

Foundations of Lunar Highland Crustal Mineralogy Derived from
Remote Sensing and Laboratory Spectroscopy of Plagioclase-
Dominated Materials

By

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A dissertation

Submitted in partial fulfillment of the requirements for the degree of Doctor of
Philosophy in the Department of Geological Sciences at Brown University

Providence, Rhode Island

May, 2014

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ACKNOWLEDGEMENTS

I am so grateful to so many people for ushering me along in this process. First, what a privilege it has been to be mentored by Carlé Pieters over the past five years. Everything good has probably already been said about her abilities as an advisor and mentor – she tends to leave a good impression on her students. I am particularly thankful for her optimism and energy, and of course for her endless patience in guiding me through the growing pains of graduate school. I admire her tenacity and confidence, and I consider Carlé one of my biggest role models.

Thank you also to my committee – to Steve, Reid, Jack, and in the early days, Alberto. You have made a great team, each with your own insights but always taking a collective interest in seeing me and my projects succeed. Committee meetings have been enlightening every time, and I have always left feeling motivated to get it right. I have an immense amount of respect for each of you. A special thank you to Steve Parman for acting as a second advisor during those first few years when I was stumbling around the experimental labs trying to understand how people can possibly *make* minerals.

I'd like also to enthusiastically thank the Carlé students who came before me – those who I got to know in Lincoln Field as well as those I had the pleasure of meeting throughout the M³ adventure. I am fortunate to have signed on to such a smart, fun, and supportive family! To Peter and Rachel in particular, I often think of how I wish we could have overlapped more in our time at Brown. Peter I'm sure will make an excellent advisor some day...he bore the brunt of my incessant questioning effortlessly.

Of course there are many others at Brown that contributed greatly to the completion of this thesis in various ways. Taki deserves a medal for dealing with the immense number of samples I kept passing his way during the infamous mixing project. He went above and beyond getting everything through quickly. Thank you to our intrepid microprobe lab manager Joe, and also his predecessor Joe. Thank you of course to Bill Collins for tons of things...teaching me how to make grain mounts at least twelve different times for instance. And for facilitating my first (and hopefully not last) film appearance. Thank you so much to Marshall, Kate, and Jamie, who showed immense patience when I was trying to learn how to run those experiments.

The group of grad students here at Brown is consistently great. To all those who were here when I arrived: thanks for lunchtime in 105, fiesta parties, introducing me to Providence (read: explaining the parking situation). Thank you to Bethany, Debra, Linda, Heather, Kate, Sam, Joe, Brendan, and all the other “older” folks who welcomed me into the fold and were always willing to chat about their experiences (in grad school and in life...). A very enthusiastic what-would-I have-done-without-you to Laura and Angela in particular. Thanks also to JR, who made the mission room seem less lonely by always having something interesting to talk about. To those in my cohort, David, Mark, Kerri, Chen, Bronwen, Jess, Rocio, Jeff, Shannon, Tina and LeAnne: I think we’ve all done a great job, and I demand a reunion “fifth-year” dinner. And to those carrying the torch, you have been an impressive bunch from the start and I have learned a lot from you. Dan and Deepak, thank you for letting me have free reign over that one mission room computer, I’ll definitely clear off that area before long. It’s been wonderful sharing the “Carle’s group” journey with you guys! Jenny and Rebecca, I’ll miss our mission room

chats. Megan and Sam, thanks for being gracious officemates, and thank you also to Steph and Terik, for being excellent additions to the third floor crew. Thank you also to Colin, who's extended conversation over the years has no doubt led to a much better thesis on this end. Thank you to another key member of Team Spinel, Kelsey, who showed me what good, true confidence looks like. Kerri and Jess in particular have been integral to the process of actually writing a thesis. Thanks to both of you for the advice, cheerleading and all-around support over the last year. Kerri, you are my life-and-thesis coach, a wealth of fantastic advice. Jess, it goes without saying that there's no other way to write a thesis than with another student who is completely nocturnal.

My family deserves the biggest thanks. It's unclear if I ever would have stumbled into geology if weren't for my dad's own interest in the subject as a chemist-turned-geologist-turned-chemist. He was always talking about how neat the Earth is and suggested that I do an Earth Science project for my 8th grade science class. He's the only reason I sought out an intro geology class in college, and so this thesis likely wouldn't have happened without him. Thanks to my mom for reminding me recently that I had always been particularly interested in "nature and the stars" as a kid. Maybe following my dad's geo suggestion was less arbitrary than I had thought? Thanks to Angie and John for moving to the Adirondacks so that I can see some anorthosite whenever visiting (little Kate has no choice but to become an enthusiastic and world-class geologist, in my opinion). And thanks most of all to Tim – although these last couple of years in grad school were consistently challenging and anxious, I couldn't look back on this stage and remember being anything but happy.

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INTRODUCTION

Understanding the composition and structure of the lunar crust is a major goal in planetary science. The processes that produced the Moon's primitive outer layer in the aftermath of a lunar-forming impact are likely repeated, in various forms and at many scales, throughout the histories of numerous planetary bodies. The Moon represents a unique laboratory in which to investigate these processes using a combination of geologic samples and remote sensing techniques. This thesis aims to provide a framework for interpreting orbital spectroscopy data for the Moon's most ancient crustal materials: the anorthositic highlands. The major results provide new insight into the mineralogic character of lunar anorthosites in the context of what is known from the sample collection.

Crustal lithologies such as anorthosites, Mg-suite materials, and mare basalts are the only igneous components of the Moon that are readily accessible to orbital sensors. Of these, only the anorthosites are thought to represent primary differentiates of the lunar magma ocean (LMO) – both the basalts and the Mg-suite rocks likely formed by secondary melting. These later-formed products offer important insights into mantle compositions and provide key information on the Moon's thermal history. The anorthosites, on the other hand, represent a direct link to the crystallized LMO itself [e.g., *Wood et al.*, 1970].

Anorthosites are well-represented in the lunar sample collection. Their abundance in returned Apollo samples was the main impetus for development of the LMO models that now serve as a framework for understanding nearly all aspects of lunar crustal formation [e.g., *Smith et al.*, 1970; *Wood et al.*, 1970]. Orbital geochemical

measurements have demonstrated that these anorthosites, or similar plagioclase-dominated rocks, should be pervasive across the lunar surface based on the remote identification of iron-poor, aluminum-rich materials [e.g., *Adler et al.*, 1972; *Davis and Spudis*, 1985]. However, remote characterization of anorthosite **mineralogy** has been severely limited in the preceding decades, due primarily to the many challenges associated with identifying plagioclase on the lunar surface in orbital near-infrared (NIR) reflectance data.

Broad absorptions in the NIR wavelength region are diagnostic of mineralogy. They are caused primarily by electron transitions in iron atoms contained in specific crystallographic sites, and therefore easily distinguish common minerals such as olivine, pyroxene, plagioclase, and spinel [e.g., *Burns*, 1993]. The mafic silicates and many oxide minerals contain iron as a major element; their associated NIR absorptions are strong and easily identifiable in a range of observational environments [e.g., *Sunshine et al.*, 1998; *Klima et al.*, 2007]. However, iron typically occurs as only a minor element in plagioclase, and the resulting diagnostic absorption near 1250 nm for plagioclase is relatively weak and easily masked when other minerals are present in moderate abundances [e.g., *Nash and Conel*, 1974; *Crown and Pieters*, 1987]. Additionally, the plagioclase structure that gives rise to the diagnostic absorption is known to easily transform into a diaplectic glass at relatively low shock pressures [e.g., *Stöffler*, 1971]. Thus, not only should the orbital identification of the diagnostic ~1250 nm plagioclase absorption be limited to locations containing exceedingly high plagioclase abundances, but the plagioclase must also occur in its crystalline form in spite of the intense bombardment history of the Moon's surface. These challenges, in addition to combined

limitations from the wavelength coverage, spectral resolution, and spatial resolution of many previous spectrometers, have often prohibited the identification of the diagnostic plagioclase absorption in NIR data despite the fact that the Moon's crust is highly feldspathic.

A suite of modern spectrometers, however, have recently identified the diagnostic plagioclase absorption in numerous locations across the lunar surface [*Ohtake et al.*, 2009; *Pieters et al.*, 2009; *Donaldson Hanna et al.*, 2013]. Many of the recent plagioclase detections are found in small kilometer-scale rocky exposures surrounded by spectrally featureless materials. This important development now allows the distribution of fresh, rocky exposures of the primitive lunar anorthosites to be mapped across the Moon's surface and evaluated in terms of their manner of exposure and their lateral and vertical extents throughout the crust.

In addition to *identification* of anorthositic exposures with NIR spectroscopy, small spectral variations also provide information about plagioclase composition and abundance. Previous workers have described a dependence of absorption band characteristics on plagioclase An content and FeO abundance specifically [e.g., *Bell and Mao*, 1973a; *Adams and Goullaud*, 1978]. Further, although studies of mineral mixtures have rarely focused on materials with high plagioclase abundances, it is clear that small amounts of mafic minerals (~5%) exert substantial effects on the spectra of plagioclase-dominated materials [e.g., *Crown and Pieters*, 1987]. The aim of this thesis is 1) to characterize in detail the spectral effects of plagioclase chemistry and plagioclase abundance, and 2) to apply these findings to case studies of two anorthosite exposures

measured by the Moon Mineralogy Mapper (M³) instrument. The major components of each specific chapter are outlined in detail below.

Chapter 1 is dedicated to characterizing the spectral reflectance properties of a diversity of well-characterized plagioclase samples in the laboratory. Previous studies have demonstrated that plagioclase commonly displays a diagnostic absorption band centered near 1250 nm [e.g. *Conel and Nash*, 1970; *Bell and Mao*, 1973b]. The exact center position of this band appears to vary with An content of the plagioclase [*Adams and Goullaud*, 1978], and the band strength is correlated with iron abundance [*Bell and Mao*, 1973a]. We examine reflectance spectra of particulate plagioclase samples (1) from a range of terrestrial sources, both volcanic and plutonic, (2) sintered at low oxygen fugacity for a range of iron abundances, and (3) collected from several Apollo landing sites on the Moon. The characteristics of natural bulk anorthosites are compared with the spectra of the plagioclase separates. Band center and band depth are calculated for each spectrum, and evaluated in terms of compositional data for the sample. The findings emphasize the difficulties in obtaining “good” 1250 nm absorption bands for many terrestrial samples, although we show that samples with an observable band can be obtained from a variety of sources. The spectral parameters (i.e., band center and depth) for these samples are consistent with previous observations, but emphasize the high sensitivity of NIR measurements to very small changes in structure and composition from sample to sample. The lunar samples typically display much more regular spectral properties, although the small amounts of mafic minerals in the Apollo 16 anorthosites are clearly expressed in some samples. We anticipate that data presented in Chapter 1 will be pared down in preparation for journal submission, perhaps focusing on the lunar

anorthosite spectra and select terrestrial plagioclase or anorthosite samples. Additional data from Mössbauer spectroscopy will be incorporated, drawing on the expertise of Darby Dyar at Mount Holyoke College who will participate as a coauthor.

Chapter 2 focuses on laboratory spectroscopy of binary mixtures that contain high abundances of plagioclase plus small amounts of various mafic or oxide components. The results provide a framework for interpreting the relative abundances of these minerals from remote spectral measurement of anorthositic lithologies. We have created seven series with a restricted particle size range (45-75 μm), each consisting of seven individual mixtures at varying abundances. The same plagioclase endmember, a gem-quality volcanic labradorite, was used in all mixtures. The mafic endmembers include: a forsteritic olivine, an intermediate olivine, an enstatite, a diopside, and two Mg-spinel with slightly different iron abundances. A major goal of this project is to emphasize the dependence of mixture spectral properties on the specific compositions of the mafic endmembers. The mafic components of most lunar anorthosites are typically ferroan relative to the compositions within the Mg-suite, but most previous mixing studies have typically focused on Mg-rich mineral endmembers such as forsterite or enstatite [e.g. *Mustard and Pieters*, 1987; *Crown and Pieters*, 1987]. The proportions of mafic minerals vary throughout each series. Select mixtures are recreated with a wider particle size distribution for each endmember, from 0-1000 μm , to test the sensitivity of the mixture properties to variations in particle size from a simulated “mature” soil to a simulated “immature” soil. The measured spectra of the laboratory mixtures are compared with spectra calculated from the appropriate endmembers using Hapke modeling [*Hapke*, 1993; 2002]. The results demonstrate that different mafic minerals exert distinguishable

effects on the spectra of plagioclase-dominated materials, and that these differences should in many cases be detectable by orbital measurements. Hapke modeling is observed to accurately predict the abundances of mineral constituents to within a few percent. Chapter 2 is in preparation for submission to a special issue of *American Mineralogist* summarizing the major outcomes of the Second Conference on the Lunar Highland Crust.

Chapters 3 and 4 represent case studies using M^3 data for two different anorthositic locations on the Moon. Chapter 3 focuses on spectral analysis of the Orientale basin, a nearly 1000 km diameter multiring impact structure that has been previously inferred to contain abundant anorthosite in its Inner Rook Ring due to a notable lack of mafic mineral signatures [e.g., *Spudis et al.*, 1984]. The results of our study confirm the ubiquity of highly pure anorthosite by identification of the diagnostic ~ 1250 nm absorption feature. Further, a weak absorption due to low-calcium pyroxene is observed in some spectra that display a plagioclase band, and the strength of the pyroxene band varies across the basin. Importantly, the “purest” anorthosite, that containing the lowest proportion of pyroxene as inferred from the absence of a pyroxene absorption, is concentrated in the Inner Rook Ring. This unique spatial variation has been noted previously [e.g., *Spudis et al.*, 1984], but we estimate that the abundance of plagioclase in the purest sections of the Inner Rook Ring may approach 99-100% based on Hapke mixing calculations for representative laboratory minerals. This estimated high level of purity suggests that vast portions of the lunar anorthositic crust must contain a lower abundance of mafic minerals than commonly anticipated based on analysis of lunar samples [e.g., *Warren et al.*, 1990]. This observation places important constraints on

magma ocean crystallization processes that must include some mechanism for removing all but tiny amounts of non-plagioclase phases from the bulk anorthosite. Chapter 3 is in press at the Journal of Geophysical Research.

Chapter 4 presents a detailed M³ investigation into the lithologies exposed in the central peak of Tsiolkovskiy crater, a ~200 km diameter crater situated in the lunar farside highlands. Unlike Orientale, none of the plagioclase-dominated spectra are free from contributions of additional mineral components. Even the “purest” plagioclase spectra from the central peak have absorption bands centered at slightly shorter wavelengths than expected for lunar anorthositic plagioclase, consistent with mixing with tiny amounts of a mafic component that is absorbing near ~1000 nm. Many of the plagioclase-dominated spectra display a pyroxene absorption superimposed on the ~1250 nm plagioclase band, and the relative strengths of the plagioclase and pyroxene bands vary substantially on the pixel level. The most pyroxene-rich spectra display absorption centers near ~990 nm, somewhat longer than the pyroxenes at Orientale. The long-wavelength absorption band occurs near 2100 nm, suggestive of an iron-rich pyroxene endmember. This observation implies that the anorthosites exposed at Tsiolkovskiy share key characteristics with the ferroan anorthositic suite in the sample collection [e.g., *Dowty et al.*, 1974; *McGee et al.*, 1993]. We intend to prepare Chapter 4 in a shortened form for submission to Geophysical Research Letters.

The final chapter, Chapter 5, briefly summarizes the main conclusions of this work and outlines several future directions that we anticipate will be fruitful avenues of research building on the contributions of this thesis.

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CHAPTER 1: Spectroscopy of diverse plagioclase and anorthosite samples in support of new remote sensing observations of the lunar crust

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Abstract

Scientific analyses of remote sensing data for anorthositic lithologies, such as the Moon's highland crust, require a detailed understanding of the origin and character of the diagnostic plagioclase absorption feature near 1250 nm in reflectance spectra. Here, we present a detailed laboratory study of the absorption properties of a diversity of well-characterized plagioclase and anorthosite samples. Lunar and terrestrial plagioclase and anorthosite samples, as well as a suite of synthetic plagioclases produced for the study, are investigated in terms of their composition and bulk spectral properties. The wavelength position and absorption depth of the diagnostic plagioclase feature is analyzed in the context of iron abundance and An content ($An = \text{molar } [Ca/(Ca+Na+K)]$). The results confirm that the addition of small amounts of divalent iron in plagioclase systematically increases absorption band depth. However, variations in the An content of plagioclase do not produce clear systematic trends for this dataset, and there is considerable scatter in the band centers measured for various plagioclases. The spectral effects of a glass component in synthetic plagioclase-dominated materials are discussed, as well as the character of a second, less prominent plagioclase crystal field absorption at longer wavelengths. Although the primary absorption characteristics of plagioclase are systematic and repeatable for a range of sample types, the plagioclase structure and chemistry is clearly complex.

1. Introduction

Plagioclase feldspars are some of the most common igneous minerals in the solar system, comprising major proportions of the crusts of the Earth, Moon, and other rocky bodies such as asteroids. Like other common rock-forming minerals, plagioclase displays unique absorption characteristics when viewed with near-infrared (NIR) reflectance spectrometers [e.g., *Conel and Nash*, 1970; *Bell and Mao*, 1972]. Small variations in these absorption characteristics are linked to aspects of mineral chemistry, such as An content and the specific abundance of minor amounts of iron [*Bell and Mao*, 1973; *Adams and Goullaud*, 1978]. However, unlike some of the more common mafic silicates [e.g., *Sunshine et al.*, 1998; *Cloutis and Gaffey*, 1991; *Klima et al.*, 2007], the details of these variations in spectral properties have not been thoroughly investigated for a range of well-characterized samples. This task has recently become particularly necessary in light of modern remote sensing data for the Moon's anorthositic crust. For the first time, the major diagnostic plagioclase absorption, centered near 1250 nm, is identified in numerous locations across the Moon's surface [*Ohtake et al.*, 2009; *Pieters et al.*, 2009; *Yamamoto et al.*, 2012; *Donaldson Hanna et al.*, In Review]. Detailed laboratory studies are needed in order to facilitate interpretation of these new data.

2. Background

2.1 Origin of Absorption Features in the NIR

Reflectance spectra of many geologically common minerals display diagnostic absorption features in the near-infrared portion of the electromagnetic spectrum. These absorptions are caused by electrons transitioning among the five d-orbitals of certain

transition metal ions as a result of interaction with incident photons [e.g., *Burns*, 1993].

The energy of the transition, which corresponds to the wavelength position of the absorption, is largely dependent on the coordination environment of the absorbing species. Because of differences in the crystal structures of common minerals, the wavelength positions corresponding to these transitions are distinct and diagnostic of mineralogy. Thus, even if the same absorbing species is present in plagioclase as in a pyroxene, for example, the resulting absorptions will be completely distinguishable from one another.

The most abundant absorbing species in typical rock-forming minerals is Fe^{2+} . Increasing proportions of this cation in a specific crystallographic site lead to a greater number of electronic transitions and stronger, deeper absorptions centered near a wavelength that is dictated by mineral structure [e.g., *Bell and Mao*, 1973]. Iron is present as a major element in olivines and pyroxenes, giving rise to strong, easily identifiable absorption features [e.g., *Adams*, 1974; *King and Ridley*, 1987]. Plagioclases, by contrast, typically only contain up to 1 wt% total iron [e.g., *Corlett and Ribbe*, 1967], and their NIR characteristics are therefore more subtle. For many plagioclases, the specific abundance of iron is correlated with An content, which is a measure of the relative abundance of the anorthite and albite components in the mineral, given by the formula $\text{An} = \text{Ca}/[\text{Ca}+\text{Na}+\text{K}]$ (molar). Increasing An content from albites to bytownites (An0-An90) generally correspond to an increase in iron abundance, whereas anorthites (An90-An100) display more variation [*Ribbe and Smith*, 1966; *Corlett and Ribbe*, 1967; *Adams and Goullaud*, 1978]. Higher iron abundances are noted in high temperature, volcanic plagioclases as compared to lower temperature, more slowly-cooled samples

and those from terrestrial high-grade metamorphic sources [Sen, 1960; Smith, 1971].

Plagioclases from lunar ferroan anorthosites typically contain low amounts of iron, often ~0.1-0.2 wt%, although anorthosites with several tenths of a percent iron are known [Dixon and Papike, 1975; Hansen et al., 1979; Phinney and Morrison, 1990; Phinney, 1991; McGee, 1993; Jolliff and Haskin, 1995].

Crystal field absorptions in olivines and pyroxenes are primarily caused by Fe^{2+} occurring in a range of octahedral M-sites. The energies of transitions within octahedral environments typically correspond to absorptions centered near 1000 nm [e.g., Adams, 1974; Cloutis and Gaffey, 1991]. In pyroxenes, the M2 site is so distorted that an additional splitting among the three lower-energy orbitals generates an additional absorption near 2000 nm [Goldman and Rossman, 1977]. Long-wavelength absorptions near 2000 nm and beyond can also result from electron transitions of Fe^{2+} in tetrahedral coordination [e.g., Slack, 1964; Bates et al., 1966]. Strong tetrahedral absorptions are common for spinels [e.g. Slack, 1964].

2.2 Origin of the Plagioclase Absorption

Near-infrared reflectance spectra of particulate plagioclase samples, both lunar and terrestrial, commonly display a broad crystal field absorption near 1250 nm [e.g., Conel and Nash, 1970; Bell and Mao, 1972; Adams and Goullaud, 1978]. Recent spectral analyses of plagioclase clasts in eucrites have noted ~1250 nm absorptions that are similar in character to the lunar and terrestrial examples [Hiroi et al., 2012]. There is disagreement over the position of Fe^{2+} within the plagioclase structure, discussed further below, but it is clear that the coordinating environment is distinct from that of olivines, pyroxenes, and spinel. As a result, the plagioclase absorption is easily distinguished from other common igneous minerals using reflectance spectroscopy.

The plagioclase feldspars are tectosilicates consisting of four-member rings of corner-sharing Si and Al tetrahedra, the T-sites, stacked to form crankshaft structures that are linked in a framework (Figure 1) [Megaw, 1962]. Larger cations such as Ca, Na, K, and Ba are accommodated in irregular A-sites corresponding to the large cavities in the structure. The number of coordinated oxygen atoms for this site are variable, probably 7-12, depending on which can be considered “neighbors” to the A cation [e.g., Megaw, 1962]. Across the plagioclase solid solution series, Ca and Al replace Na and Si in a coupled substitution ranging from albite ($\text{NaSiAl}_3\text{O}_8$) to anorthite ($\text{CaSi}_2\text{Al}_2\text{O}_8$). Early Mössbauer studies predicted that minor Fe^{2+} substituted on both the A and T sites [e.g., Appleman *et al.*, 1971 Hafner *et al.*, 1971; Schurmann and Hafner, 1972]. Distribution coefficients between synthetic plagioclase and basaltic glass also support ferrous iron substituting on tetrahedral sites [Longhi *et al.*, 1976], as do oxidation experiments on terrestrial plagioclase crystals [Behrens *et al.*, 1990]. Sen [1960] suggests that Fe^{2+} likely replaces the calcium ion based on consideration of ionic size and charge. He notes that replacement of Al^{3+} should also be possible, however. Predictions based on optical spectroscopy are also variable. Bell and Mao [1972] considered substitution on T-sites the most consistent with the fact that the wavelength position of the dominant plagioclase absorption band (~ 1250 nm) is longer than expected for crystal field absorptions due to octahedral coordination environments (typically ~ 1000). However, Mao and Bell [1973] suggest that its position intermediate to 1000 and 2000 nm may indicate averaging of absorptions due to iron in both an M and a T site. Hofmeister and Rossman [1984], based on optical and electronic paramagnetic resonance spectroscopy, reported Fe^{2+} mainly on

the distorted A-sites, possibly in a range of micro-environments. Indeed, the presence of multiple cation sub-positions within the A-site has been suggested [Megaw, 1962].

Transmission spectra of oriented plagioclase crystals from the Earth and Moon show the prominent ~1250 nm band in addition to a secondary absorption near 2200 nm. This longer-wavelength feature, which is typically weaker, may be due either to a secondary, lower-energy transition within the A-site, or from iron situated in tetrahedral coordination [e.g., Bell and Mao, 1972; Burns and Vaughan, 1975; Hofmeister and Rossman, 1984; Behrens et al., 1990]. Burns and Vaughan [1975] have suggested that while the ~2200 nm absorption is not explicitly observable in reflectance data, it may be expressed simply as the lowered reflectance values across long wavelengths that resemble an asymmetric long-wavelength “shoulder” of the primary ~1250 nm absorption.

To illustrate the differences between these two measurement modes for near-infrared data, reflectance and transmission spectra for the same plagioclase material are compared in Figure 2. For the reflectance measurement, 12 individual, homogeneous labradorite crystals (1-2 cm) were crushed together and sieved to a constrained particle size fraction of 45-125 μm (Figure 2a). The average composition of these plagioclases is given in Table 1, under the sample name “GemLabr 1-12”. Analysis by Mossbauer spectroscopy, performed by Darby Dyar at Mount Holyoke College, suggests that approximately 70% of the total iron is present as FeO. The radiation reflected by the particulate surface from an incident beam at 30 degrees to the normal was collected by the Bidirectional Reflectance spectrometer (BDR) in RELAB at Brown University [Pieters, 1983]. A separate crystal of the same material was broken in order to reveal a

natural cleavage plane, and a ~4.2 mm section was cut parallel to this face (Figure 2b). The sample was mounted vertically in a Fourier Transform Infrared spectrometer (FTIR) in RELAB and the radiation transmitted through the crystal by an incident beam on one side was detected emerging from the other side. The signal from each type of measurement is shown in Figure 2c. Both spectra are characterized by relatively high albedo and a prominent absorption near 1250 nm. However, the transmission spectrum displays both a stronger ~1250 nm band and enhanced absorption at the long wavelengths. A weak ~2200 nm absorption may be apparent in the transmission spectrum. These differences could be attributable to the fact that the strengths of both the ~1250 and ~2200 nm absorptions vary significantly depending on optical orientation [e.g., *Hofmeister and Rossman*, 1984]. The orientation of the crystal measured in transmission mode here clearly facilitates a very strong absorption, but it is expected that measurement along the other two axes would result in shallower features. The reflectance data represent a combination of the signals from the various crystallographic orientations, and the result is a decrease in spectral contrast in this case. We note that differences in the path length of the light passing through the samples could also be playing a role in the differences in absorption strength between the two spectra in Figure 2c. For instance, the many interfaces presented by the 45-125 μm particles measured in reflectance mode may scatter much of the signal back to the detector before a sufficient number of electronic transitions have occurred to generate absorptions of comparable strength to those observed in the transmission measurement (~4.2 mm path length).

2.3 Variations with Composition

For olivine and pyroxene, numerous laboratory studies have been carried out to relate spectral properties to specific variations in mineral chemistry. For example, it has

been demonstrated that the Mg# of olivines ($\text{Mg\#} = \text{molar Mg}/[\text{Mg} + \text{Fe}]$) can be predicted based on the exact wavelength positions of each of the three overlapping absorptions near 1000 nm [e.g., *Sunshine et al.*, 1998]. Similarly, variations in both the iron and calcium contents of pyroxenes result in systematic shifts in the wavelength positions of the ~ 1000 and ~ 2000 nm absorptions [e.g., *Klima et al.*, 2007, 2011]. These shifts in wavelength position arise from variations in the crystal field associated with compositional changes along the solid solution series. The An content of plagioclase may therefore also be expected to exert a measurable control on spectral properties, since the biggest change to the crystal field results from the coupled substitution of Ca and Si for Na and Al throughout the plagioclase solid solution series. Indeed, a dependence of ~ 1250 nm band position on An content has been documented [*Adams*, 1975; *Adams and Goulland*, 1978]. Specifically, these studies found that the plagioclase absorption band center increases from ~ 1100 to ~ 1300 nm from An₀-An₆₅, but decreased again from An₆₅-An₁₀₀. It therefore appears that near-infrared spectroscopy may have the capability to distinguish very low An samples (albite) from more intermediate and high An samples, but distinguishing typical alkali anorthosite compositions (andesines, for example) from anorthitic plagioclase carries more ambiguity. In addition, *Bell and Mao* [1973] successfully demonstrated that the strength of the ~ 1250 nm plagioclase absorption is strongly dependent on the abundance of FeO incorporated into the plagioclase structure.

2.4 Challenges

Although it is clear that both iron content (specifically, FeO) and An content affect plagioclase absorption characteristics, a number of factors have hampered further detailed study of these relationships. For example, the ~ 1250 nm plagioclase absorption

is generally weak and therefore difficult to detect, largely due to the fact that iron is only a minor element in plagioclase. Even the most iron-rich plagioclases, containing ~0.5-1.0 wt% total iron, are not expected to generate a strong absorption in comparison with the mafic silicates.

Additionally, on the Earth, a significant fraction of the small amount of total iron is trivalent, which does not contribute to the strength of the ~1250 nm plagioclase absorption. Alteration to clays is also often pervasive in terrestrial plagioclase samples, and even small amounts of alteration can weaken the main plagioclase band and introduce vibrational absorptions, principally at ~1.4 μm and 1.9 μm [Clark *et al.*, 1990], that can obscure weak plagioclase absorptions.

Even in environments that lack aqueous alteration, such as the Moon, the presence of non-plagioclase phases in the host rock easily obscures the plagioclase absorption feature. For example, exceedingly small proportions of common mafic silicates in plagioclase-bearing rocks are known to suppress the ~1250 nm absorption [Adams and McCord, 1971; Nash and Conel, 1974; Mustard and Pieters, 1987; Crown and Pieters, 1987; Serventi *et al.*, 2013; Chapter 2]. In addition to the mafic silicates, oxides such as ilmenite and magnetite have been shown to exert a dominant effect on bulk spectral properties, even when occurring in trace abundances as inclusions within plagioclase grains [e.g., Mustard and Pieters, 1987; Isaacson *et al.*, 2011].

These various effects are demonstrated in Figure 3 for a set of terrestrial plagioclase samples. Major element compositions of these samples are given in Table 1, along with data for the additional terrestrial samples that are discussed below. In Figure 3, all spectra were obtained for plagioclase separates from various rock types. However,

none of these examples display strong ~1250 nm absorption features due to the reasons outlined above. Other plagioclase spectra, that do display prominent 1250 nm absorptions, are the focus of this work.

3. Goals

The goal of this paper is to investigate the range of spectral properties exhibited by plagioclase feldspars in the near-infrared, focusing on the compositional controls on the diagnostic 1250 nm crystalline plagioclase absorption band. Previous foundational studies by *Bell and Mao* [1973] and *Adams and Goullaud* [1978] have motivated the current work by demonstrating that compositional parameters affect absorption characteristics even for the relatively weak and easily obscured plagioclase feature. Testing these relationships for a wider range of samples will better constrain the extent to which detailed mineralogic information can be extracted from remote reflectance measurements of plagioclase and plagioclase-dominated rocks on other planetary bodies. This is a particularly important goal in the context of new remote reflectance data for the Earth's moon, in which the enigmatic plagioclase absorption is detected ubiquitously across the lunar highlands [e.g., *Ohtake et al.*, 2009; *Yamamoto et al.*, 2012; *Donaldson Hanna et al.*, In Review].

In support of these new lunar data, we investigate the spectral properties of plagioclase samples from a wide range of environments. Natural terrestrial plagioclase samples, from both volcanic and plutonic sources, are evaluated in terms of the positions and depths of their 1250 nm absorptions. Synthetic plagioclases were produced experimentally to document the effects of small systematic variations in iron content. Spectra of lunar plagioclase and anorthosite samples are also evaluated in order to

provide a link between laboratory measurements and the plagioclase-dominated spectra recorded by remote NIR spectrometers across the Moon.

4. Methods

4.1 Terrestrial Plagioclase and Anorthosite

Thirteen terrestrial plagioclase samples were acquired from a variety of sources for this study. These samples were obtained from several different rock types, including anorthosites, gabbro-norites, and volcanic sources. Most samples were received as plagioclase separates from bulk rocks. These were inspected using a binocular microscope, and an additional attempt was made to remove remaining impurities. However, small amounts of non-plagioclase phases, such as pyroxene, oxides, and clays, are still present in nearly all samples. Some other samples (i.e., Miyake-jima and GemLabr1-12) were received as large single crystals, which were crushed using a DiamoniteTM mortar and pestle. All samples were sieved to 45-125 μm to minimize spectral variations due to particle size differences. In addition to the thirteen plagioclase separates, we have also obtained four bulk terrestrial anorthosites. These were crushed and sieved as above, but no attempt was made to remove non-plagioclase phases. These samples are intended to serve as a comparison between the spectral properties of 1) nominally pure plagioclase, and 2) rocks (i.e., anorthosites) that are dominated by the plagioclase component but may contain small amounts of additional phases.

Grain mounts were prepared for each terrestrial plagioclase and anorthosite sample. Major element data for all samples was acquired at Brown University using a Cameca SX500 electron microprobe, with the exception of sample BS-16 for which major element data was obtained from *Lundgaard et al.* [2006]. Spectral reflectance data

for the 45-125 μm particle size fraction of each sample were acquired in the RELAB facility at Brown University [Pieters, 1983].

4.2 Synthetic Plagioclase

One of the limitations in using natural samples to study the compositional controls on spectral properties is the difficulty in isolating the specific compositional variable of interest. For instance, each of the samples discussed above differ not only in iron and calcium, but also in the concentrations of various trace elements, the presence of inclusions, degree of alteration, mineral grain size, cooling rate, and other factors, all of which may variably influence spectral characteristics. In order to systematically characterize the effect of iron content on plagioclase spectra, we have synthesized a range of plagioclase compositions at variable iron concentrations, keeping constant all other variables.

The starting compositions for the iron series experiments were anorthite- and albite-composition glass powders that were combined in proportion by mass to produce a mixture consisting of ~85 wt% anorthite-composition glass. The mixture was homogenized by mixing with an agate mortar and pestle for 20 minutes under methanol and left to dry overnight. The mixture was then glassed in a Pt crucible in a box furnace at 1550° C in five separate batches for 2 hours each. The resultant glass was crushed with a steel mortar and pestle to a particle size of ~1/4 inch, and further pulverized in an alumina shatterbox. The powders were again mixed, dry, in an agate mortar and pestle for ~10 minutes. One weight percent Fe_2O_3 (half ^{56}Fe , half ^{57}Fe) was then added to one split of the homogenized glass. The iron-bearing split was homogenized by the same procedure: mixing under methanol, glassing in a box furnace, and pulverizing with a steel

mortar and pestle followed by shatterboxing. Major element analyses for the two glass powder starting compositions are shown in Table 2.

The two bulk glass powders were combined in variable proportions to produce a series of eleven glass compositions that vary in iron content. The nominal iron abundance for each sample, based on the weighed proportion of each glass endmember, is shown in Figure 4. Each of the compositions in the series was homogenized by tumbling and rolling their individual vials for ~5 minutes each, followed by mixing with an agate mortar and pestle (dry) for ~20 minutes each, followed by again tumbling and rolling each vial for ~5 minutes each. An example spectrum of a glass produced by this method is shown in Figure 5, and has an absorption minimum near 100 nm. The 11 samples were pressed into pellets (dry) and placed onto alumina boats containing a bed of zirconia beads that were loaded into a horizontal gas mixing furnace. The samples were run at 1275° C for 64 hours. Oxygen fugacity within the tube was controlled by a CO/CO₂ gas flow at $pO_2 \sim 10^{-10.5}$, corresponding to ~IW. The samples were cooled at a rate of 6° C per minute. Spectroscopy of the run products are discussed in more detail below.

Fragments of each sintered pellet were analyzed by electron microprobe. These analyses were conducted using both a Cameca SX500 microprobe at Brown University, and a JXA-8530F Field Emission Electron Probe Microanalyzer (EPMA) at Yale University. Much of the remainder of each sample was crushed in a DiamoniteTM mortar and pestle and sieved to the same particle size fraction that was investigated for the terrestrial samples (45-125 µm). Spectral reflectance measurements were carried out for samples loaded into Teflon-coated dishes in RELAB at Brown University, using an incidence angle of 30 degrees and an emission angle of zero degrees [Pieters, 1983]. X-

Ray Diffraction data was acquired at Brown University for splits of the 45-125 μm fractions of PL13b, PL15b, and PL21b.

4.3 Lunar Plagioclase and Anorthosites

Four lunar ferroan anorthosites were obtained from the curatorial facility at Johnson Space Center (JSC) for spectral analysis. Most lunar ferroan anorthosites in the sample collection are relatively homogeneous in terms of their plagioclase compositions, with iron contents typically between 0.1 and 0.2 wt%, and An contents greater than An₉₅, [e.g., *McGee*, 1993; *Papike et al.*, 1991, 1998]. As such, the four samples were chosen primarily to represent a range in their degree of shock metamorphism, as reported by previous workers., rather than a compositional range. For example, sample 60025 has been noted as having relatively minor shock damage, whereas sample 60015 has more severe shock textures and local melting as described by *Dixon and Papike* [1975]. Sample 65315 is an example of an anorthosite showing extensive recrystallization [*Dixon and Papike*, 1975], and *McGee* [1993] reported abundant maskelynite in sample 69955. Maskelynite is a diaplectic glass formed from plagioclase crystals that are shocked to pressures between ~25 and ~45 GPa [e.g. *von Engelhardt and Stöffler*, 1968; *Stöffler*, 1971]. As an amorphous phase, maskelynite does not have the plagioclase crystal structure that gives rise to the diagnostic ~1250 nm absorption feature. Increasing proportions of maskelynite in a sample therefore cause the plagioclase absorption to weaken and ultimately disappear in reflectance spectra [e.g., *Adams et al.*, 1979; *Johnson et al.*, 2003]. A spectrum of lunar maskelynite, displaying absorptions diagnostic of glass, is shown in Figure 6 [*Pieters*, 1996]. However, it is expected that even lesser degrees of shock metamorphism, resulting in fracturing and the redistribution of minor elements such as iron, will affect the way incident light interacts with the sample.

The lunar samples obtained for this study consisted mainly of both particulates and chips, with the exception of sample 69955 that arrived as three large (cm-sized) chips only. This sample was gently crushed with an agate mortar and pestle to generate sufficient particulate material for an initial bulk measurement. Spectral reflectance data for the lunar anorthosite samples, loaded into Teflon-coated dishes, were acquired in RELAB, for ~40 mg splits of each bulk sample. The measurement geometry was identical to the conditions for the terrestrial plagioclases and anorthosites, described above. A 45-75 μm split was then prepared from the bulk samples and measured in the same way. An attempt was then made to remove visible contaminating phases from a fraction of the bulk 45-75 μm split. A grain mount was prepared with 2-5 plagioclase grains of each sample and analyzed for major element composition by electron microprobe at Brown University. Spectra of plagioclase separated from lunar basalts obtained from the RELAB database are also investigated for comparison with the anorthosite spectra.

5. Sample Characterization: Composition and Spectroscopy

5.1 Terrestrial Plagioclase

Major element compositions for plagioclases from each terrestrial sample investigated in this study are shown in Table 1. They represent a diversity of compositions, ranging from An₀-An₉₆ (primarily >An₅₀) and 0-0.52 wt% total iron. A plot of total iron versus An content in plagioclase is shown in Figure 7, and the terrestrial samples are annotated according to their origin from either anorthosites, gabbro-norites from the Bushveld Igneous Complex, or other sources. The data for the anorthositic plagioclases and those from gabbro-norites both display considerable scatter and overlap

substantially, ranging from ~0.1 to 0.5 wt% FeO regardless of An content. The scatter in these data is far greater than in the terrestrial plagioclases measured by *Adams and Goullaud* [1978], hereafter referred to as *AG78*. The reason for more tightly constrained compositional relationships in the *AG78* data is unclear, since they also used samples consisting of a range of volcanic and plutonic sources and many of the spectra display evidence of alteration. The five samples from “other” sources in Figure 7 generally increase in iron abundance with increasing An content. Four of these samples are plagioclases from volcanic sources, and one is from a pegmatitic dike.

Not all of the samples in Table 1 and Figure 7 display a prominent ~1250 nm diagnostic plagioclase absorption. Those samples consisting of plagioclase separates lacking a diagnostic ~1250 nm feature were described in Figure 3. Reflectance spectra of those terrestrial plagioclase separates that do display ~1250 nm plagioclase absorptions are shown in Figure 8a. Reflectance spectra for the four bulk anorthosites, regardless of whether or not they display a ~1250 nm feature, are shown in Figure 9 and discussed following the plagioclase separates.

Most, but not all, plagioclases in Figure 8a are bright, with reflectance values near 0.8 in some parts of the spectrum. Offsetting each spectrum in reflectance (Figure 8b) facilitates comparison of the different samples. Differences in the strengths of the ~1250 nm plagioclase absorption are apparent between samples, and small shifts in the center position of this feature are also visually discernable. Also apparent in Figure 8b are the variable strengths of the sharp vibrational absorptions. These features near 1.4 and 1.9 μm are attributable to combinations and overtones of OH and H₂O fundamental vibrations, respectively, and indicate some amount of alteration of the plagioclase

structure, likely to that of a phyllosilicate mineral such as montmorillonite [e.g., *Clark et al.*, 1990]. Additional sharp features at longer wavelengths (e.g., near 2200 nm, 2300 nm, and longer) are attributable to various combinations and overtones of metal-OH fundamental vibrational absorptions in small amounts of alteration minerals [e.g., *Clark et al.*, 1990].

In order to more directly compare the strengths of the ~1250 nm absorption in all samples, variations in brightness and overall spectral slope must be minimized. This is done by removing from each spectrum a continuum defined as a straight line calculated between the reflectance maximum between 750-1000 nm and the reflectance maximum between 2300-2500 nm. Continuum-removed spectra are shown in Figure 8c. In addition to highlighting variations in absorption band strength, differences in band position are also more apparent when viewed in this way. For instance, visual inspection of the continuum-removed spectra shows that sample 4512-A-L has both the strongest and longest-wavelength band of all samples. Offsetting the continuum-removed spectra (Figure 8d) highlights the same general characteristics as in Figure 8b.

The spectra of four bulk terrestrial anorthosite samples are plotted separately in Figure 9. In general, the anorthosite spectra display a similar range of characteristics as the plagioclase separates shown in Figures 3 and 8. For instance, the anorthosite spectrum from the Banded Series of the Stillwater igneous complex displays a very strong ~1250 nm plagioclase absorption as well as some minor hydration features. Two spectra, one from the St. Urbain anorthosite massif in Quebec [e.g., *Dymek and Gromet*, 1984] and one representing the An-II anorthosite of the Stillwater Complex [e.g., *Haskin and Salpas*, 1992], display very weak ~1250 nm absorptions. The Stillwater An-II spectrum

in particular displays extensive alteration. The spectrum of the Shawmere anorthosite from an Archean complex in Ontario displays no observable ~ 1250 nm absorption, probably due to the exceedingly low total iron in its plagioclase (<0.1 wt%).

Interestingly, none of these four anorthosite spectra display obvious absorptions due to other primary igneous minerals that are expected to be present in small abundances.

5.2 Synthetic Plagioclase

Major element compositions for the synthetic plagioclase samples produced by the experimental method described above are shown in Table 3. The range of iron abundances in each sintered sample, which are consistently lower than the iron abundance in the starting glass, are shown in Figure 4. Although the amount of iron generally increases across the series, there is considerable scatter and some overlap between samples. This within-sample heterogeneity is especially pronounced in the samples containing >0.5 wt% FeO. Variation on the order of 5-10 mol% An also exists among grains of a given sample (Figure 10). The average An content of plagioclase in each sample is plotted against iron abundance in Figure 7. Because the synthetic samples are intended to isolate the effects of iron abundance on plagioclase spectral properties, their An content was nominally held constant resulting in a near vertical trend near An₈₇ in Figure 7. Powder X-Ray Diffraction spectra for splits of PL13b, PL18b, and PL21b, shown in Figure 11, demonstrate that the bulk characteristics are dominated by plagioclase.

A sample backscattered electron (BSE) image from the lowest FeO synthetic sample is shown in Figure 12. Individual plagioclase grains are typically 5-10 μm , and are not strongly zoned. However, an additional phase, labeled “glass” in Figure 12 is apparent interstitial to plagioclase grains. Analysis of this image using Environment for

Visualizing Images (ENVI) software to classify pixel brightness indicates that the additional minor phase is approximately 8% of the image (excluding the large voids). Although the amount of this interstitial phase is variable within each sample and across the sample suite, we estimate that the volumetric abundance ranges between 5-10% of the total sample everywhere.

Compositional analysis of select samples was performed using a higher-resolution electron microprobe (spot size $\sim 1\ \mu\text{m}$) at Yale University in order to better characterize the minor interstitial phase noted in BSE images for the sample suite. Example higher-resolution BSE images are shown in Figure 13. A wide field of view for two samples, a low-iron (PL13b) and a high-iron sample (PL21b), is shown in Figure 13a and 13b. Higher-magnification images are shown in Figure 13c-f, which reveal a third component, labeled “Al-phase,” occurring as needle-like crystals within the darker interstitial material. The interstitial material is also observed to be comparatively bright in samples with the highest FeO abundances, suggesting that they are particularly enriched in heavier elements relative to the background plagioclase. Figure 14 shows compositional analyses of two of the samples, PL15b and PL13b, obtained with the higher-resolution microprobe. Average compositions for all three phases are shown in Table 4. These analyses suggest that the main interstitial phase is variable in composition but generally high in elements that are incompatible in plagioclase, such as iron and magnesium, and lower in calcium and aluminum. Although there is significant variation in the composition of the main interstitial phase, on average it contains over ten times as much FeO as the plagioclase. Based largely on its texture and highly variable major element composition, we interpret this main interstitial phase as unreacted starting glass material.

Only two analyses were attempted for the needle-like phase due to its extremely small size ($<1\ \mu\text{m}$). Both analyses contained relatively high abundances ($>30\ \text{wt}\%$) of aluminum and silicon and low abundances of all other phases, including calcium.

Reflectance spectra for the synthetic plagioclase series are shown in Figure 15. In all samples except for PL11b, which nominally contains no iron, two broad absorption bands are clearly present, one centered near 1250 nm, and another at longer wavelengths, near 2100 nm. The lowest FeO sample does display a very weak $\sim 1250\ \text{nm}$ band, however, despite having $<0.1\ \text{wt}\%$ total iron. Addition of small amounts of iron into the plagioclase structure causes the albedo of the whole spectrum to decrease, and increases the absorption strengths of both absorption bands in all spectra. The continuum-removed spectra in Figure 15b show that the increase in band strength is regular, particularly for the lower-FeO samples. The apparent gap between samples PL13-b and PL15-b represents a compositional gap: a sample PL14-b was created with an iron abundance intermediate to those two samples, but was contaminated during the powder pressing stage prior to the experimental run and was not sintered. Mid-infrared spectra of all run products, shown in Figure 16, more closely resemble feldspars than the starting material, demonstrating that a significant fraction of the sample was successfully crystallized.

However, the spectra of these sintered products do show key differences from spectra of natural terrestrial plagioclases. Principal among these differences is the greater width of the $\sim 1250\ \text{nm}$ absorption and the presence of an observable $\sim 2100\ \text{nm}$ absorption. The long-wavelength absorption is similar to the weak feature observed in transmission spectra (Figure 2c), but occurs at a slightly shorter wavelength and is much stronger. In addition, the absorption band center for the main absorption seems to occur at

relatively short wavelengths, particularly for the highest-FeO samples. These first order differences suggest that some aspect of the coordination environment of iron in the synthetic samples is different from most natural plagioclases. Possible explanations are discussed in more detail elsewhere in the paper, but we suggest that the secondary glass phase is the main cause of both the width and the short-wavelength center of the ~1250 nm absorption as well as the prominent long wavelength (~2100 nm) absorption.

5.3 Lunar Plagioclase and Anorthosite

Major element compositions for plagioclases in the lunar anorthosites obtained for this study are shown in Table 5. Also shown are analyses for plagioclase separates from lunar basalts [Isaacson *et al.*, 2011] obtained from the RELAB database. Plagioclases from the four anorthosites are remarkably similar in composition, with total iron between 0.13 and 0.17 wt% and An contents of 96-97 (Table 5 and Figure 7). The four plagioclase separates from lunar basalts have higher and more variable iron abundances, from 0.35 to 0.61 wt%. Both types of plagioclase samples, anorthositic and basaltic, are consistent with the lunar data of *AG78*, which displayed an extremely large range in iron abundance despite having a restricted range of An content (anorthite in most cases).

Reflectance spectra for the Apollo 16 anorthosites are shown in Figure 17. The bulk samples as measured without controlling particle size (other than lightly crushing the large chips of 69955 to generate particulate material) are shown in Figure 17a. Three of the samples generally consist of fine particulates, but sample 60015 also contained several mm-sizes grains. These larger particles in 60015 could explain the lower albedo in this sample compared to the other three bulk anorthosites. As expected, none of the spectra in Figure 17a show evidence of the hydrous alteration that complicate many terrestrial plagioclase and anorthosite spectra. Sample 60015 shows significant spectral

contribution from a pyroxene component, expressed as a weak ~1000 nm absorption superimposed on the short-wavelength shoulder of the plagioclase absorption. A weak, broad 2000 nm absorption is also visible in this sample. Sample 65315 shows similar effects due to pyroxene, although they are not as prominent as in 60015. Samples 60025 and 69955 both resemble “pure plagioclase” even in their bulk anorthosite form. These types of spectra are analogous to the pure plagioclase detections discussed in *Donaldson Hanna et al.* [In Review] for diverse locations throughout the lunar crust in M³ data. We note that the spectrum of 69955 does not show clear evidence for maskelynite, reported in this sample by *McGee* [1993], which in its pristine form is identifiable by absorption bands near 1000 and 2000 nm (Figure 6). The absence of glass bands in this spectrum could indicate that the particular split obtained from JSC contained less maskelynite than the split studied by *McGee* [1993]. Alternatively, if the maskelynite has been highly fractured by shock metamorphism, the near-infrared feature may have been substantially subdued by enhanced internal scattering.

We note that the presence of well-developed, prominent ~1250 nm absorptions in all four lunar anorthosite spectra is perhaps striking given that all have experienced some level of shock metamorphism. This observation suggests that while the plagioclase absorption may be more easily diminished by shock than mafic minerals, the feature is often times preserved. Indeed, the recent observations of numerous “crystalline” plagioclase exposures, namely spectra that display prominent ~1250 nm absorptions, on the Moon’s surface support this conclusion [e.g. *Ohtake et al.*, 2009; *Donaldson Hanna et al.*, In Review; *Yamamoto et al.*, 2012].

Figure 17b shows the bulk anorthosite samples sieved to 45-75 μm . The removal of the larger particles in 60015 increased the albedo of its spectrum to more closely match those of the other anorthosites. The pyroxene signature is slightly stronger in the 45-75 μm splits for 60015 and 65315. This could be due to the removal of potentially plagioclase-dominated finer particles [e.g., *Cintala and Hörz, 1992*], or may indicate that the mafic component commonly occurs with a particle size within the range of 45-75 μm . Alternatively, this enhancement of the mafic signature may reflect heterogeneity in the bulk sample: in order to fill the same sized sample dish with the 45-75 μm split as the bulk split, some bulk sample that was not measured in Figure 17a was incorporated into the sieving process. Figure 17c shows the spectra of a portion of the 45-75 μm split from which most of the visible non-plagioclase components were removed. Clearly, the process of “purification” did not remove the mafic component, rather the pyroxene absorptions were enhanced in these splits for 60015 and 65315. This likely reflects heterogeneity in the 45-75 μm split, and emphasizes the high sensitivity of plagioclase-dominated spectra to small amounts of mafic minerals [Chapter 2]. Further, the attempt to purify the samples was directed primarily at removing discrete non-plagioclase phases; plagioclase grains with small inclusions were more challenging to identify and therefore were not fully removed. This implies that much of the mafic signature in the bulk anorthosite spectra for samples 65315 and 60015 may derive from small inclusions within plagioclase crystals. For the remainder of this paper, we focus on characterizing the spectra of the bulk 45-75 μm split, those spectra in Figure 17b for which no “purification” attempt was made.

The four lunar anorthosite spectra are shown in Figure 18 with spectra of plagioclase separates from lunar basalts that were obtained from the RELAB database. We note that the samples in this plot do not represent the same particle size fractions. For lunar samples, the limited quantities typically prohibit measurement of many different particle size fractions, so comparisons must often be made without the particle size variable strictly controlled. In this case, the basaltic plagioclase spectra represent a wider range of particle sizes, from 0-125 μm , than the anorthosites, which were constrained to 45-75 μm . We anticipate however that general comparisons of the absorption characteristics of each type of material are valid. In general, the basaltic plagioclases have a lower albedo than the anorthosites. Two of the plagioclase spectra, from 15058 and 70035, also display weak ~ 2000 nm absorptions. It is likely that these additional features represent a very minor pyroxene component, either as inclusions within plagioclase grains or as a few discrete grains that were not removed during sample preparation. The interpretation that the ~ 2000 nm absorptions are due to pyroxene rather than a second plagioclase crystal field absorption is supported by the fact that these two spectra also display a lower albedo and flattened short-wavelength shoulders of their plagioclase bands, possibly reflecting a minor pyroxene absorption near 1000 nm. Continuum-removed spectra, shown in Figure 18b, demonstrate that the depths of the plagioclase absorptions in the basaltic separates are greater than in the anorthositic samples. This is likely attributable to the higher iron content in the basaltic plagioclases (Table 5 and Figure 7).

6. Controls on Absorption Band Center and Depth

6.1 Approach

Variations in plagioclase An content and iron abundance are the major compositional parameters expected to control absorption band characteristics for plagioclase and anorthosite spectra [e.g., *Bell and Mao, 1973; Adams and Goullaud, 1978*]. Figures 19 and 20 describe how these two variables affect both the absorption band center and depth for the suite of terrestrial, synthetic, and lunar plagioclase and anorthosite. Plagioclase An content and total iron content were obtained from the electron microprobe data described above. Absorption band centers and depths were calculated by fitting a 5th order polynomial to each of the continuum-removed spectra in the interval from 900-1600 nm. Band centers correspond to the wavelength of the minimum reflectance value of the polynomial, which is less influenced by small-scale instrumental noise than the measured continuum-removed spectrum. Absorption depths were calculated by subtracting the minimum reflectance value from one. The band centers and depths calculated for each spectrum are given in Table 1. It is important to note that for the one bulk anorthosite sample included in the band parameter analysis, the band center and depth were calculated for spectra of the bulk particulate sample, whereas the An content and iron abundance were calculated for electron microprobe spot analyses of plagioclase grains.

6.2 Band Depth

Variation in the ~1250 nm band depth is plotted as a function of both total iron abundance and An content in Figure 19. Based on crystal field theory [*Burns, 1993*], the band depth of a crystal field absorption should be strongly related to the abundance of the absorbing species (FeO in this case). A positive correlation between the ~1250 nm band depth and total iron is indeed observed in the synthetic plagioclase samples in Figure 19a, which were designed specifically to isolate this effect. Although there is considerable

scatter in the iron abundance for the highest-FeO samples in particular, an increase in plagioclase FeO from 0 to ~0.7 wt% FeO corresponds to a total increase in band depth, at the reflectance minimum for the principle band, of ~90%. However, it is important to note that an overlapping absorption due to the glass phase identified in the microprobe data for these samples is likely contributing to this band depth measurement. This is expected particularly because of the enhanced iron abundance in the interstitial glass phase relative to the plagioclase.

The lunar sample data also show an increase in band depth with iron content. The data are clustered, however, due to the large difference in iron abundance between the basaltic and anorthositic samples. Within each compositional grouping, there is some scatter in absorption depth. This is particularly interesting for the anorthositic samples, which vary overall by a factor of two in band depth while their iron abundances are all within 0.1 wt%. Comparison of the lunar data and the synthetic data shows that the lunar anorthosite spectra in particular reach greater band depths for a given iron abundance. The terrestrial samples are scattered to lower band depths than the lunar or synthetic samples, which is likely a function of the variable amounts of ferric iron contained in terrestrial plagioclases. Ferric iron contributes substantially to the total iron abundance measured by electron microprobe for terrestrial samples, but will not affect the strength of the ~1250 nm absorption because their electron configurations prohibit abundant spin-allowed transitions [e.g., Burns, 1999]. Analyses of samples SS, 1382a, and GemLabr1-12 by Mössbauer spectroscopy suggests that between ~30 and 50% of the total iron in these samples is trivalent. Re-evaluating the band depths of these three examples in terms of estimated divalent iron shows a trend similar to that seen in the lunar and synthetic

samples in which total iron more closely approximates Fe^{2+} abundance (Figure 19b).

There are no obvious differences between the plutonic and volcanic terrestrial samples in terms of the relationship between band depth and iron abundance.

The depth of the plagioclase ~ 1250 nm band is plotted as a function of An content in Figure 19c. The An content of plagioclase should only affect the ~ 1250 nm absorption depth insofar as it controls the proportion of iron atoms in the site which gives rise to the major transition. The data for the lunar samples as well as the synthetic plagioclases lack noticeable trends, although both of these datasets occupy a very restricted range of An contents (between An86 and An96). We expect that the large range in band depths that corresponds to only small variations in An content is reflecting differences in iron content among the different samples. The terrestrial samples display a wide scatter in both An content and band depth, but do not show any obvious relationship.

6.3 Band Center

The relationship between the An content of plagioclase and the band center position in plagioclase or anorthosite spectra is illustrated in Figure 20a. The four terrestrial volcanic samples generally follow the trend observed by AG78, which is characterized by a general increase in band center with An content, until a maximum of ~ 1310 nm at $\sim \text{An}65$. This increase in band center is followed by a decrease between An65 and An100. The rest of our terrestrial data are concentrated in the labradorite (An50-An70) – bytownite (An70-An90) compositional range, and generally overlap with the AG78 data and have band centers between 1270-1315 nm. Both the anorthite (Miyake-jima) and the andesine (Q5) have slightly short-wavelength centers: 1255 and 1200 nm, respectively. The lunar data in Figure 20a are distinguishable in terms of An content based on whether the samples are basaltic or anorthositic in origin. However, the

band centers for the two classes of samples overlap. While the basaltic plagioclases cluster in terms of both An content and band center, the lunar anorthosite samples show a range from 1245 to 1285 nm. This variation in band center is not correlated with the presence or absence of mafic signatures in the bulk anorthosite spectra. The synthetic samples are clearly offset to lower band center values than terrestrial or lunar samples with similar An contents. Although the synthetics exhibit a wide range in band centers, from 1175 to 1225 nm, they vary only slightly in An content (2 mol% anorthite). From Figure 20b it appears that some of this variation for the synthetic samples is correlated with iron abundance: an increase in total iron in plagioclase from ~0 to nearly 0.7 wt% corresponds to a regular decrease in band center of nearly 50 nm. The exceedingly low abundance of iron atoms in the structure, compared with the major cations, likely does not alter the iron-bearing site sufficiently to produce this level of variation in average band center. Instead, we suggest that this decrease in band center is related to an increase in the depth of a glass absorption, between 1000 and 1100 nm, superimposed on the short-wavelength shoulder of the plagioclase ~1250 nm feature. As iron increases in the plagioclase component, so does it increase in the glass component that was measured by high-resolution electron microprobe (Table 4). The expected result is an increase in absorption strength on the short-wavelength shoulder of the main plagioclase band. The low volumetric proportion of the glass phase may prohibit a discrete ~1000 nm absorption to develop, however. This interpretation is supported by the fact that neither the terrestrial nor lunar samples display a relationship between total iron in plagioclase and plagioclase band center. Again, the lunar samples are separated from one another compositionally, with the volcanic plagioclases displaying higher iron abundances.

7. Discussion

7.1 Plagioclase 1250 nm Absorption Characteristics

There are many factors that may prevent development and preservation of a diagnostic absorption in plagioclase, such as very low iron abundance, shock metamorphism, the propensity to alteration, and contamination by strongly absorbing mafic minerals (Figure 3). However, the diverse samples analyzed here demonstrate that even small amounts of divalent iron situated in a regular, but poorly characterized site in crystalline plagioclase generate a prominent absorption feature that is repeatable across many samples. Lunar samples in particular reliably display the most prominent and well-preserved ~1250 nm bands, likely owing to the absence of terrestrial alteration. Samples of bulk anorthosites from both the Earth and Moon display spectra with similar characteristics as separates of “pure” plagioclase: some anorthosite bulk samples exhibit characteristics of plagioclase only, while others resemble plagioclase plus small amounts of alteration or mafic minerals (Figures 3 and 9). Both anorthosite and “pure” plagioclase may sometimes lack crystal field absorptions altogether, particularly when plagioclase iron abundance is especially low (<0.1 wt%). The wide range of laboratory measurements presented here emphasize that plagioclases and plagioclase-dominated rocks are sometimes indistinguishable when viewed with near-infrared spectroscopy.

We have demonstrated that the depth of the primary plagioclase absorption feature, situated near 1250 nm, is highly dependent on the abundance of ferrous iron contained in plagioclase, in support of the observations by *Bell and Mao* [1973]. This relationship is clearly demonstrated in the synthetic plagioclases produced in this study, and to some extent in the lunar plagioclase and anorthosites. In contrast, we interpret the

high degree of scatter in the ~1250 nm band depths of terrestrial samples as resulting largely from the relative amounts of divalent and trivalent iron in the plagioclase.

The terrestrial samples analyzed here, which cluster in the labradorite and bytownite compositional ranges, exhibit relatively long band centers, between 1270 and 1315 nm, consistent with the data from *AG78*. The variation (~50 nm) in band centers for samples with similar An contents emphasizes that even within a relatively narrow range of plagioclase compositions other factors may also be exerting some control on crystal structure and absorption band center. We note that the short band center for sample Q5, near 1200 nm, is well outside the scatter for the other terrestrial samples and suggest that this may be due to its low An content (An₃₄). Although band centers approaching 1200 nm can apparently also result from very anorthitic compositions (e.g., Figure 20a), if the band center is strongly controlled by An number, as suggested particularly by sample Q5, then high-resolution spacecraft data [e.g., *Green et al.*, 2011] may be able to broadly distinguish highly albitic samples from other compositions. This is an important capability that may be useful as independent verification for remote thermal infrared measurements of the Moon that are highly sensitive to plagioclase An content [e.g., *Donaldson Hanna et al.*, In Review].

7.2 Origin of the ~2000 nm Absorption

Although transmission spectra of oriented plagioclase crystals commonly exhibit a second absorption at long wavelengths [e.g., *Hofmeister and Rossman*, 1984], this feature is generally not strong enough to be observable in reflectance data. Thus, the 2000 nm absorption in the synthetic plagioclase samples presented in Figure 15 is somewhat unexpected if its origin is due to the plagioclase component of the samples. The high temperatures and relatively fast cooling rates in preparation of these samples may

preserve a higher degree of disorder in the plagioclase structure, possibly leading to a wider range of coordination environments for ferrous iron atoms and thus stronger absorptions at wavelengths other than ~1250 nm. However, we suggest that the interstitial glass phase observable in BSE images for these samples (Figures 12 and 13) may be contributing significantly to enhancing both the width of the ~1250 nm absorption and the strength of the ~2000 nm feature. Silicate glasses are known to display at least two broad absorption bands in the near-infrared, one near 1000 and one near 2000 nm, attributable to Fe^{2+} in pseudo-octahedral and tetrahedral coordination, respectively [e.g. *Mao et al.*, 1973, *Bell et al.*, 1976]. The shorter wavelength absorption near 1000 nm is typically several times stronger than the ~2000 nm absorption. Both glass absorptions are evident in the spectrum of the starting composition for the synthetic plagioclase experiments, shown in Figure 4, but were observed to change substantially during sintering to more closely reflect pure plagioclase spectra in which the main absorption is near 1250 nm.

Heat treatment of one of the terrestrial plagioclases with small amounts of alteration discussed in this study, from Split Rock, offers additional perspective on the relative contributions of plagioclase and glass on bulk experimental samples. A portion of the Split Rock sample was heated at 1300 °C for 90 hours under reducing conditions, near the IW buffer. Significant “melt” textures are observed in BSE images of the resulting sample (Figure 21), that may be similar in composition to the unreacted glasses apparent in the sintered iron series. However, there are key differences between the spectral properties of the heat-treated natural sample and the sintered plagioclase samples. For example, while the main absorption near 1200 nm in NIR spectra of the

sintered plagioclase series is broader and positioned at a shorter wavelength than the terrestrial or lunar plagioclases (Figure 15), it is still clearly dominated by a plagioclase absorption rather than a glass absorption (Figure 5). Near-infrared spectra of the experimentally treated Split Rock sample, however, are more dominated by a glass component, as evidenced by the very short-wavelength center position, near 1100 nm, of the main absorption feature (Figure 22a). However, we note that this feature near 1100 nm is not strictly analogous to a pure glass (c.f. Figure 5), and appears to still represent a combination of glass and plagioclase absorption bands in this spectral region.

We expect that the Split Rock sample may have undergone partial melting because of its intermediate An content and the presence of additional phases such as potassium-feldspar suggest a lower melting temperature. Importantly, the MIR spectra of this sample primarily reflect a feldspar structure with well-developed Reststrahlen bands between 8-12 μm (Figure 22). This example illustrates the high sensitivity of the NIR region to the abundance and coordination environment of ferrous iron. Both the sintered plagioclase series and the Split Rock heat-treated sample exhibit spectra indicative of the feldspar structure at MIR wavelengths. However, partial melting leading to higher proportions of iron in the glass of the Split Rock sample result in NIR spectral properties that are more dominated by a ferrous glass. Further, this comparison suggests that the spectra of the iron series of synthetic plagioclases likely represent a combination of plagioclase and glass spectral features resulting in the broader than expected absorption centered near ~ 1200 nm as well as the relatively strong ~ 2000 nm absorption. Nevertheless, the sintering process for this series clearly produced a substantial amount of crystalline feldspar, as evidenced by the microprobe analyses, the NIR spectra

exhibiting the main plagioclase absorption band near 1250 nm (rather than the original ~1000 nm glass band), and the MIR spectra dominated by feldspar Reststrahlen bands (Figure 16).

8. Conclusions

Plagioclase feldspars commonly display a prominent near-infrared absorption centered near 1250 nm. The depth of this absorption is related to the abundance of trace amounts of FeO within the plagioclase: greater amounts of divalent iron correspond to deeper absorption bands for terrestrial, lunar, and synthetic plagioclase. Band centers may be controlled to some extent by the An content of plagioclase, consistent with a trend observed by *Adams and Goullaud* [1978]. Specifically, band centers are longest for labradorites and bytownites, although the considerable scatter within this compositional range suggests that additional factors should be taken into account. The ranges of band depths and band centers for lunar and terrestrial plagioclases overlap substantially. The lunar samples investigated here are compositionally distinguishable from one another based on whether they are from plutonic (anorthosite) or volcanic (basalt) sources.

The results of this study indicate that, for plagioclases formed under reducing conditions, only ~0.1 wt% total iron is necessary to generate the diagnostic ~1250 nm absorption band. Further, although the effects of minor mafic components are observable in spectra of lunar anorthosite bulk samples, the plagioclase absorption is also clearly an important, if not dominant, component of the bulk spectrum. The spectral characteristics of terrestrial plagioclases are more easily confounded by additional factors, such as the influence of ferric iron and the propensity to alter to clays. In locations on the lunar surface where the primary crust of the Moon is exposed, crystalline plagioclase should be

readily identifiable by modern spectrometers. In such locations, the ~1250 nm plagioclase feature is expected to be rather uniform, as long as the plagioclases are highly calcic, as is observed in the lunar sample collection.

Acknowledgements: We are grateful to Keith Milam and Darby Dyar for providing most of the terrestrial plagioclase separates used in this study. Thanks to Ralph Milliken for providing the sample of the Shawmere anorthosite. Thanks to Taki Hiroi for the BDR, FTIR, and transmittance measurements, and to Joe Devine, Joe Boesenberg, and Jim Eckert for assistance with electron microprobe analyses at various points. Reid Cooper provided the starting material for the synthetic plagioclases, and we are grateful for the use of the horizontal gas mixing furnaces in his lab. Reid and Stephen Parman also provided significant guidance for the experimental component of this project that is greatly appreciated. This research was supported through the NASA Lunar Science Institute (NNA09DB34A).

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Table 1. Electron Microprobe Analyses and Major Spectral Parameters for Terrestrial Plagioclase¹

Sample Name	5851	SS	Miyake-jima	GemLabr 1-12	Q5	BT-1	BT-13	BS-16	BS1
Source	Amelia Courthouse	Lake County, OR	Miyake-jima, Japan	Mexico	Quizapu Volcano	Bushveld Main Zone	Bushveld Main Zone	Bushveld Main Zone	Bushveld Main Zone
Provenance	Pegmatitic dike	Volcanic	Volcanic megacrysts	Volcanic	Volcanic	Gabbro-norite	Gabbro-norite	Gabbro-norite	Gabbro-norite
n	18	18	65	123	15	18	18	--	15
Na₂O	9.80	3.55	0.49	4.53	6.75	3.51	3.12	4.25	3.99
MgO	0.00	0.14	0.08	0.11	0.00	0.02	0.01	n/a	-0.01
Al₂O₃	21.98	30.92	35.67	30.11	25.40	31.29	31.74	28.74	27.94
SiO₂	69.08	51.35	44.23	52.94	60.04	51.85	50.88	53.43	55.15
K₂O	0.10	0.12	0.00	0.28	0.55	0.20	0.21	0.33	2.20
CaO	0.13	13.52	19.22	12.19	6.81	13.55	14.26	11.54	10.06
TiO₂	0.00	0.04	0.00	0.07	0.02	0.02	0.02	n/a	0.04
MnO	0.00	0.01	n/a	n/a	0.00	0.00	0.00	n/a	0.00
FeO(T)	0.00	0.42	0.47	0.35	0.31	0.18	0.31	0.19	0.45
Total	101.08	100.07	100.16	100.58	99.89	100.63	100.56	98.48	99.82
An	1	67	96	59	35	67	71	60	50
Cations per 8 O	4.89	5.00	5.01	5.01	4.96	4.99	4.99	5.00	4.99
2 s.d. FeO(T)	0.02	0.02	0.09	0.03	0.08	0.05	0.06	--	0.84
2 s.d. An	2.09	0.82	1.30	2.02	9.99	3.00	7.82	--	42.41
Band Center (nm)	n/a	1285	1255	1270	1200	n/a	1285	1275	n/a
Band Depth	n/a	0.18	0.10	0.14	0.11	n/a	0.09	0.06	n/a

¹Electron microprobe analyses acquired at Brown University (with the exception of BS-16; *Lundgaard et al.*, 2006). Band center and Band depth parameters calculated only for those spectra displaying strong ~1250 nm absorptions (45-125 µm particle size fraction).

Table 1 Continued. Electron Microprobe Analyses and Major Spectral Parameters for Terrestrial Plagioclase¹

Sample Name	0022b	4512A-L	1382a	Split Rock	Split Rock Annealed	Stillwater An II	Stillwater Banded Ser.	St. Urbain	Shawmere
Source	Tupper Lake, NY, USA	Nain, Labrador, CA	Crystal Bay, MN, USA	Split Rock, MN, USA	Split Rock, MN, USA	Stillwater Complex	Stillwater Complex	St. Urbain, Quebec	Ontario, CA
Provenance	Anorthosite ?	Anorthosite (Igneous Complex)	Anorthosite	Anorthosite	Anorthosite	Anorthosite (Igneous Complex)	Anorthosite (Igneous Complex)	Anorthosite (Massif)	Anorthosite
	17	18	18	8	12	10	11	6	12
Na₂O	5.40	4.73	2.72	2.69	1.39	3.07	2.38	6.90	2.72
MgO	0.00	0.00	0.12	0.10	2.75	0.01	0.05	0.01	0.00
Al₂O₃	28.30	28.82	31.98	32.55	31.18	32.34	33.11	26.90	33.28
SiO₂	56.20	54.98	49.82	48.68	47.96	49.09	47.66	57.63	48.13
K₂O	0.36	0.38	0.12	0.08	0.08	0.09	0.06	0.46	0.02
CaO	9.83	10.94	14.97	15.45	15.02	15.17	16.27	8.41	15.80
TiO₂	0.00	0.01	0.04	0.04	0.05	0.02	0.03	0.01	0.00
MnO	0.00	0.00	0.01	n/a	n/a	n/a	n/a	n/a	n/a
FeO(T)	0.10	0.28	0.47	0.39	0.32	0.42	0.52	0.13	0.07
Total	100.18	100.15	100.25	99.97	98.75	100.23	100.07	100.45	100.02
An	49	55	75	76	84	73	79	39	76
Cations per 8 O	4.98	4.98	4.99	5.01	5.00	5.02	5.02	5.03	5.02
2 s.d. FeO(T)	0.03	0.03	0.11	0.06	0.33	0.08	0.04	0.04	0.11
2 s.d. An	3.06	1.00	7.86	1.37	6.26	4.13	2.54	1.33	1.79
Band Center (nm)	n/a	1315	1290	1270	1105	1190	1295	1270	n/a
Band Depth	n/a	0.24	0.19	0.11	0.19	0.07	0.31	0.03	n/a

¹Electron microprobe analyses acquired at Brown University (with the exception of BS-16; *Lundgaard et al.*, 2006). Band center and Band depth parameters calculated only for those spectra displaying strong ~1250 nm absorptions (45-125 µm particle size fraction).

Table 2. Electron microprobe analyses for synthetic glass starting compositions¹.

	PL11 Glass	PL12 Glass
<i>n</i>	50	20
Na₂O	1.52	1.51
Al₂O₃	35.56	35.34
SiO₂	46.94	46.30
K₂O	0.06	0.06
CaO	15.27	14.98
FeO(T)	0.04	0.96
Total	99.38	99.16
2 s.d. FeO(T)	0.05	0.13

¹Acquired at Brown University.

Table 3. Electron microprobe analyses for synthetic plagioclase¹.

	PL11b	PL13b	PL15b	PL16b	PL17b	PL18b	PL19b	PL20b	PL21b	PL12b
<i>n</i>	10	14	13	12	11	12	15	11	13	16
Na₂O	1.40	1.44	1.38	1.38	1.25	1.36	1.49	1.33	1.41	1.32
MgO	0.10	0.10	0.14	0.09	0.08	0.09	0.11	0.10	0.11	0.09
Al₂O₃	35.28	34.83	34.90	34.88	32.07	34.85	34.75	34.59	34.57	34.62
SiO₂	46.52	46.72	46.46	46.58	42.47	46.22	46.51	46.30	46.62	46.25
K₂O	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02
CaO	16.87	17.02	16.88	16.85	15.42	17.10	16.47	17.01	16.82	17.17
FeO(T)	0.04	0.09	0.23	0.32	0.31	0.36	0.56	0.60	0.67	0.59
Total	100.24	100.22	100.02	100.13	91.63	100.00	99.93	99.97	100.21	100.06
An	87	87	87	87	87	87	86	87	87	88
2 s.d. FeO(T)	0.02	0.02	0.09	0.08	0.12	0.07	0.37	0.18	0.49	0.33
2 s.d. An	2.02	3.58	2.92	1.78	3.14	1.86	3.45	2.32	3.82	2.96
Band Center (nm)	1205	1225	1225	1215	1210	1205	1200	1185	1185	1175
Band Depth	0.02	0.06	0.15	0.18	0.20	0.23	0.24	0.25	0.29	0.31

¹ Acquired at Brown University. Values reported are average compositions. Operating conditions were 15keV and 15nA. A focused beam was used due to the small grain size (commonly ~10 µm).

Table 4. Microprobe analyses of synthetic plagioclase versus glass component¹

	PL15b Plagioclase	PL15b Glass	PL21b Plagioclase	PL21b Glass	PL13b Al-Si Phase
<i>n</i>	3	16	4	3	1
Na₂O	1.29	0.97	1.42	1.01	0.42
MgO	0.11	0.85	0.10	1.35	0.32
Al₂O₃	33.96	20.03	34.86	25.16	52.16
SiO₂	49.69	71.23	46.77	58.01	43.87
K₂O	0.02	0.79	0.02	0.79	0.25
CaO	16.24	3.31	17.09	1.17	2.40
FeO(T)	0.20	2.61	0.46	15.74	0.29
Total	101.51	99.80	100.72	103.24	99.70
An	87.32	51.74	87	29.74	69.23
2 s.d. FeO(T)	0.15	1.03	0.21	2.33	--
2 s.d. An	1.26	20.05	2.29	15.60	--

¹Acquired using a Field Emission Electron Probe Microanalyzer at Yale University. All analyses were conducted with a focused beam, with the exception of the PL21b plagioclase analyses that were conducted with a 2µm beam. Operating conditions were 10 kV and 10 nA.

Table 5. Electron microprobe analyses of plagioclase from lunar samples

	69955, 65	60025, 885	65315, 153	60015, 801	15555, 965	15058, 276	70017, 535	70035, 188
	Anorthosite¹	Anorthosite¹	Anorthosite¹	Anorthosite¹	Basalt²	Basalt²	Basalt²	Basalt²
<i>n</i>	20	22	10	25	--	--	--	--
Na₂O	0.43	0.44	0.35	0.38	0.98	1.05	1.43	1.47
MgO	0.08	0.05	0.08	0.15	0.24	0.17	0.20	0.24
Al₂O₃	35.78	35.74	35.98	35.80	33.20	33.40	32.70	33.00
SiO₂	44.26	44.28	44.16	44.33	45.80	46.30	46.80	46.90
K₂O	0.01	0.01	0.00	0.01	0.03	0.05	0.06	0.06
CaO	19.24	19.18	19.49	19.32	18.10	18.00	17.30	17.30
TiO₂	0.01	0.01	0.01	0.01	---	---	---	---
FeO(T)	0.14	0.17	0.13	0.17	0.51	0.61	0.36	0.35
Total	99.95	99.87	100.22	100.17	98.86	99.70	98.90	99.32
An	96	96	97	96	91	90	87	86
2 s.d. FeO(T)	0.04	0.05	0.03	0.36	--	--	--	--
2 s.d. An	1.03	1.14	1.35	1.26	--	--	--	--
Band Center	1245	1285	1270	1245	1270	1280	1275	1280
Band Depth	0.15	0.18	0.19	0.12	0.44	0.36	0.36	0.35

¹Data acquired for this study at Brown University.

²Data acquired previously by Isaacson et al., 2011.

Figure Captions.

Figure 1. Four-membered tetrahedral rings, linked to form part of the feldspar framework. Tetrahedra contain Al and Si atoms, and the larger charge-balancing cations are held in the cavities formed among the rings. Image obtained from Krbetschek et al. [1997].

Figure 2. Figure 2. Example plagioclase spectra. Sample consists of a gem quality labradorite from Mexico and is used elsewhere in this study (Sample name GemLabr1-12). (a) Particulate sample (45-125 μm) loaded into a teflon-coated dish for reflectance measurement. The diameter of the sample surface is 3 mm. (b) Single crystal (4.2 mm thick) used for the transmission measurement, with a 1 inch sample box shown for scale. This crystal is the same material as the 12 crystals that were crushed together to generate the sample in part (a). (c) Bidirectional reflectance of the particulate sample from part (a) is shown with a dashed line. Transmittance through the crystal in part (b) is shown with a solid line. Both spectra were acquired in RELAB for this study.

Figure 3. Bidirectional reflectance spectra of particulate plagioclase samples that are not easily identifiable by a ~ 1250 nm absorption. 1) 5851, 2) BT1, 3) 0022b, 4) BS1. All samples have been sieved to 45-125 μm .

Figure 4. Total iron in each synthetic plagioclase sample. Black diamonds show the iron content of the starting glass for each sample, calculated based on the proportions of the high and low-iron glass endmembers that were combined to generate starting materials with a range of compositions. Colored symbols denote the microprobe data for plagioclase in the sintered run products. All good analyses are shown (Totals 98-102 wt%; Cations 4.97-5.03 per 8 oxygen). Microprobe data were obtained at Brown University using a Cameca SX500 electron microprobe (15 keV and 15 nA).

Figure 5. Example glassed starting material (approximately An90) containing nominally 0.3 wt% total iron, sieved to 45-125 μm . The center position of the absorption minimum is near 100 nm, shorter than typical plagioclase spectra.

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Figure 12. Backscattered electron image for sample PL11b, acquired at Brown University. Plagioclase grains are $\sim 5\text{-}10\ \mu\text{m}$ and appear medium grey. The glass phase occurs interstitial to the plagioclase and appears dark grey. The scale bar at bottom left is 20 μm .

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Figure 20. Compositional controls on band center estimation. (a) An content ($An = [Ca / (Na + Ca + K)]$) of plagioclase versus band center estimated by polynomial fitting to the plagioclase spectrum between 900 and 1600 nm, excluding any hydration absorptions between 1375 and 1430 nm. (b) Total iron in plagioclase versus band center estimation.

Figure 21. Backscattered electron image of Split Rock plagioclase following a reducing experimental run, acquired at Brown University. The pits are estimated to be similar in size (5-20 μm) to those in the BSE image in Figure 11. Textures are similar to those of the sintered plagioclases shown in Figure 11, although the melting appears to have been more thorough in this sample. Small, bright linear features are enriched in zirconium, the result of reaction with small amounts of the zirconium beads on which the sample was resting during the experiment. This reaction was not observed for the sintered plagioclase series.

Figure 22. Comparison of the Split Rock plagioclase sample before and after treating with similar experimental conditions as used for the synthetic plagioclase series (Experimental run: 1300° C, ~IW, 90 hours). The natural, untreated sample is shown in blue, whereas the experimentally treated sample is in black. (a) Near-infrared data, showing the prominent plagioclase absorption near ~1250 nm for the untreated sample, in addition to hydration bands near 1400 and 1900 nm, and turning down toward 3000 nm. Glass bands near 1000 and 2000 nm are present in the experimentally treated sample. (b) Mid-infrared data shown as 1-Reflectance for ease of comparison with emissivity data for plagioclase. The original natural sample displays a prominent water absorption near 3 μm (inverted here). The experimental sample is shown in black, and has slightly weaker Reststrahlen bands between 8-12 μm .

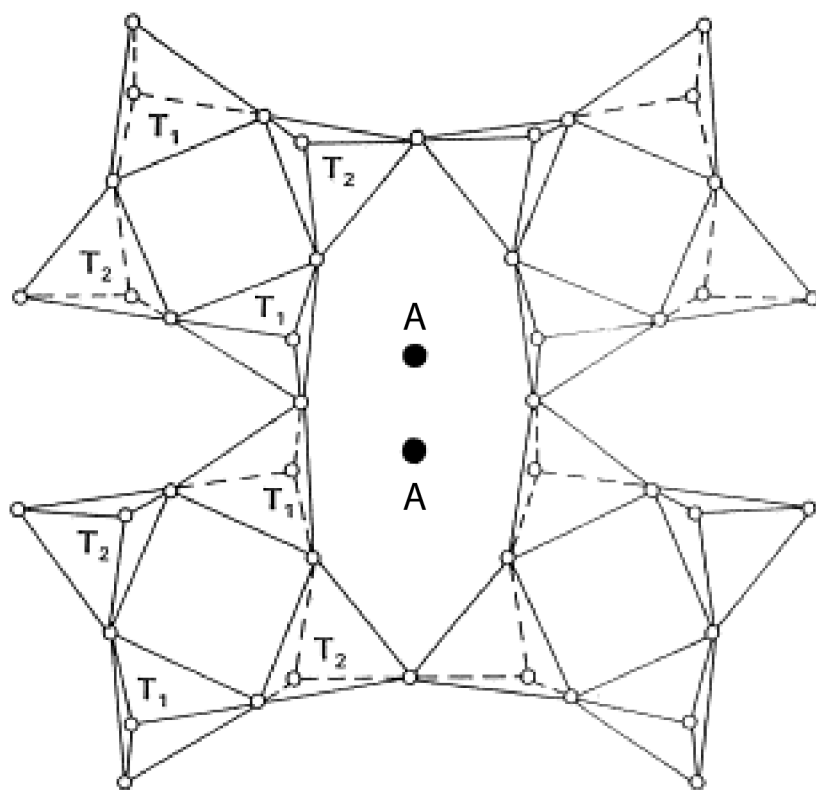


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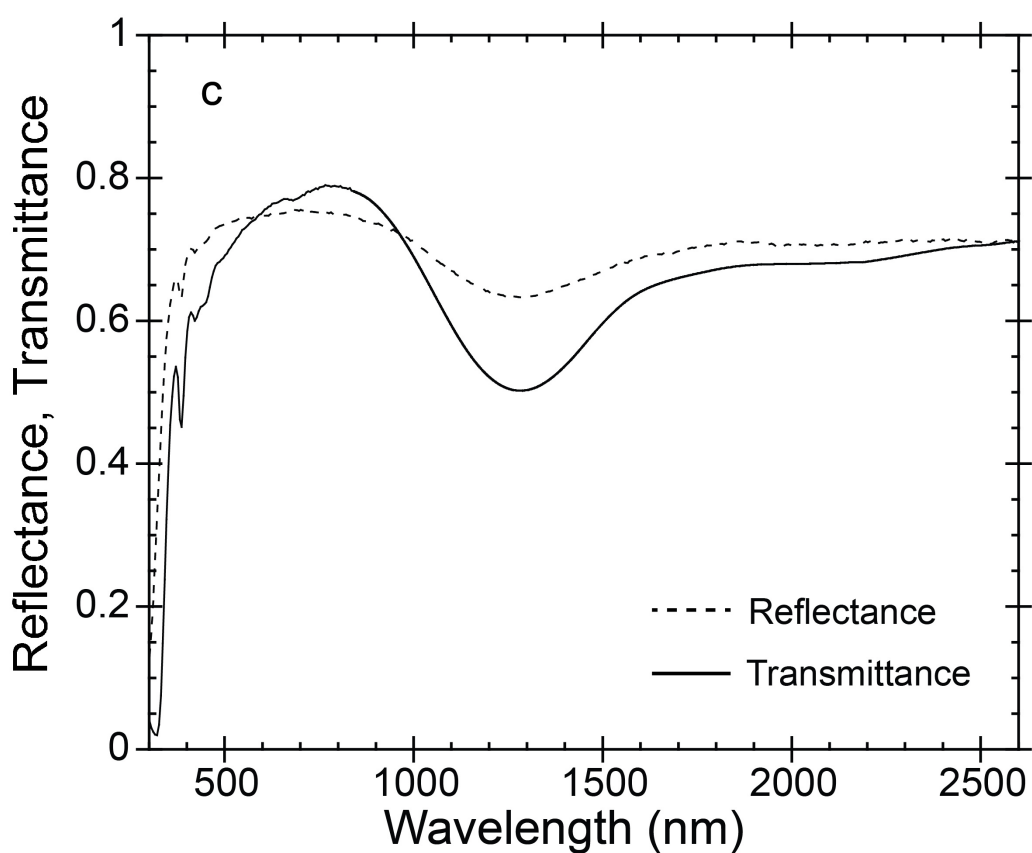
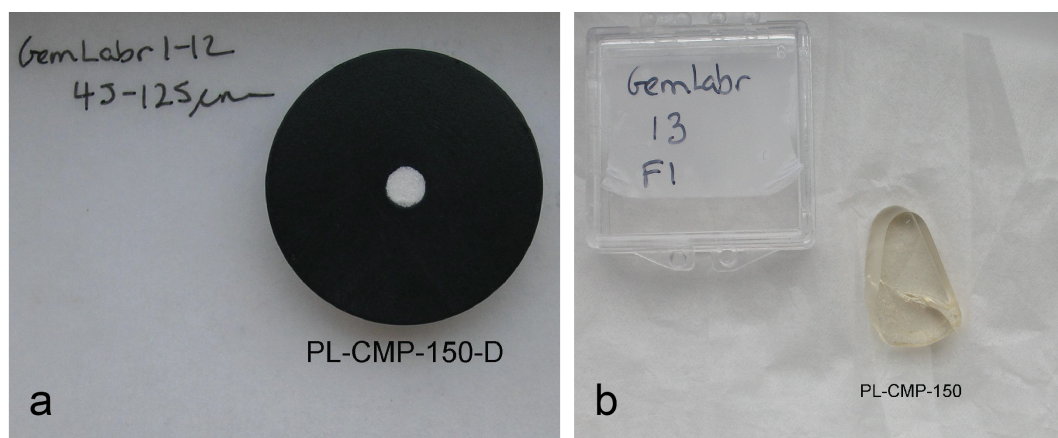


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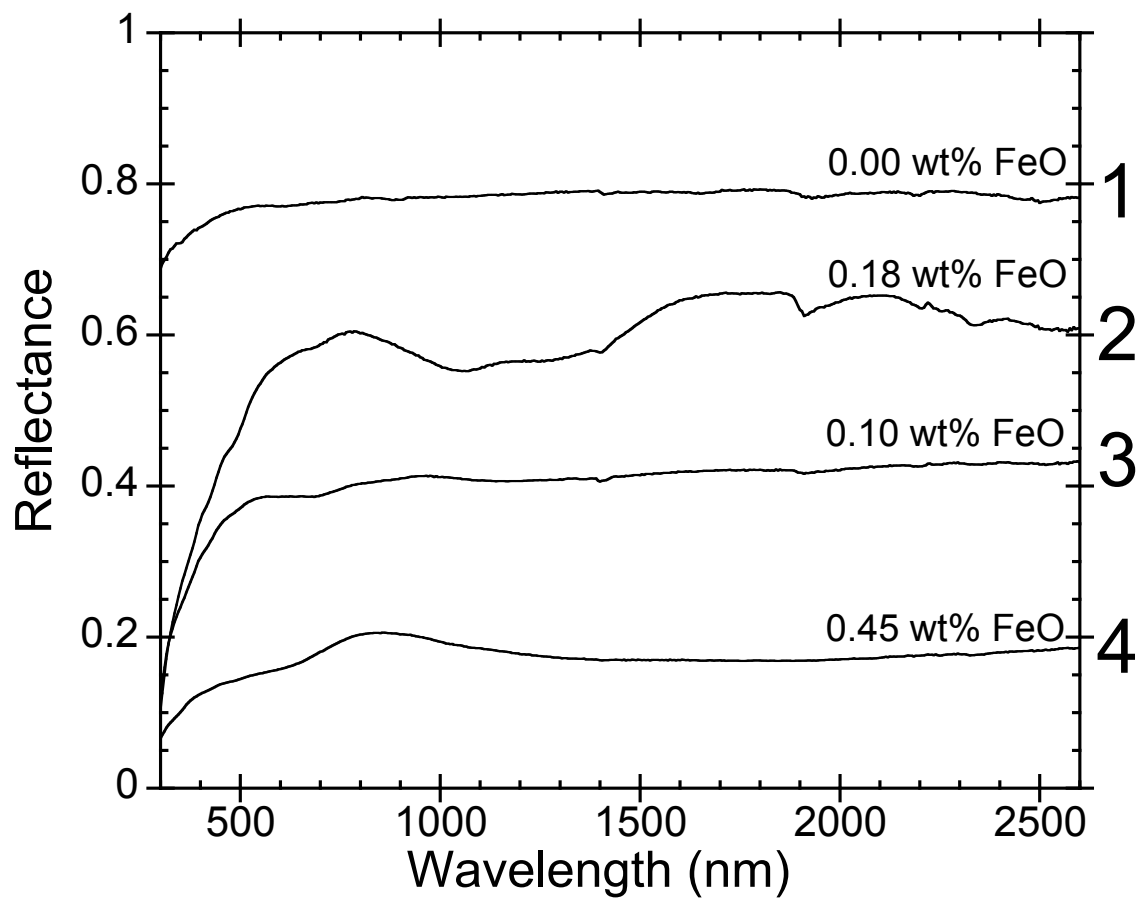


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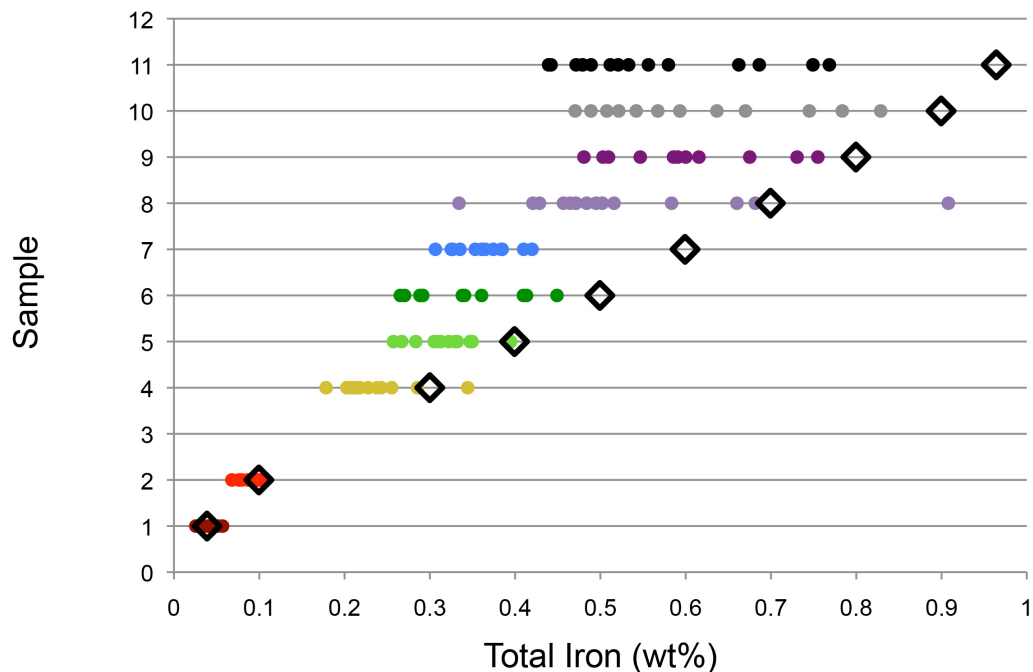


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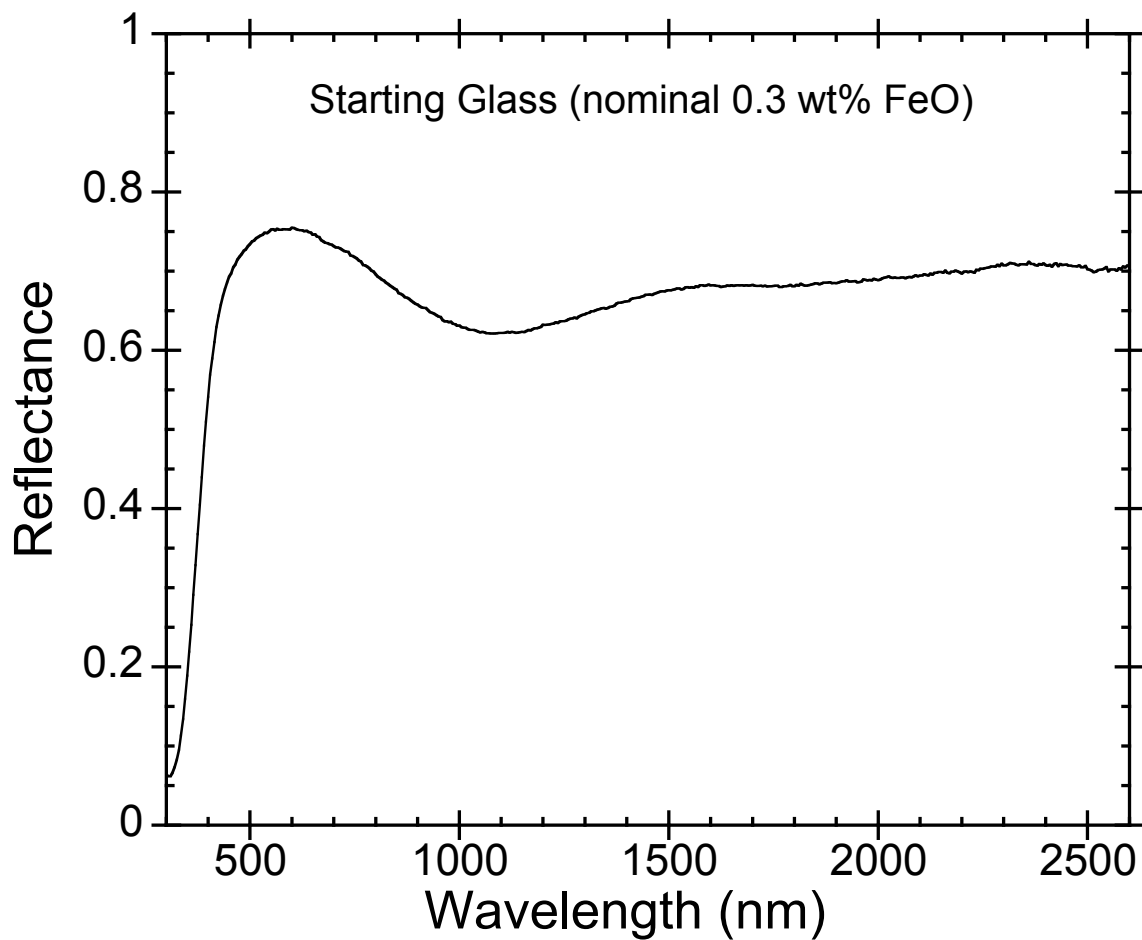


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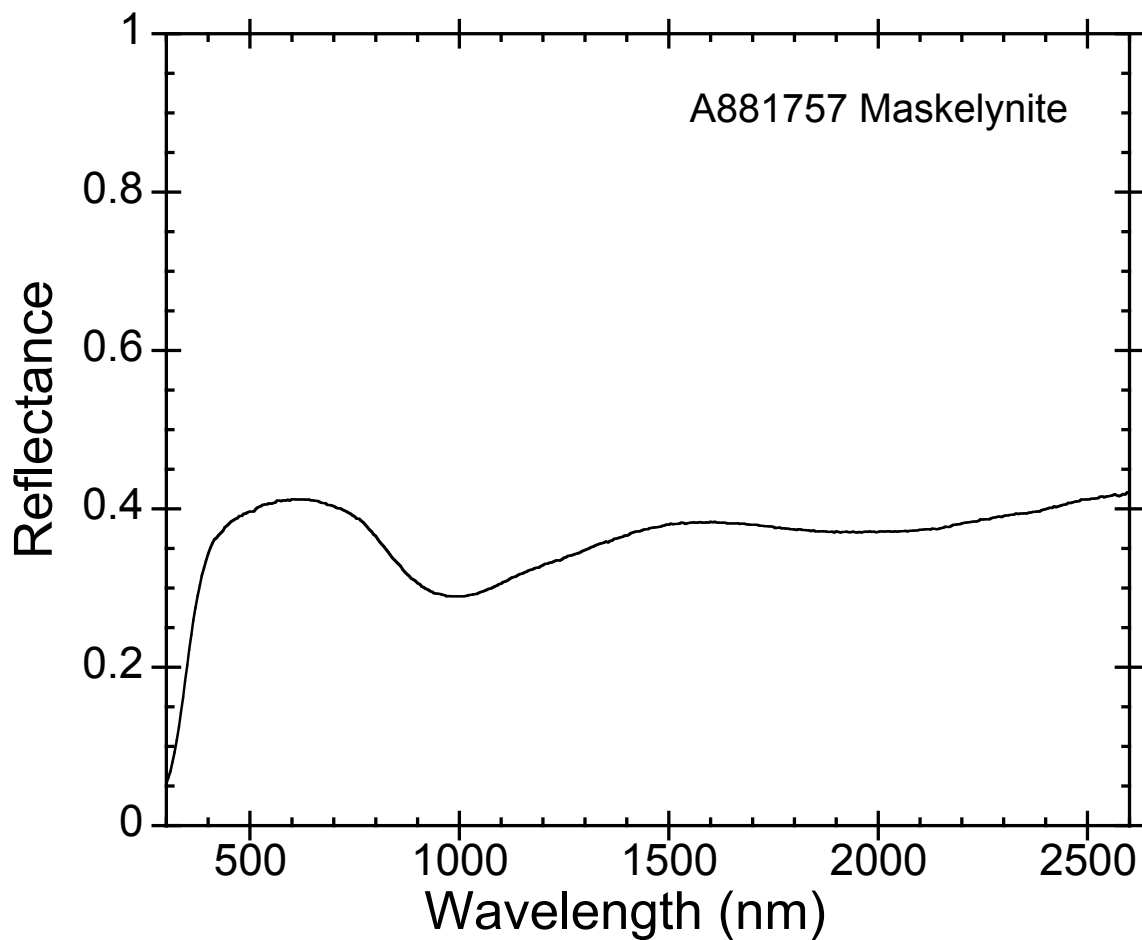


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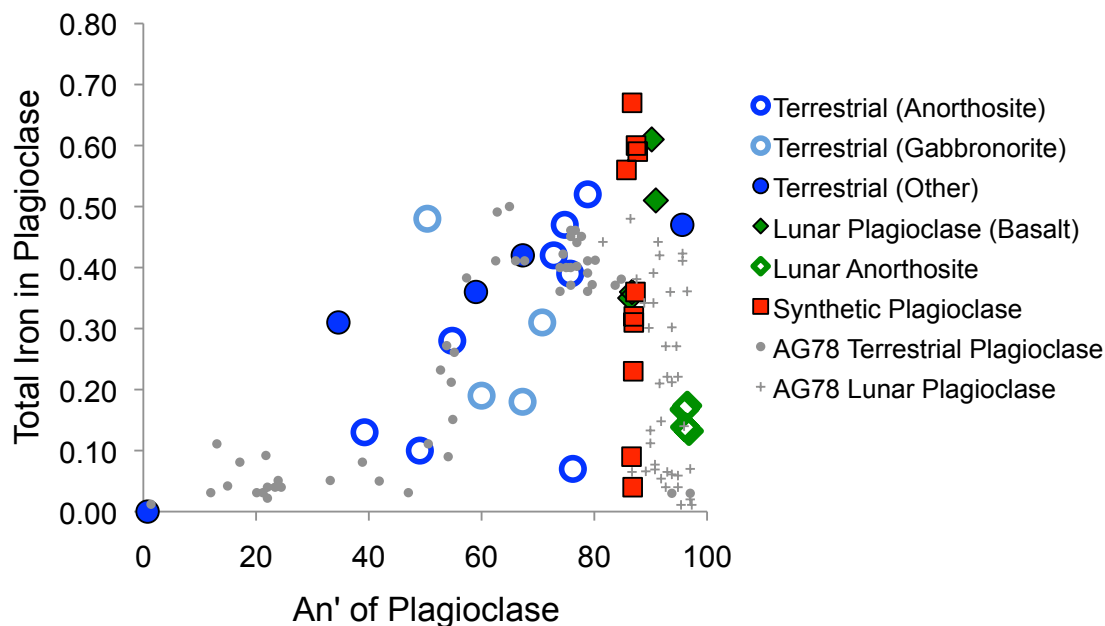


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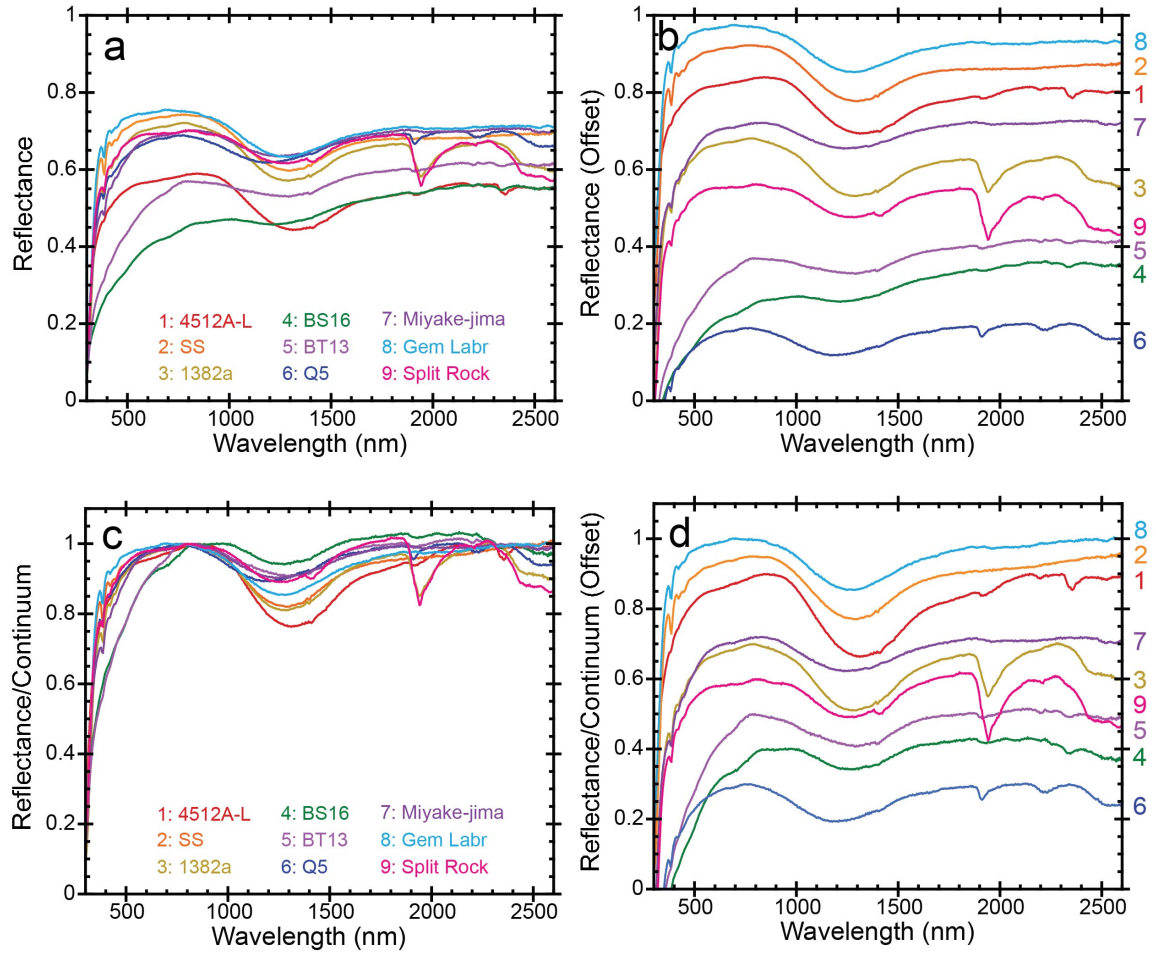


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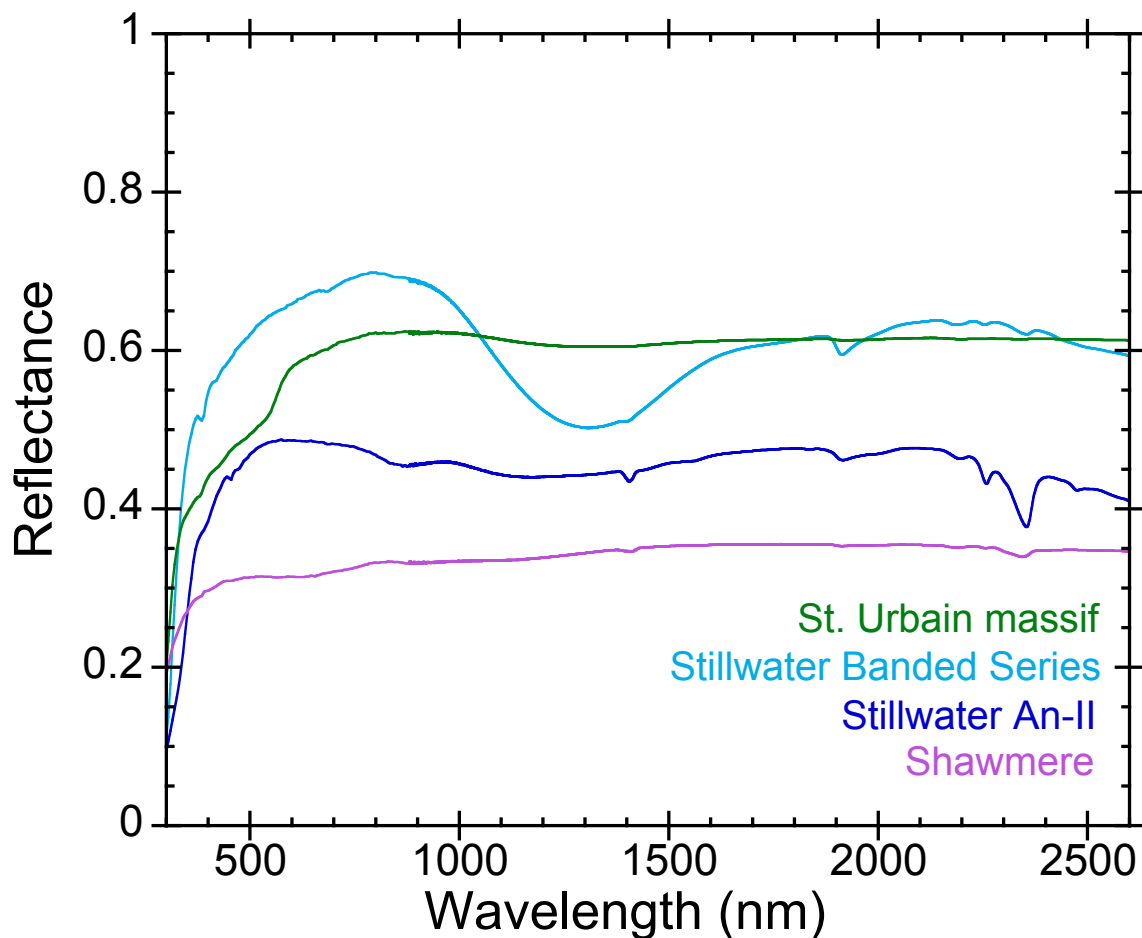


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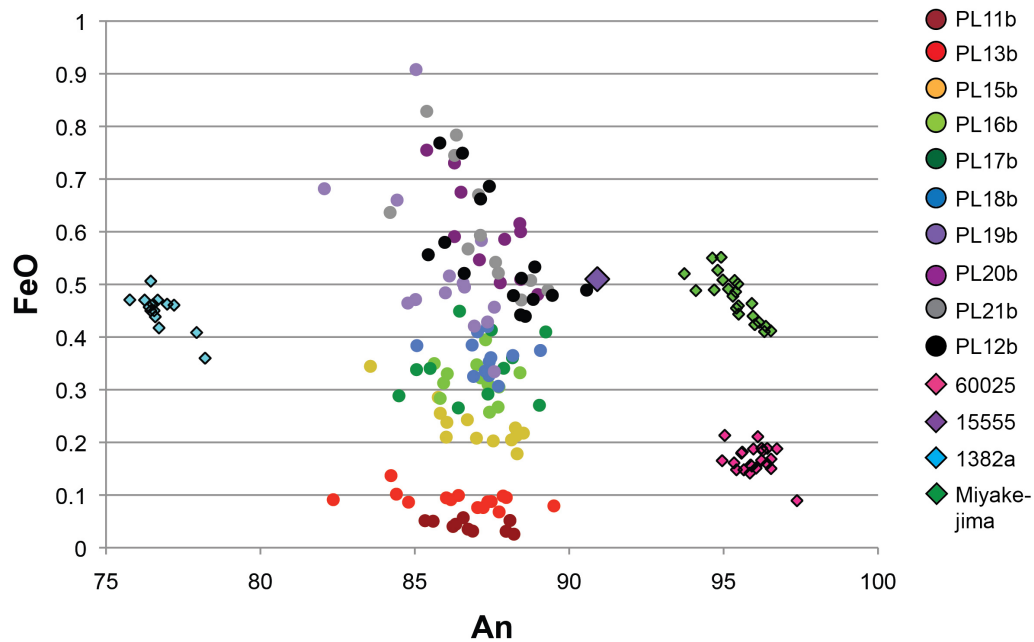


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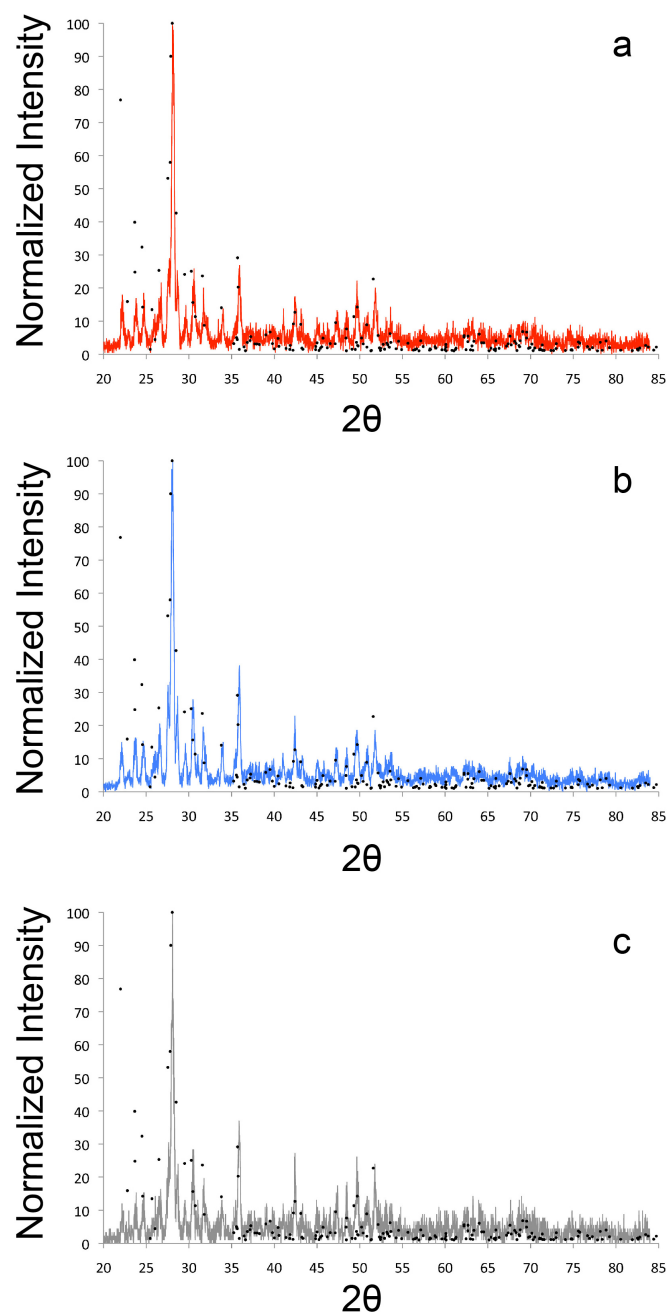


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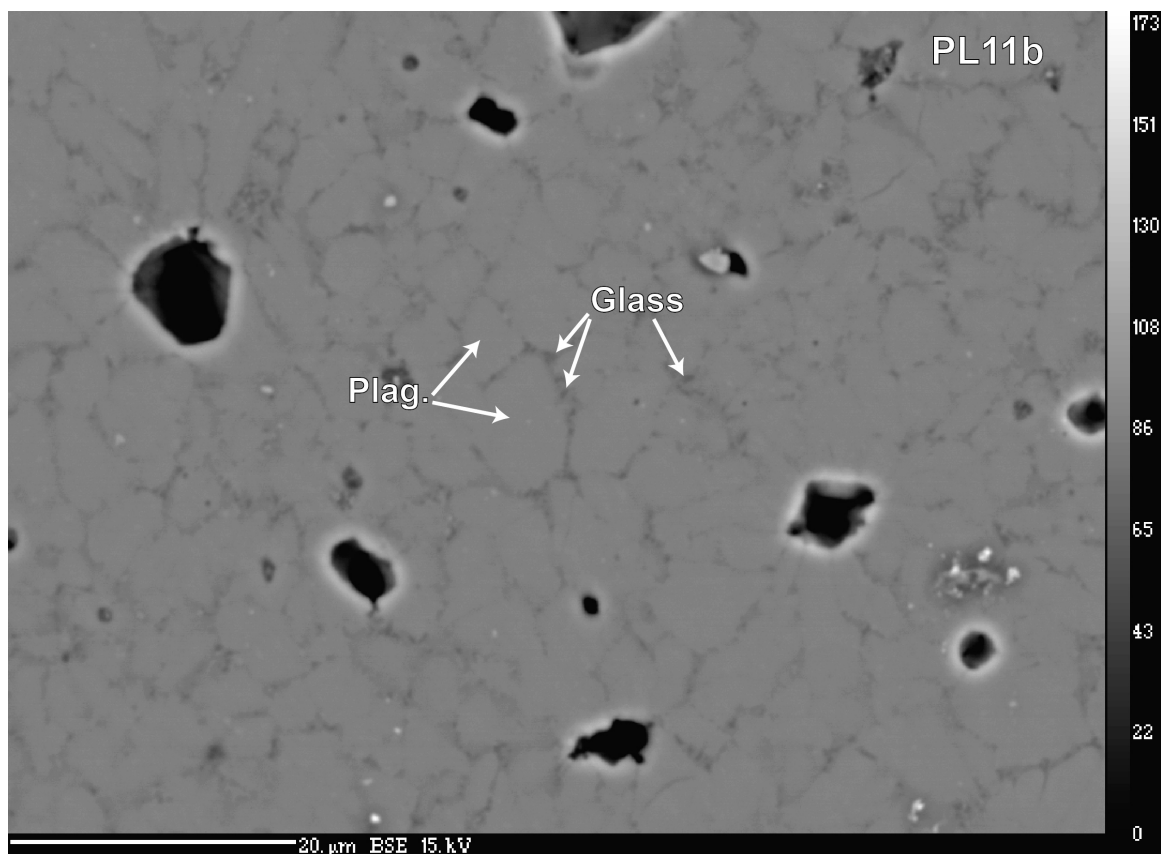


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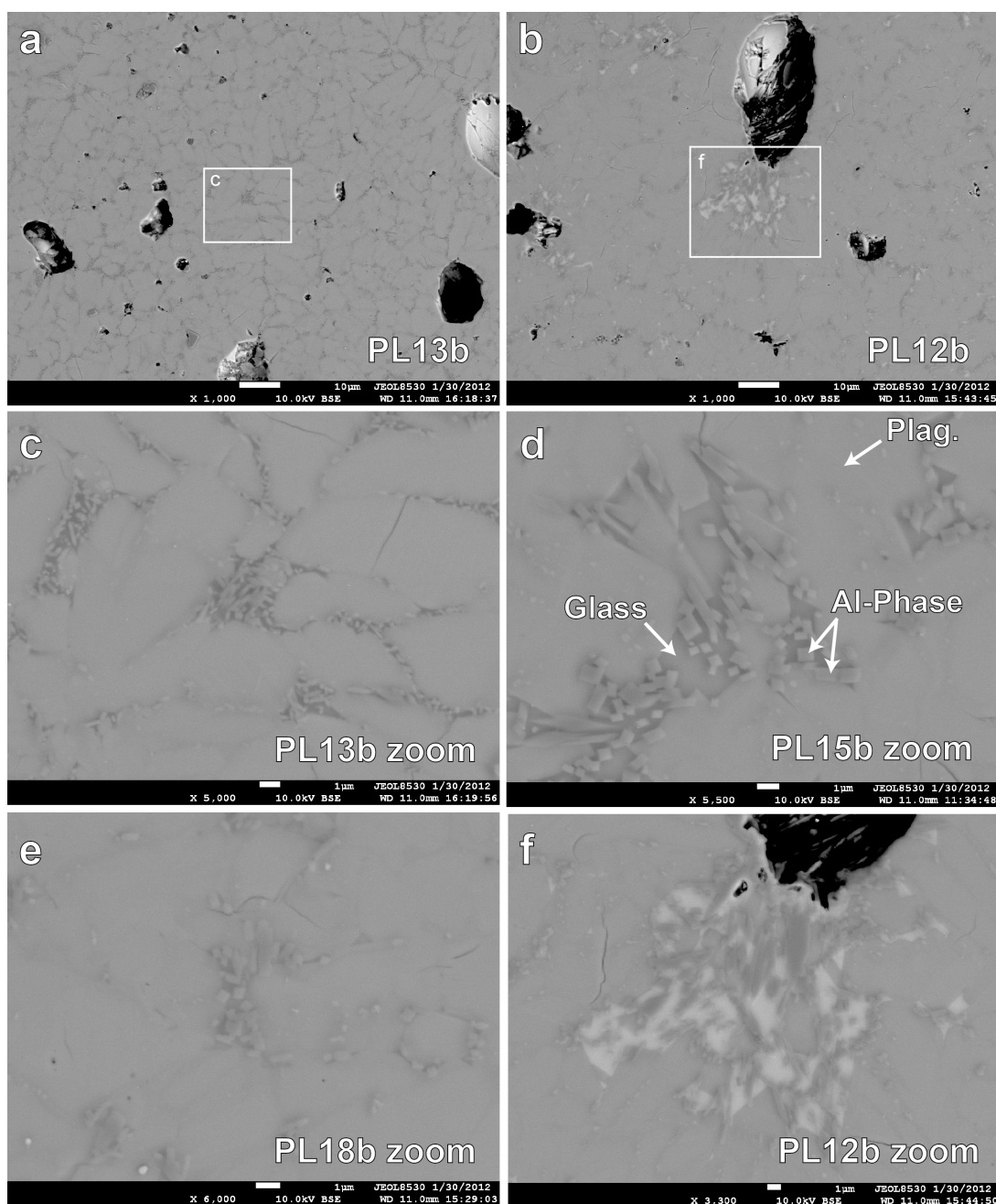


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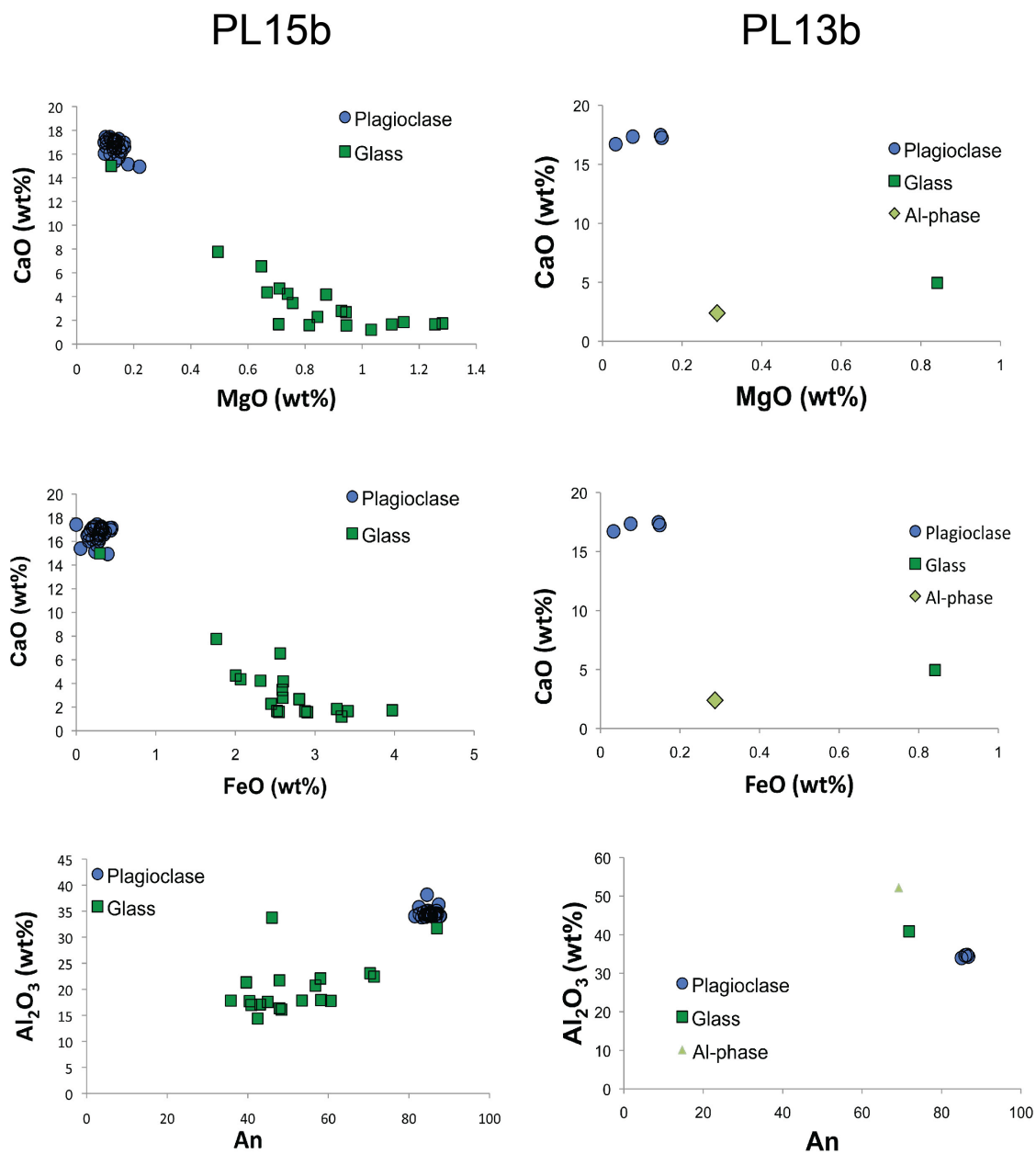


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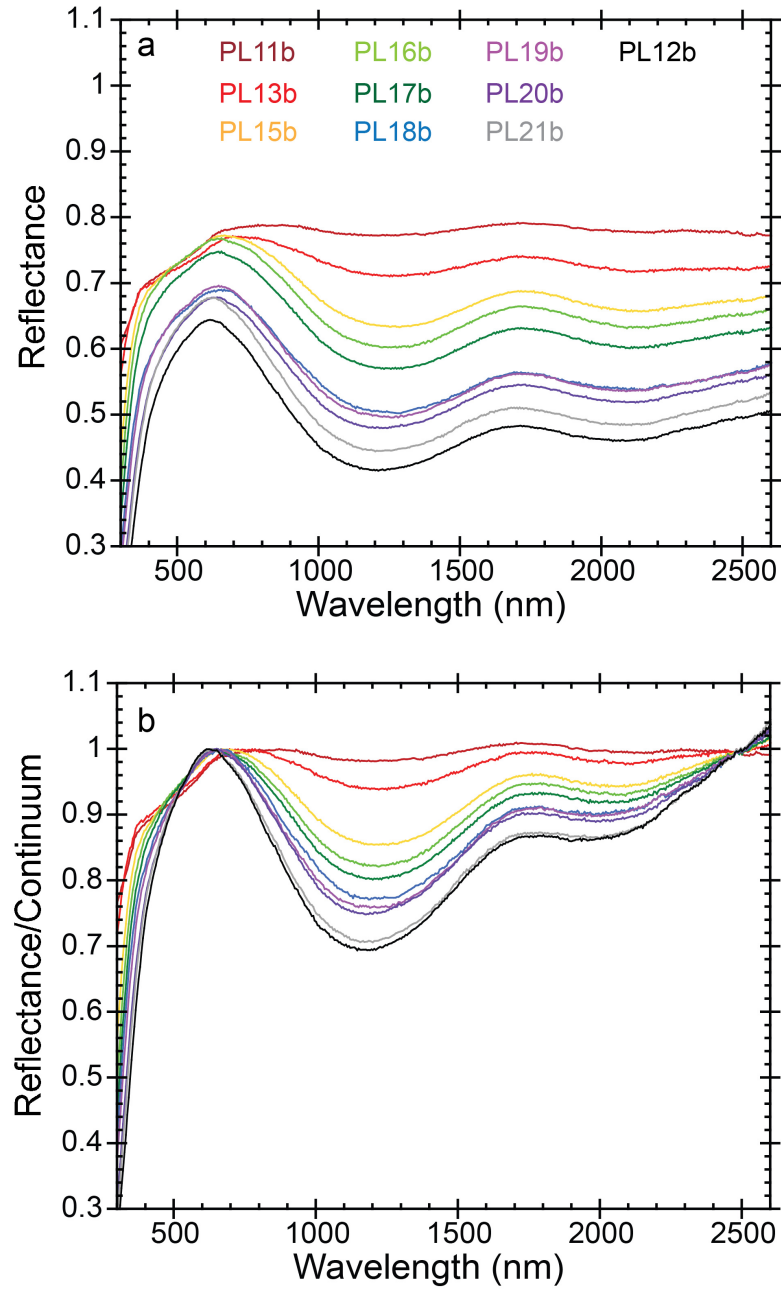


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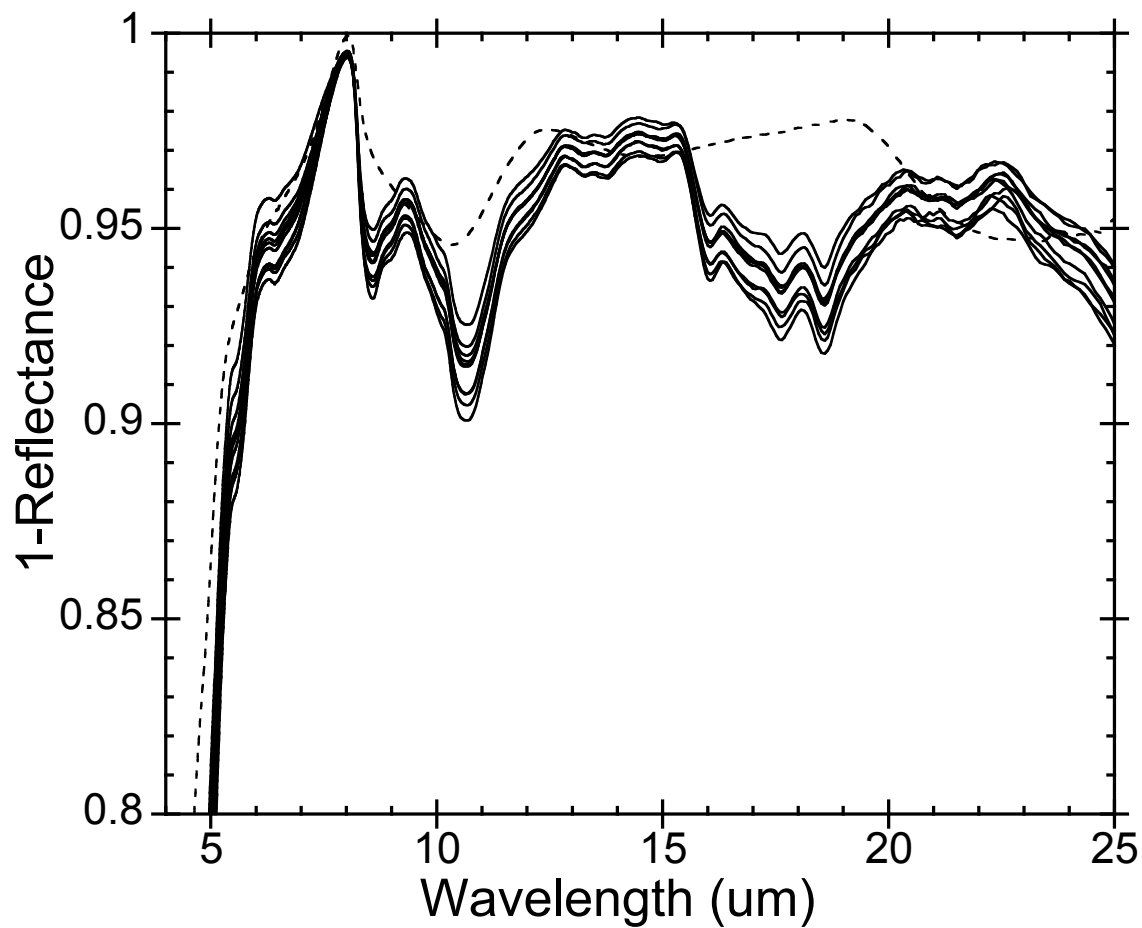


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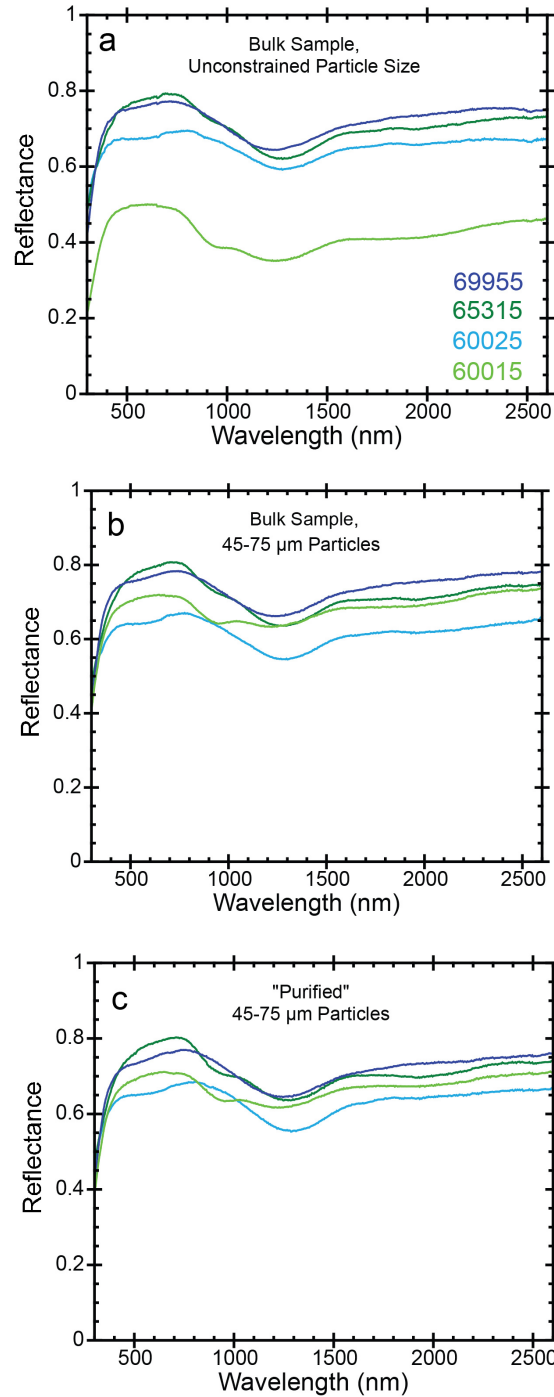


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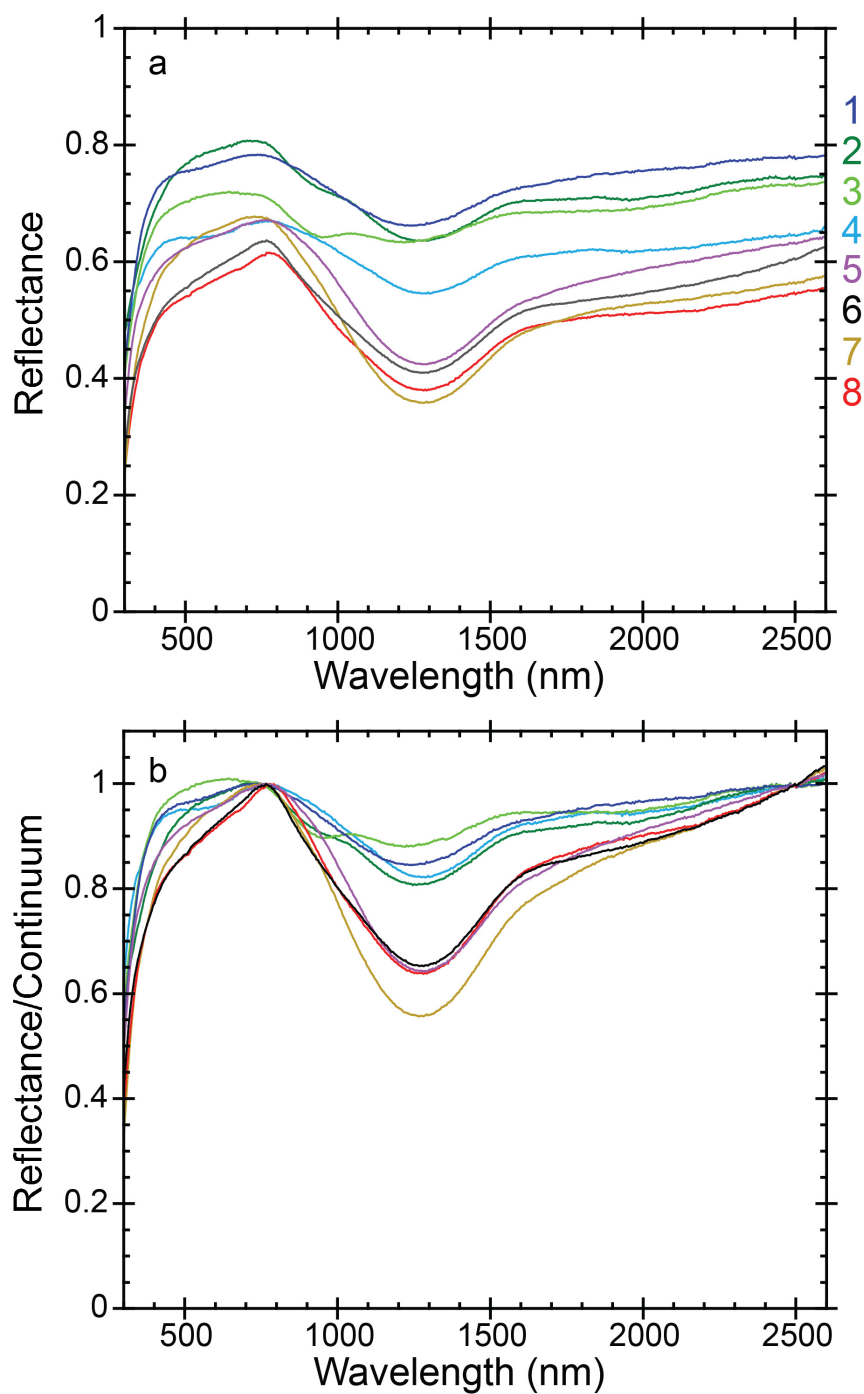


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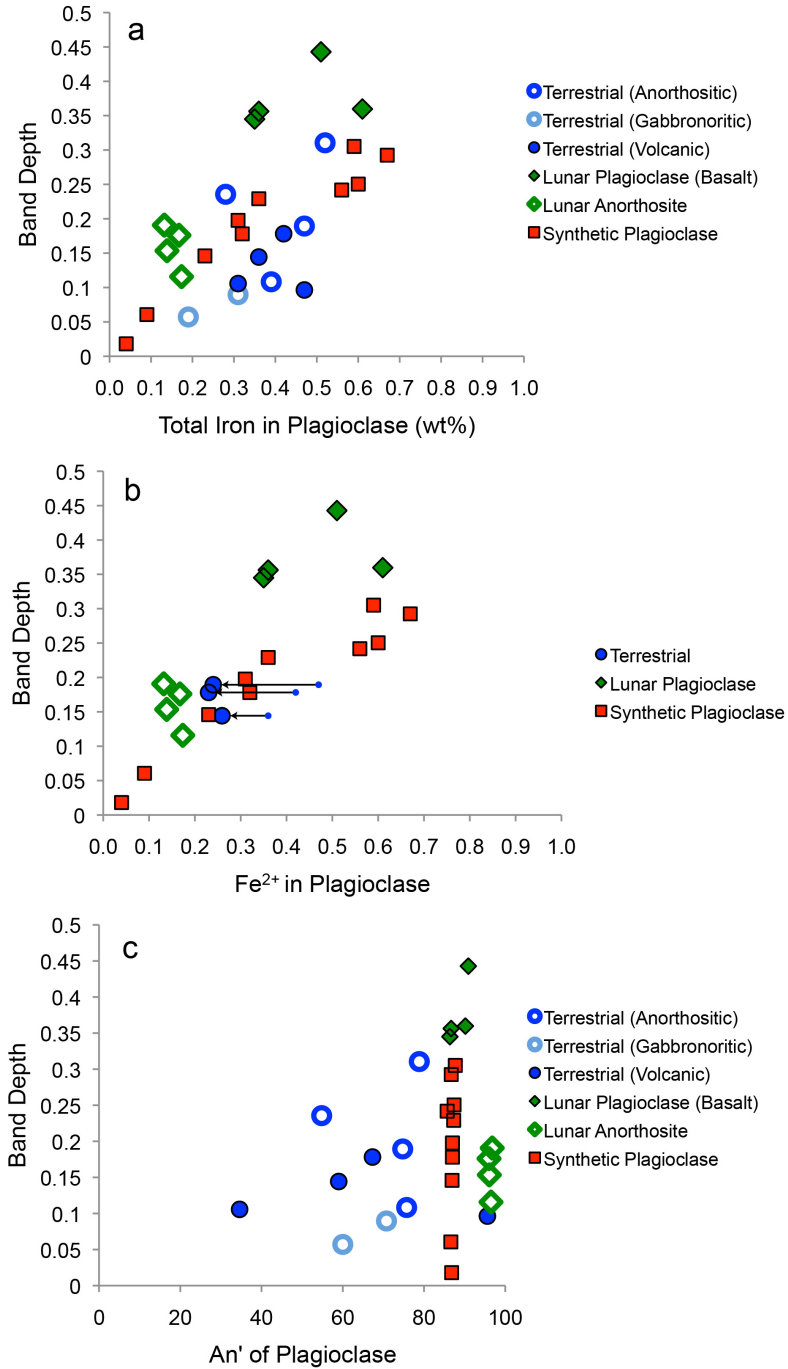


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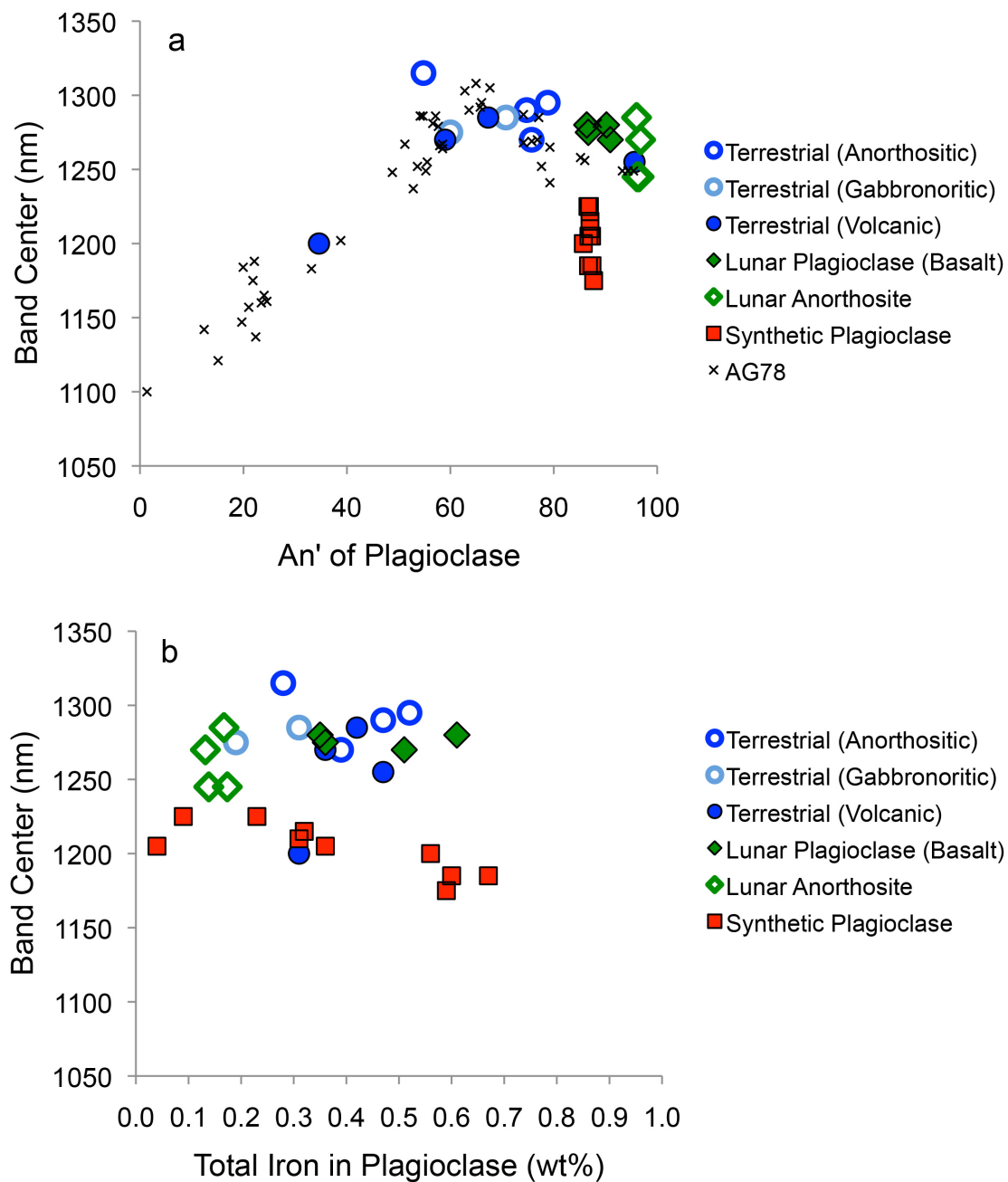


Figure 20. Compositional controls on band center estimation. (a) An content ($An = [Ca / (Na + Ca + K)]$) of plagioclase versus band center estimated by polynomial fitting to the plagioclase spectrum between 900 and 1600 nm, excluding any hydration absorptions between 1375 and 1430 nm. (b) Total iron in plagioclase versus band center estimation.

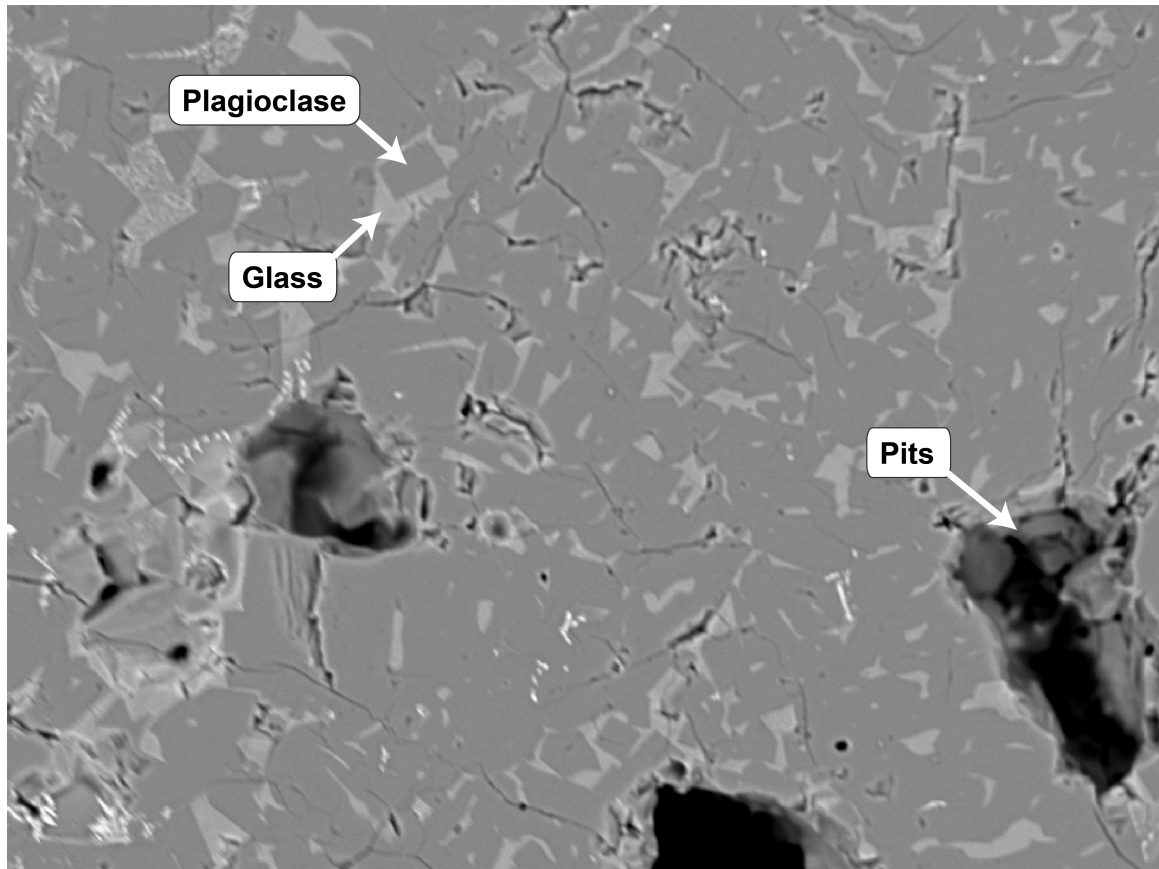


Figure 21. Backscattered electron image of Split Rock plagioclase following a reducing experimental run, acquired at Brown University. The pits are estimated to be similar in size (5-20 μm) to those in the BSE image in Figure 11. Textures are similar to those of the sintered plagioclases shown in Figure 11, although the melting appears to have been more thorough in this sample. Small, bright linear features are enriched in zirconium, the result of reaction with small amounts of the zirconium beads on which the sample was resting during the experiment. This reaction was not observed for the sintered plagioclase series.

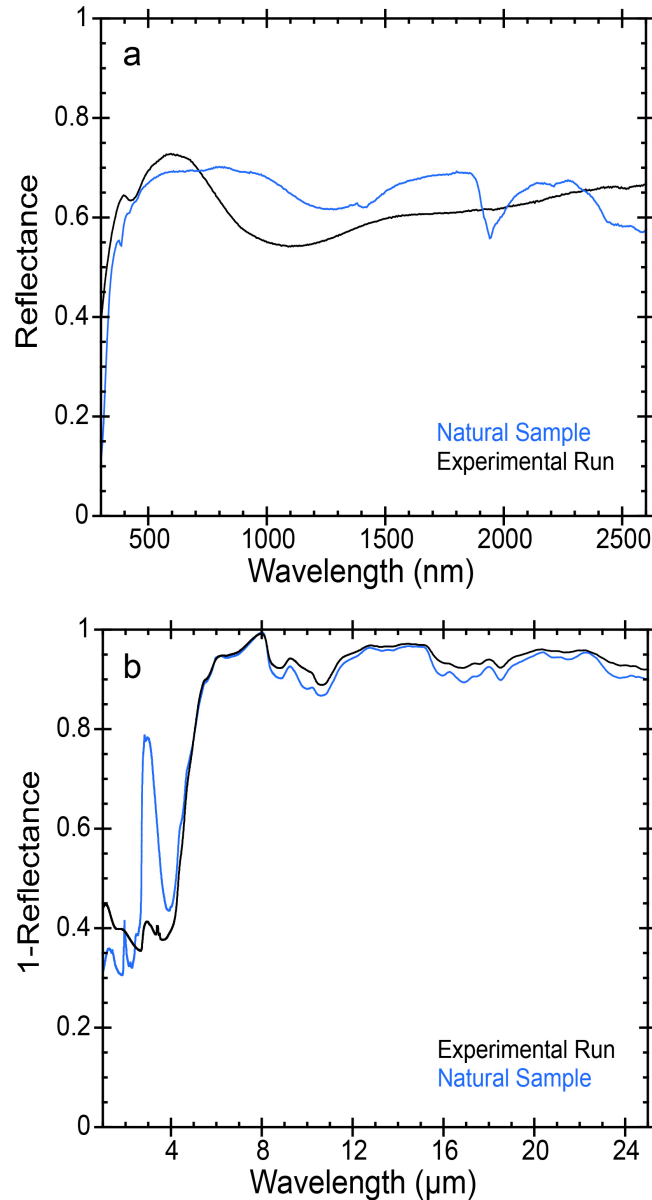


Figure 22. Comparison of the Split Rock plagioclase sample before and after treating with similar experimental conditions as used for the synthetic plagioclase series (Experimental run: 1300° C, ~IW, 90 hours). The natural, untreated sample is shown in blue, whereas the experimentally treated sample is in black. (a) Near-infrared data, showing the prominent plagioclase absorption near ~1250 nm for the untreated sample, in addition to hydration bands near 1400 and 1900 nm, and turning down toward 3000 nm. Glass bands near 1000 and 2000 nm are present in the experimentally treated sample. (b) Mid-infrared data shown as 1-Reflectance for ease of comparison with emissivity data for plagioclase. The original natural sample displays a prominent water absorption near 3 μm (inverted here). The experimental sample is shown in black, and has slightly weaker Reststrahlen bands between 8-12 μm.

CHAPTER 2: Reflectance spectroscopy of plagioclase and mafic mineral mixtures: Implications for remote sensing of lunar anorthosites

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Abstract

Anorthosites dominate the lunar upper crust and consist of high proportions of plagioclase plus small amounts of various mafic minerals. Remote near-infrared (NIR) reflectance data that can detect the plagioclase component of these rocks, namely the diagnostic 1250 nm crystalline plagioclase absorption, have only recently become available for the Moon with the success of new high-resolution orbital spectrometers. Deriving accurate mineralogic information from NIR spectra of the Moon's widespread anorthositic regions requires understanding how this plagioclase absorption combines with well-known mafic mineral absorption features in a bulk spectrum. Here, we present results of laboratory analyses that characterize the spectral properties of well-controlled binary mixtures of plagioclase with various mafic minerals. When present in high abundance (e.g., >85 vol%), plagioclase has measurable effects on the bulk spectrum. Nevertheless, even small amounts of mafic minerals (>2-5 vol%) are readily detected in a mixture with plagioclase. Variations in both mafic mineral composition and abundance produce substantial changes in bulk spectral properties of plagioclase-rich mixtures. In the mixtures produced for this study, orthopyroxene produces a strong contribution to mixture spectral properties at only 2 vol% abundance, but does not mask the plagioclase absorption unless present at high (>10 vol%) abundances. On the other hand, small (<10 vol%) amounts of olivine easily obscure the distinctive plagioclase absorption in a mixture. The character of the plagioclase-spinel mixtures are strongly dependent on spinel composition, and anorthosites in which spinel is the dominant mafic mineral should be affected by the spinel component even at 2 vol% abundance of spinel. The

systematic spectral variations observed in these controlled mixtures are not significantly affected by realistic particle size distributions for “mature” and “immature” soils.

Modeling of mixtures produced using a Hapke nonlinear approach accurately estimates relative plagioclase-mafic abundances in laboratory measured spectra to within 3 vol% for “anorthositic” mixtures and within 8 vol% for mixtures with >10 vol% mafics.

1. Introduction

Reflectance spectroscopy is a valuable tool for investigating the mineralogy of planetary surfaces remotely [e.g., *Adams and McCord*, 1970; *McCord et al.*, 1981]. Most of the major rock-forming minerals found in the lunar sample collection can be distinguished by the positions of their diagnostic broad absorption bands across near-infrared (NIR) wavelengths [e.g., *Conel and Nash*, 1970; *Hazen et al.*, 1978; *Burns*, 1993; *Sunshine et al.*, 1998]. Laboratory spectra for several of these key mineral types are shown in Figure 1. Rarely, however, do minerals occur in isolation on a planetary surface. Typically, they are “mixed” on a variety of spatial scales, occurring together in a range of rock types and soils. When the scale of mixing is on the order of millimeters such that incident light interacts with multiple components, referred to as “intimate mixing”, the bulk reflectance spectrum is not a simple linear combination of the endmember spectral properties [e.g., *Hapke*, 1981]. Instead, certain minerals, such as pyroxenes, dominate spectra disproportionately to their abundance. Detailed laboratory and modeling studies are therefore required to accurately characterize the spectra of materials consisting of more than one component [*Nash and Conel*, 1974; *Singer*, 1981; *Johnson et al.*, 1983; *Crown and Pieters*, 1987; *Mustard and Pieters*, 1987]. These types of studies are crucial for enabling mineralogic analyses from remote spectroscopy data for the Moon and other planetary bodies.

This study focuses on the spectral effects of plagioclase in mineral mixtures. Although pure plagioclase exhibits a diagnostic absorption near 1250 nm [*Conel and Nash*, 1970], it is highly transparent and difficult to distinguish in mixtures when more strongly absorbing components are present. *Crown and Pieters* [1987] noted that in

laboratory mixtures with pyroxene, plagioclase must be present in ~ 85 or 90 vol% abundance in order for its diagnostic absorption, centered near 1250 nm, to be apparent. In addition, experimental studies have noted that the ~1250 nm plagioclase absorption can be erased even in the absence of mafic minerals by the transformation of plagioclase crystals into a diaplectic glass by shock melting [e.g., *von Engelhardt and Stöffler, 1968; Stöffler, 1971*]. This latter process has often been invoked to explain the lack of a plagioclase absorption in remote sensing data for the Moon [e.g., *Adams et al., 1979; Spudis et al., 1984*]. For these reasons, the contributions of the 1250 nm crystalline plagioclase absorption to a plagioclase-dominated bulk spectrum has not been explored systematically for a wide range of mafic mineral compositions and abundances [c.f., *Nash and Conel, 1974; Singer, 1981; Johnson et al., 1983; Crown and Pieters, 1987; Mustard and Pieters, 1987; Serventi et al., 2013a*].

Understanding the spectral characteristics of materials with very high plagioclase abundances is crucial for mineralogic analyses of the Moon's highland crust, which is dominated by anorthosites. Anorthosites, which contain $\geq 90\%$ plagioclase [*Stöffler et al., 1980*], are believed to have formed the upper crust of the Moon by accumulation of buoyant plagioclase crystals at the top of a solidifying magma ocean early in lunar history [e.g., *Smith et al., 1970; Wood et al., 1970; Herbert et al., 1977; Warren and Wasson, 1980; Elkins-Tanton et al., 2011; Suckale et al., 2012*]. The newest generation of spectrometers orbiting the Moon have, for the first time, identified the diagnostic plagioclase absorption feature in numerous locations across the lunar surface [e.g., *Ohtake et al., 2009; Donaldson Hanna et al., 2012; Yamamoto et al., 2012*]. In addition, many locations also exhibit spectral properties that may indicate combinations of

crystalline plagioclase plus small abundances of mafic minerals [Chapters 3 and 4]. Examples of these types of spectra are shown in Figure 2, including spectra from the Orientale basin and Copernicus and Tsiolkovski craters. These examples are examined in detail in a subsequent section of this paper.

The goal of this study is to document the spectral characteristics of well-controlled laboratory mixtures of plagioclase plus various mafic minerals. A secondary goal is to use the results of the laboratory mixtures to test a nonlinear model for predicting mixture spectra from endmember spectra. Using both the laboratory and modeled mixture spectra, we provide a framework for constraining mafic mineral composition and relative abundance in remote sensing data for the anorthositic regions of the Moon's crust.

2. Background

Broad mineral absorptions in the near-infrared are caused by electronic transitions among the d-orbitals of certain transition metal atoms, predominately iron. These transitions are brought on by asymmetries imparted to the d-orbitals by the location of the atom within a crystal structure [e.g., *Burns*, 1993]. Differences in the crystallographic sites that contain iron atoms in different rock-forming minerals result in distinguishable absorption features. Laboratory spectra of the major lunar minerals that are considered here are shown in Figure 1: plagioclase, pyroxene, olivine, and spinel. The most diagnostic characteristics of these minerals are described below. The effects of glass and opaque minerals, such as ilmenite, on bulk spectral properties are not evaluated here, although future mixing studies should explore the effects of these additional important components of lunar rocks.

Reflectance spectra of unweathered, inclusion-free plagioclase samples are characterized by a broad absorption centered near 1250 nm [e.g. *Conel and Nash*, 1970; *Bell and Mao*, 1973; *Adams and Goullaud*, 1978; Chapter 1]. This absorption is caused by trace amounts of Fe^{2+} incorporated into the plagioclase structure, likely into the large 8-12 fold Ca^{2+} site. Increasing FeO content generally corresponds to increasing ~1250 nm absorption strength [*Bell and Mao*, 1973]. Variations in An content (molar $\text{Ca}/[\text{Ca}+\text{Na}+\text{K}]$ in plagioclase) correspond to small shifts (tens of nanometers) in the exact center position of the broad ~1250 nm absorption [*Adams and Goullaud*, 1978]. Pyroxene spectra, by contrast, are characterized by strong absorptions near 1000 and 2000 nm that are due primarily to Fe^{2+} within the M2 octahedral site [e.g., *Hazen et al.*, 1978; *Cloutis and Gaffey*, 1991; *Burns*, 1993]. Orthopyroxenes typically display relatively short-wavelength absorption centers, near ~930 and ~1900 nm, that shift to longer wavelengths with increasing FeO content. Samples that are particularly high in iron also display a weaker band centered near 1200 nm due to Fe^{2+} partitioning onto the smaller, octahedral M1 site [e.g., *Klima et al.*, 2007; 2011]. Increasing Ca content in pyroxenes also shifts the major M2 absorptions to longer wavelengths, and spectra of high-calcium clinopyroxenes display absorptions centered near 1000 and 2200 nm [e.g., *Cloutis and Gaffey*, 1991; *Klima*, 2011]. Spectra of olivines display a broad, composite absorption centered near 1000 nm. This feature is comprised of a central absorption centered between 1000 and 1010 nm caused by Fe^{2+} transitions within the octahedral M2 site. Ferrous iron situated in the M1 site generates two absorptions that overlap the M2 absorption on either side [e.g., *Burns*, 1970; *Hazen et al.*, 1977]. The composite feature shifts to longer wavelengths as the Mg number of the olivine decreases [e.g., *King and*

Ridley, 1987; Sunshine *et al.*, 1998]. Unlike the mafic silicates, Fe^{2+} in normal Mg-spinel favors the tetrahedral Al-site. This substitution results in strong absorptions at slightly longer wavelengths, near 2000 and 3000 nm [e.g. Cloutis *et al.*, 2004]. For spinel with higher iron abundances, some Fe^{2+} partitions onto the octahedral site, generating smaller absorptions near 650 and 950 nm [Cloutis *et al.*, 1993; Jackson *et al.*, 2012].

Anorthosites occupy a unique compositional range in which the highly absorbing minerals, such as pyroxenes, spinel, and to a lesser extent olivines, are present in exceedingly low abundance (<10 vol%, nominally). By contrast, plagioclase, which is relatively transparent, is present in high abundances. As a result, anorthosite spectra are more likely than other rock types to display absorption features due to *both* plagioclase and mafic minerals. This provides significant leverage in determining mineral composition and abundance because the composite absorptions that arise from combining overlapping minerals absorptions should be unique to a relatively restricted range of mineralogies.

3. Mineral Endmembers

Six binary mixture series of plagioclase plus each of the following six different mafic endmembers were generated in variable proportions for this study: a high-Mg olivine (Fo91), an intermediate olivine (Fo50), an orthopyroxene (En88), a diopside (En46), and two Mg-spinel (Mg 87 and Mg98). Spectra of all seven endmembers are shown in Figures 3 and 4. Additional details of their character and sample preparation are given in the Appendix, and major element compositions are shown in Table 1. Terrestrial endmembers were used because, unlike lunar samples, they are available in large quantities, which allows flexibility in exploring a wide range of mixture proportions

created from the same endmembers. The specific endmembers used are not intended to be direct analogs for lunar minerals, which include a range of complicated optical effects due to shock metamorphism and space weathering [e.g., *Adams et al.*, 1979; *Hapke*, 2001]. They were instead selected to be representative of the range of mineral compositions that may be expected to occur in lunar anorthosites. Thus, the major objective was to select a diversity of pure samples available in sufficient quantities to enable a systematic investigation of variations in spectral reflectance characteristics of mixtures.

A spectrum of the plagioclase endmember, a gem-quality labradorite, is shown in Figure 3, compared with a spectrum of lunar anorthosite 60025 and a plagioclase separate from highland soil 62241. Plagioclase in lunar anorthosites is typically very calcium-rich ($>An_{95}$) and iron-poor ($FeO \sim 0.1$ wt%) [e.g., *McGee et al.*, 1993]. Although An content has an effect on the exact wavelength center position of the diagnostic plagioclase absorption, this effect is only on the order of ~ 50 nm for the labradorite – anorthite compositional range and there is commonly additional variation not readily attributable to An content [*Adams and Goullaud*, 1978, Chapter 1]. Thus, the spectral characteristics of mixtures produced from the labradorite endmember are expected to be representative for these purposes. Further, it was important in selecting the plagioclase endmember to find a sample that displays a 1250 nm plagioclase absorption with sufficient spectral contrast to be comparable to laboratory measurements of lunar plagioclase. Previous mixing studies have generally only considered plagioclase with a very weak absorption or with substantial contamination from alteration signatures [*Crown and Pieters*, 1987; *Mustard and Pieters*, 1987], but recent remote sensing data have demonstrated that the plagioclase

feature is an important, visually distinguishable component of numerous spectra for the crust [Yamamoto *et al.*, 2012]. We find that the spectral properties of the plagioclase selected for analysis here are similar to lunar highland plagioclase and anorthosites measured in the laboratory. In addition to the similarities of its spectral properties to lunar examples, this sample was also chosen because of the availability of >10 grams of homogeneous material.

Spectra of the six mafic minerals used in this study are shown in Figure 4. The mafic component of lunar anorthosites is typically dominated by pyroxene (predominately low-calcium pyroxene) and minor olivine [e.g., Dixon and Papike, 1975; Warren, 1990; McGee, 1993]. The compositions of these mafic minerals are typically more ferroan, ranging from ~Mg40-Mg70, than the mafic component of the pristine Mg-suite rocks, which range up to nearly Mg90 [e.g., Ryder and Norman, 1978; Warren and Wasson, 1980; James *et al.*, 1989; McGee, 1993; Warren, 1993]. Occasionally, cumulus olivines comprise the bulk of the mafic component in lunar anorthosites. For instance, troctolitic anorthosite sample 62237 contains roughly 85 vol% plagioclase and ~15 vol% of Mg60 olivine [Dymek *et al.*, 1975; Warren and Wasson, 1977], while additional phases such as low-calcium pyroxene make up 1% or less of the bulk rock. The mafic component of troctolitic anorthosite sample 76535 is dominated by olivine (12 vol% of the bulk rock) with a much more forsteritic composition (Fo87) [Warren and Wasson, 1977].

In order to assess the spectral effects of different compositions of these mafic silicates in mixtures with plagioclase, we have created binary mixture series using plagioclase plus two different olivine samples, a High-Mg Olivine and an Intermediate

Olivine (Figure 4a), and plagioclase plus two pyroxene samples, an Orthopyroxene and a Diopside (Figure 4b). The orthopyroxene and diopside represent nearly endmember cases for the wavelength position of the ~ 1000 nm pyroxene absorption, and are therefore expected to generate different bulk spectral characteristics when mixed with large amounts of plagioclase. The two olivine spectra also differ substantially from one another. The Intermediate Olivine displays a very broad composite absorption that should overlap substantially with the 1250 nm plagioclase feature. The composite absorption observed for the High-Mg Olivine, by contrast, is more narrow. Analysis of lunar anorthosites suggests that, although most contain relatively ferroan olivines that are more analogous to the Intermediate Olivine endmember, examples of more forsteritic compositions do occur in a few cases (e.g., anorthosite sample 76535) [Warren and Wasson, 1977]. Furthermore, the primitive nature of High-Mg dunites makes their identification on the lunar surface an important objective in lunar science. The fact that these olivines have absorption features that overlap substantially with the plagioclase absorption calls for an understanding of how much plagioclase could be “hidden” in spectra resembling pure olivine. These types of data are necessary to distinguish whether spectra resembling olivine could represent anorthositic lithologies rather than troctolites or dunites, which would each require very different petrogenetic interpretations.

While spinel anorthosites have not been noted in the sample collection, recent remote sensing data have suggested their presence in numerous locations across the Moon’s surface based on spectra that display spinel absorptions but lack absorptions due to olivine or pyroxene [e.g., Pieters *et al.*, 2011; Pieters *et al.*, 2013; Yamamoto *et al.*, in press]. Although these spinel-bearing spectra also lack the diagnostic crystalline

plagioclase absorption near 1250 nm, a large amount of plagioclase could be present in a “featureless” form in which the plagioclase absorption has been erased by processes of shock metamorphism [e.g., *Adams et al.*, 1979; *Johnson et al.*, 2003]. Alternatively, the crystalline plagioclase absorption may simply be “hidden” by the strongly absorbing spinel component. We have selected two aluminate spinel samples to independently mix with plagioclase in order to place constraints on the abundance of crystalline plagioclase that is necessary to generate a ~1250 nm absorption when in an intimate mixture with spinel. The two spinel samples are both highly magnesian but differ slightly in iron content and overall albedo.

4. Experimental Procedure

Each of the seven endmember minerals were crushed in a DiamoniteTM mortar and pestle into the following size fractions: <45 μm , 45-75 μm , 75-125 μm , 125-250 μm , 250-500 μm , and 500-1000 μm . All size fractions except the finest were rinsed with deionized water after sieving to remove adhering fine particles. Binary mixture series were created from the 45-75 μm fractions of the plagioclase endmember plus each mafic endmember of the same size fraction in the following proportions (in terms of vol% mafic): 2%, 5%, 7%, 10%, 15%, 25%, and 50%. The 45-75 μm particle size fraction was selected for the above series for two reasons: 1) to maximize the spectral contrast for mixtures [e.g., *Crown and Pieters*, 1987; *Pieters*, 1983] and 2) a narrow particle size range limits the extent to which any observed variation in mixture spectra may be attributable to variations in particle size.

For each mixture, the desired proportions of each endmember were calculated in terms of volume percent of solids rather than mass percent. This was done so that the

weighting factor of each component would be analogous to the weighing factor given by *Hapke* [1981] for describing the bulk scattering properties of a linear combination of multiple components expressed in terms of single scattering albedo. For a two-component mixture, this weighting factor for component 1 would be:

$$\frac{\frac{M_1}{\rho_1 D_1}}{\frac{M_1}{\rho_1 D_1} + \frac{M_2}{\rho_2 D_2}}$$

where M_i is the bulk density $M_i = N_i \rho_i D_i^3 (\pi/6)$, ρ_i is the solid density, and D_i is the diameter, and N_i is the number of particles per unit volume for all particles of type i [*Hapke*, 1981; *Johnson et al.*, 1983; *Mustard and Pieters*, 1987]. If the particle sizes of the two components are assumed to be equal, the above equation reduces to the volume proportion of solids of component 1. To create the mixtures at the desired volume proportions, the mass needed for each component was calculated from the target volume proportion, the desired total mass of the mixture, and the solid density of each component. The total mass of each mixture varied slightly depending on the total amount of sample available, but was typically either 220 or 250 mg for the mixtures with >5 vol% mafics and 400 mg for mixtures with ≤ 5 vol% mafics. The extra sample for the mixtures with the lowest mafic abundances was desirable so that at least 10 mg of each component would be present. After weighing out each component for a given mixture, they were combined into a 4 mL glass vial and homogenized by tumbling and rotating for 5 minutes (mixtures with >5 vol% mafics) or 10 minutes (mixtures with ≤ 5 vol% mafics).

The use of a restricted particle size range in the above mixtures was intended to isolate the effects of mineral abundance on bulk spectral properties. However, natural

soils collected from the lunar surface are known to have a wide range of particle sizes that vary as a function of surface maturity [e.g., *McKay et al.*, 1974]. Particle size is known to have a strong effect on spectral properties, particularly albedo and absorption band depth [e.g., *Pieters*, 1983]. *Crown and Pieters* [1987] demonstrated that the detectability of the plagioclase absorption in mixtures with small amounts of enstatite was enhanced for particle sizes $>45\text{ }\mu\text{m}$. To test the sensitivity of the plagioclase-dominated mixtures to particle size variations, selected mixtures from the above set were duplicated using two different grain size distributions that both range from 0 to $1000\text{ }\mu\text{m}$. The first size distribution is referred to as the “immature” distribution and contains a higher proportion of large particles intended to represent relatively fresh surfaces on the Moon, such as steeply sloping crater central peaks. The second distribution, referred to as the “mature” size distribution, contains a higher proportion of small particles and is intended to represent areas on the lunar surface that have been comminuted to a greater degree by micrometeorite bombardment and impact gardening. For mixtures created with the immature distribution, both mineral components consist of $<45\text{ }\mu\text{m}$ particles, $45\text{-}250\text{ }\mu\text{m}$ particles, and $250\text{-}1000\text{ }\mu\text{m}$ particles in the following proportions, by weight: 20%, 30%, 50%, respectively. For the mixtures created with mature size distributions, the total mass of each component was divided into the same $<45\text{ }\mu\text{m}$, $45\text{-}250\text{ }\mu\text{m}$, and $250\text{-}100\text{ }\mu\text{m}$ size fractions, but in proportions of 50%, 30%, and 20%, respectively. After creating each endmember distribution, the two endmembers were combined in the desired total volume proportions. Each of these two distributions was created for mixtures of 93 vol% plagioclase plus 7 vol% high-Mg olivine, orthopyroxene, and Very-High-Mg Spinel. We note that these two particle size distributions are not direct analogs to real lunar soils,

which are characterized by a complicated range of effects such as agglutinates and nanaophase iron that have large consequences for bulk spectral properties [e.g., *Noble et al.*, 2007]. Rather, the aim of these few size distribution experiments is to isolate the effect of one of the major unknown variables, particle size, for comparison with the more restricted particle sizes of the six binary mixtures described above.

Each of the mixtures created above were loaded into 9-mm diameter Teflon-coated sample dishes (note: the mixtures containing $\geq 15\%$ of the Intermediate Olivine endmember were loaded into 5-mm dishes, due to limited sample volume). The surface of the each sample was smoothed by gently passing the edge of a piece of weighing paper, angled at ~ 30 degrees, over the sample. Reflectance spectra of the six 45-75 μm mixture series and the additional six 0-1000 μm mixtures were acquired using the Bidirectional Reflectance spectrometer (BDR) in RELAB at Brown University, with an incidence angle of 30° and a 0° emergence angle [*Pieters*, 1983].

5. Results

5.1 Controlled Particle Size

Spectra of all six 45-75 μm mixture series show systematic variations with mafic mineral abundance (Figure 5). In general, an increase in mafic abundance results in a decrease in albedo and increase in mafic mineral absorption strength for all spectra. This section describes the varying spectral characteristics that arise from combining plagioclase plus variable amounts of different mafic minerals, focusing primarily on the mixtures with $>90\%$ plagioclase.

The varying effects of different mafic minerals at the same modal proportions are shown in Figure 6, for mixtures with ≤ 10 vol% mafics. Just 2 vol% of any mafic mineral

exerts a visible effect on the bulk spectrum (Figure 6a). While the precise detectability of each mafic mineral in these mixtures may not be directly analogous to their detectability in lunar anorthosites due to small differences in mineral composition and particle size, this observation emphasizes the disproportionate spectral effects of mafic phases compared to plagioclase.

The mixtures containing 2 vol% of the High-Mg Olivine, the Intermediate Olivine, or the Diopside share similar spectral characteristics: in general they resemble a wide distorted plagioclase absorption. The 2 vol% Orthopyroxene mixture, however, differs significantly from the other mafic silicates: 2 vol% of this strongly absorbing phase results in an orthopyroxene absorption near 950 nm that is nearly subequal in strength to and distinguishable from the plagioclase absorption. This observation is similar to the results of *Nash and Conel* [1974]. Their data, which consisted of plagioclase – orthopyroxene mixtures of <50 μm particles, showed a depression of the short-wavelength plagioclase shoulder and a weak orthopyroxene band at even 1% abundance (by mass).

Spectra of both 2 vol% mixtures containing spinel display a characteristic negative slope resulting from the influence of strong 2000 and 3000 nm spinel absorptions. The major difference between the two 2 vol% spinel mixtures is the strength of the plagioclase absorption near 1250 nm: addition of a darker, more FeO-rich spinel (Mg-Spinel) subdues the plagioclase absorption almost completely at even the 2 vol% level. Mixing with a more transparent, iron-poor spinel (Very High-Mg Spinel) allows the 1250 nm plagioclase absorption to persist even when the spinel represents more than 10 vol% of the bulk material.

Addition of 5, 7, and 10 vol% mafic minerals further enhances the differences between mixtures of different minerals. For example, both the 5 vol% High-Mg Olivine and the 5 vol% Intermediate Olivine mixtures have a flat-bottomed shape, but the mixture containing the Intermediate Olivine has a much broader composite absorption that extends to wavelengths shorter than 1000 nm. By visual inspection, the mixtures containing 5, 7, and 10 vol% Intermediate Olivine simply resemble the intermediate olivine endmember with subdued spectral contrast. At the 5 vol% level, the local minimum of the diopside endmember, centered near 1050 nm becomes apparent, as does a weak 2000 nm absorption. The ~2000 nm orthopyroxene absorption is also apparent at the 5 vol% level. For both pyroxenes, the effect of the plagioclase absorption on the bulk spectrum decreases from being observable in the 2 vol% and 5 vol% mixtures to being expressed simply as a flattening of the reflectance maxima near 1250 nm in the 7 vol% and 10 vol% mixtures. This type of effect is discussed in *Crown and Pieters* [1987] for mixtures of plagioclase and orthopyroxene at varying particle sizes. Importantly, the long-wavelength absorptions in the mixture containing 5 vol% Very High-Mg Spinel is more clearly resolved into two components: one centered near 2000 nm and the other near 3000 nm that is just beyond the wavelength coverage of the BDR measurements shown here. This type of structure in the long wavelengths can be used to identify spinel in remote sensing data by distinguishing these absorptions from weak single-component “absorptions” that can result from instrumental effects.

Variations in the relative absorption depths of the plagioclase and mafic silicate (i.e., olivine and pyroxene) components can be characterized by comparing the minimum reflectance values in the ~1000 and ~1250 nm regions in a given spectrum. To make this

comparison, we find the minimum reflectance value between 850-1050 nm for each spectrum after continuum-removal. The slope of a line anchored by this reflectance minimum and the reflectance value at 1250 nm is used to compare the relative plagioclase vs. mafic absorption depths for all spectra. A schematic of this relative band depth parameter is shown in Figure 7. For a given series, higher proportions of mafic minerals correspond to more positive slope values measured in this way. For continuum removal on all spectra, we use a linear continuum with tie points at the reflectance maximum between 550-900 nm (short-wavelength tie-point) and 1350-1900 nm (long-wavelength tie point).

A comparison of the relative plagioclase – mafic absorption depths, calculated using the parameter described above, is shown in Figure 8 for the olivine and pyroxene series. For all four series, most of the change in relative band depths occurs with the addition of only <10 or <15 vol% mafics. This observation illustrates that anorthosites represent an important compositional range in which small changes in mineralogy represent large changes in bulk spectral properties. Further, it is apparent that both of the pyroxene mixture series reach significantly higher slope values (e.g., stronger mafic absorptions relative to the plagioclase absorption) than the olivine series. This reveals an important difference between the manner in which the plagioclase absorption combines with the absorptions of these two types of common mafic minerals. Specifically, because the plagioclase band overlaps with a reflectance maximum in pyroxenes, the addition of a pyroxene component weakens the absolute strength of the absorption near 1250 nm while at the same time increasing the strength of the pyroxene absorption near 1000 nm. Olivines, by contrast, have an absorption that overlaps with the plagioclase feature. As a

result, the 1250 nm region in an olivine – plagioclase mixture represents contributions from both mineral components. This observation suggests that it may be easier to “hide” a plagioclase absorption in a bulk mixture that contains only minor olivine.

5.2 Particle Size Distributions

The spectral effects of mixing mineral components that each have a wide distribution of particle sizes is shown in Figure 9. Spectra in Figure 9 a-c are unscaled, and no continuum-removal has been applied. Mixtures with a high proportion of fine, <45 μm particles (the simulated “mature” soil distribution), have a higher albedo than the mixtures with a higher proportion of large, 45-250 μm particles (the simulated “immature” soil distribution). The albedo of the comparable 45-75 μm mixtures generally falls between the two analog soil distributions. Spectra of these mixtures that are scaled to a reflectance of 1 at the wavelength of maximum reflectance for the 45-75 μm mixture are shown in Figure 9 d-f (no continuum-removal has been applied). Wavelength-dependent variations in absorption depths are apparent for the different particle size distributions. The Orthopyroxene mixtures are the most straightforward: the 45-75 μm mixtures have greater spectral contrast than either of the grain size distributions over the entire spectrum (Figure 9e). For the Very High-Mg Spinel, the immature soil particle size distribution displays a comparable absorption near 1250 nm to the 45-75 μm distribution, but the 2000 nm absorption is weaker (Figure 9f). The mature size distribution displays an even weaker 2000 nm absorption, and decreased spectral contrast in the 1250 nm region of the spectrum. The High-Mg Olivine mixtures are more complicated (Fig 9d): the 1050 nm olivine absorption is subdued for the immature size distribution, but the mature size distribution is comparable to the 45-75 μm mixture. The mature size

distribution also displays an enhanced short-wavelength absorption near 850 nm relative to the other 7 vol% olivine mixtures.

The differences in spectral contrast over different wavelengths in Figures 9 d-f may be reflecting real properties of the absorbing minerals. For example, the observation that the 2000 nm absorption in spinel decreases uniformly for both the immature and mature size distribution in Figure 9f could suggest that the 45-75 μm fraction is ideal for maximizing spectral contrast in the spinel component. However, the wide range of particle sizes in each of these samples increases the likelihood that the spectral measurement is not representative of the bulk material. For instance, for the mixtures containing a high proportion of large particles, the incident light may be sampling a fewer number of particles before it is returned to the sensor, increasing the likelihood that the plagioclase and mafic endmembers were not sampled homogeneously in the intended proportions. Given these uncertainties, we hesitate to draw important conclusions from the particle size dataset, other than to note that the scale of variation in spectral properties due to particle sizes is on the order of a percent or so variation in mafic mineral abundance. The effect on relative absorption strengths in bulk spectra would, however, be greater if the plagioclase and mafic components were given different particle size distributions. Indeed, the spectral consequences of a mafic component that is smaller on average than the plagioclase component, as is the case for typical lunar anorthosites in the sample collection [e.g., *McGee et al.*, 1993], is an important avenue for further study.

6. Nonlinear Mixing Model

Previously, laboratory mineral mixtures have been used to validate models aiming to predict mineral abundances in a given reflectance spectrum comprised of intimately

mixed components [e.g., *Johnson*, 1983; *Mustard and Pieters*, 1987, 1989]. For particulate materials in which the particles are smaller than the wavelength of light and components are intimately mixed on millimeter or centimeter scales, the spectral properties of the bulk mixture are not a simple linear combination of the spectral properties of each component. Non-linear models must be used to account for the disproportional contribution from highly absorbing components that arises when light interacts with a number of particles before returning to the sensor. Here, we use the well-characterized mixture spectra of known abundances, produced above, to test the ability of the Hapke model [*Hapke*, 1981; 1993; 2002] to predict the reflectance spectrum of each mixture based on the endmember spectra. Specifically, we are interested in determining how well the mixture spectra can be predicted for this highly non-linear regime in which the bright, relatively transparent plagioclase component is an important contributor to the bulk spectrum. We also test which mafic components lead to more accurate modeled spectra, and for which type of mixtures the models may be inappropriate.

The Hapke model approximates the reflectance of a bulk particulate mixture in which the endmember components do not combine linearly. The approach is based on relating reflectance values of each endmember component to a parameter called single scattering albedo (SSA), which depends only on the absorption characteristics of individual minerals. The SSA of each component at each wavelength can be combined linearly in proportion to the relative geometric cross section of each component. Here, we have assumed that the endmembers have the same particle size (wet-sieved to 45-75 μm), and so the relative geometric cross section can be considered analogous to volume fraction, as described above. We calculate the SSA at each wavelength for each measured

endmember spectrum by comparing with a look-up table of reflectance values calculated using equation 37 of *Hapke* [1981] at a step size of 10^{-3} in SSA. We have assumed an isotropic phase function, a backscattering term of zero, and implement the *Hapke* [2002] H-function approximations to account for multiple scattering. Linear combinations of the endmember SSA spectra, weighted by volume fraction, were calculated specifically for the proportions measured in the laboratory. The resulting mixture spectra were converted to reflectance (technically, radiance coefficient), for comparison with the laboratory measured spectra.

Comparisons between the laboratory prepared mixture spectra and the modeled mixture spectra for the same mineral proportions are shown in Figure 10. In general, the modeled mixtures are good approximations to the corresponding measured mixtures. For the olivines and the diopside, the modeled mixtures are typically slightly offset toward higher reflectance in the region of the composite absorption features between 900 and 1500 nm (Figure 10 a,b,d). The visibly largest discrepancy between measured and modeled spectra occurs for the mixtures containing the Intermediate Olivine endmember at proportions >10 vol%. This might be expected, since the Intermediate Olivine spectrum contains an absorption with significant overlap with the plagioclase absorption, making it more difficult for the model to distinguish the relative contributions of each. However, this discrepancy may also be attributable to the laboratory preparation of these samples. This particular olivine endmember was passed through a magnetic separator in two separate batches (Appendix A): one that went to form the 90, 93, 95 and 98 % plagioclase mixtures and one that formed the 0, 50, 75, and 85% plagioclase mixtures. Because this purification step was iterative, it's possible that one split was left with more

contaminating phases, including plagioclase from the bulk Kiglapait sample, than the other. Such a difference in the two Intermediate Olivine endmember splits might also be expected to give rise to the differences observed within this particular series. It is also worth noting that the Intermediate Olivine mixtures with >10% olivine were the only mixtures measured in a smaller 5 mm dish. If a higher proportion of incident photons passed completely through the sample and were extinguished by the dish, this might lead to an overall lower albedo for these samples in particular.

The slope parameter estimation of relative absorption depths in the 900-1500 nm region (described above) was calculated for the modeled mixture spectra for the four olivine and pyroxene series. The same continuum removal procedure was applied to the modeled spectra prior to this calculation. A comparison of the relative absorption band depths for the measured versus modeled mixtures is shown in Figure 11. For the mixtures containing higher mafic abundances (Figure 11a), most of the modeled spectra appear displaced to lower slope values than the measured mixtures, indicating slightly deeper relative plagioclase bands. This effect is small, however, and not generally discernable by inspection of the spectra in Figure 10. For the mixtures corresponding to mafic abundances ≤ 10 vol% (Figure 11b), the High-Mg Olivine series displays the highest discrepancy. For nearly all mafic abundances, the Orthopyroxene series displays the best match between measured and modeled relative absorption depths.

In addition to calculating mixture spectra at the specific proportions for comparison with the laboratory measured mixtures, model spectra were calculated at 0.1 vol% increments for each pair of endmembers from 10-100% mafic abundance. For each measured spectrum in a given series, the best-fit model spectrum calculated from the

corresponding endmembers was found by minimizing the root mean square error between the measured and modeled spectra. The proportions of each endmember for the best fit spectrum were constrained to sum to one. Comparison of the nominal measured mafic abundance and the mafic abundance of the best fit model spectrum is shown in Figure 12, and the best fit proportions for each mixture are listed in Table 2. In general, the best fit model spectra match the measured spectra to within <10 vol% mafics for all mixtures in all series. The best fit spectra for the mixtures containing 10 vol% or less of mafic minerals matched the nominal laboratory mafic abundances the most closely, to within 3 vol% mafic abundance. The series that produced the best estimation of mineral abundance was the orthopyroxene. Inspection of Figure 12 and Table 2 reveals that best fit model spectra nearly always predict a slightly higher proportion of mafic minerals than expected for the nominal compositions of the laboratory mixtures.

Because the non-linear modeling approach can accurately reproduce laboratory mixture spectra to within a few percent, the same approach can be used to predict mixture spectra for lunar sample endmember spectra. Example spectra of a lunar plagioclase and a lunar olivine, obtained from the RELAB database, are shown in Figure 13a and major element compositions are given in Table 3. The principal differences between the lunar plagioclase and the terrestrial sample described above include a lower albedo, a weaker absorption and a slightly steeper continuum slope for the lunar example. Although the effects of varying plagioclase composition are not discussed here [c.f., *Serventi et al.*, 2013b], examination of this sample is intended to demonstrate that the general mixing systematics described above are likely valid for a range of compositions. The lunar olivine endmember shares similar spectral characteristics with the Intermediate Olivine

investigated in this study, but also exhibits a broad long-wavelength feature near 2000 nm that is likely attributable to chromite inclusions [e.g., *Isaacson and Pieters*, 2010].

Mixture spectra calculated for these lunar endmembers using the above approach are shown in Figure 13b. Although the absolute albedo for the mixtures of lunar endmembers is lower than the terrestrial examples, the overall band character for each mixture is similar to the modeled mixtures shown in Figure 5b using terrestrial endmembers. For instance, the mixtures calculated for anorthositic proportions ($\leq 10\%$ mafics) display broad, flat-bottom spectra in both cases.

7. Discussion

7.1 Plagioclase + Mafic Silicates

Mixing small amounts of mafic minerals with plagioclase leads to a variety of spectral characteristics that are distinguishable in many cases from either endmember and therefore may be identifiable by remote spectrometers. Mafic mineral composition and abundance are the largest controls on variations in bulk spectral properties; varying the particle sizes of each component simultaneously is not observed to have a strong effect (Figure 9). However, future studies aimed at characterizing the spectral effects of varying the particle sizes of each component independently are necessary to more closely approximate the textures of lunar anorthosites in which the plagioclase grains are in many cases larger than the mafics [e.g., *McGee et al.*, 1993].

Addition of only 2 vol% of any mafic component exerts an observable effect on the bulk spectrum (Figure 6a). Although the contribution of mafic minerals may be enhanced in these mixtures by the specific particle size chosen (45-75 μm), it is clear that small amounts of these mafic components in lunar anorthosites are expected to be

important components of the bulk spectral properties. For mixtures containing ≤ 10 vol% olivine and pyroxene, the bulk spectra display a variety of composite absorptions between 900-1500 nm. Specifically, mixtures containing small amounts (2 vol% here) of orthopyroxene are uniquely identified by spectra displaying two clearly resolved components in the wavelength range of interest: one at ~ 950 nm due to orthopyroxene and one near 1250 nm attributable to plagioclase. Further, addition of just a few additional percent orthopyroxene (Figure 6b) results in large changes in the bulk spectrum: although the same two mineral absorptions may be observable, the plagioclase band is significantly weakened relative to the orthopyroxene band. This high sensitivity to orthopyroxene abundance suggests that not only are small amounts of orthopyroxene identifiable in anorthosites, but also that the relative orthopyroxene – plagioclase absorption depths may be a useful indicator of orthopyroxene content. An application of this relationship has recently been discussed for the Orientale basin [Cheek *et al.*, 2013].

The composite absorptions that result from addition of a few percent olivine or diopside, however, are not as uniquely identifiable. Flat-bottomed absorptions between ~ 900 and 1500 nm characterize many of the mixtures of these components at various abundances (Figure 6). However, the two olivine endmembers can be distinguished from each other in mixtures with plagioclase by the breadth of the composite absorption. For all olivine mixtures, those produced from the Intermediate Olivine endmember display a broader absorption, one that extends below 1000 nm, than the mixtures with the High-Mg Olivine endmember. This distinction is so pronounced and regular that we suggest it may be useful in distinguishing olivine compositions in remote sensing data for the Moon. We caution that mixtures of plagioclase plus low abundances (≤ 5 vol%) of diopside may be

indistinguishable from mixtures with forsteritic olivine, but this may not pose a major challenge to interpretation simply because anorthosites dominated by a high-calcium pyroxene mafic component are not commonly observed in the sample collection.

The spectral characteristics of the mixtures with very low mafic abundances (≤ 10 vol%) are in some cases nearly indistinguishable from spectra that contain higher proportions of mafic silicates. This is especially true for mixtures with the Intermediate Olivine endmember. However, even for mixtures with the High-Mg Olivine, the 15 vol% olivine mixture strongly resembles the mixtures containing much higher proportions of olivine. Spectra of 50/50 mixtures of plagioclase plus each mafic endmember are shown in Figure 14. In all cases, the 50/50 mixtures are indistinguishable from the 100% mafic endmembers except for small differences in albedo. This observation highlights the importance of considering the possible presence of large proportions of plagioclase in spectra that resemble dunite, for example.

7.2 Plagioclase + Spinel

Addition of small amounts of spinel to a plagioclase matrix results in different types of bulk spectral properties that depend heavily on small differences in spinel composition. Recent M^3 observations of spectra displaying strong ~ 2000 and ~ 3000 nm spinel absorptions are notoriously lacking in mineral absorptions attributable to plagioclase or other mafic minerals [Pieters *et al.*, 2011; Dhingra *et al.*, 2011; Yamamoto *et al.*, in press]. The strongly absorbing character of the common mafic silicates, discussed above, suggests that these components cannot be present in more than a few percent abundance to remain consistent with the absence of their absorption features in the spinel-bearing spectra. The abundance of plagioclase that may be present in these materials has been somewhat unconstrained. The results presented in this paper

demonstrate that spectra displaying only spinel absorptions can be produced by mixing exceedingly small amounts (~5 vol%) of a dark, highly absorbing spinel even if the more abundant plagioclase endmember displays a prominent 1250 nm crystalline absorption band (Figure 6). However, the short-wavelength absorption features in spinel containing more than ~5 wt% FeO (centered near 550 and 900 nm) [Cloutis *et al.*, 2000; Jackson *et al.*, 2012] begin to be expressed in a bulk spectrum when mixed with plagioclase in more than ~5 vol% abundance (Figure 6). Thus, in the laboratory, generating a bulk spectrum that displays neither a plagioclase absorption nor short-wavelength spinel absorptions requires somewhere between 2 and 7 vol% spinel if the spinel has a few percent FeO. However, if the spinel endmember is more transparent (e.g., the Very High-Mg Spinel), the plagioclase absorption is still discernable in the 15 and 25 vol% spinel mixtures.

While these results provide a general constraint for the amount of crystalline plagioclase that can be “hidden” by the addition of various amounts of spinel, it is likely that other factors such as space weathering or shock deformation could cause plagioclase absorptions to be substantially weakened independently of addition of spinel. Shock deformation in particular, such as transformation of crystalline plagioclase to a diaplectic glass that does not display a diagnostic absorption [e.g., von Engelhardt and Stöffler, 1968; Stöffler, 1971; Adams *et al.*, 1979], is the most likely to weaken the plagioclase absorption relative to spinel. Additional work that is underway is aimed at constraining the amount of such “shocked” plagioclase that would be consistent with the observed spectral properties of the M³ spinel-bearing detections.

7.3 Nonlinear Mixing Model

Comparison of the measured mixture spectra with spectra calculated for the same endmember proportions using the Hapke model [Hapke, 1981] demonstrates that the

nonlinear model can accurately reproduce the spectral characteristics of plagioclase – mafic mixtures (Figure 10). Further, unmixing each measured mixture spectrum using the model is shown to predict endmember abundances to within 10 vol% (Figure 12 and Table 2). The model works best for describing mixture spectra in which both the plagioclase and mafic mineral absorptions exert a measurable effect on spectral properties, namely when mafic mineral abundances are low and when the plagioclase and mafic absorptions do not overlap substantially. For example, the abundances of each endmember were predicted to within 3 vol% for any mixture containing ≤ 10 vol% mafic minerals, whereas mixtures containing > 10 vol% mafics were predicted to within 8 vol%. Among those mixtures containing ≤ 10 vol% mafics, the best fit proportions differed from the measured (laboratory prepared) mixtures by less than 1 vol% for all mixture series except the Diopside and High-Mg Olivine. Because the error in predicting abundances for the Diopside series generally increases with diopside content, we anticipate that much of the discrepancy arises from contamination in the mafic endmember, expressed as a broad absorption near 750 nm and sharp hydration features near 2400 nm. For those mixtures containing > 10 vol% mafics, the Orthopyroxene series is predicted most accurately. The Intermediate Olivine series, by contrast, had the largest discrepancies between measured and predicted abundances, possibly because of the significant overlap between the plagioclase and olivine absorptions.

An important implication of these results is that, especially for high plagioclase abundances, the Hapke model [Hapke, 1981] can be used to accurately predict mixture spectra of endmembers for which measured mixtures cannot be prepared. Above, we have shown that modeled mixtures of a lunar plagioclase and lunar olivine generally

resemble the characteristics of similar terrestrial mixtures produced in the laboratory. Because we have focused mostly on mafic endmembers with highly divergent spectral characteristics (i.e. orthopyroxene versus diopside), additional applications of this capability include calculating anorthosite-like mixtures for mafic endmembers with more intermediate spectral properties. In addition, we can produce modeled mixtures from the terrestrial endmembers used in this study at a wider range of abundances than were measured. For instance, to better constrain how much of the Very High-Mg Spinel is necessary to completely mask the expression of the plagioclase absorption, we can calculate mixtures at 5 vol% increments over the compositional range for which this transition is expected to occur (Figure 15). By simple inspection of the modeled spectra, we see that the plagioclase absorption is essentially flattened by around 40 vol% spinel, keeping in mind that the error in this range is on the order of 4-7 vol% for this sample. More detailed parameterizations of modeled spectra produced in this way could be used to more fully characterize the systematics of these various mixing series. However, the implication of this simple application is that the lack of a plagioclase absorption in spinel-bearing M^3 spectra for the Moon [e.g., *Pieters et al.*, 2012] could indicate very high proportions of spinel if the spinel composition is very low in iron. Future modeling focusing on additional spinel endmember spectra would be beneficial for placing realistic constraints on the proportion of spinel versus plagioclase in these important lithologies recently observed in remote data.

8. Application

The implications of these results can be discussed in terms of M^3 spectra with characteristics suggestive of mixtures with high proportions of crystalline plagioclase.

Representative M^3 spectra from three different regions that display a range of possible mixture characteristics are shown in Figure 2. For each of the three regions, we identify areas that resemble relatively pure plagioclase (Figure 2a), areas that display composite absorption features between 900 and 1500 nm (Figure 2b), and areas with spectra dominated by a mafic component (Figure 2c).

The examples from the Orientale basin have been described in detail in *Cheek et al.* [2013]. In general, they represent a clear progression from a pure plagioclase component (Figure 2a) to spectra containing two distinguishable absorptions that are similar to the mixtures of plagioclase plus small amounts of orthopyroxene described here (Figure 6). These types of composite absorptions are analogous to the Class B spectra in *Cheek et al.*, 2013. The more mafic-dominated spectrum shown for Orientale in Figure 2c is unlikely to be a pure orthopyroxene, rather the “flattening” of the spectrum in the 1250 nm region indicates high proportions of plagioclase are present, but the exact abundance is difficult to estimate without detailed modeling of the spectrum.

At Copernicus, spectra resembling pure plagioclase are observed in restricted areas in the northern wall (Figure 2a). In addition, a number of locations in the walls and central peaks strongly resemble spectra of forsteritic olivine [e.g., *Pieters*, 1982; *Yamamoto et al.*, 2010]. These spectra have been interpreted to suggest that either deep-seated crustal material in the form of Mg-suite plutons, or mantle material have been exposed by the Copernicus impact. The results of this study supports the interpretation that either troctolites or dunites are exposed in these locations, although we emphasize that it is difficult to distinguish between these two possibilities based on the NIR data alone. Close inspection with M^3 data, however, reveals that a few small areas within the

central peaks display spectra with the flat-bottomed absorptions (Figure 2b) that may represent a combination of the plagioclase feature expressed in the northern wall and olivine signatures elsewhere in the crater. These exposures are on the order of a few hundred meters and are likely too small to have been detected with telescopic data, which typically had a footprint of about 5 km on the lunar surface. We have shown here that these types of flat-bottomed absorptions are characteristic of laboratory mixtures containing plagioclase plus small amounts of High-Mg olivine, possibly analogous to troctolitic anorthosite sample 76535. For the Copernicus example, the limited geologic extent of these composite absorption features within the crater suggests that they could represent relatively localized regions of enhanced plagioclase abundance in a layered pluton. This interpretation is supported by the high-Mg content suggested for the olivine component by the narrow flat-bottomed absorption. Olivine observed in lunar ferroan anorthosites in the sample collection is typically much more ferroan and would be expected to generate composite absorptions that are much broader, as in Figure 5b.

The origins of the range of spectral features in the central peak of Tsiolkovskiy crater are more ambiguous. A number of locations within the peak display strong absorptions that generally resemble plagioclase, but are likely too broad to be considered as pure as the examples at Orientale and Copernicus (Figure 2a). Most of these plagioclase-like spectra also display weak 2000 nm absorptions, suggesting the presence of small amounts of pyroxene or a spinel-bearing olivine. Although Tsiolkovskiy displays a wide range of spectral characteristics throughout the central peak, perhaps the most unambiguous example of a mafic-dominated component resembles a pyroxene dominated spectrum that is likely more calcium and iron-rich than the Orientale example (Figure

2c). The example shown in Figure 2b represents certain exposures within Tsiolkovskiy's central peak that display spectra with a broad, flat-bottomed shape. These spectra are distinguished from the flat-bottomed spectra in Copernicus, however, by the fact that the absorption covers a spectral range that extends below 1000 nm and a distinct absorption near 2000 nm is observed. This type of wide, completely flat composite absorption, with an associated 2000 nm absorption is not observed in any of the binary laboratory mixtures presented in this paper. We suggest that this type of composite feature may simply be the result of mixing plagioclase with small amounts of a pyroxene component that has a relatively long-wavelength absorption, allowing for overlap between the plagioclase and pyroxene bands. Alternatively, some small amount of olivine may be present along with plagioclase and pyroxene, suppressing the reflectance in the middle of the composite band sufficiently to cause it to flatten. The spectral characteristics of the Tsiolkovskiy central peak are further discussed in Chapter 4.

9. Conclusions

Elucidating the relative proportions of mineral phases in bulk NIR reflectance spectra is a major goal in planetary science. For the crust of the Moon, this task will commonly involve distinguishing small variations in the relative amounts of minor mafic minerals present in anorthosites: olivine, pyroxene, and spinel. The results of this study demonstrate that plagioclase is not simply a featureless high-albedo component in bulk spectra, but rather an important spectral component that exerts measurable control on bulk spectral properties. At the same time, very small amounts of mafic minerals are also shown to have a large effect. The combinations of the plagioclase and mafic absorption bands present for mixtures with $\leq 10\%$ olivine and pyroxene are diagnostic of anorthosite-

like mixtures, although their individual characteristics depend on the type and composition of the mafic mineral. In some cases, such as mixtures with olivine, differences in Mg number are discernable even when the olivine is present in $\leq 10\%$ abundance. The extent to which the plagioclase absorption can be distinguished in the presence of small amounts of mafic minerals depends largely on the degree of overlap between the plagioclase and mafic mineral absorption features: plagioclase is easily “hidden” by a few percent olivine, whereas orthopyroxene and very high-Mg spinel spectra, with reflectance maxima near the location of the plagioclase band, are highly distorted by the presence of plagioclase across a wider range of mixture proportions. Iron abundance is also observed to have a major effect on whether the plagioclase absorption feature can be discerned in the presence of a few percent spinel. For most mixing series explored here, mixtures containing >10 vol% of the mafic component generally resemble spectra of the mafic endmember. This observation emphasizes the importance of using caution when interpreting remote sensing spectral data that do not display evidence for a plagioclase absorption.

Not only is the plagioclase component visibly distinguishable in bulk spectra, but nonlinear models can accurately predict mineral abundances in laboratory mixture spectra to within 3 vol% (and often <1 vol%) when ≤ 10 vol% mafics are present. The accuracy of the nonlinear approach should enable further investigation of the range of spectral characteristics expected for lunar anorthosites through study of mixture spectra modeled from different endmembers and in different abundances than those specifically investigated here. Future studies aimed at testing the nonlinear unmixing approach for spacecraft data are now necessary in order to fully describe the mineralogies of remote

sensing spectra that resemble mixtures of plagioclase plus small amounts of various mafics minerals, such as those observed at Orientale, Copernicus, and Tsiolkovskiy.

Acknowledgements: We are grateful to Taki Hiroi for his immense help getting all of the laboratory mixtures measured in RELAB, and to Tim Goudge for the Hapke mixing code. Colin Jackson was also a great help in acquiring the mineral endmembers.

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Table 1. Endmember compositions (wt%)^a

	Plagioclase	Olivine (Fo91)	Olivine (Fo50)	Diopside (En46)	Opx (En88)	Very High-Mg spinel (Mg98)	Mg-spinel (Mg87)
Source	Mexico	San Carlos	Kiglapait	Madagascar	Bamble, Norway	Tanzania	Amity, NY
<i>n</i>	123	40	40	40	54	60	10
Na ₂ O	4.48	0.01	0.00	0.16	0.01	n/a	n/a
MgO	0.11	49.98	21.48	16.15	33.96	27.48	23.49
Al ₂ O ₃	29.98	0.02	0.00	4.42	0.15	70.36	69.51
SiO ₂	52.81	41.06	34.22	51.42	57.43	0.02	0.03
K ₂ O	0.28	0.00	0.00	0.00	0.00	n/a	n/a
CaO	12.06	0.08	0.06	24.64	0.29	0.00	0.00
TiO ₂	0.07	0.00	0.01	0.28	0.06	0.00	0.03
Cr ₂ O ₃	n/a	0.02	0.00	0.00	0.01	0.10	0.07
MnO	n/a	0.13	0.57	0.07	0.05	0.03	0.13
FeO	0.35	9.01	43.59	2.64	7.90	1.10	6.02
NiO	n/a	0.38	0.01	0.00	0.02	0.00	0.01
ZnO	n/a	n/a	n/a	n/a	n/a	0.78	1.05
Total	100.14	100.69	99.94	99.78	99.88	99.87	100.34
An ^b	58.88	n/a	n/a	n/a	n/a	n/a	n/a
Mg ^c	n/a	90.82	46.76	91.59	88.45	97.80	87.43
En ^d	n/a	n/a	n/a	45.70	87.97	n/a	n/a
Fs ^e	n/a	n/a	n/a	4.20	11.49	n/a	n/a
Wo ^f	n/a	n/a	n/a	50.10	0.54	n/a	n/a
Density (g/cm ³) ^g	2.70	3.33	3.85	3.34	3.30	3.57	3.64

^a All mineral compositions analyzed using a Cameca SX100 electron microprobe at Brown University.

^bAn = molar [Ca/(Ca+Na+K)]; ^cMg= molar [Mg/(Mg+Fe)]; ^dEn = molar [Mg/(Mg+Fe+Ca)]; ^eFs = molar [Fs/(Mg+Fe+Ca)]; ^fWo = molar [Ca/(Mg+Fe+Ca)]; ^g Density values were calculated for each endmember from the mass and volume of the unit cell based on the cell parameters given in *Deer et al.*, [1992].

Table 2. Measured (laboratory prepared) and Modeled (best fit) abundances

Nominal Vol% Mafic	Measured Vol% Mafic^a	Modeled Vol% Mafic^b	Measured - Modeled Vol% Mafic	Measured Wt% Mafic^c
<i>High-Mg Olivine</i>				
2	2.00	2.80	-0.80	2.45
5	5.00	6.60	-1.60	6.10
7	6.98	9.40	-2.42	8.47
10	10.02	11.10	-1.08	12.08
15	14.94	19.00	-4.07	17.80
25	24.97	27.60	-2.63	29.10
50	48.64	55.60	-6.96	53.87
<i>Intermediate Olivine</i>				
2	2.00	1.70	0.30	2.82
5	5.01	5.20	-0.19	7.00
7	7.00	7.40	-0.41	9.69
10	10.03	10.90	-0.87	13.71
15	15.04	21.50	-6.46	20.16
25	24.89	32.10	-7.21	32.09
50	50.16	56.30	-6.14	58.93
<i>Orthopyroxene</i>				
2	2.06	2.20	-0.14	2.51
5	5.05	5.20	-0.16	6.10
7	6.75	7.30	-0.55	8.13
10	10.08	10.70	-0.62	12.05
15	15.09	14.40	0.68	17.84
25	24.93	23.60	1.33	28.87
50	50.14	49.00	1.14	55.14
<i>Diopside</i>				
2	2.02	1.50	0.52	2.49
5	5.06	5.70	-0.64	6.19
7	6.99	8.30	-1.32	8.50
10	9.96	11.80	-1.84	12.04
15	15.03	16.60	-1.57	17.95
25	24.94	30.10	-5.16	29.13
50	49.90	56.10	-6.20	55.20
<i>Very High-Mg Spinel</i>				
2	2.03	1.80	0.23	2.66
5	5.00	5.60	-0.60	6.51
7	7.00	7.50	-0.50	9.05
10	10.07	10.40	-0.33	12.89
15	15.05	16.70	-1.65	18.97

25	25.04	28.80	-3.76	30.64
50	49.95	57.00	-7.05	56.89
<i>Mg-Spinel</i>				
2	1.98	2.10	-0.13	2.65
5	5.05	5.10	-0.05	6.69
7	6.94	7.30	-0.36	9.14
10	10.01	10.30	-0.29	13.05
15	15.05	16.50	-1.45	19.28
25	24.96	27.70	-2.74	30.96
50	50.04	54.20	-4.16	57.45

^aCalculated from the mass of each component weighed out on a balance and the densities given in Table 1.

^bProportion of the mafic endmember that best fit the measured (laboratory prepared) mixture spectrum.

^cMass proportion of the mafic component as weighed out on a balance.

Table 3. Lunar sample endmember compositions (wt%)

	Olivine ^a	Plagioclase ^b
Na ₂ O	n/a	0.49
MgO	22.40	n/a
Al ₂ O ₃	n/a	35.30
SiO ₂	34.20	44.10
K ₂ O	n/a	0.03
CaO	0.37	19.20
TiO ₂	0.00	n/a
Cr ₂ O ₃	0.14	n/a
MnO	0.40	n/a
FeO	42.00	0.12
Total	99.54	99.24
An# ^b	n/a	95
Mg# ^c	49	n/a

^aRELAB ID: LR-CMP-169

^bRELAB ID: LR-CMP-183.

Figure Captions.

Figure 1. NIR reflectance spectra of common lunar minerals measured in RELAB. All are 0-125 μm with the exception of the spinel, which are large, 1-2 mm crystals. (a) Plagioclase separate from highland soil 62240 (RELAB: LR-CMP-183). (b) Olivine separate from low-Ti basalt 15555 (RELAB: LR-CMP-169). The weak absorption near 2000 nm is likely due to chromite inclusions. (c) Orthopyroxene separate from low-Ti basalt 15058 (RELAB: LR-CMP-173). (d) Clinopyroxene separate from high-Ti basalt 70017 (RELAB: LR-CMP-175). (e) Gem quality pink spinel from Sri Lanka (RELAB: SP-SWP-028).

Figure 2. Example continuum removed Moon Mineralogy Mapper (M^3) spectra, for three different areas, displaying a range of spectral characteristics that may indicate mixing of plagioclase with variable proportions of mafic minerals. (a) Spectra from Copernicus, Tsiolkovskiy, and Orientale that resemble pure plagioclase. We interpret the Tsiolkovskiy spectrum as representing plagioclase plus very small amounts of either olivine or pyroxene causing the absorption to broaden. (b) Spectra from all three areas that display composite absorptions likely indicative of anorthositic mineralogies. (c) Spectra from each of the three areas that are dominated by the spectral properties of a mafic endmember.

Figure 3. The plagioclase endmember used in the laboratory mixing analyses presented here (top spectrum, solid line). Shown for comparison are a plagioclase separate from a lunar highland soils (dotted line) and lunar anorthosite 60025 (dashed line). The terrestrial endmember and the lunar anorthosites both consist of 45-75 μm particles. The highland soil plagioclase has a particle size of 0-125 μm (RELAB ID: LR-CMP-183). The terrestrial sample was wet-sieved with deionized water to remove adhering fine particles.

Figure 4. Mafic mineral endmembers used in the laboratory mixing study presented here. All samples were wet-sieved with deionized water to 45-75 μm . (a) The two olivine endmembers: a high-Mg olivine (Mg91) from San Carlos, AZ (top spectrum), and an intermediate olivine (Mg47) separated from a sample from the Kiglapait intrusion (bottom spectrum). (b) The two pyroxene endmembers: an orthopyroxene (enstatite) from Bamble, Norway, and a diopside from Madagascar. (c) The two spinel endmembers: a very high Mg spinel (Mg98) from Tanzania (top spectrum), and an Mg-spinel from Amity, NY (bottom spectrum).

Figure 5. All six binary mixture series with particle sizes 45-75 μm produced in this study. (a) Plagioclase plus variable amounts of the high-Mg olivine endmember. The legend and color scheme are the same in subsequent parts of the figure, (b) Plagioclase plus the intermediate olivine endmember, (c) plagioclase plus the orthopyroxene endmember, (d) plagioclase plus the diopside endmember, (e) plagioclase plus the very high-Mg spinel endmember, (f) plagioclase plus the Mg-spinel endmember.

Figure 6. Mixture series (45-75 μm particles) displayed according to the volume percent mafic minerals in each mixture. Only the mixtures that are strictly analogous to anorthosites, containing ≥ 90 vol% plagioclase, are shown (a) The six binary mixtures containing plagioclase plus 2 vol% mafics. The spectra are labeled in part a only, but their order and color is maintained throughout all parts of the figure. (b) Mixtures containing plagioclase plus 5 vol% mafic minerals, (c) mixtures containing plagioclase plus 7 vol% mafics, (d) plagioclase plus 10 vol% mafics.

Figure 7. Schematic of the parameter for estimating relative band depths of the plagioclase and mafic components in a given spectrum, shown for two of the plagioclase plus high-Mg Olivine mixtures. A negative slope, shown for the 2 vol% olivine mixture, corresponds to a relatively strong plagioclase component. A positive slope, shown for the 10 vol% olivine mixture, indicates a more dominant mafic component.

Figure 8. Slope parameter estimating relative absorption strengths shown for the mafic silicates olivine and pyroxene. Higher slope values correspond to a relatively stronger mafic absorption. (a) Slope parameter values shown for all mixtures in the four mafic silicate series. (b) Slope parameter values shown for only the mixtures containing ≤ 10 vol% mafics.

Figure 9. Mixtures with wide particle size distributions (0-1000 μm). Parts a-c show unscaled mixture spectra. Parts d-f show the same spectra as in a-c, scaled to one at the maximum reflectance value (between 650 and 800 nm) for the 45-75 μm spectrum. (a) and (d) Three particle size distributions for the 7 vol% High-Mg olivine plus 93 vol% plagioclase mixtures. (b) and (e) Three particle size distributions for the 7 vol% Orthopyroxene plus 93 vol% plagioclase mixtures. (c) and (f) Three particle size distributions for the 7 vol% very-high Mg spinel plus 93 vol% plagioclase mixtures.

Figure 10. All six laboratory mixture series (solid lines), the same as in Figure 5, plotted with the mixtures calculated at the same abundances using the Hapke modeling approach (dotted lines).

Figure 11. Proportion of mafic minerals in each modeled spectrum compared with the proportion of mafics in the corresponding laboratory prepared mixture. More positive slope values correspond to a higher mafic mineral abundance. A slope of zero corresponds to equal plagioclase and mafic absorption band depths, and values below zero indicate that the plagioclase absorption is deeper than the mafic absorption in the continuum-removed spectrum. (a) Comparison of measured vs modeled absorption depths for all mixtures. (b) Comparison of measured vs. modeled absorption depths for just the mixtures containing mafic abundances ≤ 10 vol%.

Figure 12. The mafic abundance of the best fit modeled spectrum plotted against the nominal mafic abundance prepared in the laboratory. See Table 2 for difference between the nominal mafic abundance and actual prepared mafic abundance for each mixture (typically within 0.1 vol%). The mafic mineral abundances for the best fit spectrum are

slightly higher than the mafic abundance of the measured spectrum except for in the orthopyroxene series.

Figure 13. Modeling mixture spectra of lunar endmember spectra measured in RELAB. (a) Comparison of terrestrial and lunar endmembers: Plagioclase (Top gray line), 2: Lunar Plagioclase (Top black line), 3: Terrestrial Olivine (Bottom gray line), 4: Lunar Olivine (Bottom black line). The terrestrial endmembers are each 45-75 μm particles prepared for this study. The Lunar endmembers are each <125 μm particles, from Isaacson et al. (2011). (b) Mixture spectra of the lunar plagioclase and olivine endmembers described in part a (spectra 2 and 4). Mixtures were calculated using the Hapke approach described in the text for the same proportions that were prepared for all laboratory mixture series.

Figure 14. Laboratory prepared mixtures containing 50 vol% mafics, for all series (45-75 μm particles).

Figure 15. Mixture spectra modeled from 15-50 vol% mafic abundance (in 5 vol% increments) using the Hapke approach for the Plagioclase and Very High-Mg Spinel endmembers. The percentages denote mafic abundance. Spectra have been offset for clarity.

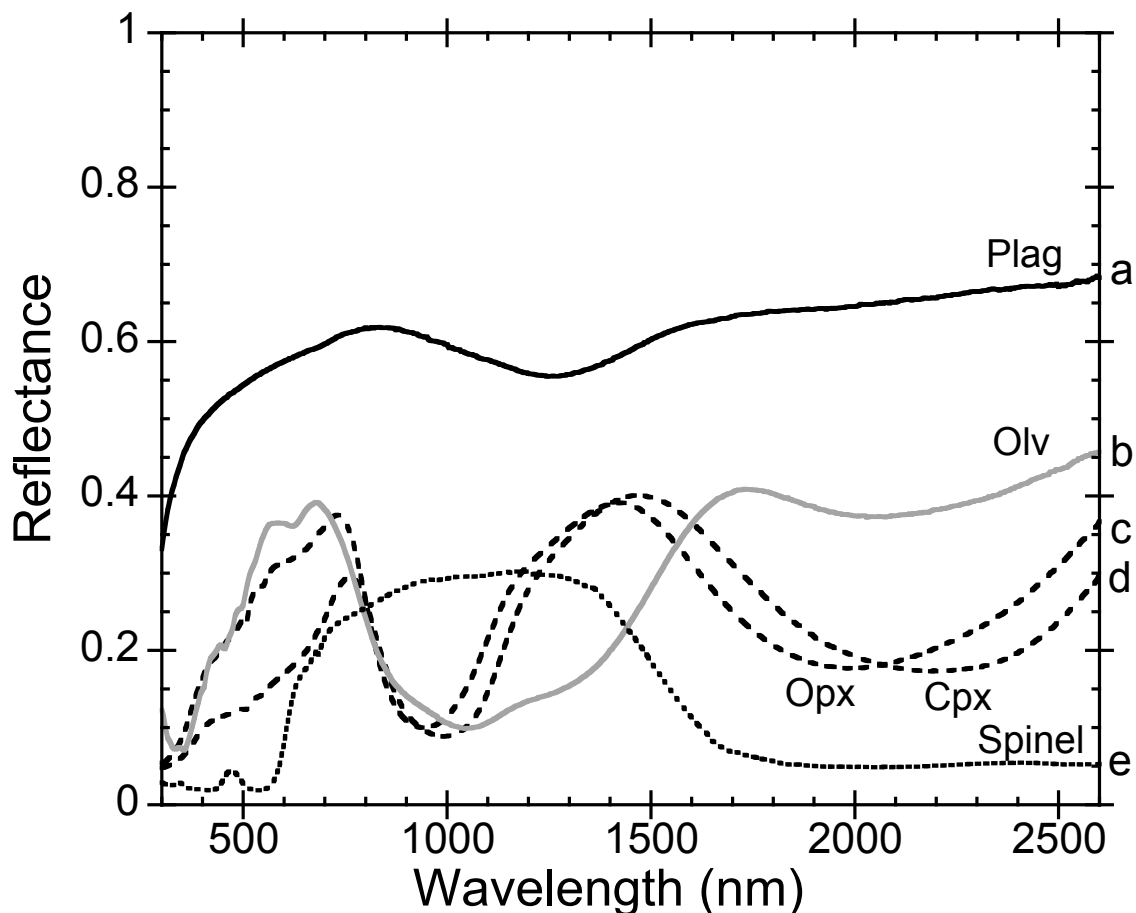


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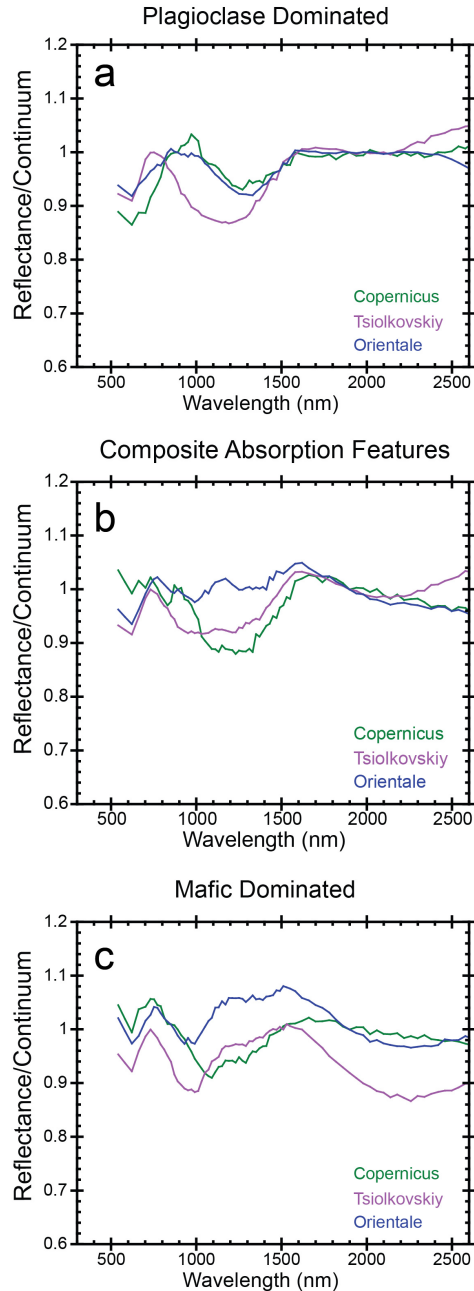


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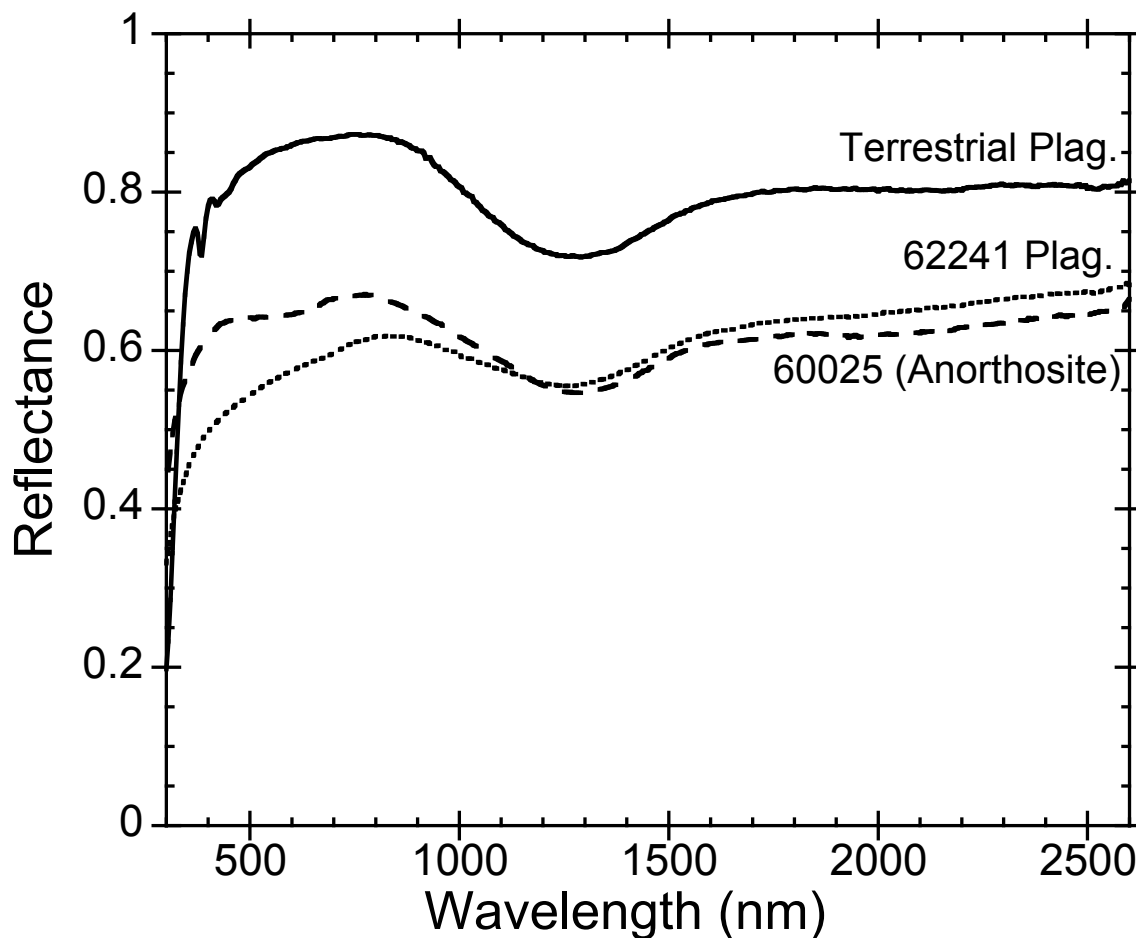


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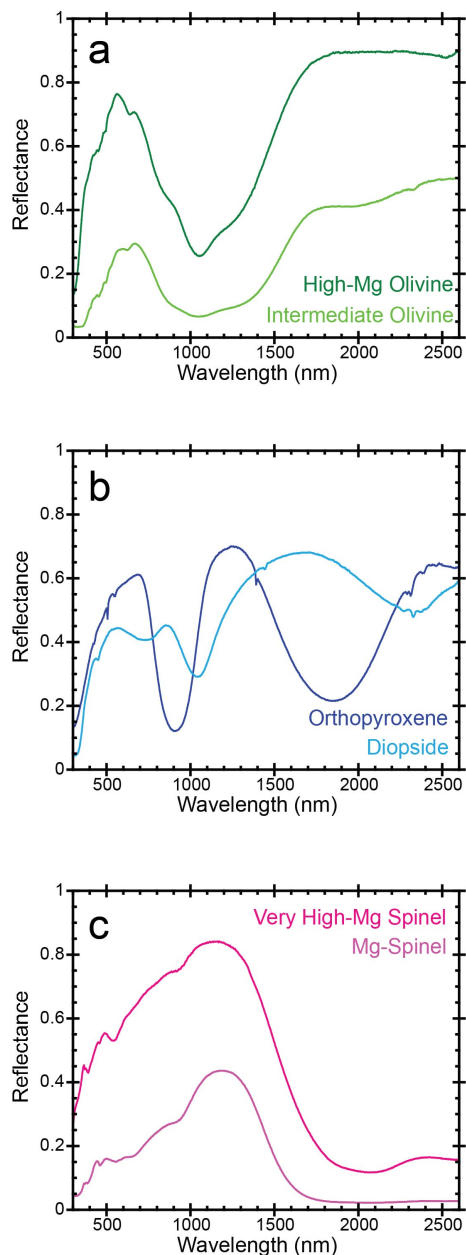


Figure 4. Mafic mineral endmembers used in the laboratory mixing study presented here. All samples were wet-sieved with deionized water to 45-75 μm . (a) The two olivine endmembers: a high-Mg olivine (Mg91) from San Carlos, AZ (top spectrum), and an intermediate olivine (Mg47) separated from a sample from the Kiglapait intrusion (bottom spectrum). (b) The two pyroxene endmembers: an orthopyroxene (enstatite) from Bamble, Norway, and a diopside from Madagascar. (c) The two spinel endmembers: a very high Mg spinel (Mg98) from Tanzania (top spectrum), and an Mg-spinel from Amity, NY (bottom spectrum).

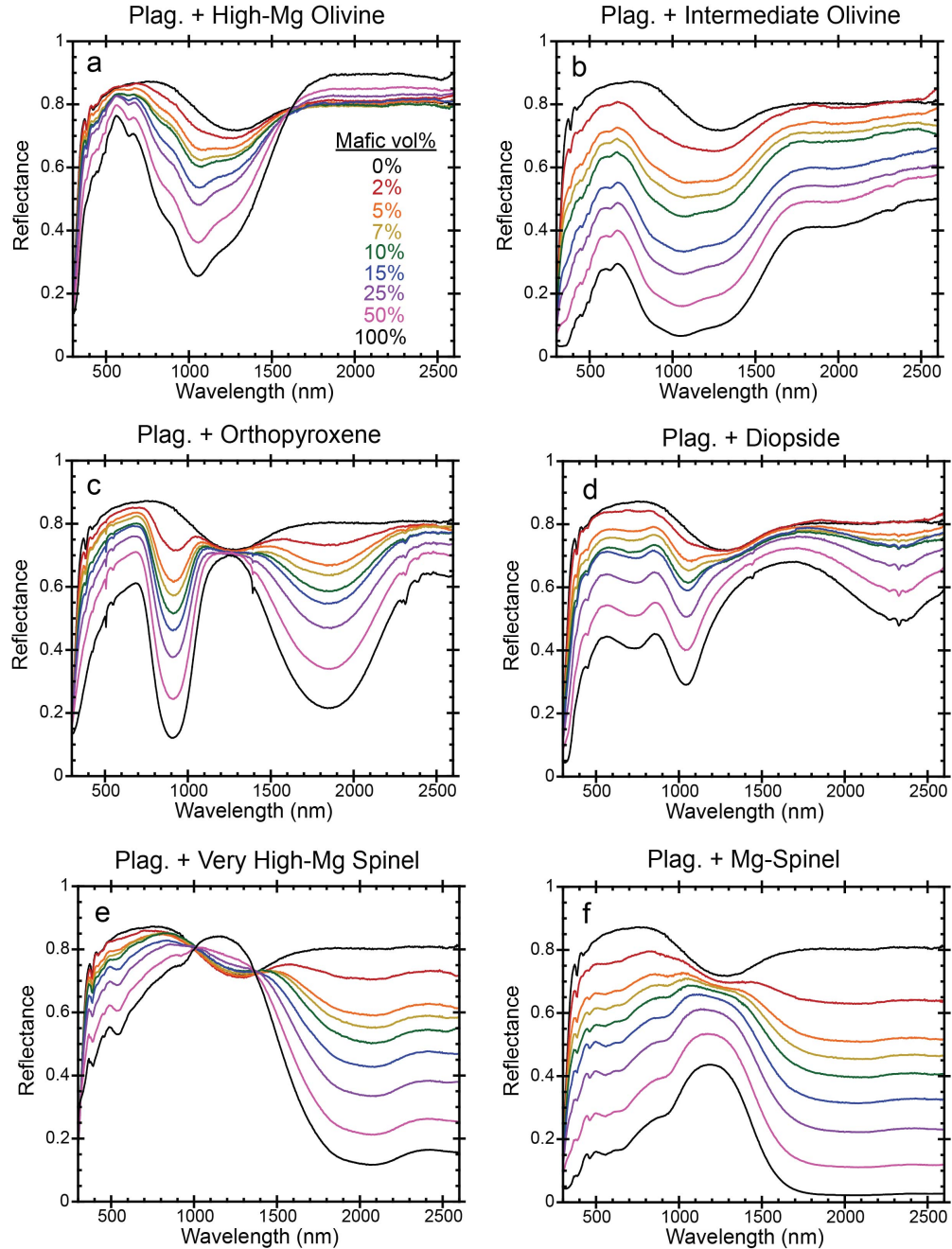


Figure 5. All six binary mixture series with particle sizes 45-75 μm produced in this study. (a) Plagioclase plus variable amounts of the high-Mg olivine endmember. The legend and color scheme are the same in subsequent parts of the figure, (b) Plagioclase plus the intermediate olivine endmember, (c) plagioclase plus the orthopyroxene endmember, (d) plagioclase plus the diopside endmember, (e) plagioclase plus the very high-Mg spinel endmember, (f) plagioclase plus the Mg-spinel endmember.

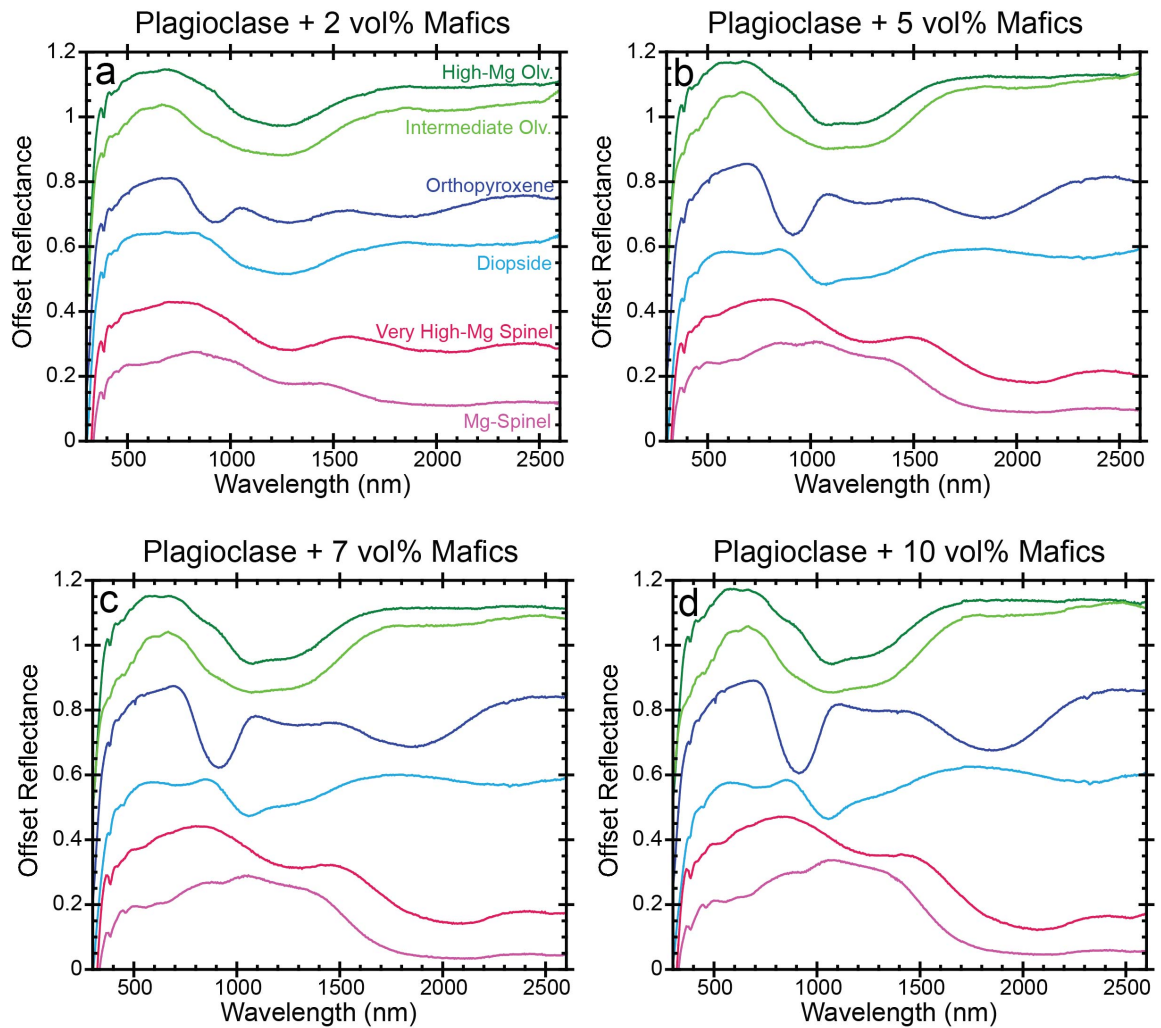


Figure 6. Mixture series (45-75 μm particles) displayed according to the volume percent mafic minerals in each mixture. Only the mixtures that are strictly analogous to anorthosites, containing ≥ 90 vol% plagioclase, are shown (a) The six binary mixtures containing plagioclase plus 2 vol% mafics. The spectra are labeled in part a only, but their order and color is maintained throughout all parts of the figure. (b) Mixtures containing plagioclase plus 5 vol% mafic minerals, (c) mixtures containing plagioclase plus 7 vol% mafics, (d) plagioclase plus 10 vol% mafics.

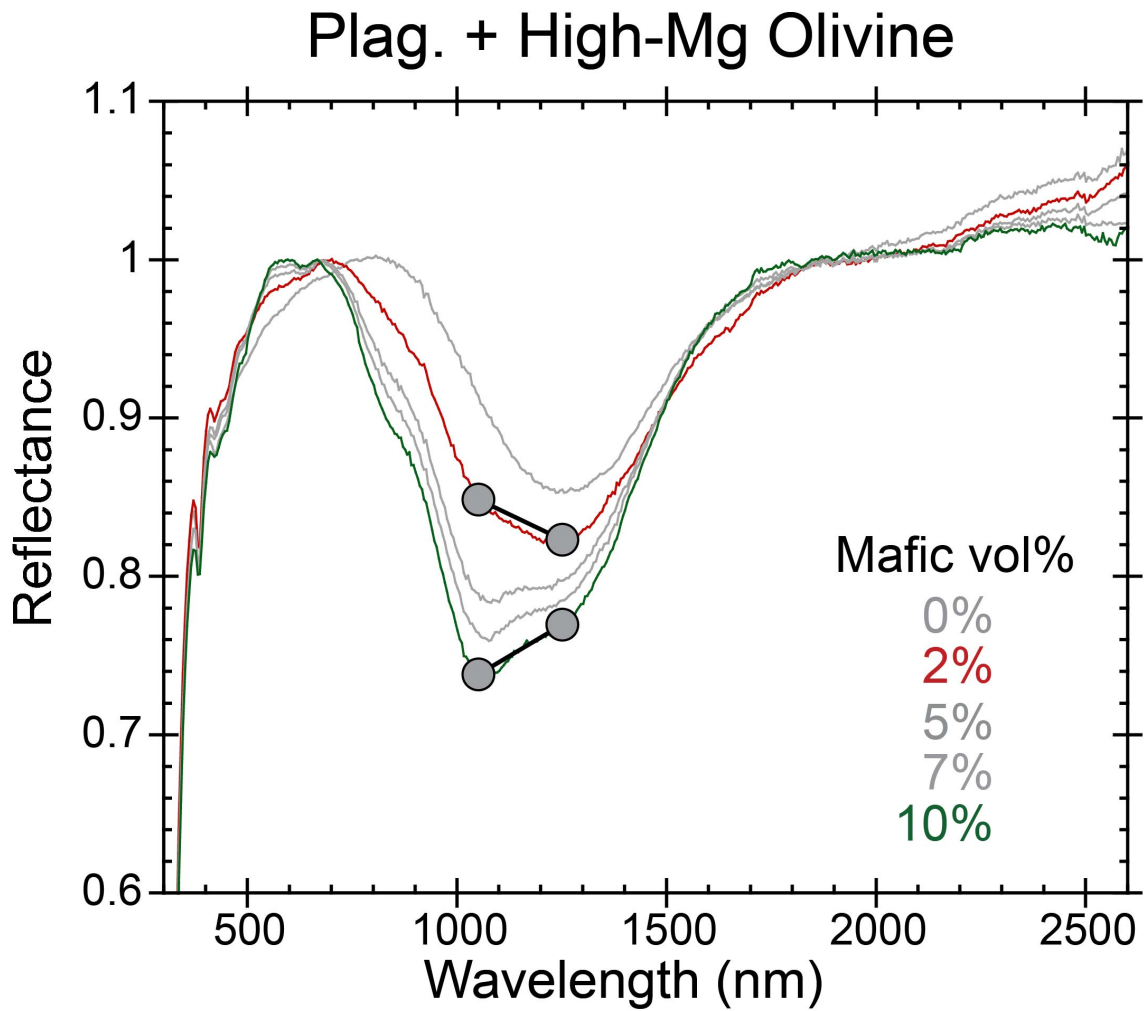


Figure 7. Schematic of the parameter for estimating relative band depths of the plagioclase and mafic components in a given spectrum, shown for two of the plagioclase plus high-Mg Olivine mixtures. A negative slope, shown for the 2 vol% olivine mixture, corresponds to a relatively strong plagioclase component. A positive slope, shown for the 10 vol% olivine mixture, indicates a more dominant mafic component.

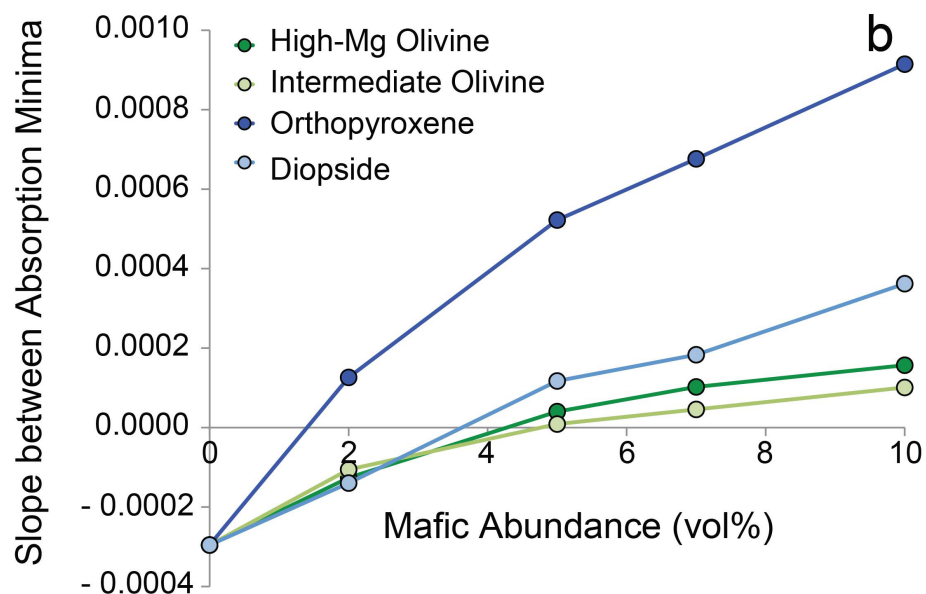
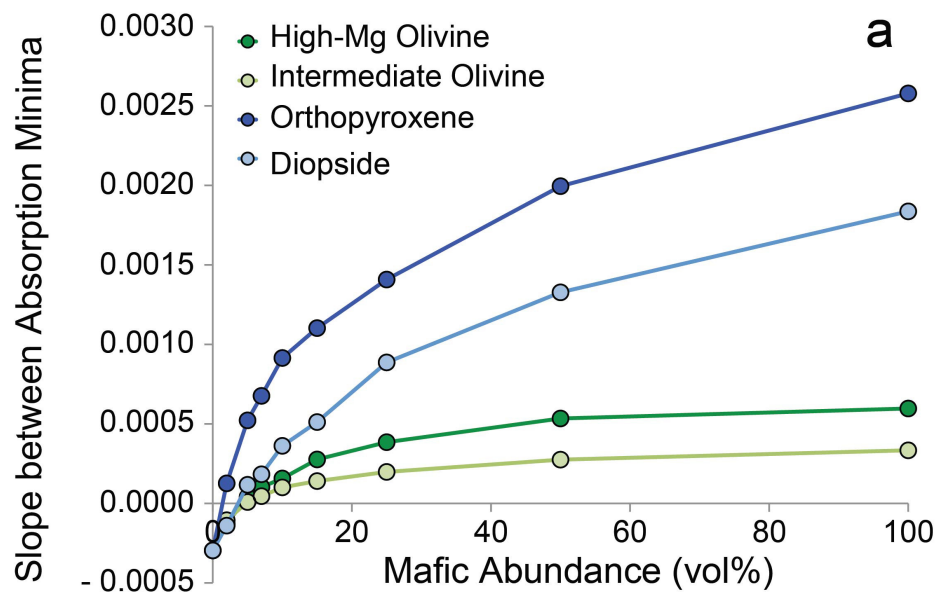


Figure 8. Slope parameter estimating relative absorption strengths shown for the mafic silicates olivine and pyroxene. Higher slope values correspond to a relatively stronger mafic absorption. (a) Slope parameter values shown for all mixtures in the four mafic silicate series. (b) Slope parameter values shown for only the mixtures containing ≤ 10 vol% mafics.

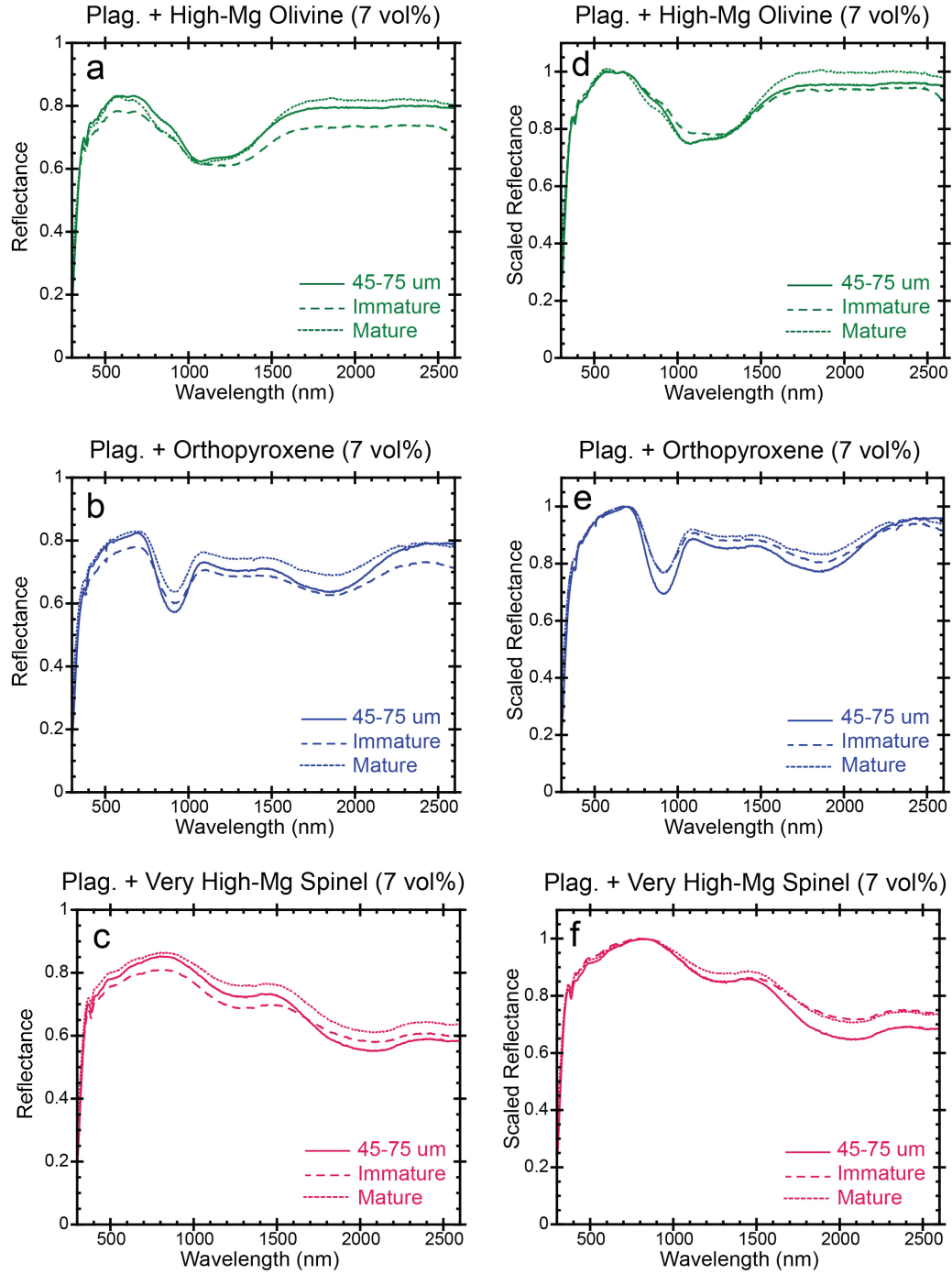


Figure 9. Mixtures with wide particle size distributions (0-1000 μm). Parts a-c show unscaled mixture spectra. Parts d-f show the same spectra as in a-c, scaled to one at the maximum reflectance value (between 650 and 800 nm) for the 45-75 μm spectrum. (a) and (d) Three particle size distributions for the 7 vol% High-Mg olivine plus 93 vol% plagioclase mixtures. (b) and (e) Three particle size distributions for the 7 vol% Orthopyroxene plus 93 vol% plagioclase mixtures. (c) and (f) Three particle size distributions for the 7 vol% very-high Mg spinel plus 93 vol% plagioclase mixtures.

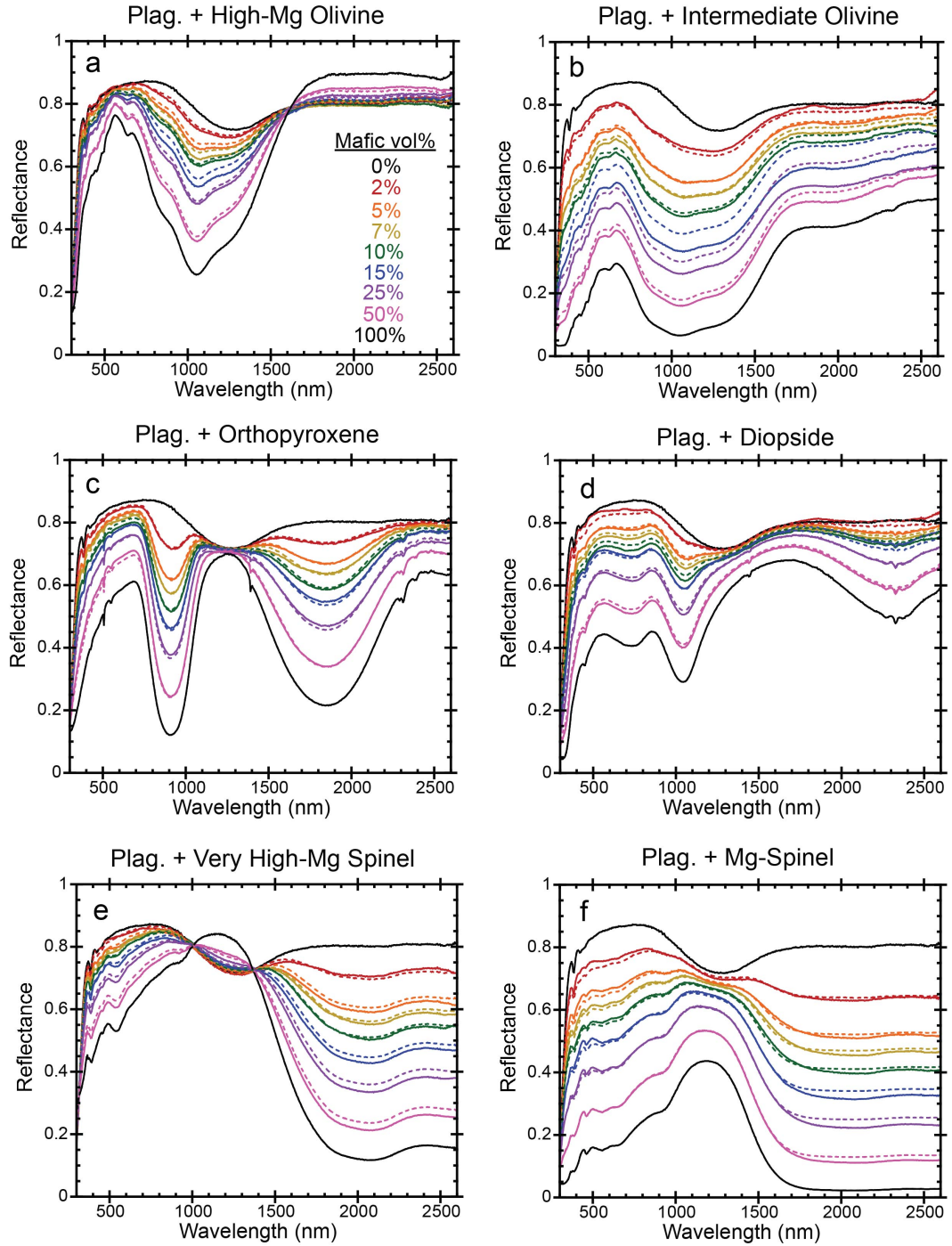


Figure 10. All six laboratory mixture series (solid lines), the same as in Figure 5, plotted with the mixtures calculated at the same abundances using the Hapke modeling approach (dotted lines).

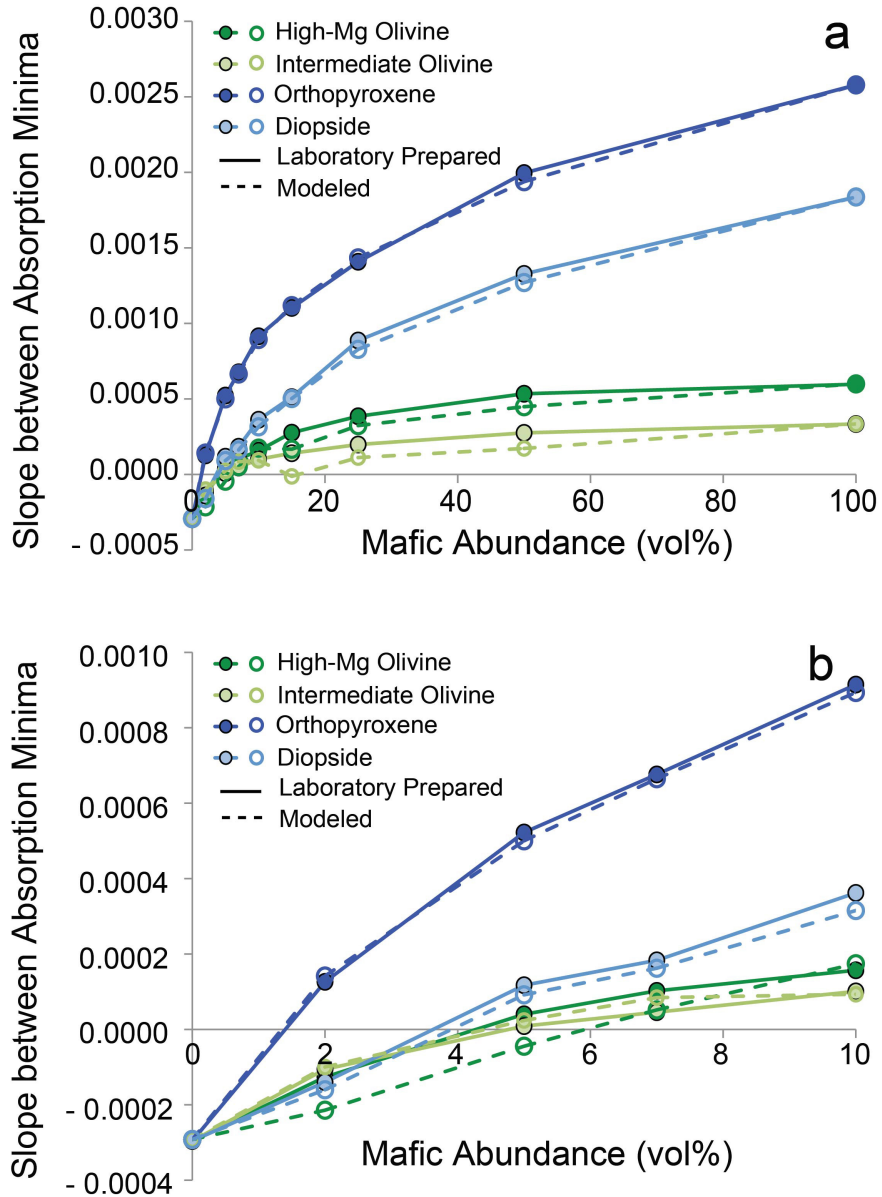


Figure 11. Proportion of mafic minerals in each modeled spectrum compared with the proportion of mafics in the corresponding laboratory prepared mixture. More positive slope values correspond to a higher mafic mineral abundance. A slope of zero corresponds to equal plagioclase and mafic absorption band depths, and values below zero indicate that the plagioclase absorption is deeper than the mafic absorption in the continuum-removed spectrum. (a) Comparison of measured vs modeled absorption depths for all mixtures. (b) Comparison of measured vs. modeled absorption depths for just the mixtures containing mafic abundances ≤ 10 vol%.

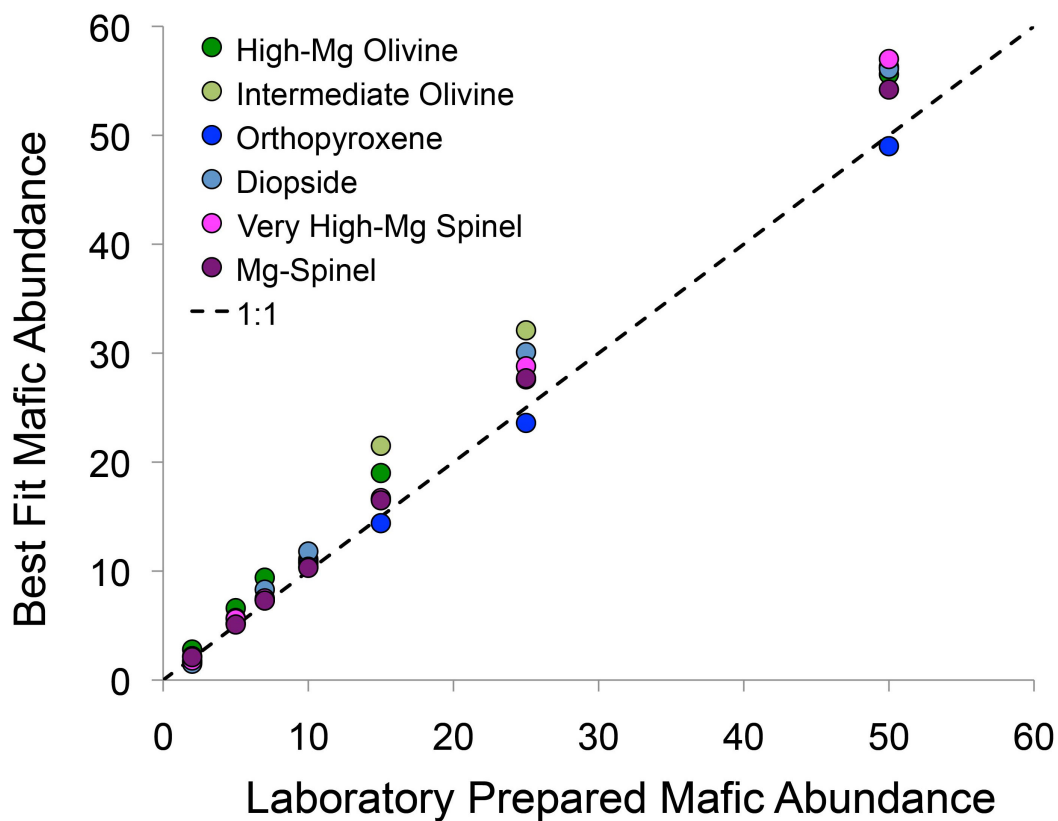


Figure 12. The mafic abundance of the best fit modeled spectrum plotted against the nominal mafic abundance prepared in the laboratory. See Table 2 for difference between the nominal mafic abundance and actual prepared mafic abundance for each mixture (typically within 0.1 vol%). The mafic mineral abundances for the best fit spectrum are slightly higher than the mafic abundance of the measured spectrum except for in the orthopyroxene series.

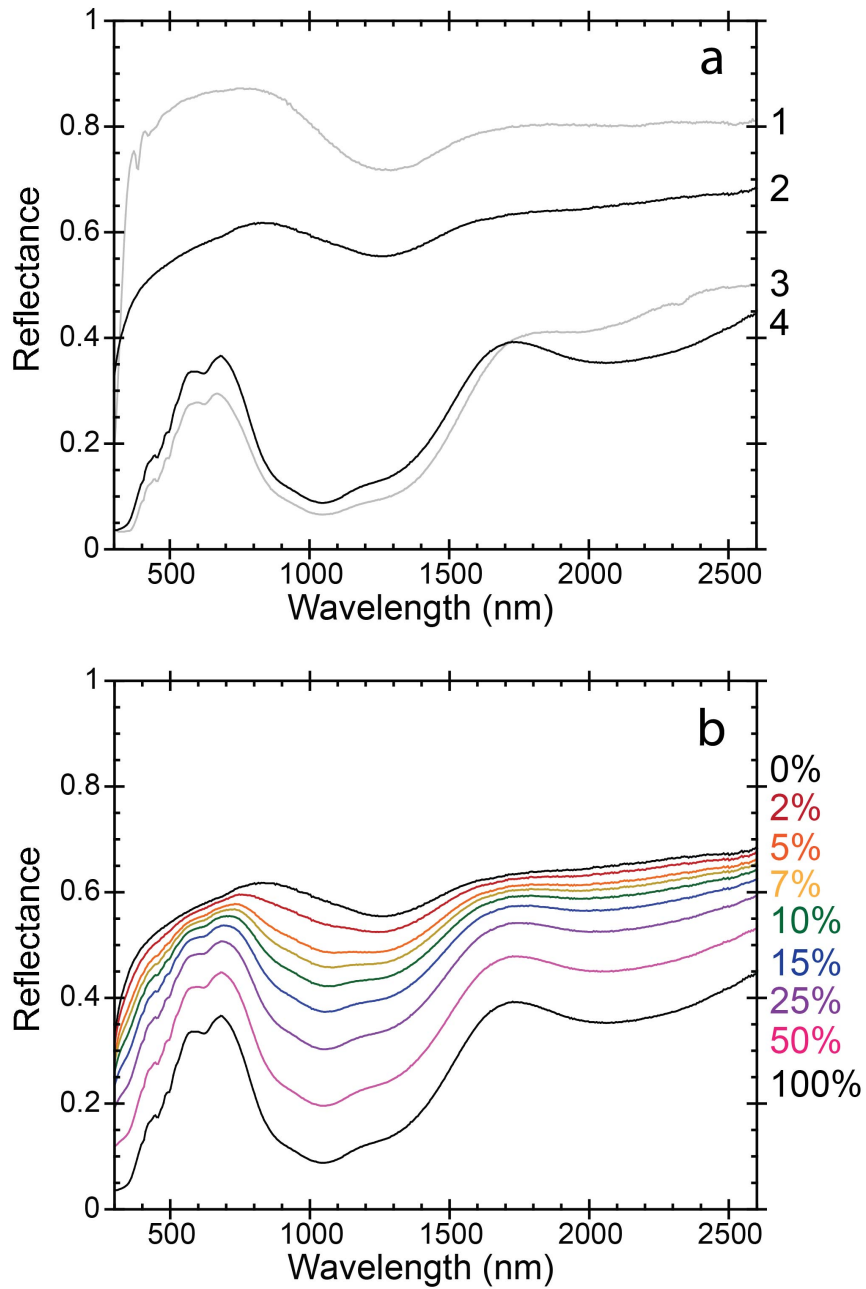


Figure 13. Modeling mixture spectra of lunar endmember spectra measured in RELAB. (a) Comparison of terrestrial and lunar endmembers: Plagioclase (Top gray line), 2: Lunar Plagioclase (Top black line), 3: Terrestrial Olivine (Bottom gray line), 4: Lunar Olivine (Bottom black line). The terrestrial endmembers are each 45-75 μm particles prepared for this study. The Lunar endmembers are each $<125 \mu\text{m}$ particles, from Isaacson et al. (2011). (b) Mixture spectra of the lunar plagioclase and olivine endmembers described in part a (spectra 2 and 4). Mixtures were calculated using the Hapke approach described in the text for the same proportions that were prepared for all laboratory mixture series.

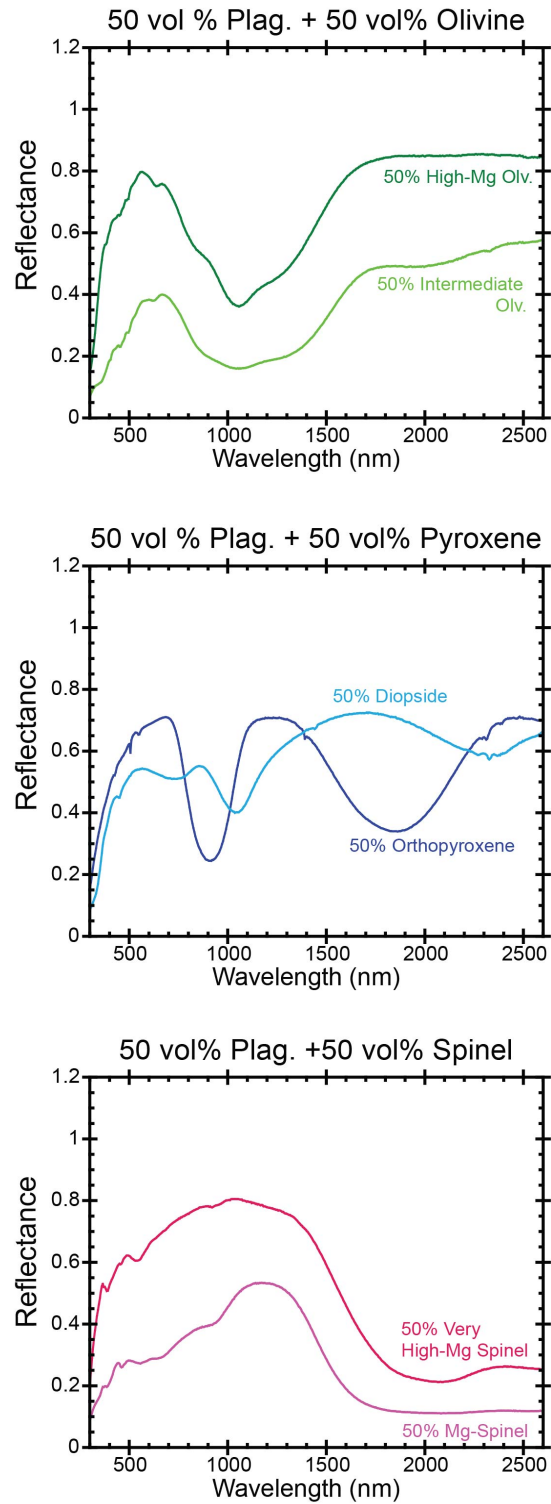


Figure 14. Laboratory prepared mixtures containing 50 vol% mafics, for all series (45-75 μm particles).

Plag. + Very High-Mg Spinel (Modeled)

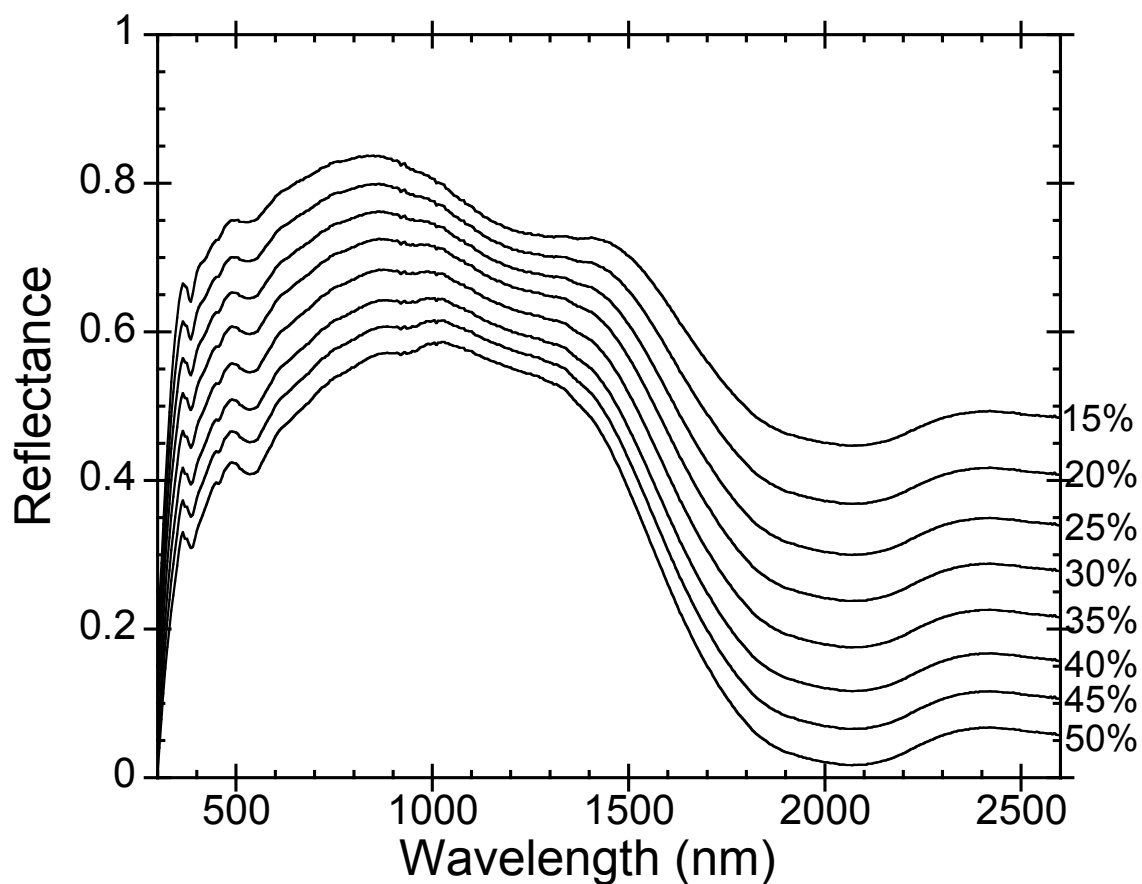


Figure 15. Mixture spectra modeled from 15-50 vol% mafic abundance (in 5 vol% increments) using the Hapke approach for the Plagioclase and Very High-Mg Spinel endmembers. The percentages denote mafic abundance. Spectra have been offset for clarity.

CHAPTER 3: The Distribution and Purity of Anorthosite across the Orientale Basin: New Perspectives from Moon Mineralogy Mapper Data

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Submitted to:

Journal of Geophysical Research

December 31, 2012

Revised:

August 8, 2013

Accepted:

August 11, 2013

Abstract

The Orientale basin is a multiring impact structure on the western limb of the Moon that provides a clear view of the primary lunar crust exposed during basin formation. Previously, near-infrared reflectance spectra suggested that Orientale's Inner Rook Ring (IRR) is very poor in mafic minerals and may represent anorthosite excavated from the Moon's upper crust. However, detailed assessment of the mineralogy of these anorthosites was prohibited because the available spectroscopic datasets did not identify the diagnostic plagioclase absorption feature near 1250 nm. Recently however, this absorption has been identified in several spectroscopic datasets, including the Moon Mineralogy Mapper (M³), enabling the unique identification of a plagioclase-dominated lithology at Orientale for the first time. Here we present the first in-depth characterization of the Orientale anorthosites based on direct measurement of their plagioclase component. In addition, detailed geologic context of the exposures is discussed based on analysis of Lunar Reconnaissance Orbiter (LRO) Narrow Angle Camera (NAC) images for selected anorthosite identifications. The results confirm that anorthosite is overwhelmingly concentrated in the IRR. Comparison with non-linear spectral mixing models suggests that the anorthosite is exceedingly pure, containing >95 vol% plagioclase in most areas, and commonly ~99-100 vol%. These new data place important constraints on magma ocean crystallization scenarios, which must produce a zone of highly pure anorthosite spanning the entire lateral extent of the 430 km diameter IRR.

1. Introduction

The Orientale basin, on the western limb of the Moon, is the youngest and most well-preserved multiring impact structure on the lunar surface [e.g., *Hartmann and Kuiper*, 1962; *Head*, 1974, 1977, 2012; *Howard et al.*, 1974; *Moore et al.*, 1974; *McCauley*, 1977; *Scott et al.*, 1977; *Croft*, 1981; *Wilhelms et al.*, 1987; *Spudis*, 1993]. Lunar Orbiter Laser Altimeter (LOLA) topography of the basin, shown in Figure 1, reveals three prominent concentric rings associated with Orientale: (1) the ~ 930 km diameter Cordillera Ring, (2) the ~ 620 km diameter Outer Rook Ring (ORR), and (3) the ~ 430 km diameter Inner Rook Ring (IRR). The Cordillera Ring forms an inward-facing relatively continuous scarp, while the ORR form a continuous to discontinuous set of inward-facing massifs and scarps mantled by the Montes Rook Formation. The IRR consist of isolated massifs, and clusters of massifs, similar in morphology to central peaks in complex craters and to rings and clusters of peaks in peak-ring basins [e.g., *Baker et al.*, 2011, 2012]. The IRR are draped and surrounded by the Maunder Formation, interpreted to be impact melt deposits.

The excellent morphological preservation of the Orientale basin rings offers a clear window into the composition of the highland crust that was exposed during basin formation [e.g., *Head et al.*, 2010a]. Lunar magma ocean (LMO) models predict an extensive zone of anorthosite, a rock type consisting of ≥ 90 vol% plagioclase [*Stöffler et al.*, 1980], in the Moon's upper crust [e.g., *Smith et al.*, 1970; *Wood et al.*, 1970; *Herbert et al.*, 1977; *Longhi*, 1977; *Warren and Wasson*, 1980; *Warren*, 1985, 1990; *Snyder et al.*, 1992; *Elkins-Tanton et al.*, 2011]. As primary crystallization products of the LMO, these anorthosites hold key information regarding magma ocean composition and

crystallization history (see *Shearer et al.* [2006] for a recent synthesis). However, early basin-forming impacts along with continued bombardment from smaller bodies [e.g., *Wilhelms et al.*, 1987; *Head et al.*, 2010b; *Fassett et al.*, 2012] produced a compositionally mixed “megaregolith” layer several kilometers thick across the Moon’s surface [e.g., *McGetchin et al.*, 1973; *Hartmann*, 1980; *Hörz et al.*, 1991; *Hawke et al.*, 2003; *Petro and Pieters*, 2008]. This mixed layer of impact ejecta obscures the anorthosites, as well as other ancient crustal lithologies such as the Mg-suite, from view by remote instruments. Exposures of igneous crustal materials are therefore mostly limited to the uplifted central peaks and peak rings of craters and basins that excavated primary crustal material from below the megaregolith [e.g., *Tompkins and Pieters*, 1999; *Matsunaga et al.*, 2008; *Cahill et al.*, 2009].

Numerous studies, discussed below, have noted the presence of anorthosite in the Orientale basin rings, particularly the IRR. The work described here represents the first dedicated analysis of the Orientale anorthosites that is based solely on exposures displaying the diagnostic plagioclase absorption feature, centered near 1250 nm. To distinguish these exposures from the bright, spectrally featureless materials discussed in numerous previous studies, we refer to the present identifications as “crystalline anorthosite.” Our specific goals are (1) to map the distribution of discrete crystalline anorthosite exposures throughout the Orientale basin, as indicated by the presence of a 1250 nm absorption in Moon Mineralogy Mapper (M^3) spectra, and (2) to estimate the “purity”, or plagioclase abundance, of the various anorthosite exposures by comparing the relative strengths of the plagioclase and mafic mineral absorptions in M^3 spectra.

2 Background

2.1 Indirect Spectral Evidence for Anorthosite

Spectral evidence for anorthosite in large craters and basins, including Orientale, has been documented previously using Earth-based telescopic data, the Clementine UVVIS camera, and the Galileo solid-state imager [e.g., *Spudis et al.*, 1984, 1989; *Pieters*, 1986; *Hawke et al.*, 1991, 2003; *Head et al.*, 1993; *Pieters et al.*, 1993; *Bussey and Spudis*, 1997, 2000]. Importantly, these instruments did not readily detect the diagnostic plagioclase absorption feature near 1250 nm, which would uniquely identify plagioclase or a plagioclase-dominated lithology. Instead, they identified areas that were consistent with anorthosite based on spectra that exhibited other characteristics of plagioclase-dominated rocks, namely (1) a high albedo, and (2) a lack of mafic mineral absorptions, indicating low modal proportions of olivine and pyroxene. The interpretation that these bright, mafic-poor regions were rich in plagioclase was supported by lower resolution orbital geochemical data, which noted high aluminum and low iron abundances in similar highland areas covered by the Apollo 15 and 16 spacecraft [e.g., *Adler et al.*, 1972a, b; *Spudis and Davis*, 1986].

Within the Orientale basin, evidence for anorthosite was found primarily in the IRR; other units in the basin appeared to have higher proportions of mafic minerals [e.g., *Spudis et al.*, 1984; *Bussey and Spudis*, 2000]. The distribution of these bright, spectrally featureless materials are shown in M^3 data for Orientale in Figures 2 and 3. In particular, Figure 2 demonstrates that the brightest pixels in the Orientale region, those with the highest reflectance values at 1489 nm, are concentrated in basin rings. Variations in the 1000 nm absorption strength, which is related to the abundance of mafic minerals, predominately pyroxene, is illustrated in Figure 3. The most feldspathic, mafic-poor

materials (dark in Figure 3) are clearly located in the non-mare portions of the basin interior. Upon closer inspection, the areas with the lowest proportion of mafic minerals in the scene correspond to the massifs of the IRR. The observation that different rings of the basin may have exposed different crustal lithologies makes Orientale a compelling laboratory for studying the distribution of primary products of the lunar magma ocean within the Moon's crust.

2.2 The Diagnostic Plagioclase Absorption

Anorthosites, which are dominated by a single mineral, should be easily identifiable on the lunar surface by near-infrared (NIR) spectrometers because plagioclase has a diagnostic crystal field absorption near 1250 nm. This absorption is caused by electronic transitions in Fe^{2+} cations substituting for Ca^{2+} in an irregular 8-12-fold site [e.g., *Conel and Nash*, 1970; *Bell and Mao*, 1973; *Adams and Goullaud*, 1978]. Figure 4 illustrates the ~1250 nm absorption in example plagioclase spectra. Only trace amounts of FeO (~0.1 wt%) in the crystal structure are necessary to generate the plagioclase absorption.

The plagioclase absorption is easily distinguished from the diagnostic ferrous absorptions of common lunar mafic minerals. For example, pyroxene absorptions occur near 1000 and 2000 nm [e.g., *Hazen et al.*, 1978; *Cloutis and Gaffey*, 1991; *Klima et al.*, 2007, 2011] whereas olivines typically display a composite absorption centered near 1050 nm [e.g., *Burns*, 1970, 1993; *Hazen et al.*, 1977]. Importantly, the relatively low concentration of iron in plagioclase coupled to the transparent nature of the mineral causes the 1250 nm absorption feature to appear very weak in comparison with the mafic silicate absorptions. Laboratory and modeling studies of mineral mixtures have shown that the diagnostic plagioclase absorption feature is distinguishable only if plagioclase

comprises more than ~85 vol% of the bulk material measured by the spectrometer (assuming intimate mixture with typical lunar minerals such as olivine or pyroxene) [Nash and Conel, 1974; Crown and Pieters, 1987; Cheek and Pieters, 2012]. The dominant effect of small amounts of pyroxene on bulk spectral properties is demonstrated in Figure 5. Here, terrestrial laboratory mixtures consisting of 95 and 98 vol% plagioclase (remainder pyroxene) are shown. In this example, the laboratory mixture containing only 2 vol% pyroxene results in a ~1000 nm pyroxene absorption that is comparable in strength to the 1250 nm plagioclase absorption. Figure 5 also shows calculated mixtures of 95 and 98% plagioclase produced using the method described in Section 3. These calculated mixtures are discussed in more detail below.

The absence of the diagnostic plagioclase feature in telescopic data for Moon, which commonly has high spectral resolution covering the 1250 nm region, has typically been attributed to the effects of shock metamorphism on plagioclase crystals [e.g., Spudis *et al.*, 1984]. Relatively low shock pressures (between ~ 10 and 30 GPa) are known to cause internal fragmentation in feldspars [e.g., Stöffler, 1971; Hörz and Quaide, 1973]. Such fragmentation in transparent materials is expected to subdue crystal field absorptions by increasing light scattering and decreasing the effective path length for photons passing through mineral grains [e.g., Pieters, 1983]. In addition, beginning at moderate pressures of ~25 GPa, plagioclase crystals transform to a diaplectic glass called maskelynite [e.g., von Engelhardt and Stöffler, 1968; Stöffler, 1971]. Because maskelynite does not have the plagioclase structure necessary to generate the crystal field electronic absorption at ~1250 nm, increasing proportions of this amorphous phase produced by extensive shock causes the strength of the diagnostic plagioclase band to

progressively weaken and ultimately disappear [Adams *et al.*, 1979; Bruckenthal and Pieters, 1984; Johnson and Hörz, 2003]. Importantly, diaplectic glasses are only known to form in tectosilicates such as feldspars and quartz; olivines and pyroxenes, by contrast, retain their spectral features even when subjected to relatively high shock pressures (e.g., ~ 60 GPa for pyroxene) [e.g., Hörz and Quaide, 1973; Adams *et al.*, 1979; Hörz *et al.*, 1991].

Recently, the Multiband Imager (MI) and Spectral Profiler (SP) onboard Japan's Kaguya mission have identified the plagioclase absorption in numerous locations across the Moon, including Orientale [e.g., Matsunaga *et al.*, 2008; Ohtake *et al.*, 2009; Yamamoto *et al.*, 2012]. Observations from M³ have also identified the plagioclase absorption in the IRR of Orientale [Pieters *et al.*, 2009], and a thorough global assessment of crystalline plagioclase at numerous basins and craters has recently been undertaken using M³ data [Donaldson Hanna, 2012, Donaldson Hanna, *in review*]. Because plagioclase must occur in high abundances in order to be distinguished spectroscopically in a bulk material (e.g., Figure 5), identification of the ~1250 nm plagioclase absorption feature in NIR spectra is essentially analogous to an anorthosite detection. The unambiguous identification of crystalline anorthosite at Orientale in several new datasets has motivated a detailed investigation of the distribution and purity of this plagioclase-dominated lithology exposed within this important lunar basin. In addition, we take advantage of the capability of M³, a high-resolution imaging spectrometer, to measure mineralogy in geologic context on both local and basin-wide scales.

3 Methods

3.1 Data

3.1.1 Moon Mineralogy Mapper (M^3)

M^3 is a hyperspectral imaging spectrometer that acquired near-global coverage of the Moon in 86 spectral channels from 430-3000 nm [Boardman *et al.*, 2011; Green *et al.*, 2011]. Here, we use publicly released Level 2 data from the instrument's Optical Period 2c2, when the spectrometer was at 200 km altitude and the spatial resolution was $\sim 280 \times 140$ m/pixel. Although the Orientale basin was covered extensively by M^3 during several different Optical Periods, the Op2c2 data for this region was found to be the most reliable and self-consistent. Seventeen Op2c2 data strips covering the basin, acquired when the detector temperature was 158 ± 1 K, were combined into a full-resolution mosaic. Although the mosaic covers the entire basin extent, we focus only on the non-mare portions of the scene; the nature, distribution and mineralogy of the mare deposits associated with Orientale are treated in Whitten *et al.* [2011].

3.1.2 Lunar Reconnaissance Orbiter Narrow Angle Camera

To evaluate the local geologic context of mineral exposures, Lunar Reconnaissance Orbiter (LRO) Narrow Angle Camera (NAC) images were analyzed for twelve massifs that contained regions displaying 1250 nm plagioclase absorptions. The images were processed and projected using the USGS Integrated Software for Imagers and Spectrometers (ISIS), imported into ESRI's Geographic Information System (GIS) software ArcMap, and georeferenced with M^3 data. Overlaying the M^3 data on NAC images reveals meter-scale information about the terrain contained in individual M^3 pixels. The specific NAC images examined are given in Table S1 of the Auxiliary Material.

3.2 Spectroscopy of Plagioclase – Pyroxene Mixtures.

A major goal of this paper is to estimate the relative plagioclase abundances in crystalline anorthosite exposures within Orientale. Our approach is based on comparing the relative strengths of the ~ 1000 nm pyroxene absorption and the ~ 1250 nm crystalline plagioclase absorption in individual M^3 spectra. First, spectra are classified into three groups based on relative plagioclase and pyroxene absorption strength. The range of plagioclase abundances predicted for each group is then estimated by comparison with calculated spectra of different proportions of well-characterized endmembers. Non-linear calculations are required in order to account for the disproportionate effect of the pyroxene component on bulk spectral properties. Our approach for calculating mixture spectra involves:

- (1) converting endmember reflectance values (technically, radiance coefficient) to single scattering albedo (ω) with a look-up table that uses Equation 37 from *Hapke* [1981] for reflectance and the H-function approximations from *Hapke* [2002],
- (2) combining the ω spectra linearly over a range of mixture proportions weighted by the relative geometric cross section of each component, and
- (3) converting the resulting ω spectrum for each mixture to reflectance again using Equation 37 from *Hapke* [1981], which assumes that the two components are intimately mixed and that particles are spherical, closely spaced and large compared to the wavelength of light (e.g., particles that are tens of microns in diameter). We have also assumed an isotropic phase function and a backscattering term of zero.

Assuming that the two endmember components have the same particle size, their relative geometric cross sections are approximately equal to volume fraction (see Equation 17 in *Hapke* [1981]). Thus, plagioclase percentages discussed in this section and throughout the paper refer to volume proportions. We note that although the “mixing” step (step 2) is carried out linearly using single scattering albedo, we refer to the approach broadly as “non-linear mixing” because the relationship between single scattering albedo and measured reflectance is highly non-linear.

This modeling approach was tested by calculating mixture spectra for terrestrial plagioclase and pyroxene endmembers that could be validated against laboratory-prepared mixtures of the same endmembers. The compositions for these terrestrial endmembers are shown in Table 3. Two laboratory-prepared mixtures of these endmembers are compared to the corresponding mixtures calculated using the forward modeling approach (described above) in Figure 5. Additionally, we calculated mixtures in 0.1 vol% increments from 80 to 100 vol% plagioclase and found the calculated spectrum with the lowest root mean square error to the measured spectra of the laboratory-prepared mixtures containing 98 and 95% plagioclase. The best fit to the laboratory-prepared spectra for the 98 and 95% plagioclase mixtures are the calculated mixture spectra for 97.8 and 94.8% plagioclase, respectively. For these two examples, the mixture modeling approach is accurate to better than half a percent of plagioclase volume proportion. We emphasize that the endmembers used in the calculation shown in Figure 5 are not intended to be lunar analog spectra, so their absorption strengths may not represent the specific mineral compositions or textures at Orientale.

Because the non-linear mixing approach described above is shown to be successful in modeling controlled mixtures prepared in the laboratory, we have confidence in using this approach to produce modeled mixtures of lunar sample input spectra, for which laboratory mixtures cannot be prepared. Using lunar sample endmembers with mineral compositions similar to those found in lunar anorthosites improves the fidelity of the modeled spectral characteristics to those observed at Orientale. The modeled mixtures produced from laboratory spectra of lunar endmembers are described in Section 4.

4 Results

4.1 Exposures with Discrete Mineral Absorptions

Many lunar surface materials consist of well-developed soils, and crystal field absorptions of constituent minerals are commonly subdued by prolonged exposure to the space environment [e.g., *Adams and McCord*, 1970, 1973; *Pieters et al.*, 2000]. In this analysis, we focus instead on non-mare regions of Orientale with spectra displaying clear absorption features that can be confidently assigned to either mafic minerals or plagioclase. Small, discrete exposures are distinguished from background soils using a combination of spectral parameters, described in Table 1, that are designed to highlight pixels with prominent NIR absorptions due to plagioclase, pyroxene, olivine, or spinel in M^3 data. The 1000 nm absorption strength map in Figure 3 shows that non-mare basin materials generally lack strong ferrous absorptions on a regional scale, indicating a feldspathic character. Individual massifs or small craters, however, often exhibit small areas with distinct NIR absorption features. Inspection of the spectra for these areas

suggests that the dominant mafic mineral is pyroxene, and the short-wavelength positions of the pyroxene absorptions indicate a low-Ca composition. Olivine and spinel are uncommon or absent in the region. Thus, characterizing the varying abundances of plagioclase across the basin (below) predominately involves comparing the relative strengths of the plagioclase and low-Ca pyroxene absorptions.

When the three parameters in Table 1 are viewed simultaneously in an RGB image and stretched to highlight the strongest absorptions, areas that contain pure plagioclase are generally distinguished from areas with spectra displaying only pyroxene absorptions. Spectra that contain a combination of the plagioclase and pyroxene absorptions (e.g., a composite feature between 1000 and 1500 nm), are also apparent. Ignoring well-developed soils with weak features (absorption strengths less than ~1%) and small scale mixed materials, we have identified nearly 800 representative discrete areas across the region with clear absorptions attributable to either plagioclase, pyroxene, or both. Individual spectra of these areas were evaluated for internal consistency and classified as described below. The locations of these discrete exposures, irrespective of their relative plagioclase and pyroxene absorption strengths, are shown in Figure S1 of the Auxiliary Material. We note that the region exterior to the Cordillera Ring in the southwestern portion of the scene displays an interesting concentration of small, mafic-rich craters that have not been mapped here. We have focused on a representative selection of these materials since they appear to be uniformly pyroxene-dominated, but a detailed investigation of these locations in the context of other mafic-rich basin materials warrants further study.

4.2 Spectral Classes

The discrete areas across the basin with distinct NIR absorptions can be broadly classified into three types based on their relative plagioclase and pyroxene absorption depths. These three spectral types include: (1) spectra that are dominated by a crystalline plagioclase absorption near 1250 nm and lack evidence for a pyroxene absorption near 1000 nm (Class A), (2) spectra that display composite absorptions (a “w” shape), in which the pyroxene ~1000 nm absorption is approximately subequal to the plagioclase ~1250 nm absorption (Class B), and (3) spectra with a ~1000 nm pyroxene absorption that dominates or is clearly stronger than the plagioclase absorption (Class C). These classes of non-mare materials across Orientale are described in Table 2, and a spectrum representing each spectral type is shown in Figure 6. In this analysis, we have focused mainly on the ~1000 nm pyroxene band, rather than both the ~1000 nm and ~2000 nm pyroxene absorptions, because of the difficulty in accurately measuring subtle ~2000 nm absorptions due to possible residual thermal emission contributions to the spectrum.

The three spectral types of non-mare material across Orientale are intended to be easily distinguished from one another by inspection of M^3 spectra in order to serve as a general framework for classifying anorthosite purity across the Moon. This approach takes advantage of the unique nature of anorthosite spectra, namely that small variations in the strongly absorbing pyroxene component result in large, easily distinguishable differences in bulk spectral properties of a plagioclase-dominated rock (e.g., the presence vs. absence of a pyroxene absorption feature). Several automated approaches for evaluating relative mineral abundances (such as absorption band thresholds) were tested for assigning each spectrum to a class, but such tools are found to be unreliable and very sensitive to other variables, largely instrumental, in addition to mineral abundance, that

are not easily controlled. Manual inspection using the above criteria to evaluate the plagioclase and pyroxene absorption features observed in continuum-removed spectra proved to be the most reliable method to avoid false positive identification of absorptions. This is partly due to the fact that most spectra from this feldspathic region do not display strong spectral contrast, and absorption strengths are typically on the order of 5% - 10% or less of the total continuum-removed reflectance.

4.3 Plagioclase Abundances

Comparison of each spectral class with calculated mixtures of lunar plagioclase and pyroxene spectra demonstrates that many spectra from the Orientale basin represent very high plagioclase abundances. Model spectra calculated from lunar endmembers using the non-linear method described in Section 3 are shown in Figure 7. The lunar sample endmembers for this calculation were selected to be within the compositional range expected for the plagioclase and pyroxene in lunar anorthosites based on the sample collection [e.g., *Ryder and Norman*, 1978; *Warren and Wasson*, 1980; *James et al.*, 1989; *McGee*, 1993; *Warren*, 1993]. Specifically, we have chosen a plagioclase endmember with 0.1 wt % FeO from highland soil 62241, and a low-calcium pyroxene separate (En₆₄Fs₂₉Wo₇) from basalt 15058. The use of a basaltic low-calcium pyroxene rather than a spectrum of an anorthositic pyroxene was dictated by the availability of measured lunar pyroxene separates in the RELAB database. The major element compositions of the lunar sample endmembers used in the mixture calculations are described in Table 3. A discussion of other factors such as mineral composition and grain size that may influence the modeling of absorption features is given in the Appendix C. Although it is difficult to quantify the absolute error associated with each of these

additional factors, their effect on *relative* absorption strengths is likely small and should not significantly affect the results described here.

As demonstrated in Figures 5 and 7, pyroxene is the optically dominant component in a plagioclase-pyroxene mixture. The addition of small amounts of pyroxene to the bulk mixture leads to systematic effects on bulk spectral properties. Calculated spectra for only the 99% and 100% plagioclase mixtures lack a detectable ~1000 nm pyroxene absorption and are analogous to Class A spectra from Orientale. Calculated spectra corresponding to 96-98% plagioclase are analogous to Orientale Class B spectra because they contain composite absorptions with ~1000 nm pyroxene features that are subequal in strength to the ~1250 nm plagioclase feature. Class A and Class B both clearly represent highly pure anorthosite, containing <5% pyroxene. In the following discussions we refer to Classes A and B collectively as ‘anorthosite’. We emphasize that the distinction between Classes A and B is defined only in terms of their spectral properties. The differences in mineralogy represented by these two classes is small, but detectable with the current spectroscopic data.

For Class C spectra, however, the dominant absorptions are due to pyroxene. Locations exhibiting Class C spectra have not been further analyzed for mafic content, but can represent a variety of compositions that are <95 vol% plagioclase. We note that many Class C locations may therefore also represent anorthosites, *sensu stricto*, and we believe this to be the case for many of the exposures within the basin rings.

4.4 Local Geologic Context of Crystalline Anorthosite Exposures

Crystalline anorthosite exposures in Orientale are commonly small (<1 km), which likely precluded their identification in Earth-based telescopic data that have spatial resolutions typically between 2 and 10 km [see *Ohtake et al.*, 2009]. As illustrated with

high spatial resolution NAC images in Figure 8 and the Auxiliary Material, the exposures principally occur on massif crests and in small fresh craters. Analysis of the NAC images showed that the plagioclase detections are typically, but not exclusively, correlated with morphologically fresh material such as meter-scale blocks or small bright craters. In nearly all cases the plagioclase detections are surrounded by spectrally featureless material rather than mafic material. In Figure 8a, M^3 pixels containing crystalline anorthosite are highlighted based on the IBD1250 parameter and overlain on a portion of a co-registered NAC image. M^3 spectra corresponding to each of the six locations annotated in Figure 8a are shown in Figure 8b, and continuum-removed spectra are shown in Figure 8c. A selection of four additional NAC images, with M^3 plagioclase detections overlain, is provided in the Auxiliary Material.

4.5 Distribution of Crystalline Anorthosite Exposures

The distribution of non-mare exposures with strong mineral absorptions that were examined in this analysis is shown in Figure 9, with each location color coded to indicate the spectral class based on the criteria in Table 2. Exposures estimated to contain more than ~95% plagioclase, namely Class A and Class B, are represented by red and yellow symbols, respectively. The remaining locations (black symbols) are classified as Class C and are estimated to contain less than ~95% plagioclase. Crystalline anorthosite with more than ~95% plagioclase is shown to be overwhelmingly concentrated in the IRR, although a few examples can be found in the ORR, near the Cordillera Ring, and associated with large craters such as Maunder, Kopff, and Schlüter. Further, Figure 9 also demonstrates that the majority of crystalline anorthosite exposures in Orientale are of the highest purity distinguishable by NIR spectroscopy (Class A) and are estimated to contain 99-100 vol% plagioclase on the basis of non-linear spectral modeling.

5 Discussion

5.1 Implications for Orientale Basin Formation

5.1.1 Crystalline Anorthosite

The distinctly crystalline nature of the numerous, small anorthosite exposures described here offers insight into the formation of the complex but well-preserved Orientale basin. Specifically, a strong 1250 nm absorption in spectra of these exposures requires that most of the plagioclase in the local target rocks either (1) never experienced shock pressures sufficient to produce maskelynite during the basin forming impact (~ 25-30 GPa), or (2) transformed into maskelynite during the impact event but later recrystallized back into feldspar. Determining the peak shock pressures experienced by the rocks of the IRR requires additional detailed modeling of peak-ring formation, and resulting estimates will depend heavily on the location, relative to the sub-impact point, from which these complex structures were derived. Numerical simulations of the terrestrial Chicxulub impact basin (180 km in diameter) do suggest that peak shock pressures experienced by material uplifted to form its peak ring could exceed 25 GPa [e.g., *Morgan et al.*, 2011]. On the Moon, such peak shock pressures would be sufficient to enable transformation of plagioclase to maskelynite, although it is unclear how such estimates would scale to an Orientale-sized impact. For example, some numerical simulations of the Orientale impact suggest that sampling depths for the IRR could be in the lower crust and mantle [e.g., *Potter et al.*, 2013], seemingly inconsistent with the abundance of highly pure anorthosite described here.

A number of experimental studies have shown that annealing maskelynite at temperatures of ~800-1000° C results in a restoration to the original plagioclase structure in under an hour [*Arndt et al.*, 1982; *Ostertag and Stöffler*, 1982]. This type of

recrystallization was invoked by *Gibson and Reimold* [2005] in describing the shock pressures experienced by the granofelses in the center of the Vredefort impact structure. While the apparently high post-shock temperatures in the Vredefort dome maybe related to subsequent magmatic events [*Gibson and Reimold*, 2005], it is prudent to consider recrystallization having occurred in lunar craters and basins as well. Ultimately however, if the effects of recrystallization could be well-characterized by estimating the post-shock thermal environment of the rings of Orientale, these undisputed observations of the presence of crystalline plagioclase can be used to constrain a lower limit for the distribution of peak shock pressures within the basin.

5.1.2 Spectrally Featureless Anorthosite

Bright, spectrally featureless materials, which have been previously been attributed to “shocked” anorthosite [e.g., *Spudis et al.*, 1984], nevertheless occur commonly throughout the basin (Figures 2 and 3). In fact, M³ pixels displaying the crystalline plagioclase absorption feature are typically surrounded by spectrally featureless materials rather than by materials displaying mafic mineral absorption features (e.g., Figure 8). In the twelve different NAC images examined, spectrally featureless M³ pixels always correspond to well-developed, relatively block-free regions or soils. Examples of four of the NAC images examined are described in the Auxiliary Material. This observation suggests that other processes in addition to shock metamorphism of plagioclase grains (e.g., fracturing or transformation to maskelynite) may contribute to the origin of spectrally featureless material within Orientale. For instance, the production of abundant nanophase iron on soil grains by prolonged exposure to the space environment is also known to substantially weaken absorption bands [*Pieters*

et al., 2000; *Hapke*, 2001; *Lucey*, 2002; *Noble et al.*, 2007], suggesting that soil maturation processes may play an important role. However, these processes must be somewhat limited in the Orientale areas in order to remain consistent with the observed brightness of the IRR [e.g., *Pieters et al.*, 2000; *Hapke*, 2001]. More extensive analyses of the spatial relationship between crystalline exposures and spectrally featureless anorthositic terrain may reveal clues about the complex shock history experienced by basin materials.

5.1.3 Peak Ring Formation

Regardless of the shock history of the anorthosite in Orientale, the concentration of the crystalline plagioclase-dominated materials within the inner ring of the basin must be linked to its formation. The overall lack of mafic minerals observed in Orientale non-mare basin materials has long suggested that the impact event did not expose and eject significant amounts of material from deep in the lower crust or mantle [e.g., *Head et al.*, 1993, 2010a; *Pieters et al.*, 1993, 2009], even if the transient cavity may have penetrated to those depths [e.g., *Head*, 2010; *Baker et al.*, 2011, 2012]. It is important to note that the IRR shares key properties with peak-rings of smaller peak-ring basins – two-ringed basin structures that characterize the transition from complex craters (smaller) to multi-ring basins (larger). Recent studies of peak-ring basins characterized on the basis of new LRO LOLA data and LROC images [*Baker et al.*, 2011, 2012] show that over the diameter range from ~200 to ~600 km many morphometric characteristics change in substantial ways. Trends are observed for peak-ring basins [*Baker et al.*, 2011, 2012] that are consistent with a model in which, at the onset diameter of peak-ring basins, the volume and depth of melting affects the interior morphology of the basin and suppresses

central peak formation [Cintala and Grieve, 1998; Head, 2010; Baker and Head, in review]. Peak rings are thought to be associated with centro-symmetric collapse and bulking of the collapsing transient crater rim, which is rotated into position by extreme uplift of the crater floor. An important prediction of this model is that the sampling depths of peak rings should be relatively shallow, predominantly in the upper crust [e.g., Baker and Head, 2012]. Such a perspective for the formation of the Orientale basin is consistent with our findings of upper crustal anorthosite being the dominant component of the Inner Rook Ring (Table 2, Figure 9). It is important to note that several other lunar basins, such as Nectaris, Grimaldi, and Humorum have also been reported to expose anorthosite in their inner rings based on telescopic and Clementine data [Spudis *et al.*, 1989; Hawke *et al.*, 1991; Bussey and Spudis, 2000]. Such anorthosite identifications are confirmed by the more recent Kaguya and M³ data [Ohtake *et al.*, 2009; Donaldson Hanna *et al.*, 2012; Donaldson Hanna *et al.*, in review; Yamamoto *et al.*, 2012].

5.2 Implications for the Lunar Magma Ocean

Determining the abundance of plagioclase in the Moon's anorthositic crust is an important goal in lunar science because of the implications for magma ocean composition and crystallization history. In most LMO models, the anorthositic crust is generally thought to have formed by flotation and accumulation of plagioclase crystals from a dense, high-FeO residual liquid after ~80% solidification [e.g., Snyder *et al.*, 1992; Elkins-Tanton *et al.*, 2011]. However, the details of this process remain somewhat unclear in terms of predictions of the actual modal abundance of plagioclase in the resultant crust. Feldspathic lunar meteorites, which likely represent averages over large areas of the Moon's crust, tend to be significantly more mafic than the anorthosites discussed here for Orientale, ranging from 76-89 vol% normative plagioclase [Korotev *et*

al., 2003]. However, the most reliably pristine ferroan anorthosite samples, which are more analogous to the materials exposed at Orientale, average 93.7 +/- 6.7 vol% plagioclase [Warren, 1990]. The range of plagioclase modes for these pristine anorthosite samples is large, and includes compositions that are too mafic to be considered anorthosites, *sensu stricto*. Other examples in this ferroan anorthosite suite, however, clearly range up to plagioclase abundances similar to those reported here for Orientale and for other areas across the Moon measured by the MI and SP spectrometers onboard Kaguya [Ohtake *et al.*, 2009; Yamamoto *et al.*, 2012].

A key difference between lunar sample data and the new remote sensing measurements is spatial scale. Although study of lunar samples can provide detailed information on the composition and textures of lunar anorthosites, limitations in either geographic extent sampled (e.g., Apollo and Luna samples) or available geographic context (e.g., feldspathic lunar meteorites) make it difficult to obtain a comprehensive view of magma ocean crystallization history solely from the currently available samples. As demonstrated in Figure 7 of this paper, high-spectral-resolution NIR data are sensitive to percent-level changes in the abundance of the mafic component of plagioclase-dominated rocks, and this level of detail can be now measured at outcrop scale. At Orientale, these new observations of crystalline anorthosite require that magma ocean crystallization must produce vast contiguous regions of anorthosite that contain no more than a few percent pyroxene in the upper crust. These pure, crystalline anorthosites are well exposed at the IRR in particular, with remnants presumably also currently below the surrounding megaregolith. The mechanism by which plagioclase is accumulated in terrestrial anorthosites is poorly understood, even when detailed stratigraphic context and

cumulus textures are preserved [e.g., *Irvine, 1980; Raedeke and McCallum, 1980; Ashwal, 1993; Namur et al., 2011*]. Indeed, study of cumulus rocks in layered mafic intrusions has shown that perfect adcumulus, monomineralic rocks are more rare than troctolites and norites, suggesting that crystal-crystal and/or crystal-liquid separation processes are commonly inefficient [e.g., *Raedeke and McCallum, 1980; Snyder et al., 1992*]. In general, the low density of plagioclase compared to the residual liquid and coexisting mafic minerals [e.g., *Elkins-Tanton et al., 2011; Suckale et al., 2012*] is thought to have facilitated the formation of a relatively pure plagioclase flotation crust at the top of the LMO [e.g., *Herbert et al., 1977*]. During the last stages of solidification, the plagioclase-dominated crust may have been further purified by the extraction of residual liquids via compaction and diffusion processes [*Morse, 1982; Parmentier and Liang, 2010*]. At Orientale, we have shown that these processes together must produce a massive and coherent zone of at least ~ 95% plagioclase over several hundred-kilometers.

6 Conclusions

Abundant exposures of crystalline anorthosite are identified and mapped across the Orientale basin based on the presence of the highly diagnostic plagioclase absorption feature in M^3 spectra. The anorthosite is concentrated overwhelmingly in the Inner Rook Ring, in agreement with previous data that indicated an abundance of mafic-poor materials in the region. The advantage of the high spectral resolution NIR data analyzed here, however, is that the presence of the diagnostic plagioclase absorption feature permits unambiguous identification of crystalline anorthosite as well as estimation of anorthosite purity at outcrop-scale over the full basin extent. The IRR anorthosite is exceedingly mafic-poor: most spectra from the inner ring either lack any discernable

mafic mineral absorptions, or have a mafic mineral absorption that is subequal in strength to the ~1250 nm plagioclase feature. Comparison with non-linear mixing calculations confirm that the plagioclase abundances in these anorthosites are very high, resembling modeled spectra containing >95%, and commonly > 99%, plagioclase. These new near-infrared spectroscopic data provide direct compositional observations of the lunar crust and therefore provide constraints on models of magma ocean crystallization:

- (1) The primary crystallization sequence early in lunar history must produce regions of the crust that are composed entirely of anorthosite that is nearly free of mafic minerals,
- (2) The overall stratigraphy of the crust and processes of multi-ring basin formation must result in this crustal anorthositic zone being exposed predominantly across the IRR of the Orientale basin during the impact event,
- (3) The areal extent of this anorthosite must be large enough to include the entire zone of crust sampled by the IRR during the Orientale impact. Similar spectroscopic analyses at other lunar basins will determine the extent to which this process is repeated across the Moon.

Acknowledgements

The authors thank P. J. Isaacson for help with the processing of LROC NAC images, and D. Hollibaugh Baker. for discussions about the mechanics of multiring basin formation. Discussions with S. Wiseman were extremely valuable in implementing the non-linear mixing models, and we thank T. A. Goudge for graciously providing the code. Support

for this research through the NASA Lunar Science Institute at Brown University
(NNA09DB34A) is gratefully acknowledged.

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Table 1. Spectral parameters used to evaluate near-infrared absorptions^a

Parameter	Measures	Estimates	Definition
IBD1250	Integrated Band Depth over the 1250 nm spectral region	Plagioclase abundance	$\sum_{n=0}^{26} 1 - \frac{R(1029 + 20n)}{R_c(1029 + 20n)}$ Sum of band depths between 1029 and 1698 nm relative to local continuum
IBD1000	Integrated Band Depth over the 1000 nm spectral region	Olivine and pyroxene abundance	$\sum_{n=0}^{26} 1 - \frac{R(789 + 20n)}{R_c(789 + 20n)}$ Sum of band depths between 789 nm and 1308 nm relative to a local continuum defined between 699 nm and 1578 nm
IBD2000	Integrated Band Depth over the 2000 nm spectral region	Pyroxene and spinel abundance	$\sum_{n=0}^{21} 1 - \frac{R(1658 + 40n)}{R_c(1658 + 40n)}$ Sum of band depths between 1658 nm and 2498 nm relative to a local continuum defined between 1578 nm and 2538 nm

^aDefinitions of the three spectral parameters used to identify mineral absorption features in this analysis of M³ data for the Orientale basin.

Table 2. Spectral classes of exposures examined across the Orientale basin^a

Spectral Class	Absorptions present	Dominant absorption	Estimated plagioclase content (vol%) ^b
A	~1250 nm (plagioclase)	~1250 nm (plagioclase)	99-100
B	~1250 nm (plagioclase) and ~1000 nm (pyroxene)	~1250 nm (plagioclase), and ~1000 nm (pyroxene) absorptions are similar in strength	96-98
C	~1250 nm (plagioclase) and ~1000 nm (pyroxene);	~1000 nm (pyroxene)	≤95

^aThe three spectral classes, defined by which mineral absorption is the most prominent in an M³ spectrum over the 1000-1500 nm region.

^bEstimated plagioclase contents for each class based on the results of the non-linear mixing analyses using lunar highland plagioclase and low-calcium pyroxene spectral endmembers (Figure 7).

Table 3. Microprobe analyses (oxide wt%) of endmembers in Figures 5 and 7^a

	Validation Samples (Fig. 5) ^b		Lunar Samples (Fig. 7) ^c	
	Pyroxene	Plagioclase	Pyroxene	Plagioclase
SiO ₂	57.43	52.81	53.00	44.10
TiO ₂	0.06	0.07	0.30	0.00
Al ₂ O ₃	0.15	29.98	1.14	35.30
Cr ₂ O ₃	0.01	n/a	0.80	0.00
FeO	7.90	0.35	18.10	0.12
MnO	0.05	n/a	0.31	0.00
MgO	33.96	0.11	22.70	0.00
CaO	0.29	12.06	3.44	19.20
Na ₂ O	0.01	4.48	0.01	0.49
K ₂ O	0.00	0.28	n/a	0.03
Total	99.86	100.14	99.80	99.24
En'	88	n/a	64	n/a
Fs'	11	n/a	29	n/a
Wo'	1	n/a	7	n/a
An'	n/a	59	n/a	95

^aCompositions of the terrestrial samples were obtained by electron microprobe at Brown University, and compositions of the lunar endmembers were obtained from the RELAB database. En' = molar [Mg/(Mg + Fe + Ca)] in pyroxene. Fs' = molar [Fe/(Mg + Fe + Ca)] in pyroxene. Wo' = molar [Ca/(Mg + Fe + Ca)] in pyroxene. An' = molar [Ca/(Ca + Na + K)].

^bValidation (terrestrial) pyroxene is from Bamble, Norway. Validation (terrestrial) plagioclase is an inclusion-free sample from Mexico. Both samples wet-sieved to 45-75 μ m.

^cLunar pyroxene is a green pyroxene separate from 15058, <125 μ m particulate, RELAB ID: LR-CMP-173 [Isaacson *et al.*, 2011]. Lunar plagioclase is a separate from highland soil 62241, <125 μ m particulate, RELAB ID: LR-CMP-183 [Taylor *et al.*, 2001, 2010].

Figure Captions.

Figure 1. Figure 1. Topography of the Orientale basin, highlighting the three major topographic rings. Lunar Orbiter Laser Altimeter (LOLA) topography at 128 pixels per degree is overlain on a Lunar Reconnaissance Orbiter (LRO) Wide Angle Camera (WAC) mosaic. The image is clipped to cover the extent of the M³ data used in this analysis.

Figure 2. M³ mosaic of the Orientale basin. a) Reflectance at 1489 nm, stretched to display the total variation in brightness over the scene. Gaps in the M³ data coverage appear black. b) Reflectance at 1489 nm, stretched to show only the brightest 5% of pixels in the scene (highest reflectance values). The dashed lines indicate the three topographic rings shown in Figure 1, and demonstrate that the brightest pixels in the region are concentrated around the Inner Rook Ring.

Figure 3. Variations in 1000 nm absorption strength throughout the basin. a) M³ mosaic of the Orientale basin showing the strength of the 1000 nm absorption (IBD1000 parameter, described in Table 1). The strongest 1000 nm absorptions are bright. The white box in the southwestern portion of the IRR shows the area represented by Figures 3b and 3c. b) Close-up of the IBD1000 mosaic showing an example of one of the most mafic-poor regions within Orientale (stretch is the same as in 3a). c) Albedo image of the portion of the scene shown in 3b. Scale bar in both (b) and (c) is 10 km. The darkest, most mafic-poor pixels are clearly associated with bright massifs.

Figure 4. Example plagioclase spectra showing the diagnostic broad plagioclase absorption feature near 1250 nm (arrow indicates 1250 nm). Top spectrum in both (a) and (b) is a plagioclase separate from a lunar highland soil (particles <125 µm) (RELAB ID: LR-CMP-183), and the bottom spectrum (with symbols) is a plagioclase separate from the Stillwater complex (particles <500 µm) (RELAB ID: SW-CMP-012). a) Bidirectional reflectance measured in RELAB, b) Single scattering albedo calculated using the approach described in Section 3.

Figure 5. Spectra of example terrestrial plagioclase – pyroxene mixtures and corresponding endmembers. Note that these endmembers are not analogous to the lunar endmembers described elsewhere in the text in connection with the characterization of Orientale spectra. Rather, these samples are used to demonstrate the ability of the mixing model to accurately predict mixture spectra when tested against actual measured laboratory mixtures. Laboratory spectra are shown in solid lines and include the plagioclase and pyroxene endmember spectra as well as two measured mixtures of 95 and 98 vol% plagioclase. Modeled mixtures of 98 and 95 vol% plagioclase calculated using the approach in Section 3 are shown in black symbols and appear superimposed on the measured mixtures. The two arrows are positioned at 950 nm and 1250 nm to indicate the approximate center positions of the pyroxene and plagioclase absorption bands, respectively. Arrows at these wavelengths are added to all spectral plots that show both

plagioclase and pyroxene absorptions throughout the paper. The plagioclase endmember is a gem quality labradorite from Mexico, and the low-calcium pyroxene is from Bamble, Norway. Major element compositions of the endmembers are given in Table 3. All endmembers were wet-sieved with deionized water to 45-75 microns and reflectance spectra of endmembers and mixtures were acquired in RELAB relative to a Lambertian surface.

Figure 6. Representative M^3 non-mare spectra for each of the three classes of NIR absorptions observed in Orientale. a) Reflectance spectra offset for clarity (Class A offset + 0.05 and Class C offset – 0.05). b) Continuum-removed reflectance spectra, also offset for clarity, with continuum tie-points at 1030 and 1700 nm. Arrows are positioned at 950 nm and 1250 nm.

Figure 7. Calculated mixture spectra based on endmember plagioclase and pyroxene spectra from the Apollo sample collection. The spectra are colored according their spectral class. Class A spectra are shown in red, Class B spectra are shown in orange, with symbols. Class C spectra are shown in grey, up to 15% pyroxene. The arrows are positioned at 950 and 1250 nm. The plagioclase separate is from highland soil 62241, 21 (RELAB ID: LR-CMP-183). The low-calcium pyroxene separate (En₆₄Fs₂₉Wo₇) is from basalt 15058, 276 (RELAB ID: LR-CMP-173) [Isaacson *et al.*, 2011]. Both endmembers are particulates sieved to <125 μ m and their compositions are given in Table 3.

Figure 8. A traverse of M^3 spectra across one of the typical anorthosite-bearing IRR massifs shown in Figures 3b and 3c (–24.71°N, 260.58°E). Figure S1 in the Auxiliary Material denotes the location of this massif in the context of the basin. a) Portion of LROC NAC image M158238556RE overlaid with the M^3 pixels (light red) that exhibit a 1250 nm plagioclase absorption. Each symbol corresponds to the approximate location from which individual spectra were extracted, and is approximately the size of an M^3 pixel. Black symbols correspond to spectra that do not display the crystalline plagioclase absorption. Red symbols correspond to locations that do display the crystalline plagioclase absorption in their spectra. The arrow indicates the direction of the traverse and is correlated with the arrows in Figure 8b and c. For reference, one plagioclase-bearing M^3 pixel has been outlined in black to demonstrate scale. b) Reflectance spectra for each of the locations along the traverse shown in (a). The spectra are separated by one M^3 pixel along a diagonal. c) Continuum-removed versions of the spectra shown in (b).

Figure 9. Non-mare locations with strong mineral absorption features, shown classified according to their spectral properties. Class A (99-100% plagioclase) are represented by red symbols and Class B (96-98% plagioclase) are represented by yellow symbols. The remaining locations (black) are Class C ($\leq$ 95% plagioclase).

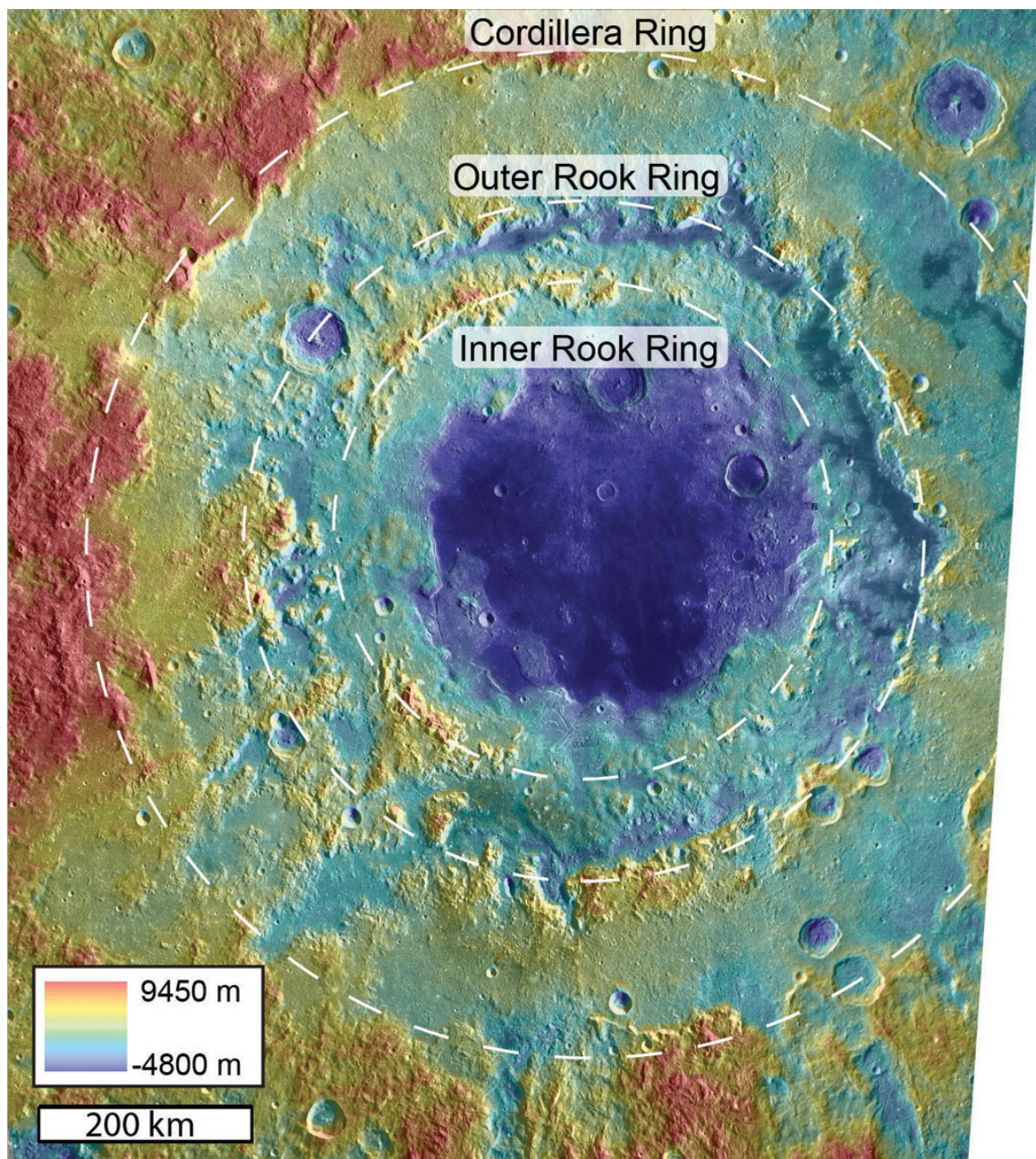


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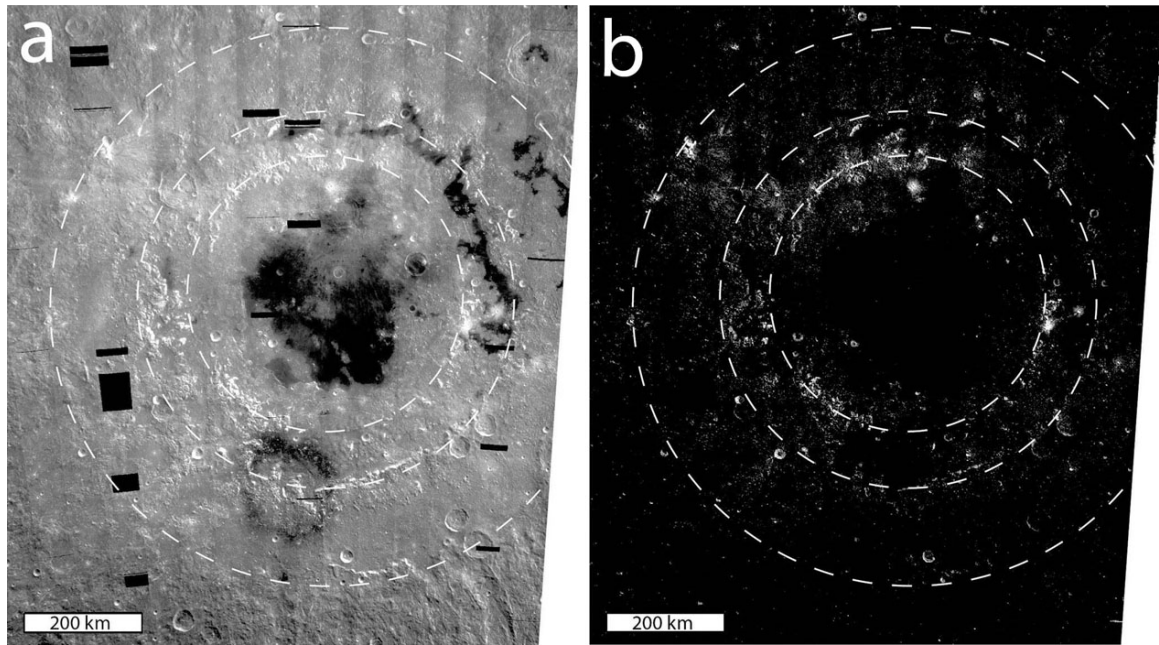


Figure 2. M³ mosaic of the Orientale basin. a) Reflectance at 1489 nm, stretched to display the total variation in brightness over the scene. Gaps in the M³ data coverage appear black. b) Reflectance at 1489 nm, stretched to show only the brightest 5% of pixels in the scene (highest reflectance values). The dashed lines indicate the three topographic rings shown in Figure 1, and demonstrate that the brightest pixels in the region are concentrated around the Inner Rook Ring.

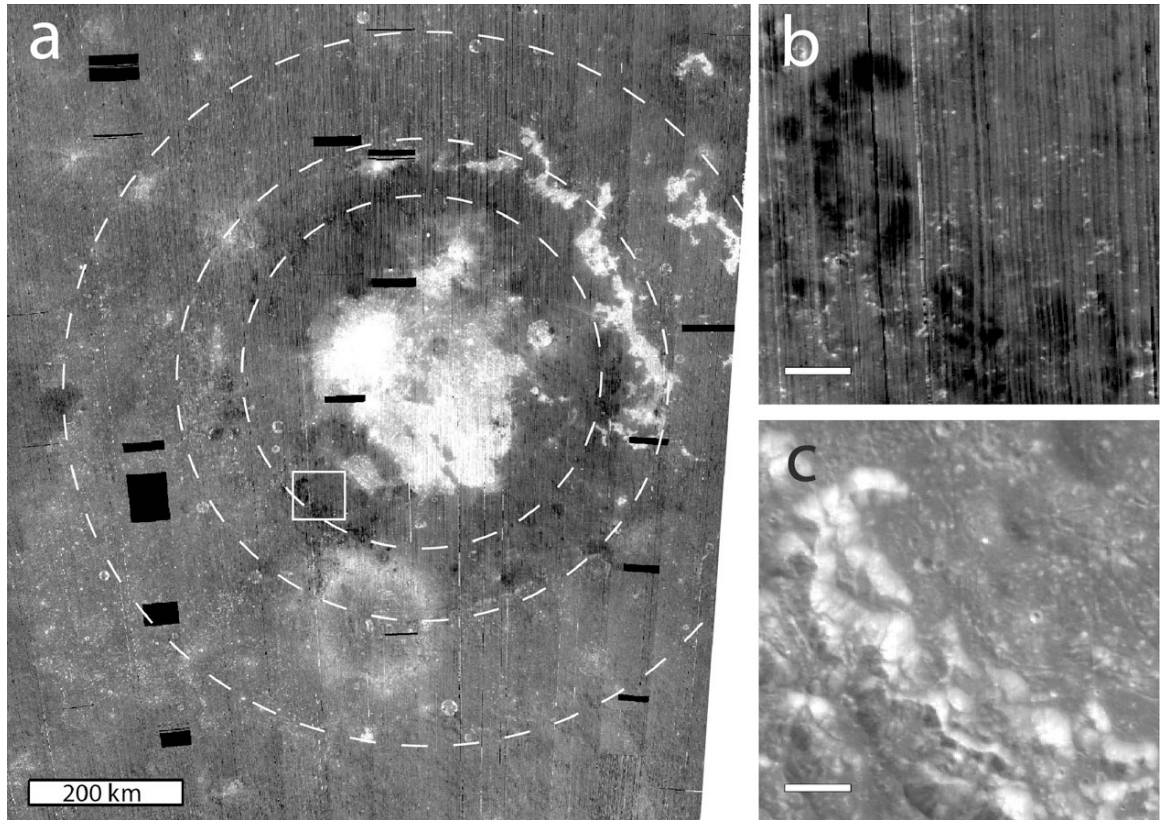


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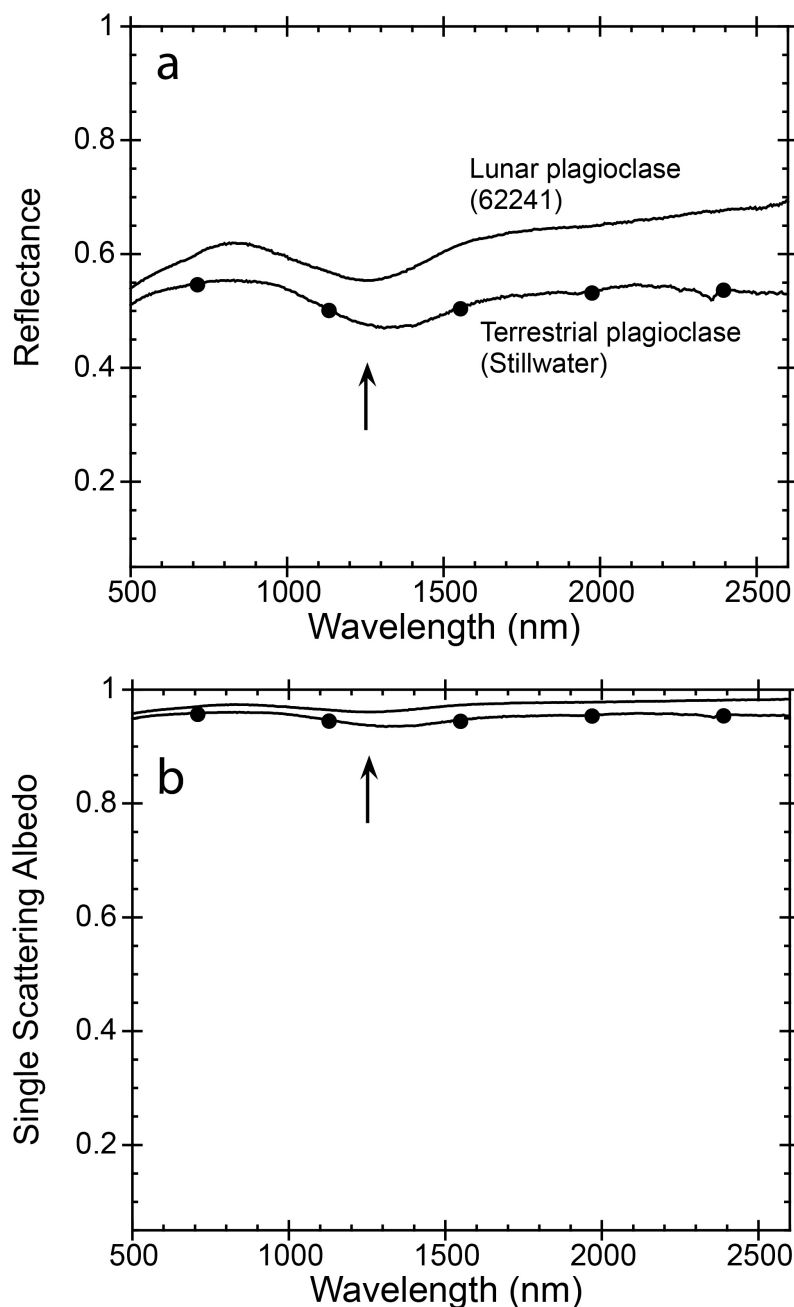


Figure 4. Example plagioclase spectra showing the diagnostic broad plagioclase absorption feature near 1250 nm (arrow indicates 1250 nm). Top spectrum in both (a) and (b) is a plagioclase separate from a lunar highland soil (particles $<125\ \mu\text{m}$) (RELAB ID: LR-CMP-183), and the bottom spectrum (with symbols) is a plagioclase separate from the Stillwater complex (particles $<500\ \mu\text{m}$) (RELAB ID: SW-CMP-012). a) Bidirectional reflectance measured in RELAB, b) Single scattering albedo calculated using the approach described in Section 3.

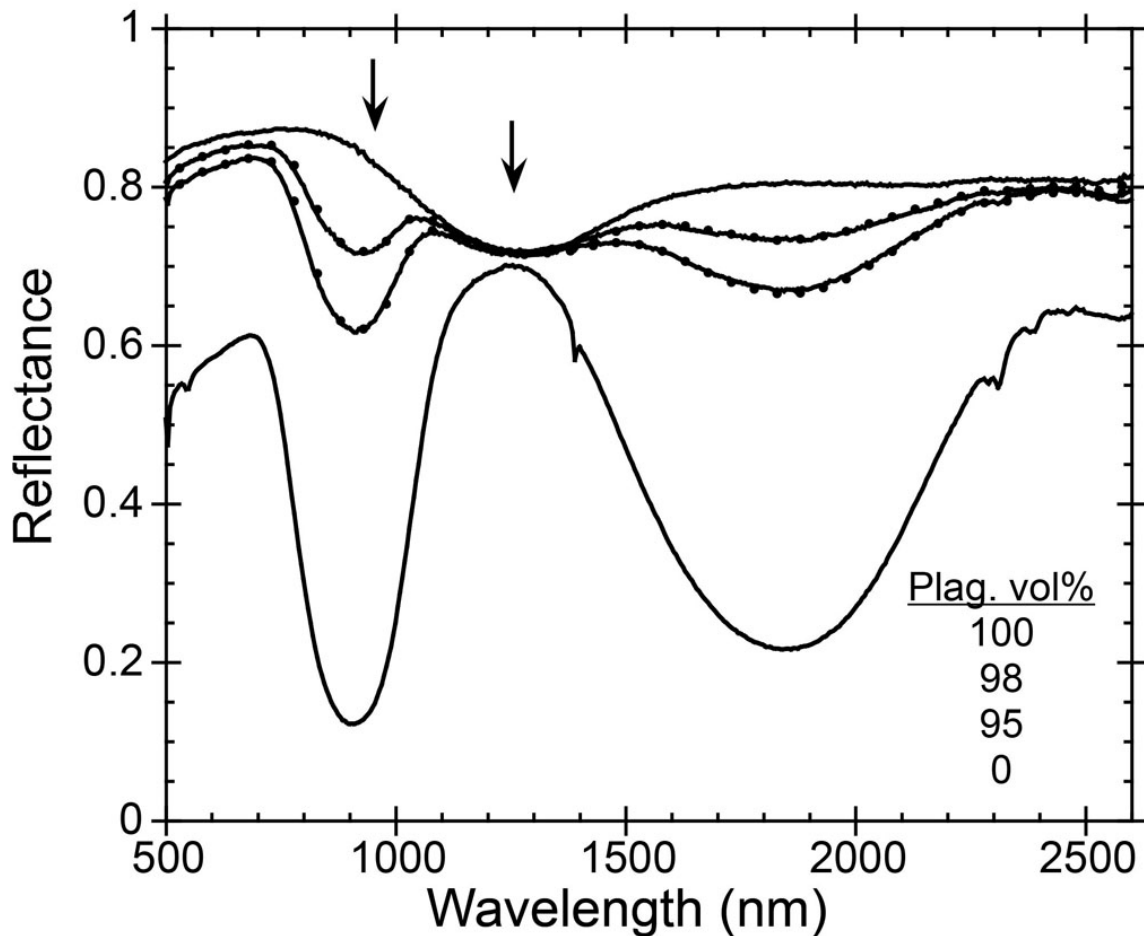


Figure 5. Spectra of example terrestrial plagioclase – pyroxene mixtures and corresponding endmembers. Note that these endmembers are not analogous to the lunar endmembers described elsewhere in the text in connection with the characterization of Orientale spectra. Rather, these samples are used to demonstrate the ability of the mixing model to accurately predict mixture spectra when tested against actual measured laboratory mixtures. Laboratory spectra are shown in solid lines and include the plagioclase and pyroxene endmember spectra as well as two measured mixtures of 95 and 98 vol% plagioclase. Modeled mixtures of 98 and 95 vol% plagioclase calculated using the approach in Section 3 are shown in black symbols and appear superimposed on the measured mixtures. The two arrows are positioned at 950 nm and 1250 nm to indicate the approximate center positions of the pyroxene and plagioclase absorption bands, respectively. Arrows at these wavelengths are added to all spectral plots that show both plagioclase and pyroxene absorptions throughout the paper. The plagioclase endmember is a gem quality labradorite from Mexico, and the low-calcium pyroxene is from Bamble, Norway. Major element compositions of the endmembers are given in Table 3. All endmembers were wet-sieved with deionized water to 45-75 microns and reflectance spectra of endmembers and mixtures were acquired in RELAB relative to a Lambertian surface.

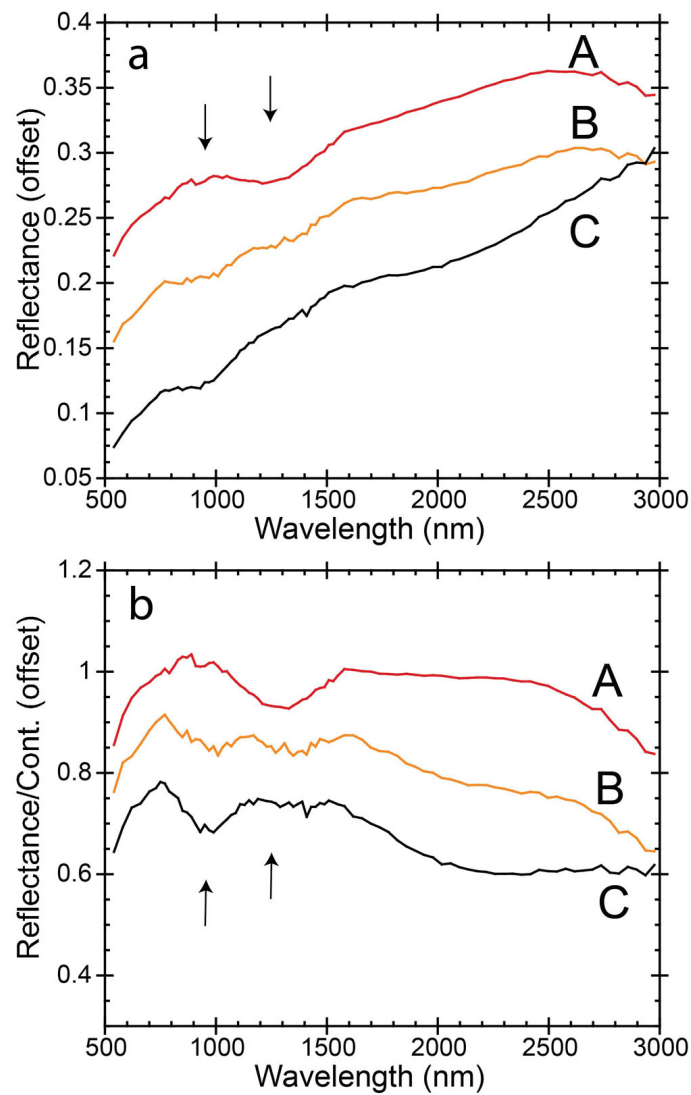


Figure 6. Representative M^3 non-mare spectra for each of the three classes of NIR absorptions observed in Orientale. a) Reflectance spectra offset for clarity (Class A offset + 0.05 and Class C offset - 0.05). b) Continuum-removed reflectance spectra, also offset for clarity, with continuum tie-points at 1030 and 1700 nm. Arrows are positioned at 950 nm and 1250 nm.

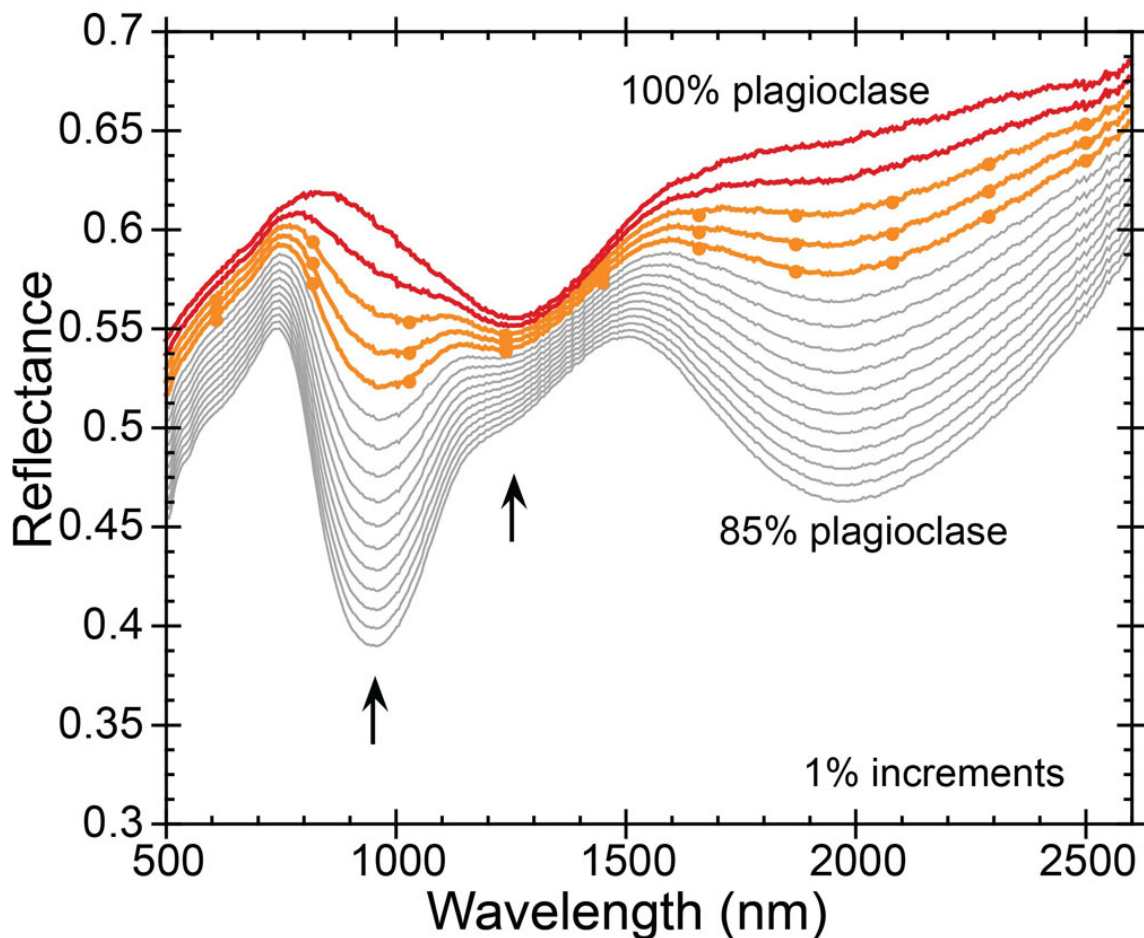


Figure 7. Calculated mixture spectra based on endmember plagioclase and pyroxene spectra from the Apollo sample collection. The spectra are colored according to their spectral class. Class A spectra are shown in red, Class B spectra are shown in orange, with symbols. Class C spectra are shown in grey, up to 15% pyroxene. The arrows are positioned at 950 and 1250 nm. The plagioclase separate is from highland soil 62241, 21 (RELAB ID: LR-CMP-183). The low-calcium pyroxene separate (En₆₄Fs₂₉Wo₇) is from basalt 15058, 276 (RELAB ID: LR-CMP-173) [Isaacson *et al.*, 2011]. Both endmembers are particulates sieved to <125 μm and their compositions are given in Table 3.

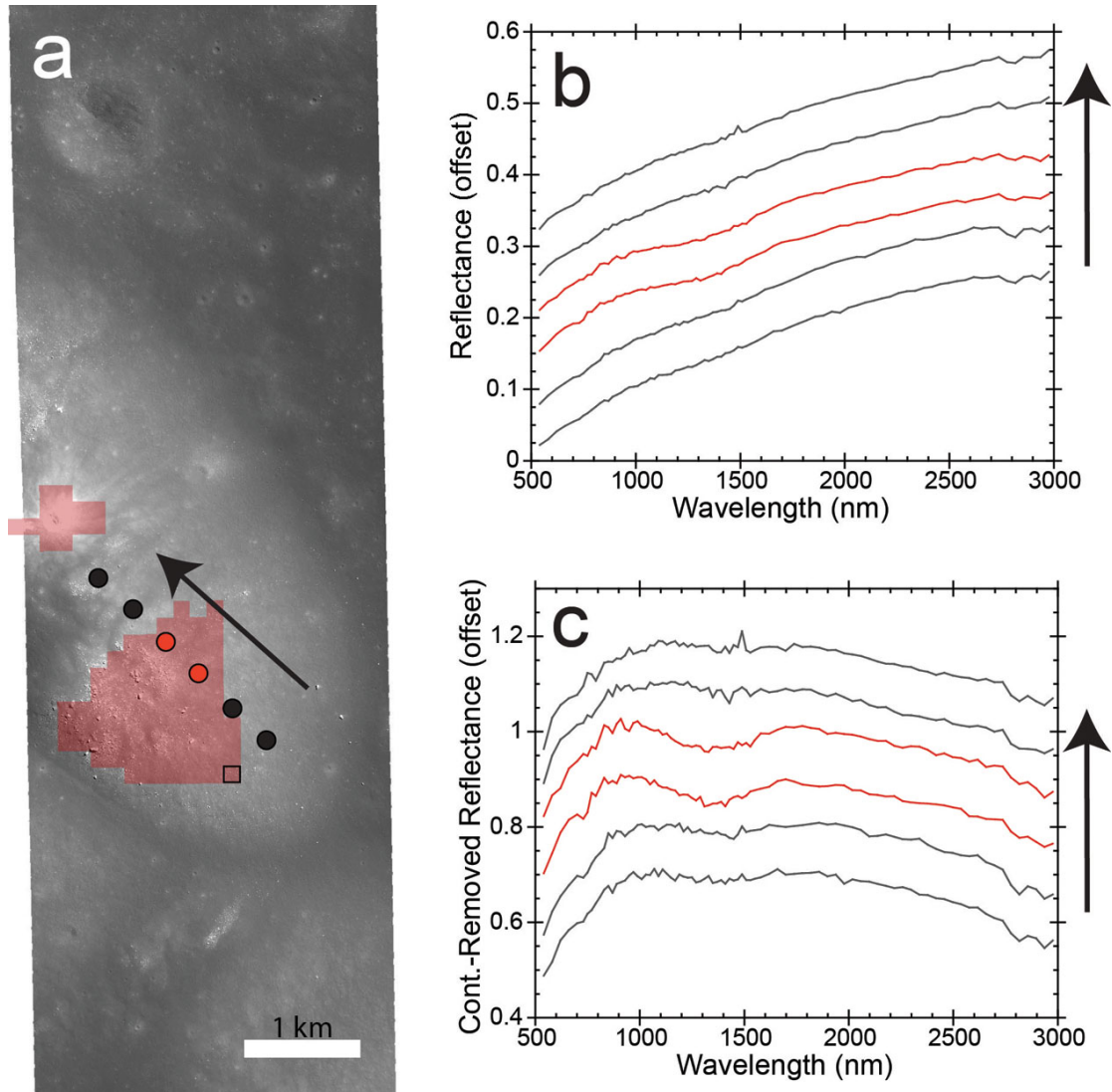


Figure 8. A traverse of M^3 spectra across one of the typical anorthosite-bearing IRR massifs shown in Figures 3b and 3c (-24.71°N , 260.58°E). Figure S1 in the Auxiliary Material denotes the location of this massif in the context of the basin. a) Portion of LROC NAC image M158238556RE overlaid with the M^3 pixels (light red) that exhibit a 1250 nm plagioclase absorption. Each symbol corresponds to the approximate location from which individual spectra were extracted, and is approximately the size of an M^3 pixel. Black symbols correspond to spectra that do not display the crystalline plagioclase absorption. Red symbols correspond to locations that do display the crystalline plagioclase absorption in their spectra. The arrow indicates the direction of the traverse and is correlated with the arrows in Figure 8b and c. For reference, one plagioclase-bearing M^3 pixel has been outlined in black to demonstrate scale. b) Reflectance spectra for each of the locations along the traverse shown in (a). The spectra are separated by one M^3 pixel along a diagonal. c) Continuum-removed versions of the spectra shown in (b).

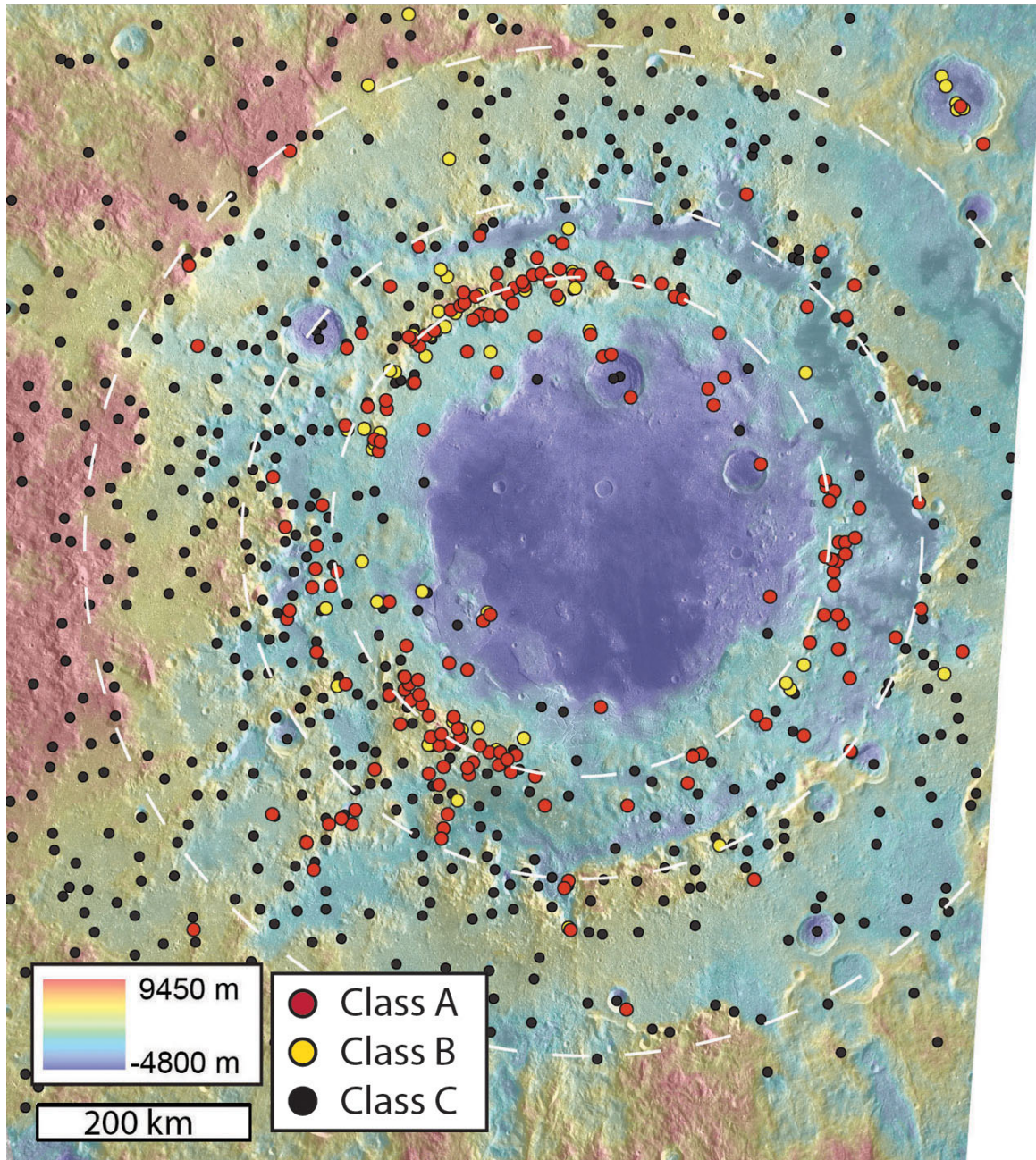


Figure 9. Non-mare locations with strong mineral absorption features, shown classified according to their spectral properties. Class A (99-100% plagioclase) are represented by red symbols and Class B (96-98% plagioclase) are represented by yellow symbols. The remaining locations (black) are Class C ($\leq 95\%$ plagioclase).

CHAPTER 4: Anorthosites at Tsiolkovskiy crater:
Mineralogic variations and connections to “ferroan” anorthosites

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Abstract

The mineralogy exposed in the central peak of Tsiolkovskiy crater is investigated in detail using new data from the Moon Mineralogy Mapper (M^3). Spectral parameters mapped across the central peak indicate that relatively mafic-free anorthosite is concentrated in a coherent zone along ridge crests. Analysis of spectra from this region indicates, however, that even the “purest” examples of this anorthosite contain subtle effects from a minor mafic component. Thus, the anorthosite at Tsiolkovskiy is distinguished from the completely mafic-free anorthosite observed elsewhere on the Moon. Further, the mafic component within the Tsiolkovskiy anorthosites is variable in both composition and abundance across the peak. The diagnostic spectral effects of a pyroxene endmember are clearly expressed in many areas that contain smaller abundances of plagioclase. The composition of this pyroxene is higher in calcium and/or iron than typical pyroxenes of the Mg-suite, and suggests the anorthosites exposed at Tsiolkovskiy share key mineralogic properties with the ferroan anorthositic suite observed in the lunar sample collection.

1. Introduction

The Moon's primary crust is believed to be comprised mainly of anorthosite, a rock type consisting of ≥ 90 vol% plagioclase, formed during the solidification of a magma ocean early in the Moon's history [e.g., *Smith et al.*, 1970; *Wood et al.*, 1970; *Dowty et al.*, 1974; *Snyder et al.*, 1992; *Elkins-Tanton et al.*, 2011]. The evidence for an anorthositic crust originated from the preponderance of plagioclase-dominated materials, including hand-sample sized anorthosites, in the returned samples from the Apollo missions [e.g., *Wood et al.*, 1970]. Additional confirmation has since come through the study of feldspathic lunar meteorites and various remote sensing observations that suggest large volumes of plagioclase must be present in the lunar crust [e.g., *Adler et al.*, 1972a, b; *Spudis et al.*, 1984, 1989; *Davis and Spudis*, 1985; *Spudis and Davis*, 1986; *Bussey and Spudis*, 1997, 2000; *Hawke et al.*, 2003; *Korotev et al.*, 2003]. Although a great deal of compositional information has been obtained for anorthosites in the sample collection, these examples either represent very restricted areas on the lunar surface (e.g., Apollo missions), or represent large averages of crustal composition in the absence of detailed geologic context (e.g., lunar meteorites). Remote sensing with near-infrared (NIR) sensors is capable of measuring detailed mineralogic information from rock exposures across the lunar surface based on broad absorption bands that are diagnostic of many of the rock forming minerals [e.g., *Burns*, 1993]. Examples of NIR spectra for plagioclase, olivine, pyroxene, and spinel are shown in Figure 1.

Orbital NIR measurements of the Moon have only recently identified the diagnostic crystalline plagioclase absorption feature, centered near 1250 nm [e.g., *Matsunaga et al.*, 2008; *Ohtake et al.*, 2009; *Donaldson Hanna et al.*, In Review;

Yamamoto et al., 2012]. Many locations displaying a crystalline plagioclase absorption display no indication of mafic mineral absorptions in their spectra, which would occur near 1000 and 2000 nm. These plagioclase-only spectra require an exceeding high level of “purity” or plagioclase abundance [e.g., *Donaldson Hanna et al.*, In Review, Chapter 2]. Other areas exhibit spectra that appear to be combinations of plagioclase and mafic (commonly pyroxene) absorption bands [*Donaldson Hanna et al.*, In Review; *Cheek et al.*, 2012]. To a first order, relative mineral absorption band depths are correlated with relative mineral abundance [Chapter 2]. In order to estimate the relative abundances of multiple mineral phases in a spectrum, it is necessary to identify their respective absorption bands. Laboratory mineral mixing studies suggest that exceedingly small amounts of mafic minerals or oxides exert a disproportionately large effect on bulk spectral properties [e.g., *Nash and Conel*, 1974; *Crown and Pieters*, 1987; *Mustard and Pieters*, 1987; *Serventi et al.*, 2013a]. This is an advantage in estimating relative mineral abundances for plagioclase-dominated rocks: percent-level variations in the strongly-absorbing mafic mineral content in plagioclase-dominated rocks produces measurable changes in the bulk spectrum [Chapter 2].

The present study aims to take advantage of this sensitivity in studying the spatial variations in relative mineral abundances at Tsiolkovskiy crater. Tsiolkovskiy is a 180 km diameter Late Imbrian central peak crater that is easily distinguished on the lunar farside by its mare filled interior. Central peaks of large craters such as Tsiolkovskiy are thought to represent deep-seated target material that was uplifted and exposed at the surface during the impact process [e.g., *Cintala and Grieve*, 1994]. These locations are important targets for NIR compositional studies because they provide rare windows into

primary crustal lithologies that are commonly obscured by a thick megaregolith layer on the Moon [e.g., *Hartman*, 1980; *Tompkins and Pieters*, 1999; *Hawke et al.*, 2003]. At Tsiolkovskiy, it is estimated that the central peak excavated on the order of 10-30 km into the surface, well into the crust [e.g. *Melosh*, 1989; *Cintala and Grieve*, 1994]. The steep ridges of Tsiolkovskiy's peak have been identified as having strong mineral absorptions that in many places are inconsistent with the low-calcium pyroxene dominated lithologies that are ubiquitous in central peak craters across the lunar surface [e.g., *Tompkins and Pieters*, 1999]. Previous multispectral analyses have suggested both plagioclase and olivine signatures in the central peak ridges [*Pieters and Tompkins*, 1999; *Heather and Dunkin*, 2002]. More recent analyses using hyperspectral data from the Spectral Profiler onboard the Kaguya spacecraft have identified mixtures of plagioclase and pyroxene (interpreted to be low-calcium) in the peak [*Matsunaga et al.*, 2008]. Here, we investigate the NIR signatures of the central peak using Moon Mineralogy Mapper (M³) data, an imaging spectrometer with high spectral resolution (83 bands) and 140 - 280 m spatial resolution. We take advantage of the combination of high spatial resolution, high spectral resolution, and wide spectral coverage to investigate variations in the mineralogy of the anorthosites and other lithologies within the central peak.

2. Data and Methods

Spectral image cubes from the Moon Mineralogy Mapper (M³) are analyzed for mineralogic variations within Tsiolkovskiy crater. A mosaic of six publicly available Level 2 M³ data strips were combined into a full-resolution mosaic covering the extent of the crater. The data were acquired when the detector was “warm” during Optical Period 2c1. Analysis of crater materials focuses primarily on the central peak,

using various spectral parameters that are mapped across the region. We focus on four parameters in particular. Three of these parameters calculate integrated band strengths across the major absorption features of interest: the ~1000 and ~2000 nm mafic absorptions, and the ~1250 nm plagioclase absorption. These are referred to as the 1000 IBD, 2000 IBD, and 1250 IBD parameters. Equations for these parameters are given in Table 1 of Chapter 3. A fourth parameter was developed to capture small variations spectra displaying both a pyroxene absorption near ~1000 nm and a plagioclase absorption near 1250 nm. This parameter was only calculated for the pixels displaying the strongest ~1000 nm and/or ~1250 nm absorption features. A 2-part continuum was removed from each of these strongly absorbing spectra [see *Moriarty et al.*, in review], which were then smoothed with a 3-point median filter to minimize the level of noise in each channel. The slope between the reflectance values at 1250 and 990 nm was calculated for all selected pixels as follows:

$$\text{1250-990 Slope} = \frac{R_{1250} - R_{990}}{1250 - 990}$$

Areas with relatively deeper pyroxene bands should have positive 1250-990 nm slope values. Spectra with negative 1250-990 nm slope values should correspond to plagioclase-dominated spectra. Areas with pyroxene and plagioclase bands that are similar in depth should have 1250-990 nm slope values close to zero. Spectra 1 and 4 in Figure 8 have been annotated to show the slope calculated using this parameterization. A similar approach was used to measure relative band depth variations for laboratory mixture spectra in Chapter 2.

3. Results

3.1 Basin Characteristics

Context images for Tsiolkovskiy crater are shown in Figure 2. An albedo image of the region, shown in Figure 2a, illustrates the location of Tsiolkovskiy within bright, uniform, and morphologically degraded highland terrain. The distinctive mare fill in the crater's interior has not covered the central peak, which is preserved in the center. When the region is viewed in a standard color composite (RGB), shown in Figure 2b, that is commonly used to show first-order mineralogic distinctions in M^3 data, additional complexity is evident in the central peak in particular. The RGB is mainly sensitive to the strengths of the major mafic silicate absorptions. In this depiction, highland materials and most of the central peak appear bright blue due to the absence of strong mafic absorptions. Mare units are combinations of reds, oranges, and yellows, depending on the relative proportions of olivine and pyroxene and their compositions. In Figure 2b, not only are the highland and mare portions of the scene distinguishable, but the ridges of the central peak also appear as a unique pink color, indicating some composition that is absorbing near 1000 nm (the red channel) but not near 2000 nm (green channel), and is also likely relatively bright (blue channel). Examination of the spectral properties of these ridges are the focus of the remainder of this paper.

3.2 Central Peak Characteristics

Some of the unique absorption properties of Tsiolkovskiy's central peak can be described using the band parameters shown in Figure 3. An albedo image of the peak is shown in Figure 3a. In general, most of the material is bright relative to the surrounding mare. The absorption strength of the 1000 nm spectral region is shown in Figure 3b. This parameter sums the absorption depths over an important spectral range, from 790 nm to

1309 nm, which covers nearly the full extents of typical olivine and pyroxene (short-wavelength) absorptions, and at least half of the plagioclase absorption. The ~1000 nm absorption strength is clearly enhanced on the ridges. The strength of the absorption across 1250 nm is shown in Figure 3c, which is also strong in the central peak.

Comparison of Figure 3 parts (b) and (c) shows that in general, many of the same regions are enhanced in both 1000 and 1250 nm absorption strengths. This is expected because the wavelength ranges of the plagioclase, olivine, and pyroxene absorptions all overlap to some extent in this region; the shoulders of any of these three mineral absorption bands could be measured by either of the two parameters shown in Figure 3b and 3c. It is also possible that the overlap in the spatial distributions of areas with high 1000 IBD and 1250 IBD values indicates that the spectra for these ridges are mixtures of plagioclase and mafic silicates. The distribution of the 2000 nm absorption feature, shown in Figure 3d, further distinguishes materials of the peak. Specifically, areas that display 1000 and/or 1250 nm absorptions but lack strong 2000 nm absorptions are representative of olivine or plagioclase.

3.3 Pyroxene and Plagioclase Components

The complexities associated with distinguishing overlapping mineral absorptions calls for a more detailed examination of individual spectra in order to make interpretations of central peak mineralogy. Close-up images for a region on the western ridge of the peak are shown in Figure 4, displayed in the same parameters as in Figure 3. The region covered by these images is outlined in Figure 3a and covers most of the westernmost ridge, which is apparent cutting diagonally through the albedo image in Figure 4a. Location 1 in Figure 4 displays high 1000 nm and 2000 nm parameter values but lacks strong 1250 nm parameter values, indicating that the spectrum is dominated by

a mafic component. A spectrum representing an average of seven pixels from Location 1 is shown in Figure 5a and b. The spectral signature from this area is clearly dominated by a pyroxene component as expected. Examination of the continuum-removed spectrum (Figure 5b) shows that the major pyroxene bands are centered near 990 nm and 2100 nm. These relatively long-wavelength center positions imply that the pyroxene composition is more iron and/or calcium rich than typical Mg-suite pyroxene, which have absorption centers below ~930 and 1900 nm [Cloutis and Gaffey, 1991; Klima *et al.*, 2011]. The shallow absorption feature near 1200 nm superimposed on the ~990 absorption could be due either to an M1 absorption in the pyroxene, to some small amount of plagioclase, or both. An average spectrum for six areas across the central peak representing some of the best pyroxene-dominated exposures is shown in Figure 6. Also shown in Figure 6 is an average spectrum representing typical pyroxene dominated spectra from the northeastern and southwestern walls of Tsiolkovskiy. As shown in the RGB image in Figure 2b, these pyroxene-dominated materials in the walls likely represent material that was derived from relatively shallower depths than the central peak and deposited as a heterogeneous mix along the rim of the final crater [e.g., Pieters and Tompkins, 1999]. Comparison of the pyroxene-dominated spectra in Figure 6 show that the examples from the walls of Tsiolkovskiy have shorter-wavelength band positions, near 2000 nm, and lack a ~1200 nm shoulder. Thus, to a first order it is clear that the central peak has tapped a unique portion of the crust that is not accessible by study of other surface materials in this region. The relationship between the pyroxene component and other central peak materials is discussed in the following sections.

Location 2 in Figure 4 displays relatively low 2000 nm parameter values, but is enhanced in the 1250 nm and 1000 nm parameter, suggesting that the spectra are dominated either by plagioclase or olivine. An average spectrum from this location displays strong absorptions resembling plagioclase, shown in Figure 5c and d. Note that as in Figure 5b, the y-axis scale for the continuum-removed spectrum has been expanded in order to better show spectral characteristics. It is important to note that this feature is not completely analogous to the pure plagioclase observed in the Orientale basin [Chapter 3] or many other locations across the lunar surface [Donaldson Hanna *et al.*, In Review]. Rather, the primary absorption is centered at relatively short wavelengths, near 1200 nm, and there is a weak absorption feature just long of 2000 nm. Further, the reflectance maximum on the short-wavelength side of the absorption occurs near 700 nm, whereas pure plagioclase observed elsewhere commonly has this maximum closer to 1000 nm [c.f., Chapter 3]. This recession of the short-wavelength maximum has been shown to be diagnostic of just a few percent mafic minerals in mixture with plagioclase, even if the primary mafic bands are not directly observable [Chapter 2]. A comparison of plagioclase spectra from Tsiolkovskiy and the Orientale basin illustrating these differences is shown in Figure 7. We interpret the unique characteristics of plagioclase-dominated spectra in Tsiolkovskiy to represent the spectral effects of very small amounts of mafic minerals in the bulk material. Although it appears that most of the “plagioclase” spectra in Tsiolkovskiy contain some small influence from a mafic component near 1000 and 2000 nm, we refer to spectra like those in Figures 5c and 5d as plagioclase. Spectra containing greater influences from a mafic component are discussed in more detail below.

3.4 Pyroxene and Plagioclase spectral mixtures

In addition to units spectrally dominated by either pyroxene or plagioclase, many locations resemble spectral combinations of the two, as described by *Matsunaga et al.* [2008]. These types of “mixture” spectra, shown in Figure 8, are characterized either by 1) highly asymmetric composite bands in which a plagioclase or pyroxene absorption is superimposed on the shoulder of the other (e.g., spectrum 4 in Figure 8), 2) by flat-bottomed spectra that have absorption minima spanning the entire spectral range from ~990 to ~1300 nm (e.g., spectra 1 and 2 in Figure 8), or 3) by spectral shapes intermediate to these two, often displaying two distinct absorptions (e.g., spectrum 3 in Figure 8). Spectra with two distinct absorption features near 990 and ~1250 nm, such as spectra 3 and 4 in Figure 8, are easily consistent with anorthositic rocks containing percent-level amounts of pyroxenes. Many exposures within the Orientale basin, particularly in the Outer Rook Ring, were interpreted in a similar manner [Chapter 3]. The wide, flat-bottomed shapes of spectra 1 and 2, however, are slightly more ambiguous. It is possible that they represent mixtures of the same components as spectra 3 and 4, but with a relatively weaker pyroxene band causing the two main absorptions in this wavelength region to overlap. These types of spectra were not observed at Orientale, but could be attributed to the slightly longer wavelength position of the pyroxene band at Tsiolkovskiy. However, similar composite spectra with relatively long-wavelength pyroxene bands observed in Spectral Profiler data [*Ogawa et al.*, 2010] data did appear to have two resolvable bands in this spectral region in most cases. This may suggest that the flattening observed for the Tsiolkovskiy spectra reported here is simply an artifact. Alternatively, these types of flattened spectra could represent mixing with a third minor

component that is absorbing between 1000 nm and 1250 nm, such as an olivine or very high-calcium pyroxene.

The relative strengths of the plagioclase and pyroxene absorptions in these composite spectra are variable across the peak and are related to the relative abundances of each component. To capture these subtle spectral variations, we use the 1250-990 nm slope parameter described above to group spectra across Tsiolkovskiy's central peak into three main classes: pyroxene-dominated (Class 1), intermediate (Class 2), and plagioclase-dominated (Class 3). Figure 9 demonstrates this classification for a small area on the western ridge. In Figure 9, spectra 1 and 2 correspond to the pyroxene-dominated spectral class. Spectra in this class may display both pyroxene and plagioclase absorptions, but the pyroxene component near 990 nm is deeper than the plagioclase component near 1250 nm. This class includes spectra resembling a pyroxene endmember as well as pyroxene-dominated spectral mixtures. Spectra in an intermediate class, represented by spectra 3 and 4, display plagioclase and pyroxene absorptions that are similar in depth to one another such as spectra 1-3 in Figure 8. The plagioclase-dominated class, corresponding to spectra 5 and 6 in Figure 9, contains the purest plagioclase endmember as well as spectra with a small pyroxene component superimposed near 990 nm. It is important to note that while these spectral classes are similar to those used to describe variations in the Orientale basin [Chapter 1], they are not directly analogous. While the "purest plagioclase" class in Orientale contained no mafic mineral signatures near 1000 nm, the plagioclase-dominated spectra in Tsiolkovskiy commonly display hints of a small mafic component that are subtle and not easily captured with the simple parameter used here (e.g., a shift of the main absorption to short

wavelengths and a slight widening in the absorption minimum, which is described in more detail below).

The spectra shown in Figure 9a and b correspond to a traverse down one of the ridge slopes, shown in Figure 9c. Each of the spectra in part (a) and (b) correspond to single pixels that are adjacent to one another along a diagonal. The pixels in Figure 9c are color-coded according to their spectral class, and delineate spatially coherent zones that are spectrally distinct. Moving from spectrum 1 to spectrum 6, the traverse first covers areas spectrally dominated by pyroxene (Class 1). Subsequent spectra contain subequal pyroxene and plagioclase absorption depths (Class 2), followed by spectra with dominant plagioclase absorption bands (Class 3). This example illustrates the abrupt spatial variations in mineral spectral signatures that were noted by *Pieters and Tompkins* [1999]. This classification scheme applied to all strongly-absorbing spectra of the central peak is shown in Figure 10. The strength of these absorption features are commonly 5 or 10%, although band strengths as low as about 1% were examined. As in the subset shown in Figure 9, it is clear that variations in the relative plagioclase and pyroxene abundances correspond to coherent, distinct zones in the central peak. Most of the plagioclase-dominated Class 3 locations are restricted to the ridge crests, whereas intermediate spectra in Class 2 are found downslope. Spectra that are dominated by pyroxene absorptions near 990 nm (Class 1) occur throughout the peak both on the ridge crests and as relatively small isolated exposures.

3.5 Possible third mineral component

Figure 10 describes major spectral variations in terms of the relative absorption depths at 990 and 1250 nm. However, closer inspection of many spectra from the peak suggests that not all may be simple combinations of these two endmember components.

For instance, many flat-bottomed spectra are considerably more narrow than those in Figure 8, with absorption minima extending from only ~1030 to 1250 nm. The band depths of the 2000 nm absorptions are typically shallower in these examples. Example spectra are shown in Figure 11, compared with examples of the wider, flat-bottomed spectra discussed above. These additional types of spectra could be analogous to the concave down (across 800-1000 nm) spectra attributed to an olivine-bearing lithology by *Pieters and Tompkins* [1999]. Laboratory mineral mixtures described in Chapter 2 suggest that these types of spectra could be consistent with mixing of plagioclase plus either olivine or a high-calcium pyroxene, and similar spectral characteristics are indeed observed in Copernicus crater, which is known to contain abundant forsteritic olivine [Pieters, 1982; Yamamoto *et al.*, 2010]. However, these spectra may also simply represent mixing of the same plagioclase and pyroxene endmembers but with even smaller proportions of pyroxene than in the wider flat-bottomed spectra shown above. The laboratory mixtures in Chapter 2 suggest that 2-5 vol% mafic minerals have the effect of distorting the main plagioclase band, but the local minima across all composite absorptions generally coincide with the band center positions of each endmember component. By comparison with these laboratory examples, shown in Figure 12, mixing a component with an absorption minimum near 990 nm may not be expected to generate composite absorptions with minima at longer wavelengths. However, distinguishing such small variations in band minima may be more difficult for remote data, and the origin of the more narrow composite absorptions is considered ambiguous at this point.

4. Discussion and Synthesis

The mineralogic variation in Tsiolkovskiy's central peak can now be characterized in geologic context using modern spectrometers with high spatial and spectral resolution. Much of the material along the ridge crests of the central peak is dominated by a relatively pure anorthosite containing only a few percent mafic minerals. An important new result of this work is the observation that even the purest plagioclase-dominated component in this central peak commonly contains sufficient mafic material to subtly influence its spectral properties. Comparison with laboratory and modeled mixtures [Chapter 2] suggests that the mafic component should not be present in more than ~2-5 vol% abundance for these plagioclase-dominated spectra, or a distinct mafic band minimum would be apparent in the bulk spectrum. Nonetheless, its presence clearly distinguishes the most plagioclase-rich material at Tsiolkovskiy from the purest crystalline anorthosite that has been noted at Orientale and elsewhere across the lunar surface [Donaldson Hanna *et al.*, 2012; Chapter 3]. This observation emphasizes the diversity of anorthositic crustal materials on the Moon. The comparison between the plagioclase-dominated materials at Orientale and Tsiolkovskiy is particularly compelling because of stark differences in the manner of their exposure. At Orientale, individual massifs of the Inner or Outer Rook rings are typically dominated by either spectrally pure plagioclase or by anorthosites with a detectable mafic signature. Massifs characterized by spectrally pure plagioclase occur abundantly throughout the entire 400 km Inner Rook Ring. At the central peak of Tsiolkovskiy, however, which is only a few times larger than individual Orientale massifs, variations in the character of the anorthosites are present nearly on the pixel scale. Determining whether these small variations in anorthosite

mineralogy across the globe are due to lateral heterogeneity, vertical heterogeneity, or both, should rely on similar detailed analyses for a wide range of lunar craters and basins.

Key compositional properties of the mafic component of Tsiolkovskiy's central peaks area also apparent. Specifically, the pyroxene component is higher in iron and/or calcium than expected for Mg-suite materials, based on the estimated band position of the long-wavelength pyroxene band [e.g., *Klima et al.*, 2011]. This new observation is enabled by the high spectral resolution of the M³ instrument across the entirety of the NIR spectral region. Spectral coverage of the 2000 – 2500 nm region is particularly key, since subtle variations in pyroxene composition are more readily expressed at these wavelengths than near 1000 nm (Figure 6). The observation of a more iron- or calcium-rich pyroxene within the peaks has important implications for crustal mineralogy. Detection of a relatively ferroan pyroxene within the anorthosites of the peak ridges suggests that these anorthosites have a mafic component that is similar in composition to those found in the ferroan anorthosites (FANs) of the sample collection [e.g., *Dowty et al.*, 1974; *Warren and Wasson*, 1980; *McGee et al.*, 1993]. These important rocks are considered the most primitive remnants of the lunar magma ocean and are characterized by highly calcic plagioclase compositions coupled with intermediate, but variable, magnesium numbers for their mafic components. Magnesium number is defined as molar [Mg/(Mg+Fe)], and typically ranges from ~0.4 to 0.7 for the FANs whereas Mg-suite mafic compositions are typically >0.8 [e.g., *Warren and Wasson*, 1980]. The present analysis therefore demonstrates a connection between the anorthosites identified at Tsiolkovskiy crater and those characterized within the sample collection. Further analysis using thermal infrared wavelengths from the DIVINER instrument are needed in order to

asses the An content of plagioclase component and determine whether the Tsiolkovskiy examples are truly representative of the ferroan anorthositic suite rocks. Similar combined analyses of NIR and thermal-IR data for anorthosite exposures across the Moon will ultimately enable detailed characterization of the distribution and composition of what is thought to be one of the most pervasive lunar rock types.

Acknowledgements: Many thanks to Dan Moriarty for continuum-removal of the Tsiolkovskiy image cube, and to Kerri Donaldson Hanna for helpful discussions regarding the plagioclase composition of anorthosites on the Moon. We gratefully acknowledge support for this work through the NASA Lunar Science Institute (NNA09DB34A).

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Figure Captions.

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Figure 3. Spectral parameter maps of the central peak of Tsiolkovskiy specifically chosen to highlight mineralogic differences: (a) reflectance at 1489 nm. Scale bar is 10 km, (b) integrated band strength across 1000 nm, (c) integrated band strength across 1250 nm, (d) integrated band strength across 2000 nm.

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Figure 6. Comparison of pyroxene-dominated spectra from the central peak (blue) and walls (black) of Tsiolkovskiy crater. (a) Reflectance, (b), continuum-removed reflectance following *Moriarty et al.*, in review.

Figure 7. Comparison of plagioclase-dominated spectra from Tsiolkovskiy (black spectrum, deeper absorption) and the Orientale basin (blue spectrum, weaker absorption). The Tsiolkovskiy spectrum represents an average of 7 pixels, whereas the Orientale example is a single-pixel spectrum. Spectra have been continuum-removed following *Moriarty et al.*, in review.

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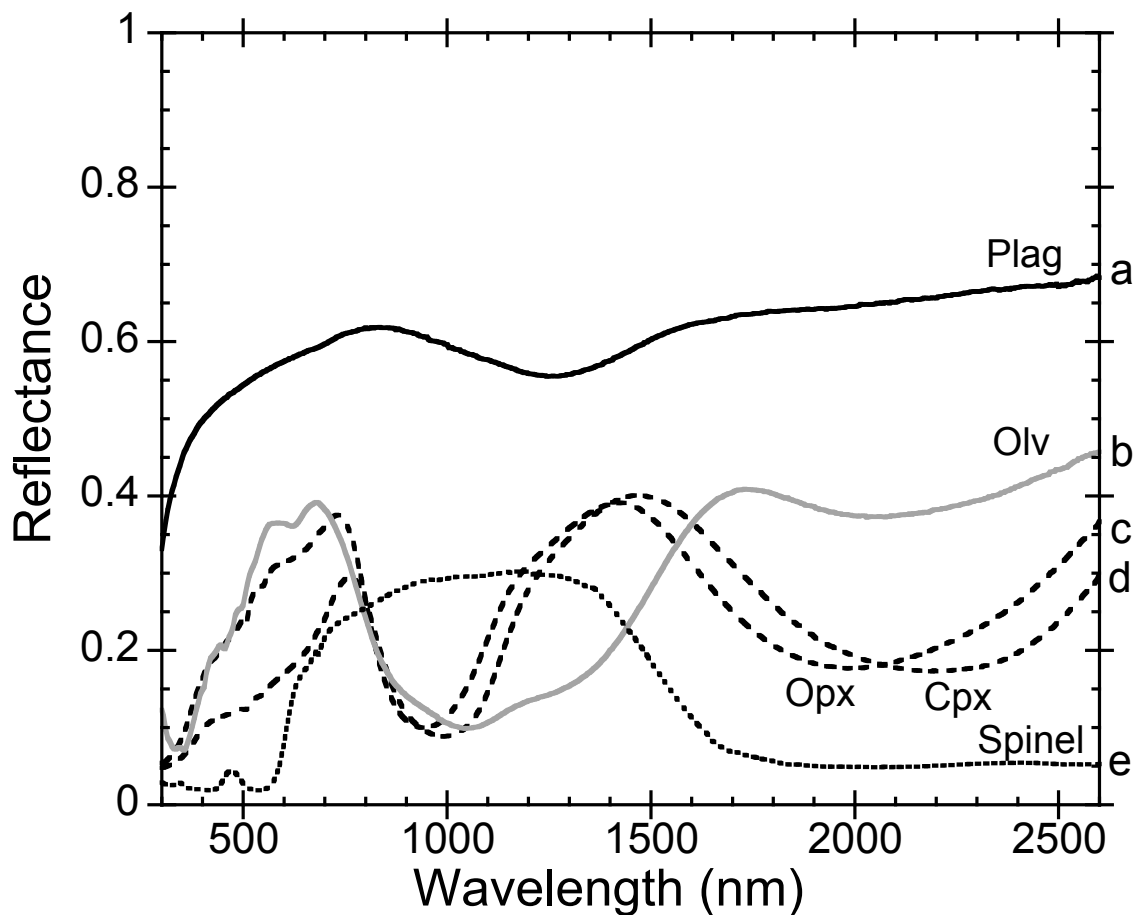


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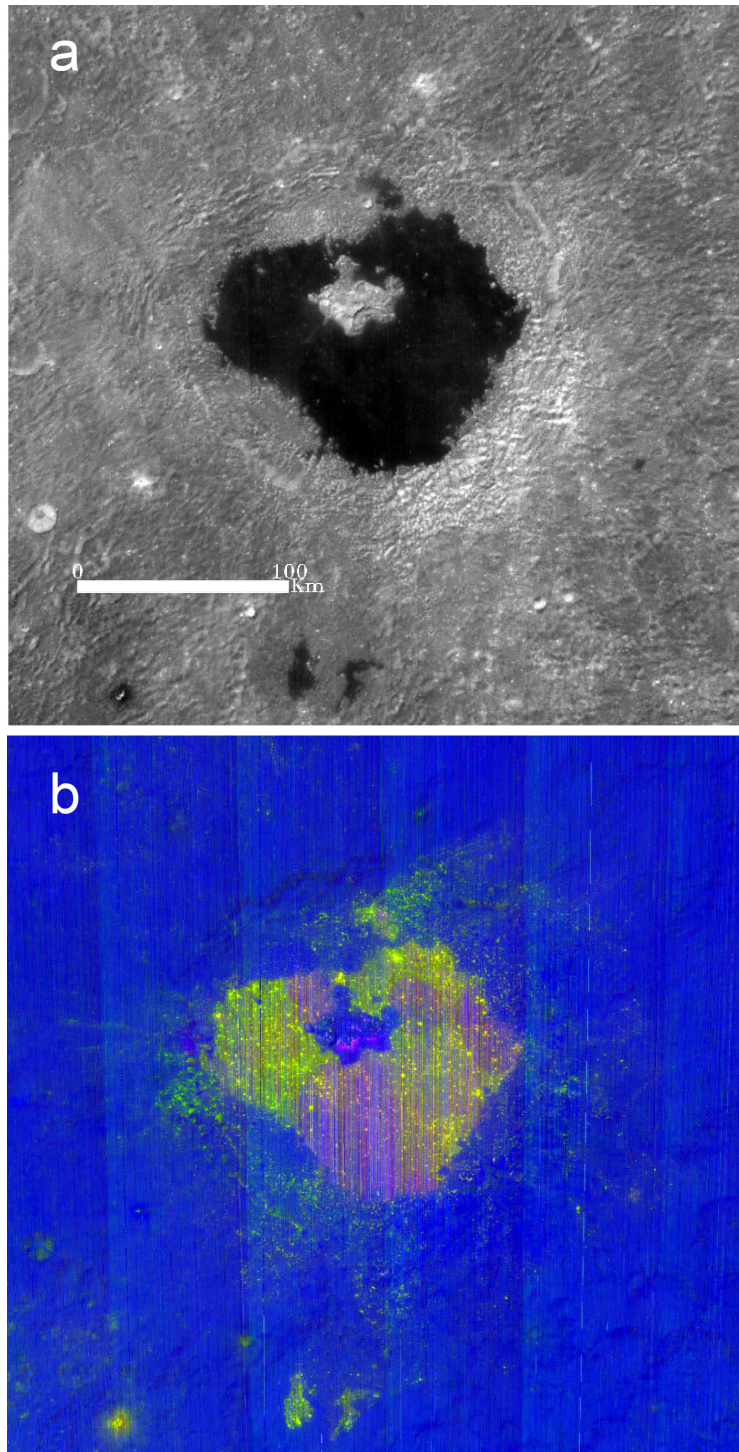


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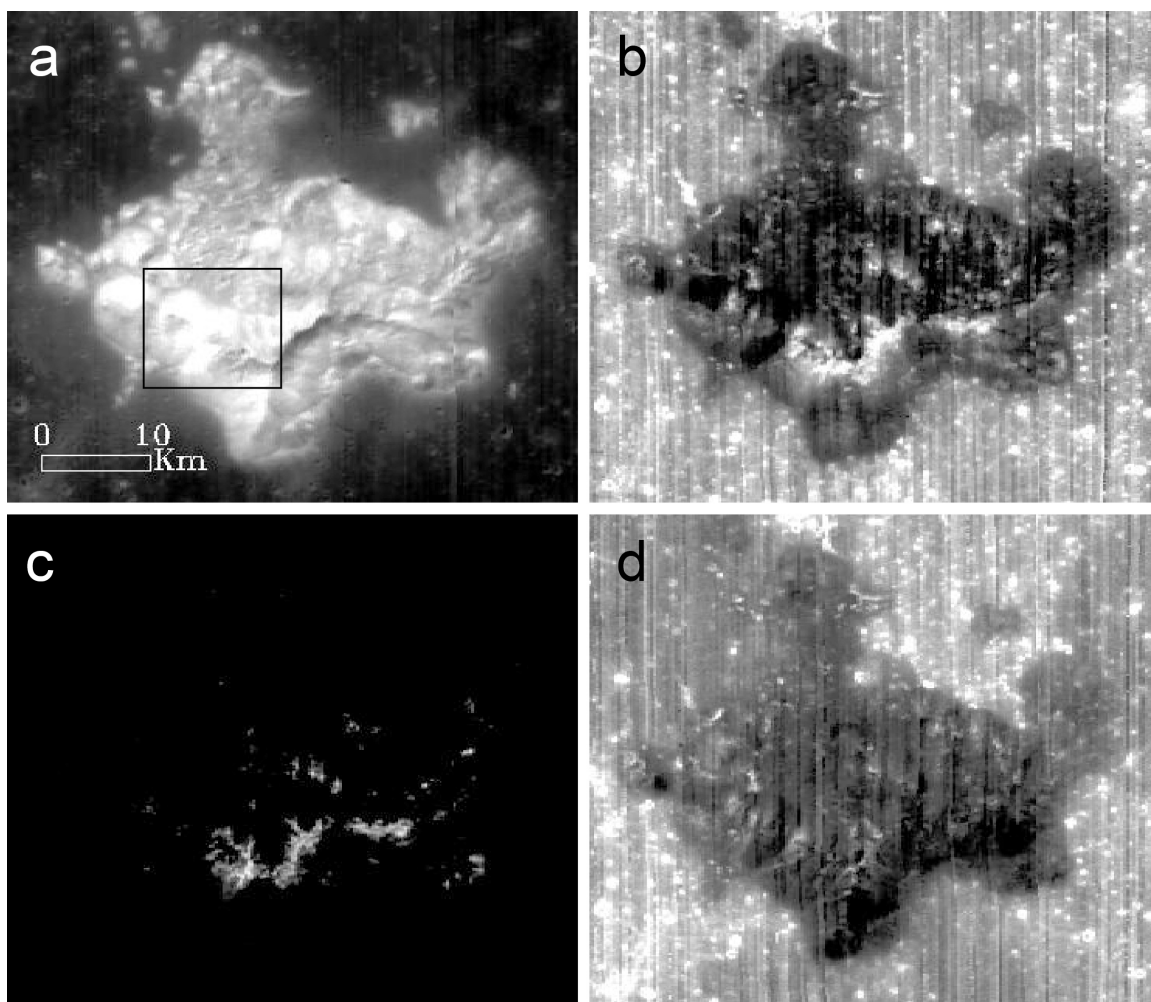


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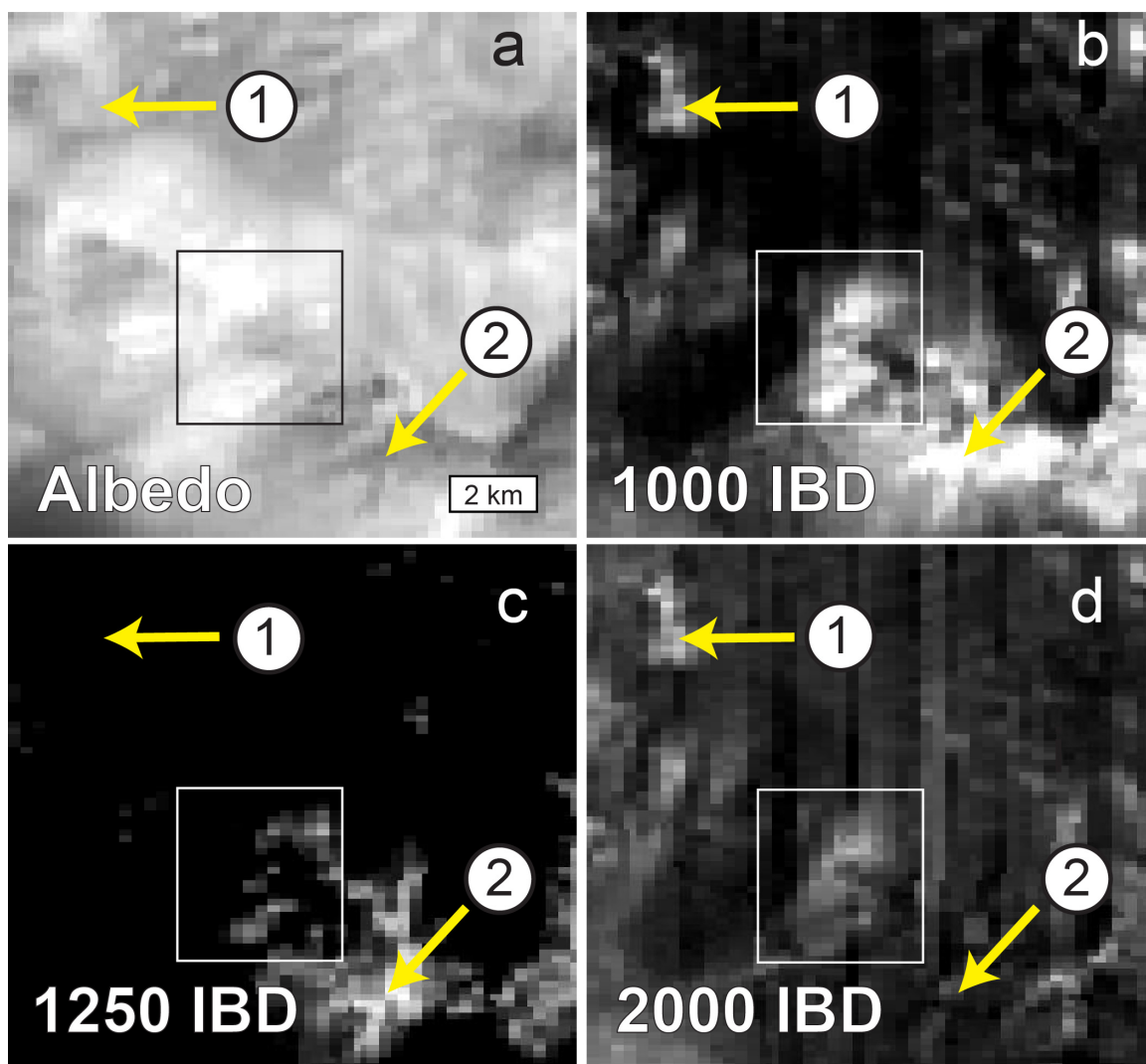


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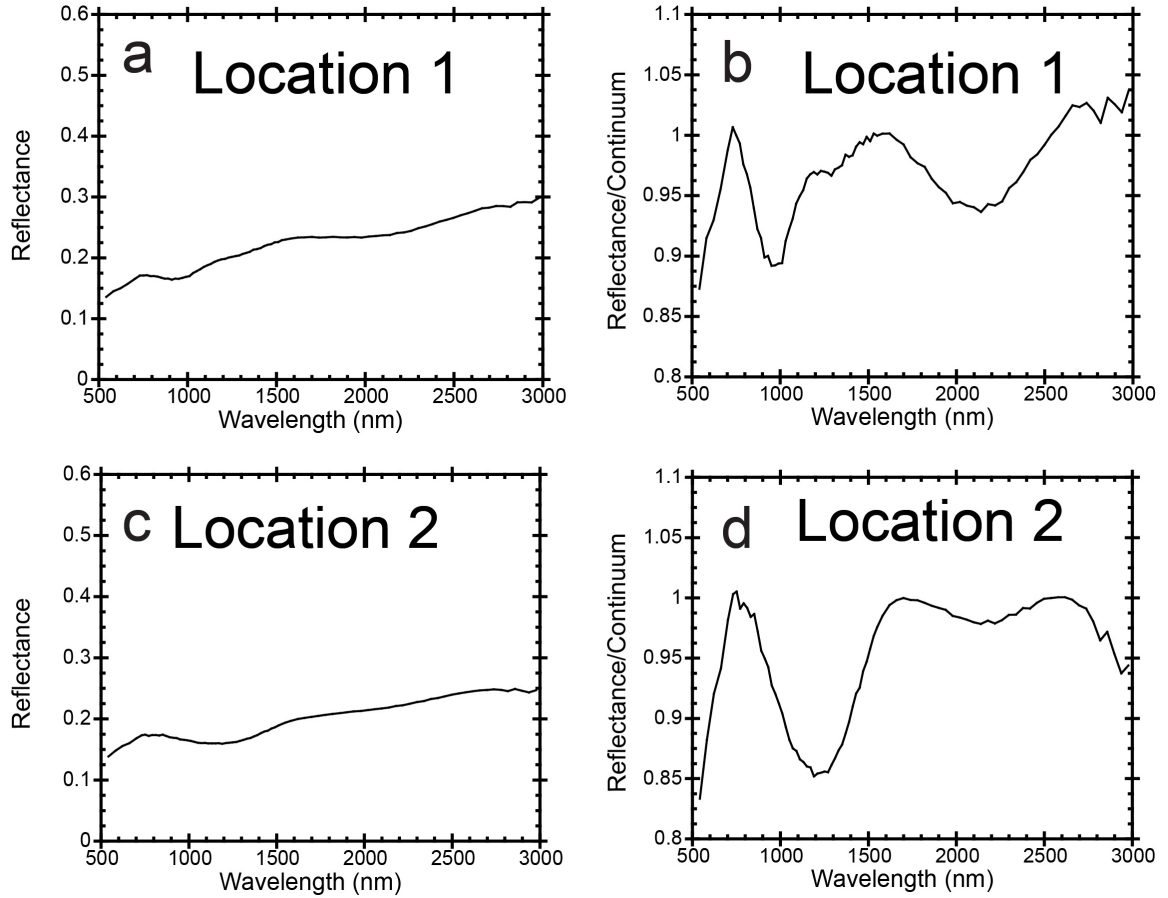


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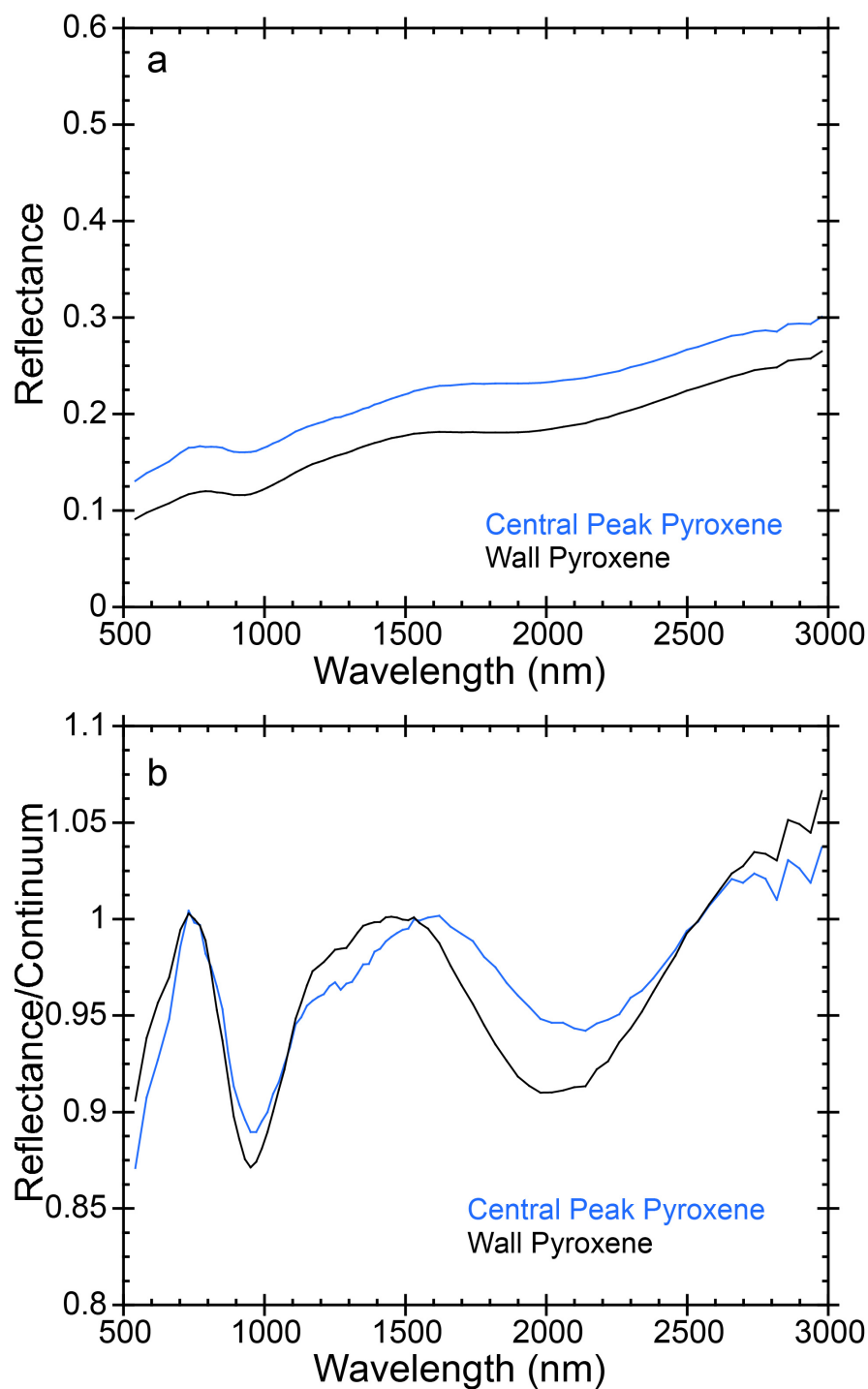


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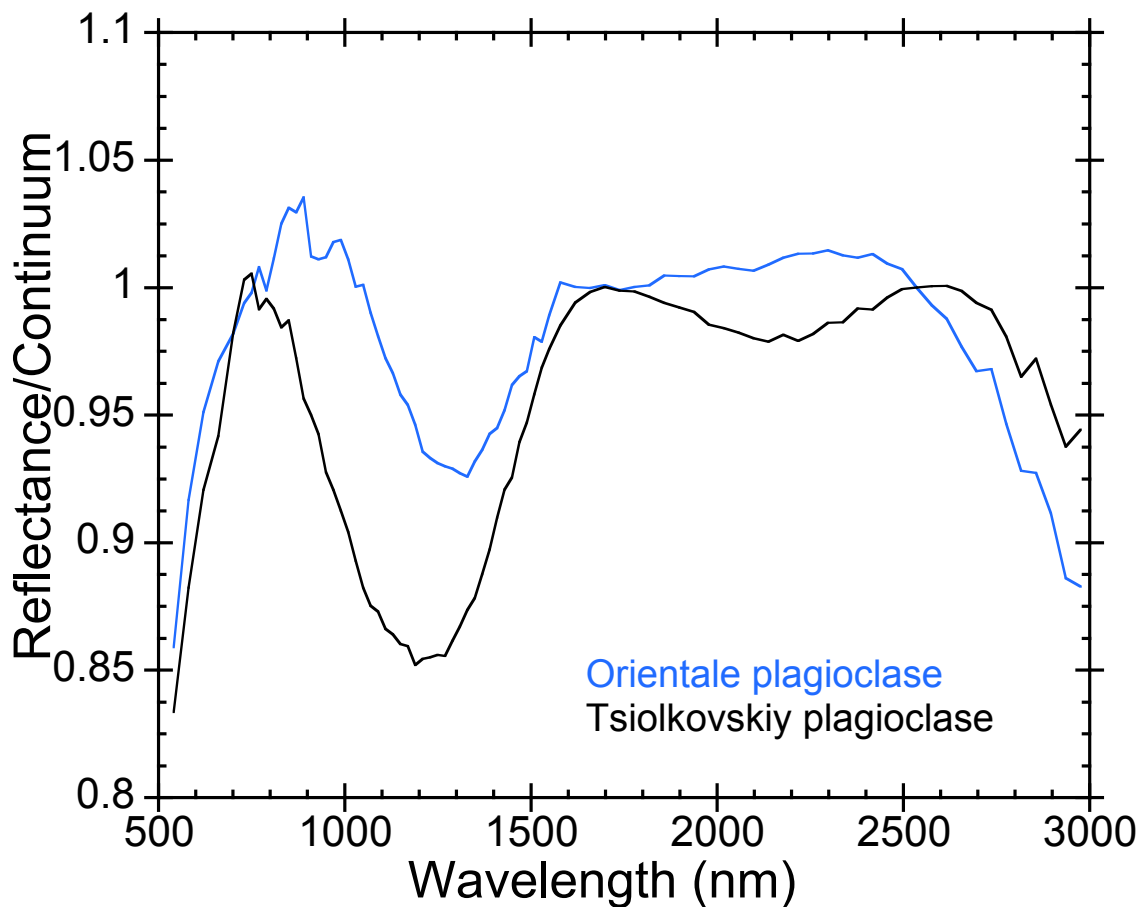


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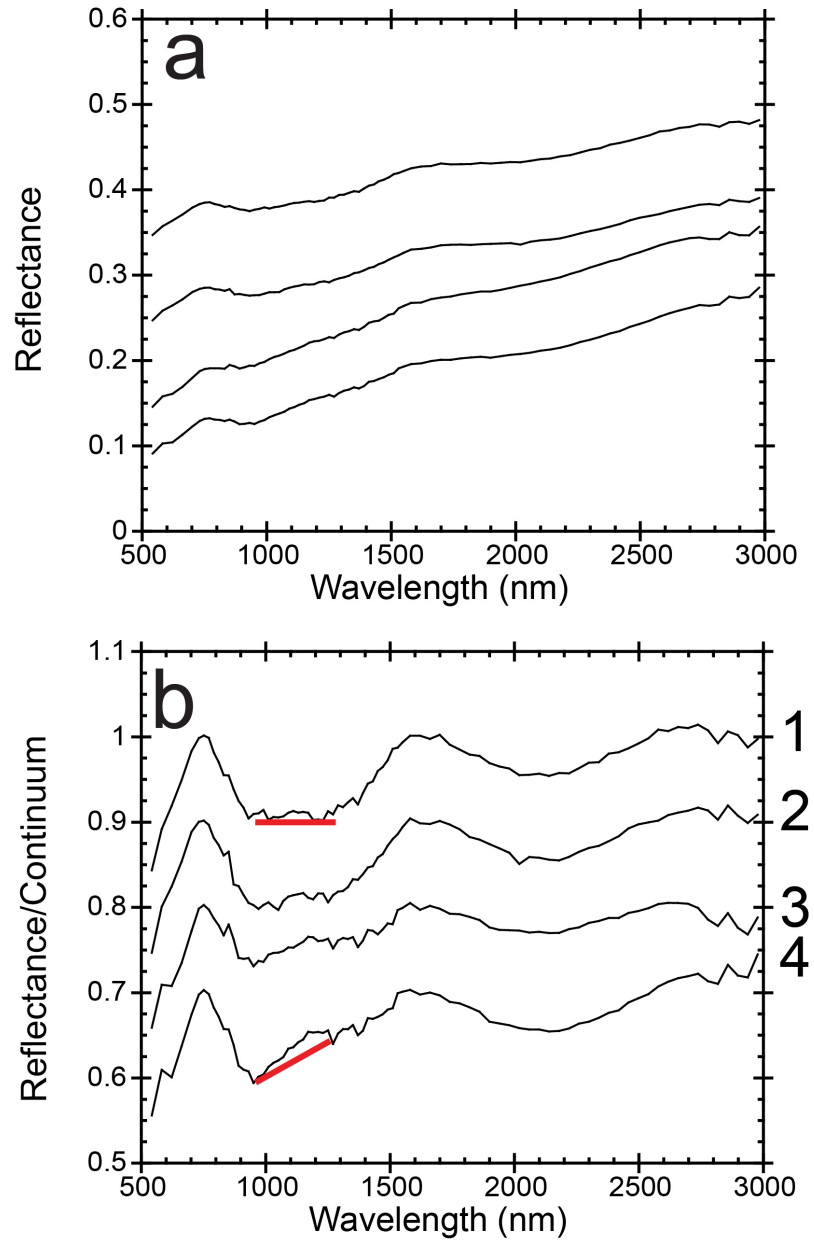


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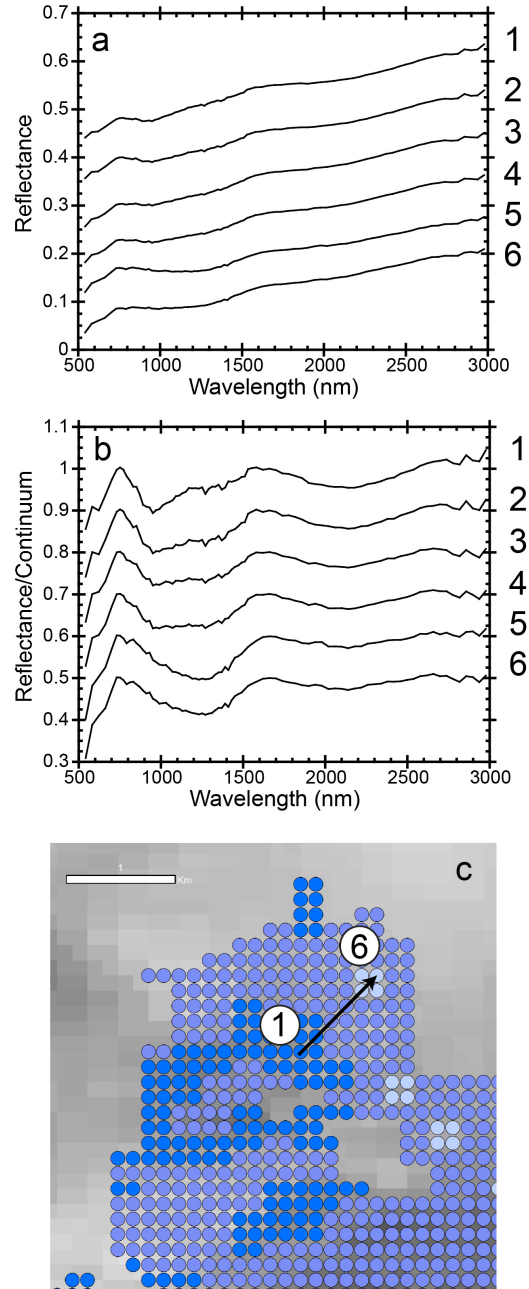


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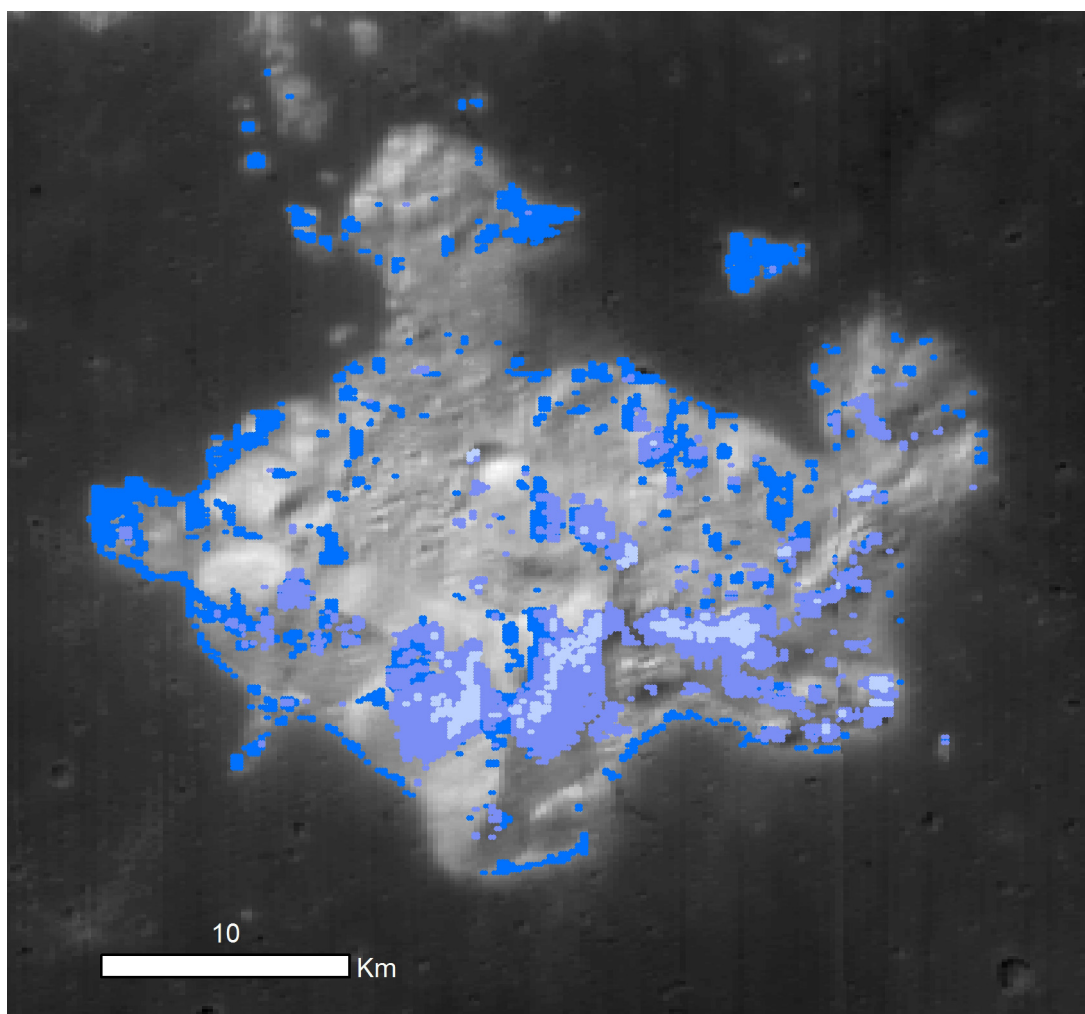


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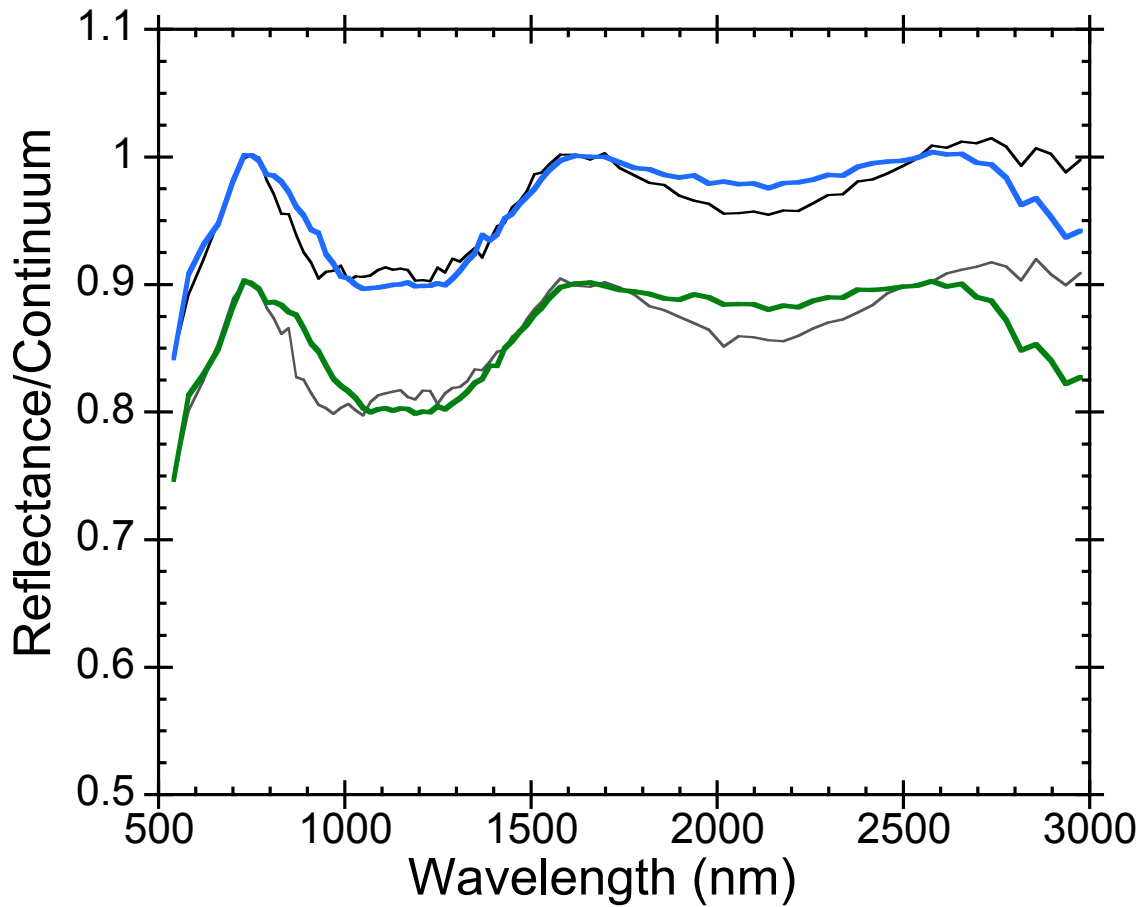


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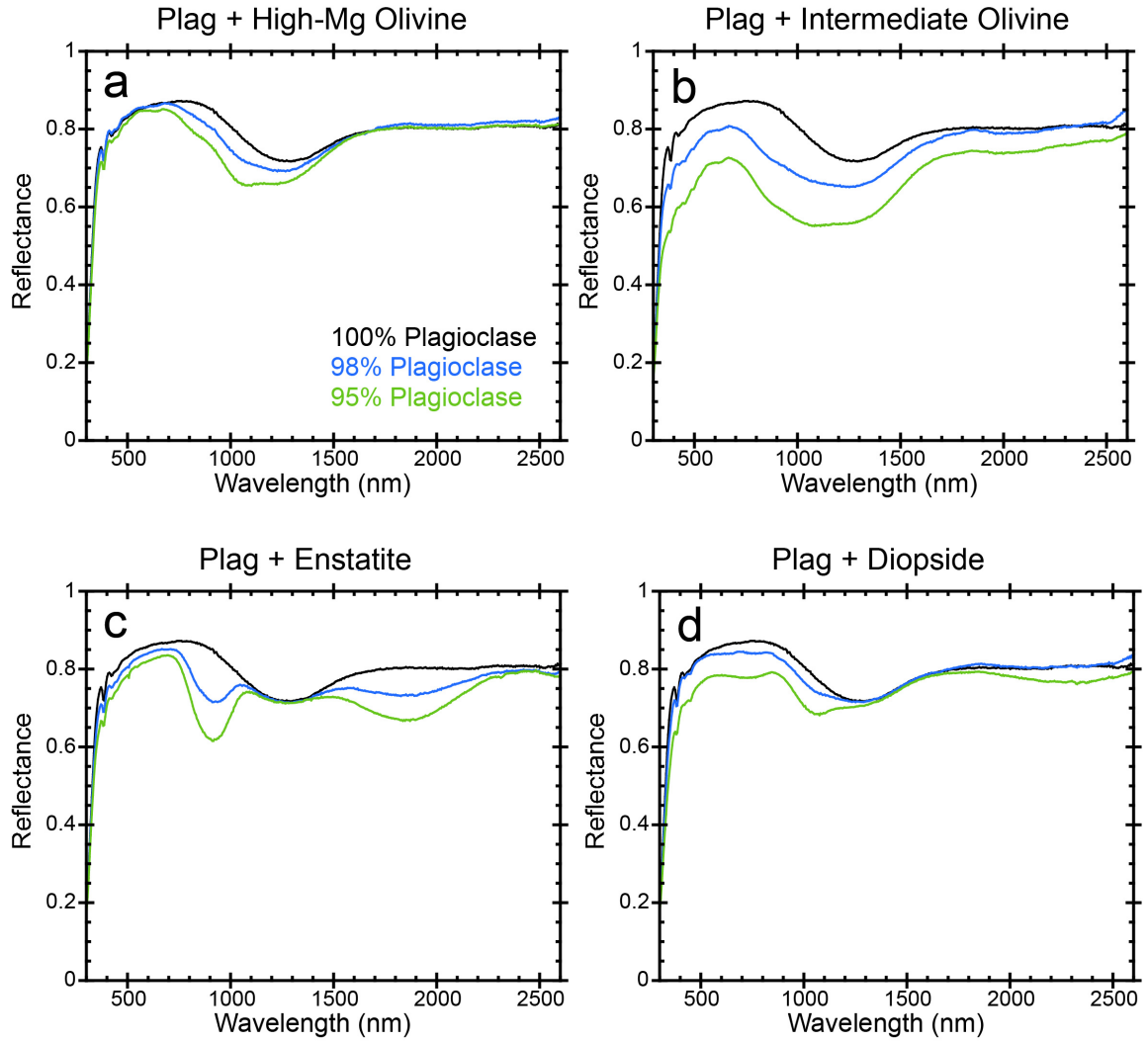


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CHAPTER 5: Synthesis and Future Directions

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1. Motivation

The plagioclase-rich nature of the lunar crust has been obvious since the first results of the Apollo 11 mission [*Smith et al.*, 1970; *Wood et al.*, 1970]. The implications for crustal petrogenesis were compelling, and spurred the development of the magma ocean hypothesis that has served as a framework for understanding planetary-scale magma differentiation processes throughout the solar system [e.g., *Elkins-Tanton et al.*, 2011]. However, limitations in remote mineralogic data have left a number of fundamental questions about crustal composition and structure largely unresolved. For instance, while there is evidence for variations in mafic mineral content throughout the crust, with more mafic-rich lithologies apparently occurring in deeper stratigraphic zones [*Tompkins and Pieters*, 1999; *Cahill et al.*, 2009], the relative thicknesses of the upper and lower crustal zones, and to what extent their compositions continuous and homogeneous across the globe, are relatively unknown. Accurate estimates of the variation in crustal plagioclase content across the globe are crucial for understanding large-scale aspects of magma ocean crystallization processes as well as constraining the bulk chemical make-up of the Moon. Answering these questions requires high resolution mineralogic analyses of primary igneous exposures throughout all reaches of the crust.

Any thorough mineralogic analysis of the anorthositic crust requires information about the plagioclase component of lunar rocks. One of the greatest frustrations of lunar geologists over the past decades has been the invisibility of this ubiquitous and important mineral to near-infrared spectrometers. Because the absence of plagioclase detections could be easily attributable to shock processes or to the “weakness” of the plagioclase spectral signature in general, the literature on lunar spectroscopy has evolved to focus

instead on the distribution and character of more mafic lithologies such as the Mg-suite or the mare basalts, which do have strong near-infrared signatures. Detailed laboratory studies of plagioclase and anorthosite spectral properties are notably sparse in comparison with data on olivine and pyroxenes. With the recent success of modern spectrometers, however, the plagioclase mineral structure is now clearly detectable across the Moon's surface [Matsunaga *et al.*, 2008; Ohtake *et al.*, 2009; Yamamoto *et al.*, 2012; Cheek *et al.*, 2013; Donaldson Hanna *et al.*, In Review]. We are finally poised to make direct measurements of the full mineralogic nature of the primary anorthositic crust, using spectroscopy to probe all major components of plagioclase-dominated rocks simultaneously. It is in this context of enhanced instrumental capabilities that this thesis has been written.

2. Summary of Major Contributions

This thesis has been geared toward enabling the remote analysis of lunar crustal rocks from the improved vantage point offered by a discernable plagioclase near-infrared absorption band. We began with an in-depth spectral characterization of plagioclase and anorthosite samples in Chapter 1. This first project focused on the analysis of samples for which the compositions are well-known, and in some cases, controlled experimentally. Our findings have reinforced previous studies that documented a dependence of absorption characteristics on iron and An content, but we have also emphasized the striking complexity of natural terrestrial samples. It is apparently difficult to discern detailed compositional information from samples that have been formed and modified by natural terrestrial geologic processes. Spectra of lunar plagioclase and anorthosite, however, are quite regular, and our observation that bulk spectra of four Apollo 16

anorthosites all display prominent ~ 1250 nm plagioclase absorptions is particularly important. Despite a low iron abundance (between 0.1 and 0.2 wt% FeO), the presence of small proportions of naturally co-occurring mafic minerals, and the effects of shock metamorphism, the plagioclase band in all four lunar anorthosites is strong and easily discernable. We suggest that future studies of plagioclase spectral properties focus on more detailed analysis of well-controlled lunar anorthosite samples, with special attention paid to the minor and trace phases. Particularly important will be simultaneous characterization of the modal mineralogy of samples allocated for spectral measurements, following on the approach of *Isaacson et al.* [2011]. In addition, pure synthetic plagioclase samples that are relatively free from contaminating or unreacted phases should be sought in order to systematically characterize variations in spectral properties across a wide compositional parameter space, following the approach of *Klima et al.*, [2007] for pyroxenes.

Chapter 2 builds on the results of Chapter 1 by exploring the spectral characteristics that result when small proportions of mafic mineral powders are added to pure plagioclase samples. We have found that although mafic minerals do have an overwhelming effect on bulk spectral properties, at anorthositic proportions (i.e. very high proportions of plagioclase) the plagioclase feature still exerts a measurable influence on the spectrum. In many cases, the mixture spectra resemble either distorted plagioclase bands (i.e., anorthositic mixtures containing olivine or diopside), or distorted mafic bands (i.e., anorthositic mixtures containing orthopyroxene). The precise character of the composite spectrum is dependent, however, on both the type (e.g., olivine or pyroxene) or abundance of the mafic phase, suggesting that variations in the chemical and mineralogic

make-up of anorthosites should be distinguishable on the lunar surface using near-infrared techniques. Indeed, we believe that the new remote data already show spectral evidence for a diversity of anorthosite compositions for several locations, such as at Tsiolkovskiy crater and the Orientale basin.

The third and fourth chapters were dedicated to characterizing two examples of anorthosite exposures using Moon Mineralogy Mapper data, leveraging the lessons learned from the well-controlled samples studied in Chapters 1 and 2. Comparison of the two examples, from Tsiolkovskiy crater and the Orientale basin, demonstrates that variations in the plagioclase abundance within the lunar crust are clearly discernable with the new data. For instance, it is clear that the vast upper crustal zone exposed at Orientale is more plagioclase-rich than generally expected for typical highland materials [e.g., *Warren, 1990; Korotev et al., 2003*]. At the same time, the material exposed at Tsiolkovskiy crater, which likely sampled much deeper stratigraphic levels, is slightly more mafic rich on average and also shows greater variability over small spatial scales. The exposures at Tsiolkovskiy are also compelling because the mafic component of their spectra are clearly consistent with the abundantly sampled ferroan anorthosites. Thus, not only are highly pure anorthosites ubiquitous [*Ohtake et al., 2009; Yamamoto et al., 2012; Donaldson Hanna et al., In Review*], but examples of more mafic-rich anorthosites are also present across the Moon. The diversity apparent in the two case studies explored here suggests that expanded analysis of plagioclase-dominated crustal exposures from a variety of locations and depths within the crust will undoubtedly begin to complete our conception of the vertical and lateral compositional structure of the Moon's crust.

3. Future Directions

A number of specific projects are envisioned that build on the various results of this thesis. Some of the most compelling directions are mentioned briefly below. These future avenues of research are directed at more fully exploring aspects of both plagioclase composition and its relationship to other minerals important to lunar geologic history.

(1) The relationship between the “crystalline” plagioclase discussed in this thesis (displaying a ~1250 nm absorption band) and the “featureless” plagioclase discussed using previous datasets [e.g., *Spudis et al.*, 1984; *Hawke et al.*, 2003] will be a particularly important avenue of future research. Both featureless spectra and spectra displaying only a plagioclase absorption likely represent materials that are poor in mafic minerals and rich in plagioclase. However, the reasons for their spectral differences are probably related to important and ubiquitous aspects of lunar surface evolution. For instance, the spectrally featureless nature of much of the anorthositic material on the Moon’s surface is likely due either to shock metamorphism, such as fracturing or maskelynitization [e.g., *Adams et al.*, 1979; *Johnson and Hörz*, 2003], or to optical maturity caused by the development of nanophase iron or reduction of optical path length by comminution and soil development [e.g., *Hapke*, 2001; *Noble et al.*, 2007; *Taylor et al.*, 2001]. Discerning which of these factors, or which combination of factors, is affecting lunar highland soils in various locations across the globe will be important for interpreting surface characteristics. Remote sensing analysis of those areas containing *both* featureless and crystalline plagioclase will likely be a key approach for learning about these processes. At the same time, further laboratory analyses are envisioned that may help constrain the variable effects of shock metamorphism and optical maturity. For

instance, progressive, controlled, shock experiments similar to those described in *Johnson and Hörz* [2003] may be carried out on uniform, gem-quality crystals and measured spectroscopically. Additionally, spectroscopic studies of lunar anorthosites should be carried out in concert with detailed petrographic study of coordinated thin sections in order to establish a better link between shock metamorphic textures and spectral properties. The spectral characteristics of samples, either natural or experimental, for which varying proportions of the plagioclase grains have been transformed to maskelynite will be a particularly important aspect of this problem.

(2) Plagioclase is not the only new mineral identified on the Moon by the recent suite of modern NIR spectrometers. Mg-spinel and Cr-spinel have also been detected in numerous exposures across the lunar surface [*Pieters et al.*, 2009; *Jackson et al.*, 2012; *Yamamoto et al.*, 2013]. While spinel is certainly an important mineral found in lunar rocks of the sample collection [e.g. *Haggerty et al.*, 1971] this new capability to identify its spectral features from orbit enables a more global characterization. These exposures are widespread across the globe, although they are generally concentrated in the highlands in association with feldspathic materials that do not display strong plagioclase absorption features. Chapter 2 has included mixing analyses of Mg-spinel plus a plagioclase endmember displaying a prominent ~1250 nm absorption. These analyses are intended to constrain the spinel abundance in these lunar exposures if the other major component were crystalline plagioclase. However, the context of many of the spinel exposures suggests that much of the associated material represents “featureless” plagioclase that has been shocked or space weathered sufficiently to erase the main absorption band. Thus, an important direction for future research involves characterizing

the spectra of mixtures of spinel plus varying amounts of a featureless plagioclase endmember. In a laboratory mixing study, endmembers representing this featureless plagioclase component could include any of the terrestrial plagioclase spectra from Chapter 1 that do not display plagioclase bands. However, terrestrial samples do not display the “red” continuum slope, which gradually decreases into the UV. The continuum is a particularly important component in spectra lacking strong mineral absorption features. Although lunar samples (principally soils) that are good representatives of the desired plagioclase spectral properties are found in the sample collection, they are generally too valuable to allocate in quantities sufficient to produce series of mixtures that would capture a range of bulk spectral characteristics. Instead, we suggest leveraging the nonlinear mixture modeling described in Chapters 2 and 3 to predict mixture spectra from input endmember spectra. The endmember spectra could then comprise a range of measured spectra from the RELAB database that do display various continua and overall brightness values. The effects on the shorter wavelengths, which have been proposed as useful indicators of spinel Mg number [*Jackson et al.*, 2012] also need to be explored with well-controlled analyses.

(3) The relationship between the crystalline plagioclase absorption at ~1250 nm and the M1 pyroxene band is another important topic that has implications for interpretation of anorthositic spectra. The pyroxene M1 band occurs centered near 1200 nm, and overlaps substantially with the plagioclase band. Its strength is variable, depending on the composition and cooling history of the mineral [*Klima et al.*, 2008]. Until now, any absorptions in this 1200-1250 nm wavelength region have typically been attributed to the pyroxene M1 bands whenever strong pyroxene M2 bands are also

present [*Klima et al.*, 2008]. However, our work has shown that the crystalline plagioclase absorption is an important spectral component in a range of materials, and should be considered in analyses of targets that contain appreciable plagioclase. For instance, our analysis of M³ data for Tsiolkovskiy crater on the Moon shows a pyroxene component with a strong ~1200 nm shoulder. The context of these spectrally pyroxene-dominated exposures within a clearly anorthositic region suggests that plagioclase is likely contributing to this feature. Distinguishing the relative contributions of pyroxene and plagioclase near 1200 nm is a challenging task that may be best approached with detailed laboratory and/or modeled mixtures of plagioclase with a range of pyroxene endmembers for which particle size, composition, cooling history, and other important variables are well-controlled. These analyses can be coordinated with spectroscopy of various Apollo and eucrite samples. The results would have important implications for predicting mineral abundances on planetary surfaces. Laboratory spectral analyses of some eucrites for instance, which are comprised mainly of plagioclase and pyroxene in variable proportions, are known to display strong ~1250 nm absorptions due to plagioclase, but this feature is not distinguishable without careful targeting of plagioclase-dominated clasts in the bulk sample [*Hiroi et al.*, 2012]. Mixing analyses will therefore be important for distinguishing the variable contributions of plagioclase and pyroxene when viewed on larger scales by remote spectrometers.

(4) Finally, we emphasize that the spectral properties of many more anorthosite samples from the Apollo and lunar meteorite collections should be measured in controlled environments such as RELAB. Reflectance spectroscopy is a non-destructive technique that requires only a few tens of milligrams per measurement. These data are

relatively simple to collect, and can offer crucial insight for scientific analyses of the lunar crust. For instance, the spectra of four Apollo 16 anorthosites measured in Chapter 1 differ subtly in their plagioclase absorption properties, but differ greatly in the depths of absorptions due to minor amounts of mafic minerals in the anorthosite. These variations likely hold clues regarding differences in the geologic histories in these samples. It is inevitable that a detailed understanding of the chemical, structural, or textural causes of these variations in a wide range of anorthosite samples will improve interpretations of the anorthosites that are variably exposed on the lunar surface and measured with comparable sensors.

4. Final Thoughts

Lunar science is entering new era of discovery that is motivated largely by advances in remote sensing technology. This thesis in particular describes several new perspectives that emerge from the spectroscopic analysis of plagioclase-dominated materials on the Earth and Moon. First, we now know that plagioclase can be readily detected with near-infrared sensors, particularly in the absence of ferric iron or terrestrial alteration products (Chapter 1). Further, it appears that near infrared spectroscopy offers substantial leverage for measuring small, percent-level variations in the mafic content of anorthositic materials (Chapter 2). From analysis of plagioclase-rich exposures on the Moon using new spectroscopic data, we have learned that vast reaches of the lunar crust consist of mountains of exceedingly pure anorthosite – containing ~2% or less mafic minerals (Chapter 3), but that other areas, such as Tsiolkovskiy crater, contain more “impure” anorthosites (Chapter 4). These differences that are apparent in the analysis of just two examples of crustal exposures suggest that a diversity of compositions have

resulted from crystallization of the magma ocean, and that this diversity is readily observable with the new data.

This thesis has focused primarily on new science coming from sensors that are sensitive to mineralogy, although these lessons are accompanied by developments in our understanding of lunar gravity, topography, geomorphology, volatile budget, and a host of other topics. These improvements afford lunar geologists the chance to continuously re-evaluate with fresh eyes the collection of samples derived from the Moon. Continued refinement of planetary formation and evolution hypotheses based on constraints from remote sensing and a large, diverse, and well-characterized sample suite is a unique opportunity available to lunar scientists. The lessons from this integrated approach have implications across the solar system for the range of terrestrial bodies shaped by the same fundamental geologic processes as those under investigation at our Moon.

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APPENDIX A: Brief descriptions of endmembers used in laboratory mineral mixing study (with Chapter 2)

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A1. Sample Descriptions

The following are brief descriptions of the endmembers used in the mixing study in Chapter 2. Major element compositions are given in Table 1 of Chapter 2.

Plagioclase: The plagioclase endmember used in these mixing analyses is a yellow labradorite from Mexico. Seven 2-3 cm transparent, inclusion-free stones were crushed together to create a homogeneous sample.

High-Mg Olivine: The high-Mg olivine sample was a San Carlos olivine that consisted of four ~1 cm grains with very minor inclusions that were removed by handpicking.

Intermediate Olivine: The Kiglapait olivines were obtained from a cut slab of a bulk rock sample, which also contained abundant plagioclase and some pyroxene. Most of the olivine was separated by crushing the bulk sample and passing the particulate material (principally 125-500 μm) through a magnetic separator. The olivine split was further crushed and again passed through a magnetic separator in order to remove most inclusions (likely spinel).

Orthopyroxene: The orthopyroxene endmember is an enstatite from Bamble, Norway that was obtained from Ward's. Most grains are tan or grey in color. Inspection under a binocular microscope indicates the presence of a minor fibrous component, suggested to be tremolite by *Singer* [1981]. The orthopyroxene was

previously separated from a bulk rock by David Crown [*Crown and Pieters*, 1987].

Diopside: The diopside endmember is from Madagascar and was obtained from Ward's. The grains with the least amount of oxidation and impurities were selected for the analysis. These were crushed and additional impurities were removed by hand-picking.

Very High-Mg Spinel: The very high Mg spinel endmember consists of six transparent inclusion-free crystals from Tanzania. Each crystal was 1-2 cm in size and displayed a deep purple color.

High-Mg Spinel: The high-Mg spinel endmember consisted of a number of 1-2 cm black spinel crystals (many euhedral) from Amity, New York that were separated from a calcite-dominated rock manually. Adhering calcite was removed by dissolving in 6N HCl for 12-48 hours.

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APPENDIX B: Mid-infrared spectra of select laboratory mineral mixtures (with Chapter 2)

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B1. Example mid-infrared spectra for three representative mixture series

Chapter 2 discusses in detail the near-infrared spectra properties of plagioclase – mafic mineral mixtures. Here, we show the mid-infrared spectra for three representative series: Plagioclase + Intermediate Olivine (Figure B1), Plagioclase + Orthopyroxene (Figure B2), Plagioclase + Very high-Mg Spinel (Figure B3). For all series, systematic changes are apparent as the proportion of mafic mineral increases.

Figure Captions.

Figure B1. Mid-infrared spectra for the binary plagioclase + Intermediate olivine series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend. Particle size 45-75 μm .

Figure B2. Mid-infrared spectra for the binary plagioclase + Orthopyroxene series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend of Figure B1. Particle size 45-75 μm .

Figure B3. Mid-infrared spectra for the binary plagioclase + Very high-Mg spinel series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend of Figure B1. Note the slightly expanded y-axis scale. Particle size 45-75 μm .

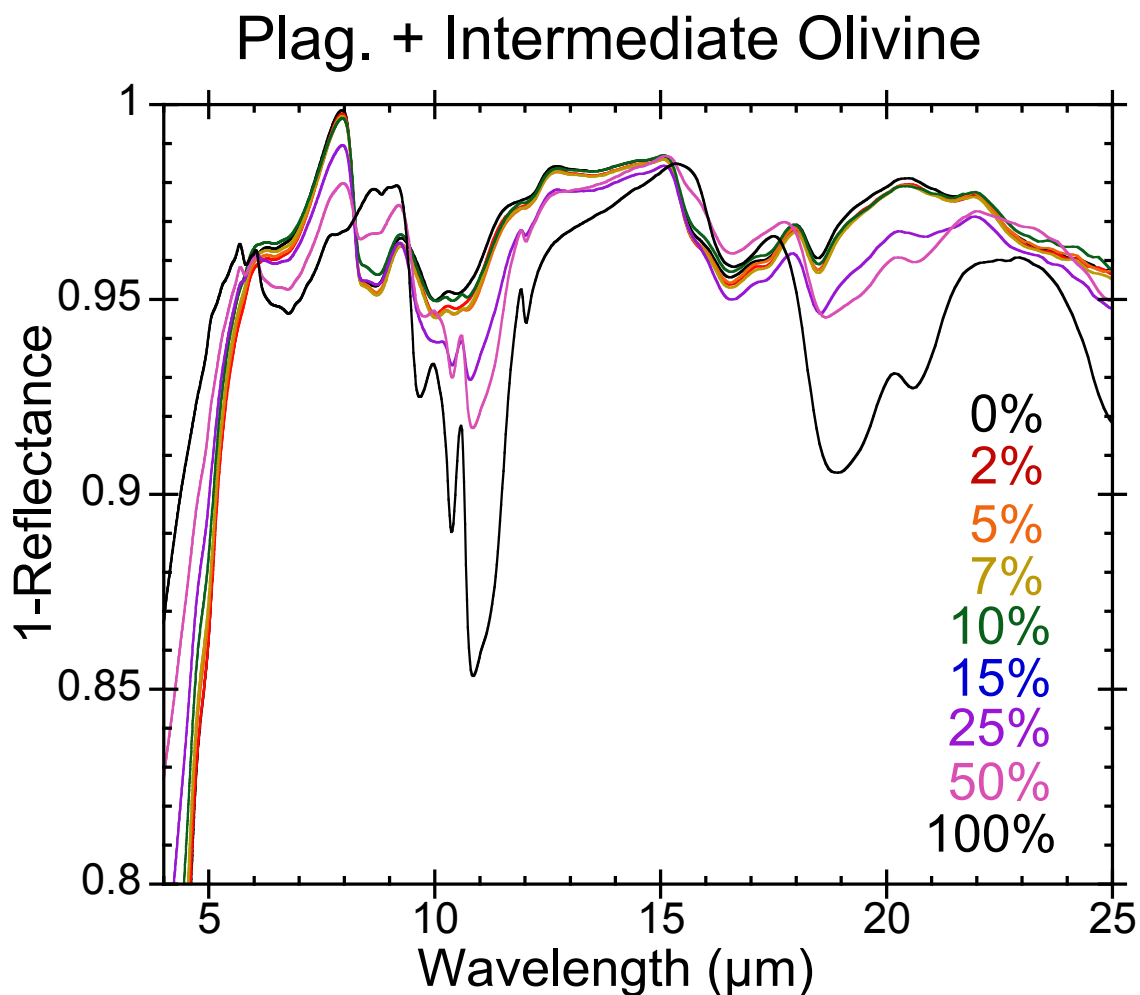


Figure B1. Mid-infrared spectra for the binary plagioclase + Intermediate olivine series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend. Particle size 45-75 μm.

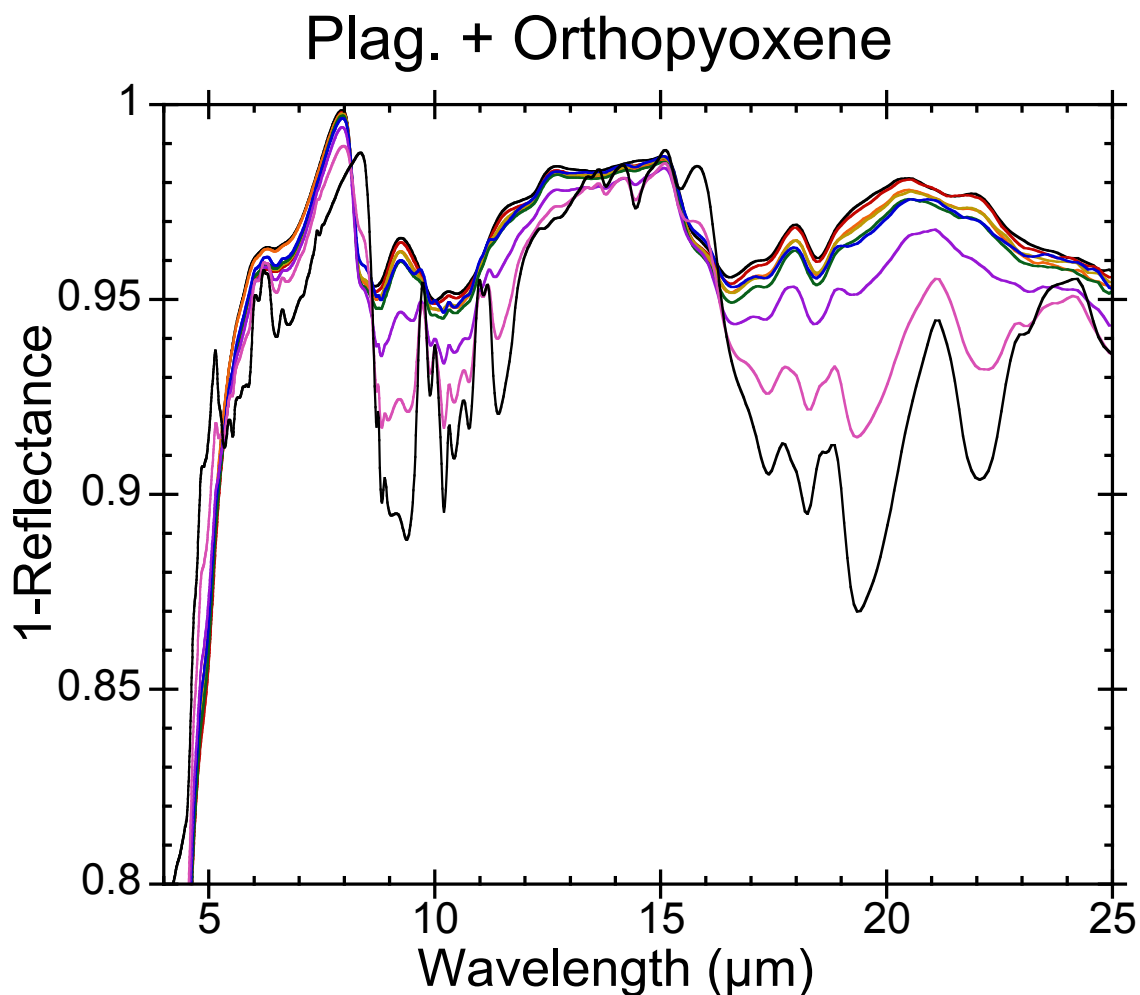


Figure B2. Mid-infrared spectra for the binary plagioclase + Orthopyroxene series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend of Figure B1. Particle size 45-75 μm.

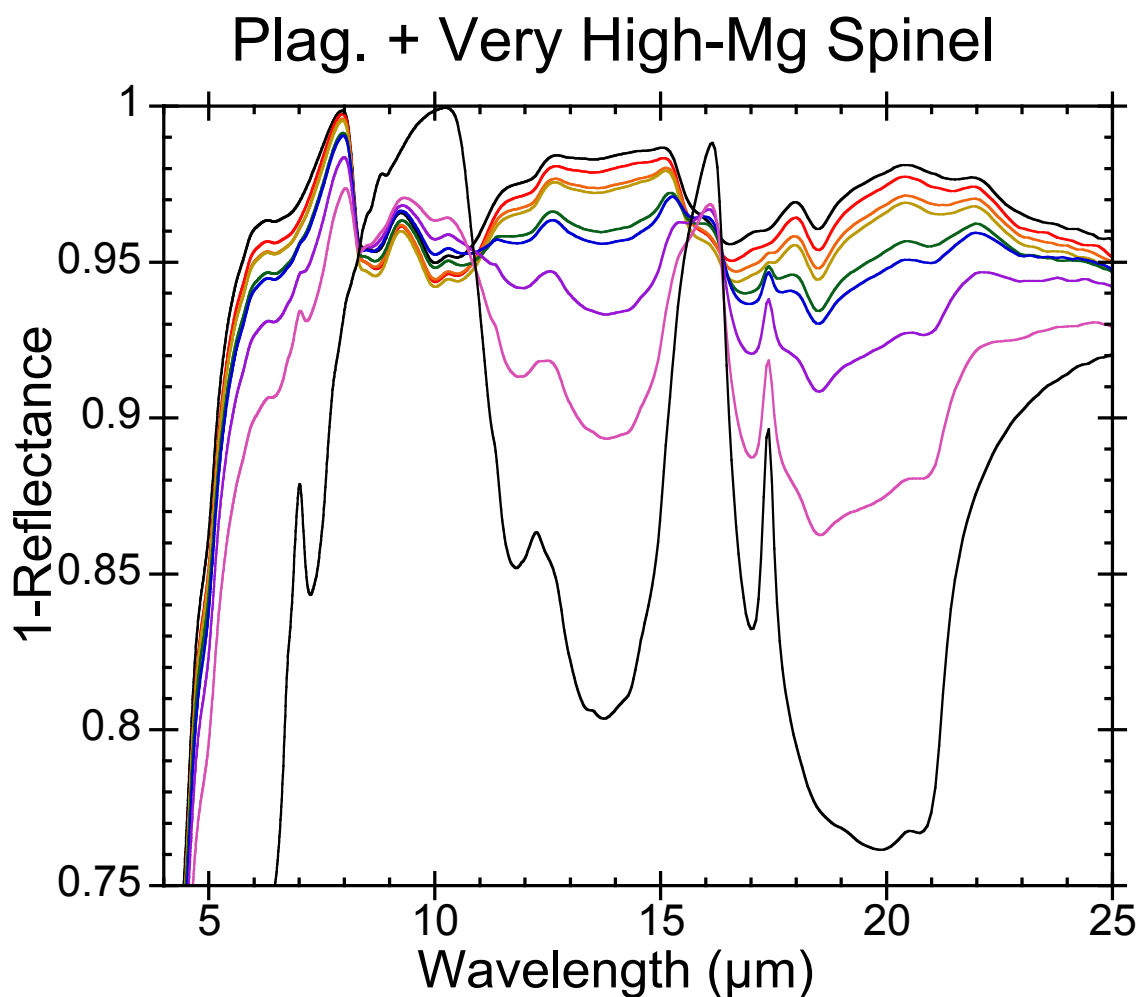


Figure B3. Mid-infrared spectra for the binary plagioclase + Very high-Mg spinel series. The spectra are colored the same as the near-infrared data in Figure 5 of Chapter 2, and correspond to the mafic abundance (vol%) in each mixture given in the legend of Figure B1. Note the slightly expanded y-axis scale. Particle size 45-75 μm .

APPENDIX C: Additional Considerations for Mineral Abundance Estimates (with Chapter 3)

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Submitted to:

Journal of Geophysical Research

December 31, 2012

Revised:

August 8, 2013

Accepted:

August 11, 2013

An important component of this work is constraining the range of plagioclase abundances that are consistent with each of the major spectral classes found in the Orientale region. Because the approach relies on estimating the relative band strengths in both calculated mixtures and in M^3 spectra, it is important to consider what factors, besides mineral abundance, might affect absorption strength. Although there are a number of parameters, such as space weathering, photometry, local topographic effects, particle size, spatial (linear) mixing, and mineral composition, that are known to affect absorption strengths in minerals, only those factors that could lead to substantial differences in the *relative* strengths of the plagioclase and pyroxene absorptions are likely to influence the classification used here. These effects are discussed below.

C.1 Pyroxene Composition

Mineral composition is perhaps one of the most important considerations in predicting relative absorption band strengths. For plagioclases, FeO content is the most significant chemical control on absorption strength [e.g., *Bell and Mao*, 1973; *Adams and Goullaud*, 1978]. Fortunately, the FeO concentrations in plagioclase from most sampled lunar anorthosites are remarkably consistent, typically ~0.05-0.2 wt% [e.g., *Papike et al.*, 1991; *McGee*, 1993]. This gives us confidence that the plagioclase endmember used in the mixing calculation (containing 0.1% FeO) is representative of the absorption strength of highland plagioclase that is observed at Orientale (plagioclases in mare basalts, however, often contain > 0.3 wt% FeO [*Isaacson et al.*, 2011]). The compositions of pyroxenes found in lunar anorthosites are more variable. We focus on low-calcium pyroxenes here, which are the most common mafic mineral found in lunar anorthosites [*McGee*, 1993]. Low-calcium pyroxenes typically have short-wavelength absorption

features below ~ 950 nm [*Klima et al.*, 2007, 2010], similar to those observed at Orientale. Because of the low calcium content in pyroxenes found in lunar anorthosites, typically <5 wt% CaO [*McGee*, 1993], the major control on absorption strength for the ~ 1000 nm pyroxene absorption is the relative magnesium and iron contents of the sample. Relative FeO contents of low-calcium pyroxenes are approximated by comparing their Mg# (Mg# = molar Mg/[Mg+Fe]). Analyses in the literature suggest that compositions of low-calcium pyroxenes in anorthosites vary substantially, ranging from $\sim$ Mg40 to $\sim$ Mg70 [e.g., *Ryder and Norman*, 1978; *Warren and Wasson*, 1980; *James et al.*, 1989; *McGee*, 1993; *Warren*, 1993].

To demonstrate the effect that different Mg# values for low-calcium pyroxene could have on the estimates of plagioclase abundance illustrated in Figure 7, we produced similar non-linear mixing models using four different pyroxene compositions from *Klima et al.* [2007, 2010] that span the range of low-calcium pyroxenes found in lunar anorthosites. The four pyroxene endmembers are shown in Figure A1, and the modeled mixtures use the same lunar plagioclase endmember as in Figure 7. The modeled mixture spectra for these four pyroxenes are shown in Figure A2. Pyroxene compositions are referred to by En' rather than Mg# to accommodate the small amount of calcium in one of the samples. Figure A2 illustrates that the same general pattern is observed for all pyroxene compositions. For three of the pyroxenes (En50Fs50, En35Fs65, and En30Fs59Wo5), variation in relative absorption strengths between calculated mixtures containing the same modal proportions are on the order of only $\sim 1\%$ variation in pyroxene abundance. The models produced with the En70Fs30 pyroxene, however, show ~ 1000 nm absorptions that are notably weaker than for the other pyroxene samples,

requiring higher abundances of pyroxene for detection in the bulk calculated material. Although these synthetic pyroxenes are useful for demonstrating trends of absorption strength over a given compositional range, it is difficult to directly compare their absorption strengths to lunar samples (partly due to particle size effects).

Shown in Figure A3 are modeled spectra produced using a lunar Mg-Suite low-calcium pyroxene from norite 78235, 9002A (En76Fs17Wo6). Here, it is apparent that even a pyroxene endmember with very low FeO (relative to the range expected for sampled lunar anorthositic pyroxenes) would not change the plagioclase abundance estimate for either Class A or Class B by more than ~1%. Thus, it does not appear that pyroxene composition will substantially affect the plagioclase abundance estimates for Orientale that are described in Table 2.

C.2 Particle Size Variations

Particle size can have a strong effect on absorption strength. The mixing calculations described in Section 3 have been carried out assuming, for simplicity, that both the plagioclase and pyroxene endmembers are equal in particle size. Petrography of lunar anorthosites in the sample collection has shown that plagioclase crystals commonly form millimeter-sized laths, whereas pyroxenes are only tens of microns in diameter [e.g., *McGee*, 1993]. All other constraints being equal, the optical path length would thus on average be shorter for the pyroxene, and this difference would result in weaker pyroxene absorption than if grains were equal in size. This effect would produce a slight overestimate of the plagioclase abundance associated with each spectral class. If however, as expected, the exposed surfaces contain particulate material derived from small-scale impact gardening, the size discrepancy should diminish as plagioclase

crystals are expected to break down more easily than pyroxenes by comminution [*Cintala and Hörz*, 1992]. Thus, it is not possible to reliably estimate the relative grain sizes of plagioclase and pyroxene represented by the Orientale spectra and the assumption of comparable grain size is compatible with most regolith evolution models. However, it is clear that systematic grain size variations over even a relatively large interval would not result in Class A or Class B areas containing less than anorthositic proportions of plagioclase.

C.3 Linear vs. Non-linear Mixing

The physical scale of mixing, here assumed to be on the order of millimeters, can affect the relative absorption strengths of plagioclase and pyroxene in a bulk spectrum. For example, in a strictly intimate mixing scenario, the contribution of pyroxene to the bulk spectrum will be the most highly non-linear. However, if any mafic component exists concentrated in large-scale heterogeneities such as discrete pyroxene-rich boulders, the mixing behavior would be more linear and the measured regional spectrum could exhibit a relatively weaker pyroxene absorption than in the intimate mixing scenario described above. Petrography of returned lunar anorthosites suggests that the assumption of an intimate mixture, in which light interacts with a number of grains before being absorbed or returned to the sensor, is appropriate for these applications [e.g., *Pieters*, 1983]. For instance, the largest grains in anorthosites, typically plagioclases, are usually only a few millimeters in length and occur in a matrix of smaller (<1 mm) mafic mineral grains [e.g., *McGee*, 1993]. Further, although our analysis of several NAC images in this region did not suggest that discrete pyroxene-dominated blocks are common on IRR massifs, additional analyses would be useful to address the importance of areal mixing on

the scale of an M^3 pixel as well as regolith mixing issues. We note, however, that even under a strictly linear mixing scenario, calculations using the same lunar endmembers as described above (Table 3) result in Class A spectra that correspond to 92-100 vol% plagioclase. Thus, even in the most extreme case (e.g., very pure plagioclase areas distinct from large blocks of pyroxene within an M^3 pixel), Class A spectra, which dominate the mineral exposures in the IRR, are representative of anorthosite, *sensu stricto*.

C.4 M^3 Data Considerations

The data used in this analysis was Level 2 as delivered to PDS. We evaluated whether the “ground-truth” correction described by *Isaacson et al.* [2013] affects the result. Although this correction is now recommended for M^3 data, we found that it did not significantly alter the spectral characteristics of the crystalline non-mare material in the Orientale region that is the focus of this analysis. A subset of ~100 Class A spectra were examined with and without ground truth applied, and the level of the correction was found to be well below that of varying plagioclase abundance.

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Table C1. LROC NAC images analyzed in this study^a.

Image ID	Center Latitude (°N)	Center Longitude (360°)
M145210647RE	-24.98	271.14
M114613998LE	-13.54	259.84
M114613998RE	-13.54	259.75
M129852054LE	-19.31	273.8
M129947051LE	-23.94	259.19
M142835956LE	-21.9	273.61
M145210647LE	-24.98	271.22
M158191296RE	-11.55	268.2
M158232013RE	-11.91	261.94
M158238556RE	-24.71	260.58
M160587105RE	-12.27	262.37
M168856058LE	-12.1	261.06

^aNAC images corresponding to 12 anorthosite identifications were examined for geologic context and surface morphology. General findings are discussed in Section 4. Spectra for these regions are classified as Class A and represent anorthosite with the highest plagioclase abundance observed in the Orientale basin.

Figure Captions.

Figure C1. Figure C1. The locations of the discrete areas across the Orientale basin exhibiting strong NIR absorption features that were evaluated in this study. These locations are shown in Figure 9, classified according to their spectral properties. Red asterisk symbols denote the locations of the NAC images shown in Figure 8a and in Figures C5-C8.

Figure C2. Four synthetic pyroxenes discussed in *Klima et al.* [2007, 2011] that generally span the compositional range expected for low-calcium pyroxenes in lunar anorthosites. Each of these samples was input into the non-linear mixing model described in Section 3, and the results are given in Figure C3. The arrow indicates 950 nm. Spectra were obtained from the RELAB database. Sample numbers correspond to those given in *Klima et al.*, [2007, 2011] and refer to their RELAB IDs: DL-CMP-026, DL-CMP-004, DL-CMP-025, DL-CMP-008.

Figure C3. Non-linear mixture models for various pyroxene compositions produced using the approach described in Section 3. The input plagioclase spectrum for all models is a separate from highland soil 62241 (the same as used for the modeled spectra shown in Figure 7). The pyroxene endmembers correspond to the four synthetic pyroxenes shown in Figure C2. The plagioclase abundances that were assigned to the Class A spectra of Figure 7 are shown in red. The plagioclase abundances that were assigned to the Class B spectra in Figure 7 are shown in orange, with symbols. The plagioclase abundances that were assigned to the Class C spectra in Figure 7 are shown in grey. The only pyroxene endmember that remains undetectable at the 1% level is the highest-Mg sample. Arrows are positioned at 950 and 1250 nm.

Figure C4. Calculated mixture spectra using a lunar pyroxene endmember that is more Mg-rich (En76Fs17Wo6) than the endmember in Figure 7 (the plagioclase endmember is the same). The pyroxene endmember is a spectrum of an orthopyroxene separate from norite 78235, 9002A (0-250 μm). The plagioclase abundances that were assigned to the Class A spectra of Figure 7 are shown in red. The plagioclase abundances that were assigned to the Class B spectra in Figure 7 are shown in orange, with symbols. The plagioclase abundances that were assigned to the Class C spectra, up to 15% pyroxene, in Figure 7 are shown in grey. Arrows are positioned at 950 and 1250 nm.

Figure C5. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC images M114613998RE and M114613998LE. Detections in the lower right may correspond to blocky material apparent in the scene, but the detections in the upper left are not obviously associated with morphologically fresh, large blocks. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

Figure C6. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M129947051LE. These detections occur on the slope of an IRR massif. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

Figure C7. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M142835956LE. This detection is correlated with a small, bright crater. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

Figure C8. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M160587105RE. These detections are associated with bright, blocky material near the crest of an IRR massif. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

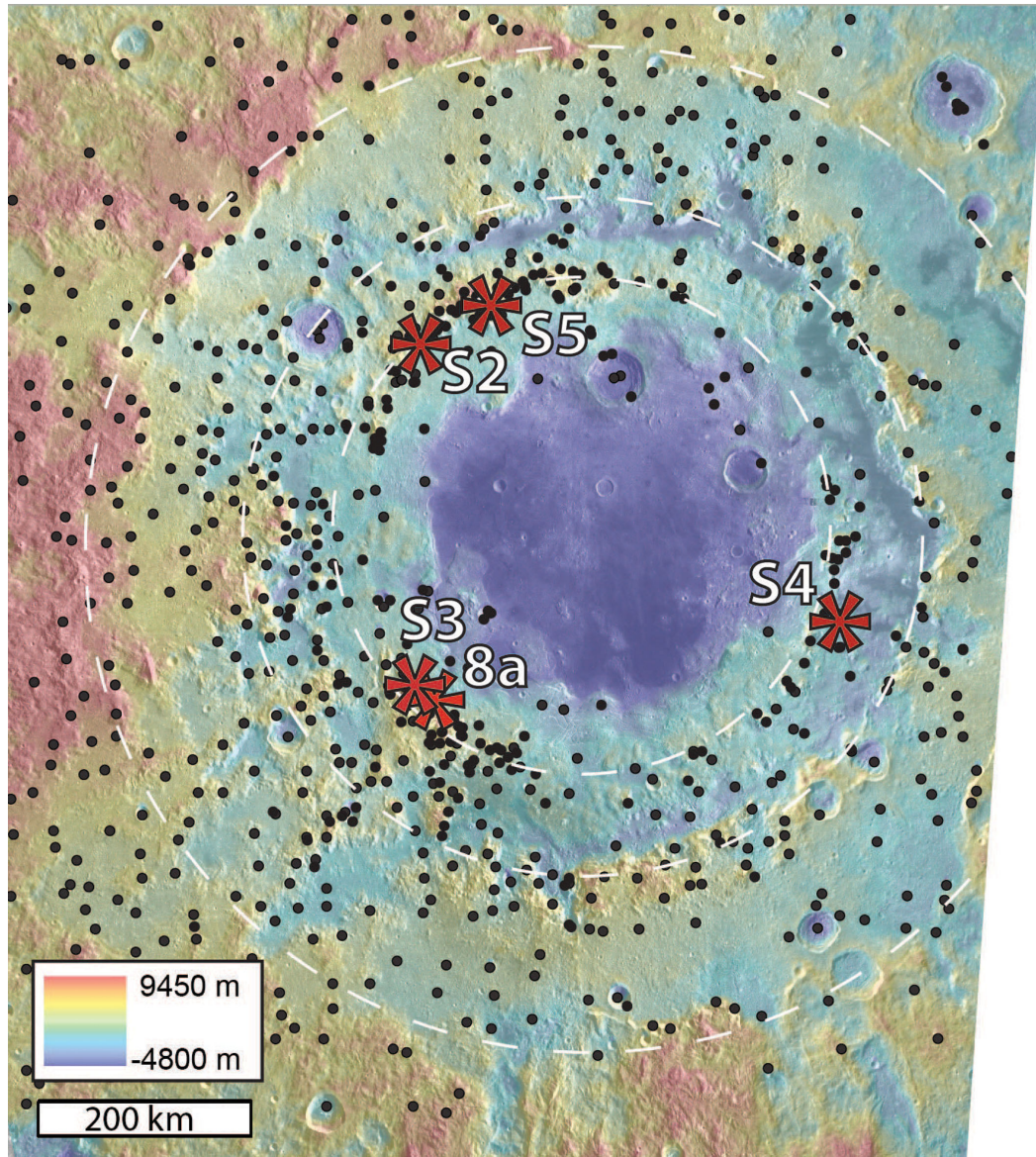


Figure C1. The locations of the discrete areas across the Orientale basin exhibiting strong NIR absorption features that were evaluated in this study. These locations are shown in Figure 9, classified according to their spectral properties. Red asterisk symbols denote the locations of the NAC images shown in Figure 8a and in Figures C5-C8.

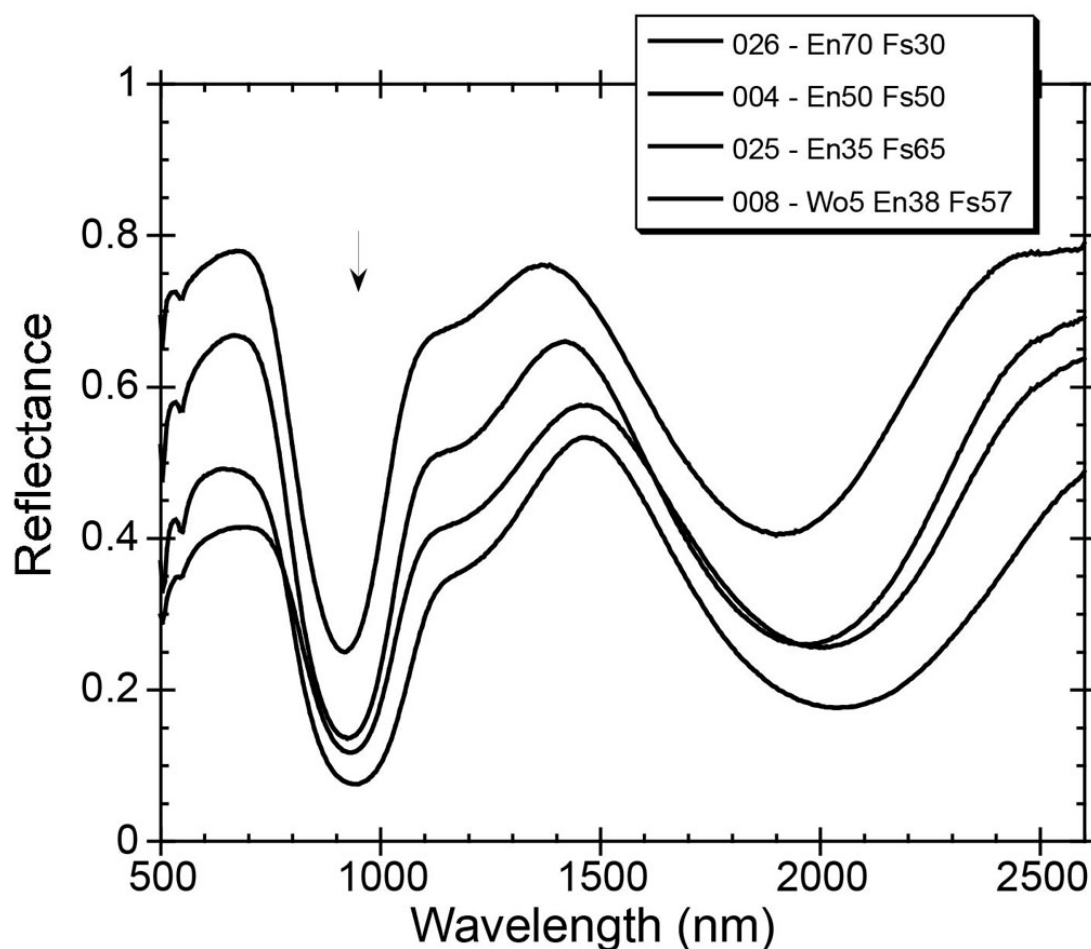


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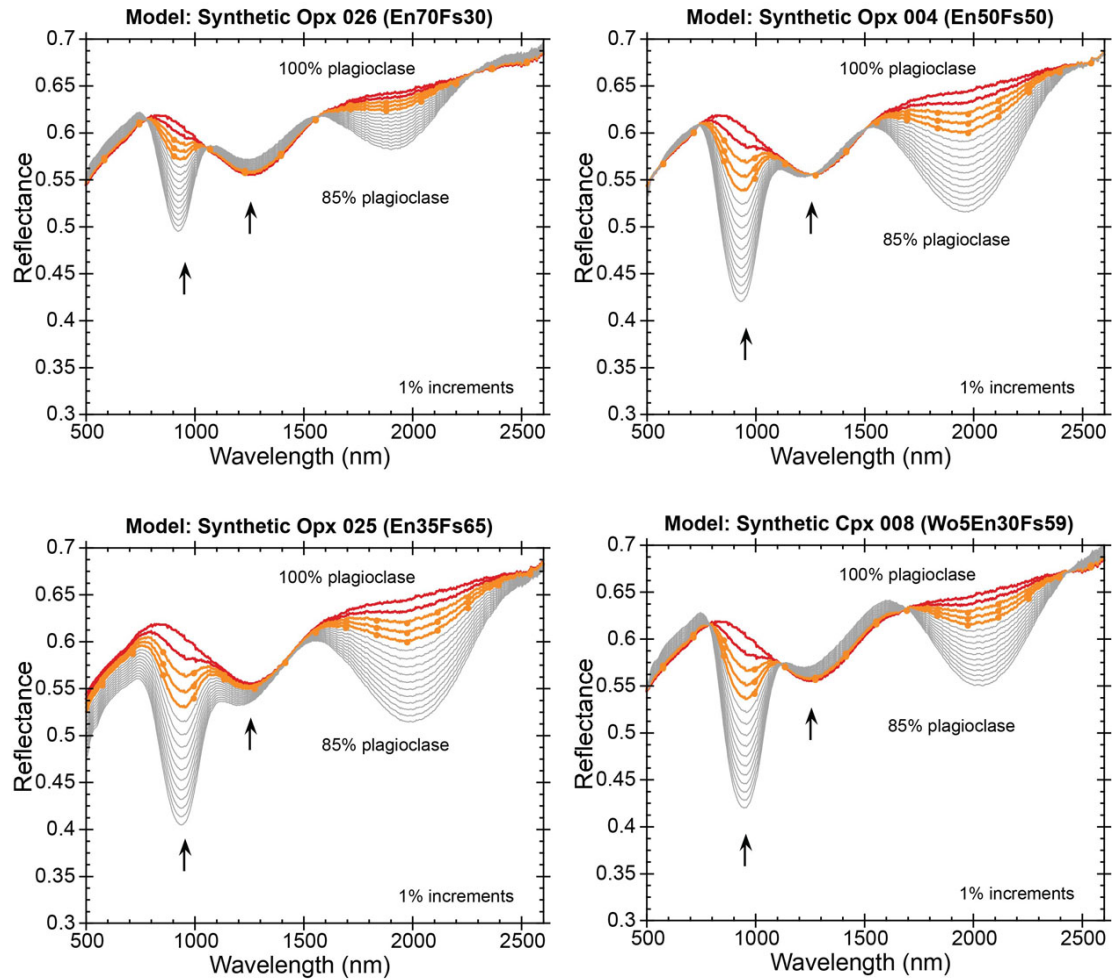


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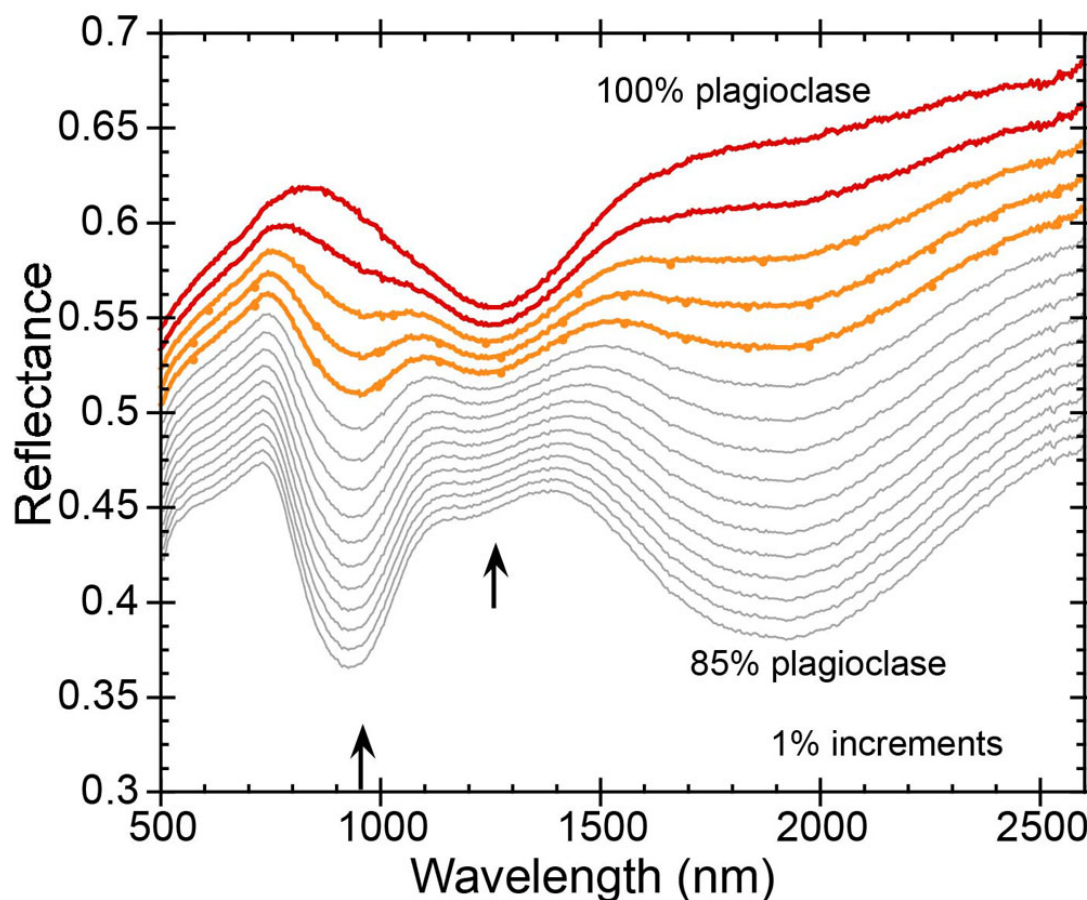


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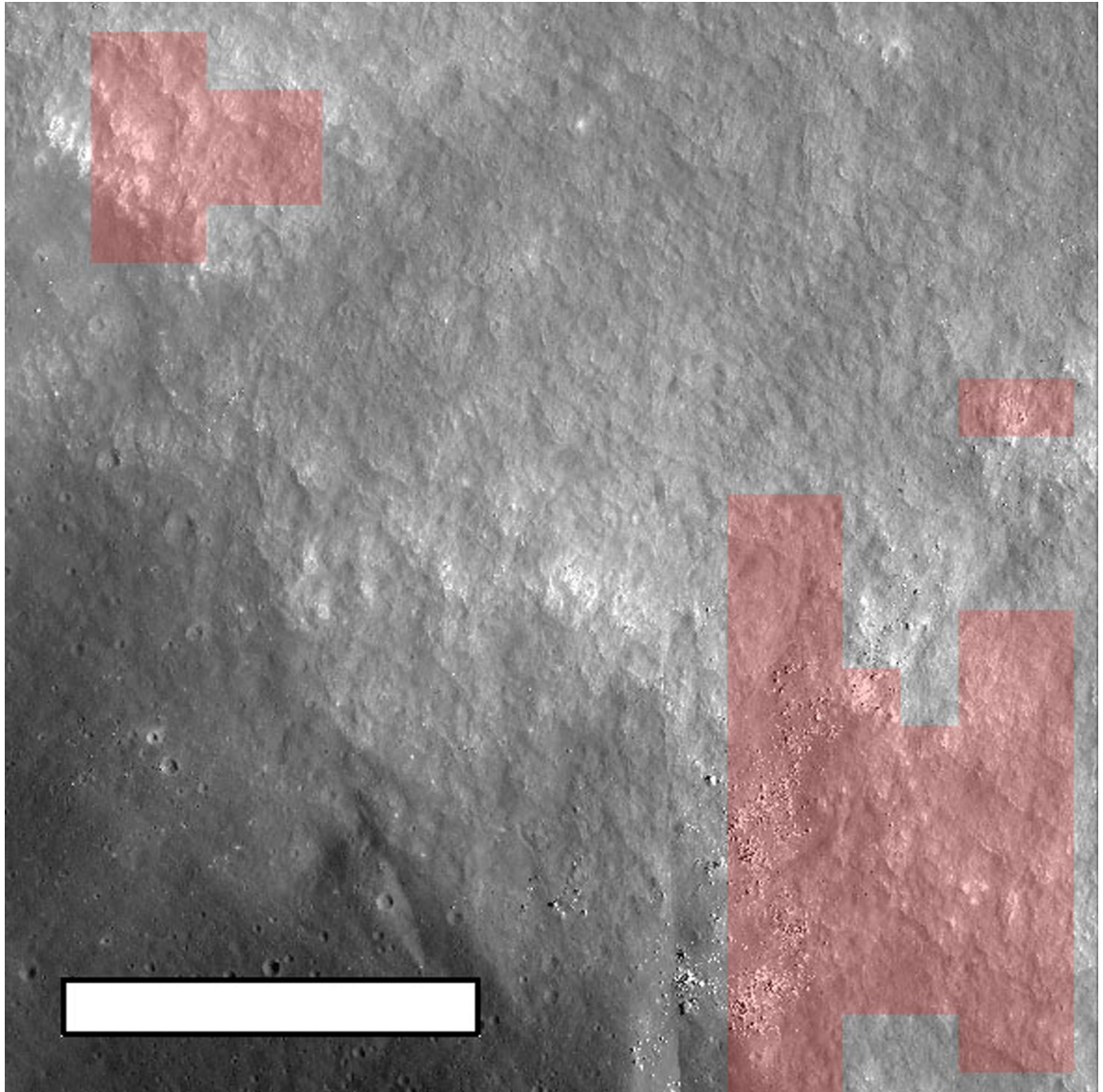


Figure C5. M³ pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC images M114613998RE and M114613998LE. Detections in the lower right may correspond to blocky material apparent in the scene, but the detections in the upper left are not obviously associated with morphologically fresh, large blocks. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

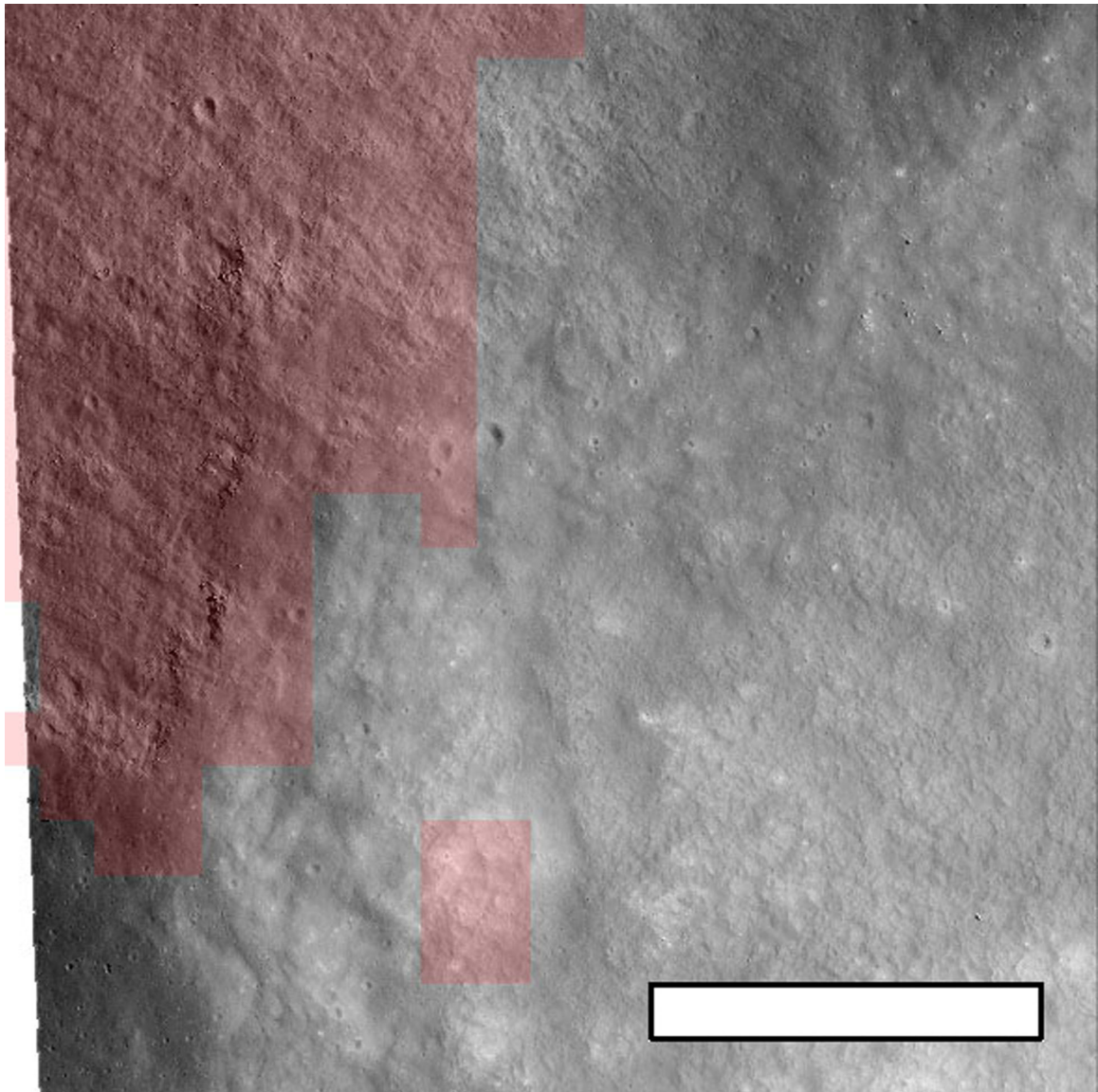


Figure C6. M³ pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M129947051LE. These detections occur on the slope of an IRR massif. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

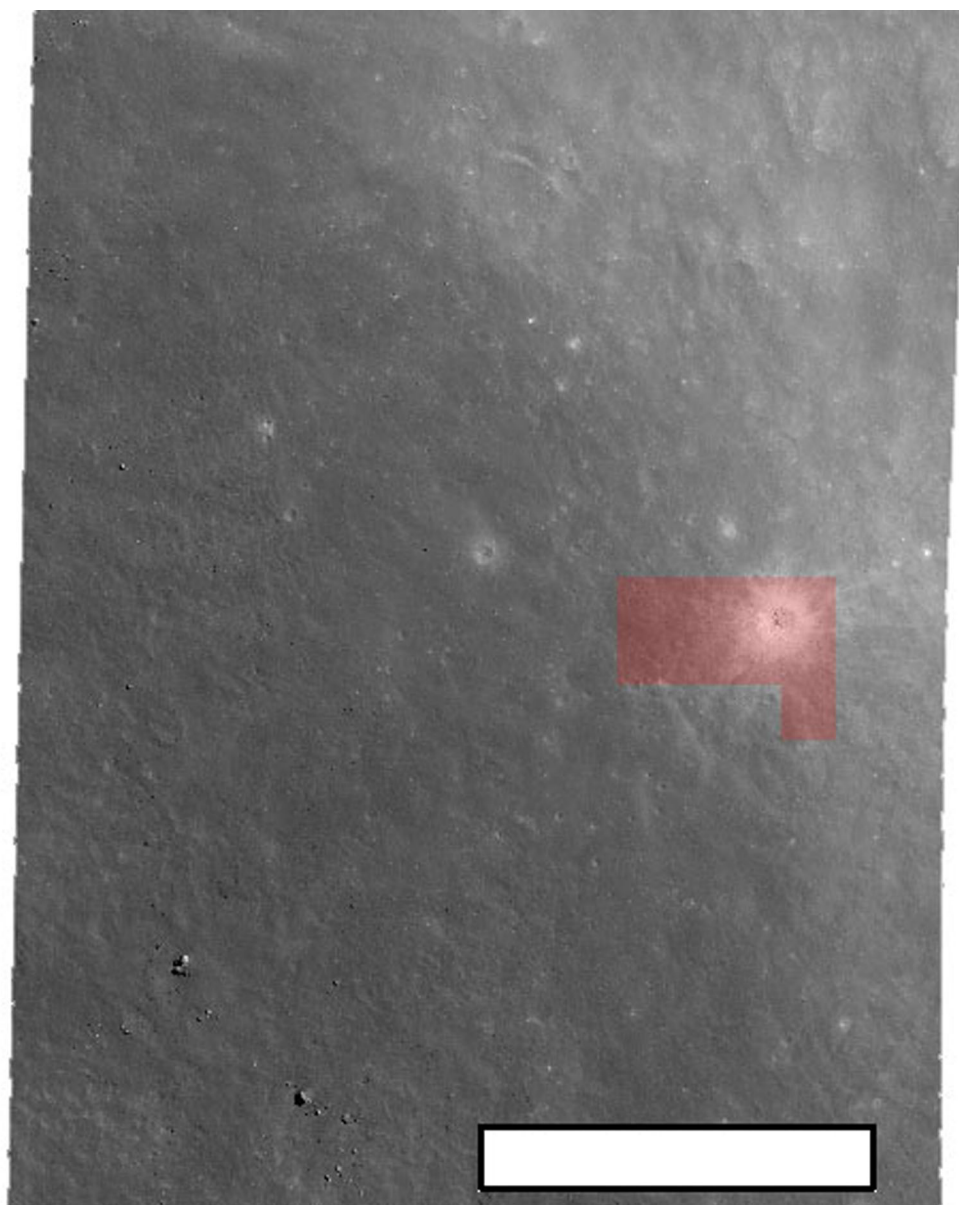


Figure C7. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M142835956LE. This detection is correlated with a small, bright crater. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.

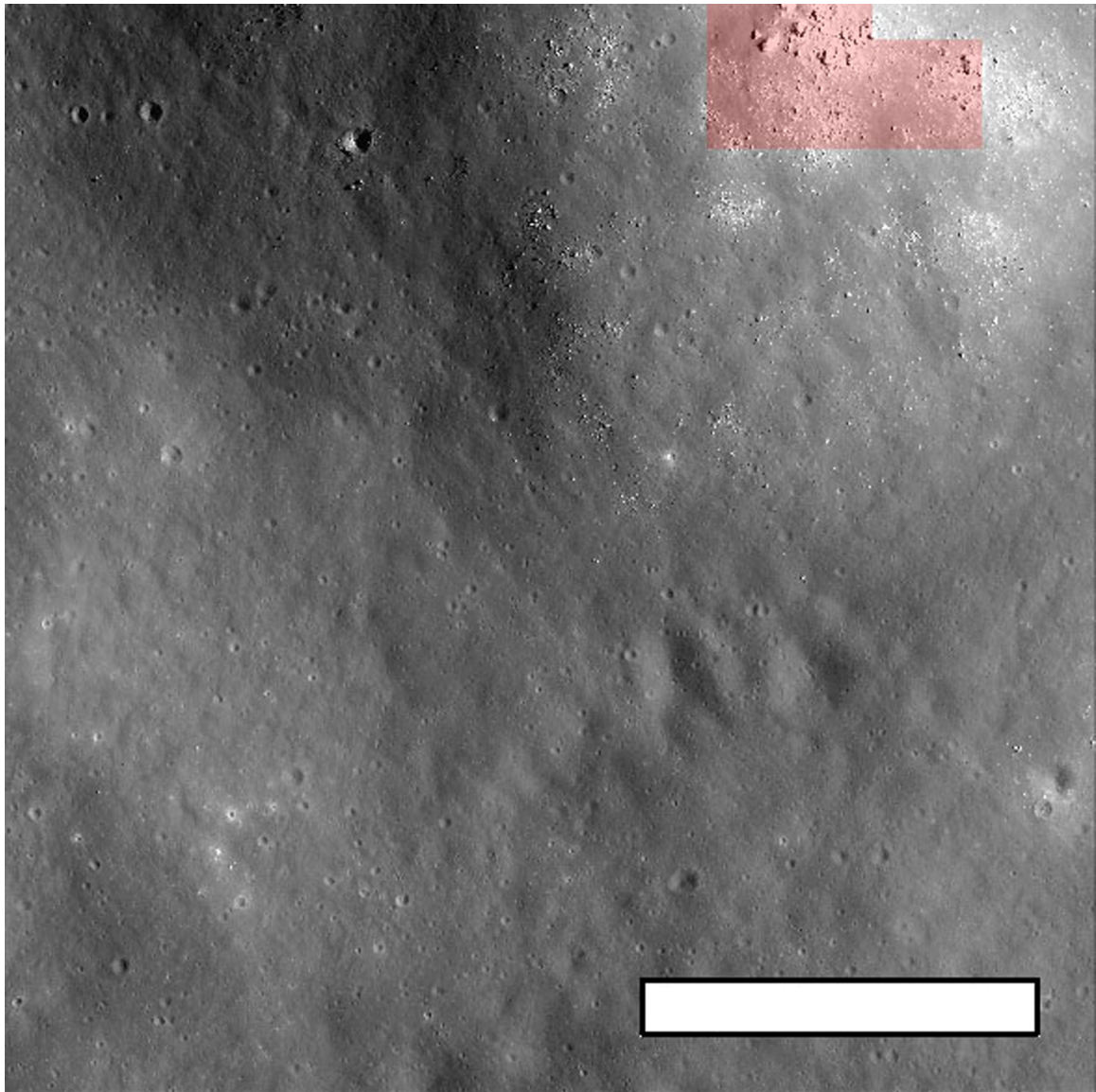


Figure C8. M^3 pixels displaying a strong 1250 nm plagioclase absorption are shown in light red overlain on a portion of LROC NAC image M160587105RE. These detections are associated with bright, blocky material near the crest of an IRR massif. Areas of the scene not overlain with light red correspond to spectrally featureless material. The locations of this massif is indicated in Figure C1. Scale bar is 1 km.