mineralogy Mapper (M³)

instruments [*Pieters et al.*, 2009]. Although EPOXI and Cassini VIMS data provide excellent spectral coverage, these datasets are rather limited because of their low spatial resolution (>10 km/pixel) compared with the size of pyroclastic deposits and lack of global coverage. In contrast, M^3 data provide global NIR coverage at ~ 280 m/pixel spatial resolution or better, but wavelengths >2 μm are commonly affected by the presence of thermally contributed radiation that can weaken and mask potential water absorption features [*McCord et al.*, 2011]. These issues were mitigated in previous studies of M^3 data by employing a first-order thermal correction developed by *Clark et al.* [2011] and by examining regions at mid to high latitudes where surface temperatures are colder and such effects are weak or absent [e.g., *Pieters et al.*, 2009]. A study by *McCord et al.* [2011] integrated M^3 spectra with surface temperatures estimated from Lunar Reconnaissance Orbiter (LRO) thermal infrared Diviner measurements in a more detailed approach to remove thermal effects, but only for select study regions.

A new empirical thermal correction model for M^3 data was recently developed by *Li and Milliken* [in review] based on an observed correlation in reflectance values at wavelengths of ~ 1.55 and 2.54 μm for laboratory spectra of a wide range of lunar samples, including isolated volcanic glass beads and soils with pyroclastic components (e.g., orange soils from the Apollo 17 site). The reflectance correlation observed in the lab spectra was also observed in M^3 data that were independently corrected using Diviner-based temperatures in conjunction with a Hapke-based radiative transfer model [*Li and Milliken*, in review]. These results demonstrated that thermal radiance could be estimated, and subsequently removed, at M^3 wavelengths without the need for concurrent

temperature measurements, yielding a significant improvement in the retrieval of surface reflectance properties at wavelengths $>2\text{ }\mu\text{m}$ from M^3 data.

Reflectance values for the new thermally corrected data were estimated to be within $\pm 2\%$ or better of expected values at $2.54\text{ }\mu\text{m}$ for a wide range of compositions that typify the lunar surface, including highland, mare, and pyroclastic soils [*Li and Milliken*, 2016 under review]. The resulting thermally-corrected M^3 data thus provide a new and improved perspective on surface reflectance properties for regions of the Moon where residual thermal contributions were previously problematic, including equatorial and mid-latitude regions where surface temperatures can be in excess of 400K.

As discussed in detail by *Li and Milliken* [Chapter 2], fundamental OH and H_2O absorptions observed in M^3 data near $\sim 3\text{ }\mu\text{m}$ can be used to estimate the absolute water content of lunar surface materials. Previous studies have shown that Hapke's Effective Single Particle Absorption Thickness (ESPAT) parameter is linearly related to water content when derived at a wavelength of $\sim 2.9\text{ }\mu\text{m}$ [e.g., *Milliken and Mustard*, 2005; *Milliken and Mustard*, 2007a; 2007b; *Li and Milliken*, Chapter 2]. The slope of the ESPAT-% H_2O trend was demonstrated to be largely invariant with composition for a number of hydrated minerals and lunar-relevant materials, including hydrated volcanic glasses and a sample of anorthosite [*Milliken and Mustard*, 2005; 2007a; 2007b; *Li and Milliken*, Chapter 2]. However, both laboratory experiments and numerical simulations show that the slope of the ESPAT-% H_2O trend is dependent on particle size [*Milliken and Mustard*, 2007a; 2007b; *Li and Milliken*, Chapter 2].

Adopting a conservative estimate of $\sim 60\text{--}80\text{ }\mu\text{m}$ for the optically dominant component of lunar regolith, *Li and Milliken* [Chapter 2] estimated the water content of

the lunar surface to be <100 ppm at latitudes of $\pm 30^\circ$ and up to ~ 1000 ppm at high (polar) latitudes. The lower values are in the range of water contents measured for lunar soils via pyrolysis [Epstein and Taylor, 1970], and such surface-correlated volatiles are likely the result of solar wind implantation (though a component of terrestrial contamination cannot be ruled out) [DesMarais *et al.*, 1974; Boynton *et al.*, 1975]. Furthermore, water absorptions observed in M^3 data exhibited evidence for diurnal variation at latitudes < 55° N/S, where absorptions disappeared and water contents approached values at or near 0 during local noon and early afternoon [Li and Milliken, Chapter 2]. This variation was not observed at high latitudes where surface temperatures are lower and diffusion processes may be slower.

All of these observations are consistent with the primary water signature seen in M^3 data being the result of solar wind interaction with the uppermost surface of the lunar regolith, in agreement with previous observations of M^3 data [Pieters *et al.*, 2009; McCord *et al.*, 2011], laboratory measurements [Stephant and Robert, 2014], and theoretical models [Poston *et al.*, 2013; Farrell *et al.*, 2015]. The maximum water content of ~ 100 ppm that was observed for $\pm 30^\circ$ latitude [Li and Milliken, Chapter 2], the decrease of this signature during the course of a lunar day, and the quantitative agreement with pyrolysis measurements for bulk lunar soils suggest that ~ 100 ppm is an appropriate ‘background’ water content for bulk surface materials at this latitude range.

Any estimated water content that is in excess of this value at these latitudes may therefore be indicative of non-solar wind sources, including impact delivery or volatile-bearing magmas. The goal of this work was to search for anomalously high water contents at the lunar surface that may be indicative of such sources, with an emphasis on

analyzing pyroclastic deposits and purported silicic domes. The former are believed to result from fire fountain eruptions caused by ascent and eruption of volatile-rich magmas [Heiken *et al.*, 1974], where the size of the pyroclastic deposit (i.e., areal range) may correlate with the total volatile content of the magma source [Wilson and Head, 1981]. Silicic domes may be formed through fractional crystallization of magmas or ascent of silica-rich melts due to their immiscibility and low density [Glotch *et al.*, 2010; Jolliff *et al.*, 2011]. Water and other volatiles in the source region could have been concentrated in these melts and brought to the surface, thus both silicic domes and pyroclastic deposits have potential to provide evidence of water sourced from the lunar interior.

3. Data and Methods

3.1. Mapping Lunar Surface Water with M³ Data

The $\pm 30^\circ$ latitude zone was chosen as the focus of this study because of the low background (solar wind contribution) water contents expected for this region and because it hosts numerous pyroclastic deposits [Head, 1975; Head, 1976; Gaddis *et al.*, 2003] as well as the Apollo landing sites. Methods for thermal correction, processing, derivation of ESPAT values, and mapping of M³ data were the same as those described in Li and Milliken [in review; Chapter 2]. To estimate absolute water content for this region it was necessary to choose a representative particle size to adopt an appropriate ESPAT-%H₂O trend (slope value). We chose to follow our previous methods and used a conservative average particle size of 60 – 80 μm , consistent with values measured from Apollo soil samples [Heiken *et al.*, 1991].

Our experiments with lunar-relevant materials, which included a variety of basaltic glasses and an anorthosite, suggest $\%H_2O = 0.59 \cdot ESPAT$ for particles of this size [Li and Milliken, 2016 in prep.]. The water content for the lunar surface at $\pm 30^\circ$ latitude is thus derived from our previously derived ESPAT maps assuming a conservative value of 50% of the calculated ESPAT value (i.e., $\%H_2O = 0.5 \cdot ESPAT$). As described above, a value of 100 ppm is then subtracted from the bulk water content map to produce an ‘excess’ water content map for these latitudes (Figure 1).

3.2. Estimating Volcanic Glasses with Moon Mineralogy Mapper (M^3) Data

The concentration of volatiles such as water that are sourced from pyroclastic eruptions and that are hosted in volcanic glass may be expected to exhibit a positive correlation with glass abundance. That is, if the most significant water-bearing component in a soil is volcanic glass, then water content of the bulk soil should increase with glass content of that bulk soil. Evaluating the relationship between water content and glass abundance can thus provide an independent check to determine if the latter is the primary host of the former.

Multiple approaches can be applied to estimate the abundance of volcanic glass on the lunar surface, including radiative transfer modeling [Hapke, 1981; Shkuratov *et al.*, 1999], modified Gaussian modeling (MGM) [Sunshine and Pieters, 1993], and empirical models [Pieters *et al.*, 2002; Li, 2006; Korokhin *et al.*, 2008; Li *et al.*, 2012]. It has been shown that applying radiative transfer models to estimate the abundance of lunar surface minerals is constrained by the presence of nanophase iron [Li and Li, 2011]. Though MGM is appropriate for quantifying the position and strength of absorption bands at NIR

wavelengths, the method is restricted in its ability to quantify mineral abundances, especially for volcanic glasses that can have weak absorptions at these wavelengths.

An empirical model called partial least squares and back propagation neural network (PLS-BPNN) was designed by *Li et al.* [2012] for estimating lunar surface minerals with M³-like spectral data and validated with the lunar soil characterization consortium (LSCC) dataset. This model is advantageous compared with other empirical models, such as partial least squares and principle component regression [*Pieters et al.*, 2002; *Li*, 2006] in that it takes into account the nonlinearity of spectral mixing [*Pieters et al.*, 2002; *Li*, 2006; *Li et al.*, 2012]. However, the uncertainty of the PLS-BPNN model increases as the mineral abundance of a given component begins to exceed that of the training dataset.

The most reliable range for volcanic glass abundance is from 0 to 20 volume percent based on the model developed in *Li et al.* [2012], which was the model adopted in this study. The model was applied to eleven large pyroclastic deposits at $\pm 30^\circ$ latitude to examine correlations between independently estimated glass contents and corresponding values from the ‘excess’ water maps. Only M³ images acquired in a single optical period that provided the most spatial coverage for a given deposit were modeled in order to avoid uncertainties that might be introduced by different instrument responses under the different temperature conditions for each M³ optical period. We used OP1B images for Sinus Aestuum, Montes Harbinger, SW Humorum, Rima Bode, and SE Nectaris; OP2C images for Aristarchus, Montes Carpatus, Sulpicius Gallus, Taurus Littrow, and S Vaporum; and OP1A images for S Moscoviense.

3.3. Estimating Total Volatiles in Magma Sources with Magma Eruption Models

The magma eruption model (explosive) developed by *Wilson and Head* [1981] was used to estimate the volatile content that would be required to generate different sizes of pyroclastic deposits. Assuming the eruption is adiabatic, then equation (1) from [*Wilson and Head*, 1981] can be rewritten as:

$$\int_0^v v dv - \int_h^0 g dh - \int_h^0 \frac{fv^2}{4r} dh = \frac{\gamma}{\gamma-1} \frac{nQT}{m} \quad (1)$$

where v is the velocity of erupted melt, h is the depth where the eruption is initiated, g is gravitational constant, f is the friction factor, r is the half width/radius of the dike/conduit, γ is the ratio of heat capacity of gases, n is the mole of gasses, Q is the gas constant, T is the gas/melt temperature, and m is the gas molecular weight. The terms on the left side of equation (1) describe the kinetic energy, potential energy, and friction energy, respectively. The right side of the equation describes total energy in the volatile system assuming the eruption is adiabatic.

We can rewrite equation (1) as follows using similar manipulation procedures as [*Wilson and Head*, 1981].

$$H_2O\% = \frac{(R + 2h + Rhf / 2r)gm(\gamma-1)}{2QT\gamma} w \quad (2)$$

where R is the radius of the pyroclastic deposits, which can be estimated from orbital imagery or water maps, $h = \sim 1000$ m [*Wetzel et al.*, 2015], $T = \sim 1300$ K, $\gamma = 1.3$, $m = 28$ (all gases are converted to CO [*Wilson and Head*, 1981]), $g = 1.622$ g/s² (for the

lunar case), $f = \frac{24}{\text{Re}} + 0.01$ (Re: $10^2 - 10^5$) [Wilson and Head, 1981], w is the percentage of water in total volatiles (n) and is set to $\sim 1\%$ based on results from [Wetzel *et al.*, 2015].

Equation (2) can then be used to estimate the initial water content of magma sources for pyroclastic deposits of different areal extents. In this study we place an upper limit on water content in the source region by using the maximum measured radius for each pyroclastic deposit, though in reality a deposit may consist of numerous smaller eruptions associated with different vents that coalesce/overlap to form a larger coherent deposit. The radius (range) of each pyroclastic deposit is determined from the extent of any observed ‘excess’ water signature at each of the eleven locations. The pyroclastic ranges used in this study are listed in Table 1.

3.4. Hydration Diffusion Modeling for Volcanic Glass

A 1-D diffusion model designed for silicate melts and validated with laboratory experiments [Zhang and Ni, 2010] was applied to examine potential water loss by degassing under different cooling rates. Initial water content values were set based on estimates from the magma eruption model described in the previous section. The model is of the form

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial X}{\partial t} \right) \quad (3)$$

where $X = \frac{c/_{18.015}}{c/_{18.015} + 100 - c/W}$ is the mole fraction of water, c is wt% of water, W is molecular weight of basaltic melt, $D = c \cdot \exp(-8.56 - 19110/T)$ is the hydration diffusion

coefficient for basaltic melts [Zhang and Ni, 2010], T is the temperature of the melt and varies with the time (t), and x is the diffusion distance.

We used a finite difference algorithm to solve equation (3) [Crank, 1979]. The two boundary conditions are set as (1) $c(0, t) = 10$ (the water content in the vapor cloud is 10 ppm as indicated by [Saal et al., 2008]); (2) $c(end, t) = c(end-1, t)$ (the water content at the center equals the adjacent layer of a glass bead). The radius of volcanic glass beads is set as 50 μm . The initial temperature of melt is set at 1450 $^{\circ}\text{C}$ and the glass transition temperature is set as 850 $^{\circ}\text{C}$, which are the same value as used in [Saal et al., 2008].

A variety of cooling rates are modeled, ranging from 1 $^{\circ}\text{C/s}$ to 200 $^{\circ}\text{C/s}$. The diffusion time lasts from 0 s to the maximum fly time of melts calculated from the range of pyroclastic deposits [Wilson and Head, 1981]. The modeled diffusion curves are the average water retention percentage of all volcanic glasses for a given pyroclastic range (from 0 s to the maximum fly time). The volcanic glasses are assumed to be evenly distributed from the vent (0 s fly time) to the edge of the deposit (the maximum fly time). However, it is expected that higher abundances of volcanic glass are present near the vents than at the edge of the deposits, so the modeled water retention percentages may be considered lower limits.

4. Results

4.1. Water in Lunar Pyroclastic Deposits

As discussed above, the background water content at $\pm 30^{\circ}$ latitude (i.e., 100 ppm) is attributed to the likely maximum contribution from solar wind implantation, and this value is subtracted from all pixels within this latitude zone (Figure 1). The resulting

‘excess’ water map reveals a number of locations that have anomalously high water contents compared to adjacent regions. All large, spatially coherent regions of excess water correspond to regions previously recognized as pyroclastic deposits [*Gaddis et al.*, 2003]. No large regions of excess water appear to be associated with impact craters, ejecta, or other distinct morphologic units.

In addition, estimated water contents range up to several hundred ppm and persist during the course of the lunar day, unlike the lower contents and loss of water that is typically observed for water of solar wind origin at these latitudes [*Li and Milliken*, Chapter 2]. These observations suggest excess water associated with pyroclastic deposits is stable in the thermal environment of these locations and thus not likely to be entirely due to solar wind implantation. Instead, these signatures may represent endogenous sources, including water derived from magma source regions. To further explore this possibility we focus only on the eleven large pyroclastic deposits ($>1000 \text{ km}^2$) identified by *Gaddis et al.* [2003] in this latitude zone to avoid ambiguity associated with identification of small pyroclastic deposits in M^3 data ($\sim 280 \text{ m/pixel}$).

The correlation between water content and volcanic glass abundance at the pyroclastic deposits can be examined to further validate whether or not the observed water signature is sourced from the lunar interior. Volatiles associated with magmatic eruption may be emplaced on the surface in two different ways: condensation of vapor clouds on surface materials [*Meyer et al.*, 1975] and/or quenched inside the glass itself [*Saal et al.*, 2008]. Either mechanism leads to the prediction that bulk water content of the regolith should exhibit a positive correlation with glass content if glass is in fact the dominant carrier of excess water.

The estimated volcanic glass abundances (based on the PLS-BPNN model) and corresponding water contents for each pyroclastic deposit are shown in Figure 2, and it is clear that the spatial distribution of these components is highly correlated. This is further demonstrated in Figure 5, where modeled glass abundances for all pixels within the 11 large pyroclastic deposits are plotted against their corresponding ESPAT values. Mapped volcanic glass abundances are generally less than 10%, which is in the reliable range of the PLS-BPNN model. The average reflectance spectra of pixels with glass abundances $> \sim 5\%$ for each deposit are presented in Figure 3 and continuum-removed versions are plotted in Figure 4. Their spectra exhibit similar features in the visible to near-infrared region, including low reflectance and stronger Fe^{2+} absorptions at $1\mu\text{m}$ compared with $2\mu\text{m}$, which is in accordance with spectra of Apollo volcanic glasses (Figure 4). However, the narrow shape of the short wavelength portion of the $1\mu\text{m}$ band in the continuum-removed M^3 spectra is consistent with the presence of pyroxene in addition to volcanic glass, which is not unexpected given that the deposits are not entirely composed of glass.

As stated above, if the water observed in pyroclastic deposits is representative of a magmatic source, then a positive correlation between the size of a pyroclastic deposit (acting as a proxy for pyroclastic range) and water content may be expected. The results from the magma eruption model discussed above are presented in Figure 6, where it is assumed that water may only represent 1% of the total volatile content of the magma [Wetzel *et al.*, 2015]. As expected, modeled water contents increase with the size of each pyroclastic deposit (blue line in Figure 6). These values provide upper limits because they assume materials from a single eruption can span the entire observed range of a given deposit.

The observed mean water contents for each pyroclastic deposit are also shown on Figure 6 for comparison, and it is clear that the observed values lie below the trend predicted from the magma eruption model. These deviations may result from a number of factors, including 1) uncertainties in the model or estimated water contents, 2) inaccurate estimates of pyroclastic range, 3) differences in degassing history, 4) differences in water content of magma source regions, and 5) post-emplacement loss of water. In addition, it can be observed that there are two distinct trends for the estimated water contents, corresponding to a set of ‘high’ and ‘low’ water contents (red and green trends, respectively, in Figure 6). Previous studies have identified these 11 pyroclastic deposits as likely high- or low-Ti compositions [e.g., *Hawke et al.*, 1990; *Lucey et al.*, 2000; *Shkuratov et al.*, 2005], and using these designations reveals that pyroclastics with higher water content correspond with inferred high-Ti deposits and lower water contents with low-Ti deposits.

Though speculative, these differences may represent different volatile contents within the magma source regions, where volatiles such as water are concentrated in the high-Ti magmas. Alternatively, the two trends may represent different cooling rates and thus degassing history between high- and low-Ti magmas. The latter effect was explored to a first order using the 1-D diffusion model described above, assuming that the major water loss mechanism during eruption is likely to be diffusion [*Wetzel et al.*, 2015]. Different cooling rates were explored for initial magma water contents based on values derived from the magma eruption model, which are considered likely upper limits.

Results from the diffusion model are compared with observed water content values for the high- and low-Ti deposits in Figure 7. For consistency, and to allow direct

comparison to the diffusion model, percent water retention for the large pyroclastic deposits are based on mean observed values of water content for each deposit and assuming an initial magma water content based on values from the magma degassing model. It can be seen from Figure 7 that low-Ti deposits fall in the region corresponding to cooling rates of $\sim 1\text{-}20^\circ\text{C/s}$, which is consistent with cooling rate estimates for Apollo green glasses [Arndt *et al.*, 1984]. Estimated water retention values for high-Ti deposits fall in the range of $\sim 40\text{-}100^\circ\text{C/s}$, which is also in broad agreement with cooling rates of $\sim 100^\circ\text{C/s}$ that have been determined for Apollo orange glasses [Arndt and Engelhardt, 1987]. However, one high-Ti data point deviates from this trend and plots above a cooling rate of 200°C/s (Figure 7). If it is instead assumed that water represents 2% of the total initial volatile content (as opposed to 1%), then water contents for all high-Ti pyroclastic deposits fall within a cooling rate range of $\sim 30\text{-}200^\circ\text{C/s}$ (Figure 8), a range that is consistent with Apollo volcanic glasses [Arndt and Engelhardt, 1987; Saal *et al.*, 2008].

4.2. Water Content of Silicic Regions on the Moon

Another type of volcanism called highland or nonmare volcanism was recognized on the lunar surface by its high albedo, domical morphology features, and compositions that are different from mare volcanism [Head *et al.*, 1978; Head and McCord, 1978]. Evidences from visible-near infrared spectra, mid-infrared thermal spectra, and modeling work on the eruption conditions suggest that the magma might be more silicic rich than mare volcanism [Head *et al.*, 1978; Head and McCord, 1978; Wilson and Head, 2003; Glotch *et al.*, 2010; Glotch *et al.*, 2011; Jolliff *et al.*, 2011]. The highland/nonmare

volcanism could be formed by the ascending of silicic rich melts due to its immiscibility and low density or fractional crystallization [Hess, 1989; Glotch *et al.*, 2010; Jolliff *et al.*, 2011]. Water (if any) from the source can be concentrated in the silicic rich melts due to its incompatibility. We examined the water content of seven possible Si-rich regions on the Moon, previously interpreted to represent evolved magmas, including reported silicic domes [Glotch *et al.*, 2010; Glotch *et al.*, 2011; Jolliff *et al.*, 2011]. The water maps for each feature were extracted from the global water content map of Li and Milliken [2016 in prep.] and are presented in Figure 9. These maps show that the Gruithuisen, Compton-Belkovich, and Mairan domes regions all exhibit enhanced water contents compared with surrounding terrains. Enhanced water signatures in Compton Belkovich have previously been reported by [Petro *et al.*, 2013], though our quantitative mapping results indicate the feature is enriched in water by only ~100-300 ppm compared to surrounding terrains. Of the four Si-rich domes in the Mairan region that have been previously identified and studied [e.g., Scott and Eggleton, 1973; Head and McCord, 1978; Head and Wilson, 2003; Glotch *et al.*, 2011], only the “middle” dome exhibits a significant (~100-300 ppm) increase in water content relative to surrounding terrains.

In contrast to these three regions, the remaining four silicic regions exhibit no clear evidence for the presence of water (Figure 9). As such, purported silicic regions exhibit water content values that span a much broader range than is observed for the large pyroclastic deposits, ranging from 0 (undetected) to ~1000 ppm. Though some of these features (e.g., Compton Belkovich) are at higher latitudes where abundance of water sourced from solar wind increases [Li and Milliken, Chapter 2], the ‘hydrated’ Si-rich locations all exhibit water contents above background values observed in adjacent

terrains. Also, spectra for both the Mairan “middle” dome and the Gruithuisen dome exhibit water absorptions even when surrounding terrains lack such features (Figure 9).

5. Discussion

To summarize these findings, a number of locations in the $\pm 30^\circ$ latitude zone exhibit water contents that are in excess of values expected due to solar wind implantation. No clear associations between enhanced water signatures and crater or crater ejecta were observed at the spatial scale of this study, suggesting these enhanced water signatures are likely not the result of volatile-rich impactors. In contrast, the majority of these locations correspond to previously identified pyroclastic deposits, including 11 large pyroclastic deposits described in *Gaddis et al.* [2003]. It is worth noting that Sinus Aestuum, one of the largest pyroclastic deposits, exhibits relatively low water contents and only a fraction of the mapped deposit exhibits evidence for hydration, an issue that is discussed in more detail below. Several previously reported Si-rich locations also exhibit enhanced water signatures, though the association between water and Si-content is not as ubiquitous as the apparent association between water content and pyroclastic materials. Together, these observations suggest that a significant portion of water observed in pyroclastic deposits and certain silicic domes are representative of water derived from interior sources, i.e. magma source regions.

Different pyroclastic deposits exhibit different ranges and mean values in water content, and these differences may be the result of a number of different processes. However, it is not possible to use water contents observed from orbit to uniquely determine the petrologic history (ascent rate, duration, speed, degassing history, initial

volatile content of magma, etc.) for each pyroclastic deposit. Rather, the above comparison of water contents estimated from M^3 data with 1-D diffusion and magma eruption models simply provides a ground-level assessment of whether or not the observed values are consistent with processes that occur in pyroclastic eruptions and thus water sourced from the lunar interior.

To a first order the answer to this question is yes; estimated water contents appear to scale with the size of the pyroclastic deposit, bulk water content is positively correlated with modeled volcanic glass abundance, inferred high- and low-Ti pyroclastic deposits exhibit distinct trends in water content, and estimated water retention values can be modeled to be in agreement with predicted values based on cooling rates determined for Apollo volcanic glasses. Although each of these approaches has associated uncertainty, the observations and modeling results are in broad agreement and we conclude that the excess water observed in lunar pyroclastic deposits is wholly consistent with an origin from the lunar interior.

It is well documented for Apollo samples that volatiles originating from the solar wind are surface-correlated and, although the water contents we observe for pyroclastic deposits are up to several hundreds of ppm higher than values expected from solar wind, it is necessary to consider similar effects. Photons that interact with the lunar surface and that are subsequently scattered in the direction of the M^3 detector have interacted with a volume of surface material and thus record bulk, volumetric information. As such, it is not possible to determine from M^3 spectra how water is physically distributed in the volcanic glass. Some of the water signature observed from orbit may be representative of volatiles in the interior of the glasses, similar to components measured in Apollo volcanic

glasses by *Saal et al.* [2008]. However, some of the water contents we estimate are an order of magnitude higher than what were observed in that study. This may imply that some portions of the erupting magma experienced little degassing during eruption and emplacement, which would imply magmas with very high water contents (up to several hundred ppm).

Alternatively, water in the vapor cloud produced by the eruption may diffuse back into or condense on the outermost surfaces of glass beads. This could lead to higher water contents in the rims of glasses compared with the interiors (which may still exhibit diffusion profiles such as those described in *Saal et al.* [2008]). M^3 spectra would also be sensitive to this water, and perhaps even be biased towards its detection because it would be the first encounter of a strongly absorbing species for photons at $\sim 3 \mu\text{m}$ wavelength. The path length of photons ($\sim < 500 \mu\text{m}$) at NIR wavelengths is still an order of magnitude greater than the likely thickness of water-enriched rims ($\sim$ several hundred Å), thus M^3 spectra are expected to be sensitive to water distributed throughout the glass, but the apparent values may be biased towards concentrations in the outermost portion of the beads. Therefore, it must be considered that water contents estimated from M^3 data may not be equivalent to (and perhaps be greater than) water contents observed in SIMS and other in situ analyses of lunar glasses where volatile-rich rims are typically avoided. Despite these potential concerns, enhanced water signatures at pyroclastic deposits as seen in M^3 data would still reflect an origin from the lunar interior, but whether these spectral signatures are representative of vapor cloud-magma interaction during eruption and emplacement or bulk water contents of volcanic glass warrants additional study.

The reason for the general lack of high water contents in Sinus Aestuum compared with other large pyroclastic deposits is unclear. This observation could be the result of 1) dilution or covering by ejecta from Copernicus, 2) high diffusion rates during eruption (possibly as a result of multiple small eruptions that have thin vapor clouds), or 3) a water-poor magma source region. The intriguing hydration state of Sinus Aestuum will be investigated in more detail in a future study.

The simplest way to explain the observed variance in water content associated with silicic-rich regions is that these magmas had significantly different water contents. However, the observed differences may also be related to their distinct formation processes. Silicic domes may result from fractional crystallization of melts or ascent of silicic melts due to their immiscibility and lower density [Glotch *et al.*, 2010; Jolliff *et al.*, 2011]. In contrast, pyroclastic deposits are believed to have formed as volatile-charged, explosive fire fountains [Heiken *et al.*, 1974]. The former may have more pulses of thermal events and much slower cooling rates than the latter, which could lead to higher degrees of water loss in the Si-rich magmas.

However, the identification of these regions as Si-rich is not without ambiguity. These features are characterized by their high reflectance at visible to near infrared wavelengths, distinct wavelength position of the Christiansen feature (CF) at mid-infrared wavelengths, and association with positive thorium anomalies [Glotch *et al.*, 2010; Glotch *et al.*, 2011]. However, none of these three characteristics are unique to Si-rich materials. Increased reflectance at VNIR wavelengths could be due to other factors such as higher abundance of plagioclase and smaller particle size, and the thorium data

acquired by the Lunar Prospector (LP) mission are very low spatial resolution (>10s of kilometers per pixel) and not capable of resolving individual silicic materials.

Wavelength position of the CF is a key indicator of the Si content of geologic materials [e.g., *Greenhagen and Paige*, 2006; *Glotch et al.*, 2010], but the Diviner instrument has only three wavelength channels that can be used to estimate the position of this feature on the lunar surface, leading to uncertainty in these interpretations. In addition, the position of the CF can vary for a given material when measured under lunar-like conditions versus ambient terrestrial conditions, primarily due to strong thermal gradients that are established in particulate materials when exposed to solar illumination in a vacuum [*Donaldson Hanna et al.*, 2012]. However, additional work is needed to understand and quantify how such factors may affect compositional interpretations based on estimated CF positions. We simply note that one explanation for the apparent lack of hydration signatures in some silicic regions may be that they are in fact not enriched in silica. Despite these issues, the observation that some silicic domes exhibit increased water contents supports previous studies that have highlighted these locations as regions of intriguing composition, and our observations are consistent with volatile enrichment in Si-rich magmas on the Moon.

6. Conclusions

Water contents within the $\pm 30^\circ$ latitude zone on the Moon were evaluated using thermally corrected M^3 spectra to search for water that may be of endogenous origin. Pyrolysis measurements of bulk Apollo soil samples and M^3 -based estimates of water content for typical soils in this latitude zone suggest water sourced from solar wind

processes is on the order of ~100 ppm or less. This is taken as a background value, and water in excess of this value is consistent with a non-solar wind origin. Observed regions of excess water in this latitude range are strongly correlated with the previously mapped distribution of pyroclastic deposits, exhibiting water contents up to several hundreds of ppm assuming particles 60-80 μm in diameter.

The tight correlation between the water content of pyroclastic deposits and modeled volcanic glass abundance suggests the latter is the major host of water in these deposits, which is taken as evidence for water derived from magma source regions. High-Ti deposits exhibit higher water contents compared with low-Ti deposits, which suggests differences in volatile content of magma source regions or different degassing histories. Observed water enhancements are beyond values expected for solar wind implantation, but it is not possible to use orbital data to distinguish water enriched in the rims of glass beads due vapor cloud-glass interactions during eruption from water that is hosted in the interior of glass beads. In either case, enhanced water associated with pyroclastic deposits is consistent with an internal origin.

Three out of seven examined silicic regions exhibit enhanced levels of hydration, suggesting volatiles may be concentrated in Si-rich magmas but that this process is not necessarily unique to identified silicic deposits. Observed variations between silicic deposits may reflect variations in water content of magma sources, degassing history, or misidentification of some deposits as being Si-rich. Together, the hydration state of pyroclastic deposits and silicic domes reveals that the water is widely distributed in magma source regions and by extension the lunar interior. Volatiles measured in the lunar samples are thus reflective of global-scale processes and are not biased towards unusual,

volatile-rich sources. These results suggest the bulk lunar mantle is indeed water-bearing and lunar magma ocean models must take into account these volatiles.

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Table Captions

Table 1. The pyroclastic ranges used in this study.

Figure Captions

Figure 1. Lunar surface water at $\pm 30^\circ$ latitudes after subtracting a background value of 100 ppm from *Li and Milliken* [2016 in prep.], assuming mean regolith particle size 60 – 80 μm ($\text{H}_2\text{O}\% = 0.5 \cdot \text{ESPA}$) [*Li and Milliken*, 2016 in prep.]; the locations of pyroclastic deposits are from [*Gaddis et al.*, 2003].

Figure 2. Our mapped water contents (the left column) and volcanic glasses (the right column) for those 11 large pyroclastic deposit ((a) – (k)) at $\pm 30^\circ$ latitudes.

Figure 3. The average spectra of pixels with glass contents $> \sim 5\%$ for the 11 large pyroclastic deposits.

Figure 4. Continuum removal of the spectra shown in Figure 3 compared with those of Apollo 15 green glass and Apollo 17 black beads.

Figure. 5. Comparison between ESPA and modeled volcanic glass abundance at all eleven pyroclastic deposits, this trend indicates that volcanic glasses are the major hosts for the water from the lunar interior.

Fig. 6. Average water contents vs. pyroclastic ranges for 11 large pyroclastic deposits at $\pm 30^\circ$ latitudes.

Figure 7. Water retention percentages for different cooling rates based on a simple 1-D diffusion model (colored lines).

Figure 8. Water retention percentages for different cooling rates based on a simple 1-D diffusion model (colored lines), assuming water takes 2% of total volatiles in magma sources for both low and high-Ti deposits (markers).

Figure 9. The hydration states of silicic domes without removing the ‘background’ water.

Tables

Pyroclastic Deposits	Pyroclastic Range (km)
Carpatus	118
Nectaris SE	241
Moscoviense	1193
Harbinger	2349
Aristarchus	4258
Humorum	10360
Taurus Littrow	657
Vaporum	1848
Sulpicius Gallus	3272
Rima Bode	3400
Sinus Aestuum	74

Figures

Figure 1

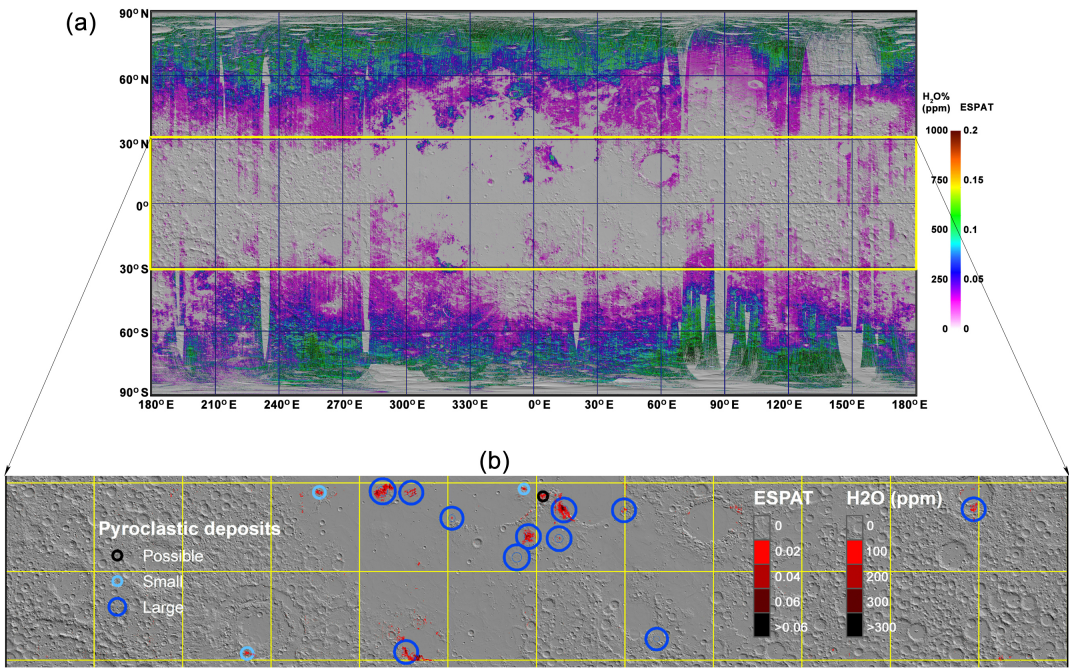


Figure 2

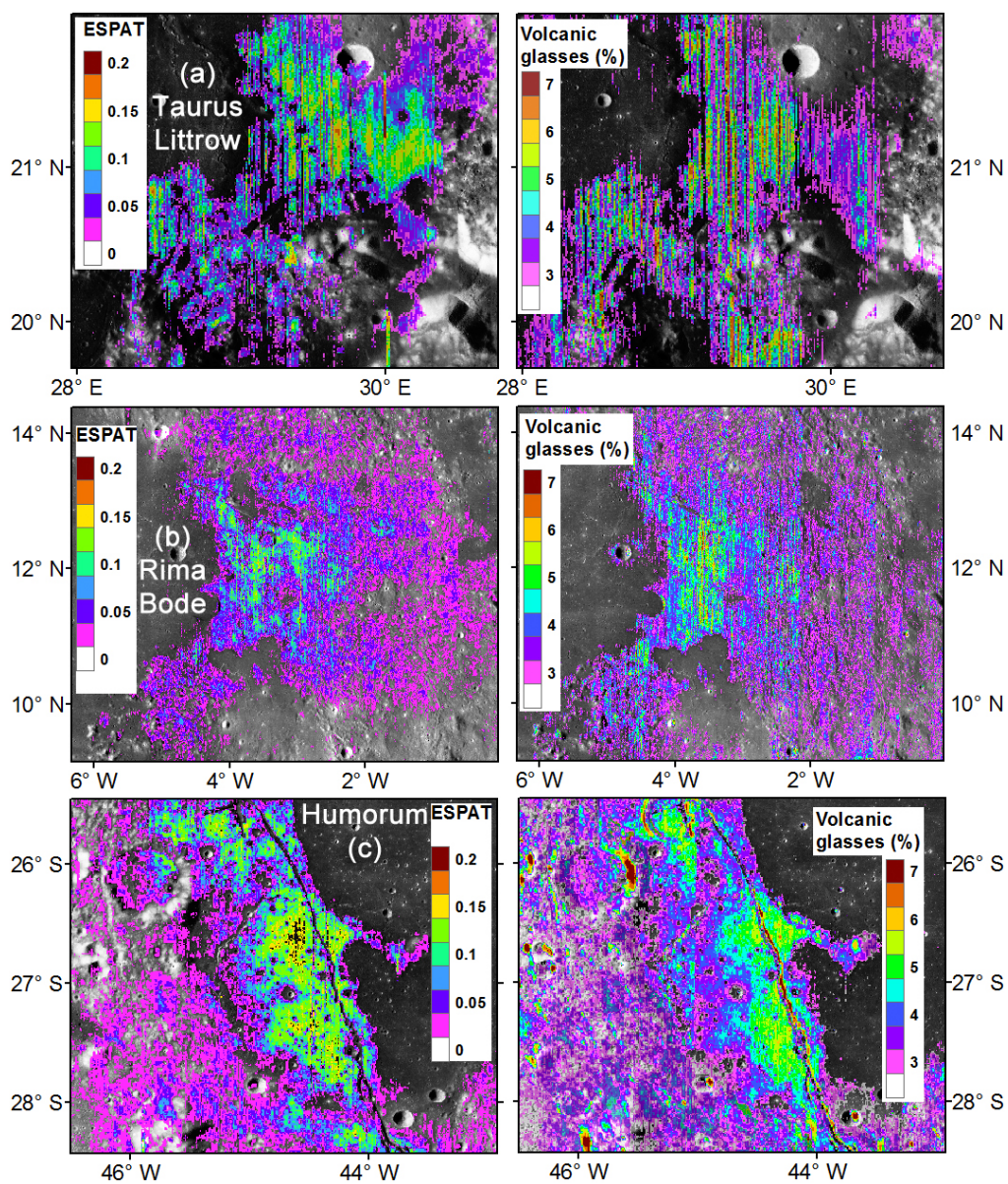


Figure 2 - continued

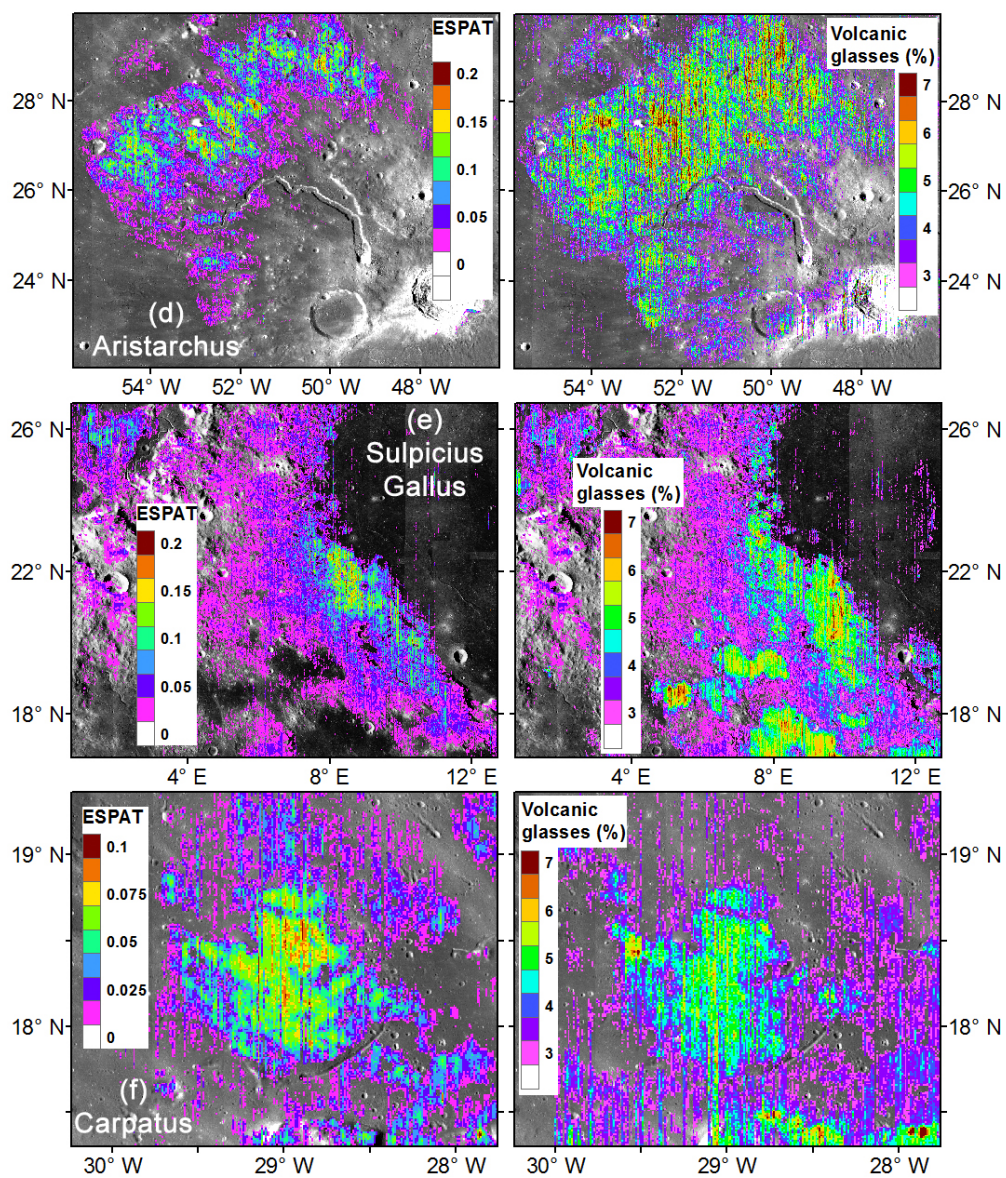


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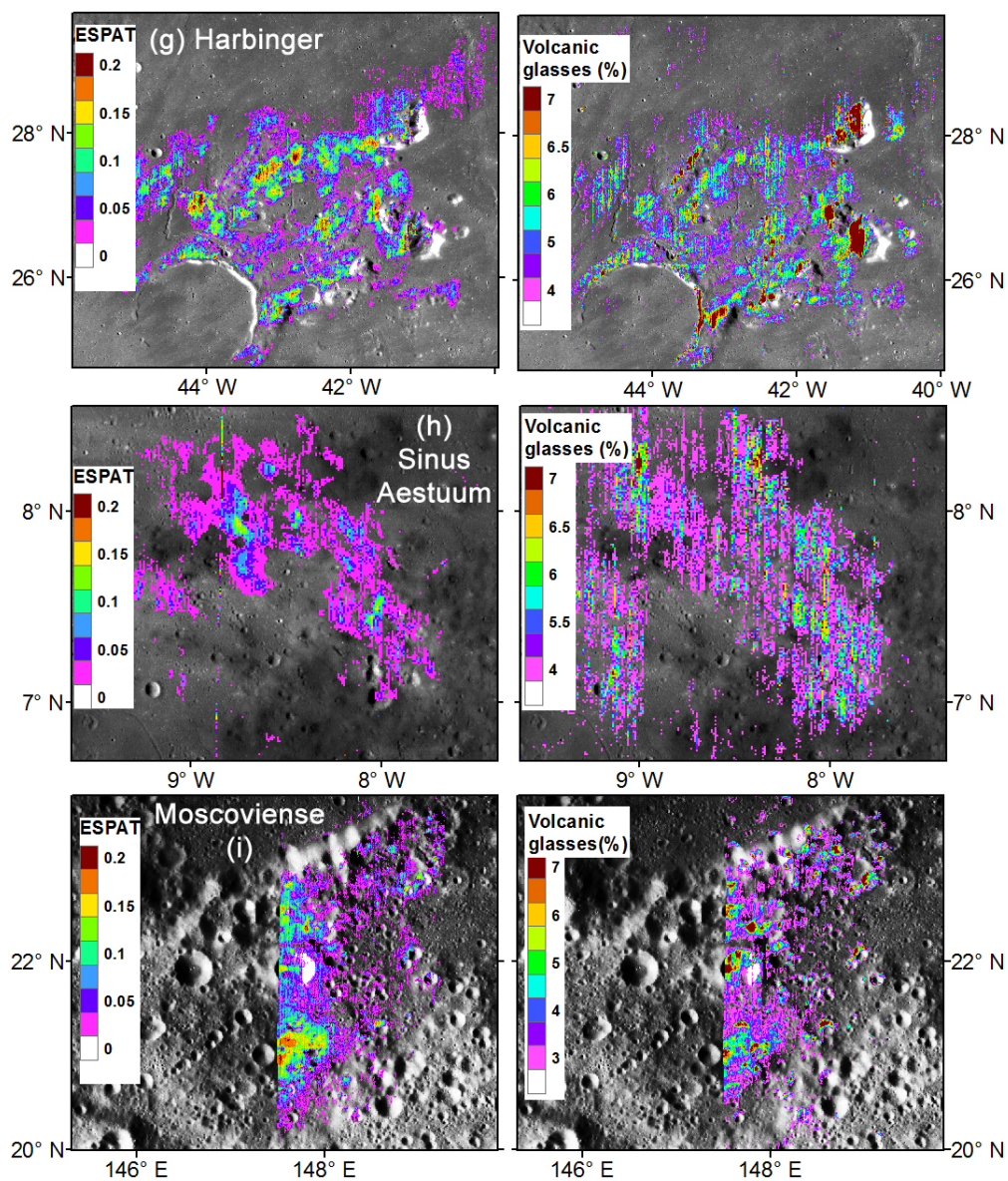


Figure 2 - continued

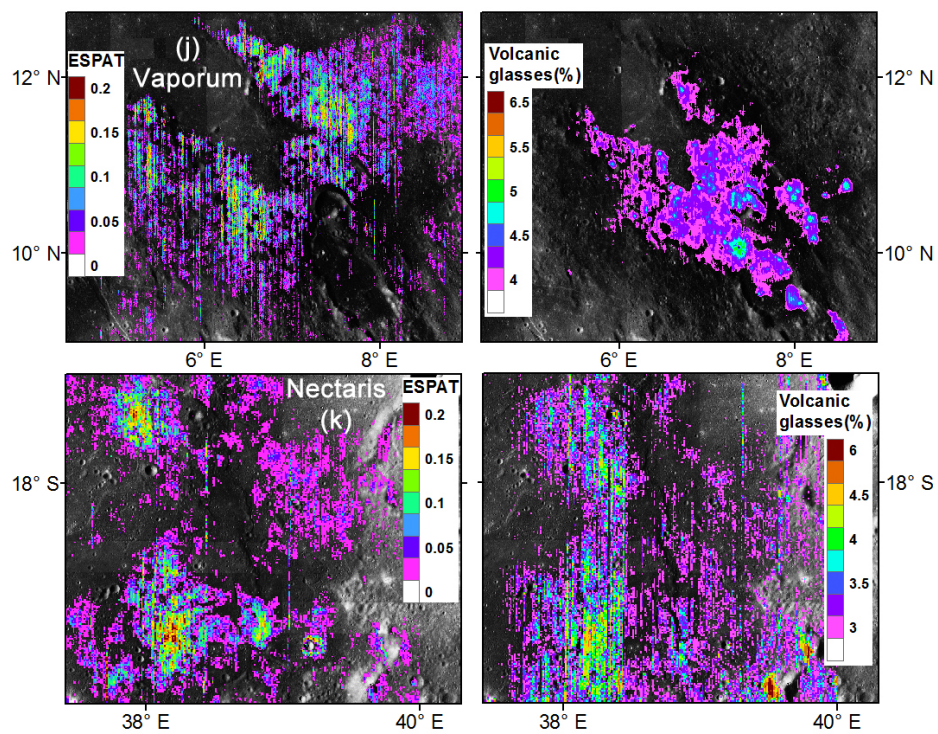


Figure 3

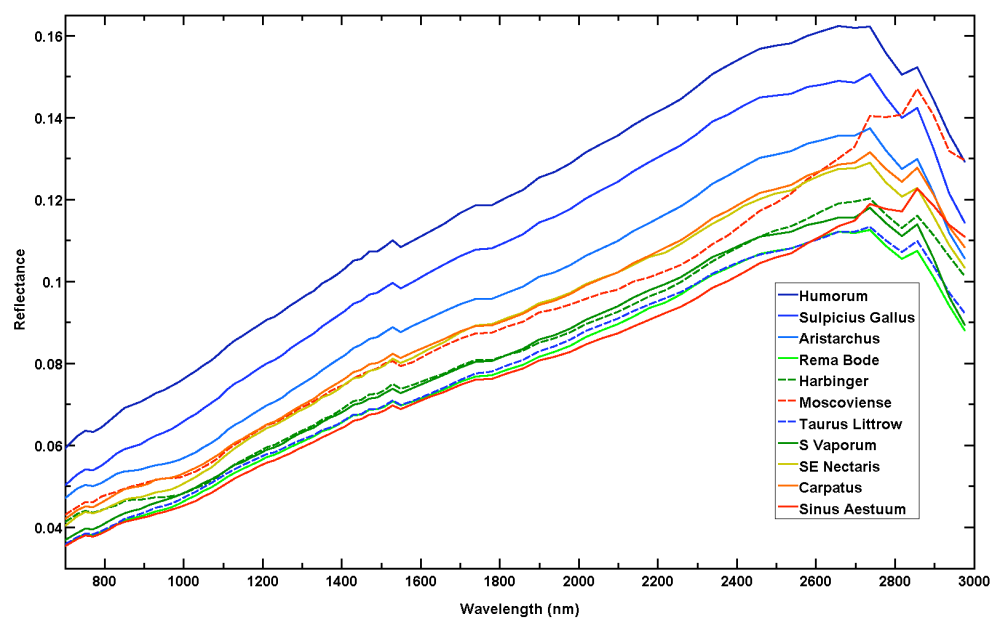


Figure 4

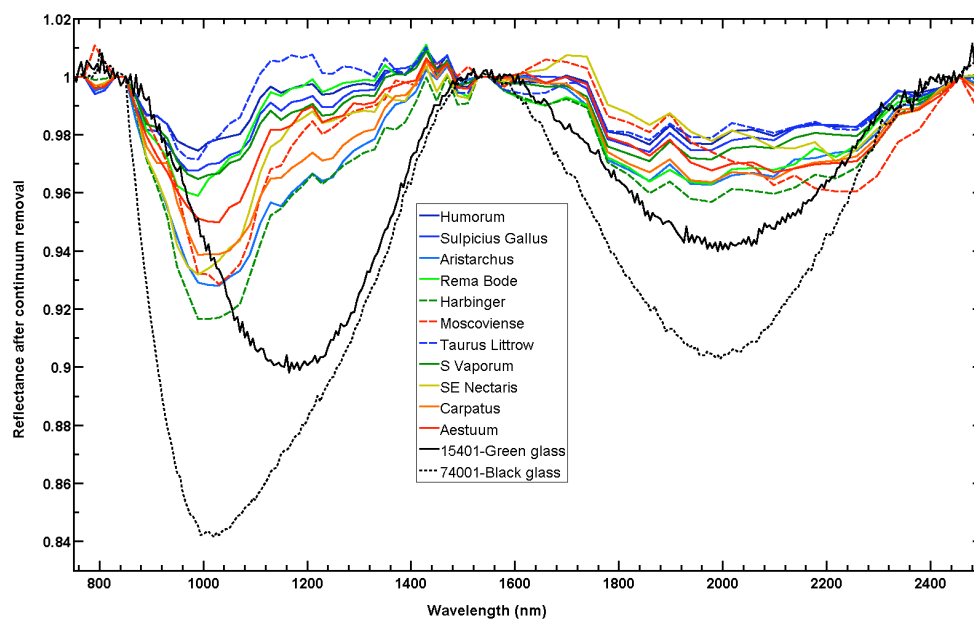


Figure 5

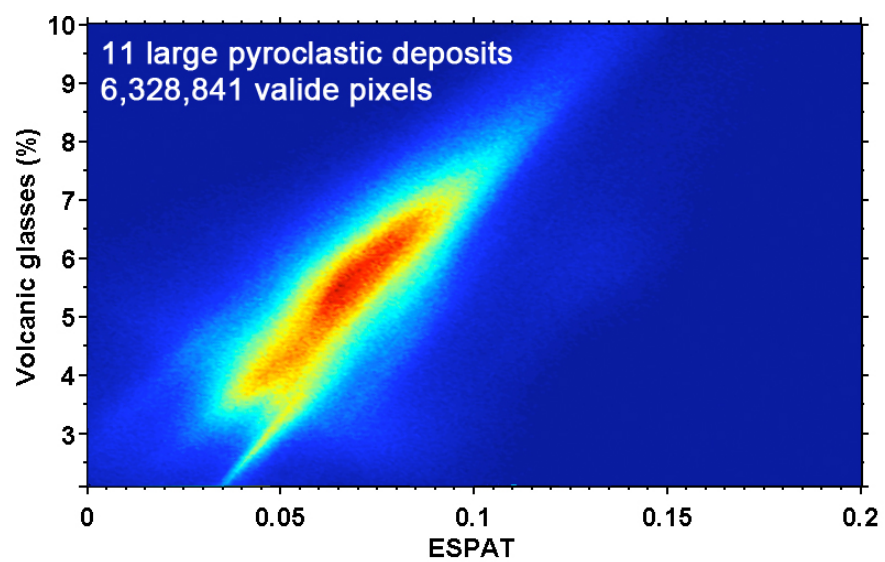


Figure 6

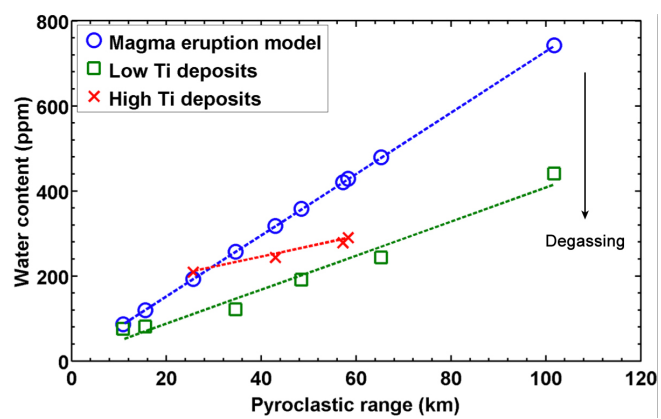


Figure 7

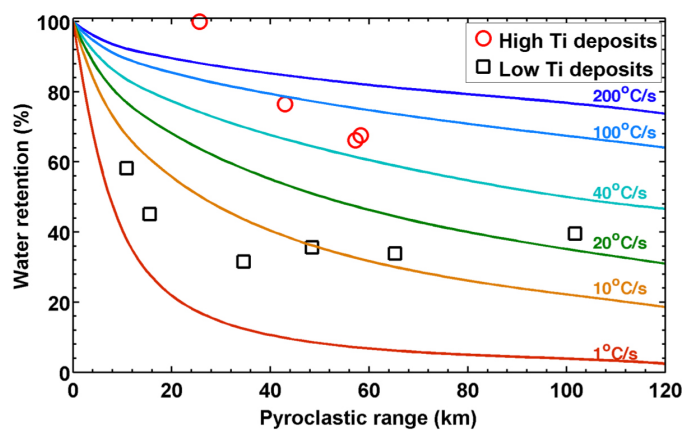


Figure 8

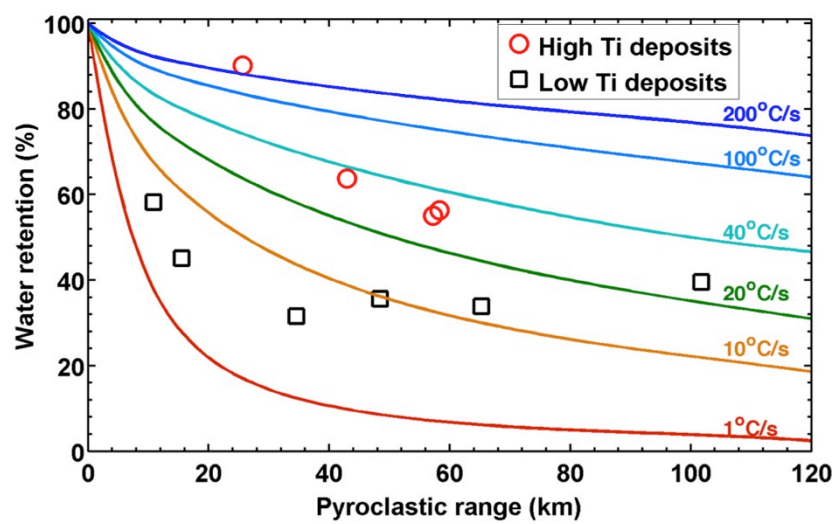
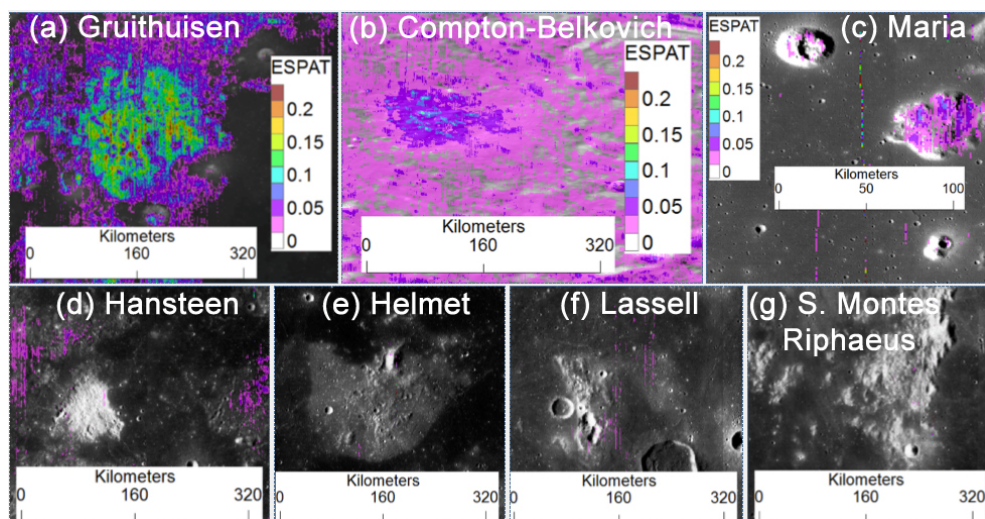


Figure 9



Chapter 4: Geomorphological and Mineralogical Mapping at Pyroclastic Deposit

Sinus Aestuum and Rima Bode: Insights into Their Magmatism

Shuai Li

and

Ralph E. Milliken

Abstract

Sinus Aestuum and Rima Bode are two adjacent very large ($> 1000 \text{ km}^2$) pyroclastic deposits. Previous studies suggest Sinus Aestuum is the only one out of eleven large pyroclastic deposits that shows no detectable water originating from the lunar interior [*Chapter 3*]. Sinus Aestuum is also the only pyroclastic deposit associated with exposures of spinel [*Pieters et al.*, 2014]. In this study we perform detailed geomorphological and mineralogical studies at both Sinus Aestuum and Rima Bode to understand: 1) why deposits at Sinus Aestuum differ from Rima Bode in their apparent water content; 2) the connection between the lack of indigenous water and the presence of spinel at Sinus Aestuum; and 3) implications for differences in the magma source between Sinus Aestuum and Rima Bode. We examine images acquired at 750 nm wavelength acquired by the Multiband Imager (MI) onboard the Japanese KAGUYA (SELENE) mission to outline major geomorphologic units ($\sim 20 \text{ m/pixel}$ at the equatorial region) at the two pyroclastic deposits. Spectral band parameters and band ratios of MI data are used to assess compositional variations at Sinus Aestuum and Rima Bode. Results show that surface units at Sinus Aestuum may contain a component of ejecta from the Copernicus impact. We perform nonlinear spectral unmixing analyses using radiative transfer modeling in conjunction with MI and new thermally corrected Moon Mineralogy Mapper (M^3) data. These quantitative assessments suggest that the abundance of a pyroclastic-rich spectral endmember is approximately five times higher at Rima Bode than at Sinus Aestuum. This suggests that the apparent lack of water absorptions at Sinus Aestuum cannot be entirely due to dilution by anhydrous components, thus a dry magma source at Sinus Aestuum is plausible. We also

quantitatively mapped spinel abundance at Sinus Aestuum using radiative transfer modeling in conjunction with M^3 data. Spectral features in the purest spinel pixels exhibit steeper slopes from 0.5 to 1.5 μm and two very weak absorptions at 0.5 – 0.65 μm and 0.65 – 0.8 μm . The former absorption may be introduced by octahedral Cr^{3+} in Cr spinel [Williams *et al.*, 2016] and the latter may be caused by octahedral Fe^{2+} in aluminate spinel. The potential presence of octahedral Fe^{2+} in aluminate spinel suggests fast cooling rates that require thin/no vapor clouds during pyroclastic eruptions, which is in accordance with the dry magma source hypothesis at Sinus Aestuum [Jackson *et al.*, 2014]. However, it is also possible that any water that may have been emplaced at Sinus Aestuum during the eruptions has subsequently diffused out due to post-emplacement thermal events.

1. Introduction

Lunar pyroclastic deposits (LPD), also called dark mantling deposits (DMD), were erupted at the surface by magmas sourced from the deep lunar interior (~400 - 500 km) in the form of explosive fire fountains enriched in volatiles [Adams *et al.*, 1974; Head, 1974; Heiken and McKay, 1974; Pieters *et al.*, 1974; Head, 1975; Head, 1976; Heiken and McKay, 1977; Delano and Livi, 1981; Gaddis *et al.*, 1985; Hawke *et al.*, 1989; Head and Wilson, 1989]. The formation of these deposits may be associated with the major episode of volcanism in the early history of the Moon [Head, 1974]. Thus, these pyroclastic deposits provide clues to the interior of the early Moon, which is critical for understanding lunar formation and evolution (e.g., the lunar magma ocean).

Lunar pyroclastic deposits are compositionally, and thus spectrally, distinct from other major geological units (i.e., mare and highland). Pyroclastic deposits exhibit extremely low albedo at visible wavelengths due to iron/titanium charge transfer absorptions and/or the presence of opaque minerals (e.g., ilmenite), which makes them readily identifiable with telescopic and orbital reflectance data [Pieters *et al.*, 1973; Adams *et al.*, 1974; Pieters *et al.*, 1974; Gaddis *et al.*, 1985; Hawke *et al.*, 1989; Gaddis *et al.*, 2003]. Pyroclastic materials are typically glass-rich and lack crystallinity, which explains why their reflectance spectra at near infrared wavelengths show very weak 1 and 2 μm absorptions [Pieters *et al.*, 1973; Adams *et al.*, 1974; Burns, 1993]. Because of their unique spectral features, global surveys of pyroclastic deposits have been performed using Clementine multiband spectral data, Lunar Reconnaissance Orbiter camera data, and M³ data [Gaddis *et al.*, 2003; Gustafson *et al.*, 2012; Besse *et al.*, 2014], in which the latter two studies focused on small deposits that were previously unidentified. Detailed

studies on the geological and morphological features of these pyroclastic deposits can inform us on the nature of processes associated with their formation and may also help to identify possible vents. Assessments of compositions of pyroclastic materials can indirectly provide information about the composition of the potential magma sources, and consequently inform us of the heterogeneity/homogeneity of the lunar interior.

In this study, we examine two adjacent very large (areal extent $> 1000 \text{ km}^2$ [Gaddis *et al.*, 2003]) pyroclastic deposits: Sinus Aestuum and Rima Bode. Studies of water ($\text{H}_2\text{O}/\text{OH}$) contents at eleven very large pyroclastic deposits between latitudes $\pm 30^\circ$ with new thermally corrected M^3 data suggested that Sinus Aestuum is the only large pyroclastic deposit that lacks clear spectral evidence for the presence of lunar interior water [Chapter 3]. Interestingly, global surveys of spinel using M^3 data confirmed that Sinus Aestuum is the only pyroclastic deposit that contains exposures of that mineral group [Sunshine *et al.*, 2010; Pieters *et al.*, 2014]. Spectral features of Sinus Aestuum spinel were carefully examined with MI and Spectra Profiler (SP) data by Yamamoto *et al.* [2013]. The presence of absorptions at $\sim 0.65 \text{ }\mu\text{m}$, $1 \text{ }\mu\text{m}$, and $1.3 \text{ }\mu\text{m}$ suggested that Sinus Aestuum spinel might be Cr/Fe-rich [Yamamoto *et al.*, 2013]. In contrast, pyroclastic materials at an adjacent very large pyroclastic deposit Rima Bode exhibit signs of water originating from the lunar interior [Chapter 3], but no spinel was found at this location [Sunshine *et al.*, 2010]. The apparent link between water content and spinel content for the large pyroclastic deposits may reflect differences in formation conditions, processes, post deposition modifications, and magma sources.

We focus on the following questions in our study. 1). Why does Sinus Aestuum lack evidence for lunar interior water as compared to other very large pyroclastic

deposits? 2). Is there any connection between the absence of lunar interior water and the presence of spinel at Sinus Aestuum? 3). Can the absence of lunar interior water and presence of spinel at Sinus Aestuum allow us to characterize its formation conditions, formation processes, post deposition modifications, and/or magma sources? To address these questions, we first perform detailed geomorphological mapping at both Sinus Aestuum and Rima Bode using MI 750 nm reflectance data. We then apply empirical band parameters and band ratios derived from Clementine data on MI data to understand compositional differences among the mapped geomorphological units. We perform nonlinear spectral unmixing analyses using radiative transfer modeling and in-scene endmembers on MI and M^3 data to investigate the lateral/vertical mixing at the two pyroclastic deposits. We examine whether the absence of lunar interior water at Sinus Aestuum is associated with specific geologic settings, compositions, or dilution due to lateral/vertical mixing. Spinel is mapped using radiative transfer modeling in conjunction with M^3 data. The spatial connection between spinel and pyroclastic materials is used to understand whether its formation is associated with pyroclastic eruption. The spectral features of pixels with highest abundance of spinel (i.e., > 90%) are examined to understand spinel speciation (e.g., Cr or Al spinel), which may inform us about magma sources and formation processes.

2. Data

We use MI data to identify distinct geomorphological units and to map their boundaries. We also use spectral band ratios and spectral unmixing to assess compositional variations at each of the two study regions. New thermally corrected M^3

data are used to perform nonlinear spectral unmixing analyses with in-scene endmembers to investigate lateral and vertical mixing of compositional units and to estimate spinel abundance at Sinus Aestuum. Digital elevation model (DEM) data are integrated with these data to create 3D perspective views for our geomorphological and mineralogical mapping results to help reveal stratigraphic relationships and and geologic contacts of key morphological and mineralogical units.

2.1. Multiband Imager (MI) Data

The Multiband Imager onboard the KAGUYA (SELENE) mission has two cameras, VIS and IR, with a spatial resolution ~ 20 and 62 m per pixel, respectively [Ohtake *et al.*, 2008]. The VIS camera has five bands centered at 0.415 , 0.75 , 0.9 , 0.95 , and 1.0 μm , while the IR camera has four bands centered at 1.0 , 1.05 , 1.25 , 1.55 μm [Ohtake *et al.*, 2008]. Only VIS bands were used for geomorphological mapping and band ratios. VIS and IR data are both utilized in the nonlinear spectral unmixing model that relies on in-scene endmembers.

The MI data were downloaded from the SELENE Data Achieve (<http://l2db.selene.darts.isas.jaxa.jp/index.html.en>). We utilize the MI MAP products that have been photometrically and topographically corrected. All MI map reflectance data have been converted to the standard viewing geometry ($i = 30^\circ$, $e = 0^\circ$, $g = 30^\circ$) (see label files of MI Map products and [Ohtake *et al.*, 2009]). We searched for all available image cubes with given latitude and longitude ranges (Rima Bode: 8.5° N - 16° N, 353.5° E - 360° E; Sinus Aestuum: 0° - 9° N, 343° E - 357° E). The coordinates for each MI MAP product are also available and are based on simple cylindrical projection method (see

product explanation of MI Map products). We constructed Matlab codes to mosaic all MI image cubes within our research area based on the simple cylindrical projection.

2.2. Moon Mineralogy Mapper (M³) Data

The M³ radiance images, location files, and observation files are downloaded from the M³ PDS archive (<http://pds-imaging.jpl.nasa.gov/volumes/m3.html>). We adopt the same procedures as the M³ team [Lundeen *et al.*, 2011] to convert the radiance data to reflectance, but the new thermal correction model developed by Li and Milliken [in review] is applied for removing thermal effects. There are different optical periods (OPs) of M³ data available at our research area. We only use OP1B data that cover our entire research area at Sinus Aestuum in order to minimize errors/uncertainties between different OPs [Boardman *et al.*, 2011]. Matlab codes were used to mosaic the M³ data using the same map projection scheme as applied to MI data.

2.3. Digital Elevation Model (DEM) Data

A DEM product SLDEM2015 derived from LOLA and KAGUYA terrain camera data was downloaded (<http://imbrium.mit.edu/EXTRAS/SLDEM2015/TILES/>) and used in this study. This DEM dataset has a horizontal spatial resolution of ~59 m per pixel at equatorial regions and a vertical accuracy ~3 - 4 m. The spatial resolution of MI data is ~20 m per pixel (IR data are resampled to VIS resolution), whereas M³ data have a spatial resolution of ~280 m per pixel. This DEM is higher resolution than M³ data, but it may not be capable of resolving all geological details seen in the higher resolution MI data.

3. Methods

One of the major goals in this study was to understand the link between the absence of lunar interior water and the presence of spinel at Sinus Aestuum. A parallel study for comparison was performed at Rima Bode, which exhibits evidence for lunar interior water but lacks exposures of spinel. Mapping different geological and morphological features at the two regions could provide improved geological context for each deposit. Empirically derived band parameters and band ratios from Clementine data are applied to MI data to understand compositional differences among the mapped geomorphological units. Nonlinear spectral unmixing is performed on MI and M³ data using Hapke's radiative transfer model as well as in-scene endmembers to estimate spinel content at Sinus Aestuum and to investigate the lateral/vertical mixing at the two pyroclastic deposits.

3.1. Geomorphological Mapping Methods

We outline major geomorphological features at our research area using the 750 nm albedo map of MI data. Three main and two sub units are defined according to brightness. The three main units are high albedo, low albedo, and very low albedo (dark). The two sub-units are dark materials mixed with high and low albedo materials, respectively. Six additional units are defined according to their morphology. They are smooth and dark regions, lumpy and dark regions, lava flow regions, vents, rilles, and craters. We employ the polygon tool in the ArcGIS software to outline boundaries for these eleven geomorphological features.

3.2. Band Parameters and Band Ratios

Major geological units such as mare, highland, and pyroclastic deposits are identified using a combination of band ratios and band parameters. *Gaddis et al.* [2003] comprehensively described the spectral characteristics of pyroclastic deposits, mare, and highland using Clementine data (Figure 5&6 in their paper). Because the MI data have almost identical band centers as those of Clementine data [*Ohtake et al.*, 2008], we can directly select band parameters and band ratios based on *Gaddis et al.* [2003] results to discriminate mare, highland, and pyroclastic deposit regions. Ratios between band 950 nm and 749 nm are chosen and assigned as the red band. A threshold 1.08 is set for the red band. If the ratio is greater than 1.08, it could be either pyroclastic deposit or highlands material (see Figure 5 in [*Gaddis et al.*, 2003]). Albedo at 749 nm is assigned as the green band. A threshold 0.15 is set to discriminate highland (> 0.15) from other units (see Figure 5&6 in [*Gaddis et al.*, 2003]). Ratios between band 414 nm and 749 nm is assigned as the blue band. A threshold 0.65 is set; pixels with values above this threshold are not likely to be associated with pyroclastic deposits (see Figure 6 in [*Gaddis et al.*, 2003]). In the resulting RGB color map, red colors are inferred to be pyroclastic deposits; green colors are associated with highland material; and black or blue colors are likely to represent mare materials. Mixing between these three primary units results in pink (red mixed with blue), cyan (blue mixed with green), and yellow (green mixed with red).

3.3. Nonlinear Spectral Unmixing Methods

Pyroclastic materials could be diluted or muted by lateral and/or vertical mixing with non-pyroclastic materials due to regolith gardening and space weathering. Quantitative assessments of the abundance of pyroclastic materials are required for investigating the influence of lateral and vertical mixing. Hapke's radiative transfer model is applied to do nonlinear spectral unmixing for MI and M^3 data using in-scene endmembers. We use Hapke's model to convert all reflectance to single scattering albedo (SSA). Unmixing SSA is in the linear regime if all endmembers have similar particle sizes, which could be true on the lunar surface because the surface spectral characteristics are dominated by particles ~ 10 to $20\ \mu\text{m}$ in diameter [Pieters *et al.*, 1993]. A second order Legendre polynomial is applied in Hapke's model to describe the phase function, in which the coefficient b for backward scattering and c for side scattering are assigned to the mean values derived experimentally for basaltic minerals by Mustard and Pieters [1989]. We utilize the 1% error version of multiple scattering function (H) for both up- and down-welling radiation [Hapke, 1993]. The parameterization of Hapke's model in this study is the same as that of [Li and Li, 2011; Li and Milliken, 2015].

Four spectral endmembers are picked from MI and M^3 images in our study area. The pyroclastic-rich endmember is picked from the outlined pyroclastic deposit regions (dark units) in our geomorphology maps. We apply an empirical threshold at 0.1 on the 750 nm reflectance values to pick the darkest pixels ($R_{750nm} < 0.1$) [Gaddis *et al.*, 2003]. Similarly, we pick highland- and mare-rich endmembers (high and low albedo units, respectively). An empirical threshold 0.15 for 750 nm reflectance values is used for picking highland rich pixels ($R_{750nm} > 0.15$) [Gaddis *et al.*, 2003]. Highland- and mare-

rich endmembers were selected from areas far north of Rima Bode to avoid contamination from pyroclastic deposits and ejecta from the Copernicus impact. When determining endmember pixels, spectrally homogeneous and morphologically smooth areas are preferred. The fourth endmember was spinel-rich. We first use band math to create band parameters similar to those of *Pieters et al.* [2014] to get a qualitative sense where spinel might be most abundant. We then check those locations pixel by pixel to pick candidates that have no absorptions at $\sim 1 \mu\text{m}$ but the strongest absorption at $\sim 2 \mu\text{m}$. The final spectrum for each endmember represents an average of spectra from all selected pixels from the MI and M³ images.

4. Results

4.1. Geomorphological Maps at Sinus Aestuum and Rima Bode

Geomorphological mapping is performed on the MI 750 nm image at Sinus Aestuum and Rima Bode according to the morphological units and features described above (Section 3.1). Images at the two locations are mosaicked together and stretched equally (Figure 1, 2% linear stretch). Figure 2a shows our outlined major geomorphology units at Sinus Aestuum coded with different colors. In Figure 2b, we overlay the outlines of mapped geomorphology units on the water map at Sinus Aestuum. The water maps at Sinus Aestuum and Rima Bode are derived from *Li and Milliken* [Chapter 3]. No water features are associated with any units at Sinus Aestuum.

Geomorphological mapping results for Rima Bode are shown in Figure 3 a & b. Figure 3a shows our mapped geomorphology units coded with different colors and in Figure 3b, the outlines of these units are overlain on the water map of this region. The

dark and smooth units exhibit the highest water content (Figure 3b), while the water content decreases at zones representing dark materials mixed with low albedo and high albedo materials (white and yellow polygons in Figure 3b, respectively).

4.2. Band Parameters and Band Ratios Mapping

We choose band parameters and band ratios that were empirically determined by *Gaddis et al.* [2003] from Clementine data and apply them to MI images to discriminate mare, highland, and pyroclastic materials qualitatively. MI and Clementine data share common bands at 0.415, 0.75, and 0.95 μm that were used to determine band parameters and band ratios in *Gaddis et al.* [2003]. We used the same band parameters and band ratios without any modifications. We assign the band ratio between 950 nm and 750 nm to the red channel and stretch the ratio from 1.15 to 1.24 as an indicator for pyroclastic deposits (see section 3.2 and Figure 5 in *Gaddis et al.* [2003]). Band 750 nm is assigned to the green channel and is stretched from 0.15 to 0.22 as an indicator for highland materials (see section 3.2 and Figure 5&6 in *Gaddis et al.* [2003]). The band ratio between 415 nm and 750 nm is set to the blue channel and is stretched from 0.6 to 0.7 to be an indicator for mare materials (see section 3.2 and Figure 6 in *Gaddis et al.* [2003]). However, none of these indices are unique solutions, especially the indicators for highland and mare materials, because the values of these indicators partially overlap, even after using the thresholds listed above (Figure 5&6 in *Gaddis et al.* [2003]). Therefore, pixels that fall in regions of overlap (e.g., mixed colors) should be re-examined and validated with data that contain more detailed spectral information (i.e., M^3 data).

The band parameter and band ratio maps at Sinus Aestuum and Rima Bode are shown in Figure 4. Dark deposits at Rima Bode exhibit strong red colors, suggesting pyroclastic-rich materials. However, most previously mapped pyroclastic deposits at Sinus Aestuum are pink in color, indicating pyroclastic materials (red) mixed with mare materials (blue). However, *Pieters et al.* [1973] pointed out that the mare at Sinus Aestuum and Rima Bode region is less ‘blue’ than pyroclastic deposits. Therefore, areas that are bluish in color could also be pyroclastic materials, which will be examined with a more quantitative approach in the nonlinear spectral unmixing analysis section.

Figure 5a shows the geomorphology map overlain on the band ratio map at Sinus Aestuum. Green color (highland rich) matches high albedo units very well, and gray to black color (mare rich) matches with low albedo units. Red and dark red colors (pyroclastic rich) match the lumpy and dark units, whereas pink colors match well with dark and smooth units. The latter suggests that pyroclastic materials at Sinus Aestuum may have been mixed with abundant mare basalts, which could possibly mask spectral features associated with water (i.e., a spectral dilution effect). However, as mentioned above, the band ratio parameters are not unique indices for mare, highland, and pyroclastic materials. Data with more spectral information (i.e., M^3 data) are necessary to assess whether pyroclastic materials at Sinus Aestuum are mixed with mare or other non-pyroclastic material.

Our mapped geomorphological map overlain on the band ratio map at Rima Bode is plotted in Figure 5b. The color shows less variation than at Sinus Aestuum. Red (pyroclastic rich), green (highland rich), and dark (mare rich) colors match the dark and smooth, high albedo, and low albedo units very well. In the unit marked as dark materials

mixed with high albedo materials, we do not observe mixing of colors (yellow), which may suggest that one type of material superposes or is spectrally dominant over the other. Compositionally speaking, either the pyroclastic deposit superposes the highland or the highland superposes the pyroclastic material. However, it is challenging to assess whether mixing occurs at this region based on qualitative indices (a binary regime). The lateral and vertical mixing will be examined using nonlinear spectral unmixing analyses in the next section.

In summary, band parameters and band ratios of MI data suggest that compositions of our mapped geomorphologic units are relatively homogeneous. No clear spectral mixing is observed at units marked as dark units mixed with high albedo units based solely on albedo, suggesting superposition of compositions. Dark and smooth units that may be composed of pyroclastic materials show little contamination at Rima Bode, whereas the same type of units at Sinus Aestuum appear to be heavily mixed with mare basalts, which may explain the apparent absence of water features. However, as mentioned above, the interpretation of compositions from band parameter and band ratio indices is quite non-unique. The observations presented thus far could indicate a second type of pyroclastic material is present at Sinus Aestuum that exhibits greater 415 nm to 750 nm reflectance ratios, or the magma source for this region could have been water-poor. Alternatively, magma at Sinus Aestuum may have had different degassing history compared with that at Rima Bode and other pyroclastic deposits that exhibit water from the lunar interior. More detailed compositional studies at Sinus Aestuum are required to assess whether the absence of lunar interior water is associated with contamination, dry magma sources, or different degassing history.

4.3. Nonlinear Spectral Unmixing Analyses

We applied Hapke's radiative transfer model as well as MI data to do nonlinear spectral unmixing analyses at Sinus Aestuum and Rima Bode. Endmembers were picked from MI images according to the criteria and procedures described in Section 3.3. Figure 6 a and b show the selected endmember spectra and spectra of Apollo green glass, orange glass, and black beads resampled (nearest neighborhood algorithm) to MI spectral resolution, respectively. Endmember spectra of high albedo units exhibit the highest albedo at all spectral bands compared with other endmember spectra and they show a very weak absorption centered near 1 μm (Figure 6a, green lines). Endmember spectra for low albedo units show intermediate reflectance at all spectral bands and have the strongest 1 μm absorption band among all endmember spectra (Figure 6a, blue lines). Endmember spectra of dark units from both Rima Bode (Figure 6a, red lines) and Sinus Aestuum (Figure 6a, black lines) are almost identical, indicating similar compositions. Comparison of spectra between dark units and Apollo glasses (Figure 6b) suggests pyroclastic materials at Sinus Aestuum and Rima Bode might be mixtures of orange glass (Figure 6b, the brown line) and black beads (Figure 6b, the black line), indicating both iron and titanium rich compositions [Adams *et al.*, 1974]. Only the average spectra shown in Figure 6a were used for spectral unmixing analyses. It should be noted that none of the three endmembers are pure minerals. Although only three endmembers are utilized, more than three minerals are involved.

The nonlinear spectral unmixing results are shown in Figure 7. Overall, the mapped units (highland, mare, and pyroclastic deposits) match with band ratio and

geomorphological maps, but the former exhibit much sharper boundaries between different units (Figure 7 vs. Figure 2, 3, and 4). The significant difference between spectral unmixing results and the band parameter and band ratio map at Rima Bode is that mixing between pyroclastic (red) and highland materials is observed (yellow color) in the former (Figure 7b), suggesting possibly vertical mixing. Spectral unmixing results are significantly different compared with the band parameter and band ratio map at Sinus Aestuum. One major difference is that the portion of highland component estimated with spectral unmixing at Sinus Aestuum is significantly smaller than what is inferred from the band ratio map (Figure 4) and the geomorphological map (Figure 2). The spectral unmixing indicates mare basalts dominate this region, which is consistent with telescopic observations by *Pieters et al.* [1973].

The formation mechanism of dark spots in pyroclastic deposits at Sinus Aestuum is unclear (Figure 1). These dark spots can be formed by small impacts that excavate underlying, darker materials (i.e., volcanic glasses), or they may represent small volcanic eruptions in which the dark materials are juvenile volcanic glasses. We cannot assess which of the two hypotheses is correct based on geomorphology and band ratios. However, spectral unmixing results indicate these dark spots are likely associated with small craters. Some of them appear to punch through the pyroclastic deposit layer and excavate highland materials underneath it, such that the crater centers show highland components (green color) (Figure 7a). Most of them are yellowish color in the RGB map, which indicates that these impacts may not penetrate fully through the pyroclastic deposit layer (Figure 7a).

An important observation from the spectral unmixing results at Sinus Aestuum is that most of pyroclastic deposits are pink to light yellow in color (Figure 7a), suggesting the presence of mare basalts (blue) and highland (green) ejecta from the Copernicus impact, which is not apparent in the band ratio and morphologic maps. However, it is unclear whether this mixing could entirely mute water features (if any) at Sinus Aestuum. We compare the histogram of the abundance of pyroclastic components at Sinus Aestuum and Rima Bode in Figure 8. It shows that Rima Bode is around five times richer in the pyroclastic spectral endmember than at Sinus Aestuum. The most pyroclastic-rich region at Rima Bode (Figure 3b, red polygons) contains around 500 ppm water on average. If Sinus Aestuum initially had a similar amount of water, the expected water content of the bulk surface material after dilution would be around 100 ppm after, which is still above the detect limit of M^3 data (~ 10 s ppm) [*Li and Milliken*, in prep.-b]. Therefore, if Sinus Aestuum magmas or pyroclastic deposits once had water, the current abundance might be less than ~ 10 s ppm because even ‘freshly’ excavated pyroclastic materials exhibit no spectral evidence for water. It is also possible that magmas at Sinus Aestuum may have experienced a more extensive degassing history compared with other pyroclastic deposits.

4.4. Spinel at Sinus Aestuum

We applied a nonlinear spectral unmixing analysis to estimate spinel abundance at Sinus Aestuum using M^3 data (0.6 – 2.5 μm wavelength region). Spinel spectra are known for their strong absorption at 2 μm , and either a lack of or a much weaker 1 μm absorption depending on the Fe content [*Jackson et al.*, 2014]. These characteristics make

spinel readily identifiable from pyroxene (absorptions at 1 and 2 μm), olivine (broad absorption near 1.1 μm), and plagioclase (weak 1.25 μm absorption) on the lunar surface. The endmember spectra for high albedo (highland rich), low albedo (mare rich), and dark units (pyroclastic rich) were picked from the same locations used in the MI data analysis (Section 3.3 & 4.3) (Figure 9). However, an additional endmember from immature low albedo units was incorporated to accommodate the occurrence of a 2 μm absorption at low albedo units (e.g., excavated fresh mare basalts). Endmember spectra for spinel were selected according to the criteria and procedures described in section 3.3 (Figure 9). Spectral features of endmembers for high albedo, low albedo, and dark units are similar to those of MI data. The additional endmember for immature low albedo units shows strong 1 and 2 μm absorption features, suggesting high pyroxene content. The endmember spectra for spinel only exhibit a strong absorption at 2 μm and steep slopes at the 0.6 – 1.5 μm region (Figure 9).

The M^3 spectral unmixing results for high albedo, low albedo, and dark units at Sinus Aestuum are consistent with those from MI data. Estimates of spinel are overlain on the MI 750 nm map in Figure 10. Only pixels with over 30% spinel are color coded to avoid ambiguity in identification. The estimation shows that spinel is constrained within the pyroclastic deposit regions and it is mostly associated with small dark halo craters. However, not all dark halo craters have spinel exposed (Figure 10), which suggests that most spinel was excavated by impacts from the shallow subsurface (~ 10 s m according to the crater diameter to depth scaling law and [Head, 1974]). 3D views of mapped spinel at Sinus Aestuum are presented in Figure 11 and show that some spinel exposures are located on topographic high points or outside of pyroclastic deposits (yellow arrows in

Figure 11), which suggests that the spinel formation may be associated with violent explosive eruptions at Sinus Aestuum. We cannot exclude the possibility that spinel-bearing compositions and pyroclastic deposits at Sinus Aestuum may have a common magma source.

M³ spectra for pixels with different spinel contents are plotted in Figure 12. We averaged spectra of pixels with 0 to 100% spinel content at 10% bins. The spectra in Figure 12 essentially exhibit a mixing trend. The average spectra of pixels with high spinel content (e.g., > 90%) show no absorptions at ~1 and 1.3 μm as was observed in Spectral Profiler (SP) data [Yamamoto *et al.*, 2013]. The 1 μm absorption shown in Yamamoto *et al.* [2013] might be caused by pyroxene mixed with spinel (light blue spectra in Figure 12, containing 30 – 40% spinel). The 1.3 μm absorptions seen by SP data might be introduced by continuum removal because no absorption near 1.3 μm is shown before continuum removal (see original SP spectra in the supplementary materials of Yamamoto *et al.* [2013]). However, we observe strong concave up trends at wavelengths from ~500 nm to 900 nm and steep slopes from 800 nm to 1500 nm. There may be two absorptions in the 500 – 900 nm region, one absorption at ~500 – 650 nm and the other at ~650 – 800 nm. The mechanism of this strong concave up at 500 – 900 nm is still unclear. One possible mechanism is that the 500 – 650 nm absorption could be caused by octahedral Cr³⁺ in Cr spinel [Williams *et al.*, 2016], whereas the 650 – 800 nm absorption could be due to octahedral Fe²⁺ in aluminate spinel [Jackson *et al.*, 2014]. The steep slope from 800 nm to 1500 nm could be due to the presence of orange glass and black beads as indicated by MI data in Figure 6. The 1 μm absorption caused by octahedral Fe²⁺ in aluminate spinel might be counteracted or cancelled out by the

reflectance ‘peak’ observed in spectra of black beads at the same wavelength (Figure 6). The strong absorption centered at 550 nm due to octahedral Cr^{3+} in Cr spinel (Figure 6 in *Williams et al.* [2016]) coupled with octahedral Fe^{2+} in aluminate spinel (Figure 2 in *Jackson et al.* [2014]) could create strong concave up trends from 500 to 800 nm. However, this interpretation is non-unique. Other mechanisms should be explored in future studies to better understand the type(s) of spinel and glass that might be present in these regions.

Similar to the M^3 results, we also plotted the average (low spectral resolution) MI spectra of pixels with different spinel contents from 0% to 100% with 10% bin size (Figure 13, the bottom plot), and M^3 data resampled to the MI spectral bands are plotted for comparison (Figure 13, the top plot). It is clear from Figure 13 that the two datasets are in excellent agreement with respect to the spectral properties of these pixels. The wiggles observed in resampled M^3 data are mostly artifacts (see the original data in Figure 12 before resampling), whereas wiggles of MI data at 1 μm might be due to the imperfect alignment of VIS and IR cameras of the MI instrument.

In summary, the emplacement of spinel may be associated with explosive eruptions at Sinus Aestuum and the spinel may share the same magma source as the pyroclastic deposits in this region. The spectral features of spinel at Sinus Aestuum indicate octahedral Cr^{3+} in Cr spinel and octahedral Fe^{2+} in aluminate spinel, although the absolute abundance might be very low (according to their very weak absorptions), which is distinct from Mg spinel at other locations on the lunar surface. The presence of octahedral Fe^{2+} in aluminate spinel may suggest fast cooling rates during formation, which requires thin or no vapor clouds during pyroclastic eruptions at Sinus Aestuum

[*Jackson et al.*, 2014]. This is also in accordance with a relatively dry magma source at Sinus Aestuum.

5. Discussion

Three hypotheses are proposed for the absence of lunar interior water at Sinus Aestuum pyroclastic deposits. Lateral and/or vertical mixing introduced by the Copernicus impact may mute water absorptions at Sinus Aestuum. Alternatively, the magma source(s) of pyroclastic deposits at Sinus Aestuum may have been H₂O-poor. Finally, water may have been present in the pyroclastic deposit but has since diffused out by post-emplacement thermal events. The spectral unmixing analyses show that pyroclastic materials at Sinus Aestuum are only around five times less abundant than those at Rima Bode, which is not sufficient to mute water features completely at our level of detection in M₃ data. The absence of water features at ‘fresh’ pyroclastic materials excavated by young craters also suggests that the pyroclastic materials are inherently dry, at least prior to excavation. Water (if any) in pyroclastic materials that were ejected far from the vents and thus less affected by thermal events would have been more likely to be retained. However, no such case is observed through the Sinus Aestuum deposits. All the above observations indicate that the hypothesis of dry magma sources at Sinus Aestuum deposits is more plausible, suggesting heterogeneity of water content in the lunar interior. Additionally, the lack of water in the magma source may produce thin vapor clouds during eruption, which may provide the environment (fast cooling) for the formation of octahedral Fe²⁺ in aluminite spinel [*Jackson et al.*, 2014]. However, it is unclear whether pyroclastic materials can be ejected far enough to avoid effects from

post-deposition thermal events. So, we cannot entirely rule out that water was initially present in the Sinus Aestuum pyroclastic deposits and has subsequently been lost via diffusion during post-deposition thermal events.

There are two unresolved uncertainties in our nonlinear spectral unmixing analyses. One is from the assumption that all particle sizes at our research area are identical. Although the spectral properties of the lunar surface are controlled by particles with 10 – 20 μm size [Pieters *et al.*, 1993], the particle size of samples from the same location could vary from several to hundreds of micrometers [Heiken *et al.*, 1991], which could introduce non-negligible uncertainties. However, our nonlinear spectral unmixing analyses are sufficient to provide relative abundances of endmembers by accommodating the effects from viewing geometry, phase function, porosity, back surge, and multiple scattering, which is sufficient to support the conclusions presented here. The other uncertainty is from the selection of endmembers from the images. Using endmembers selected from images has several advantages. First, systematic errors from different instruments (i.e., in laboratory and onboard orbiters) are negated. Second, effects from space weathering (i.e., nanophase iron) on the lunar surface cannot be resolved explicitly in radiative transfer modeling [Li and Li, 2011], but those effects are included in spectra of in-scene endmembers. A remaining concern is whether our selected endmembers are representative for the research areas. We apply several approaches to constrain this uncertainty and to validate our model results. As described in section 3, all endmembers are carefully picked and compared with laboratory spectra to guarantee that purest and unique endmembers are selected for each study region. We also examine the curve fittings of our spectral unmixing analyses. The residuals of curve fittings are very small,

generally on the order of 10^{-3} , indicating nearly all spectral variability within a region is appropriately captured by our chosen endmembers. Spectra from different regions within each scene were also examined to assess whether the endmembers were representative. Therefore, our nonlinear spectral unmixing analyses are capable of providing a first-order understanding of the relative abundance of the selected endmembers, though we acknowledge that the composition of these regions is inherently more complex than can be accommodated by our narrow range of endmembers.

6. Conclusions

We mapped geomorphological features for two large pyroclastic deposits at Sinus Aestuum and Rima Bode using the MI 750 nm images (~ 20 m/pixel). Empirically derived band parameters and band ratios were applied to examine the compositional variations of different geomorphological units. Results from band ratios suggest that compositions in individual units are relatively homogeneous. Pyroclastic materials at Sinus Aestuum are heavily contaminated (mixed with other lithologies) when compared with those at Rima Bode. Nonlinear spectral unmixing analyses (radiative transfer modeling) were performed at Sinus Aestuum and Rima Bode with MI data to understand the effects of lateral and/or vertical mixing and the degree to which such processes may mask water absorptions at Sinus Aestuum. The spectral unmixing results show that pyroclastic materials at Sinus Aestuum may have been diluted around five more times than those at Rima Bode. However, this dilution is not sufficient to explain the entire absence of water feature at Sinus Aestuum given our current understanding of detection limits for water absorptions in M^3 data. The hypothesis of a water-poor magma source at

Sinus Aestuum remains plausible. However, water loss via degassing during emplacement or by post-emplacement heating events cannot be ruled out. Pixels of M^3 data that represent purest spinel were selected as in-scene endmembers and used in spectral mixing models to estimate the relative spinel content at Sinus Aestuum. The weak absorptions at 500 – 650 nm and 650 – 800 nm of spinel spectra at Sinus Aestuum may be indicative of octahedral Cr^{3+} in Cr spinel and octahedral Fe^{2+} in aluminate spinel, respectively, whereas the 1 μm absorption paired with a 0.7 μm feature are both caused by octahedral Fe^{2+} . The latter might be cancelled out by the reflectance ‘peak’ in spectra of black beads at 1 μm (Figure 6), but this interpretation is non-unique and further study is warranted. If confirmed, the presence of octahedral Fe^{2+} in aluminate spinel suggests fast cooling rates that require thin/no vapor clouds during the pyroclastic eruption [Jackson *et al.*, 2014], which is in accordance with the dry magma source hypothesis at Sinus Aestuum.

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Figure captions

Figure 1. The 750 nm albedo map of Multiband Imager (MI) data at the two pyroclastic deposits Sinus Aestuum and Rima Bode, 2% linearly stretched.

Figure 2. (a) Color coded geomorphological units outlined with MI 750 nm images at Sinus Aestuum; (b) outlines of our mapped geomorphological units overlain on the water map from *Li and Milliken* [in prep.-b] at Sinus Aestuum, no water feature is observed, the base map is WAC mosaics; explanation of legends: DarkSmooth: smooth and dark (very low albedo) units; DarkHighMix: mixing zones between dark and high albedo units; HighAlbedo: high albedo units; LowAlbedo: low albedo units; DarkLowMix: mixing zones between dark and low albedo units; DarkSpoty: lumpy and dark units; Lava channel: riles.

Figure 3. (a) Color coded geomorphological units outlined from MI 750 nm images at Rima Bode; (b) outlines of our mapped geomorphological units overlain on the water map from *Li and Milliken* [in prep.-b] at Rima Bode; explanation of legends: DarkSmooth: smooth and dark (very low albedo) units; DarkHighMix: mixing zones between dark and high albedo units; HighAlbedo: high albedo units; LowAlbedo: low albedo units; DarkLowMix: mixing zones between dark and low albedo units; LavaFlow: morphology associated with lava flows; Lava channel: riles.

Figure 4. False color map of band parameters and band ratios of MI data at Sinus Aestuum and Rima Bode, assignments of each band are listed in the map.

Figure 5. Outlines of our mapped geomorphological units overlain on the band ratio maps at Sinus Aestuum (a) and Rima Bode (b).

Figure 6. (a) Single scattering albedo of endmembers of MI data for nonlinear spectral unmixing analyses at Sinus Aestuum and Rima Bode; (b) laboratory measured spectra of Apollo green glass, orange glass, and black beads resampled to MI spectral resolution.

Figure 7. Nonlinear spectral unmixing results using MI data and endmembers shown in Figure 6 for Sinus Aestuum (a) and Rima Bode (b); note that each endmember is not pure in composition.

Figure 8. Histograms of abundances of pyroclastic rich endmember at Sinus Aestuum (top) and Rima Bode (bottom).

Figure 9. Endmember spectra of M^3 data for nonlinear spectral unmixing analyses at Sinus Aestuum.

Figure 10. Estimates of spinel at Sinus Aestuum overlain on the MI 750 nm images, only pixels composing > 30% spinel are color coded.

Figure 11. A 3D view of mapped spinel at Sinus Aestuum, the base map is MI 750 nm mosaics (~20 m/pixel) and the DEM data is SLDEM2015 derived from LOLA and KAGUYA terrain camera data (~59 m horizontal resolution, 3 – 4 m vertical resolution).

Figure 12. Average single scattering albedo of pixels from M³ images with estimated spinel from 0 to 100% with a bin size 10% (top) and they were offset for clarity (bottom).

Figure 13. Average single scattering albedo shown in Figure 12 are resampled to MI spectral bands to compare with those of MI pixels composing the same amount of spinel, note that wiggles of the M³ green spectrum (50-60% spinel) are introduced by artifacts of M³ data (see Figure 12, the brown spectrum with 50 – 60% spinel); while the wiggles of MI data at ~1 μm might be due to the imperfect alignment of MI VIS and IR cameras, this plot suggests data consistency between M³ and MI data.

Figures

Figure 1

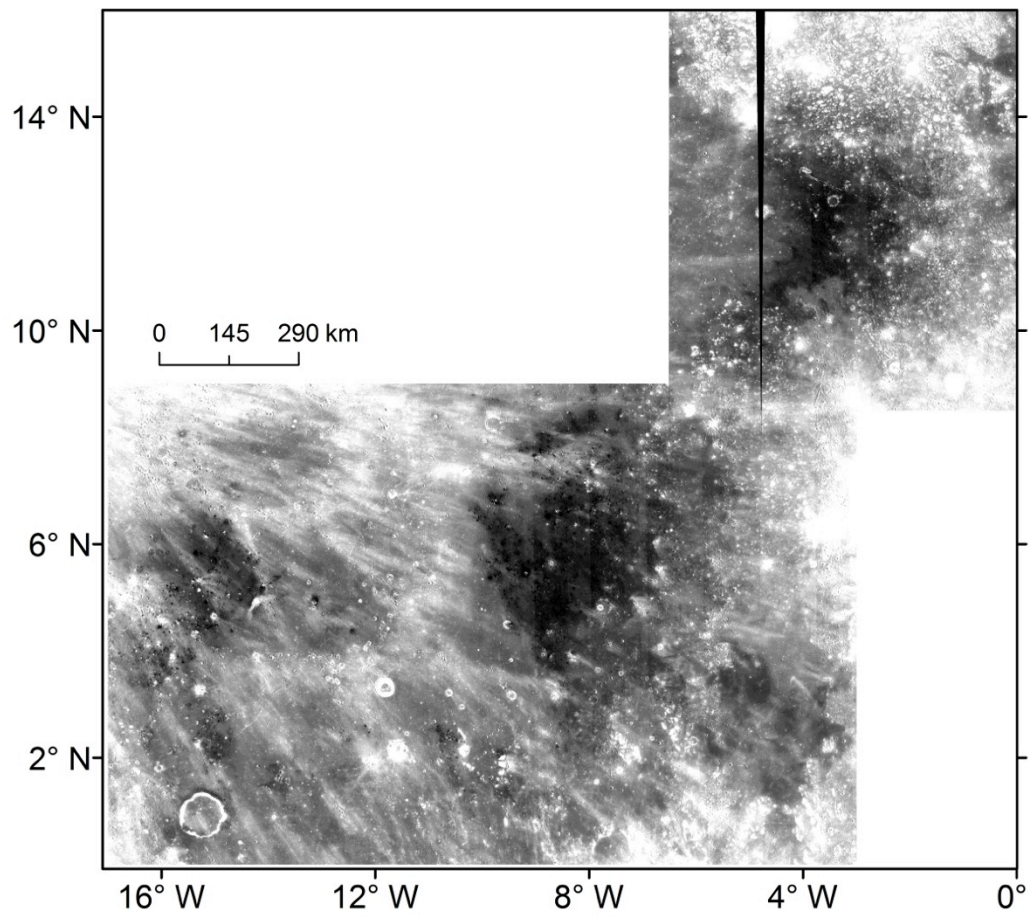


Figure 2

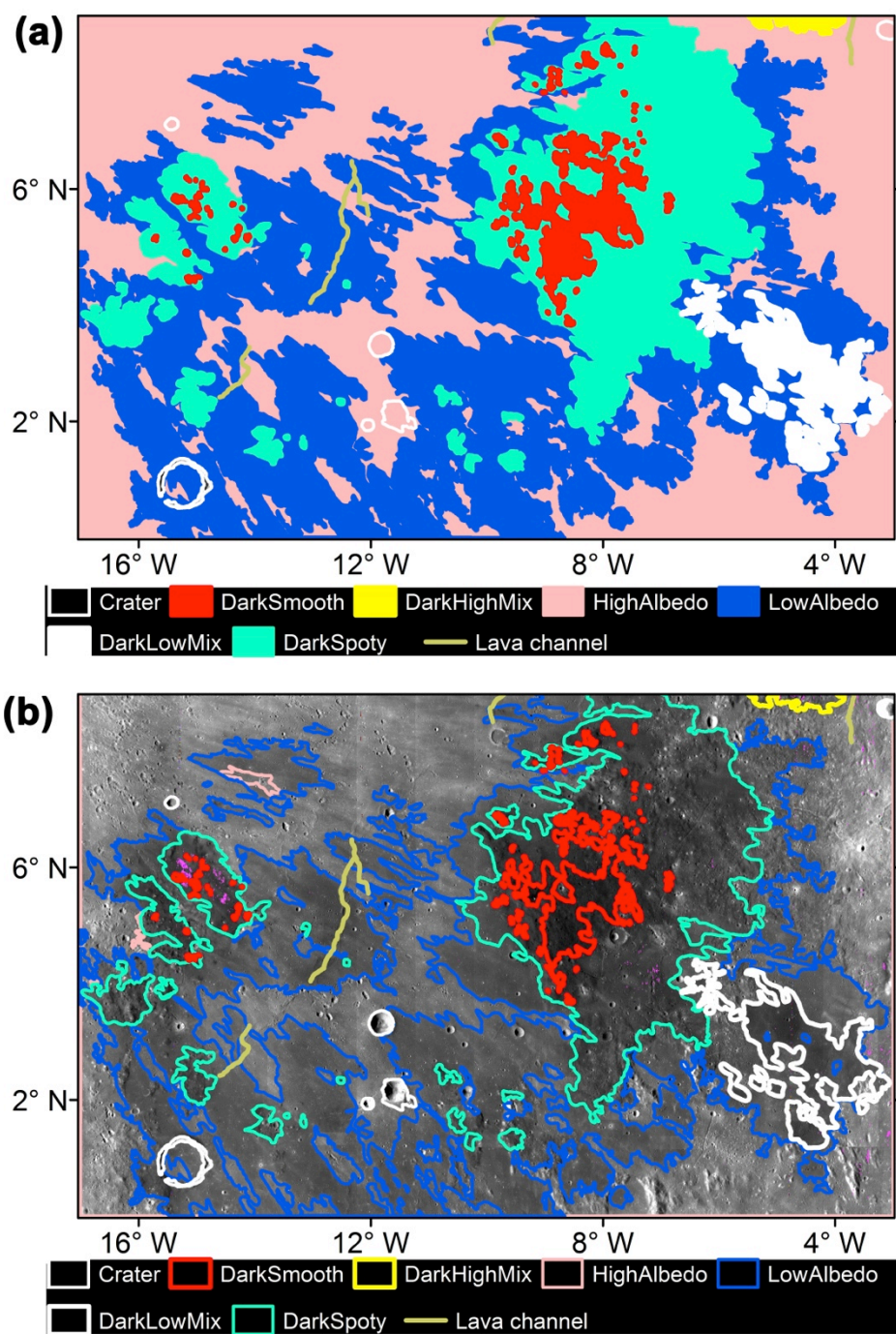


Figure 3

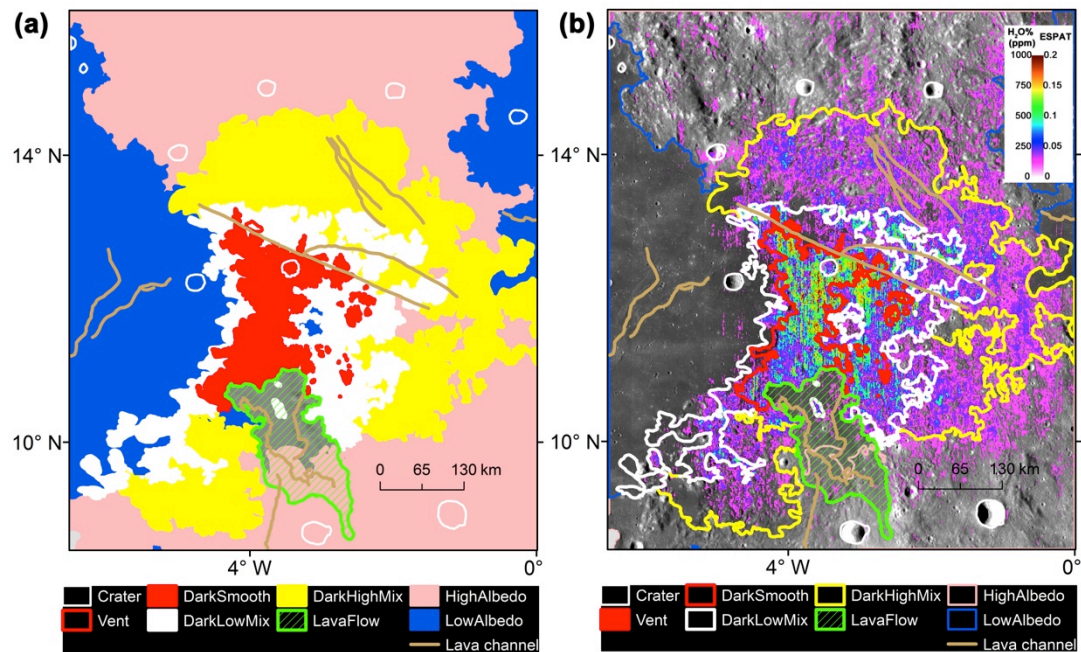


Figure 4

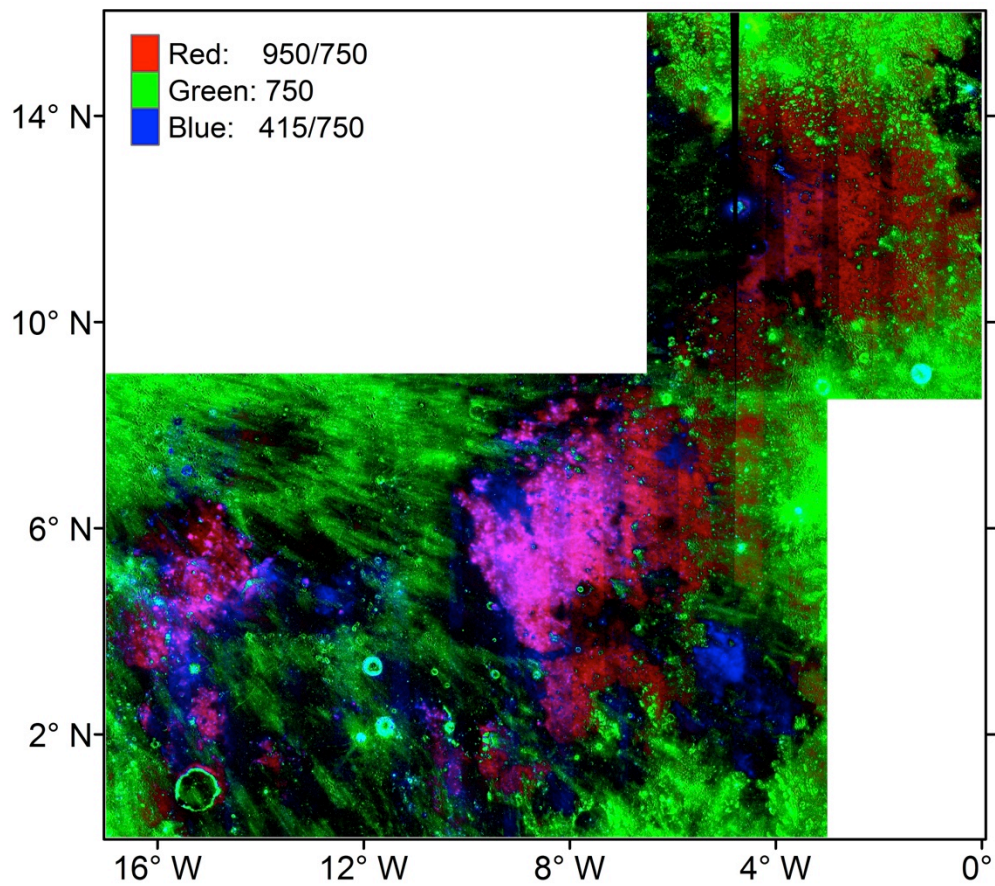


Figure 5

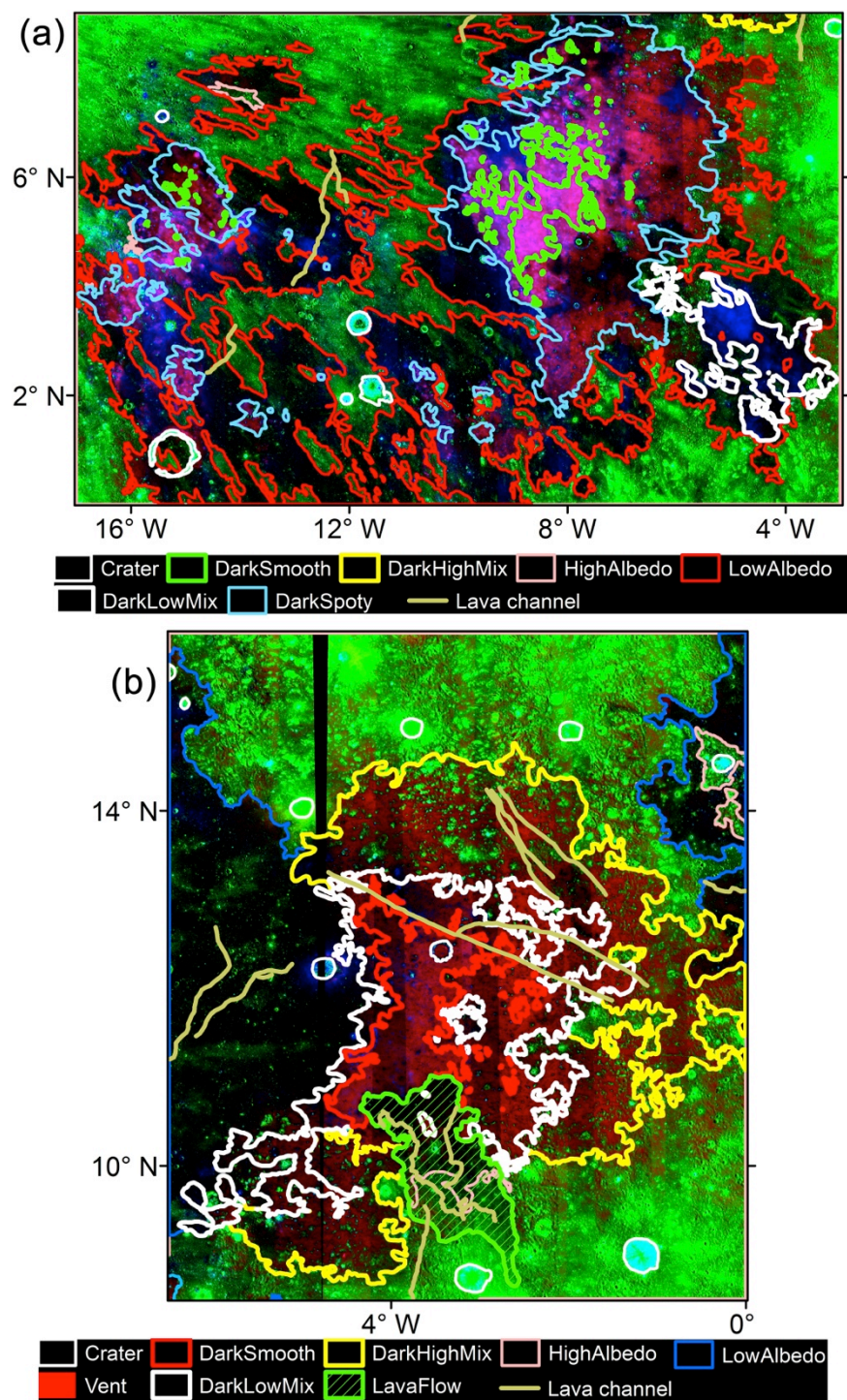


Figure 6

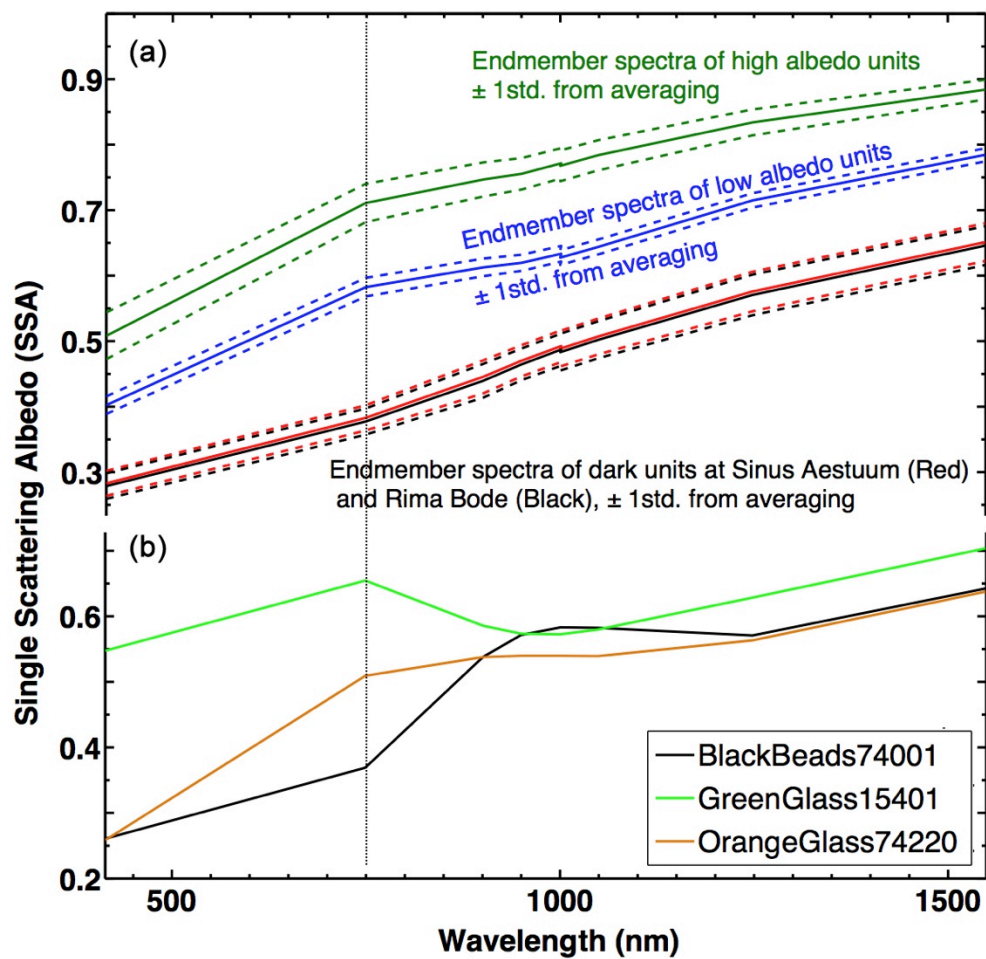


Figure 7

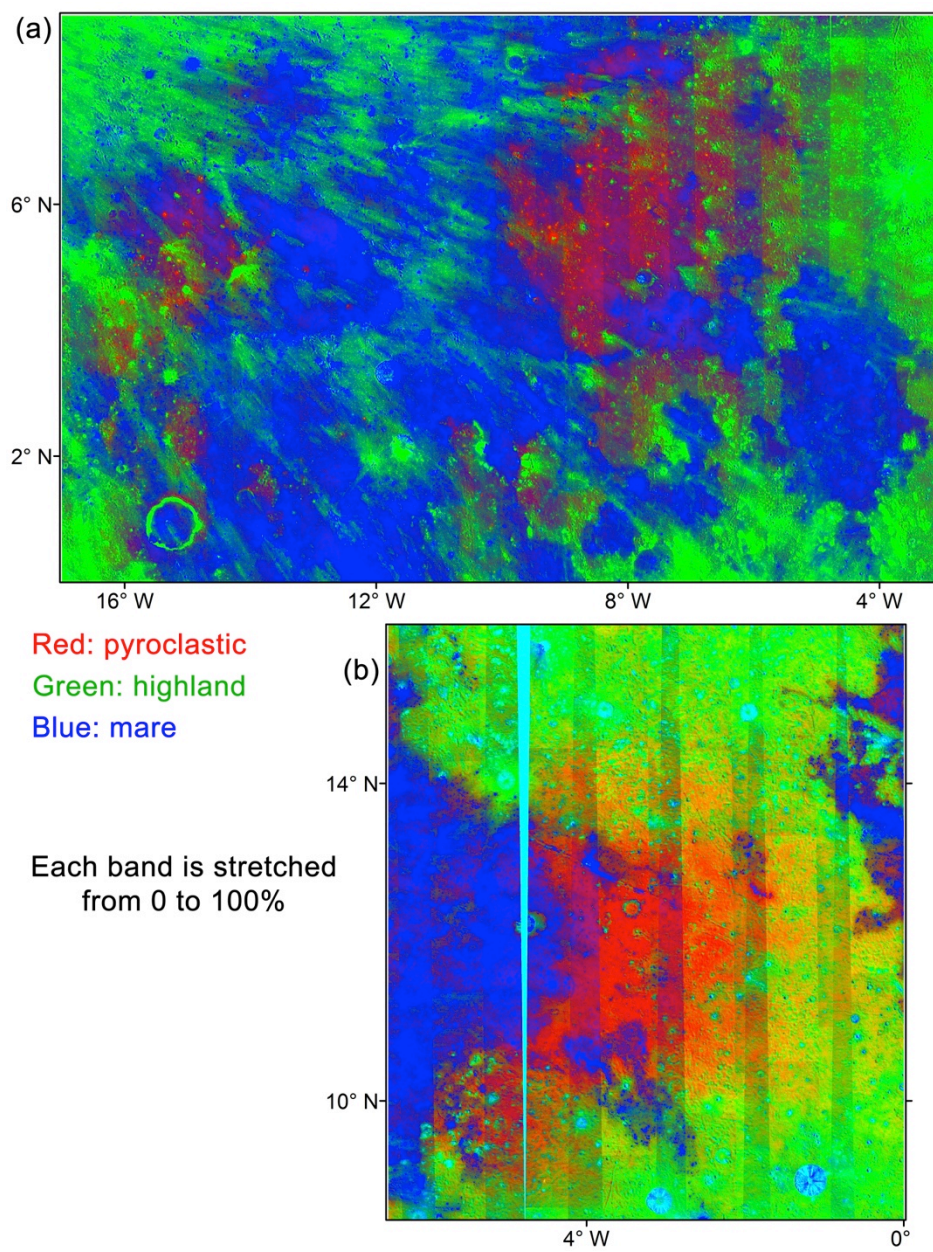


Figure 8

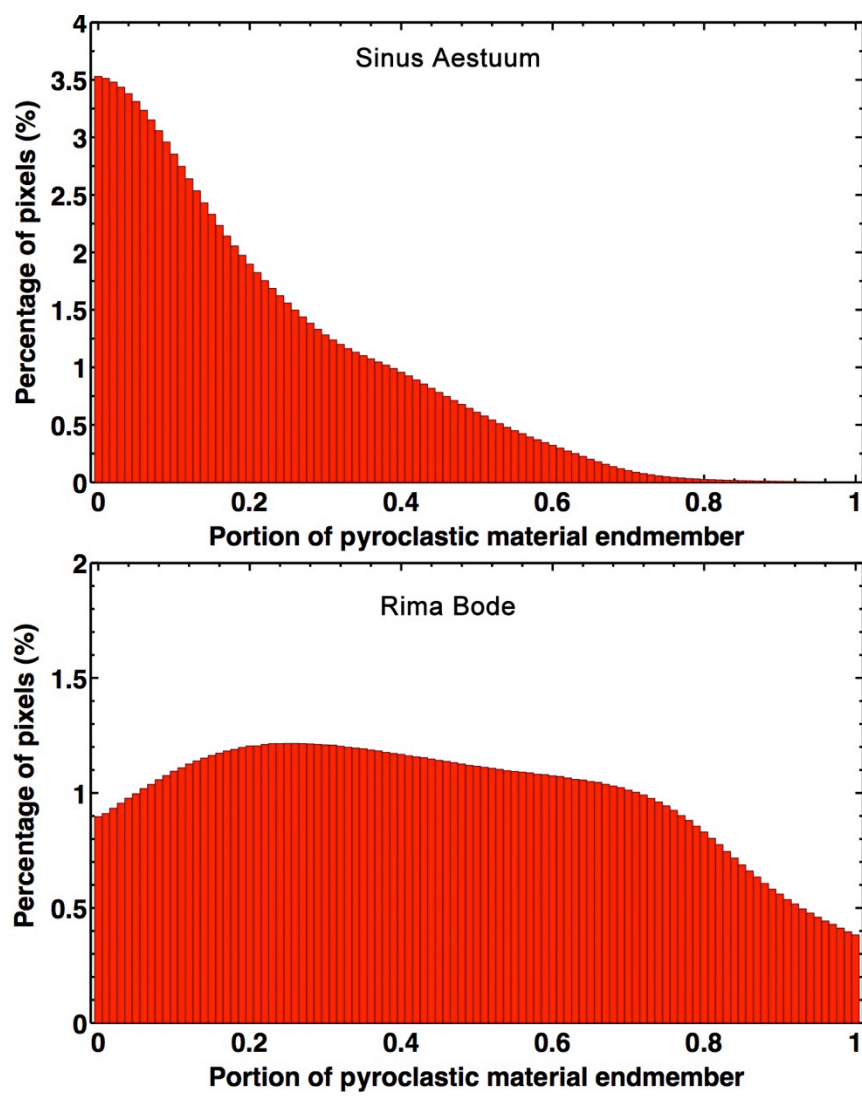


Figure 9

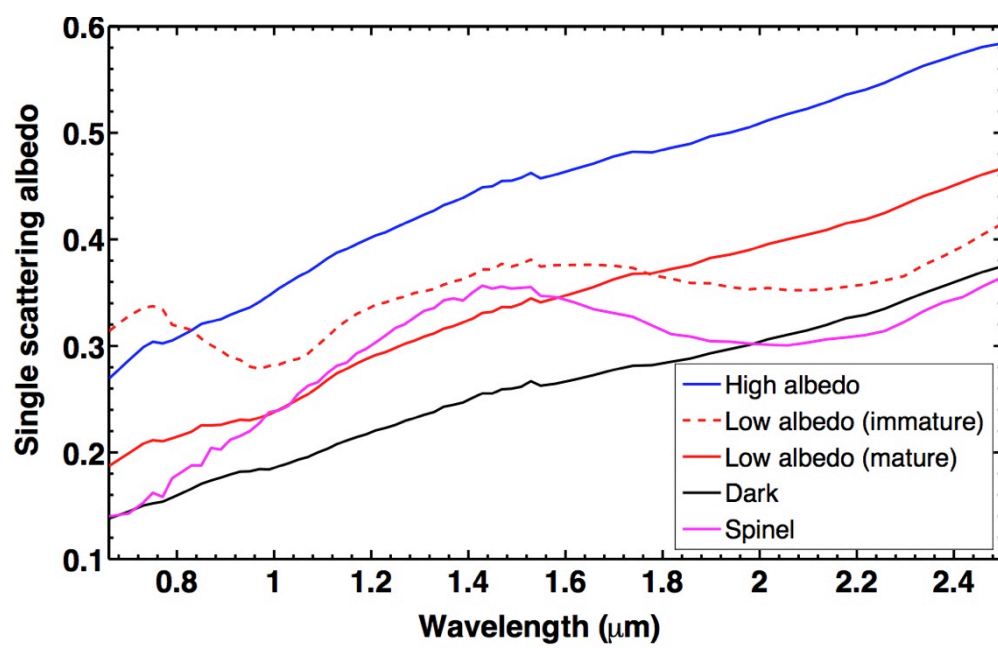


Figure 10

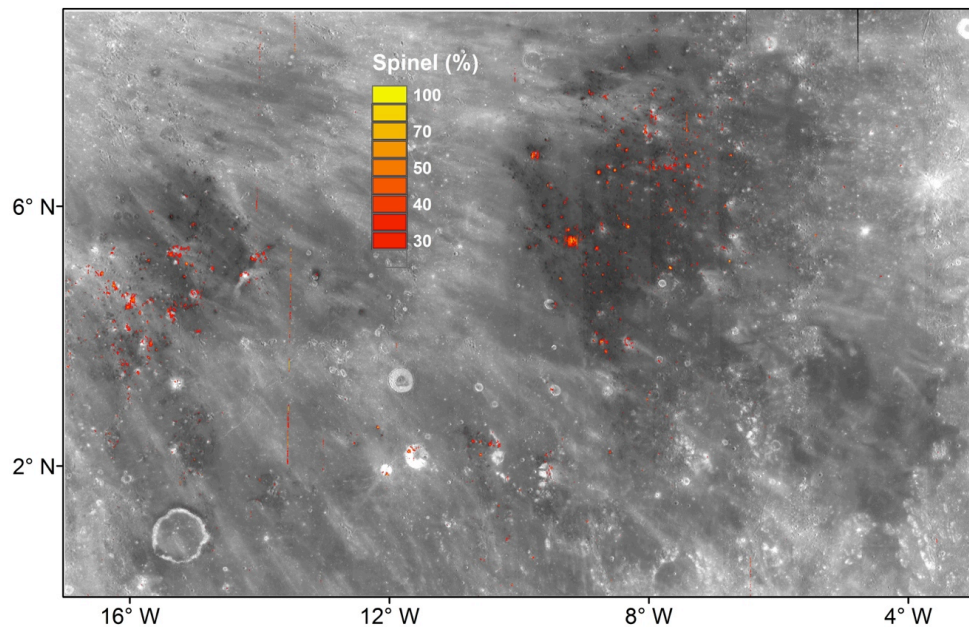


Figure 11

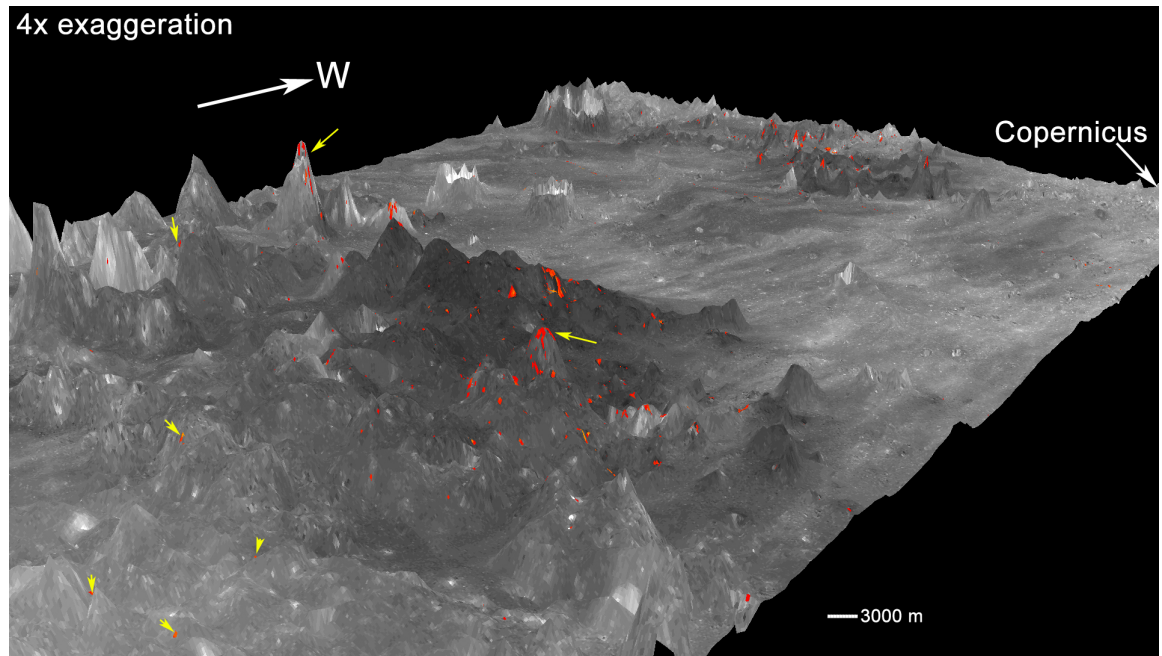


Figure 12

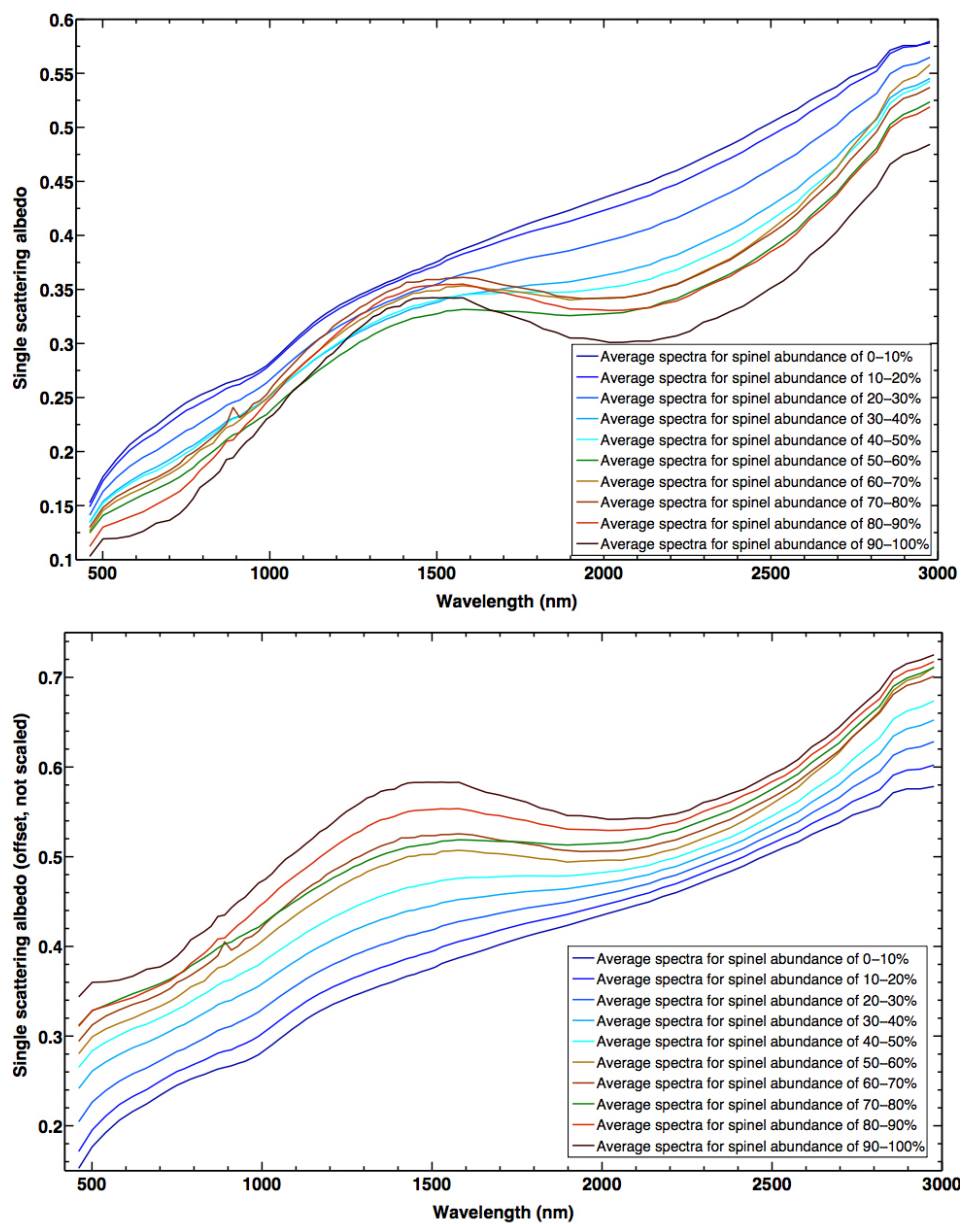
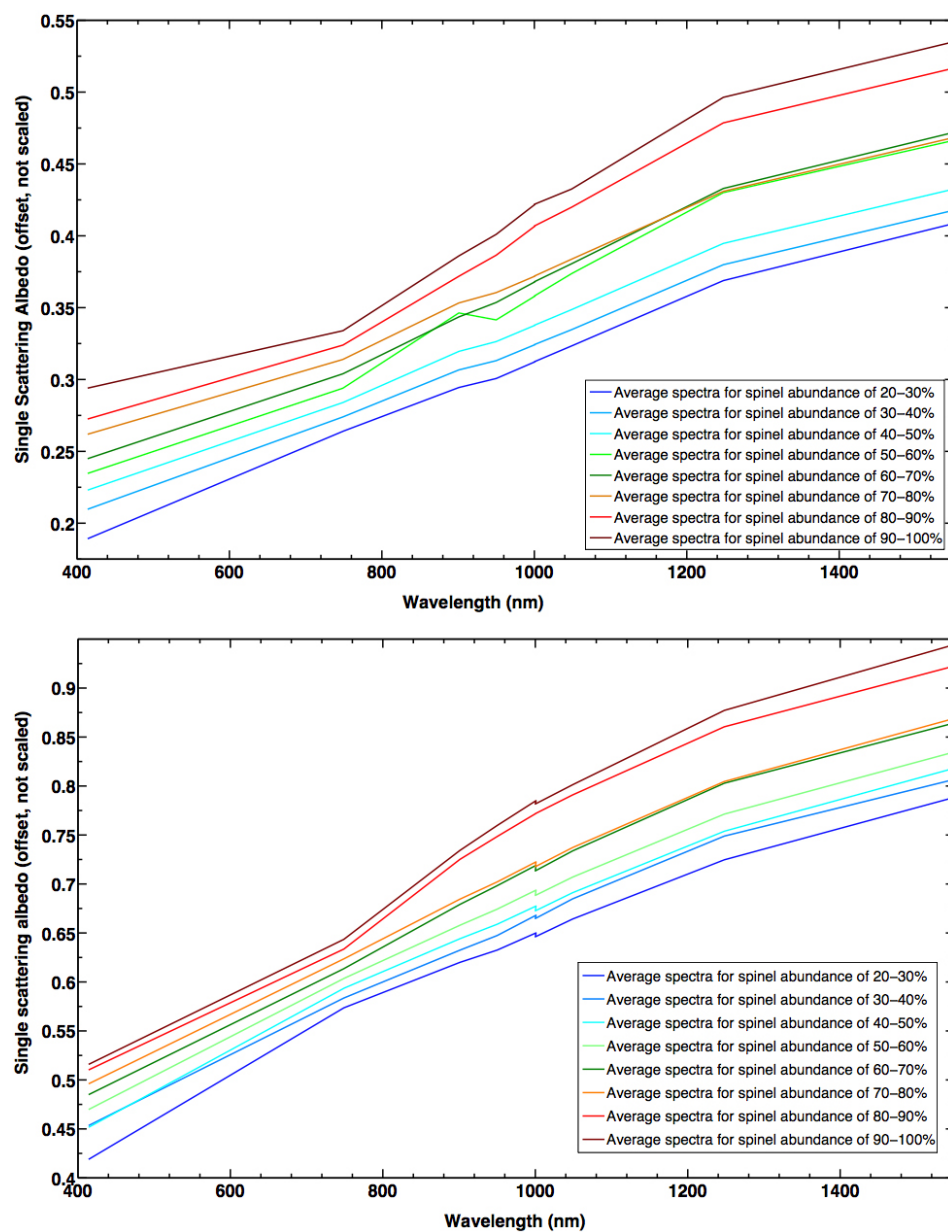


Figure 13



Water at the Optical Surface of the Moon: A Summary

The bulk of this thesis focuses on understanding the distribution and origin of ‘water’ (OH/H₂O) on the Moon. Whether or not the lunar surface should record hydration signatures from solar wind, cosmic rays, impacts, and/or magmatic processes has been debated since the pre-Apollo era [Watson *et al.*, 1961]. Using lunar samples to address these questions at a global scale, however, is difficult due to terrestrial contamination [Epstein and Taylor, 1970] and limited sampling locations [Elkins-Tanton and Grove, 2011]. Orbital detection of lunar surface water provides an alternative way to assess the sources of lunar surface water and its abundances. Following quickly on the unambiguous detection of water in lunar volcanic glasses [Saal *et al.*, 2008], absorption features indicative of water was observed in near-IR reflectance spectra acquired by the EPOXI [Sunshine *et al.*, 2009], Cassini VIMS [Clark, 2009], and Chandrayaan-1 Moon Mineralogy Mapper (M³) instruments [Pieters *et al.*, 2009].

However, the interpretation of these observations was complicated by a combination of low spatial resolution data (>10 km/pixel for EPOXI and VIMS) and the presence of thermally emitted radiation at wavelengths >2 μm in M³ data [McCord *et al.*, 2011]. As part of this thesis, a new model was developed for M³ data to address the thermal effects present in current publicly available data, the details of which are presented in Chapter 1. My research combined M³ data, thermal infrared measurements from the LRO Diviner instrument, and lab spectra of Apollo samples with radiative transfer models to develop a novel semi-empirical thermal correction model for the entire M³ dataset [Li and Milliken, in review]. The resulting thermally-corrected M³ data were then combined with a Hapke radiative transfer model and laboratory experiments to provide the first global quantitative maps of ‘water’ at the optical surface of the Moon.

This allows a new perspective on the spatial and temporal distribution of lunar surface water, which in turn can be compared with models of solar wind implantation, surface migration of volatiles, and retention of volatiles sourced from the lunar interior.

Key findings of Chapter 2 are that lunar surface hydration is variable both spatially and temporally, and these observations are consistent with a solar-wind origin. Importantly, this work demonstrates that surface hydration varies strongly as a function of latitude and thus its retention is likely controlled by diurnal variations in surface temperature, with surface composition (e.g., mare vs. highland) having little or no effect. Indeed, water mapping results presented in Chapter 2 demonstrate that surface hydration is dynamic over the course of a lunar day at latitudes $<60^\circ$, whereas higher latitudes are characterized by increased water content and apparent thermal stability of that water. In addition, at high latitudes it was found that regions of increased optical maturity (increased degree of space weathering) exhibit higher water contents than ‘immature’ regions, suggesting the latter may not yet have reached steady state. This work broadens our knowledge on the distribution, variation, and origin of the lunar surface water and provides quantitative estimates for comparison with theoretical and experimental rates of hydroxyl formation and destruction at the lunar surface.

The mapped water content at the Apollo sampling zone (i.e., $\sim\pm 30^\circ$ latitude) is found to be broadly consistent with water contents measured from bulk Apollo soil samples. This suggests that water produced by solar wind produced is the major contributor to the lunar surface water reservoir at a global scale [*Liu et al.*, 2012; *Li and Milliken*, in prep.], and water contents attributable to solar wind are on the order of ~ 100 ppm at $\pm 30^\circ$ latitude. Thus regions with ‘enhanced’ water contents, which may indicate

impact or magmatic sources, can be identified by locating areas in excess of this value, which is discussed in Chapter 3 and 4.

The major findings of that work are that lunar pyroclastic deposits and silicic rich domes exhibit strong and persistently higher water contents than surrounding terrains, indicating some of this signature may represent endogenous water associated with magmatic sources. I combined M^3 , *SELENE* MI, *LROC* NAC, and Earth based radar data with radiative transfer modeling, lab-based empirical modeling, magma ascent models, and finite difference numerical modeling to examine and quantify the potential endogenous water content of lunar pyroclastic and silicic rich domes, which provides a broader picture of magma volatile content and variations in magma degassing history on the Moon.

Results from this integrated study show that volcanic glasses at pyroclastic deposits are the major host for observed excess water signatures. This water may be both quenched within and vapor deposited on the glass. Interestingly, high-Ti deposits show higher water content than low-Ti ones, indicating either different water contents in magma source regions, different degassing history, or both. The hydration state of silicic rich domes exhibits more complicated processes compared with pyroclastic deposits. Only three out of seven of these identified locations exhibit enhanced hydration levels. Several possible scenarios are proposed, such as 1) silicic domes have a more complicated degassing history than pyroclastic deposits; 2) the water content in their magma sources has much larger variations than that of pyroclastic deposits; 3) The distinct lithologies between pyroclastic deposits and silicic rich domes show different

effects on the water retention; 4) The identification of their composition as being silicic-rich is ambiguous.

The work presented in Chapters 1 – 3 emphasizes scientific questions related to water on the Moon at large (global) spatial scales. Localized water anomalies seen through these global scale studies remains an area of future research and exploration. Intriguingly, Sinus Aestuum is the only one of the large pyroclastic deposits that shows weak evidence for hydration. In addition, Sinus Aestuum is the only pyroclastic deposit that has spinel exposed at the surface [Pieters *et al.*, 2014]. Is there any link between the apparent lack of lunar interior water in this deposit and the formation of spinel? What can the presence of these factors tell us about magmatic evolution in this region? To explore this question in more detail a detailed geomorphological and mineralogical study was performed at Sinus Aestuum and, for comparison, at Rima Bode (Chapter 4).

That study shows that the absence of a lunar interior water signature at Sinus Aestuum can be attributed to a dry magma source region. However, the hypothesis that lunar interior water was initially present but diffused out due to post-deposition thermal events cannot be ruled out. Weak absorptions at 500 – 650 nm and 650 – 800 nm in M^3 spectra for spinel-rich regions at Sinus Aestuum may be indicative of octahedral Cr^{3+} in Cr spinel and octahedral Fe^{2+} in aluminite spinel, respectively, whereas the 1 μm absorption paired with a 0.7 μm absorption (both caused by octahedral Fe^{2+}) may be cancelled out or masked by spectral features observed at 1 μm for black volcanic glass beads. Despite these spectral complexities, the presence of octahedral Fe^{2+} in aluminite spinel suggests fast cooling rates that require thin/no vapor clouds during the pyroclastic

eruption [Jackson *et al.*, 2014], which is in accordance with the dry magma source hypothesis at Sinus Aestuum.

1. Outstanding Questions

1.1. Thermal Issues of Reflectance Spectra at Wavelength $>2 \mu\text{m}$ on the Lunar Surface

The new semi-empirical thermal correction model in Chapter 1 has uncertainties from the deviation of the $1.54\text{-}2.54 \mu\text{m}$ trend. Although uncertainties from this deviation have been assessed and will not change the global trends of water distribution and variation in Chapter 2, it will be challenging to apply this model to reflectance data acquired on the lunar surface with different spectral and spatial resolutions. For instance, what are the uncertainties if applying this model to Clementine multiband spectral images or hyper-spectral data acquired by Spectral Profiler onboard KAGUYA (SELENE) mission? Will this model work on reflectance data acquired by spectrometers on a rover or lander (e.g., Chang'E 3&5)? Laboratory studies are required for understanding the thermal behaviors of lunar surface materials at the optical depth under vacuum and strong solar irradiation conditions.

1.2. Lunar Surface Water Speciation, Variation, and Origin

What is the speciation of the water seen by M^3 data is an important unresolved question. The abundance of the lunar surface water ($\text{H}_2\text{O}/\text{OH}$) is too low that only the fundamental stretching absorptions (both H_2O and OH) centered $\sim 3 \mu\text{m}$ are visible at the M^3 wavelength region ($\sim 0.4 - 3 \mu\text{m}$). The fundamental bending absorption of H_2O

centered $\sim 6 \mu\text{m}$ can be applied to discriminate it from OH. Alternatively, a full $3 \mu\text{m}$ absorption bands from ~ 2.6 to $4 \mu\text{m}$ will be helpful for telling the lunar surface water speciation. The presence of H_2O will make the spectra exhibit broader absorption with the center shifted towards longer wavelengths than OH [Milliken, 2006]. A spectrometer or imager with spectral wavelengths at least including $2.6 - 4 \mu\text{m}$ bands onboard orbiters or rovers/landers are necessary to discriminate the speciation of lunar surface water at different scales.

The diurnal variation of lunar surface water has been observed by different instruments that sense different depths. Analyses of data acquired by the Lyman Alpha Mapping Project (LAMP) instruments onboard the NASA Lunar Reconnaissance Orbiter (LRO) suggest that lunar surface water within the sensing depth of several microns varies diurnally [Hendrix *et al.*, 2012]. Near infrared reflectance spectra acquired by EPOXI and M^3 sensing around $100 \mu\text{m}$ also suggest the diurnal variation of lunar surface water [Sunshine *et al.*, 2009; Li and Milliken, in prep.]. Interestingly, statistics of data acquired by the Lunar Exploration Neutron Detector (LEND) onboard LRO that senses $\sim 1 \text{ m}$ thick of the lunar surface also indicate that water at this zone varies diurnally but the minimum value does not appear at local noon as shown by the UV and Near infrared data but shifts to $\sim 2:30$ local afternoon. What can the diurnal variations of lunar surface water at different depths inform us about its origin and distribution beneath the surface (at least 1 m)? What does the shift of the minimum water abundance at daytime sensed by LEND mean? Is the shift associated with diffusion processes driven by temperature? However, the temperature profile of the lunar surface shows that it reaches steady state at around 0.5 m [Vasavada *et al.*, 1999].

1.3. Questions Raised by the Wet Yet Heterogeneous Lunar Interior Seen by M³ Data

Multiple lines of evidence suggest that the excess water signature observed at pyroclastic deposits in Chapter 3 is from the lunar interior. The anomalies of water at silicic rich domes may be also associated with magmatic activities and sources from the interior. Several outstanding questions are raised according to these new finds in Chapter 3. Can we estimate the absolute water content of magma sources before degassing and consequently the water content in the mantle from the mapped water at pyroclastic deposits and silicic domes? How was water retained in the catastrophic giant impact that is hypothesized to create the Moon? If water was depleted entirely in the giant impact, what are the sources of the lunar interior water observed in Apollo samples and by orbital data? What can the heterogeneity of the lunar interior water inform their origin and retention? How will the presence of lunar interior water change our understanding about the evolution of the Moon (i.e., lunar magma ocean)? Is there any connection between the heterogeneously hydrated lunar interior and the long lived lunar core dynamo [*Stegman et al.*, 2003; *Evans et al.*, 2014]? Do we need to reexamine all previous work that assumed a completely dry lunar interior? Where else do we expect to detect the lunar interior water besides pyroclastic deposits and silicic rich domes?

1.4. Other Localized Water Anomalies Need to Be Explored

Sinus Aestuum one of the most interesting localized water anomalies is investigated in details with high spatial (KAGUA/SELENE MI) and spectral (M³) resolution data in Chapter 4. The magma source properties and emplacement processes of

pyroclastic deposit are revealed by the analyses of combined datasets. There remain multiple localized water anomalies waiting for future exploration. They include but are not limited to the Plato crater (enhanced water content at the crater center and rim), a small mare region near Mons Pico located at the north east of mare Imbrium (enhanced water content), mare Australe (enhanced water content), and the mare Humboldtianum-crater Compton region (suppressed water content). More locations showing water anomaly can be found in the water map shown in Chapter 2.

2. Applications

I am interested in the water budget within the ‘snow line’ in our solar system. The framework I developed for examining hydration features of the lunar surface can also be applied to Vesta (*Dawn* VIR data), C-type asteroids (e.g., the upcoming OSIRIS-REx and Hayabusa2 missions) as well as data acquired in past and future for other airless planetary bodies. As such, I hope to continue this part of my research in order to further improve our understanding of how the solar wind interact with different materials, the distribution and origin of volatiles on planetary bodies, how they evolve through time, and what can it inform the solar system formation and evolution.

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