Effects of Regolith Properties on UV/VIS Spectra and Implications for Lunar Remote Sensing

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Effects of Regolith Properties on UV/VIS Spectra and Implications for Lunar Remote Sensing

by

Ecaterina “Oana” Coman

A dissertation presented to
The Graduate School
of Washington University in
partial fulfillment of the
requirements for the degree
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“If I have seen further, it is by standing upon the shoulders of giants”

-Sir Isaac Newton

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Washington University in St. Louis

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Abstract of the Dissertation

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by

Ecaterina “Oana” Coman

Doctor of Philosophy in Earth and Planetary Science

Washington University in St. Louis, 2017

Professor Bradley L. Jolliff, Chair

Lunar regolith chemistry, mineralogy, various maturation factors, and grain size dominate the reflectance of the lunar surface at ultraviolet (UV) to visible (VIS) wavelengths. These regolith properties leave unique fingerprints on reflectance spectra in the form of varied spectral shapes, reflectance intensity values, and absorption bands. With the addition of returned lunar soils from the Apollo and Luna missions as ground truth, these spectral fingerprints can be used to derive maps of global lunar chemistry or mineralogy to analyze the range of basalt types on the Moon, their spatial distribution, and source regions for clues to lunar formation history and evolution.

The Lunar Reconnaissance Orbiter Camera (LROC) Wide Angle Camera (WAC) is the first lunar imager to detect bands at UV wavelengths (321 and 360 nm) in addition to visible bands (415, 566, 604, 643, and 689 nm). Sato et al. [2017] has used the relationship between returned lunar soil TiO$_2$ concentrations and ratios of the lunar reflectance at 321 and 415 nm at the corresponding landing sites to derive a global TiO$_2$ map of the Moon. This dissertation uses a combination of laboratory and remote sensing studies to examine the relation between TiO$_2$ concentration and WAC UV/VIS spectral ratio and to test the effects of variations in lunar
chemistry, mineralogy, and soil maturity on ultraviolet and visible wavelength reflectance, particularly on the 321/415 ratio (the ratio of reflectance intensity at 321 nm to that at 415 nm). The research comprises three parts:

1) An introduction to the dissertation that includes some background in lunar mineralogy and remote sensing.

2) Coordinated analyses of returned lunar soils using UV-VIS spectroscopy, X-ray diffraction, and micro X-ray fluorescence.

3) Comparisons of local and global remote sensing observations of the Moon using LROC WAC and Clementine UVVIS TiO$_2$ detection algorithms and Lunar Prospector (LP) Gamma Ray Spectrometer (GRS)-derived FeO and TiO$_2$ concentrations.

Of all possible ratio combinations in the laboratory using the WAC bandpasses, the 321/415 ratio correlates best with TiO$_2$ and ilmenite abundances, supporting the use of this ratio for the creation of a global TiO$_2$ map using the LROC WAC images. The 321/415 ratio correlation with TiO$_2$ concentration is strongest for submature to mature soil, suggesting the LROC WAC-derived relationship between 321/415 ratio and TiO$_2$ is strong because the WAC senses mostly mature soil at 400 meter/pixel resolution. Analysis of mineral and glass components and TiO$_2$ mass balance reveals that the mineral ilmenite (FeTiO$_3$) contributes the majority of TiO$_2$ in lunar soils containing more than 2 wt. % TiO$_2$, and it is the effect of ilmenite on the spectra that controls the 321/415 ratio for submature to mature lunar soils. For soils with low TiO$_2$ values, other phases can be the main TiO$_2$ contributors and the 321/415 ratio may no longer behave in a consistent fashion and thus should not be used to estimate TiO$_2$ at concentrations < 2 wt. %.
From observations of regions of interest using TiO\textsubscript{2} concentrations derived from Clementine, WAC, and LP-GRS, WAC TiO\textsubscript{2} values more closely match LP-GRS TiO\textsubscript{2} values. The WAC TiO\textsubscript{2} derivations overestimate TiO\textsubscript{2} values in the high-Ti basalts near Lichtenberg crater and the Chang’e-3 landing site, and may slightly overestimate TiO\textsubscript{2} values at the Luna 24 landing site in Mare Crisium, all areas with high FeO.

Global comparisons of WAC 321/415 ratio and LP-GRS TiO\textsubscript{2} and FeO revealed that FeO can affect 321/415 ratios for high- and low-Ti regions. At low TiO\textsubscript{2} concentrations (< 4 wt. %), increasing FeO increases the 321/415 ratio. Because all low-Ti basalts have ages greater than 2.5 Ga, this correlation may result from increasing submicroscopic metallic iron in high-Fe, mature soils. At high Ti, increasing FeO lowers the 321/415 ratio. We interpret this relationship to result from increasing FeO in pyroxene for soils with a range of maturities. No correlation with FeO exists at intermediate TiO\textsubscript{2}, possibly owing to a complex interplay between different mineral and glass phases on the WAC spectra or simply because of the competing (and opposite) trends between submicroscopic iron and pyroxene that exist at low- and high-Ti.

Finally, the global studies show that increasing TiO\textsubscript{2} corresponds to an increase in the 321/415 nm ratio at all but the highest FeO concentrations (> 23 wt. % FeO). Though FeO can affect the 321/415 ratio, TiO\textsubscript{2} controls the 321/415 ratio to first order. These findings support the use of the WAC 321/415 ratio for TiO\textsubscript{2} (and ilmenite) detection on the Moon.

References
Chapter 1: Introduction to the Dissertation

Our closest celestial neighbor has fascinated mankind for generations. The lunar landscape comprises dark, volcanic plains surrounded by light, heavily cratered anorthositic highlands. Probing this lunar surface can unravel clues to not only the history of the Moon, but also that of our own Earth and the Solar System.

The tenuous lunar atmosphere permits remote sensing spacecraft to directly examine the lunar surface with little to no attenuation of signals at a wide range of wavelengths and energy levels. The lack of plate tectonics or an atmosphere on the Moon generally allows for lunar geology to stay preserved for billions of years, allowing us to look back at the lunar past and gain a deeper understanding of the formation and evolution of the Moon. On finer scales, bombardment by micrometeorites, solar wind, and cosmic rays can both comminute and coalesce lunar regolith grains in addition to altering the chemistry of the impacted material.

Since the late 1950s, humans have sought to investigate this planetary body with spacecraft and manned missions, beginning with the first successful mission to the Moon in 1959 by the Soviet Luna 2 impactor. The United States Apollo 11 mission in 1969 landed the first humans on the Moon and returned the first lunar samples to Earth for examination. Lunar samples from subsequent Apollo manned and Luna unmanned Soviet robotic sample-return missions make up the rest of the lunar return-sample suite. These samples have provided crucial ground truth for remote observations of the lunar surface, allowing scientists to compare remote sensing measurements to laboratory analyses of soils from those locations, though care must be taken when interpreting remote sensing data. For example, remote sensing data commonly covers areas much larger than those from which Apollo and Luna returned soil samples, so
relationships between remote sensing observations and laboratory studies of returned soils may suffer from the difference in spatial scale between them. Moreover, the surface sensed is not homogeneous despite the homogenizing effects of billions of years of macro- and micrometeorite impacts, solar wind, and cosmic rays.

1.1 Lunar Remote Sensing and Spectroscopy

Lunar remote sensing studies have employed spectroscopy from the ultraviolet to the infrared to investigate lunar mineralogy. This technique can detect light reflected from the upper millimeter of the lunar surface. When light with energy similar to the electronic transitions in a molecule’s orbitals strikes a sample, the molecule absorbs part of the light’s energy and the associated electrons jump to a higher molecular energy level. Every wavelength induces a different absorption response in the sample, and a spectrum is created by plotting intensities owing to absorption or related sample reflection on the y-axis and the corresponding wavelength on the x-axis. The positions of these absorption bands are characteristic of sample mineralogy.

The Moon is a relatively dry, airless body with low oxygen fugacity in its mantle. As a consequence, the lunar surface lacks secondary minerals and exhibits limited mineralogy consisting mainly of the silicates plagioclase \((\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8)\), pyroxene \(((\text{Fe,Mg,Ca})_2\text{Si}_2\text{O}_6)\), and olivine \(((\text{Mg,Fe})_2\text{SiO}_4)\) along with the oxide ilmenite \((\text{FeTiO}_3)\). The silicates comprise solid solution series, with each combination of elements along the solid solution series exhibiting variations in absorption band positions and strengths, and a diverse spectral response at ultraviolet to visible wavelengths. Minor lunar minerals include spinels, phosphates, sulfides, K-feldspar, various silica mineral phases (quartz, cristobalite, tridymite), and iron metal. Ilmenite contributes most of the \(\text{TiO}_2\) on the lunar surface, but other Ti-bearing minerals include ulvöspinel \((\text{Fe}_2\text{TiO}_4)\), chromite \((\text{FeCr}_2\text{O}_4, \text{with Ti in solid solution})\), armalcolite
((Fe,Mg)Ti$_2$O$_5$), rutile (TiO$_2$), and tranquillityite (Fe$_8$Ti$_3$Zr$_2$Si$_3$O$_{24}$). All the iron in these minerals is in the divalent state.

In addition to silicates, ilmenite, and a variety of minor minerals, the lunar surface also contains various forms of glass. Pyroclastic glasses formed from fire fountaining of lava during volcanic eruptions in the Moon’s geologic past, and impact glasses form from the collision of meteorites with the lunar surface and the resulting formation and ejection of impact melt. Micrometeorite impacts melt tiny bits of regolith to create small, vesicular glassy breccias consisting of welded rock and mineral fragments; these breccias, called agglutinates, cannot be found anywhere on Earth.

On the Moon, the presence and proportions of plagioclase, Fe$^{2+}$ in silicates or glasses, maturation products (sub-microscopic Fe (SMFe) or agglutinate glass), and opaque minerals such as ilmenite have been shown to have the largest effects caused by chemistry and mineralogy on the observed spectral response at ultraviolet to infrared wavelengths [Hapke et al., 1975; Rava and Hapke, 1987; Pieters et al., 2000; Hapke, 2001; Loeffler et al., 2009]. In addition, grain-size differences can affect reflectance values and associated absorption bands [Adams and Filice, 1967; Pieters, 1997].

1.2 Remote TiO$_2$ Detection

Returned lunar samples exhibit a wide range of TiO$_2$ concentrations, from <1 to >10 wt. % TiO$_2$ in lunar soils, <1 to >14 wt. % TiO$_2$ in lunar basalts, and <1 to >16 wt.% TiO$_2$ in volcanic glasses, leading to various lunar basalt classification schemes based on TiO$_2$ concentrations [Papike and Vaniman, 1978b; Neal and Taylor, 1992; Gillis et al., 2003]. Color differences across the lunar surface have been attributed to differences in mare basalt TiO$_2$ concentrations based on the known TiO$_2$ concentrations from Apollo and Luna sampling sites.
[Whitaker, 1972; Pieters and McCord, 1976; Papike and Vaniman, 1978b]. Lunar TiO$_2$ maps created using various algorithms comparing spectra of the Moon to known TiO$_2$ values at the Apollo and Luna landing sites expanded TiO$_2$ estimates to unsampled areas of the Moon [Charette et al., 1973; Pieters and McCord, 1976; Johnson et al., 1977; Johnson et al., 1991a; Lucey et al., 1996; Blewett et al., 1997; Robinson et al., 2007; Robinson et al., 2011; Sato et al., 2015; Sato et al., 2017].

The mineral ilmenite, which is the main host of TiO$_2$ on the Moon has a low reflectance spectrum that exhibits a reflectance maximum at 1 µm and a generally flat spectral response throughout the visible wavelengths [Cloutis et al., 2008; Isaacson et al., 2011; Hapke, 2016]. The ilmenite spectral response (reflectance) increases into the ultraviolet wavelength region and exhibits a reflectance maximum at 250 nm [Cloutis et al., 2008; Isaacson et al., 2011; Hapke, 2016]. This ilmenite spectrum contrasts with silicate spectra, which have high reflectance and show large decreases in reflectance towards shorter wavelengths caused by an Fe$^{2+}$ absorption near 250 nm [Cloutis et al., 2008; Hapke, 2016]. Some algorithms using ultraviolet to visible reflectance ratios use the ilmenite spectral response as a proxy for TiO$_2$ and actually detect ilmenite, not TiO$_2$ directly [Robinson et al., 2007; Robinson et al., 2011; Sato et al., 2015; Sato et al., 2017].

Mare basalts permit a glimpse into the lunar interior where they formed. Characterizing these basalts and their compositional variations on the lunar surface gives us clues about the lunar interior and its history through the evolution of basalt compositions over time. For example, from a relationship between a Lunar Reconnaissance Orbiter Camera (LROC) Wide Angle Camera (WAC) spectral UV/VIS ratio and TiO$_2$ concentration, Sato et al. [2017] created a global lunar TiO$_2$ map and noted that the last low-Ti basalts erupted on the Moon over 2.5 billion
years ago. From this TiO\(_2\) data, *Sato et al.* [2017] inferred a change in global lunar volcanism at 2.5 Ga from a system driven by internal lunar heating to one driven by local radioactive element decay in high-Ti cumulates. Understanding and improving available TiO\(_2\) detection algorithms will result in more accurate lunar TiO\(_2\) maps and identification of diverse mare basalt types and regions on the Moon. The mineral ilmenite in and of itself is equally important; it provides the best efficiency extraction of oxygen, an element important for both life support and spacecraft propulsion in potential future human habitats on the Moon. Additionally, ilmenite is highly retentive of solar wind gases such as H\(_2\), which is also a key lunar resource [*Allen et al.*, 1996b].

### 1.3 Topics of the Dissertation

This dissertation focuses on analysis of the relatively new relationship found between the Lunar Reconnaissance Orbiter Camera (LROC) Wide Angle Camera (WAC) 321/415 nm reflectance ratio and TiO\(_2\) concentration [*Robinson et al.*, 2011; *Sato et al.*, 2015; *Sato et al.*, 2017]. We perform laboratory observations using ultraviolet (UV) to visible (VIS) spectroscopy, X-ray diffraction, and X-ray fluorescence to look for effects from chemistry and mineralogy on the 321/415 nm ratio, and conduct a related study using known mixtures of ilmenite and silicates. We also conduct remote sensing studies to compare TiO\(_2\) concentrations derived from LROC WAC data ([*Sato et al.*, 2017]) and Clementine UVVIS data ([*Lucey et al.*, 2000]) as well as Lunar Prospector Gamma Ray Spectrometer data.

#### 1.3.1 Chapter 2

*Robinson et al.* [2007], *Robinson et al.* [2011], *Sato et al.* [2015], and *Sato et al.* [2017] showed a good correlation between TiO\(_2\) concentration and an ultraviolet- to visible-wavelength reflectance ratio (UV/VIS ratio) from Hubble Telescope and LROC WAC observations. Chapter 2 contains results from analyses of lunar soils collected on Apollo missions. These analyses use
ultraviolet to visible spectroscopy, X-ray diffraction, and micro X-ray fluorescence to study the effects of mineralogy and chemistry on the spectral response, particularly at the 321 and 415 nm wavelengths corresponding to the LROC WAC bands.

We compared the contribution of TiO$_2$ to the bulk lunar soils from ilmenite, pyroxene, and other phases, and found that ilmenite contributes the most TiO$_2$ to soils containing > 2 wt. % TiO$_2$. For soils with < 2 wt. % TiO$_2$, pyroxenes and other phases may contribute more TiO$_2$ than ilmenite. We noted that the 321/415 ratio correlates more strongly with ilmenite than with bulk TiO$_2$, so ilmenite must control the spectral response at these wavelengths. Because ilmenite is the main contributor of TiO$_2$ to lunar soils, this leads to the good relationship between TiO$_2$ and the 321/415 ratio.

We analyzed all possible UV/VIS ratio combinations using the WAC bandpasses and found that the 321/415 ratio correlates best with TiO$_2$ and ilmenite concentrations. More importantly, TiO$_2$ and ilmenite concentrations correlate with the 321/415 ratio best for submature to mature soils, implying that the LROC WAC is sensing mostly mature soil at 400 meter/pixel resolution.

1.3.2 Chapter 3

Chapter 3 includes both local and global remote sensing observations of the Moon to further analyze the LROC WAC TiO$_2$-detection algorithm. We first compare the LROC WAC and Clementine detection algorithms at five areas of interest corresponding to landing sites and other calibration sites. The LROC WAC method uses an ultraviolet to visible spectral ratio (321/415 nm), whereas the Clementine algorithm uses a short-visible to long-visible wavelength algorithm (415/750 nm). Lunar Prospector Gamma Ray Spectrometer (LP-GRS)-derived FeO and TiO$_2$ concentrations provide additional evidence along with returned soils (Apollo and Luna).
and results from the Active Particle-induced X-ray Spectrometer (APXS) TiO$_2$ concentration at the Chang’e-3 (CE-3) landing site.

Comparisons of WAC and Clementine TiO$_2$ at the five areas of interest show that WAC TiO$_2$ more closely corresponds to LP-GRS TiO$_2$ than does Clementine TiO$_2$, but that WAC TiO$_2$ does not always correlate well with LP-GRS TiO$_2$. The WAC TiO$_2$ algorithm overpredicts TiO$_2$ at the Luna 24 landing site and in the high-Ti mare regions near Lichtenberg crater and the Chang’e-3 landing site, all regions with high FeO concentrations according to LP-GRS, returned soil, and CE-3 APXS FeO measurements.

We also study the WAC 321/415 ratio globally as a function of FeO and TiO$_2$ using the LP-GRS FeO and TiO$_2$ values. Regions with low LP-GRS TiO$_2$ (<4 wt. %) show a positive correlation between 321/415 ratio and LP-GRS FeO. This effect may be a result of increasing fine-grained iron in mature low-Ti mare soils. No obvious relationship exists for intermediate TiO$_2$ regions (4-8 wt. %). For regions with high TiO$_2$, the 321/415 ratio decreases with increasing FeO, possibly owing to increasing Fe-rich pyroxene concentrations lowering the 321/415 ratio.

1.4 Statement of Labor

Ecaterina Coman performed all work in this dissertation, unless otherwise stated, under the guidance of the dissertation chair, Bradley L. Jolliff. Paul Carpenter completed original X-ray diffraction (XRD) and micro X-ray Fluorescence (μXRF) measurements (as reported in Chapter 2). Additional XRD and μXRF measurements were done by Ecaterina Coman with assistance from Paul Carpenter. Hiroyuki Sato processed and provided global Lunar Prospector Gamma Ray Spectrometer data. Additional processing of Lunar Prospector Gamma Ray Spectrometer data was done by Ecaterina Coman.
References


Johnson, T. V., R. S. Saunders, D. L. Matson, and J. A. Mosher (1977), A TiO$_2$ abundance map for the northern maria, paper presented at 8th Lunar Science Conference, Pergamon Press, Houston, TX.


Chapter 2: Effects on Reflectance Spectra and Remote Sensing Observations from Mineralogy and Chemistry of Ti-Bearing Lunar Soils

This paper presents results of coordinated ultraviolet and visible wavelength reflectance measurements, X-ray diffraction analyses of mineral components, and micro X-ray fluorescence analyses of Ti concentrations of 13 lunar soil samples (<210 μm) that span a range of maturity and TiO$_2$ contents. Results of these analyses are used to determine the effects of soil maturity, TiO$_2$ concentration, and specific mineralogical makeup, especially ilmenite content, on the ultraviolet/visible (UV/VIS) ratio for application to remote sensing observations of the Moon and other airless bodies. We find that measured ilmenite weight percent correlates highly with measured TiO$_2$ concentrations. Thus, the ilmenite content is a good predictor of TiO$_2$ concentration. Ilmenite is the main contributor of TiO$_2$ for soils with greater than about 2 weight percent TiO$_2$, so we take the effects of TiO$_2$ on reflectance spectra to be essentially those of ilmenite. Constraining the data set to eight mature Apollo soils, we find that among the UV/VIS ratios from laboratory-measured spectra, the 320/415 nm ratio shows the best correlation with TiO$_2$ and ilmenite. Moreover, for soils with similar maturity in the submature to mature range, soils with higher TiO$_2$ have higher 320/415 UV/VIS ratios. Finally, the correlation between TiO$_2$ content and 320/415 ratio in samples measured in the lab appears weaker than for the same relationship using the Lunar Reconnaissance Orbiter (LRO) Wide Angle Camera (WAC) spectral data for the 320/415 ratio of Apollo ground-truth sites. The correlation between lab-derived 321/415 ratios and TiO$_2$ content for measured samples improves when low-maturity
samples are excluded from the dataset, implying that the LROC WAC spectra at 400 m/pix spatial resolution senses mostly mature soil.

2.1 Introduction

The Moon reveals a diversely colored surface under remote-sensing observations [e.g., Pieters et al., 1993b; Nozette et al., 1994; Sato et al., 2014]. Variations in color result from differences in chemical composition, mineralogy, grain size, and maturity of the soils. Diagnostic spectral responses can be used to quantify these characteristics and in some cases, to infer abundances of mineral or chemical constituents.

Ilmenite (FeTiO₃), an opaque mineral, can be distinguished spectrally from the most common lunar minerals (plagioclase, pyroxene, and olivine) because of its contrasting spectral response; ilmenite spectra exhibit low reflectance and relatively flat slopes at visible wavelengths, which rise to slightly higher reflectance values toward the UV, whereas silicate spectra display high reflectance at visible wavelengths and sharp declines in reflectance toward the UV [Wagner et al., 1987; Hapke, 2001] (Figure 2.1). Ilmenite is the main Ti-bearing mineral on the Moon, and the distinction between ilmenite and silicate spectra at visible and UV wavelengths can be used as a proxy for TiO₂ detection in the form of a UV to VIS spectral ratio. These UV/VIS spectral ratios have been shown to correlate

![Figure 2.1](image-url)
with TiO$_2$ concentrations in lunar soils, allowing for Ti content of the lunar surface to be empirically derived from remote sensing measurements [Charette et al., 1974; Johnson et al., 1991a; b; Blewett et al., 1997; Robinson et al., 2007; Robinson et al., 2011].

Analyses of lunar TiO$_2$ or ilmenite contents using pre-existing remote sensing data have proven difficult in part owing to variability in spatial resolution (footprint on the surface). Clementine UV-VIS data are nearly global in extent at ~400 meters per pixel (mpp), but included 415 nm as the only UV band. With only two months of mapping, the photometric correction of the data was also of limited quality. High-resolution data taken by the Hubble Space Telescope at 60 mpp exist for only three nearside locations of the Moon [Robinson et al., 2007]. Pieters [1978] obtained Earth-based telescopic observations of the nearside, but those data are at a low spatial resolution of area 10-20 km in diameter. The Lunar Prospector Gamma Ray Spectrometer (LP-GRS) could only sense Ti at about 2 degrees per pixel or lower effective resolution, and the Ti signal is not particularly strong [Lawrence et al., 1998; Gillis et al., 2004]. The Lunar Prospector Neutron Spectrometer (LP-NS) data can also be used to derive TiO$_2$, but the method requires knowledge of other neutron-absorbing elements and has no better resolution than the LP-GRS [Elphic et al., 1998b; Elphic et al., 2016]. Moreover, absolute accuracy of these methods has been called into question in areas outside of calibration sites because of substantial differences between TiO$_2$ concentrations derived from different sensors (e.g., Clementine-derived TiO$_2$ and LP-derived TiO$_2$) [Gillis et al., 2004; Elphic et al., 2016].

Of the most recent imagers orbiting the Moon (Chang’e 1 [Zhao et al., 2009], the Chandrayaan-1 Moon Mineralogy Mapper (M$^3$) [Green et al., 2011], and the SELENE (Kaguya) Multispectral Imager (MI) [Ohtake et al., 2008]), only the Lunar Reconnaissance Orbiter Camera (LROC) Wide Angle Camera (WAC) has obtained spectra at the true UV wavelengths that are
well suited for detection of ilmenite (and, by correlation, TiO$_2$) on the Moon [Robinson et al., 2010]. The LRO WAC has a 400 m/pix resolution for the UV bands, 321 and 360 nm [Robinson et al., 2010]. Sato et al. [2015] and Sato et al. [2017] reported LRO WAC UV/VIS spectral ratios and found a good correlation between these spectral ratios and TiO$_2$ concentrations based on soil sample analyses for sample stations at the Apollo landing sites. The resulting global TiO$_2$ map helped Sato et al. [2017] interpret a transition in lunar volcanism at about 2.6 Ga; mare older than 2.6 Ga contain a diversity of TiO$_2$ concentrations and represent global volcanic eruptions from a variety of depths. In contrast, mare basalts younger than 2.6 Ga may correlate with enrichment in radioactive elements and compositions of only medium- to high-TiO$_2$, corresponding to localized eruptions.

Much work has been done to elucidate the effects of maturity, mineralogy, and grain size on spectral parameters [Pieters, 1978; Pieters et al., 1993b; Taylor et al., 2001a; Taylor et al., 2001b], yet understanding the full effects of these variables on TiO$_2$ concentrations derived from the spectral ratios requires further studies. Expanding the current understanding of the relationship between UV/VIS ratios and TiO$_2$ will further improve detection of TiO$_2$ (and ilmenite) and provide additional clues to lunar volcanic history and the distribution of Ti-bearing materials at the Moon’s surface. Here we present coordinated compositional, mineralogical, and spectroscopic observations of Apollo lunar soil samples and examine the effects of composition and maturity on UV-VIS reflectance spectra and on various UV/VIS ratios as sampled by the LRO WAC. We also determine the best spectral ratio for remote TiO$_2$ determination and analyze the accuracy and applicability of determining TiO$_2$ content from orbit using LRO WAC UV/VIS spectral ratios.
2.2 Methods

2.2.1 Lunar Samples

We have measured soil samples in the laboratory from Apollos 11, 12, 15, 16, and 17 (Table 2.1) using ultraviolet to visible reflectance spectroscopy (UV-VIS), X-ray diffraction (XRD), and micro X-ray Fluorescence (µXRF). The allocated soils are all from <1 mm sieved fractions (sieved to <1 mm by the Lunar Sample Curatorial Facility at Johnson Space Center).

We further sieved the samples to remove fragments coarser than 210 µm and refer to the <210 µm soil samples as *bulk samples*. Soils have TiO$_2$ concentrations of 0.46 to 9.43 wt. %, and Is/FeO maturity values range from 5.1 to 81 as measured on the < 1 mm fraction by Morris [1978] (Table 2.1). Appendix A includes complete major-element compositions from the literature for the 13 lunar soils. The same bulk samples were used throughout all UV-VIS, XRD, and µXRF measurements to ensure consistent relationships and avoid variations resulting from use of different soil subsamples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2^a$</th>
<th>Std. Dev.</th>
<th>Ilmenite$^a$</th>
<th>Std. Dev.</th>
<th>320/415</th>
<th>Std. Dev.</th>
<th>Is/FeO$^b$</th>
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<td>10084</td>
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<td>8.46</td>
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<td>2.99</td>
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<td>0.041</td>
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</tr>
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<td>0.017</td>
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<td>0.005</td>
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<td>0.004</td>
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<td>6.39</td>
<td>0.17</td>
<td>0.85</td>
<td>0.025</td>
<td>81</td>
</tr>
</tbody>
</table>

$^a$TiO$_2$ and Ilmenite values are measured in wt. %.

$^b$Is/FeO values measured by Morris et al. [1983].
2.2.2 UV-VIS Reflectance Spectroscopy

We collected bi-directional reflectance measurements of the 13 lunar soils using a UV-VIS Ocean Optics Jaz spectrometer with a 2,048 element CCD detector and 200 Hz frequency pulsed xenon light source. An anodized aluminum case enclosed the sample and fiber optics, preventing any intrusion of stray light. Approximately 25 mg of soil were placed into a 2 mm central depression in a shallow-well anodized aluminum sample holder. Using a sliding access drawer, samples were placed inside the analysis chamber at a reproducible distance and geometry relative to the light source and detector (Figure 2.2).

The fiber optics of the spectrometer were fixed at a 30 degree incidence angle and 0 degree emission angle. This geometry approximates a common image illumination geometry in lunar orbital remote sensing for more simple correlation of lab spectra with remote observations. The LRO WAC collects images that cover a wide swath and incorporate a wide range of illumination conditions (60° field of view in 7-color mode, from 321 to 689 nm) in the cross-track direction [Robinson et al., 2010]. For spectroscopic interpretation, these LROC WAC images can be corrected to a uniform illumination geometry [e.g., Sato et al., 2014].

We acquired reflectance spectra with minimal noise from 300 to 700 nm using the Ocean Optics OceanView software. Measurements of standard deviations between spectra show a reduction in noise when using 25- vs. 5-spectra averaging, but no significant change between 25
and 50 or 100 averaged spectra. Increasing integration times beyond 220 ms per spectrum oversaturated the CCD detector and resulted in erroneous reflectance measurements. For best results and to optimize measurement time, we used a 25-spectra average with 220 ms integration time per spectrum.

During a typical set of analyses of reflectance standards, reflectance values varied as much as 3% throughout the span of one hour. The sample measurements exhibited an average standard deviation of 0.68% reflectance between all measured reflectance values from 300 to 700 nm and a maximum average reflectance standard deviation of 0.84% (Table 2.2).

Despite careful loading of the sample into the holder, sample roughness effects typically caused small spectral variations. Obtaining multiple measurements mitigated roughness effects and we therefore used multiple sample measurements at different rotations of the sample holder to create an average sample spectrum. We averaged four reflectance spectra of the sample at 90 degree intervals, and also averaged spectra taken on different dates. Using a Labsphere 99% reflectance standard, we collected reference and dark spectra before each soil sample analysis in order to correct for systematic variations in the spectrometer response with time and for variations in electronic noise from the CCD. Spectra of Labsphere reflectance standards at 5%, 10%, and 20%
reflectance were also taken at the end of every soil run to verify and compare successive reflectance measurements.

The final spectra were smoothed in Matlab using a 34-point moving average to remove residual noise after collection while retaining the spectral shape. These processed spectra were then plotted and analyzed using Microsoft Excel.

2.2.3 X-ray Diffraction (XRD)

A Bruker d8 Advance X-ray Diffractometer coupled with Rietveld refinement were used to quantitatively determine the mineralogy of the soil samples. The Rietveld refinement uses the entire XRD pattern to model the proportion of each mineral present along with the percentage of an amorphous component [Rietveld, 1969b; a; Young et al., 1977]. Because the diffraction peaks of pyroxene and plagioclase (the two main minerals present in lunar soils) do not interfere with the main ilmenite diffraction peaks around 32.5 and 35 degrees 2-theta, XRD can be used to unambiguously identify the presence of ilmenite.

The Bruker instrument is equipped with a Cu X-ray tube and was used with 40 kV accelerating voltage and 40 mA tube current, a Ni filter, an anti-scatter fin, and a sample spinner. The same 25 mg subsamples of soil used in the spectral measurements were placed in the recessed cavity of a zero-background-diffraction silicon holder and scanned from 5 to 80 degrees 2-theta at ~0.2 degree steps with 0.5 seconds per step. The sample was spun at 15 rotations per minute to minimize preferred orientation effects. After acquiring XRD patterns, mineral proportions (reported in weight percent) were retrieved through Rietveld refinement calculations via Bruker Topas software. The refinements were based on structure files for plagioclase, augite, pigeonite, olivine, ilmenite, troilite, and kamacite.
Refinement of the broad peak centered at ~28 degrees 2-theta was used to determine the amorphous component of the sample. We chose to model the amorphous component with a peak at 28 degrees because this 2-theta value best matched the highest point on the broad peak observed in the measured soil patterns. A model crystal size of 1 nm constrained the amorphous 28 degree peak to a component with an arbitrarily small particle size. Uncertainties in the refinements were estimated using the goodness of fit of the least-squares peak fitting. Figure 2.3 shows an example powder pattern and final XRD Rietveld refinement for bulk soil sample 10084 and its amorphous component.

Analyses of powdered samples can result in preferred orientation peaks, but various techniques exist to correct for these effects. Peaks can be fit using analytical methods such as Rietveld refinement to correct for prominent high-intensity peaks. Preferred orientation effects can also be mitigated by rotating the sample (thus we use a sample spinner during data acquisition). In addition, one can average multiple diffraction patterns suspected to exhibit preferred orientation effects. Samples can further be ground to a very fine grain size (e.g. <5 µm). Because grinding and revealing fresh grain surfaces alters the reflectance spectra, we chose not to routinely grind samples. For the experiments mentioned in this paper, sample rotation, averaging of multiple measurements, and Rietveld refinement helped to mitigate effects from preferred orientation peaks. Final ilmenite values and associated uncertainties derived using XRD and Rietveld refinement can be found in Table 2.1.
Figure 2.3. Quantitative analysis of mineral concentrations using XRD with Topas Rietveld refinement for bulk soil 10084. Different mineral phases show distinct peak positions, and the amorphous component has a broad peak. Residual values are acceptable but show some peaks that could be due to preferred orientation effects.
2.2.4 Micro X-ray Fluorescence (µXRF)

Micro X-ray Fluorescence measurements of the same 25 mg bulk soil samples used in the UV-VIS and XRD analyses were used to determine quantitatively the concentration of TiO$_2$ present in those samples. We measured samples placed in the same zero-background silicon holders as used in the XRD analyses. We used an EDAX Orbis X-ray fluorescence analyzer with a Rh X-ray tube (350 mA current, 40 kV accelerating voltage) and silicon drift detector to collect µXRF spectra of the soil samples at ambient temperature and 1 atmosphere pressure. The 1-atmosphere analysis condition sacrifices the low-energy X-rays of Na and to some extent Mg and Al in order to measure fine-grained lunar soil samples without disturbing the samples during vacuum operation.

For each sample, we gathered and summed 10 replicate acquisitions with separate, non-overlapping 2 mm diameter sample areas and 100-second count time per acquisition. Ti intensity values were corrected using EDAX Orbis Combine software with a least-squares peak-area determination, which included modifications for fluorescence and absorbance effects from elements in the sample. The calibration curve made using published oxide wt. % data for the 13 soils translated corrected Ti intensity values to wt. % TiO$_2$ concentrations. To adjust for non-representative replicate acquisitions, we discarded the highest and lowest calculations of TiO$_2$ and averaged the remaining 8 measurements. We use the largest errors, calculated as the sample standard deviation between the 8 replicate acquisitions, to determine the uncertainties (Table 2.1).

2.3 Results

Mineralogy and Chemistry. TiO$_2$ wt. % published values for <1 mm lunar soils plotted against Ti intensity of our analyses of the <210 µm bulk soils measured using µXRF shows an
excellent correlation, with an $R^2$ value of 0.996 (Figure 2.4). Intensities were corrected for effects from fluorescence and absorbance of elements in the sample; the fit of published TiO$_2$ wt. % and corrected TiO$_2$ wt. % derived from µXRF intersects the origin within uncertainty and has an $R^2$ value of 0.999 (Figure 2.5).

TiO$_2$ concentration measured by µXRF for the bulk soils vs. ilmenite concentration measured using XRD and Rietveld refinement also reveals an excellent linear fit, with an $R^2$ value of 0.96 (Figure 2.6). The wt. % TiO$_2$ occurring in bulk-sample ilmenite was calculated by multiplying sample ilmenite wt. %, measured by XRD, by the average TiO$_2$ concentration in lunar ilmenite, given by Papike et al. [1998] (Table 2.3). Comparing the resulting wt. % TiO$_2$ in ilmenite to the bulk sample TiO$_2$ wt. %, we find that between 32.1 and 66.3 percent of the bulk sample TiO$_2$ (on average 52.6%) is contributed by ilmenite (Table 2.3). Data reveal a strong positive correlation between bulk sample TiO$_2$ and the percent of the bulk TiO$_2$ contributed by ilmenite (Figure 2.7).

We calculated the wt. % TiO$_2$ contributed by pyroxene using values for the average TiO$_2$ wt. % in lunar pyroxene given by Papike et al. [1998] (Table 2.4). We calculated the wt. % contributed by other phases (e.g. glasses, rutile, armalcolite, etc.) by removing the total TiO$_2$ contributed to the sample by both ilmenite and pyroxene (Table 2.4). Plotting these three sample TiO$_2$ contributors (ilmenite, pyroxene, and other phases) reveals that ilmenite remains the main contributor of TiO$_2$ for all samples except those with low TiO$_2$ concentrations (less than ~2 wt. %) (Figure 2.8, Table 2.4). Glasses (impact and agglutinate) are by far the main TiO$_2$ contributors among the “other phases.”
Figure 2.4. Measured µXRF Ti net intensities (counts/s) and published TiO$_2$ concentrations in 13 bulk soil samples (<210 µm). Net intensities and published values are highly correlated. Data collection and reduction by P. Carpenter.

\[ y = 88.671x + 14.061 \]
\[ R^2 = 0.996 \]

Figure 2.5. Published TiO$_2$ wt. % and calibrated µXRF TiO$_2$ wt. %. Calibrated µXRF TiO$_2$ concentrations show improved correlation compared to Figure 2.4 owing to corrections for effects from fluorescence and absorption of X-rays in the sample. Data collection and reduction by P. Carpenter.

\[ y = 0.999x - 0.007 \]
\[ R^2 = 0.999 \]
Figure 2.6. Measured µXRF TiO\textsubscript{2} wt. % and ilmenite wt. % from XRD. The µXRF TiO\textsubscript{2} concentrations correlate well with XRD ilmenite concentrations. Data collection and reduction by P. Carpenter.

Figure 2.7. Measured µXRF bulk TiO\textsubscript{2} and TiO\textsubscript{2} contributed from ilmenite. Bulk TiO\textsubscript{2} correlates well with calculated TiO\textsubscript{2} contributed by ilmenite using average concentrations of TiO\textsubscript{2} in ilmenite from Papike et al. [1998].
Table 2.3. TiO$_2$ contributed to the sample by ilmenite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ilmenite (wt. %)</th>
<th>Avg. TiO$_2$ in Ilmenite$^a$ (wt. %)</th>
<th>TiO$_2$ From Ilmenite (wt. %)</th>
<th>Total Sample TiO$_2$ (wt. %)</th>
<th>Percent of TiO$_2$ From Ilmenite$^b$ (%)</th>
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</thead>
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</table>

$^a$Average TiO$_2$ in lunar ilmenite is given by Papike et al. [1998].

$^b$The calculated average percent of total sample TiO$_2$ contributed from XRD-derived ilmenite contents is 52.6 wt. %.

Figure 2.8. TiO$_2$ contributed to the bulk sample TiO$_2$ by different phases. Ilmenite has the greatest contribution of TiO$_2$ for samples with total bulk TiO$_2$ greater than ~2 wt. %. Below ~2 wt. % TiO$_2$, pyroxene and other phases, especially glasses, can contribute much of the TiO$_2$.  

25
Table 2.4. TiO$_2$ contributed to the sample by pyroxene and other phases.

<table>
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<tr>
<th>Sample</th>
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<th>TiO$_2$ from Ilmenite (wt. %)</th>
<th>TiO$_2$ from Other Phases$^b$ (wt. %)</th>
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<td>1.14</td>
<td>0.52</td>
<td>1.58</td>
<td>0.70</td>
</tr>
<tr>
<td>15601$^a$</td>
<td>51.46</td>
<td>1.32</td>
<td>0.68</td>
<td>0.59</td>
<td>0.56</td>
</tr>
<tr>
<td>67511</td>
<td>7.13</td>
<td>0.96</td>
<td>0.07</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>70181</td>
<td>38.61</td>
<td>1.91</td>
<td>0.74</td>
<td>4.23</td>
<td>3.52</td>
</tr>
<tr>
<td>71501</td>
<td>36.73</td>
<td>1.91</td>
<td>0.7</td>
<td>4.82</td>
<td>3.95</td>
</tr>
<tr>
<td>72501</td>
<td>15.85</td>
<td>1.91</td>
<td>0.3</td>
<td>0.89</td>
<td>0.30</td>
</tr>
<tr>
<td>73131$^a$</td>
<td>11.34</td>
<td>1.91</td>
<td>0.22</td>
<td>0.32</td>
<td>0.42</td>
</tr>
<tr>
<td>73261</td>
<td>17.45</td>
<td>1.91</td>
<td>0.33</td>
<td>0.93</td>
<td>0.55</td>
</tr>
<tr>
<td>74241</td>
<td>33.43</td>
<td>1.91</td>
<td>0.64</td>
<td>5.08</td>
<td>2.08</td>
</tr>
<tr>
<td>76501</td>
<td>16.22</td>
<td>1.91</td>
<td>0.31</td>
<td>1.50</td>
<td>1.44</td>
</tr>
<tr>
<td>78501</td>
<td>26.83</td>
<td>1.91</td>
<td>0.51</td>
<td>3.09</td>
<td>1.68</td>
</tr>
<tr>
<td>79221</td>
<td>27.93</td>
<td>1.91</td>
<td>0.53</td>
<td>3.39</td>
<td>2.69</td>
</tr>
</tbody>
</table>

$^a$For underlined samples, the largest contributors of TiO$_2$ to the sample are phases other than ilmenite.

$^b$Values calculated by mass balance (TiO$_2$ from other phases = Bulk TiO$_2$ – TiO$_2$ from pyroxene – TiO$_2$ from ilmenite).

**Spectroscopy.** The spectra of soils measured in this study ranged from ~4 to ~35% reflectance (at 415 nm) (Figure 2.9). For easier comparison, we plot the same spectra grouped according to low (Is/FeO 5.1-36) or medium to high (Is/FeO 40-81) maturity in Figure 2.10 and Figure 2.11. Mature samples (Is/FeO values ranging from 58-81) show a steady horizontal flattening and increasing UV/VIS ratio with increasing TiO$_2$ concentration (Figure 2.12). Likewise, increasing sample TiO$_2$ concentration flattens and increases UV/VIS ratio for submature samples (Is/FeO 40-58), with the exception of sample 12057 (Figure 2.13). Sample 12057 has one of the largest ratio uncertainties and could have a ratio value fitting the trend within uncertainties (Table 2.1). Immature soils do not exhibit similar relationships with changing TiO$_2$ (Figure 2.10).

For high-Ti soils between ~6.5 and 9.5 wt. % TiO$_2$, reflectance decreases with increasing maturity (Figure 2.14). The pattern of decreasing reflectance with increasing maturity also
appears in a plot of very low ~0.4 to 1.5 wt. % TiO₂, but the sample size is small for these concentrations (Figure 2.16). Weak relationships exist for soils with TiO₂ concentrations between 1.4 and 3 wt. %; neither reflectance nor slope changes correlate consistently with maturity (Figure 2.15).

When examining all 13 soils, laboratory UV/VIS ratios calculated using all possible LROC WAC bandpasses show weak to no correlation with measured TiO₂ and ilmenite (Table 2.5). The 321/415 ratio has the best correlation with both TiO₂ and ilmenite. Comparison of this 321/415 ratio and TiO₂ wt. % for all samples does not reveal a strong correlation (Figure 2.17, Table 2.5), with an R² of 0.30. For sub-mature to mature samples with Iₘ/FeO values greater than 40, the correlation coefficients for all ratios improve, and the 321/415 ratio again has the best correlation with TiO₂ and ilmenite, although that for 360/415 is nearly as good (Table 2.6). Removal of immature soils improves the correlation between the 321/415 ratio and TiO₂ wt. % to an R² value of 0.78 (Figure 2.17).
Figure 2.9. Spectra of 13 lunar soils with varying chemistry, mineralogy, and maturity.
Reflectance of samples with low maturity ($I_S/FeO \leq 40$).

Reflectance of submature to mature samples ($I_S/FeO \geq 40$).

Figure 2.10. Reflectance of samples with low maturity ($I_S/FeO \leq 40$).

Figure 2.11. Reflectance of submature to mature samples ($I_S/FeO \geq 40$).
Figure 2.12. Reflectance of mature samples with a range of TiO$_2$ contents. Samples exhibit increased 320/415 ratio with higher TiO$_2$ wt. %.

Figure 2.13. Reflectance of submature samples with a range of TiO$_2$ contents. Similar to the mature samples, submature samples also show bluing and flattening with increasing TiO$_2$ wt. %. Sample 12057 has the largest ratio error (± 0.03) and follows the trend within the error of 76501 (0.02).
Samples with Similar High TiO$_2$ but Different Maturities

Figure 2.14. High-Ti soils with TiO$_2$ concentrations between 6.5 and 9.5 wt. %. Reflectance decreases with increasing maturity for high-Ti soils.

Samples with Similar Low TiO$_2$ but Different Maturities

Figure 2.15. Low-Ti soils with TiO$_2$ concentrations between 1.4 and 3 wt. %. No clear relationship exists between maturity and reflectance, possibly owing to large variations in iron concentrations in these samples.
Figure 2.16. Very low-TiO soils with TiO₂ concentrations between 0.45 and 1.5 wt. %. Reflectance decreases with increasing maturity for soils with very low TiO₂, but sample size is limited.
### Table 2.5. Coefficients of determination ($R^2$) between UV/VIS ratios and wt. % TiO$_2$ or Ilmenite.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>TiO$_2$ Coefficient of Determination</th>
<th>Ilmenite Coefficient of Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>321/415</td>
<td>0.30</td>
<td>0.22</td>
</tr>
<tr>
<td>321/566</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>321/604</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>321/643</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>321/689</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>360/415</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>360/566</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>360/604</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>360/643</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>360/689</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

### Table 2.6. Coefficients of determination between UV/VIS ratios of submature to mature soils and wt. % TiO$_2$ or Ilmenite.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>TiO$_2$ Coefficient of Determination</th>
<th>Ilmenite Coefficient of Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>321/415</td>
<td>0.78</td>
<td>0.88</td>
</tr>
<tr>
<td>321/566</td>
<td>0.66</td>
<td>0.77</td>
</tr>
<tr>
<td>321/604</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td>321/643</td>
<td>0.61</td>
<td>0.71</td>
</tr>
<tr>
<td>321/689</td>
<td>0.61</td>
<td>0.70</td>
</tr>
<tr>
<td>360/415</td>
<td>0.75</td>
<td>0.87</td>
</tr>
<tr>
<td>360/566</td>
<td>0.41</td>
<td>0.49</td>
</tr>
<tr>
<td>360/604</td>
<td>0.33</td>
<td>0.40</td>
</tr>
<tr>
<td>360/643</td>
<td>0.28</td>
<td>0.34</td>
</tr>
<tr>
<td>360/689</td>
<td>0.26</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Figure 2.17. Comparisons of 320/415 nm reflectance ratio measured using OceanOptics spectrometer and TiO$_2$ wt. % measured using µXRF. Gray circles represent immature samples with $I_s$/FeO less than 40. Black squares represent submature to mature samples with $I_s$/FeO greater than or equal to 40. The fit between 320/415 ratio and TiO$_2$ wt. % is not strong when considering all soils ($R^2 = 0.30$) but improves when considering only submature to mature soils ($R^2 = 0.78$).
2.4 Discussion

2.4.1 Relationship Between TiO$_2$ and Ilmenite Concentrations

Experiments to determine chemistry and modal mineralogy of the 13 lunar samples reveal good agreement between measurements. Measured µXRF Ti intensity and calibrated µXRF TiO$_2$ wt. % values correlate well with published TiO$_2$ concentrations for soils <1 mm (Figure 2.4, Figure 2.5). We compared these results to measurements of ilmenite wt. % based on XRD and Rietveld refinement to determine the characteristics of the relationship between bulk TiO$_2$ and ilmenite contents in the soils; the TiO$_2$ wt. % measured using µXRF correlates linearly (with high correlation coefficient) with the ilmenite wt. % as determined using XRD and the Topas Rietveld refinement (Figure 2.6).

2.4.2 TiO$_2$ Contributed by Various Phases

At all concentrations of TiO$_2$, a strong correlation also exists between bulk sample TiO$_2$ and the percent of bulk TiO$_2$ contributed to the sample by ilmenite, illustrating that lunar soil TiO$_2$ concentrations change linearly with ilmenite concentrations (Figure 2.7). Although there is a consistent relationship between bulk sample TiO$_2$ concentrations and the concentrations of TiO$_2$ contributed to the sample by ilmenite, the relationship is not 1:1, because not all of the sample TiO$_2$ is contributed by ilmenite. Using the average concentration of TiO$_2$ in ilmenite from Papike et al. [1998], ilmenite contributes between ~1/3 to ~2/3 of the bulk sample TiO$_2$, with an average of 52.6 wt. % TiO$_2$ contributed (Table 2.3). Plots of various TiO$_2$ contributors reveal that ilmenite dominates the TiO$_2$ contribution for samples with total TiO$_2$ concentrations greater than ~2 wt. % (Figure 2.8). At a total TiO$_2$ concentration less than ~2 wt. %, pyroxene, glasses, and other more minor phases can become the main contributors of TiO$_2$; for low bulk TiO$_2$ samples 15601 and 73131, ilmenite only contributes ~33 wt. % to the total sample TiO$_2$ (Table 2.4, Figure 2.8). Because ilmenite is the main Ti-bearing mineral on the Moon for soils with bulk
TiO$_2$ concentrations greater than ~2 wt. %, it is appropriate to use the differences in spectral response between silicates and ilmenite at UV-VIS wavelengths to predict and constrain lunar TiO$_2$ concentrations using the ilmenite spectral response.

### 2.4.3 Soil Reflectance Effects Owing to TiO$_2$

Specific components of maturity have different effects on the UV-VIS-NIR reflectance spectrum of a soil. The maturity of the lunar surface is defined as the amount of alteration a regolith (unconsolidated rock and mineral fragments) exposed at the lunar surface exhibits over time owing to micrometeorite impacts, solar wind and solar flares, and galactic cosmic ray interactions. Two of the components contributing to maturity, micrometeorite impact vaporization and particle irradiation and sputtering, result in the preferential removal of oxygen from ferrous iron phases and subsequent re-deposition of submicroscopic and nanophase Fe$^0$ (henceforth referred to as SMFe) and amorphous coatings from the vapor phase on grain surfaces [Hapke, 2001; Hapke et al., 1973; Loeffler et al., 2009]. In this paper, we use the I$_S$/FeO maturity index (henceforth referred to as “maturity”) to observe the effects of SMFe on the spectral response; I$_S$/FeO is the ratio of ferromagnetic resonance (FMR) signal intensity (I$_s$) of Fe$^0$ between 4 and 33 nm (SMFe) to the total concentration of FeO in the soil [Housley et al., 1974; Morris, 1978]. An I$_S$/FeO value of 0-30 corresponds to immature samples, 30-60 to submature samples, and >60 to mature samples.

A plot of all lunar soil spectra (Figure 2.9) does not reveal a clear relationship between TiO$_2$ concentrations and 321/415 ratio. To limit effects of maturity on this spectral reflectance, we chose to keep maturity constant and plot soils of various TiO$_2$ concentrations as a function of maturity. Plots of only immature to submature soils (Figure 2.10) indicate that TiO$_2$ content does not appear to consistently affect reflectance. When comparing only submature to mature soils,
samples with higher Ti generally have higher UV/VIS ratios and flatter slopes (Figure 2.11, Figure 2.12, Figure 2.13). The lack of correlation of the 321/415 ratio with TiO$_2$ between a wide range of maturities or between low maturity soils implies that in immature soils, effects other than ilmenite content may dominate the UV/VIS ratio. Denevi et al. [2014] observed that soils with I$_S$/FeO values less than 40 had increasing 321/415 ratios with increasing I$_S$/FeO, but that 321/415 ratios did not show large variations for I$_S$/FeO values greater than 40. The more systematic relationship between TiO$_2$ concentrations and UV-VIS slopes for submature to mature soils is likely a combination of the maturity effects reaching saturation as noted by Denevi et al. [2014] and equalizing grain size and glass contents so as to allow the spectral effects of ilmenite to dominate; spectral trends of ilmenite are complementary to those of TiO$_2$ and show increasing UV/VIS ratios and flatter slopes with increasing ilmenite shortward of 500 nm [Wagner et al., 1987; Cloutis, 2010].

2.4.4 Soil Reflectance Effects with Maturity

Increasing soil maturity results in overall darkening, reduction in the amount of absorption in absorption bands, and reddening of the spectra in the VIS-NIR region [Adams et al., 1973; Hapke et al., 1975; Wagner et al., 1987; Pieters et al., 1993a; Pieters et al., 2000; Hapke, 2001; Noble et al., 2001; Hendrix and Vilas, 2006; Noble et al., 2007; Cloutis et al., 2008]. For the freshest materials, changes in maturity have a greater influence on UV reflectance than on VIS region reflectance [Hendrix and Vilas, 2006; Denevi et al., 2014]. Increasing maturity increases the UV reflectance with decreasing wavelength and shallows absorption band depths, resulting in a flatter spectrum from 200-400 nm than immature lunar soil or silicates [Hapke et al., 1975; Wagner et al., 1987; Hapke, 2001; Hendrix and Vilas, 2006; Cloutis et al., 2008].
To limit effects of TiO$_2$ on lunar soil reflectance, we analyzed the effects of maturity on spectra separated into three groups by ranges of TiO$_2$: very low TiO$_2$ (~0.4 to 1.5 wt. %), low TiO$_2$ (~1.5 to 2.8 wt. %), and high TiO$_2$ (~6.5 to 9.5 wt. %). Our analyses exhibit a tendency for overall reflectance to decrease with increasing maturity, likely owing to a greater presence of submicroscopic Fe$^0$ (SMFe). Reflectance decreased with increasing maturity for samples with high TiO$_2$ contents and very low TiO$_2$ contents (Figure 2.14, Figure 2.16). Samples with low TiO$_2$ contents were mostly submature to mature soils and did not show a clear relationship between maturity and reflectance (Figure 2.15). Low TiO$_2$ soils exhibited a wide range of FeO concentrations, likely resulting in the lack of relationship between maturity and reflectance. Soils with lower FeO concentrations (73261, 8.5 wt. % FeO and 72501, 8.7 wt. % FeO) had higher reflectance than soils with much higher FeO concentrations (12057, 16.7 wt. % FeO and 15601, 19.9 wt. % FeO).

The observations of decreasing reflectance with increasing maturity are consistent with previous published findings [Adams et al., 1973; Hapke et al., 1975; Wagner et al., 1987; Pieters et al., 1993a; Pieters et al., 2000; Hapke, 2001; Hendrix and Vilas, 2006; Noble et al., 2007; Cloutis et al., 2008], but only three very low TiO$_2$ soils were examined, so the relationships between maturity and reflectance for these very low TiO$_2$ soils should be interpreted with caution. Because of the limited sample size of very low TiO$_2$ soils and the lack of consistent relationships between maturity and reflectance for low TiO$_2$ soils, maturity is most likely correlated with reflectance for our samples only when comparing high TiO$_2$ soils. Petrographic factors that include FeO, such as pyroxenes, olivines, or glasses, may have a stronger effect on lower TiO$_2$ soils.
For similar high TiO$_2$ soils, submature and mature samples had flatter slopes at UV wavelengths than the immature sample 74241 (Figure 2.14). Likewise, for the very low TiO$_2$ soils, the mature sample 72501 had a flatter slope than the immature samples (67511 and 73131). The flat slopes for mature samples at UV wavelengths parallel findings by Hendrix and Vilas [2006] and Denevi et al. [2014] showing flatter spectra towards UV wavelengths for the more mature soils.

### 2.4.5 UV/VIS Ratio Correlations with TiO$_2$ and Ilmenite Concentrations

Ratios comparing short- to long-wavelength visible reflectance values have been shown to correlate well with TiO$_2$ concentrations, but these strictly empirical relationships are not well understood and may also be marred by maturity and other effects [Blewett et al., 1997; Charette et al., 1974; Gillis-Davis et al., 2006; Gillis and Jolliff, 2003; Johnson et al., 1991a; b; Lucey et al., 1998]. The properties of the ilmenite spectral response have shown promise for TiO$_2$ detection on the Moon. The optical properties of ilmenite are controlled by surface scattering owing to ilmenite’s high opacity. For powdered samples of small grain size, spectra generally appear flat and low in reflectance at ultraviolet (UV) to visible (VIS) wavelengths. The ilmenite spectrum shows a slight increase in reflectance from 500 nm towards the UV and shorter wavelengths (Figure 2.1) [Wagner et al., 1987; Hapke, 2001]. In contrast, silicate powders display relatively high reflectance values from near-infrared to visible wavelengths and exhibit decreasing reflectance towards the UV owing to an absorption edge and transition to surface scattering of UV wavelengths [Wagner et al., 1987]. The distinction between silicate and ilmenite spectra can be used to create a ratio comparing reflectance values at various wavelengths to discern differences in the amount of ilmenite present in a soil. To distinguish the
effects of ilmenite from other lunar soil components, one of the ratio bands used must occur below 350 nm [Cloutis et al., 2008].

Using the spectral properties of ilmenite as a proxy for TiO$_2$ detection, Robinson et al. [2007] analyzed the relationship between Hubble Space Telescope 502/250 ratios at the Apollo 17 landing site and returned sample TiO$_2$ concentrations at those locations, revealing a strong negative correlation between TiO$_2$ concentrations and 502/250 ratios that did not show a dependency on maturity effects [Robinson et al., 2007]. This promising study spurred subsequent global TiO$_2$ observations and derivations using a similar UV/VIS ratio, and comparisons of LROC WAC 321/415 ratios to Lunar Prospector and soil sample TiO$_2$ values also showed a strong positive correlation [Robinson et al., 2011; Sato et al., 2015; Sato et al., 2017]. These ratios are seemingly less affected by maturity than ratios involving wavelengths only in the visible part of the spectrum. The 321/415 ratio may be a more effective tool for determining the abundance of TiO$_2$ contributed by ilmenite from remotely sensed observations.

Two models may explain the strong relationship between UV/VIS ratios and TiO$_2$. The first model posits that opaques control lunar soil spectral properties at ultraviolet to visible wavelengths [Wells and Hapke, 1977; Rava and Hapke, 1987]. The spectral response for the main contributor of TiO$_2$ to lunar soils, the opaque mineral ilmenite, could control the overall spectral response for UV/VIS ratios of lunar soils; spectra of soils with higher ilmenite (and, therefore, TiO$_2$) contents should have higher UV/VIS ratios due to the upturn in reflectance towards UV wavelengths contributed by the ilmenite (Figure 2.1).

A second model presented by Pieters et al. [1993b] argues that Fe-Ti charge transfer absorption bands in lunar glasses at ultraviolet to visible wavelengths would decrease the reflectance at these wavelengths with increasing TiO$_2$ [Bell et al., 1976]. The opaque nature of
high-Ti lunar soil contributors like ilmenite could also result in a dominance of surface scattering from grain surfaces over volume scattering, strongly masking the effects of compositional variations other than Ti on the spectral response at UV-VIS wavelengths and resulting in a darker, flatter spectrum. This model would predict a scatter in low-Ti lunar soil UV/VIS ratios as volume scattering in these diverse basalts allows the complex soil mineralogy to affect the spectral response. We can test these hypotheses with laboratory spectral studies.

Comparison of UV/VIS ratios of three locations from Hubble Telescope data to returned sample compositions of those locations revealed a strong relationship between TiO$_2$ concentrations and UV/VIS ratios that is less dependent on maturity effects than VIS ratios at higher wavelengths [Robinson et al., 2007]. Comparisons of LROC WAC UV/VIS ratios to Lunar Prospector and soil sample TiO$_2$ values show a similar strong relationship [Robinson et al., 2011; Sato et al., 2015]. Denevi et al. [2014] demonstrated increasing UV/VIS ratio with increasing maturity for relatively immature soils, but show that saturation of UV/VIS ratios occurs for submature to mature soils with $I_S$/FeO values greater than ~40. The LROC WAC is the only orbiting spacecraft camera detecting bands at UV wavelengths on the Moon, so we relate our laboratory observations to the LROC WAC bandpasses.

Analysis of all laboratory-derived UV/VIS ratios consistent with the LROC WAC filters revealed that the 321/415 ratio is the spectral ratio that correlates most strongly with TiO$_2$ and ilmenite concentration, and validates use of this ratio for TiO$_2$ determination by UV-VIS remote sensing (Table 2.5, Table 2.6). When examining all samples, all UV/VIS ratios have a weak correlation with TiO$_2$ and ilmenite. All ratios show an improved, stronger correlation when examining only submature to mature soils with $I_S$/FeO > 40, with the 321/415 ratio having the highest coefficient of determination (0.78). The two best-correlated UV/VIS ratios have the 415-
nm reflectance as the divisor in the ratio and a UV-wavelength reflectance (either 321 or 360 nm) as the dividend. Ilmenite has an even stronger correlation with the 321/415 ratio than TiO$_2$ has, with an $R^2$ value of 0.88.

The improved reflectance-ratio correlation with ilmenite over TiO$_2$ for all ratio combinations is not consistent with control by Fe-Ti glasses of the relationship between TiO$_2$ and UV/VIS ratios. The improved fit when removing immature soils suggests a possible spectral contrast dominated by submicroscopic iron; immature soils have less submicroscopic iron and volume scattering controls reflectance, but submature and mature soils may have enough submicroscopic iron to dominate the spectral response with surface scattering and lead to a lack of spectral contrast for high maturity soils as seen in Denevi et al. [2014]. Conversely, Denevi et al. [2014] showed that the 321/415 ratio does not depend on maturity for low-iron soils, and that the ratio generally stays constant for these soils even at low maturity. This finding contradicts the spectral contrast hypothesis, because immature soils should show variations in reflectance ratios from spectral effects owing to volume scattering in silicate phases. Furthermore, if the opaqueness of ilmenite caused a spectral contrast effect, we would not expect low-Ti/-ilmenite soils to lie along the correlation line with 321/415 ratio unless the combined effects of pyroxene, plagioclase, olivine, and glasses was (fortuitously) enough to result in the correct ratio (Figure 2.17). We would also not expect high-Ti soils to plot off the curve, as the reflectance of these soils with highly opaque phases (ilmenite being the main contributor of TiO$_2$ for high-Ti soils) should be controlled by surface scattering and generally flat-sloped (Figure 2.17). The improved correlation of the 321/415 ratio with ilmenite instead of TiO$_2$, when immature soils are removed, supports the model by Wells and Hapke [1977] and Rava and Hapke [1987] that the overall
spectral shape of opaque phases (e.g. ilmenite and submicroscopic iron), controls the spectral response at UV-VIS wavelengths.

2.4.6 321/415 vs. TiO₂ Concentration

When examining all soils, the correlation between our laboratory-derived TiO₂ contents and the 321/415 ratio (R² = 0.30) is not as strong as the correlation between the Apollo and Luna soil TiO₂ wt. % and LRO spectral ratios found by Robinson et al. [2011] (Figure 2.17). The fit improves (R² = 0.78) after removing immature samples. The strong correlation between TiO₂ and 321/415 ratios when excluding immature soils suggests that the poor fit of the laboratory-derived UV/VIS ratio and TiO₂ wt. % could be a maturity effect as originally mentioned by Charette et al. [1974]. The finest fraction of lunar soils dominates the spectral properties of those soils from ultraviolet to infrared wavelengths [Pieters et al., 1993a]; this finest fraction also has the largest quantity of fine-grained (<30 nm) single domain metallic iron in lunar grain-size separates and has been shown to cause bluing in the soil from visible to ultraviolet wavelengths [Morris, 1977; 1980].

The poor correlation between our laboratory-derived TiO₂ contents and 321/415 ratio when including immature soils could also result from sampling different petrographic components and unusual compositions and locations where the samples were found. Some of the removed immature samples contain significant TiO₂ in phases other than ilmenite. For example, pyroxene and other phases contribute the majority of TiO₂ to sample 15601, making the use of the ilmenite spectral response unsuitable for TiO₂ detection. Sample 73131 not only has most of its TiO₂ stored in pyroxene and phases other than ilmenite (Table 2.5), but it is also a friable regolith breccia that disintegrated upon transport, not a soil [Korotev and Kremser, 1992]. Furthermore, this sample has a small mare basaltic component and a very low concentration of
FeO, so it is not representative of the majority of samples analyzed in this study [Korotev and Kremser, 1992]. For both sample 15601 and 73131, ilmenite contributes only ~33 wt. % to the total sample TiO$_2$ (Table 2.3). Global derivations of low-TiO$_2$ values using the LROC WAC 321/415 ratio should be interpreted cautiously; the ilmenite spectral response may not be appropriate for soils like 73131 and 15601 where ilmenite does not contribute a substantial amount of TiO$_2$. In addition to the unusual components of 73131 and 15601, much of the TiO$_2$ in sample 74241 is hosted in volcanic glass instead of ilmenite [Korotev and Kremser, 1992]; the spectrum for this soil therefore may be anomalous and plot off the curve. Though unusual compositions could contribute to ratio irregularities, unusual compositions account for only about half of the immature soils in this study.

Denevi et al. [2014] found that laboratory-derived 321/415 ratios increase for Apollo mare and intermediate-iron highland samples for Is/FeO values below ~40. However, soils with Is/FeO values greater than ~40 results show little to no variation in 321/415 ratio values. With space weathering effects saturating in the UV for submature to mature soils, maturity becomes a smaller contributor to the 321/415 ratio values, and other soil properties like mineralogy or composition (specifically, ilmenite and TiO$_2$ content) can dominate the spectral response. Furthermore, typical immature soils occur in special or localized places, such as near fresh craters or boulders, and do not represent the majority of lunar soils [Le Mouélic et al., 2001].

Unusual compositions can have some effect on the UV/VIS ratio of lunar soils, but a lack of space weathering saturation appears to control our UV/VIS ratio and TiO$_2$ correlations. When the immature soils are removed from the 321/415 ratio and TiO$_2$ comparison, the correlation between UV/VIS ratio and TiO$_2$ improves ($R^2 = 0.78$) owing to removal of these unsaturated, atypical samples (Figure 2.17). The improved correlation and fit when removing immature soils
(Figure 2.17) resembles that of the LRO WAC ratios [Robinson et al., 2011; Sato et al., 2015; Sato et al., 2017] and suggests that the good fit is due to the sensing by the WAC of mostly mature soil at the 400 mpp UV-band resolution for the ground-truth points used by Robinson et al. [2011] and Sato et al. [2017].

2.5 Conclusions

We analyzed 13 lunar soils with a range of TiO₂ concentrations and maturities to better understand remote sensing of TiO₂ on the Moon. Samples consisted of “bulk” Apollo soils <210 µm. Coordinated analyses by X-ray powder diffraction, µX-ray fluorescence, and UV/VIS spectroscopy from 300 to 700 nm allowed for comparison of mineralogy, chemistry, and grain-size effects on the reflectance of the same sample aliquots.

Titanium intensities measured using µXRF correlate well with published TiO₂ values, and we used this correlation to calibrate TiO₂ contents for the soil subsamples. X-ray diffraction followed by Rietveld refinement allowed for determination of the proportions of mineral and amorphous components. Because pyroxene or plagioclase peaks do not interfere with ilmenite diffraction peaks, XRD accompanied by Rietveld refinement can readily estimate ilmenite modal abundances.

Ilmenite wt. % measured using XRD correlates well with bulk TiO₂ concentrations of the same soil measured using µXRF and, on average, TiO₂ in ilmenite accounts for 52.6% of the bulk TiO₂ content in the lunar soils analyzed. Correlations between UV/VIS ratios and ilmenite and TiO₂ concentrations for submature to mature samples are strong, with the UV/VIS ratios even better correlated with ilmenite than with TiO₂. A reduction in reflectance and upturn shortward of 500 nm due to ilmenite can be used to estimate the concentration of TiO₂ for samples with greater than 2 wt. % TiO₂. In samples with less than 2 wt. % TiO₂, pyroxene and
other phases contribute more TiO₂ to the sample than ilmenite. TiO₂ derived from the UV/VIS ratios using the ilmenite spectral response should be interpreted cautiously when TiO₂ so derived is low, i.e., < 2 wt.%, which includes most of the Moon’s highlands.

UV-VIS spectra of bulk soil samples show correlations between overall reflectance and TiO₂ contents or maturity. For similarly high TiO₂ contents, increasing maturity leads to decreased reflectance values. For submature to mature soils, increasing TiO₂ results in spectral flattening and increasing 321/415 ratios. Immature soils do not exhibit a consistent relationship between TiO₂ and 321/415 ratios.

Of the possible laboratory-derived UV/VIS ratios using the LRO WAC bandpasses, the 321/415 ratio shows the best correlation with TiO₂. TiO₂ generally correlates with 321/415 spectral ratios, but the correlation is poor when considering immature together with mature soils ($R^2 = 0.30$); however, when considering only the submature to mature soils ($I_s/FeO > 40$), the correlation between TiO₂ and the 321/415 spectral ratio improves ($R^2 = 0.78$) and becomes more in line with the correlation between remotely sensed LRO WAC ratios and landing-site soils described by Robinson et al. [2011], Sato et al. [2015], and Sato et al. [2017].

Based on our observations, we conclude that the LROC WAC 321/415 ratios correlate well with TiO₂ contents of landing site soil because the sample areas detected by the WAC (at 400 mpp in the UV) consist of mostly submature to mature soil.
References


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Pieters, C. M. (1978), Mare basalt types on the front side of the moon: A summary of spectral reflectance data, paper presented at 9th Lunar and Planetary Science Conference, Pergamon Press, Houston, TX.


Chapter 3: Detection and Variability of TiO$_2$ using LROC WAC Data at Landing Sites and Calibration Sites

The Lunar Reconnaissance Orbiter Camera (LROC) Wide Angle Camera (WAC) now has global photometrically corrected ultraviolet to visible (UV-VIS) spectral imaging data for the Moon at ~400 meters/pixel resolution [Sato et al., 2014]. Sato et al. [2015] demonstrated a linear relationship between TiO$_2$ (i.e., ilmenite) and the 321/415 nm WAC reflectance ratio using returned lunar soil compositions and photometrically corrected WAC sample-return-site observations at UV-VIS wavelengths. In this chapter, we analyze the WAC-derived TiO$_2$ values at Apollo landing sites and several other areas of interest among those described in Pieters et al. [2008] and compare them to the local Clementine and Lunar Prospector TiO$_2$ values as determined by Lucey et al. [2000] and Prettyman et al. [2006], respectively. Comparisons of selected regions of interest show that WAC TiO$_2$ values more closely correspond to LP-GRS TiO$_2$ values and returned soil compositions than do Clementine TiO$_2$ values. Because the Lunar Prospector Gamma Ray Spectrometer (LP-GRS) presents independent measurements of global lunar TiO$_2$ and FeO, we also analyzed the 321/415 ratio globally as a function of LP-GRS TiO$_2$ and FeO to quantify any independent effect of the bulk FeO content on the 321/415 ratio. We find that FeO has little effect for intermediate TiO$_2$ regolith but FeO content may influence the WAC 321/415 ratio for both low- and high-Ti regions. In low-Ti regions, this influence can result in an overestimation of TiO$_2$. The simplicity and consistency of the WAC TiO$_2$ algorithm, however, shows much promise for global geologic studies of the Moon’s mare regions and volcanic history.
3.1 Introduction

The Moon has a wide range of TiO$_2$ concentrations on its surface, especially in mare basalt areas, making this oxide the main compositional discriminator of different volcanic units. Mare basalt classification schemes include bimodal classifications [Neal and Taylor, 1992] and those consisting of multiple compositional divisions [Papike and Vaniman, 1978a]. In this Chapter, we categorize basalts into four groups equivalent to those of Papike and Vaniman [1978a]: very low-Ti basalts (<1 wt. % TiO$_2$), low-Ti basalts (1-5 wt. % TiO$_2$), intermediate-Ti basalts (5-9 wt. % TiO$_2$), and high-Ti basalts (> 9 wt. % TiO$_2$).

Beginning with Ewen Whitaker’s color difference photographs in 1972, ratios of short- and long-wavelength images have highlighted color differences attributed to variations in TiO$_2$ across the lunar surface. Spectral ratios leading to color differences may be related to absorptions in Fe-Ti lunar glasses or pyroxenes [Charette et al., 1973; Wells and Hapke, 1977; Pieters, 1978], reduced spectral contrast owing to surface scattering from opaque minerals such as ilmenite (FeTiO$_3$) [Pieters, 1978], bluing (proportionally lower reflectance at longer wavelengths than shorter wavelengths) and darkening effects from ilmenite [Hapke et al., 1975; Wells and Hapke, 1977], or a combination Fe-Ti absorptions and ilmenite [Wells and Hapke, 1977]. Gillis-Davis et al. [2006] inferred that the spectral effects of ilmenite, the main contributor of TiO$_2$ in lunar soils for soils with bulk TiO$_2$ greater than ~2 wt. % [Coman et al., 2016], influence the Clementine spectral ratio to a greater extent than Fe-Ti absorptions or different scattering mechanisms. The improved correlation of the 321/415 ratio with the concentration of ilmenite in lunar soil compared to lunar soil TiO$_2$, as described in Chapter 2, supports this hypothesis.
Multiple methodologies have been derived for remotely determining TiO$_2$ from spectral data [Whitaker, 1972; Charette et al., 1974; Pieters and McCord, 1976; Johnson et al., 1977; Johnson et al., 1991a; Lucey et al., 1996; Blewett et al., 1997; Robinson et al., 2007; Robinson et al., 2011]. Charette et al. [1974] and subsequent authors (Table 3.1) empirically showed that a ratio of a blue wavelength to a longer visible (VIS) wavelength reflectance correlates well with TiO$_2$ for mature mare soils, but these algorithms are either complex and require multiple regression models, or display systematic errors such as abnormally high TiO$_2$ concentrations compared to samples of lunar basalts and basaltic soils [Elphic et al., 2002; Gillis-Davis et al., 2006]. The empirical nature of the correlations and the use of a limited number of returned-sample soils means that TiO$_2$ derivation methods may not fully or representatively cover the range of spectral responses from the lunar surface. Part of the problem is that the spectral response is actually a function of mineralogy, not just chemical composition, and there are multiple mineral and glass hosts of TiO$_2$ in lunar materials (Chapter 2).

The ultraviolet (UV) to visible spectral response distinguishes the main lunar silicates (anorthite, olivine, augite, pigeonite) from ilmenite (FeTiO$_3$) (Figure 3.1). Compared to the spectral response for the silicates, ilmenite reflectance appears flat and increases towards shorter wavelengths.
wavelengths, whereas the reflectance of the silicates sharply decreases towards shorter wavelengths.

![Spectra showing reflectance vs. wavelength for different minerals](image)

**Figure 3.1.** Spectra from *Clark et al.* [2007] highlighting the difference between the spectral response of ilmenite and lunar silicates.

Ilmenite is the most important mineral host of TiO$_2$ on the Moon, and ilmenite’s spectral qualities have proven promising for TiO$_2$ detection [*Sato et al.*, 2017]. Using the contrast in UV response between ilmenite and lunar silicates, *Robinson et al.* [2007] demonstrated a good linear fit between a UV and VIS band ratio (502/250 nm) derived from Hubble Space Telescope images of the Apollo 17 landing site and TiO$_2$ concentrations of returned Apollo 17 soils. Additionally, *Robinson et al.* [2007] demonstrated that soil maturity does not affect the correlation of the 502/250 nm ratio with TiO$_2$ at the Apollo 17 landing site, in contrast with results from some previous studies comparing blue visible wavelength to red visible wavelength reflectance values for Apollo landing sites or returned soils [e.g. *Charette et al.*, 1974].
The 502/250 ratio method using the ilmenite spectral response showed potential, so the Lunar Reconnaissance Orbiter (LRO) Wide Angle Camera (WAC) was designed with filters at true UV wavelengths (Table 3.2) [Robinson et al., 2010] to determine TiO$_2$ remotely and generate a global TiO$_2$ map. Robinson et al. [2011] showed a good linear fit between LROC WAC 321/415 ratios and the TiO$_2$ concentrations from returned soils and Lunar Prospector. Sato et al. [2017] compared WAC 321/415 ratios at Apollo landing sites and the TiO$_2$ concentrations of the corresponding returned soils, and created a global lunar TiO$_2$ map from the consistent relationship between the WAC ratio and landing site TiO$_2$.

Based on laboratory spectroscopy experiments (Chapter 2), from among available combinations of UV/VIS ratios using bandpasses corresponding to those of the LROC WAC, the 321/415 ratio is found to best correlate with TiO$_2$. Regardless of the strong correlation between the WAC 321/415 ratio and TiO$_2$, some returned soils (e.g., Luna 24 and Luna 16) occur as outliers in the fit of data to the average correlation.

Outlier soils such as Luna 24 and Luna 16 may have spectral properties that deviate from the average lunar soils. Gillis et al. [2003] described these soils as having some of the lowest 415 nm reflectance values of returned lunar soils. Understanding the effects of these soils’ specific properties on the reflectance spectra at UV-VIS wavelengths can aid interpretation of UV/VIS ratio-derived TiO$_2$ values. To gain a better understanding of these effects requires identifying the impact of TiO$_2$ contributors other than ilmenite on the UV/VIS ratios, particularly for low-Ti

<table>
<thead>
<tr>
<th>LROC WAC Bands (nm)</th>
<th>Clementine Bands (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>321 (UV)</td>
<td>415 (VIS)</td>
</tr>
<tr>
<td>360 (UV)</td>
<td>750 (VIS)</td>
</tr>
<tr>
<td>415 (VIS)</td>
<td>900 (IR)</td>
</tr>
<tr>
<td>566 (VIS)</td>
<td>950 (IR)</td>
</tr>
<tr>
<td>604 (VIS)</td>
<td>1000 (IR)</td>
</tr>
<tr>
<td>643 (VIS)</td>
<td></td>
</tr>
<tr>
<td>689 (VIS)</td>
<td></td>
</tr>
</tbody>
</table>
soils and regions whose UV relationships and UV/VIS-based TiO$_2$ derivations are not well understood.

We conducted analyses of a set of local regions of interest (ROIs) and global distribution to better understand the WAC TiO$_2$ detection systematics. For specific ROIs, we analyzed the results of the WAC TiO$_2$ algorithm at several landing sites and important calibration sites as defined by Pieters et al. [2008], comparing the WAC-derived TiO$_2$ to TiO$_2$ values derived from Clementine UV-VIS data and Lunar Prospector (LP) Gamma Ray Spectrometer (GRS) data [Lucey et al., 2000; Prettyman et al., 2006]. We placed additional emphasis on the relation between Clementine-based and WAC-based TiO$_2$ owing to the popularity and widespread use of the Clementine TiO$_2$ detection algorithm, which yields TiO$_2$ at much higher spatial resolution than the LP-GRS data. The regions of interest (Table 3.3) were chosen for their variations in mare basalt TiO$_2$ concentrations and available soil calibration data.

We also analyzed the 321/415 ratio as a function of FeO and TiO$_2$ globally across the lunar surface using the independent FeO and TiO$_2$ measurements of the LP-GRS. FeO-bearing minerals other than ilmenite (e.g., pyroxene and olivine) and glasses can influence the 321/415 ratio, particularly in low-Ti areas (less than ~2 wt. % TiO$_2$) where FeO-bearing pyroxenes and other phases can be the main contributors (hosts) of TiO$_2$ [Coman et al., 2016].

### 3.2 Methods

#### 3.2.1 LRO Data

The LRO WAC is a push-frame camera with 7 bands (filters) ranging from true ultraviolet wavelengths to visible wavelengths (Table 3.2) [Robinson et al., 2010; Speyerer et al., 2012b; Mahanti et al., 2015]. The WAC images the lunar surface at ~400 meters/pixel resolution for ultraviolet wavelengths and ~100 meters/pixel for visible wavelengths. Using the 623 nm
band at low incidence angles, the WAC can also operate in monochrome mode with a nadir
ground sample distance of 75 m/pixel at a nominal 50 km altitude, with higher or lower
resolution when at perigee and apogee, respectively.

The WAC has two separate lenses, one for the UV filters and one for the visible filters.
These lenses image onto the same CCD array, which is outfitted with 7 color filters. The UV
nadir resolution is 384 m/pixel at 50 km, hence the nominal processed image resolution of
400 meters/pixel for color data.

For the work described here, we make use of the 321 nm and 415 nm bands from the 7-band WAC global mosaic, photometrically corrected to incidence and phase angles of 60 degrees [Sato et al. [2014].

*Sato et al. [2017] demonstrated a linear relationship between TiO$_2$ concentrations in returned Apollo soils and a ratio of the 321 nm to 415 nm WAC orbital reflectance values (321/415) extracted from images of the corresponding Apollo sites. The global lunar WAC TiO$_2$ concentration map was derived, in wt. %, from the WAC photometrically corrected global mosaic [Sato et al., 2014] using the 321 nm and 415 nm bands and the correlation determined by Sato et al. [2017]. This relationship uses a linear regression fit to the lunar soil TiO$_2$ and orbital 321/415 ratio. We refer to the WAC-derived TiO$_2$ images and data as “WAC TiO$_2$”.

The WAC “Nearside Dawn Mosaic,” henceforth referred to as the WAC Morphology mosaic, uses the 643 nm band LROC WAC images photometrically corrected to a common illumination geometry [Robinson, 2010; Speyerer et al., 2012a; Sato et al., 2014]. LRO did not

Table 3.3. Selected regions of interest and center lat/lon of 200 × 200 km zones for analysis.

<table>
<thead>
<tr>
<th>Area Name</th>
<th>Lat</th>
<th>Lon (° E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mare Serenitatis (MS2)</td>
<td>18.7</td>
<td>21.4</td>
</tr>
<tr>
<td>Mare Imbrium near Chang'e 3</td>
<td>44.1</td>
<td>340.5</td>
</tr>
<tr>
<td>Mare Procellarum near Lichtenberg Crater</td>
<td>31.5</td>
<td>293.0</td>
</tr>
<tr>
<td>Mare Crisium near Luna 24</td>
<td>12.7</td>
<td>60.4</td>
</tr>
<tr>
<td>Mare Tranquillitatis near Apollo 11</td>
<td>2.7</td>
<td>23.6</td>
</tr>
</tbody>
</table>
slew during imaging for this dataset, allowing for consistent lighting geometry during spectral collection and the creation of a nearly continuous 100 meters/pixel mosaic for the 643 nm band. WAC Morphology maps for the regions of interest help contextualize the derived TiO$_2$ distribution.

A digital elevation model (DEM) was used to mask large slopes, which can influence reflectance values. Section 3.2.4 contains the slope image processing method. The digital elevation model from Barker et al. [2016] uses data from both the LRO Lunar Orbiter Laser Altimeter (LOLA) and the SELENE Terrain Camera to create a DEM with approximately 80 meters/pixel resolution at the equator. This DEM covers latitudes of 60° South to 60° North with a vertical accuracy of 4 meters. We refer to this dataset as the LOLA-SELENE DEM.

We used the WAC empirically normalized 643 nm mosaic to eliminate outlier I/F values in the scene (henceforth referred to as WAC 643 reflectance or “WAC 643”), where I represents the radiance received at the detector, while F represents the solar radiance from a normally illuminated, perfectly diffuse Lambertian surface. Areas with high I/F correspond to areas with high detected reflectance. This mosaic is normalized to a 30° incidence angle and 0° emission angle using the photometric function from [Boyd et al., 2012] and has a resolution of 100 meters/pixel.

### 3.2.2 Clementine UVVIS Data

The Clementine Spacecraft [Nozette et al., 1994; McEwen and Robinson, 1997], officially named the Deep Space Program Science Experiment, was a joint mission between the Department of Defense (DoD) and National Aeronautics and Space Administration (NASA). Clementine carried an Ultraviolet/Visible (UVVIS) camera with 5 spectral bands (Table 3.2). We
used the Clementine photometrically corrected 100 meters/pixel UV-VIS mosaic [Eliason et al., 1999; Isbell et al., 1999; Robinson et al., 1999].

Instead of a direct ratio of reflectance values, the Lucey et al. [2000] algorithm uses a polar coordinate rotation. This coordinate rotation attempts to separate the effects of maturity on Clementine UVVIS reflectance values from the effect of TiO$_2$ (i.e., ilmenite) in a Clementine 750 nm reflectance vs. Clementine ratio plot. Empirically, the polar angle correlates to the elemental Ti content and the radius, to the degree of maturity. The TiO$_2$ algorithm assumes that the dark and flat ilmenite spectral response at visible wavelengths would accurately approximate TiO$_2$ owing to ilmenite’s position as the principal carrier of TiO$_2$ in lunar soils. The algorithm shows a good empirical power-law relationship between TiO$_2$ concentration of returned lunar soils and the polar angle in a Clementine 750 nm reflectance and Clementine 415/750 nm ratio plot of the corresponding landing sites (Equation 3-1, Equation 3-2) [Lucey et al., 2000]. The standard deviation of the data points around the power-law fit is 0.93 wt. %.

\[
\theta_{TiO_2} = \arctan \left( \frac{R_{415}}{R_{750}} - 0.42 \left( \frac{R_{750}}{R_{415}} \right) \right) \quad \text{Equation 3-1}
\]

\[
Clem TiO_2 = 3.78 \times \theta_{Fe}^{5.979} \quad \text{Equation 3-2}
\]

### 3.2.3 Lunar Prospector GRS Data

The concentrations of TiO$_2$ and FeO used in this work were determined from gamma ray spectra measured by the LP-GRS [Binder, 1998; Lawrence et al., 1998; Lawrence et al., 2004; Prettyman et al., 2006]. Data processing was completed by Prettyman et al. [2006] using average GRS gamma ray spectra containing 512 energy channels. A spectral unmixing algorithm of elemental concentrations derived from gamma ray data, and elemental weight fractions were then converted to weight fractions of major oxides [Prettyman et al., 2006]. Spectra represent
uncollimated, omnidirectional gamma rays detected from a few tens of cm depth of the lunar surface, produced by cosmic ray interactions with nuclei in the lunar surface and by long-lived radioactive-element decay (Figure 3.2). The resulting global TiO$_2$ and FeO data were binned to various resolutions afforded by counting statistics. For TiO$_2$, the best available binned resolution is 2 degrees/pixel (~60 km/pixel at the equator) [Lawrence et al., 2004].

### 3.2.4 Processing – Local Observations

We used the Integrated Software for Imagers and Spectrometers (ISIS) 3 to crop, resample, and project all images to a similar resolution and map projection. We coregistered the WAC photometric basemap, WAC morphology, WAC 643 reflectance, LOLA-SELENE DEM, Clementine mosaics, and LP-GRS images on the region of interest (Table 3.3) and cropped the images to approximately ~200 km × 200 km. The resulting data were then resampled to 400 meters/pixel resolution and re-projected to equirectangular projection using cubic convolution, which uses a weighted average of the 16 nearest cell centers. In order to keep the same pixel values when upsampling the LP-GRS data, resampling of the LP-GRS data to 400 meters/pixel used nearest-neighbor interpolation where new pixels take the value of the nearest neighboring pixel without any change to the actual LP-GRS values.

To properly compare WAC and Clementine data, we masked unusual areas that might affect the spectral response and resulting TiO$_2$ derivations from any calculations. We derived slope images for each region of interest from the LOLA-SELENE DEM using the ISIS function

![Figure 3.2. Formation and source processes that produce gamma rays in the lunar regolith. From Prettyman et al. [2006].](image-url)
slpmap and eliminated areas with steep slopes by masking data greater than 3°. As demonstrated at the Apollo landing site, slopes less than 3° should result in errors of less than 0.50 wt. % TiO$_2$ in the Clementine algorithm [Robinson and Jolliff, 2002]. From the remaining pixels with slopes below 3°, we masked unusually bright or dark features (e.g., fresh craters or shadowed regions) that fell outside 1σ of the average WAC 643 reflectance values at a particular site. We plotted values from the resulting image pixels from the WAC and Clementine images in a 2-dimensional histogram using edited code from Clewely and Bunting [2014].

For simpler analysis and to more easily discern variations in TiO$_2$ concentrations, we classified the WAC TiO$_2$ images using 1 wt. % TiO$_2$ bins. In the classification images, red and warm colors correspond to low TiO$_2$ values whereas blue colors correspond to high TiO$_2$ values.

3.2.5 Processing – Global Observations

We analyzed WAC 321/415 values for the whole Moon as a function of LP FeO and TiO$_2$. The WAC ratio (321/415) basemap was downsampled to the 2 degrees/pixel resolution of the LP data by averaging the WAC values corresponding to each LP pixel [Prettyman et al., 2006]. WAC and LP maps were resized to an extent spanning 60° South to 60° North latitude. Values from both mare and highlands regions contributed to the resulting plots; analyses of the plots at LP-GRS FeO values > 15 wt. % can delineate relationships at mare regions. Errors in our observations at these mare regions may result from the inclusion of highlands pixels in the downsampling at mare regions near mare-highlands boundaries.

3.3 Local Area (ROI) Results

The following sections examine the TiO$_2$ values determined from the WAC or Clementine algorithms, or derived using the LP-GRS at various regions of interest. Referenced TiO$_2$ values correspond to Table 3.4 and Table 3.5.
Table 3.4. Remotely sensed TiO$_2$ (wt. %) regions of interest within 200 × 200 km areas from LP-GRS, Clementine UVVIS, and LROC WAC.

<table>
<thead>
<tr>
<th>Site Name$^a$</th>
<th>Subset</th>
<th>Min.</th>
<th>Avg.</th>
<th>Max.</th>
<th>St. Dev.</th>
<th>N. Pixels</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lunar Prospector GRS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tranquillitatis near AP11</td>
<td></td>
<td>1.24</td>
<td>5.77</td>
<td>9.03</td>
<td>1.78</td>
<td>8</td>
</tr>
<tr>
<td>Serenitatis</td>
<td></td>
<td>0.60</td>
<td>3.97</td>
<td>8.83</td>
<td>1.76</td>
<td>8</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>High Ti</td>
<td>1.84</td>
<td>4.75</td>
<td>7.28</td>
<td>1.52</td>
<td>5</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>Low Ti</td>
<td>1.62</td>
<td>3.40</td>
<td>7.28</td>
<td>1.23</td>
<td>7</td>
</tr>
<tr>
<td>Procellarum near LC</td>
<td>High Ti</td>
<td>1.25</td>
<td>5.31</td>
<td>7.94</td>
<td>1.97</td>
<td>2</td>
</tr>
<tr>
<td>Procellarum near LC</td>
<td>Low Ti</td>
<td>0.68</td>
<td>3.94</td>
<td>7.94</td>
<td>2.02</td>
<td>8</td>
</tr>
<tr>
<td>Procellarum near LC</td>
<td>Crater</td>
<td>0.68</td>
<td>3.11</td>
<td>7.94</td>
<td>2.45</td>
<td>4</td>
</tr>
<tr>
<td>Crisium near L24</td>
<td></td>
<td>0.00</td>
<td>1.77</td>
<td>2.99</td>
<td>0.88</td>
<td>8</td>
</tr>
<tr>
<td><strong>Clementine UVVIS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tranquillitatis near AP11</td>
<td></td>
<td>1.38</td>
<td>10.25</td>
<td>16.30</td>
<td>1.57</td>
<td>176578</td>
</tr>
<tr>
<td>Serenitatis</td>
<td></td>
<td>0.85</td>
<td>5.19</td>
<td>14.98</td>
<td>1.43</td>
<td>167510</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>High Ti</td>
<td>1.10</td>
<td>7.07</td>
<td>10.89</td>
<td>1.24</td>
<td>100874</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>Low Ti</td>
<td>0.20</td>
<td>1.71</td>
<td>12.14</td>
<td>0.98</td>
<td>146371</td>
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<tr>
<td>Procellarum near LC</td>
<td>High Ti</td>
<td>0.91</td>
<td>8.41</td>
<td>13.76</td>
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<tr>
<td>Procellarum near LC</td>
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<td>4.39</td>
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<td>Procellarum near LC</td>
<td>Crater</td>
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<td>2.47</td>
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<tr>
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<td></td>
<td>0.45</td>
<td>5.17</td>
<td>9.22</td>
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<tr>
<td><strong>LROC WAC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tranquillitatis near AP11</td>
<td></td>
<td>0.31</td>
<td>6.86</td>
<td>12.37</td>
<td>1.13</td>
<td>176578</td>
</tr>
<tr>
<td>Serenitatis</td>
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<td>0.08</td>
<td>3.78</td>
<td>11.59</td>
<td>1.17</td>
<td>167422</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>High Ti</td>
<td>1.85</td>
<td>7.75</td>
<td>12.55</td>
<td>1.00</td>
<td>100874</td>
</tr>
<tr>
<td>Imbrium near CE3</td>
<td>Low Ti</td>
<td>0.00</td>
<td>2.30</td>
<td>12.78</td>
<td>1.17</td>
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</tr>
<tr>
<td>Procellarum near LC</td>
<td>High Ti</td>
<td>1.70</td>
<td>7.66</td>
<td>11.65</td>
<td>1.95</td>
<td>44243</td>
</tr>
<tr>
<td>Procellarum near LC</td>
<td>Low Ti</td>
<td>0.05</td>
<td>4.32</td>
<td>11.34</td>
<td>1.66</td>
<td>166661</td>
</tr>
<tr>
<td>Procellarum near LC</td>
<td>LC</td>
<td>0.00</td>
<td>2.51</td>
<td>8.34</td>
<td>0.89</td>
<td>68847</td>
</tr>
<tr>
<td>Crisium near L24</td>
<td></td>
<td>0.00</td>
<td>3.63</td>
<td>9.04</td>
<td>0.82</td>
<td>160646</td>
</tr>
</tbody>
</table>

$^a$AP11 = Apollo 11, CE3 = Chang’e-3, LC = Lichtenberg Crater, L24 = Luna 24
Table 3.5. Remotely sensed TiO$_2$ (wt. %) at specific landing sites.

<table>
<thead>
<tr>
<th>Landing Site</th>
<th>Lat (°)</th>
<th>Lon (°)</th>
<th>N. Pixels</th>
<th>Clementine UVVIS$^a$</th>
<th>LROC WAC$^b$</th>
<th>Returned Soils/APXS$^{cde}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apollo 11</td>
<td>0.67</td>
<td>23.47</td>
<td>1x1</td>
<td>10.83 (Avg.)</td>
<td>7.8 (St. Dev.)</td>
<td>6.84 (Min), 7.66 (Avg.), 9.00 (Max), 0.65 (St. Dev.)</td>
</tr>
<tr>
<td>Apollo 11</td>
<td>0.67</td>
<td>23.47</td>
<td>2x2</td>
<td>10.82 - 10.88 (Avg.-Max.), 0.09 (St. Dev.)</td>
<td>6.84 - 7.56 (Min-Avg. Max.), 0.46 (St. Dev.)</td>
<td>6.84 (Min), 7.66 (Avg.), 9.00 (Max), 0.65 (St. Dev.)</td>
</tr>
<tr>
<td>Apollo 11</td>
<td>0.67</td>
<td>23.47</td>
<td>3x3</td>
<td>10.61 - 10.96 (Avg.-Max.), 0.19 (St. Dev.)</td>
<td>6.84 - 7.53 (Min-Avg. Max.), 0.38 (St. Dev.)</td>
<td>6.84 (Min), 7.66 (Avg.), 9.00 (Max), 0.65 (St. Dev.)</td>
</tr>
<tr>
<td>Chang'e-3</td>
<td>-19.51</td>
<td>44.92</td>
<td>1x1</td>
<td>4.75 (Avg.)</td>
<td>3.13 (St. Dev.)</td>
<td>4.60 (Min), 4.98 (Avg.), 5.20 (Max), 0.26 (St. Dev.)</td>
</tr>
<tr>
<td>Chang'e-3</td>
<td>-19.51</td>
<td>44.92</td>
<td>2x2</td>
<td>4.5 - 4.64 (Avg.-Max.), 0.1 (St. Dev.)</td>
<td>1.49 - 2.41 (Min-Avg. Max.), 0.63 (St. Dev.)</td>
<td>0.90 (Min), 0.99 (Avg.), 1.07 (Max), 0.6 (St. Dev.)</td>
</tr>
<tr>
<td>Chang'e-3</td>
<td>-19.51</td>
<td>44.92</td>
<td>3x3</td>
<td>4.5 - 4.8 (Avg.-Max.), 0.23 (St. Dev.)</td>
<td>1.49 - 2.82 (Min-Avg. Max.), 0.64 (St. Dev.)</td>
<td>0.90 (Min), 0.99 (Avg.), 1.07 (Max), 0.6 (St. Dev.)</td>
</tr>
</tbody>
</table>

$^a$Clementine UVVIS has 200 meters/pixel resolution

$^b$LROC WAC has 400 meters/pixel resolution

$^c$Average TiO$_2$ values from soils 10084 and 10010

$^d$Average TiO$_2$ values from soils top 100 cm of soil, 24077 and 24109 [Meyer, 2009].

$^e$Average values from Table 1 in Ling et al. [2015].
3.3.1 Mare Tranquillitatis

The first human landing site on the Moon, Tranquility Base in Mare Tranquillitatis, is a relatively smooth region where basalts resurfaced the Tranquillitatis basin (Figure 3.4). The Apollo 11 mission landed on the Moon in 1969 in southwestern Mare Tranquillitatis at approximately 23.47° E, 0.67° N in an area of relatively uniform elevation and albedo (Figure 3.4C).

**ROI Observations.** WAC TiO$_2$ values in a 200 × 200 km region near the Apollo 11 landing site show a range of TiO$_2$ concentrations, from 0.3 to 12.4 wt. % with an average of 6.9 ± 1.1 wt. % TiO$_2$ (Table 3.4, Figure 3.3). The LP-GRS-measured TiO$_2$ values at this site also cover a significant range, from 1.2 to 9 wt. % TiO$_2$ with an average of 5.8 ± 1.8 wt. % (Table 3.4, Figure 3.3). Clementine values have the widest range, from 1.4 to 16.3 wt. % TiO$_2$, and the highest average TiO$_2$ value (10.3 ± 1.6 wt. %) (Table 3.4, Figure 3.3).

**Apollo 11 Landing Site Observations.** The TiO$_2$ concentration derived from WAC data is 7.5-7.8 wt. % at the Apollo 11 landing site (averages of the pixel corresponding to the landing site and a 2×2 and 3×3 pixel box centered on the landing site), which is consistent with published results from returned Apollo 11 soil samples 10084 and 10010 (average 7.7 wt. %, with a range of 6.8-9 wt. %) [Meyer, 2009] (Table 3.5). The Clementine TiO$_2$ values at the Apollo 11 landing site measure on average 10.8-11 wt. % TiO$_2$ for the pixels covering the landing site and 2×2 and
3×3 pixel boxes centered on the landing site and fall outside the range of measured soil TiO$_2$ concentrations (6.8–9.0 wt. %) [Gillis et al., 2003].

**2D Histogram Observations.** If the Clementine and WAC TiO$_2$ detection algorithms both accurately determine TiO$_2$, the derived TiO$_2$ values would plot along a 1:1 line in a 2-dimensional (2D) histogram (Figure 3.4D). At Mare Tranquillitatis, the Clementine TiO$_2$ values are, on average, higher than the WAC TiO$_2$ values and fall to the left of the 1:1 line. Clementine TiO$_2$ values in this area can reach as high as 16 wt. %, which is a TiO$_2$ concentration not found in the returned lunar soil sample suite (the highest TiO$_2$ concentration in lunar soil is ~10 wt. %) [Gillis et al., 2003]. Because of these high Clementine TiO$_2$ values, the Clementine algorithm appears to overestimate TiO$_2$ in the Mare Tranquillitatis region whereas the WAC TiO$_2$ algorithm gives values more consistent with Lunar Prospector and returned soil samples from this region.
Figure 3.4. WAC and Clementine TiO$_2$ at the Apollo 11 landing site and nearby Tranquillitatis Basin basalts. A) WAC TiO$_2$ map of Mare Tranquillitatis near Apollo 11. Yellow arrows correspond to approximate crater rays from Theophilus crater. Cyan arrow corresponds to ejecta ray from Tycho crater. B) WAC TiO$_2$ Classification image of Mare Tranquillitatis near Apollo 11. Red/warm colors correspond to low TiO$_2$, blue/cool colors correspond to high TiO$_2$. Dashed white rectangle shows LP pixel corresponding to the Apollo 11 landing site (white star). C) WAC morphology map of Mare Tranquillitatis near Apollo 11. The gold star represents the Apollo 11 landing site. D) Comparison of WAC TiO$_2$ and Clementine TiO$_2$ in Mare Tranquillitatis. In general, Clementine TiO$_2$ values are higher than WAC TiO$_2$; some Clementine TiO$_2$ values fall outside of the highest TiO$_2$ measured in returned samples.
3.3.2 Mare Serenitatis (MS2)

The region of interest in southern Mare Serenitatis is an international science coordination and calibration target used as an optical standard (MS2) in telescopic studies of the Moon [McCord et al., 1972; McCord et al., 1981; Pieters et al., 2008] (Figure 3.6). Mare Serenitatis (MS2) consists of relatively homogeneous low-Ti basalt that is younger than the high-Ti basalt of Mare Tranquillitatis to the south.

WAC TiO$_2$ images show lower TiO$_2$ to the west of the 200×200 km region centered on MS2, though many of these values correspond to unrepresentative areas as described in Section 3.2.4. To the south of the selected 200×200 km region lie basalts continuous with the Tranquillitatis basalts to the south; TiO$_2$ values in this region correspond to the high-Ti regions seen at Mare Tranquillitatis in Figure 3.4 (area number 3, Figure 3.6B; lobe number 3, Figure 3.6D). A narrow mixing zone lies between the two basalt units in the southeast (area number 2, Figure 3.6B). A branch of the high-Ti basalt unit extends to the west in the southwest corner of the 200×200 km area and represents a more extensive mixing zone.

**ROI Observations.** The WAC TiO$_2$ algorithm gives a range of 0.1-11.6 wt. % TiO$_2$ and an average of 3.8 ± 1.2 wt. % TiO$_2$ for the younger, low-Ti mare, consistent with the range of 0.6-8.8 wt. % and average of 4.0 ± 1.8 wt. % LP-GRS TiO$_2$ values in this region (Table 3.4, Figure 3.5). Clementine-derived TiO$_2$ values at MS2 have the widest range, from 0.9 to 15.0 wt. % TiO$_2$, and the highest average value (5.19 ± 1.4 wt. % TiO$_2$) (Table 3.4, Figure 3.5). Both
Clementine and WAC TiO$_2$ maximum values in this region are concentrations not found in the lunar soil sample suite, though the Clementine maximum is higher than the WAC by ~3 wt. % [Gillis et al., 2003].

**2D Histogram Observations.** Examining the WAC TiO$_2$ vs. Clementine TiO$_2$ histogram for the Serenitatis region shows the Clementine TiO$_2$ algorithm to again predict higher TiO$_2$ than the WAC algorithm (Figure 3.6D). At low TiO$_2$ values, the Clementine algorithm consistently derives higher TiO$_2$ than the WAC algorithm by about 1-2 wt. % (lobe number 1, Figure 3.6D). At the high TiO$_2$ values of the Tranquillitatis basalts (lobe number 3, Figure 3.6D), the Clementine algorithm predicts TiO$_2$ values of up to 4 wt. % greater than the WAC TiO$_2$ algorithm, with some TiO$_2$ values upwards of 14 wt. %; however, returned lunar soils lack such high TiO$_2$ concentrations [Gillis et al., 2003].
Figure 3.6. WAC and Clementine TiO$_2$ in Mare Serenitatis (MS2) basalts. A) WAC TiO$_2$ map of Mare Serenitatis (MS2). B) WAC TiO$_2$ Classification image of Mare Serenitatis (MS2). Red/warm colors correspond to low TiO$_2$, blue/cool colors correspond to high TiO$_2$. C) WAC morphology map of Mare Serenitatis (MS2). D) Comparison of WAC TiO$_2$ and Clementine TiO$_2$ at Mare Serenitatis. Lobe 1 corresponds to younger, low-Ti basalts, lobe 2 corresponds to the mixing zone between lava flows, and lobe 3 corresponds to older, high-Ti basalts.
3.3.3 Mare Imbrium at the Chang’e-3 landing site

The Chinese Chang’e-3 mission landed in 2013 in northern Mare Imbrium (340.49° E, 44.12° N) in an area with two distinct mare basalt units; younger Eratosthenian (~2.96 Ga) high-Ti mare basalt flows at the CE3 landing site overprint older Imbrian (~3.52 Ga) low-Ti mare basalt [Hiesinger et al., 2000]. We separated the two basalt flows for analysis into high-Ti and low-Ti regions using the maximum and standard deviation of the bimodal reflectance distributions in the WAC 643 reflectance histogram.

Observations on High-Ti Basalt Region. The high-Ti basalts have a range of <2 wt. % to 12.6 wt. % and an average of 7.8 ± 1.0 wt. % WAC TiO₂. Both the WAC and Clementine average TiO₂ values in the high-Ti basalt region fall about 3 wt. % higher than the 4.8 ± 1.5 wt. % average high-Ti LP-GRS basalt (Clementine measures 7.1 ± 1.2 wt. % TiO₂). The high-Ti basalt region near Chang’e-3 in Mare Imbrium is the only

Figure 3.7. WAC 643 histogram for Mare Imbrium near the Chang’e-3 landing site. The two local maxima were used to separate analyses into low- and high-TiO₂ regions.

Figure 3.8. Average TiO₂ values, ranges, and standard deviations at Mare Imbrium near the Chang’e-3 landing site. Red point represents landing site values measured by the Chang’e-3 APXS.
location we have examined where the WAC TiO$_2$ values are, on average, higher than the Clementine TiO$_2$ values (7.8 vs. 7.1 wt. %) and lie farther from the LP-GRS derived TiO$_2$ values than the Clementine TiO$_2$ (Table 3.4, Figure 3.8D).

**Observations on Low-Ti Basalt Region.** The low-Ti basalts have a range of <2 wt. % to 12.8 wt. % and an average of 2.3 ± 1.2 wt. % WAC TiO$_2$ (Table 3.4, Figure 3.8). In the low-Ti basalt region, the WAC average TiO$_2$ concentrations lie closer to the LP-GRS average TiO$_2$ concentration (3.4 ± 1.2 wt. % TiO$_2$) than does the average Clementine concentration (1.7 ± 1.0 wt. % TiO$_2$) (Table 3.4, Figure 3.8).

**Observations on Chang’e-3 Landing Site.** Chang’e-3 landed in the high-Ti basalt zone where the regolith has an average 7.8 wt. % WAC TiO$_2$ (Table 3.4, Figure 3.8). The Chang’e-3 Active Particle-induced X-ray Spectrometer (APXS) measurements characterize the landing site regolith as having intermediate TiO$_2$ (5.0 wt. %), slightly lower than the average WAC TiO$_2$ pixel values (5.5-6.2 wt%) corresponding to the exact landing site [Peng et al., 2014; Ling et al., 2015] (Table 3.5). The Clementine dataset has no data for the specific location of the Chang’e-3 landing site (it is in a data gore), so we can not compare Clementine TiO$_2$ data for this exact landing site.

The Chang’e-3 landing site is within ~10 km of the boundary between the high- and low-TiO$_2$ basaltic flows, so the regolith and TiO$_2$ content at the landing site may reflect mixing between the two units caused by ejecta contamination from small impact craters. We examined multiple profiles across the high- and low-Ti mare contact to determine the extent of this mixing zone; an example profile is shown in Figure 3.10A. On average, the width of the mixing zone between high- and low-Ti basalts is about 10 km, and the Chang’e-3 landing site falls at the edge of this mixing zone (Figure 3.10A, B). The intermediate TiO$_2$ value at the Chang’e-3 landing site
and the observation that the Chang’e-3 landing site lies at the edge of the mixing zone between high- and low-Ti basalts support the possibility that the Chang’e-3 APXS took measurements in an area where mixing of regolith has occurred between low-Ti material from the northeast and the local high-Ti basalt flow in the southwest.

**Figure 3.9.** WAC and Clementine TiO$_2$ at the Chang’e-3 landing site and nearby basalts in Mare Imbrium. A) WAC TiO$_2$ map of the Chang’e-3 Landing Site in Mare Imbrium with profile from mixing zone analyzed in Figure 3.10. B) WAC TiO$_2$ Classification image of the Chang’e-3 Landing Site in Mare Imbrium. Red/warm colors correspond to low TiO$_2$, blue/cool colors correspond to high TiO$_2$. White rectangle corresponds to the LP-GRS pixel corresponding to the Chang’e-3 landing site. C) WAC Morphology map of the Chang’e-3 landing site in Mare Imbrium. D) Comparison of WAC TiO$_2$ and Clementine TiO$_2$ in Mare Imbrium near the Chang’e-3 landing site. Lobe 1 corresponds to younger, high-Ti basalts, lobe 2 corresponds to the mixing zone between lava flows, and lobe 3 corresponds to older, low-Ti basalts.
Figure 3.10. Profile through the Chang’e-3 landing site showing TiO$_2$ mixing zone between high- and low-Ti Imbrium basalts. A) An example profile through the Chang’e-3 landing site mixing zone. The mixing zone is ~10 km wide, and the Chang’e-3 landing site lies at the edge of the mixing zone. B) The location of the profile through the mixing zone overlaid on a WAC TiO$_2$ image of the Chang’e-3 landing site.
3.3.4 Oceanus Procellarum near Lichtenberg Crater

The Lichtenberg crater region (293° E, 31.5° N) in Oceanus Procellarum is an international science coordination and calibration target as defined by Pieters et al. [2008]. Young, high-Ti basalts occur with older, low- to intermediate-Ti basalts around Lichtenberg crater. We used the WAC 643 reflectance histogram to separate the 200 × 200 km region near Lichtenberg crater into two basaltic regions for analysis using the histogram’s local maxima and standard deviations (Figure 3.11). Because the standard deviations overlapped the area between the peaks in the histogram, we chose the histogram local minima reflectance value as the maximum value for the low I/F region (high-Ti) and minimum value for the high I/F (low to intermediate-Ti) region.

The region near Lichtenberg crater consists of high-Ti and low- to intermediate -Ti basalt regions according to the WAC TiO$_2$ classification (Figure 3.9B), with low-Ti regions containing up to four separate basalt flows. The WAC and Clementine algorithms yield comparable concentrations of TiO$_2$ in the basalts surrounding Lichtenberg crater (Figure 3.12, Table 3.4, Figure 3.13D).

Observations on High-Ti Basalt Region. In the high-Ti basalt region east of Lichtenberg crater, WAC-derived TiO$_2$ values fall between 1.7 and 11.7 wt. %, with an average of 7.7 wt. % TiO$_2$ and standard deviation of 2.0. In this same region, Clementine-derived TiO$_2$ has a range of 0.9–13.8 wt. %, an average of 8.4 wt. % (slightly higher than the WAC TiO$_2$), and a standard
deviation of 2.6 wt. % (Figure 3.12, Table 3.4). Both the WAC and Clementine algorithms overestimate TiO$_2$ in this high-Ti region by 2.3-3 wt. % compared to the LP-GRS; the average LP-GRS concentration is 5.3 ± 2.0 wt. %, with a range of 1.3-7.9 wt. % (Figure 3.12, Table 3.4).

**Observations on Low to intermediate-Ti Basalt Region.** For the lower-Ti basalt region, WAC TiO$_2$ values range from < 2 to 11.3 wt. % with an average of 4.3 wt. % and standard deviation of 1.7 wt. %, and Clementine TiO$_2$ values range from 0.2 to 13.7 wt. % with an average of 4.4 wt. % and standard deviation of 2.1 wt. % (Figure 3.12, Table 3.4). LP-GRS TiO$_2$ values in the low-Ti region have a smaller range (0.7 - 7.9 wt. % TiO$_2$) but similar average TiO$_2$ concentration to both WAC TiO$_2$ and Clementine TiO$_2$ values (3.9 wt. % ± 2.0 wt. %). The maximum TiO$_2$ values for the WAC TiO$_2$ (11.6 wt. %) and Clementine TiO$_2$ (13.8 wt. %) algorithms fall significantly higher than the maximum LP-GRS TiO$_2$ concentration (7.9 wt. %) in both high- and low-Ti basalt areas. Such high WAC and Clementine TiO$_2$ values are not found in the lunar soil sample suite [Gillis et al., 2003].

**Basalt Diversity in Low- to Intermediate-Ti Region.** Up to four different basaltic units may exist in the low-Ti region near Lichtenberg Crater as identified using the LROC WAC TiO$_2$ and WAC 643 nm reflectance (Figure 3.13A, B, C). The first basalt area (Figure 3.13B, number
1) has high reflectance (Figure 3.13C) and low WAC TiO$_2$ (< 4 wt. %). The second basaltic area (Figure 3.13B, number 2) has high reflectance similar to basalt area 1, but higher WAC TiO$_2$ concentrations (2 – 6 wt.%). Basaltic region 3 (Figure 3.13B) lies in the low- reflectance region to the west of the high-Ti basalts and consists of intermediate-Ti basalts that embay southern Lichtenberg crater (4 – 6 wt.% WAC TiO$_2$). Region 4 (Figure 3.13B) has intermediate to low reflectance and intermediate TiO$_2$ values similar to those surrounding the high-Ti basalts to its northeast (5 – 6 wt.% TiO$_2$).

Stratigraphic relationships point to a younger age for the intermediate-Ti basalts in this region compared to the low-Ti basalts, consistent with crater count ages for region 4 (2.9 Ga) and regions 1 and 2 (3.47 Ga) [Hiesinger et al., 2003]. Basalt 3 likely erupted after regions 1 and 2 in the area now covered by the high-Ti basalts, followed by eruptions in two areas from the same source region as basalt 4, one to the south (area 4 in Figure 3.13B) and another on top of the preexisting basalt 3 flows. The high-Ti basalts then covered a majority of the intermediate-Ti basalts corresponding to basalt 3, though parts may still be visible on the southwestern edge of the high-Ti basalts. The high-Ti basalts have an age of 1.68 Ga (resurfacing) and cover an older, now buried surface of 3.18 Ga [Hiesinger et al., 2003]. Parts of this high-Ti region were mapped near the intermediate-Ti basalts of region 3, which could imply an age of 3.18 Ga for region 3 and 1.68 Ga for the high-Ti region. We list the regions in Figure 3.13B in order of predicted eruption history, with 1 being the oldest and 5 being the youngest.

**Observations on Lichtenberg Crater.** We also analyzed the area with the most dense occurrence of the Lichtenberg crater rays to constrain their composition. Because the Lichtenberg crater rays are not representative of the scene’s basaltic composition, we analyzed the Lichtenberg crater rays by considering all values near the crater with WAC 643 reflectance.
greater than 0.075 (the highest ~16% of reflectance values) and avoiding small, nearby craters (Figure 3.11). The Lichtenberg crater rays have low WAC TiO$_2$ values, with an average of 2.5 +/- 0.9 wt. % TiO$_2$. The WAC TiO$_2$ value for Lichtenberg’s rays is consistent with those from Hawke et al. [2004] (~2 wt. % average) and our own Clementine TiO$_2$ calculations (2.5 +/- 0.6 wt. %). The WAC TiO$_2$ value is and lower than the average Lunar Prospector Gamma Ray signature from this area (3.1 +/- 2.5 wt. %). The Lunar Prospector pixel does include surrounding higher-Ti mare basalts, which could increase the average TiO$_2$ and result in a higher value than the Clementine- and WAC-derived TiO$_2$. The Lichtenberg crater ejecta rays also have low iron concentrations (12-16 wt. % FeO). Hawke et al. [2004] inferred that the Lichtenberg crater impact excavated highlands material from beneath the thin mare basalts in this region and that the excavated low FeO highlands material, and not a maturity effect, causes Lichtenberg’s bright rays (Figure 3.13C). The low WAC TiO$_2$ values over Lichtenberg crater and the area northwest of the crater (red in Fig. 4.13B) support this interpretation (Figure 3.13B).
Figure 3.13. WAC and Clementine TiO$_2$ in Procellarum Basin near Lichtenberg Crater. A) WAC TiO$_2$ map of Lichtenberg Crater. B) WAC TiO$_2$ Classification image of Lichtenberg Crater. Red/warm colors correspond to low TiO$_2$, blue/cool colors correspond to high TiO$_2$. C) WAC 643 map of Lichtenberg Crater showing dark, younger high-Ti regions and bright, older low-Ti regions. D) Comparison of WAC TiO$_2$ and Clementine TiO$_2$ near Lichtenberg crater. Lobe numbers correspond to different basalt flows.
3.3.5 Mare Crisium at Luna 24

The Soviet Luna 24 mission landed in Mare Crisium (62.2°E, 12.7°N) in 1976. This site (Figure 3.15C) has been an ongoing topic of interest owing to the discrepancy between some remotely-calculated TiO$_2$ values at the landing site and returned samples studied in the laboratory. Soil samples returned from this site have an average of 1 wt. % TiO$_2$ in soils from the top 100 cm of the core (soils 24077 and 24109) [Blanchard et al., 1977; Ma and Schmitt, 1978; Nyquist et al., 1978], and the highest basalt rock fragment from Luna 24 has a TiO$_2$ content of 2.3 wt. % [Ma and Schmitt, 1978] (Table 3.5).

ROI Observations. The LP-GRS detected between 0 and 3 wt. % TiO$_2$ in the area, with an average value of $1.8 \pm 0.9$ wt. % TiO$_2$, consistent with returned soil and basalt TiO$_2$ concentrations. WAC TiO$_2$ values in this Mare Crisium region range from <2 wt. % to 9 wt. %, and have an average value of $3.6 \pm 0.82$ wt. %. (Figure 3.14, Table 3.4). Clementine TiO$_2$ concentrations are even higher, with a range of 0.5 to 9.2 wt. %, an average of $5.2 \pm 0.8$ wt.%. WAC and Clementine TiO$_2$ concentrations are higher than the returned soil and basaltic rock samples from the Luna 24 landing site, and Clementine values are significantly higher than LP-GRS.

Observations on Luna 24 Landing Site. The WAC TiO$_2$ value of the pixel centered on the landing site is 3.1 wt.%; the 2×2 and 3×3 pixel box surrounding the landing site pixel gives an average WAC TiO$_2$ value of 2.4 and 2.8 wt. %, respectively, with a minimum value of 1.5 wt. % TiO$_2$. These

![Figure 3.14. Average TiO$_2$ values, ranges, and standard deviations in Mare Crisium near the Luna 24 landing site. Red point represents returned Luna 24 soil values.](image-url)
values approach the returned basalt sample maximum TiO$_2$ value (2.3 wt. %, [Ma and Schmitt, 1978]). The Clementine pixel centered at the landing site has the value 4.5 - 4.8 wt. % TiO$_2$, two to four times the value of returned soil and the highest-Ti rock sample (1 wt. % TiO$_2$ and 2.3 wt. % TiO$_2$, respectively) (Table 3.5) [Ma and Schmitt, 1978].

2D Histogram Observations. As shown in the WAC TiO$_2$ classification image (Fig. 4.15B), the mare deposits in this region appear to be variable, with some areas in the 4-6 wt.% TiO$_2$ range, some in the 3-5 wt.% range, and close to the Luna 24 landing site (to the southwest), in the 0-3 wt.% range. For the entire 200 x 200 km Mare Crisium region observed, Clementine-derived TiO$_2$ values consistently plot 1-2 wt. % higher than the WAC TiO$_2$ values (Figure 3.15D).
Figure 3.15. WAC and Clementine TiO$_2$ at the Luna 24 landing site and nearby Crisium Basin basalts. A) WAC TiO$_2$ map of Mare Crisium near Luna 24. The gold star represents the Luna 24 landing site. B) WAC TiO$_2$ Classification image of Mare Crisium near Luna 24. Red/warm colors correspond to low TiO$_2$, blue/cool colors correspond to high TiO$_2$. White rectangle represents the LP-GRS pixel that falls over the Luna 24 landing site. C) WAC Morphology map of Mare Crisium near Luna 24. The gold star represents the Luna 24 landing site. D) Comparison of WAC TiO$_2$ and Clementine TiO$_2$ at Mare Crisium near Luna 24.
3.4 Global Results

We investigated the WAC 321/415 ratio as a function of TiO$_2$ and FeO across the lunar surface to understand the effect of FeO on the 321/415 ratio, particularly for low-Ti regions where pyroxene and glasses, and not ilmenite, can be the main contributors of TiO$_2$ [Coman et al., 2016]. We used Lunar Prospector Gamma Ray Spectrometer data as ground truth so we would not be limited by the available lunar sample suite.

We first examined the WAC 321/415 ratio and TiO$_2$ relationship as a function of FeO in 1 wt. % FeO increments. For each FeO value, the WAC 321/415 ratio increases with increasing TiO$_2$ (Figure 3.16). For example, for 18-19 wt% FeO (the green line in Figure 3.16), higher TiO$_2$ values correspond to higher WAC 321/415 ratios. The general shape of the plot when examining all FeO values follows a pattern of increasing WAC 321/415 ratio with increasing TiO$_2$. This direct relationship parallels that from laboratory studies of lunar soil TiO$_2$ and 321/415 ratios [Coman et al., 2015] and from returned lunar soil TiO$_2$ and LROC WAC 321/415 ratios [Robinson et al., 2011; Sato et al., 2015]. Figure 3.17 and Figure 3.18 show the individual data points for each FeO interval.

We also observed the WAC 321/415 ratio and FeO relationship as a function of TiO$_2$ in 1 wt. % TiO$_2$ intervals (Figure 3.19). Figure 3.20 and Figure 3.21 show the individual FeO and 321/415 data points for each TiO$_2$ interval. For low TiO$_2$ values (0-4 wt. %, red and orange lines in Figure 3.19), the WAC 321/415 ratio increases with increasing FeO (Figure 3.20). No clear relationship exists for intermediate TiO$_2$ values (4-8 wt. % TiO$_2$) (Figure 3.20). At high TiO$_2$ values (>8 wt. % TiO$_2$), the WAC 321/415 ratio behaves inversely to the LP-GRS FeO and increasing FeO corresponds to a decrease in the 321/415 ratio (Figure 3.21).
**Figure 3.16.** Plot of LP-GRS TiO$_2$ wt.% vs WAC 321/415 ratio as a function of FeO. Lines represent the effect of changing TiO$_2$ on the WAC 321/415 ratio while holding FeO essentially constant. Each line represents a narrow range of FeO values; black to warm colors represent lower FeO and cool colors represent higher FeO. At constant FeO, the WAC 321/415 ratio increases with increasing TiO$_2$. 
Figure 3.17. Individual plots of LP-GRS TiO$_2$ vs. WAC 321/415 at approximately constant LP-GRS FeO (9-17 wt. %).
Figure 3.18. Individual plots of LP-GRS TiO$_2$ vs. WAC 321/415 at approximately constant LP-GRS FeO (17 – 25 wt. %).
Figure 3.19. Plot of LP-GRS FeO vs. WAC 321/415 ratio as a function of TiO$_2$. Lines represent the effect of changing FeO on the WAC 321/415 ratio while holding TiO$_2$ essentially constant. Each line is of an approximately constant TiO$_2$ value; warm colors represent lower TiO$_2$ and cool colors represent higher TiO$_2$. For low TiO$_2$ values, the WAC 321/415 ratio increases with increasing FeO. FeO does not appear to affect intermediate TiO$_2$ values. At high TiO$_2$ values, there is an inverse relationship between FeO and WAC 321/415.
**Figure 3.20.** Individual plots of LP-GRS FeO vs. WAC 321/415 at approximately constant LP-GRS TiO$_2$ (0 to 8 wt. %). At low TiO$_2$, increasing FeO increases the WAC 321/415 ratio. For intermediate TiO$_2$ values, FeO does not affect 321/415 ratio.
3.5 Discussion

3.5.1 WAC and Clementine TiO$_2$ Comparisons at Regions of Interest

Apart from the Mare Imbrium high-Ti basalts, the WAC TiO$_2$ values more closely match the LP-GRS values than do Clementine TiO$_2$ values, with the Clementine algorithm commonly overestimating TiO$_2$ values compared to LP-GRS. These local observations are consistent with global findings from Sato et al. [2015] who found the Lucey et al. [2000] algorithm to give higher TiO$_2$ values than the WAC 321/415 ratio relationship.

The WAC values, however, fall outside of the LP-GRS TiO$_2$ ranges for the Luna 24 landing site. In regard to Luna 24, some authors have suggested the 2-4 wt. % remotely calculated composition at the landing site may not represent the surrounding basalts [Blewett et al., 1997; Lucey et al., 2000], but Head et al. [1978] described a similar spectral response from telescopic spectra and laboratory spectra of returned Luna 24 soils, implying a homogeneous composition in the basalt region surrounding the Luna 24 landing site. After accurately
identifying the Luna 24 landing site on the rim of a small crater, Robinson et al. [2012] concluded that soil collected from the Luna 24 site consisted of mostly excavated crater ejecta not representative of the surrounding surface basalts. Sampling of atypical material at the Luna 24 landing site would appear consistent with the detection by the WAC of a higher TiO$_2$ concentration at 400 mpp resolution (2.4-3.1 wt. %) compared to the returned Luna 24 soils (1 wt. %).

The WAC algorithm may overestimate TiO$_2$ concentrations for the high-Ti basalts inside Mare Imbrium at the CE-3 site and the high-Ti basalts near Lichtenberg crater. The high-Ti flow in Mare Imbrium is the only site where the WAC algorithm estimates higher values than Clementine. The WAC TiO$_2$ at the actual Chang’e-3 landing site is ~1.6 wt. % higher than the Chang’e-3 APXS measurement and likely represents a mixture of younger, high-Ti and older, low-Ti basalt flows, perhaps excavated by Zi Wei crater, on the rim of which Chang’e-3 landed [Ling et al., 2015].

3.5.2 Effects of FeO on WAC 321/415 Ratio: Laboratory-Based Results

The three areas where the WAC algorithm may over-predict TiO$_2$ values in relation to LP-GRS (high-Ti basalts of Lichtenberg crater and Chang’e-3, and possibly the Luna 24 landing site) all exhibit high FeO values for LP-GRS or returned samples (~20 wt. % FeO or greater). The presence of FeO in mineral or glass phases has long been shown to affect lunar soil spectra and spectral slopes (e.g., Burns et al. [1972], Hazen et al. [1978], Cloutis et al. [2008], Pieters and Englert [1993]). Also, because FeO-bearing phases such as pyroxenes, glasses, and other minerals can be the main contributors of TiO$_2$ in low-Ti soils [Coman et al., 2016], the ilmenite-based TiO$_2$ algorithms may not apply to areas like Luna 24, and spectral effects from FeO may cause these deviations.
First, we examined laboratory-based results. Chapter 2 contains our methodology for the micro X-ray fluorescence (μXRF) and UV-VIS spectroscopy. Micro-XRF-derived FeO values closely fit published values ([Morris et al., 1983; Meyer, 2009]) (Figure 3.22A), so we compared FeO to laboratory-derived 321/415 ratios (Figure 3.22B). When examining all soils, no clear relationship exists between FeO and the 321/415 ratio (Figure 3.22B, blue and orange circles). When examining only submature to mature soils (Figure 3.22B, orange circles), the 321/415 ratio appears to increase exponentially with increasing FeO, though our sample suite lacks intermediate 12-15 wt. % FeO soils to form a robust regression.

This trend may also be a second-order function of TiO$_2$. Submature to mature soils with low FeO values have low TiO$_2$ values; likewise, soils with high FeO values also have high TiO$_2$ values (soil 12057 being the exception). Because of the limitations in testing the FeO effects in the laboratory resulting from the small number of samples in our sample suite, we must consider remote sensing data and compare the LP-GRS and WAC 321/415 ratios.
Figure 3.22. Laboratory-measured FeO (wt. %) in lunar soil vs. laboratory 321/415 ratio. A) Our μXRF-derived FeO values closely match the literature. B) No strong relationship exists between FeO (μXRF) and laboratory-measured 321/415 ratio. After removing all immature soils (blue dots), the 321/415 ratio appears to increase with increasing FeO.
3.5.3 Effects of FeO on WAC 321/415 ratio – Remote Sensing

We first plot the WAC 321/415 ratio and LP-GRS TiO$_2$ as a function of LP-GRS FeO (Figure 3.16, Figure 3.17, Figure 3.18). The LP-GRS TiO$_2$ exhibits a positive correlation with 321/415 ratio. This relationship parallels findings from Robinson et al. [2011], Robinson et al. [2007], Sato et al. [2015], and Sato et al. [2017] that showed a strong positive correlation between a spacecraft UV/VIS ratio and TiO$_2$ of returned soil. Coman et al. [2015] also found a strong positive correlation between laboratory-measured UV/VIS ratios and mature lunar soil TiO$_2$. A weak dependence of the WAC 321/415 ratio on FeO is also observed, with higher WAC 321/415 ratios corresponding to higher LP-GRS FeO (Figure 3.16, Figure 3.17, Figure 3.18).

Areas with >15 wt. % FeO correspond to mare regions with less highlands contaminants, so aside from ilmenite/TiO$_2$, pyroxene, olivine, volcanic glass, and submicroscopic metallic iron (SMFe) spectra should dominate the 321/415 ratio. We focus on pyroxene as the main FeO-bearing phase because of its abundance in lunar basaltic soils and on metallic iron because of its strong effects on reflectance spectra.

*The Potential Role of Pyroxene at High TiO$_2$ Values.* Regions with high TiO$_2$ values are likely controlled by spectral effects of ilmenite and pyroxene, with little effect from plagioclase, which does not vary much in abundance. At high LP-GRS TiO$_2$ values (>8 wt. % TiO$_2$), LP-GRS FeO exhibits an inverse relationship with WAC 321/415 ratio (Figure 3.19, Figure 3.21), possibly owing to spectral effects from FeO held in pyroxenes (Figure 3.1). Pyroxenes show a steep decrease in reflectance from visible to ultraviolet wavelengths owing to strong Fe$^{2+}$-O charge transfer effects seen near 253 nm [Blazey, 1977; Cloutis et al., 2008]. With increasing FeO, this band broadens to higher wavelengths and lowers the reflectance at 321 nm, resulting in a lower ratio of 321 nm to 415 nm reflectance with increasing FeO for the high-Ti regions.
[Cloutis et al., 2008; Hapke, 2016]. With a maximum 1% change in TiO$_2$ between TiO$_2$ bins in Figure 3.21, ilmenite concentrations should remain relatively constant within the same bin, and increasing pyroxene FeO concentrations would lower the 321/415 ratio.

**Intermediate LP-GRS TiO$_2$ Values.** At intermediate LP-GRS TiO$_2$ values, the WAC 321/415 ratio does not have a defined dependence on LP-GRS FeO (Figure 3.20); locations with TiO$_2$ values between 3 and 7 wt. % have R$^2$ values less than 0.4. A lack of correlation could be a consequence of the complicated interplay at intermediate TiO$_2$ values between plagioclase at low FeO, pyroxenes and pyroclastic glasses at high FeO, and maturity effects. The high-Ti mare near both Chang’e-3 and Lichtenberg crater have intermediate LP-GRS TiO$_2$, and the WAC 321/415 ratio gives TiO$_2$ values up to 3 wt. % higher than those of the LP-GRS. The spectral signatures of these regions require further study, which are outside the scope of this work.

**Low LP-GRS TiO$_2$ Values and Luna 24.** Plots of WAC 321/415 ratio and LP-GRS FeO as a function of TiO$_2$ show a direct relationship between FeO and 321/415 ratio at low TiO$_2$ values (Figure 3.19, Figure 3.20). Very low FeO values represent highlands regions dominated by plagioclase and lacking in ilmenite, pyroxene, olivine, and volcanic glasses. These areas therefore exhibit a low 321/415 ratio. Higher FeO values (> 15 wt. %) represent mare regions. Increasing FeO in pyroxene or olivine would not be able to contribute to an increase in the 321/415 ratio as seen with increasing FeO, as these FeO hosts have even lower 321/415 ratios than plagioclase. The increase in 321/415 ratio may result from increasing submicroscopic metallic iron in mature lunar soils. We explain this hypothesis in the next section.

The soils returned from the Luna 24 landing site possess up to 20 wt. % FeO, the highest FeO concentrations of all returned samples [Papike et al., 1998]. Luna 24 soils also have very low TiO$_2$ values in returned soil and LP-GRS (~ 1-2 wt. %) [Papike et al., 1998]. Using the
relationship between LP-GRS FeO and WAC 321/415 ratio in a narrow range of low TiO$_2$ (0-2 wt. %) (Figure 3.20), we can derive a hypothetical WAC TiO$_2$ value. For a soil with 20 wt. % FeO and a 321/415 ratio of 0.71-0.72, the WAC TiO$_2$ value would be approximately 2.5 wt. % TiO$_2$. This value closely corresponds to that of ~2.4 wt. % derived at the Luna 24 landing site using the WAC algorithm. Effects from FeO may cause the WAC algorithm to overestimate TiO$_2$ slightly at this landing site and any other low- to very-low-Ti region on the Moon.

**The Potential Role of Submicroscopic Metallic Iron at Low LP-GRS TiO$_2$ Values.** The finest fraction of lunar soils dominates the spectral properties of lunar soils from ultraviolet to infrared wavelengths [Pieters et al., 1993a]; this finest fraction also has the largest quantity of fine-grained (<30 nm) single-domain metallic iron in lunar grain size separates [Morris, 1977; 1980]. The fine-grained iron darkens and reddens the lunar soil at visible and infrared wavelengths, but darkens and causes a bluing in the soil from visible (~400 nm) to ultraviolet wavelengths [Hendrix and Vilas, 2006; Riner et al., 2006; Denevi et al., 2014]. A soil with more FeO will naturally have the capability to create more submicroscopic and nanophase iron, and a soil’s amount of exposure to the lunar space environment (its maturity) controls the creation of these iron particles.

*Sato et al.* [2017] show that mare regions with TiO$_2$ concentrations less than 4 wt. % TiO$_2$ are all older than 2.5 Ga. The <4 wt. % TiO$_2$ mare regions would have had a longer exposure to micrometeorite and solar wind bombardment and greater opportunities to form fine-grained iron particles. The probability of forming these iron particles would increase with higher concentrations of available FeO, and the higher concentration of submicroscopic and metallic iron would result in an increase in the 321/415 ratio with increasing FeO as seen in Figure 3.20,
spectra in Allen et al. [1996a] and Noble et al. [2007], and 321/415 ratio and maturity relationships in Denevi et al. [2014].

Denevi et al. [2014] demonstrated that maturity (as measured by I$_S$/FeO, [Morris, 1978]) does not affect the 321/415 ratio for low FeO highlands, consistent with the points seen in Figure 3.20 at low TiO$_2$ and for FeO values < 12 wt. %. In moderate-FeO highlands and low-Ti mare, soils with higher maturities had higher 321/415 ratios [Denevi et al., 2014]. The submicroscopic iron in mature moderate-FeO highlands regions or intermediate- to low-Ti mare with TiO$_2$ < 4 wt. % and FeO > 12 wt. % may explain the increase in 321/415 ratio with increasing FeO at low TiO$_2$ values (Figure 3.19, Figure 3.20).

The Role of Maturity and Pyroxene in Decreasing Spectral Contrast. In addition to the positive and negative correlation between FeO and 321/415 ratio at low and high TiO$_2$, respectively, increasing FeO also limits the contrast in 321/415 ratio values. When examining the 321/415 as a function of TiO$_2$ in areas with >15 wt. % FeO (Figure 3.16), increasing FeO concentrations lead to progressively flatter regression lines for TiO$_2$ and WAC 321/415 ratios. This pattern also appears in the plots of constant TiO$_2$ and varying FeO, where the decrease in spectral contrast results in 321/415 ratios approaching a constant value (between 0.72-0.75) with increasing FeO (Figure 3.20). A tradeoff between the spectral effects from submicroscopic metallic iron and pyroxene likely causes this pattern.

All mare regions younger than 2.5 Ga have TiO$_2$ values greater than 4 wt. % [Sato et al., 2017], but in addition to these young regions there are also older intermediate and high-Ti regions. Because the maturity can vary for intermediate and high-Ti regions, the effects of maturity may get averaged out in our plots for these regions, allowing effects from other phases such as pyroxene at high TiO$_2$ values to dominate.
3.6 Conclusions

We compared WAC- and Clementine-derived TiO$_2$ values at five selected landing sites and calibration sites to assess the accuracy of the derived TiO$_2$ values with respect to returned lunar soils and LP-GRS detected TiO$_2$ concentrations. We find that the Clementine-derived TiO$_2$ values commonly are higher than the WAC-derived values. WAC-derived TiO$_2$ values also correspond more closely to LP-GRS TiO$_2$ values than do the Clementine-derived values. At the Luna 24 landing site and the high-Ti mare regions near Lichtenberg crater and the Chang’è 3 landing site, the WAC TiO$_2$ values are higher than those measured by the LP-GRS.

We also used the LP-GRS TiO$_2$ and FeO values as a global “ground truth” to examine the effect of FeO on the WAC 321/415 ratio. The presence of FeO in the form of pyroxenites and submicroscopic iron may influence the WAC 321/415 ratio and derived WAC TiO$_2$. For soils with low TiO$_2$ values (< 3 wt. %), such as the Luna 24 landing site, increasing FeO increases the 321/415 ratio and may result in higher than expected WAC TiO$_2$, possibly owing to increasing fine-grained, submicroscopic iron in mature low-Ti mare soils. For soils with high TiO$_2$ values (>8 wt. %), FeO has an inverse relationship with 321/415 ratios as the FeO concentration in pyroxene increases in an ilmenite-rich soil, broadening the ~250 nm Fe-O charge transfer absorption and pulling down the 321 nm band reflectance. The lower 321 nm reflectance results in lower than expected WAC TiO$_2$ values.

A fruitful area for further study would be to investigate the effects of soil chemistry and mineralogy at visible and ultraviolet wavelengths using filters similar to those of the LROC WAC. Particularly of interest would be synthetic mixtures of (Fe$^{3+}$-free) pyroxene, plagioclase, ilmenite, and fine-grained metallic iron. These synthetic mixtures would enhance the suite of lunar analog spectra at ultraviolet wavelengths and clarify the patterns with 321/415 ratio seen.
from the LP-GRS FeO and TiO$_2$ data. While soil properties other than ilmenite concentration may affect this ratio to some extent, the WAC 321/415 ratio has proven to be a simple yet accurate algorithm for TiO$_2$ detection.
References


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Chapter 4: Dissertation Summary

The ilmenite spectral response at UV-VIS wavelengths correlates well with TiO₂ content in lunar soils and thus can be used as a proxy for TiO₂ detection on the Moon despite the fact that ilmenite only accounts for some 50% of the TiO₂ in lunar soils, on average. The 321/415 (UV/VIS) ratio shows the strongest correlation with TiO₂ of all UV/VIS ratios analyzed in the laboratory using an Ocean Optics UV-VIS spectrometer and spectral data convolved to LROC WAC bandpasses. In this summary, I review effects from mineralogy, chemistry, and maturity on the 321/415 ratio independent of ilmenite and suggest precautions one must take when working with TiO₂ concentrations derived from the 321/415 ratio relationship.

A Practical Limit and Phases other than Ilmenite. The ilmenite spectral response may not be appropriate in regions with low bulk TiO₂ values (< 2 wt. %). In these low-Ti regions, phases other than ilmenite (e.g., pyroxene and glasses) that have different spectral responses (steep UV/VIS compared to ilmenite) contribute as much TiO₂ as ilmenite or even the majority of TiO₂ to the soil (Chapter 2).

Maturity. Maturity strongly affects the 321/415 ratio in soils that are immature, that is, not extensively space weathered (with I₅/FeO values < 40). Laboratory measurements of submature to mature soil spectra show a strong positive correlation between TiO₂ and the 321/415 ratio, suggesting that spectral effects from maturity as measured by I₅/FeO saturate in submature to mature soils (Chapter 2). The good correlation between LRO WAC-derived TiO₂ and landing-site ground truth TiO₂ benefits from the fact that at the 400 mpp spatial resolution of the WAC, most of the landing site soils are mature.
FeO effects on 321/415 nm ratios. Remote sensing observations of LP GRS TiO$_2$ values reveal a strong positive correlation with LROC WAC 321/415 ratios for all values of FeO < 23 wt. % (Chapter 3). For low TiO$_2$ (< 4 wt. %) soils, FeO has a second-order positive correlation with 321/415 ratio (Chapter 3). Intermediate TiO$_2$ (3–8 wt. %) soils do not show a dependence on FeO (Chapter 3). In high TiO$_2$ (> 8 wt. %) soils, FeO exhibits an inverse correlation with the 321/415 ratio (Chapter 3).

Although the WAC 321/415 ratio correlates well with TiO$_2$ concentrations at the Apollo landing sites, the relationship is best applied to mature and submature mare regions of intermediate TiO$_2$ values. It may be possible to correct for FeO in regions where TiO$_2$ values fall below 4 wt. % or above 8 wt. %.

Analyses of known (laboratory-prepared) mixtures of ferric-iron-free ilmenite, pyroxenes containing various concentrations of FeO, olivine, plagioclase, ferric-iron-free Fe-Ti-bearing silicate glass, low-Fe-Ti silicate glass (as an amorphous component), and submicroscopic metallic iron would be useful to constrain the spectral response for analog lunar mineral and glass mixtures and would help to elucidate the causes of spectral variations in the UV-VIS and further test hypotheses presented in this dissertation.
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</table>

Average Grain Size: 51<sup>h</sup> 78<sup>i</sup> 89<sup>j</sup> 64<sup>j</sup> 75<sup>j</sup> 59<sup>j</sup> 60<sup>j</sup> 87<sup>j</sup> 51<sup>j</sup> 31<sup>j</sup> 90<sup>j</sup>

<sup>a</sup>Korotev and Gillis [2001]
<sup>b</sup>Korotev et al. [2011]
<sup>c</sup>LSPET [1972]
<sup>d</sup>Korotev [1991]
<sup>e</sup>Rhodes et al. [1974]
<sup>f</sup>Korotev and Kremser [1992]
<sup>g</sup>Rose et al. [1974]
<sup>h</sup>Basu et al. [2001]
<sup>i</sup>Average of values from Quaide et al. [1971] and King et al. [1971]
<sup>j</sup>Graf [1993]