

Lunar Sample Ground Truth: A Cornerstone of Remote
Mineralogical and Compositional Analysis of Planetary
Surfaces

By

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B.S., Yale University, 2005
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A dissertation

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This dissertation by Peter J. Isaacson is accepted in its present form by the
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the degree of Doctor of Philosophy.

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Curriculum Vitae

Peter Jonas Isaacson

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Education & Honors

Brown University, Providence, RI

Master of Science, Geological Sciences, May 2007

Ph.D. expected May 2010

Master's Thesis: Origins of the Northern Imbrium Noritic Deposits.

Honors: Brown University First Year Fellowship, Geology Club Treasurer, NSF Graduate Research Fellowship Honorable Mention (2005), Sheridan Center Teaching Certificate I

Advisor: Professor Carlé M. Pieters

Yale University, New Haven, CT

Bachelor of Science, Geology and Geophysics (with honors), May 2005

Thesis: Relief change and erosion history of the Icicle Creek area, Washington Cascades, using (U-Th)/He thermochronometry.

Honors: Penfield Prize, Belknap Prize, Pat Wilde Prize, Senior Award, Environmental Studies Summer Internship Program

Advisors: Professors Mark T. Brandon and Peter W. Reiners

Research & Professional Experience

Brown University, Research Assistant to Dr. Carlé M. Pieters, 2005 – present

Involved in several original research projects dealing with remote and laboratory compositional analysis of lunar materials. Projects include remote compositional analysis of regions of the Moon with a focus on interpreting their origin, analysis of water in lunar soil with laboratory spectroscopy, and spectroscopic characterization of lunar rock and mineral samples. Results have been presented at professional meetings and published in peer-reviewed journals.

Moon Mineralogy Mapper Science Team, 2005 - present

Participated in biweekly teleconferences and numerous science team meetings. Activities include targeting support, mission planning, data calibration and validation, and data analysis.

JPL Planetary Science Summer School, July 2008

Contributed to student team development of concept New Frontiers-class mission to Io. Participated in design sessions with JPL TeamX support. Responsibilities included imaging spectrometer concept design and mission design to reach Jupiter orbit in 6:1 resonance with Io. Contributed to final report and mock New Frontiers proposal.

Yale University, Research Assistant to Prof's. Mark Brandon and Peter Reiners, 2003 – 2005

Involved in analysis of recent relief change in active convergent zones using (U-Th)/He thermochronology and inverse modeling. Projects included developing an inverse model to calculate relief change from thermochronological (cooling age) data, assisting in relief change analysis of the Italian Apennines through the NSF Continental Dynamics funded RETREAT project, and thesis research on relief change in the Washington Cascades.

Publications

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Teaching and Community Service Experience

Brown University, Teaching Assistant, GEOL 0220, Fall Semester 2009.

Responsibilities include teaching the laboratory portion of course, grading laboratory exercises and homework assignments, assisting with regular office hours/course discussion time (“drop ins”), and occasional assistance with class lecture materials.

Ladd Observatory, Brown University, Invited Lecture, July 20, 2009.

Gave introductory lecture on basic lunar science and history of lunar science and exploration, as well as the current and future eras of lunar science and exploration. Event celebrated the 40th anniversary of the first manned lunar landing. Lecture title: “Lunar geology: Apollo & Beyond”

Georgia Institute of Technology, Aerospace Engineering Design Course, *Invited Guest Lecturer*, Spring Semester 2008.

Gave lecture on lunar science, the Apollo program, and current and future lunar exploration efforts to senior undergraduate aerospace engineering design class of approximately 50 students. Provided consultations to individual design teams planning sample return missions from South Pole-Aitken (SPA) basin on the lunar farside.

Brown University, *Science Outreach Instructor, Vartan-Gregorian Elementary School, Providence RI*, 2006.

Taught overview lessons of Earth and Mars to third and fourth grade classes.

Yale University, *DEMOS participant, New Haven, CT*. 2004.

Gave demonstrations and discussion of basic science to elementary and middle school students.

Research Grants

Spectroscopy of Lunar Meteorites: Groundwork for Lunar Exploration, NASA Lunar Advanced Science and Engineering Research (LASER) Program, 2008-2010, NNX08AY89G.

Professional Memberships

American Geophysical Union, student member, 2006 – Present

Geological Society of America, student member, 2008 – Present

Mineralogical Society of America, student member, 2008 – Present

American Astronomical Society, Division for Planetary Sciences, Affiliate Member, 2009 - Present

Elected to Sigma Xi, 2008

Acknowledgments

In trying to come up with a list of all the people who have helped me get to where I am today, I realize that the task defines “impossible”. I will surely miss somebody, so I’ll do my best to keep these acknowledgments general. So, please know that even if I haven’t mentioned you here by name, I am thankful for the chance to have gotten to know and interact with everyone over the past 5 years.

The jump to starting grad school definitely is a bit jarring, but I have to say that the other grad students here when I arrived were really welcoming and made the transition a lot smoother. Sitting around the table eating lunch in room 105 with the whole group really made the program and group feel a lot more welcoming. Ralph at one point took pity on me, the poor little first year staring helplessly at a Sun workstation with no idea what to do with that empty terminal window. Along similar lines, I want to thank Caleb and Jay for always being cheerful whenever I came by with some strange (and usually silly) Arcmap question. Wes never failed to remind me not to work so hard, and even though I ignored him most of the time, it was much appreciated. It was great to be able to share the insanity of being a crazed Red Sox fan with Carolyn. I also want to thank/blame Wes and Carolyn for getting me hooked on ultimate Frisbee. Thanks to them, the undergrads sitting peacefully on the Lincoln Field green were never safe from flying plastic discs. They should know that I’ve done my best to continue the tradition of hitting innocent bystanders with flying pieces of plastic. Even though I still only understand about 75% of what he says (up from about 25% when we first met), it’s been mostly great having Gareth around for the past 5 years, especially because he’s such a good sport about losing the “RiRa hill race” every time.

I've had the good fortune to share an office with some great people. Joe and Sam were always equally ready for a stupid joke, serious discussions, beer, and usually some combination of all three. I want to thank Joe in particular for the continuing supply of the latest and greatest in delicious home-brewed beer. Although I have to admit that a few of those offerings are still somewhere in the back of the fridge, and would probably make fantastic astrobiology experiments at this point. Jenny has been a great newcomer to the office. And that Noah guy, well, I'll come back to him.

There is a big crowd of folks I've been fortunate enough to hoist a pint or six with at the GCB over the last few years. On the Lincoln Field side, I want to mention Bethany, Deb, Laura, Brendan, Ailish, Mark, Kerri and Jason, and Angela – you've all helped keep this place (and me) sane over the last few years. Across the street (apologies in advance for the long list), this cast of motley characters includes Jon, Ashley, Linda, Caitlin, Mariela, McCall and Danny, Heather and Dave, and the massive list of first and second year ~~alcoholics~~ grad students (Aron, Scott, Rocio, Colin, Bronwen, Mary, Tina, Jess, and Jeff).

I want to make special mention of “Team Carlé”, past, present, and future. I've been very fortunate to be in a group of great scientists but also great people. Pretty much every member of the group I've met and interacted with has been nothing but warm and friendly and also a great scientist and mentor. As far as the folks I overlapped with, Rachel was always there for any sort of conversation, from serious talks about mineral spectroscopy and crystal field theory to baseball. Noah really converted me into a true lunatic, is a fellow crazed Red Sox fan, and has helped me immeasurably over the last 5 years. Both Rachel and Noah are good reminders that one can do this job and still have

fun, without taking things too seriously. The newest members of the group, Leah and Deepak, are both great people and will carry on the tradition well!

I want to mention a few of my former teachers and advisers who have played a part in my route to a Ph.D. thesis in planetary science. I likely would never have considered a career (or even a degree) in science were it not for Peter Naiden, who taught my first high school science class and really introduced me to science. I want to thank my eighth-grade English teacher, Jack McMahon, who pretty much taught me how to write. Ian Ramsey's music theory class was something of an "escape" during high school, and he's still a source of good advice today. I also want to thank Samantha Langley-Turnbaugh for supervising and advising me as a summer intern at the University of Southern Maine, and letting me get my hands dirty with a large soil science study, which showed me that I really liked lab work. I want to mention Ron Smith, who taught the remote sensing course that made me decide that I wanted to do that kind of work as a graduate student. Ron put me in touch with Jack at Brown, and the rest, as they say, is history. I especially want to thank my two undergraduate research advisors, Pete Reiners and Mark Brandon. They both gave me far too much of their time as well as important roles in their research projects, and this experience was vital to my going on in science. I also want to thank my college roommate and friend, John, who convinced me to make that early-morning walk up the hill to my first geology class. Lastly, I want to mention my friends from high school and earlier, Rassul and Colin, who were always there when I needed a break from everything related to grad school.

At Brown, I've had the good fortune to interact with a number of wonderful teachers, scientists, and mentors. I won't mention everyone because I'd end up listing

most of the faculty, but I do want to mention a few people specifically. Jan and Karen were very supportive and great mentors when I was a TA for their class. Alberto was always full of enthusiasm and willing to talk about the Moon. I also want to thank Alberto for being part of my preliminary exam committee. Lastly, I want to thank Paul for being a terrific teacher and adviser. I was fortunate enough to be able to take the last classes Paul taught at Brown, and I will say that the students who came after me and weren't able to take classes from Paul really missed out. Paul is a wonderful teacher who for some reason has stuck around on my committee for my entire 5 years at Brown, and I am truly grateful.

On the Lincoln Field side, I want to thank Pete for his constant enthusiasm; Pete is so good at reminding us of how cool the stuff we do really is! Jack has had lots of good advice for me over the past 5 years, and also took the time to talk to me (and probably recruit me) when I was looking around at graduate programs without having the foggiest idea about planetary science. I also want to thank Mike for being on my committee over the past few years, and for the numerous conversations about science and life, sometimes over beer. Jim has been on my committee from the beginning, and his knowledge and ability and constant reminders to get to the bottom of things and express the big picture clearly without diluting the science have been an important part of my education. I also want to thank Clive Neal for taking the time to participate on my Ph.D. defense committee as a reader.

I also want to thank the staff around the department who have helped me so much. In particular, Rebekah, Celeste, and Peter have always been very supportive, and Nancy and Ruth are always ready to answer questions cheerfully. I also want to thank Bill for

always finding time to solve problems despite everything on his schedule, as well as the regular supply of baseball DVD's! Nancy in particular was a big help in navigating the whirlwind of my first grant proposal. I also want to acknowledge Taki for all of his work keeping the RELAB running and producing all of the high quality spectra without which this thesis would have been impossible to write. I've also learned a lot about spectroscopy and radiative transfer from conversations with Taki. I also want to thank Jeff, who has always been cheerful no matter how many demands and problems get piled on to his to-do list.

Being involved with the M³ science team has been an enormous part of my education, and I can't thank that group enough for being so open and welcoming from the get-go to a know-nothing first-year graduate student. I especially want to recognize Jessica Sunshine, Matt Staid, Joe Boardman, and Cass Runyon. They've all helped me significantly, but more importantly, they're just good people, and I'm fortunate to be able to call them friends. Jess in particular has been extremely supportive and scientifically critical in an overwhelmingly positive way. The M³ team has also demonstrated how to remain positive as a group through some bumps in the road.

After living by myself my first year in Providence, I've lived with a bunch of great people who have helped keep me sane and well plied with potent potables. Alison and Cori took a flyer on me, and I'm really glad they did. Snowman forever. Even though we couldn't convince them to stay, I got to live with other great people like Uly, Kate, and Shannon. They're quick to tell me I need to leave the office and come have fun. The more things change, the more they stay the same. And somehow, 98 Transit Street is still standing as of this writing.

I owe a special thanks to Larry Taylor. Larry heard me give a talk at an M³ science team meeting, and decided something I said was a bit off. So his solution was to invite me down to Knoxville, host me at “Tranquility Base”, give me a private course on electron microprobe analysis, and to let me break in (hopefully not literally) his brand new electron microprobe. This was a side of work with lunar samples that I did not experience while at Brown, so I owe a good portion of the breadth of my graduate education experience to Larry. I consider Larry almost as a second adviser.

I spoke glowingly of “Team Carlé”, but a good deal of the credit for this group of good people must go to the leader herself. I am extremely grateful to have had the chance to work with and learn from Carlé over the past 5 years. No matter how busy she is (and it’s usually “very”), Carlé will give you her complete, undivided attention when you walk into her office and ask if you can have a minute, even if it usually turns out to be more like an hour. I realize now that I had no idea what I was doing when deciding on graduate programs 5 years ago, but I am truly thankful that I stumbled into the decision to come to Brown and work with Carlé and everyone else mentioned above.

The person who has been with me more than anyone over the past year or so is Kate. Her positive attitude even as I was forced to spend more and more long hours in the office with my dissertation was remarkable, and made the whole process much easier. Her smiles, love, and unwavering support have meant so much to me.

Lastly, I want to thank my family. They have all been there throughout, and all of them even manage to give the impression that they’re interested in what I do. I have no doubt that the many outdoor excursions throughout my childhood played a significant role in my ending up as a geologist, and I am glad that my siblings and I were dragged

along on these ventures, even if we didn't always show it at the time! I owe so much of where I am now to them; thank you, and I love you all.

Rather than end with a series of inspirational quotes, I'll end with a few that make me smile:

"There was only one catch and that was Catch-22, which specified that a concern for one's own safety in the face of dangers that were real and immediate was the process of a rational mind. Orr was crazy and could be grounded. All he had to do was ask; and as soon as he did, he would no longer be crazy and would have to fly more missions. Orr would be crazy to fly more missions and sane if he didn't, but if he was sane, he had to fly them. If he flew them, he was crazy and didn't have to; but if he didn't want to, he was sane and had to."

-- Joseph Heller, *Catch 22*

"I've got plenty of common sense! I just choose to ignore it."

-- Bill Watterson, *Calvin & Hobbes*

And of course, I have to close with some "Moon" quotes:

"For when I look at the Moon I do not see a hostile, empty world. I see the radiant body where man has taken his first steps into a frontier that will never end."

-- David R. Scott, *Apollo 15 Commander*

"This has been far more than three men on a mission to the Moon; more still than the efforts of a government and industry team; more, even, than the efforts of one nation. We feel this stands as a symbol of the insatiable curiosity of all mankind to explore the unknown."

-- Buzz Aldrin, *Apollo 11 Lunar Module Pilot*

"It's different, but it's very pretty out here. I suppose they are going to make a big deal of all this."

-- Neil Armstrong, *Apollo 11 Commander*

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INTRODUCTION

Understanding the thermal and chemical evolution of planetary bodies is one of the pillars of planetary science and exploration. By investigating the history of solar system bodies such as the Moon, Mars, Mercury, Venus, and numerous asteroids, we continue to learn more about the evolution of the early solar system and the early history of the Earth. The processes by which planetary bodies evolve thermally (e.g., magma ocean processes, differentiation, internal convection, and volcanism) produce distinctive chemical signatures. If these chemical signatures can be detected, significant insight into the processes that shaped the body can be gained. Direct analysis of a diverse array of returned samples is the best tool for investigating the geologic history of planetary bodies, one of the reasons sample return missions are a “holy grail” in planetary exploration. Short of returned samples, surface composition of planetary bodies represents one of the best available clues for determining the thermal and chemical history of rocky bodies. Although planetary surfaces are subjected to a diverse range of processes that obscure the older record of geologic evolution, such as physical and chemical weathering, ongoing bombardment, and space weathering, those surfaces contain clues to the distinctive chemical signatures produced by the geologic processes that acted and are acting upon that planetary body.

Visible to near-infrared reflectance spectroscopy is a powerful tool for analyzing the surface composition of planetary bodies. Some of the most abundant minerals found on igneous solar system bodies, olivine, pyroxene, and spinel (although spinel is not common on planetary surfaces, being more of a high-pressure phase located in planetary

interiors) have diagnostic absorption features in visible to near-infrared reflectance spectra that enable remote detection [e.g., *Adams*, 1974; *McCord et al.*, 1981; *Pieters*, 1982; *Gaffey et al.*, 1993; *Pieters and McFadden*, 1994]. Furthermore, these absorption features change in predictable ways with the composition of the mineral, allowing not only remote identification but also remote analysis of mineral composition [*Sunshine and Pieters*, 1998]. When reflectance data are collected globally, these properties enable compositional mapping of planetary surfaces on the basis of mineral abundance. While far from the only technique available for remote compositional analysis of planetary surfaces, optical spectroscopy offers the capability of collecting compositional data with the highest spatial resolution, providing critical geologic context along with compositional information.

Like any technique, reflectance spectroscopy has limitations, as alteration processes such as those mentioned above can complicate interpretation of collected spectra [e.g., *Adams et al.*, 1979; *Pieters et al.*, 2000; *Hapke*, 2001; *Bibring et al.*, 2005], and not all mineral phases of interest exhibit diagnostic features. Analyses of mineral mixtures, of which the vast majority of igneous planetary rocks consist, can also be quite complex, and determining the exact composition of a segment of a planetary surface on the basis of reflectance spectra is often quite difficult and non-unique [e.g., *Nash and Conel*, 1974; *Singer*, 1981; *Mustard and Pieters*, 1987; *Mustard et al.*, 1998]. For this reason, predicted rock and mineral modal and chemical compositions determined from reflectance spectroscopy are typically considered approximate. Despite these limitations, the combination of potential high spatial resolution (relative to other compositional remote sensing techniques such as gamma ray or x-ray spectroscopy) and diagnostic

compositional indicators places reflectance spectroscopy in the top echelon of techniques for remote compositional analysis of planetary surfaces.

The position of the diagnostic absorption features in spectra of mafic silicates like olivine and pyroxene is linked to the specific crystal structure of the mineral, specifically the asymmetry and metal-oxygen distances of the cation sites in which transition metals reside [Burns, 1993]. Fe^{2+} is the dominant cation responsible for the diagnostic absorption features in visible to near-infrared reflectance spectra of common planetary mafic minerals. Background information about reflectance spectroscopy and reflectance measurements is presented below. While absorption properties are based in mineral physics and can be predicted theoretically, the diversity of forms and subtle variations in the natural environment is immense, and interpretations based purely on theory are often limited. This limitation is one reason that reflectance spectroscopy measurements rely on careful ground truth measurements of returned samples. Ground truth measurements are critical for calibration [Pieters, 1999], but are also important analogues against which to compare remotely-sensed data to guide compositional interpretations and constrain mapping of un-sampled terranes. Thus, high-quality measurements of a diverse library of lunar materials are essential for high-quality science using remotely-sensed reflectance data (analysis of samples we do have is critical to learning what we can through remote sensing about samples we don't have). High quality ground truth data is particularly important in the current era, with modern reflectance spectrometers recently or currently in operation around or en route to a wide range of solar system bodies. These spectrometers are producing datasets of unprecedented spatial and spectral resolution, offering the ability to perform high quality compositional analyses that address wide-

ranging questions in planetary science. In this context, the following chapters present a variety of contributions to lunar ground truth, with newly analyzed samples and with new methods for application of ground truth.

Outline of Chapters

We begin in chapter 1 with an overview of a project focused on integrated analyses of a suite of lunar mare basalt samples. The suite includes two low-Ti samples from Apollo 15, and two ilmenite-rich high-Ti samples collected during the Apollo 17 mission. This project conducted coordinated analyses of the mineralogy/petrography and reflectance spectroscopy of the bulk samples, and also prepared mineral separates from the samples that were characterized similarly. These samples and mineral separates represent, to my knowledge at this writing, the best available samples with which to test models for spectral unmixing. The samples have been characterized carefully and the endmember separates were collected from the specific sample being “unmixed” from its bulk sample reflectance spectrum. This chapter also provides a careful characterization of completely unweathered mare basalts, the “starting material” for the weathered mare soils analyzed by the Lunar Soil Characterization Consortium [*Taylor et al.*, 2001]. Chapter 1 provides an overview of the samples and the measurement procedures, and gives example applications of the results to mixture modeling and quantitative spectral deconvolution. Chapter 1 has been submitted to *Meteoritics and Planetary Science*, has been through the peer-review process, and is nearly ready for final publication.

Chapter 2 presents an application of the results described in chapter 1, focusing on the effect of ilmenite on reflectance spectra. Efforts to map ilmenite (technically, TiO_2) traditionally have relied on an empirical correlation between a ratio of wavelengths in the

UV to wavelengths in the visible (UV-Vis) and the TiO₂ content of bulk lunar soil [e.g., *Charette et al.*, 1974; *Lucey et al.*, 1995]. However, the spectral signature of ilmenite extends well beyond a flat or relatively “blue” slope across the UV-Vis wavelengths; depending on the particle size and opacity of the host material, ilmenite can cause weakened and distorted absorption features near 1 and 2 μm in spectra of basalts, and also causes prominent upturns in reflectance beyond $\sim 1.5 \mu\text{m}$. With the advent of orbital spectrometers capable of measuring reflected radiation at these longer wavelengths, such signatures can now be used to constraint the presence and abundance of ilmenite in addition to the traditional UV-Vis approach. Chapter 2 presents a correlation analysis between ilmenite abundance and spectral ratios to identify those parameters most useful for detection of ilmenite across this broader wavelength coverage. However, the results of this approach are limited by the samples available for the study, and full exploration of this issue and publication of these results will likely require analyses of additional samples. Chapter 2 also provides a short overview of the possible explanations for the features exhibited by spectra of lunar ilmenites.

Chapters 3 and 4 focus on evaluating the composition of lunar olivine with visible and near-infrared reflectance spectroscopy. The major absorption features in olivine reflectance spectra are known to shift with composition [*Burns*, 1970], and these trends can be detected by deconvolving near-infrared spectra into component absorption bands [*Sunshine and Pieters*, 1998]. Lunar olivines cannot be treated in the same way as terrestrial olivine, as lunar olivine contains chromite inclusions that alter the olivine’s spectral characteristics. Chapter 3 addresses the effect of the absorptions due to chromite, and presents a method for obtaining results consistent with those found in

laboratory analyses of terrestrial olivine. Chapter 4 addresses the additional complexities involved in applying the methods of chapter 3 to remotely-sensed spectra. Remotely-sensed spectra typically exhibit pronounced continuum slopes, which complicate analyses of olivine-dominated spectra using the approaches described in chapter 3 and by previous work [*Sunshine and Pieters*, 1998]. Chapter 4 presents a method for continuum removal that standardizes the process of analyzing remotely-sensed olivine-rich spectra. The effects of continuum removal on the deconvolved absorption band properties are addressed, and a correction method is proposed. The methods are applied to a suite of spectra collected by the Moon Mineralogy Mapper (M³), and are used to estimate the composition of the olivine measured with those reflectance spectra. Chapter 3 has been submitted to *Icarus*, and chapter 4 is in preparation for submission to the *Journal of Geophysical Research*.

Chapter 5 presents the current results of an ongoing study of the spectroscopy of lunar meteorites. Previous research suggests that the Apollo samples, despite their extraordinary value and countless contributions to lunar science, may present an incomplete view of lunar geology due to their origin from a unique geochemical terrane [e.g., *Korotev*, 2005]. Lunar meteorites represent a more diverse (but random) sampling of the lunar crust, and thus would be important contributions to the ground truth sample collection in their own right. Spectroscopic investigation of lunar meteorites offers the potential for additional important scientific advances. The diverse sampling of the crust by the lunar meteorites offers the potential for additional contributions to our understanding of lunar geology. However, the impact of the meteorite samples is limited by their unknown geologic context (beyond broad generalizations such as “mare basalt”,

“highland”, or possibly “farside highlands”). If high-quality ground truth reflectance spectra are acquired, it may be possible to constrain the geologic context of these important samples far more precisely. The work initiated in Chapter 5 ultimately will involve measurement of the bulk samples as well as analyses of their individual components (minerals and lithic clasts). Chapter 5 presents results for the bulk (chip) samples, as well as one case study of the specific components of one sample. Chapter 5 will not be published in its current form, but the results of the focused analyses of the chip components and bulk samples ultimately will be submitted for publication. Note that as chapter 5 is not a completed study, it is not meant to stand as an independent published work to the same extent as some of the other chapters. Thus, the introductory background material on reflectance spectroscopy is not repeated in chapter 5. This background information can be found below.

Chapter 6 presents an experimental approach to ground truth, as it describes experiments that attempt to measure lunar soils free from adsorbed terrestrial water. Reflectance spectra of lunar soils measured in terrestrial laboratories typically exhibit absorption features near 3 μm due to water and OH. This feature has traditionally been attributed to adsorbed terrestrial water. Chapter 6 describes heating experiments designed to remove the loosely-held component of the water. Lunar samples measured without terrestrial water would represent important ground truth constraints for remote sensing and detection of water on the lunar surface, particularly in light of the recent discoveries of diverse forms of lunar water [Clark, 2009; Pieters *et al.*, 2009; Sunshine *et al.*, 2009; Colaprete *et al.*, 2010; Spudis *et al.*, 2010]. Chapter 6 is nearly ready for

publication, likely in *Geophysical Research Letters*, although a final decision on the content of the submitted manuscript has not been made.

Finally, in Chapter 7, I summarize the key results found in the preceding chapters. I also identify a number of questions raised that suggest avenues of additional research, and identify possible applications of the work presented here.

Background: Reflectance Spectroscopy

Visible to near-infrared reflectance spectroscopy has been one of the primary tools for remote compositional analysis of planetary and asteroidal surfaces since the 1970's [e.g., *Charette et al.*, 1974; *Larson and Fink*, 1975; *McFadden et al.*, 1977; *Pieters*, 1978; *McCord et al.*, 1981; *Pieters*, 1982; 1986; *Pieters and McFadden*, 1994]. Much of this research has been based on the broad, diagnostic absorptions in visible to near-infrared wavelengths caused by electronic transitions in transition metal cations located in distorted mineral crystal lattice sites [*Burns*, 1993]. Such diagnostic absorptions are observed in spectra of mafic silicates common to planetary surfaces such as pyroxene and olivine [e.g., *Burns et al.*, 1972; *Adams*, 1974; *Hazen et al.*, 1978; *Cloutis and Gaffey*, 1991], one of the reasons visible and near-infrared (vis-NIR) reflectance spectroscopy is a powerful tool for remote compositional analysis of these surfaces. More narrow absorptions linked to molecular vibrations, bends, and stretches are also used for remote compositional analysis, typically for water-bearing alteration mineral such as clays and sulfates [e.g., *Bibring et al.*, 2005; *Gendrin et al.*, 2005; *Bibring et al.*, 2006; *Ehlmann et al.*, 2008].

The broad, diagnostic absorption features in vis-NIR reflectance spectra of mafic silicates like pyroxene and olivine are known as spin-allowed crystal field (CF)

absorptions [e.g., *Burns*, 1993]. They are caused by crystal field electronic transitions in transition metal cations located in a ligand field such as a mineral's crystal lattice structure. In mineral crystal structures, the crystallographic sites are asymmetric, causing the *d*-orbital electrons in the transition metal cation to be split into more than one energy level [*Burns*, 1993]. Incident photons with the proper wavelength can be absorbed and cause an electron to be excited to a higher energy level. Spin-allowed crystal field transitions produce substantial absorption features such as those observed in vis-NIR spectra of pyroxene and olivine, whereas spin-forbidden transitions produce features ~1-2 orders of magnitude weaker than spin-allowed transitions [*Burns*, 1993]. The strength of the spin-allowed crystal field absorptions is inversely proportional to the symmetry of the crystallographic site.

In the pyroxene structure, the M2 site is more asymmetric, and produces absorptions near 1 μm and 2 μm , while the more symmetric M1 site produces weaker absorptions near 1 μm and 1.2 μm [*Burns*, 1993]. In the olivine structure, the M1 site is more asymmetric, and produces absorptions near ~0.85 μm and ~1.25 μm [*Burns*, 1993]. In both cases, these absorption features shift with changing mineral composition. Ca-Mg-Fe pyroxene absorptions shift to longer wavelengths with increasing Ca and Fe content, while Mg-Fe olivine absorptions shift to longer wavelength with increasing Fe content [e.g., *Burns*, 1970; *Burns et al.*, 1972; *Adams*, 1974; *Hazen et al.*, 1978; *Cloutis and Gaffey*, 1991; *Klima*, 2008]. The position of these absorption features in wavelength space is controlled by the energy separation between the split *d*-orbital energy levels, which is largely determined by the metal-ligand distances of the specific crystallographic sites [*Burns*, 1993]. These shifts in the positions of absorption features in olivine and

pyroxene reflectance spectra are compositionally diagnostic, and can be used to estimate mineral composition with remotely-sensed reflectance spectra [e.g., *Sunshine et al.*, 1990].

Laboratory Reflectance Measurements

Reflectance is generally defined as the fraction of incident radiation reflected by any surface. Remotely-sensed reflectance spectra of planetary surfaces are typically acquired as bidirectional reflectance, in which incident radiation on planetary surfaces is measured only for a very specific range of incidence and emission angles. These angles are defined by the orientation and position of an orbiting spacecraft relative to the planetary body and the light source (typically the Sun). Laboratory reflectance measurements are collected in a variety of formats, including directional-hemispherical reflectance (specified incidence angle, emission measured over a hemisphere), bi-conical reflectance (incidence and emission angles span a range or “cone” of orientations), and bidirectional reflectance. While reflectance measurements not measured in bidirectional reflectance can be converted to bidirectional reflectance using approximations [e.g., *Hapke*, 1993], bidirectional reflectance measurements are the most desirable, as they can be compared directly to remotely-sensed bidirectional reflectance measurements.

Reflectance measurements in the RELAB at Brown University [*Pieters and Hiroi*, 2004], where all laboratory spectra presented in this thesis were measured, are acquired in two forms. Across the visible to near-infrared, reflectance spectra are acquired in bidirectional reflectance (BDR). Reflectance spectra are collected in biconical reflectance from $\sim 1\ \mu\text{m}$ to $\sim 50\ \mu\text{m}$ by Fourier Transform Infrared (FT-IR) spectroscopy. Typically, biconical measurements are spliced with BDR measurements by scaling the

biconical spectra to the BDR spectra at a common wavelength. As BDR measurements represent the bulk of the laboratory spectroscopy data presented in this thesis, an overview of the accuracy and precision of these measurements is provided.

Visible to near-infrared BDR spectra collected in the RELAB have very high precision for most particulate (loose and incoherent, typically with grain sizes from several hundred μm down to very fine particles) materials. The precision has been estimated as 0.25% [Pieters and Hiroi, 2004]. Samples are measured on a spinning stage, meaning that the sample effectively is measured at all radial orientations at least once for each measured wavelength (typically spaced in 5-10 nm increments). The signal is recorded continuously over the rotation, producing a variance in the signal that is due to geometry effects. This recorded signal is averaged over the rotation to produce the reported “reflectance”. This variance should not be mistaken for measurement “error”. Samples that are measured repeatedly, without being disturbed in their sample dish, exhibit very high repeatability. If samples are disturbed or re-prepared in dishes for measurement, altering the degree of packing, density, and other physical properties, differences between measured reflectance spectra (such as overall albedo and apparent absorption band strength) can vary. However, scaling such spectra at common wavelengths effectively will eliminate these differences.

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CHAPTER 1: The Lunar Rock and Mineral Characterization Consortium: Deconstruction and Integrated Analyses of Mare Basalts

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Abstract

The Lunar Rock and Mineral Characterization Consortium (LRMCC) has conducted coordinated mineralogy/petrography/spectroscopy analyses of a suite of pristine lunar basalts. Four basalt slabs (two low-Ti, two high-Ti) and paired thin sections were analyzed. Thin sections were analyzed for mineralogy/petrography, while the slabs were used to prepare particulate separates of major mineral phases and bulk samples. Mineral separates and particulate bulk samples were crushed to controlled grain sizes and their reflectance spectra measured in the NASA RELAB at Brown University. The resulting dataset provides an essential foundation for spectral mixing models, offers valuable endmember constraints for space weathering analyses, and represents critical new ground truth results for lunar science and exploration efforts.

1 Introduction

The Earth's Moon presents a unique vantage point to address a number of fundamental questions in planetary science. These questions include the mechanisms of formation of rocky planets, igneous processes such as magma ocean formation and crystallization and subsequent basaltic volcanism, impact processes and products, and space weathering of airless planetary surfaces. Despite great leaps in our understanding of the Moon made following the return of samples during the Apollo and Luna programs and subsequent orbital missions, a number of themes in lunar science remain poorly understood. The current generation of lunar exploration is rich, with a number of orbital missions in operation and future surface missions in the planning phases to address these questions. The present suite of lunar orbiters are returning global data from a range of sophisticated instruments, which will allow the lunar science community to address questions which have been poorly constrained due to limitations in the available data.

Optical instruments offer the highest spatial resolution for analyzing and mapping the Moon's surface mineralogy. A number of high-quality instruments on the current suite of orbiters provide the high spatial resolution, broad spectral coverage, and high spectral resolution data needed for accurate interpretation of lunar surface mineralogy [Ohtake *et al.*, 2007; Matsunaga *et al.*, 2008; Kiran Kumar *et al.*, 2009; Mall *et al.*, 2009; Pieters *et al.*, 2009; Tschimmel *et al.*, 2009]. Interpretation of such data, however, relies in large part on links to returned samples analyzed in terrestrial laboratories [e.g., Pieters, 1986; Pieters, 1999; Lucey *et al.*, 2000; Pieters *et al.*, 2000; Gillis *et al.*, 2003]. As such, careful measurement of samples returned by the Apollo and Luna programs is essential for the current era of lunar exploration.

Optical instruments are sensitive to surface mineralogy because highly diagnostic absorption features occur in the visible to near-infrared. The basic reflectance properties of the major lunar minerals are known and based on mineral physics. In the visible to near-infrared, the major lunar minerals have diagnostic absorption features caused by crystal field transitions in Fe²⁺ cations in distorted crystal lattice sites. Pyroxenes have diagnostic absorptions at 1 and 2 μm , while olivine has a combination absorption near 1 μm [Burns, 1970; Adams, 1974; Burns, 1993]. Both minerals' absorption features shift in generally-understood ways based on mineral composition [e.g., Burns, 1974; Cloutis and Gaffey, 1991; Sunshine and Pieters, 1998; Klima *et al.*, 2007]. Iron-bearing plagioclase has a weaker but still diagnostic absorption feature near 1.3 μm , although it is often overwhelmed by the more optically active pyroxene or olivine features in spectra of bulk rocks [Bell and Mao, 1973; Adams and Goullaud, 1978; Burns, 1993]. These references provide more background on visible-near infrared reflectance spectroscopy. Example reflectance spectra of lunar minerals are shown in Figure 1. While the major crystal field absorptions are generally well understood, minor element substitutions are sensitive to the local environment and can have a significant effect on diagnostic absorptions. The diversity of forms and combinations in natural environments is large, often making it difficult to isolate diagnostic absorptions. Because lunar conditions are often distinct in subtle ways, it is important to use real lunar materials as ground truth rather than relying on synthetic or terrestrial analogues. The Lunar Rock and Mineral Characterization Consortium (LRMCC) has conducted careful, integrated measurements of lunar materials with the goal of extending the library of well-characterized lunar materials available as ground truth.

The LRMCC builds on the work of the Lunar Soil Characterization Consortium (LSCC), which conducted coordinated mineralogy/petrography/spectroscopy analyses of a suite of lunar soils of different composition and maturity, but did not analyze the unweathered component of the lunar sample suite [Taylor *et al.*, 2001]. The LRMCC is conducting similar coordinated analyses, and has initially focused on pristine, unweathered lunar materials in the form of mare basalt samples and mineral separates prepared from the bulk rock samples. The measurement and compositional characterization of both mineral separates and the rock from which they were prepared are of particular value for spectral unmixing and space weathering models. In the case of spectral unmixing, the LRMCC samples represent exceptional constraints for models, because spectra of both bulk rock samples and their exact constituent (endmember) minerals were obtained. Mixture models typically rely on selecting endmember mineral spectra from a library, and a number of assumptions are required to unmix the spectrum of interest [e.g., Mustard and Pieters, 1987; Hiroi and Pieters, 1994; Clark, 1995; Poulet and Erard, 2004]. The LRMCC samples eliminate the need for many of these assumptions, and to our knowledge, represent the best constraints for mixture models yet obtained. Spectral unmixing is discussed in section 6.1. In the case of space weathering models, these measurements provide accurate constraints on the starting materials for the space weathering process, which, when combined with the results of the LSCC, should provide a more complete assessment of the space weathering of lunar materials [e.g., Pieters *et al.*, 2000; Hapke, 2001; Noble *et al.*, 2001; Taylor *et al.*, 2001; Sasaki *et al.*, 2003]. In total, the combined results from the LSCC and LRMCC provide a suite of well-characterized ground truth lunar materials that span a range of compositions and

maturities. These ground truth data provide a strong foundation for lunar science and exploration with these new high spectral resolution datasets.

2 Methods, Samples, and Sample Preparation

2.1 Samples, Petrography, Modal Mineralogy

The LRMCC was allocated slabs and associated thin sections of two low-Ti basalts (15058 and 15555) and two high –Ti basalts (70017 and 70035). The thin sections and slabs were created specifically for the coordinated analyses of this study. The thin sections and slab samples were prepared from adjacent portions of the parent samples to ensure similar mineralogy. The thin sections (15058,248, 15555,971, 70017,541, 70035,193) were used for detailed mineralogy and petrography analyses. The slabs (15058,276, 15555,965, 70017,535, 70035,188) were used to prepare particulate bulk samples, a portion of which were used for the separation of mineral separates. Mineral separation was done by hand picking under an optical microscope at the University of Tennessee. Mineral separates were prepared from a 125 – 250 μm size fraction and visually checked for purity. Grains rejected for purity from these separations (i.e., grains with intergrown phases) were crushed to <125 μm to remove impurities. Representative subsamples of the mineral separates were used to prepare grain mounts for chemical analyses. Because minerals were separated on the basis of color, the separations do not follow strict compositional divisions (e.g., pigeonite from augite). Thus, it is important to analyze directly the compositional ranges of the prepared separates through analysis of these grain mounts, both to verify that the separates are representative of the range of mineral compositions found in the thin section and to

understand precisely the composition of the minerals to be analyzed with reflectance spectroscopy.

The paired thin sections were used to analyze the petrography, modal mineralogy, and mineral composition of the basalt samples. Sample petrography was evaluated using a combination of optical microscopy and backscattered electron imagery. Chemical analyses of minerals were performed with the Cameca SX-50 electron microprobe (EMP) at the University of Tennessee. Operating conditions were as follows: 15 keV accelerating voltage, 20 nA beam current, and a 2 μm beam diameter, except for plagioclase analyses, in which case a 5 μm diameter beam and 10 nA current were used to minimize loss of volatile elements K and Na. Modal mineralogy was determined using the *Oxford FeatureScan* software package of an Oxford instrument energy dispersive spectrometer (EDS) interfaced to the microprobe. Threshold values of cation abundance (based on EDS measurements) were specified and used to classify the various phases in the thin section. EDS spectra are qualitative (absolute cation abundances cannot be determined). Cation abundance thresholds were thus defined as “corrected window percent” (CWPC). These values are defined as percentage of the counts in an element’s energy window (where its “peak” in EDS spectra occurs) relative to the total count over all windows after a background removal. However, these CWPC are generally comparable to the given element’s oxide weight percentage [Taylor *et al.*, 1996]. Modal mineralogy was then determined by an automated point counting procedure on the classified thin section. A detailed description of this procedure is provided by Taylor *et al.* [1996]. The CWPC values used in this study are reported in Table 1.

The chemical compositions of the prepared mineral separates were also determined by EMP analysis. A representative subset of grains from each separate was prepared as grain mounts for EMP. Compositions were compared to those obtained from thin section analyses to ensure that the prepared mineral separates were representative of the range of compositions found in the bulk sample.

2.2 Reflectance Spectroscopy

The particulate samples were used for spectroscopic measurements in the NASA Reflectance Experiment Laboratory (RELAB) at Brown University. Particulate samples were first received at Brown with a grain size range of $\sim 125 - 250 \mu\text{m}$. Initial measurements of these samples were made across a range of wavelengths, but this grain size range is too coarse for typical lunar applications. The samples were crushed and sieved to a series of finer grain sizes, first $<125 \mu\text{m}$ and then $<45 \mu\text{m}$, and measurements were collected at each grain size prior to preparation of the next. A rough estimate of grain size distribution in the $<125 \mu\text{m}$ splits was obtained prior to crushing the samples to $<45 \mu\text{m}$. Prior to crushing, the $<125 \mu\text{m}$ splits were passed through a $45 \mu\text{m}$ sieve, and the masses of the $<45 \mu\text{m}$ and $45 \mu\text{m} - 125 \mu\text{m}$ splits were measured by weighing. The results of this procedure are illustrated in Figure 2. While not a true estimate of grain size distribution, this approach provides a rough estimate of the relative abundances of coarse vs. fine particles in the $<125 \mu\text{m}$ splits. The $<125 \mu\text{m}$ separates are largely dominated by coarse particles, though most contain a non-negligible component of fine particles. These results indicate that the mean particle size of the $<125 \mu\text{m}$ separates tends to be larger than might be assumed. Several separates, most notably plagioclase, tended to have

slightly more fine particles in the <125 μm split, perhaps due to lower resistance to the crushing process.

Particle size should not be mistaken for the grain size of the samples, particularly for the bulk samples. When the samples are crushed, a mixture of single-grain and multi-grain particles is produced. In the case of multi-grain particles (either single-phase or multiple-phase), photons interact with multiple grains/phases while ‘traversing’ a single particle. This situation has optical properties very different from that in which mineral grains are physically separated from one another. Even in typical nonlinear mixture models designed to deal with intimate mixtures, particles are assumed to be fundamentally mono-minerallic, with void spaces that affect the material’s scattering properties present between grains [e.g., *Hapke*, 1993]. Multi-mineral particles represent a more complex system to model accurately, and the reader is cautioned that the samples discussed here often exhibit these additional complexities.

Spectra were acquired as bidirectional reflectance (BDR) at 30° incidence and 0° emergence from 0.28 μm to 2.6 μm , and as biconical reflectance by FT-IR to 50 μm . BDR spectra are the most applicable as ground truth and to quantitative models, because they match the observation geometries of orbital sensors. A more detailed description of the RELAB facilities is provided by Pieters and Hiroi [2004]. BDR spectra were acquired with 0.005 μm (5 nm) spectral resolution. The spectral resolution of FT-IR measurements is variable with wavelength in nm, as spectra were acquired with a spectral resolution of 4 cm^{-1} . We spliced the acquired FT-IR spectra to the BDR spectra through multiplicative scaling, which provides a better constraint of absolute reflectance and band

strength beyond 2.6 μm . Biconical measurements are not directly comparable to BDR measurements for quantitative assessments of band strengths and albedos.

Spectral reflectance results are presented by wavelength range: visible/NIR (300–2600 nm), NIR/short wavelength mid-IR (2.5 – 8 μm), and mid-IR (7 – 9.5 μm). The mid-infrared wavelength region contains a number of diagnostic mineral absorption features, although the process responsible for most features in this wavelength region is fundamentally different from that in the visible/NIR for the lunar minerals of interest to this study. In the visible/NIR, the absorption features are caused by crystal field transitions largely in Fe^{2+} ions. In the mid-infrared, absorptions are linked to vibrations, stretches, and bends in crystal lattice structures tied to Si-O bonds with fundamental absorptions occurring at longer wavelengths (e.g. $\sim 10 \mu\text{m}$). Specific features are caused by overtones and combinations of fundamental molecular vibrations, stretches, and bends; the fundamental process responsible is intimately tied to crystal vibrations, rather than electronic transitions [e.g., *Salisbury and Walter*, 1989; *Clark*, 1999; *Cooper et al.*, 2002].

3 Results

3.1 Mineralogy and Petrography

We discuss the major aspects of the mineralogy/petrology analyses of these samples, particularly those aspects most relevant to analysis of the reflectance spectra. Detailed mineralogy/petrography data are presented in the Appendix to this paper. Modal abundances determined from analyses of the thin section samples are presented in Table 2. Note that these modal abundance data for the thin sections are not equivalent to the modal abundance of the mineral separates, as separations were performed manually on

the basis of color rather than composition. This distinction is discussed further below and in section 6.1. Overall sample texture is illustrated briefly in Figure 3. Sample 15058 is generally subophitic, whereas 15555 and the high-Ti samples are generally poikilitic. Pyroxenes, the dominant mineral in these samples, were found to have compositions similar to those reported by previous studies [*Bence and Papike, 1972; Papike et al., 1974; Ryder, 1985*]. Pyroxenes are strongly zoned for all samples analyzed by the LRMCC. The low-Ti sample pyroxenes are zoned from core to rim, becoming significantly more iron-rich toward the rim. The high-Ti sample pyroxenes exhibit complex sector zoning, making a common core to rim zoning profile difficult to establish, although the pyroxenes generally become more Fe-rich in their rims. The mineral separates are all quite pure, being estimated at 98-99% purity for all prepared separates based on visual inspection. However, in many cases, when prepared for reflectance measurements, the separates show minor amounts of visible contamination by other phases, so caution should be taken when interpreting the reflectance data.

The composition of the prepared mineral separates determined from analysis of the grain mounts and of the mineral phases determined from thin section analyses are presented graphically in Figure 4. The prepared mineral separates were found to have compositional ranges consistent with those observed in the thin section analyses. Average geochemical compositions of the mineral phases analyzed in the thin sections and of the prepared mineral separates are presented in Appendix A.

Mineral separates from slab sample 15058 are identified as green pyroxene, brown pyroxene, and plagioclase. Green pyroxenes are orthopyroxenes and pigeonites, containing primarily Mg-rich compositions. Brown pyroxenes are primarily augites,

containing both Mg-rich and Fe-rich clinopyroxene compositions. Plagioclases are very Ca-rich (typical of plagioclases from mare basalts) and relatively Fe-rich (~0.6 wt.% FeO), and are compositionally indistinguishable from the plagioclases in the thin section.

Sample 15555 separates consist of greenish olivine, two varieties of pyroxene (reddish-brown and light-brown), and plagioclase. Pyroxene compositions are consistent with those observed in the polished thin sections; the reddish-brown pyroxenes are generally Mg-poor augite, and the light brown pyroxenes are generally Mg-rich subcalcic augite. Olivine and plagioclase have very similar compositional ranges to those observed in thin section, though the olivine separate lacks the fayalitic olivines (Fo₅₋₁₀) seen in thin section. The olivine contains small inclusions of Cr-rich spinel (chromite). These are volumetrically minor, but are quite significant optically. These spinels can be seen by visual inspection under a binocular microscope, and occur as inclusions (possibly nucleation sites) within olivine grains. Due to their presence within olivine grains, their strong absorption features, and their small size, they will have a disproportionally large optical effect. The plagioclase has slightly lower FeO than 15058 (~0.5 wt.%)

Mineral separates from 70017 include pyroxene, plagioclase, and opaque oxides dominated by ilmenite. The pyroxenes were separated into two classes; dark brown pyroxenes are generally augites, while light-brown ones are mostly pigeonites. The plagioclase separate has compositions consistent with those found in analysis of the polished thin section, and has lower FeO than found in the Apollo 15 plagioclase separates (~0.35 wt.%). The high-Ca pyroxenes (augites) were found to be rich in TiO₂ (up to ~3.5 wt.%).

Mineral separates from 70035 are light-brown pyroxene, dark brown pyroxene, plagioclase, and opaque oxides dominated by ilmenite. As in 70017, the dark brown pyroxenes are mainly augites, while the light brown pyroxenes are generally pigeonites. Plagioclase compositions are essentially identical to those observed in the thin section sample, and FeO content is similar to the 70017 plagioclase (~0.35 wt.%). The high-Ca pyroxenes were found to contain abundances of TiO₂ comparable to those observed in the 70017 high-Ca pyroxenes (~3.5 wt.%). The trend of TiO₂ vs. CaO content for 70035 is illustrated in Figure 5, and is discussed in the appendix. Some of the lower-Ca augites do not show enrichment in TiO₂, suggesting that the system was enriched in TiO₂ at some point during the augite crystallization sequence, but not while pigeonites and sub-calcic augites formed later in the sequence (see Appendix).

Mineral separates often span a range of compositions. For simplicity, pyroxenes are labeled as “augite” or “pigeonite” in the reflectance spectra figures (Figure 6-11), although these labels do not always correspond exactly to the composition of the separate. The key between actual separate names and the separate labels as plotted is given in Table 3, which lists the separate names as presented above, the separates’ general composition as given above, and the separates’ labeled composition in the reflectance spectra figures.

3.2 Reflectance Spectroscopy

The results of the spectral reflectance analyses are described in this section grouped by wavelength range. Labels given to spectra shown in the figures (Figures 6-11) are linked to specific mineral species in Table 3.

3.2.1 Visible/NIR Bidirectional Reflectance

The spectra of coarse and fine-particle separates are shown in Figures 6 and 7, respectively. The fine-grained sample spectra are generally consistent with the coarse-grained sample spectra, though with increased albedos and decreased band strengths.

Each basalt sample contains a range of pyroxene compositions, as well as abundant plagioclase. Only 15555 contains sufficient modal olivine to prepare a mineral separate (the other samples exhibit ~2% modal olivine or less). Pyroxenes were selected and separated into two groups on the basis of color. These pyroxenes vary in composition as indicated by Figure 4, which leads to different overall wavelength positions of the 1 and 2 μm absorption features. The separates containing more Ca-rich pyroxene (generally greater than 15-20% Ca) exhibit spectra with longer-wavelength absorption features. The pyroxene separate spectra appear to exhibit 1.2 μm absorption features, which may vary in strength between compositions. Quantitative deconvolutions (e.g. section 6.2) of the spectra are required to confirm this observation, however. The Apollo 17 samples are high-Ti basalts, and the augite separates from those rocks contain relatively high abundances of TiO_2 (up to 3.8 wt.%, section 6.1). The Apollo 17 augite spectra show a weak but perceptible feature in the visible (0.4 μm – 0.75 μm), which is essentially absent in the Apollo 17 pigeonite separate spectra. Where present, this feature is more pronounced in the coarse-grained sample pyroxene spectra.

The plagioclase spectra show relatively strong absorption features near 1.3 μm . This is likely due to their relatively high FeO content (~0.3-0.5 wt.%). The plagioclase spectra show marked drop-offs in reflectance at short wavelength (<0.4 μm), and often a shallow absorption features in the visible (0.4 μm – 0.8 μm). They also exhibit a broad

absorption or altered continuum slope beyond the principal 1.3 μm feature. The Apollo 17 plagioclase spectra differ from the Apollo 15 plagioclase spectra in strength of the 1.3 μm feature and in long wavelength continuum slope. Specifically, the Apollo 17 plagioclase spectra exhibit weaker 1.3 μm features and steeper long wavelength continuum slopes, reaching higher reflectance values at 2.6 μm . The 70035 plagioclase spectra have a weak feature near 1 μm , which is notably stronger in the fine-grained sample spectrum (Figure 7).

The olivine separate spectra for 15555 exhibit the characteristic composite absorption feature near 1 μm [Burns, 1974; Sunshine and Pieters, 1998; Dyar *et al.*, 2009], as well as an asymmetric long wavelength absorption feature. The ilmenite spectra are generally flat and featureless through the visible, with a pronounced upturn around 1.7 μm and a roll-off at long wavelengths (2.4 μm – 2.6 μm). They do exhibit a minor reflectance minimum at ~ 0.5 μm , and a peak in reflectance at ~ 1 μm , which becomes stronger at finer particle size.

The bulk basalt sample spectra generally resemble the pyroxene spectra, as pyroxene is the dominant optical phase in these samples. The 1 and 2 μm pyroxene absorptions in the bulk sample are broadened relative to the 1 and 2 μm features observed in spectra of the pyroxene separates due to the presence of a wide range of pyroxene compositions in the bulk samples. Additionally, the 15555 bulk sample spectra exhibit evidence for an olivine component in the broadened 1 μm feature and the strong absorption around 1.2 μm . The broad visible wavelength feature seen in the Ti-rich pyroxene spectra is also subtly apparent in the high-Ti bulk sample spectra. The high-Ti sample spectra exhibit notable differences from spectra of the pyroxenes separated from

those samples and from the low-Ti bulk sample spectra. The high-Ti bulk sample spectra have reduced albedos, have weakened 1 and 2 μm pyroxene absorptions (especially at the smaller particle size), and show pronounced upturns in reflectance at wavelengths beyond $\sim 1.5 \mu\text{m}$. These properties, which are not observed in the low-Ti bulk sample spectra, are due to the high abundances of ilmenite in the high-Ti bulk samples.

3.2.2 NIR/Short Wavelength Mid-IR 2.5 – 8 μm (Volume Scattering)

The spectra of coarse and fine-particle samples for the long wavelength NIR region are shown in Figures 8 and 9, respectively. Spectra are plotted in reflectance, though approximate “emissivity” spectra can be obtained by the simple Kirchhoff’s law relationship, which holds that emissivity is approximately equal to 1 - reflectance ($\epsilon=1-r$) [e.g., *Nicodemus*, 1965; *Clark*, 1999]. This approximation has been shown generally to be correct to first order [*Salisbury*, 1993]. For the purposes of this discussion, the NIR/short wavelength mid-IR wavelength region extends from 2.5 μm to 8 μm , stopping just short of the Christiansen feature for silicates. The pyroxene separate spectra exhibit several absorption features near 5 and 6 μm . Plagioclase spectra exhibit weak absorption features near $\sim 4.4 \mu\text{m}$. The Apollo 17 plagioclase separate spectra, which have slightly lower FeO contents, are somewhat brighter in the 3-4 μm range than the Apollo 15 plagioclase separate spectra. Olivine has some weak but detectable features between 5 and 6 μm that are often very diagnostic [*Pieters et al.*, 2008]. Spectra of all separates exhibit sharp features near 3.4 μm , which are likely caused by a sample preparation step where samples were exposed to ethanol (see Discussion). Ilmenite lacks major features in this wavelength region, but does show evidence for the same 3.4 μm absorption seen in spectra of the other separates. Ilmenite (FeTiO_3) is not a silicate mineral and thus does

not experience Si-O vibrational absorptions. It is darker than the other separates in the 3-4 μm region. As in the NIR, the bulk sample spectra generally follow the behavior of the pyroxene separates, though features of other minerals can be detected as well.

Spectra of all fine particle separates and some of the coarse particle separates exhibit a broad absorption feature near 3 μm . Among coarse particle samples, only plagioclase consistently has a 3 μm feature. All fine particle samples (separates and bulk) have a 3 μm feature, though the feature is strongest in the plagioclase spectra.

3.2.3 Mid-IR 7 – 9.5 μm (Volume - Surface Scattering)

This wavelength region generally contains the transition from volume to surface scattering in silicate minerals. As in the long wavelength NIR wavelength region, spectra are plotted in reflectance. Spectra for the LRMCC coarse and fine-particle samples are presented in Figures 10 and 11, respectively. This wavelength region contains spectral features that are useful compositional indicators, most notably the Christiansen feature, a reflectance minimum and an emission maximum [e.g., *Salisbury*, 1993]. The position of the Christiansen feature is controlled by the position of the fundamental vibrational absorption feature, which is in turn controlled by a material's composition. While the wavelength is physically controlled by the degree of depolymerization of the silicate material, the wavelength of the Christiansen feature has been shown to correlate with index measurements of material chemistry such as SCFM ($\text{Si}/(\text{Si}+\text{Ca}+\text{Fe}+\text{Mg})$). The feature generally moves to longer wavelengths as materials become more mafic (SiO_2 content decreases) [e.g., *Salisbury and Walter*, 1989; *Cooper et al.*, 2002].

The lunar mineral separate spectra behave as expected. The Christiansen features for the plagioclase separate spectra occur at shorter wavelengths, near 8 μm in all cases at

both grain sizes. The pyroxene Christiansen features occur at longer wavelengths, at slightly greater than 8.5 μm . The olivine separate spectra have a Christiansen feature at a very slightly longer wavelength than the pyroxene spectra, as expected from olivine's more mafic composition. They have composite features, with a second feature near 9.2 μm . The fine particle olivine separate spectrum (Figure 11) differs from the coarse particle spectrum (Figure 10) in that the longer-wavelength "component" ($\sim 9.2 \mu\text{m}$) of the Christiansen feature becomes stronger, and the reflectance minimum of the spectrum shifts to this component of the feature. Otherwise, the fine particle sample spectra are similar to their coarse-grained counterparts, albeit with increased spectral contrast. They also have steeper slopes from $\sim 7 \mu\text{m}$ to the Christiansen feature due to their higher reflectance values at shorter wavelengths. The ilmenite spectra lack a distinctive Christiansen feature in this wavelength region, and have higher reflectance throughout, particularly in the fine-grained sample spectra. Ilmenite does not have a Christiansen feature in the same wavelength region as the silicate minerals because as a Fe-Ti oxide, it does not have a Si-O vibrational absorption feature. A feature for ilmenite occurs at significantly longer wavelengths ($\sim 12.5 \mu\text{m}$). The bulk sample spectra contain composite features, due to the presence of multiple mineral species in the sample that have Christiansen features at different wavelengths.

4 Discussion

4.1 Mineralogy/Petrography

This manuscript focuses on integrated analyses of petrography and reflectance spectroscopy. The mineralogy and petrography results are presented here in the context

of the insight they provide for interpreting the reflectance spectroscopy results. More specific mineralogy and petrography results are discussed in the Appendix.

4.2 Visible/NIR Bidirectional Reflectance

The reflectance spectroscopy results for this wavelength region are presented in Figures 6 (coarse particles) and Figure 7 (fine particles). The positions of the 1 and 2 μm pyroxene absorption features are consistent with pyroxene compositions for the two pyroxene separates prepared from each sample, as the higher-Ca pyroxenes have absorption features at longer wavelengths [e.g., *Adams, 1974; Cloutis and Gaffey, 1991*]. The 15058 augite spectra appear to have slightly stronger 1.2 μm absorption features relative to the Apollo 15 pigeonite spectra, which could be suggestive of a faster cooling history [*Klima et al., 2008*], although a stronger 1.2 μm absorption could also be caused by the higher Ca content of the augites [e.g., *Burns, 1993; Klima et al., 2007; Klima et al., 2008*]. However, such conclusions cannot be drawn without quantitative deconvolutions of individual pyroxene bands in the spectra [e.g., *Sunshine et al., 1990; Klima et al., 2008*] such as those presented below.

The pyroxene separates from both Apollo 17 samples are more compositionally distinct than those prepared from the Apollo 15 samples (see Figure 4). Their reflectance spectra reflect this compositional diversity, as they exhibit clear differences in the position of the 1 and 2 μm absorptions. The Apollo 17 pyroxene spectra appear to have weaker 1.2 μm absorptions than those observed in the Apollo 15 sample spectra. On the whole, the Apollo 17 pyroxene separates have higher abundances of CaO than do the Apollo 15 separates, suggesting that in this case, the comparatively weak 1.2 μm bands are due to a slightly slower cooling history [*Klima et al., 2008*], consistent with the

results of petrographic analyses of the paired thin section samples and previous analyses of these samples, which found them to have cooled relatively slowly [Brown *et al.*, 1975]. However, confirmation of the relative strengths of the 1.2 μm absorption features in these spectra requires quantitative deconvolutions.

Several interpretations are possible for the broad visible wavelength absorption observed in the Apollo 17 augite separate spectra (observed most prominently in Figure 6). These pyroxenes have relatively high TiO_2 contents, roughly twice those observed for pyroxenes in the Apollo 15 samples. It has been suggested that the presence of Ti^{3+} cations in the pyroxene structure can cause such absorptions in the visible [Burns *et al.*, 1976; Burns, 1993], although a $\text{Fe}^{2+} - \text{Ti}^{4+}$ metal-metal charge transfer is also a possible explanation [Loeffler *et al.*, 1975; Burns *et al.*, 1976]. Ti in these pyroxenes is likely to exist in both +3 and +4 valence states, so multiple transitions could contribute to the observed absorption feature. The feature is slightly stronger in the augite separate spectra relative to the pigeonite spectra, and augites in the Apollo 17 high-Ti samples have elevated Ti contents because they co-precipitated with ilmenite in a more Ti-rich environment than pigeonites (see Figure 5 and Appendix). These pyroxenes exhibit sector zoning, and the augites typically have small inclusions of ilmenite (illustrated in Figures 3g and 3h). An alternative interpretation is that the ilmenite inclusions produce the broad feature across the visible in the Ti-rich pyroxene separate spectra. Similar features have been observed in analyses of microcrystalline ilmenite-bearing glassy phases, and have been attributed to the microcrystalline ilmenite [Pieters and Taylor, 1989]. If ilmenite were responsible for this feature, the transition responsible would likely be the $\text{Fe}^{2+} - \text{Ti}^{4+}$ metal-metal charge transfer in the ilmenite structure, in which

these are the two dominant cations [Loeffler *et al.*, 1975]. We favor the structural Ti interpretation due to the apparent high abundance of TiO₂ in the pyroxene and lack of direct visual evidence for microcrystalline ilmenite, although resolution of the structural Ti in pyroxene vs. microcrystalline ilmenite interpretation is beyond the scope of this paper and likely requires additional analytical techniques.

The broad multi-component absorption centered near 1.05 μm in the olivine separate spectra (Figures 6 and 7) is consistent with the olivine's composition ($\sim\text{Fo}_{50}$) based on the methods of Sunshine and Pieters [1998] and Isaacson and Pieters [2008]. As is commonly observed in lunar olivine spectra, the spectra also have slightly asymmetric absorption features near 2 μm . Such features are not typically observed in spectra of synthetic or terrestrial olivines. We attribute this feature primarily to the presence of small spinel inclusions in the olivine [Pieters *et al.*, 1990]. The spinel is observed as small crystalline growths within olivine crystals, a common feature of lunar olivine [Dymek *et al.*, 1975; Papike *et al.*, 1998]. Photons interacting with olivine also interact with the spinel grains without having to pass through void spaces between mineral grains. Common nonlinear models for radiative transfer in particulate media [e.g., Hapke, 1993; Hapke, 2008] do not account for this situation quantitatively, but can be used to indicate that such a situation has major effects on the overall reflectance properties of a material. Spinel has characteristic, very strong absorption features near 2 μm [Cloutis *et al.*, 2004]. Because olivine in 15555 typically intergrows with plagioclase and pyroxene, as illustrated in Figure 3, it is possible that trace amounts of pyroxene and plagioclase exist in our olivine separate. While visual inspection of the olivine separate shows it to be relatively pure, olivine is not optically active at wavelengths around 2 μm ,

and it is possible that minor quantities of pyroxene contamination could contribute to such features. However, the character of the absorption and the lack of any pyroxene features near 1 μm (confirmed with quantitative deconvolutions by Isaacson and Pieters [2010]) point to chromite being responsible for the 2 μm feature in the olivine spectra.

The Apollo 15 plagioclase spectra (Figures 6 and 7) have strong absorption features relative to other pure plagioclase separate spectra, likely due to the high Fe content [Bell and Mao, 1973] of these separates (~ 0.5 wt.% FeO). The Apollo 17 plagioclase separate spectra have slightly weaker 1.3 μm features, likely due to their lower Fe content (~ 0.3 wt.%). All plagioclase spectra presented here exhibit additional absorptions at longer wavelengths. The long wavelength edge of the 1.3 μm absorption feature has lower reflectance than its counterpart on the short wavelength side for the plagioclase spectra presented here (most apparent in the coarse particle spectra presented in Figure 6). Although the 1.3 μm feature clearly dominates, the plagioclase absorption feature is not simply a single crystal field transition in Fe^{2+} . While most absorption properties of plagioclase are understood based on mineral physics [e.g., Bell and Mao, 1973; Adams and Goullaud, 1978; Pieters, 1996], the long wavelength behavior may be related to Fe content and a separate absorption feature [Hofmeister and Rossman, 1984; Cheek *et al.*, 2009]. Lastly, the 70035 plagioclase is a somewhat less pure separate than the 70017 plagioclase, as evidenced by a weak absorption at 1 μm superimposed on the wing of the plagioclase 1.3 μm absorption (most apparent in the fine particle spectrum in Figure 7). We interpret this feature as a pyroxene absorption likely caused by minor pyroxene contamination of the plagioclase separate. The feature is stronger in the finer-particle separate spectrum, likely because the strength of the plagioclase absorption

decreases, and the more optically-active pyroxene absorption becomes proportionally stronger.

Ilmenite acts as an opaque across visible wavelengths when the grain size is significantly greater than the wavelength of the light being measured (i.e. grain size $\gg 1 \mu\text{m}$). Thus, the ilmenite separate spectra are dark and relatively featureless through the visible and part of the NIR before showing increased reflectance beyond $\sim 1.7 \mu\text{m}$. The magnitude of features in the ilmenite spectra is strongly dependent on particle size (they become more prominent with decreasing particle size), but the overall spectral properties of these lunar ilmenites are consistent with measurements of synthetic ilmenite [Riner *et al.*, 2008].

The bulk sample spectra exhibit the presence of both pyroxenes quite clearly. Pyroxene is the dominant optical phase in the samples, so this is unsurprising. The prominent inflection near $1.2 \mu\text{m}$ seen in all bulk basalt spectra (Figures 6 and 7) has many potential contributions. Pyroxene, olivine, and plagioclase all have absorption features in this region, although not all play equal roles in bulk sample spectra. Plagioclase has an absorption feature in this region, although it is quickly overwhelmed in mixtures with more strongly absorbing phases like pyroxene and olivine. Careful quantitative analysis (i.e., spectral deconvolution and quantification of the properties of individual absorption features) is required before drawing conclusions about the detectability of plagioclase in such spectra [Klima *et al.*, 2008]. The pyroxene absorption is the most dominant component, as the inflection is observed in olivine-rich and olivine-poor samples alike. The effect of olivine is apparent in a comparison of the 15555 bulk sample spectra with other bulk sample spectra; the proportionally stronger $1.2 \mu\text{m}$ feature

in 15555 relative to the 1.2 μm features exhibited by the other bulk sample spectra is attributed to the contribution of the olivine absorption.

The Apollo 17 bulk sample spectra differ markedly from the Apollo 15 bulk sample spectra. The most prominent differences are decreased albedo, significantly weakened absorption features at 1 and 2 μm , and pronounced long wavelength ($>1.7 \mu\text{m}$) reflectance upturns in the Apollo 17 bulk sample spectra. These effects are observed in both coarse-particle and fine-particle spectra, although they are exhibited more clearly by the fine-particle spectra in Figure 7. The curvature of the bulk sample spectra in the 2 μm region is caused by the reflectance upturn, and mimics an absorption feature. These properties are attributed to the abundant ilmenite, which exhibits a reflectance maximum near 1 μm , is generally opaque, and exhibits an upturn in reflectance beyond $\sim 1.7 \mu\text{m}$. These properties are similar to some of the optical effects of space weathering, which include decreased albedo, increased spectral slope, and weakened absorption features. All of these effects are observed when comparing the low-Ti (Apollo 15) to the high-Ti (Apollo 17) bulk sample spectra. These samples are completely optically immature, so these results hint at the complexity of addressing space weathering and maturity in ilmenite-rich regions of the Moon, and generally indicate that ilmenite is a major complication in interpretation of reflectance spectra [Hiroi *et al.*, 2009].

4.3 NIR/Short Wavelength Mid-IR 2.5 – 8 μm (Volume Scattering)

Many spectra presented in Figures 8 and 9 have broad absorptions at 3 μm . The feature near 3 μm is characteristic of an O-H vibrational absorption [Farmer, 1974]. We attribute this feature to adsorbed terrestrial water, which persists despite measurement in a dry air purged environment. This feature is apparently strongest in the plagioclase

separate spectra. The 3 μm feature also is generally more apparent in coarse particle sample spectra (Figure 8). A number of explanations for this observation are possible. First, plagioclase may be more susceptible to adsorption of water, perhaps due to a surface chemistry process. Additionally, although plagioclase is a nominally anhydrous mineral (it has no OH or H₂O in its chemical formula), it has been shown to contain structural water and OH [e.g., *Bell and Rossman, 1992; Seaman et al., 2006*], in some cases up to ~1000 ppm [e.g., *Johnson and Rossman, 2003; 2004*], so the 3 μm absorption may be caused partially or entirely by internal water in the plagioclase grains. Alternatively, the apparent stronger absorption feature in plagioclase may be simply an effect of the relative transparency of plagioclase relative to the other phases analyzed. The mean optical path length is greater in a transparent phase, which increases the number of times light interacts with grain surfaces. If water is adsorbed on grain surfaces, additional surface interactions due to this increased mean optical path length would produce a proportionally stronger 3 μm absorption feature. The strength of the O-H absorption may also be anti-correlated with the depolymerization state of the Si-O bond in silicates (strongest absorption in plagioclase). The 3 μm absorption is weakest for ilmenite, although this observation would be consistent with both the mean optical path length explanation and the Si-O depolymerization explanations.

Spectra of all separates show sharp absorption features near 3.4 μm , although the strength of these features is variable between spectra. These features are attributed to the C-H fundamental stretch, which is diagnostic of organic hydrocarbons [e.g., *Cruikshank and Brown, 1987; Gaffey et al., 1993; Clark, 1999*]. These features were likely imparted due to a sample preparation step in which the samples were processed in ethanol

(CH₃CH₂OH) which caused some ethanol to remain in the separates as a trace contaminant. The features are not observed in the bulk samples, because they were not subjected to this preparation step.

The pyroxene separate spectra show similar absorption properties to each other at these wavelengths. The position and strength of their absorption features do not show significant variation with mineral composition.

Absorption features in the olivine spectra between 5 and 6 μm are weak (slightly more apparent in Figure 9) but highly diagnostic. These features have potential value for remote detection, as they provide an independent indication of the presence of olivine beyond the 1 μm crystal field absorptions (which can be complicated by the presence of other absorbing phases).

Plagioclase spectra show a weak but important absorption feature near $\sim 4.4 \mu\text{m}$. Because the 4.4 μm feature occurs in a wavelength region unaffected by the mafic crystal field absorptions, the presence of this feature may allow plagioclase to be detected unambiguously.

The bulk sample spectra generally follow the behavior of the pyroxene spectra. The presence of olivine is apparent in the fine particle olivine-bearing bulk sample spectrum (15555), as evidenced most notably by the feature near 5.7 μm . The plagioclase absorption at 4.4 μm is weak-to-absent in the bulk sample spectra, suggesting that the modal abundance of plagioclase in these basaltic samples may be below the detection limit for this feature.

4.4 Mid-IR 7 – 9.5 μm (Volume - Surface Scattering)

As predicted by theory, plagioclase separates exhibit short wavelength Christiansen features, pyroxenes and olivine have features at longer wavelengths, and bulk samples show composite absorption features dominated by a variety of phases. These spectra, illustrated in Figures 10 and 11, are consistent with previous work suggesting that this wavelength range is very useful for remote detection of plagioclase [e.g., *Salisbury and Walter*, 1989]; the plagioclase “feature” is readily apparent in the bulk sample spectra as well as in plagioclase separate spectra. The 15555 olivine separate spectra exhibit an unusual property, in that the reflectance minimum appears to shift between particle size separates. This behavior is not apparent in the bulk sample spectra, suggesting that the other phases dominate the bulk sample spectra. It is not clear which phase is responsible for this behavior, as the Christiansen feature for spinel occurs at wavelengths beyond this wavelength region [*Cloutis et al.*, 2004].

5 Applications

5.1 Mixing Models

One of the principal goals of reflectance spectroscopy is remote determination of planetary surface mineralogy. Visible to near-infrared reflectance spectra contain diagnostic mineral absorption features, as discussed above. Mixtures of minerals, such as those found in rocks and rock powders, produce reflectance spectra that are effectively a composite of the individual component mineral reflectance spectra. The quantitative relationship between the mixed spectrum and the individual endmember spectra is complex, however, and is an area of ongoing research [*Mustard and Pieters*, 1987;

Hapke, 1993; e.g., Hiroi and Pieters, 1994; Clark, 1995; Shkuratov et al., 1999; Poulet and Erard, 2004].

Mixture models can be classified into linear and nonlinear varieties. Linear models are the simplest, and assume that the endmembers are physically separated by more than the wavelength of the incident radiation and that photons can interact with only one endmember prior to being reflected. Linear models can be considered spatially akin to a checkerboard. Nonlinear models treat the complexities that arise when components are intimately mixed and photons can interact with multiple endmembers prior to being scattered back to a sensor.

Mixture models rely on accurate knowledge of the endmember spectra used. Most endmember spectra, regardless of their quality, are approximations, because the mineral composition and general character cannot match exactly those of the minerals found in the mixture being studied. The LRMCC samples and mineral separates presented here offer the ability to overcome this limitation, because the endmember minerals were extracted from the exact bulk sample being analyzed. The thin sections are directly linked to the slab samples, and portions of the slabs were used to prepare separates while other portions were retained as “bulk samples”. The detailed characterization of the samples, their component mineral composition, and their modal abundances represent a very accurate understanding of the “ground truth” which a mixture model seeks to estimate. These samples thus represent the “ideal” case to test mixture models: realistic mixtures with realistic mineralogical properties (as opposed to synthetic mixtures created from laboratory mixtures of pure endmembers), and precise knowledge of the endmember mineral spectra. Models that cannot reproduce the “truth”

for the bulk samples need refinement. Although not zero, the number of unconstrained variables is significantly reduced compared to most other modeling situations.

In the case of pyroxene separates for these samples, modal abundances as reported from thin section analyses should not be equated with modal abundance of the prepared mineral separates. Modal abundances from the thin section were determined for mineral compositions, and separations were performed visually, so assumptions must be made to convert measured abundance with mineral separate abundance. The modal abundances of the specific mineral separates were estimated by classifying the mineral separates (e.g. Brown/Green Pyroxene) as combinations of mineral compositions (e.g. orthopyroxene), for which abundances were measured. This classification was performed by comparing the composition of the pyroxene separates (Figure 4, left) to the range of compositions observed in analysis of the thin sections (Figure 4, right). In the case of 15058, our assumptions are that Green Pyroxene = orthopyroxene + pigeonite, and that Brown Pyroxene = augite + Fe-pyroxene. This is not strictly true based on the mineral composition results (Figure 4), but is sufficient for approximation.

Initial example nonlinear fits calculated for one of the samples and mineral separates are illustrated in Figure 12. These fits were calculated using the methods of Hiroi and Pieters [1994], and are discussed by Hiroi et al. [2009]. Briefly, volume abundance of endmembers and surface roughness of the bulk sample were allowed to vary. Isotropic scattering was assumed. The fit in Figure 12a allows effective grain size of the endmembers to vary (“unconstrained”), while the fit in Figure 12b constrains the grain sizes to a constant value of 72 μm (“constrained”). More detail regarding the model parameters and assumptions is provided by Hiroi and Pieters [1994]. The line and

symbol styles in Figure 12 are largely the same as used in the reflectance spectroscopy figures (Figures 6 – 11). The fit is plotted as “x” symbols. The fit in Figure 12a has a calculated root mean square deviation (RMSD) of 0.55% over the full wavelength range used for the fit (0.4 μm – 2.5 μm), and the fit in Figure 12b has a RMSD of 1.68% over the same wavelength range.

The resulting modeled abundances for the fits in Figure 12 are listed in Table 4, along with the modeled effective grain sizes for unconstrained fit (Figure 12a). Also presented in Table 4 are the actual modal abundances as determined from analysis of the thin section sample, based on the groupings described above. Because only three endmembers were used to perform the unmixing, the sum of the three modeled abundances is 100%. In determining the modal mineralogy of the thin section, more phases were reported than two pyroxenes and plagioclase. To facilitate comparison between modeled and measured abundances, we also report the thin section abundances of the two pyroxene groupings after normalizing the two pyroxene plus plagioclase components to a total of 100% (analogous to the spectral unmixing results). The quality of the fits is generally good, and fitting generally is able to reproduce the modal abundances determined from the thin section, especially considering the assumptions described above. The abundances of Brown Pyroxene and Plagioclase differ significantly from the thin section values in both fits, indicating that despite the quality of these samples and spectra, questions about the mixture model remain. The deviations in effective grain size for the unconstrained fit merit further investigation, as the samples were crushed and prepared with near-identical methods. For example, plagioclase is modeled to have a much lower grain size than the pyroxene separates. It is possible that

differing physical properties for the various separates lead to varying particle sizes in the crushed bulk sample and mineral separates, although it is also possible that the optical properties of plagioclase are not fully accounted for by these models.

5.2 Quantitative Absorption Modeling

To characterize fully the specific crystal field absorption features in the spectra acquired in this study, quantitative analyses of the absorption band properties are required. Band properties such as band position, band strength, and band width are diagnostic of mineral/rock composition and are the basis of remote mineralogical analyses with reflectance spectroscopy. To use these spectra in mixture models and in interpretation of remotely acquired data, quantification of these parameters is essential.

Currently, one of the best methods for quantitative assessment of absorption features is the Modified Gaussian Model (MGM) [*Sunshine et al.*, 1990]. The MGM models the shape of a spectrum by applying a series of Gaussian curves to fit the shapes of individual absorption features. The properties of the fitted Gaussian curves can be interpreted as the properties of the individual, deconvolved component absorption features in the modeled spectrum. This approach removes ambiguity in interpretation of absorption features in reflectance spectra; the positions and strengths of the absorption features are clear, and interpretations of mineralogy based on those spectra are more reliable.

Example fits to for one of the LRMCC bulk samples are presented in Figures 13 and 14. The 15058 bulk sample spectra are the simplest example for deconvolution because the sample lacks abundant olivine or ilmenite, which complicate the other bulk sample spectra. While this sample is the simplest of the four in mineralogy, the

deconvolutions are not simple. We performed fits for both the coarse particle (Figure 13) and fine particle (Figure 14) separate spectra. We performed two fits for each spectrum, one using single pyroxene absorptions for the 1 and 2 μm features and one using 2 pyroxene absorptions for each feature. Using 2 absorption features is reasonable based on the range of pyroxenes found in the sample, but when fitting an “unknown” spectrum, one should always use the least number of bands required for a numerically and physically reasonable fit. In other words, additional bands should not be added to reduce the “error” of the fit unless there is a sound reason to do so based on mineralogy and mineral physics. As can be seen in the RMS error of our fits, the single pyroxene fit is significantly worse than the two pyroxene fit for both size separates. Additionally, the single-pyroxene fits required the use of a linear continuum slope to produce a stable fit. The 2-pyroxene fits show improved RMS error in both cases. The fine particle separate spectra showed improved RMS error for both single and 2-pyroxene fits compared to their coarse particle counterparts, suggesting that the bands may be saturated in the coarse-grained separate spectra. When two absorptions are used at 1 and 2 μm , the shorter-wavelength absorption is modeled to be stronger in both grain-size separates, consistent with the mineralogy of the sample [*Sunshine and Pieters*, 1993; *Klima et al.*, 2007; *Klima et al.*, 2008]. These MGM fits provide quantification of the specific absorption band properties observed in the spectra: band width, band strength, and band position. Such quantification is critical for reliable application of these spectra as ground truth, and will be performed for the bulk sample and selected mineral separate spectra acquired in this study.

6 Conclusions/Summary

The Lunar Rock and Mineral Characterization Consortium (LRMCC) has conducted coordinated mineralogy/petrography/spectroscopy analyses of a suite of lunar basalts. Slab samples were used to prepare particulate separates of bulk samples and mineral separates, and paired thin sections were used for mineralogy/petrography analyses. The LRMCC data are important for lunar science in many contexts. The spectra represent controlled ground truth for optical remote sensing instruments, which rely on such ground truth measurements to conduct mapping. The samples analyzed by the LRMCC are not weathered, and provide an excellent complement to the results of the Lunar Soil Characterization Consortium (LSCC), which analyzed the weathered component of lunar surface materials in a suite of lunar soils. The spectra also represent some of the best constraints on spectral mixture models yet produced, as the mineral endmembers are produced directly from the rock sample being investigated (“unmixed”), and their compositions are well known. Quantitative analyses of spectral mixing and absorption features are ongoing. The combined datasets from the LSCC and LRMCC represent an invaluable resource for current and future lunar science and exploration efforts.

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Table 1: CWPC ranges used for phase classification in modal mineralogy analyses

Mineral Phase	Cation	Inclusive Range
Olivine	Mg	11 – 50
	Si	35 – 60
	Ca	0 – 3
Orthopyroxene	Ca	0 – 3.7
	Si	50 – 75
	Mg	10 – 33
	Al	0 – 5
Pigeonite	Si	43 – 72
	Ca	2 – 15
	Al	0 – 6
	Mg	5 – 29
Augite	Si	39 – 70
	Ca	14 – 40
	Al	0 – 7
	Mg	4 – 25
Fe-pyroxene	Si	39 – 75
	Ca	3 – 30
	Mg	0 – 5
	Al	0 – 6
Plagioclase	Al	20 – 43
	Si	35 – 65
	Fe	0 – 2
	Ca	10 – 40
Silica	Si	85 – 100
	K	0 – 5
Ilmenite	Fe	20 – 50
	Ti	45 – 70
Chromite	Cr	10 – 45
	Si	0 – 10
Ulvöspinel	Ti	15 – 45
	Al	0 – 8
	Fe	40 – 75
Armalcolite	Ti	68 – 85
	Al	0 – 6
	Fe	5 – 20
Rutile	Ti	85 – 100
	Fe	0 – 7
Troilite/metal	Fe	35 – 100
	Si	0 – 12
	Ti	0 – 7
K-rich glass	Si	40 – 90
	Al	4 – 29
	K	3 – 20
Phosphates	P	20 – 70
	Ca	20 – 70

Table 2. Modal abundances from thin section analysis

Mineral Phase	15058,248	15555,971	70017,541	70035,193
Olivine	0.1 (Fayalite)	11.8	1.5	1.2
Orthopyroxene	3.7	0.3	---	---
Pigeonite	25.6	32.4	17.7	20.2
Augite	16.7	18.6	34.2	27.7
Fe-pyroxene	17.1	5.4	0.6	1.1
Plagioclase	30.1	27.3	25.7	30.1
Tridymite	3.5	0.8	1.6	0.9
Ilmenite	1.4	1.3	17.3	17.4
Chromite	<0.1	0.4	---	---
Ulvospinel	0.9	1.0	0.3	0.3
Armalcolite	---	---	0.1	0.1
Rutile	---	---	<0.1	---
Troilite/Metal	0.2	0.2	0.3	0.4
K-rich glass	0.5	0.4	0.6	0.6
Phosphates	0.1	0.1	0.1	<0.1
Total	99.9	100	100	100

Table 2. Separate identification key

Basalt Sample	Separate Name	Separate Composition	Separate Label (Figs. 6-11)
15058,276	Brown Pyroxene	Augite	Augite
	Green Pyroxene	OPX/pigeonite	Pigeonite
	Plagioclase	Plagioclase	Plagioclase
15555,965	Light Brown Pyroxene	Mg-rich subcalcic augite	Pigeonite
	Reddish-Brown Pyroxene	Mg-poor augite	Augite
	Plagioclase	Plagioclase	Plagioclase
	Olivine	Olivine	Olivine
70017,535	Light Brown Pyroxene	Pigeonite	Pigeonite
	Dark Brown Pyroxene	Augite	Augite
	Plagioclase	Plagioclase	Plagioclase
	Ilmenite	Ilmenite	Ilmenite
70035,188	Light Brown Pyroxene	Pigeonite	Pigeonite
	Dark Brown Pyroxene	Augite	Augite
	Plagioclase	Plagioclase	Plagioclase
	Ilmenite	Ilmenite	Ilmenite

Table 3. Modal mineral abundances from thin section analysis and spectral fitting for 15058

	Green Pyroxene	Brown Pyroxene	Plagioclase
Thin section [*]	29.3	33.8	30.1
Norm. thin section [*]	31.4	36.3	32.3
Spectral fitting, free ^{**}	32.1	52.3	15.6
Modeled effective grain size (μm)	55.5	58.5	30.5
Spectral fitting, constrained ^{**}	29	51	20

^{*}See discussion in section 5.1

^{**}Free refers to the fit shown in Figure 12a, in which effective grain size is allowed to vary. Constrained refers to the fit shown in Figure 12b, in which effective grain size was constrained to a constant value of 72 μm.

Figure Captions

Figure 1. Bidirectional reflectance spectra of common lunar materials. The diagnostic absorption features of pyroxene and olivine are readily apparent, as is the weaker absorption in plagioclase. Various pyroxene compositions are shown, illustrating the shift in band position with changing pyroxene composition. The long-wavelength absorption in olivine is attributed to chromite inclusions. A spectrum of mature Apollo 16 soil 62231 is plotted, and exhibits the characteristic decreased albedo, reduced band strengths, and red-sloped continuum of lunar soil reflectance spectra. The band centers of the Moon Mineralogy Mapper (M^3) imaging spectrometer on Chandrayaan-1 in its two resolution modes are plotted for reference. Note that M^3 's spectral coverage extends to 3 μm , but data for these samples extend only to 2.6 μm .

Figure 2. Particle size distribution results for the <125 μm separates obtained from weighing experiments. The analytical technique is discussed in the text. The coarse particle samples are largely dominated by larger (45 – 125 μm) particles, but have non-negligible abundances of fine particles. Plagioclase separates tend to have more fine particles.

Figure 3. Photomicrographs of LRMCC thin sections illustrating sample texture. (a) and (c) were collected with reflected light, and the other images with transmitted light (plane-polarized for (b) and (h), cross-polarized for (d), (e), (f), (g)). (a) demonstrates the subophitic texture characteristic of 15058. (b) 15555 thin section showing euhedral chromite grain within pyroxene and poikilitic enclosure of olivine in plagioclase. The sample exhibits poikilitic enclosure of pyroxene and olivine by plagioclase. (c) shows the typical poikilitic texture of plagioclase in 70017, with elongated pyroxenes intergrown with ilmenite and plagioclase. (d) shows the poikilitic texture of plagioclase in 70035. (e) shows zoning from pigeonite core to augite rim in a pyroxene grain from 15058; a similar trend is observed in pyroxenes from 1555 (f). (g) and (h) show the complex sector zoning observed in pyroxenes from 70017 (g) and 70035 (h). Inclusions of ilmenite within pyroxenes are apparent in both cases.

Figure 4. Compositions of major silicate mineral phases found in LRMCC samples. The left column shows the composition of the prepared mineral separates, while the right column illustrates the compositions found in the thin section analyses. The compositions of the prepared separates generally reflect those found in thin section. Note that an olivine separate was obtained only from 1555,965. While olivine is present in the other samples, its modal abundance is too low to allow the preparation of a separate.

Figure 5. CaO vs. TiO_2 abundance for 70035,188 pyroxene separates in weight percent. The data were determined by EMP analysis of grain mounts prepared from subsets of the mineral separates. Separates are labeled as augite and pigeonite, but as discussed in the text, there is some compositional overlap. High-Ca pyroxenes show significant increases in TiO_2 content above a certain CaO content, suggesting that the system became enriched in TiO_2 during augite crystallization, and thus that the augite grains largely crystallized in a Ti-rich environment.

Figure 6. Visible and near-infrared spectra of coarse particle samples. Pyroxenes are labeled as pigeonites and augites for labeling simplicity, but some compositional overlap exists, and the “pigeonite” separates do contain some minor orthopyroxene.

Figure 7. Visible and near-infrared spectra of fine particle samples.

Figure 8. Mid-infrared spectra of coarse particle samples in the volume-scattering wavelength region.

Figure 9. Mid-infrared spectra of fine particle samples in the volume-scattering wavelength region.

Figure 10. Mid-infrared spectra of coarse particle samples in the wavelength region of transition from volume to surface scattering.

Figure 11. Mid-infrared spectra of fine particle samples in the wavelength region of transition from volume to surface scattering.

Figure 12. Examples of preliminary nonlinear spectral unmixing models using the coarse particle 15058,276 bulk sample and mineral separate spectra. Line styles and symbols follow the approach employed for the reflectance spectroscopy figures (Figures 6-11), with some minor changes. The bulk sample spectrum is no longer plotted as a heavier line, and its cross symbols have been hidden. The calculated fit is plotted as “x” symbols. The unmixing method follows the approach of Hiroi and Pieters [1994] (a) Fit with effective grain size for the endmembers (mineral separate spectra) allowed to vary (“unconstrained”). This fit has a calculated root mean square deviation (RMSD) of 0.55% over the full wavelength range used for the fit (0.4 μm – 2.5 μm). (b) Fit with effective grain size for the endmembers constrained to a constant value of 72 μm . This fit has a RMSD of 1.68% over the wavelength range used for fitting (0.4 μm – 2.5 μm).

Figure 13. MGM deconvolutions of the 15058,276 bulk sample coarse particle separate spectrum. Example deconvolutions are shown using one (a) and two (b) absorption features to fit the one and two μm pyroxene absorption features. The principal pyroxene absorptions are plotted in black and dashed (in the case of the two-pyroxene fit) lines, and the 1.2 μm pyroxene absorption in dotted lines. Other absorption features are plotted in grey.

Figure 14. MGM deconvolutions of the 15058,276 bulk sample fine particle separate spectrum. Example deconvolutions are shown using one (a) and two (b) absorption features to fit the one and two μm pyroxene absorption features. The principal pyroxene absorptions are plotted in black and dashed (in the case of the two-pyroxene fit) lines, and the 1.2 μm pyroxene absorption in dotted lines. Other absorption features are plotted in gray. RMS error is plotted offset from 0 by 0.2 for clarity.

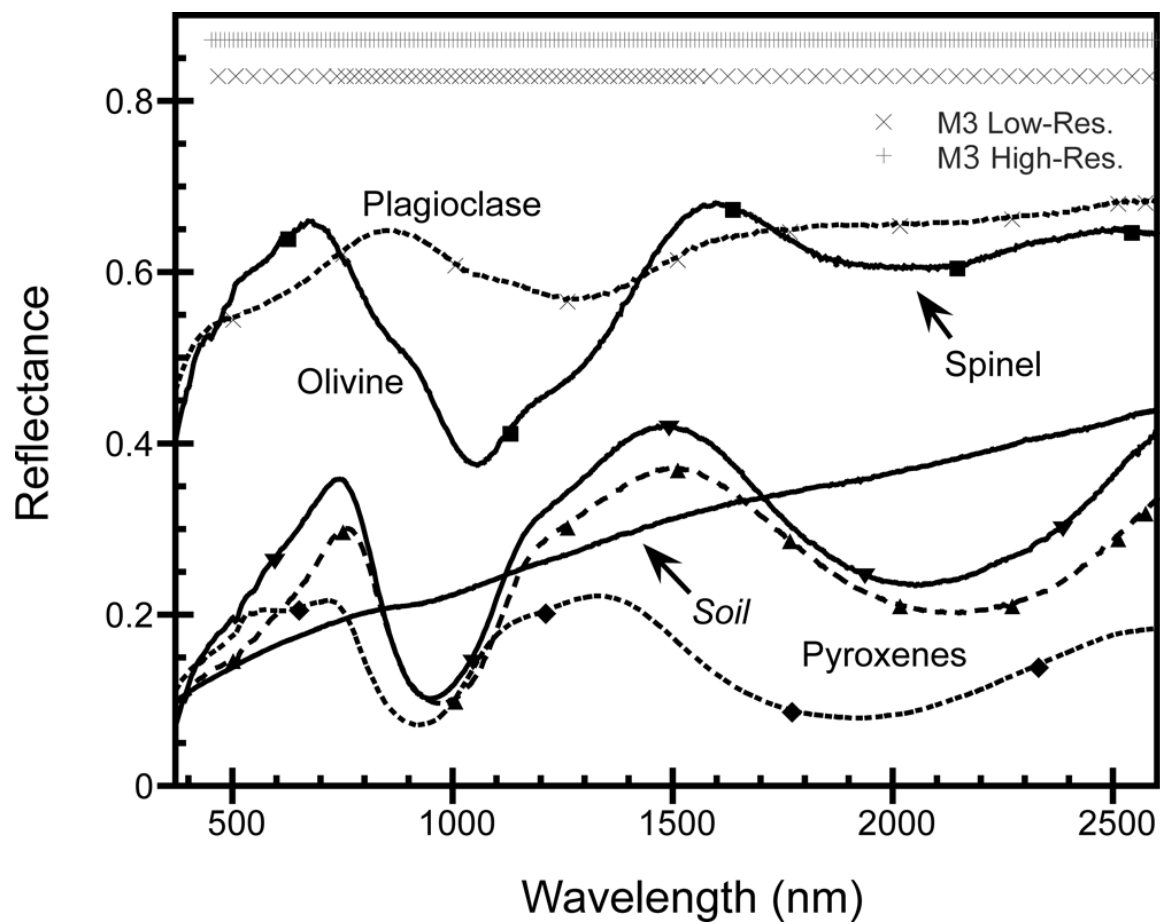


Figure 1.

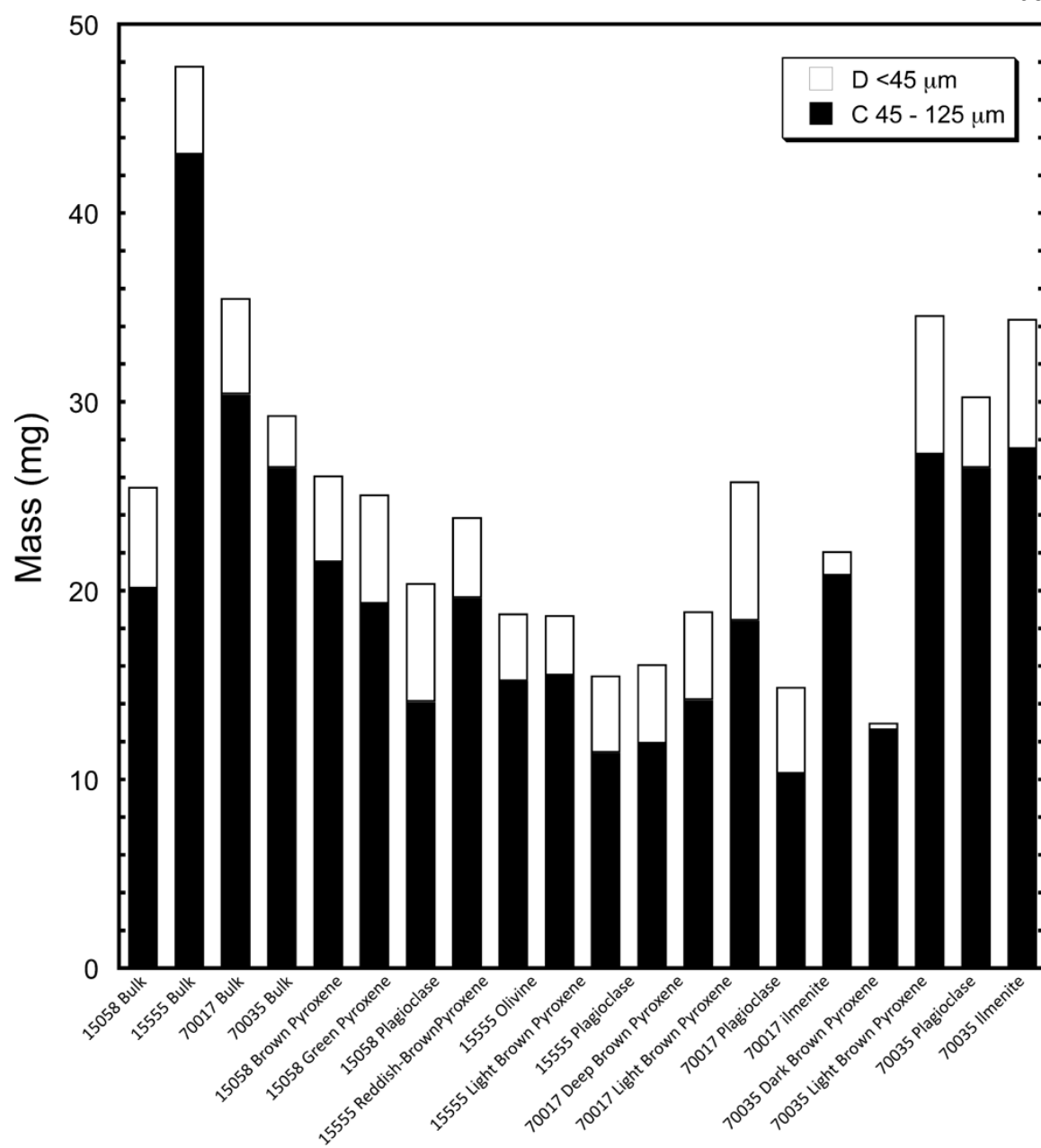


Figure 2.

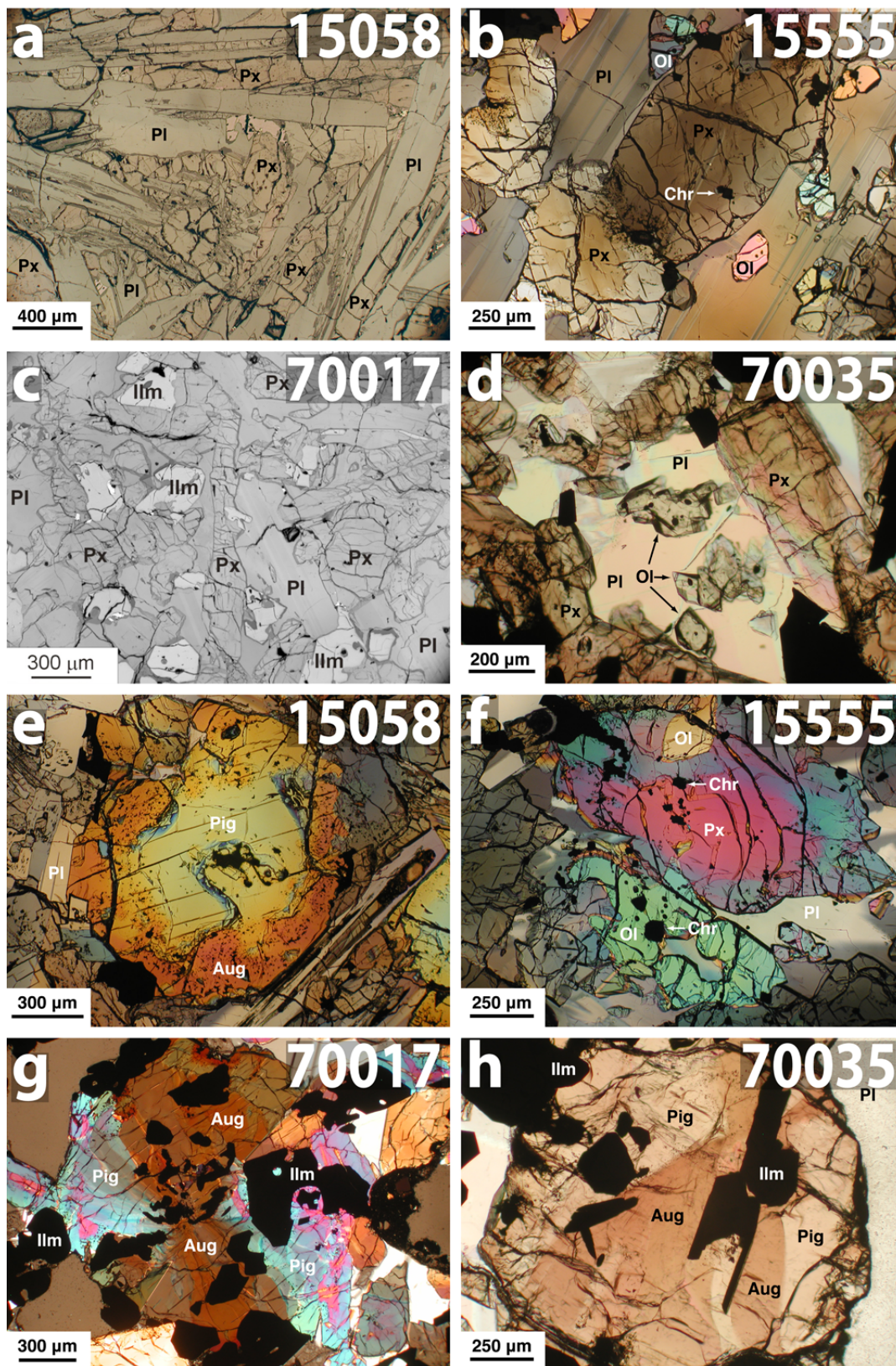


Figure 3.

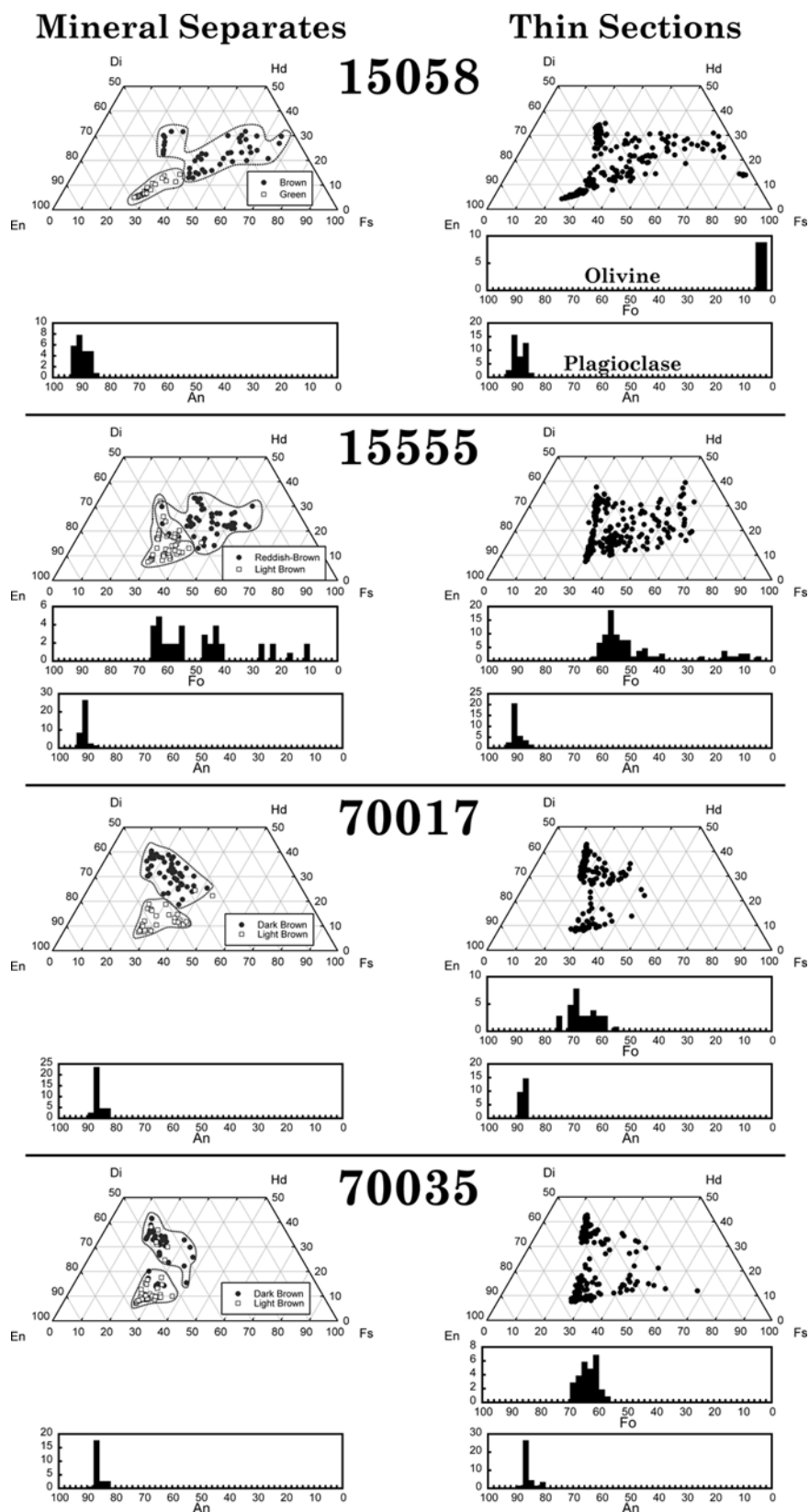


Figure 4.

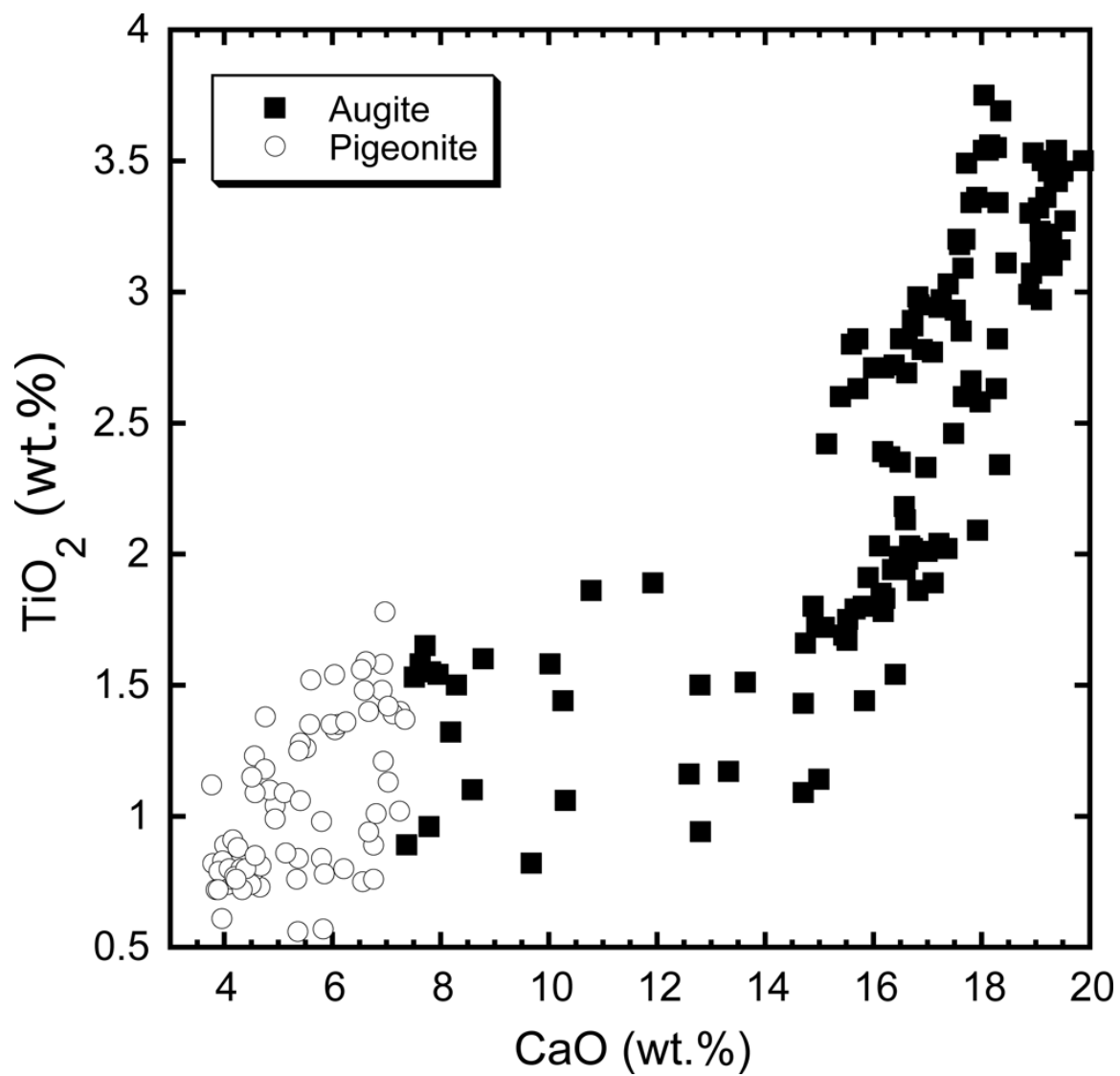


Figure 5.

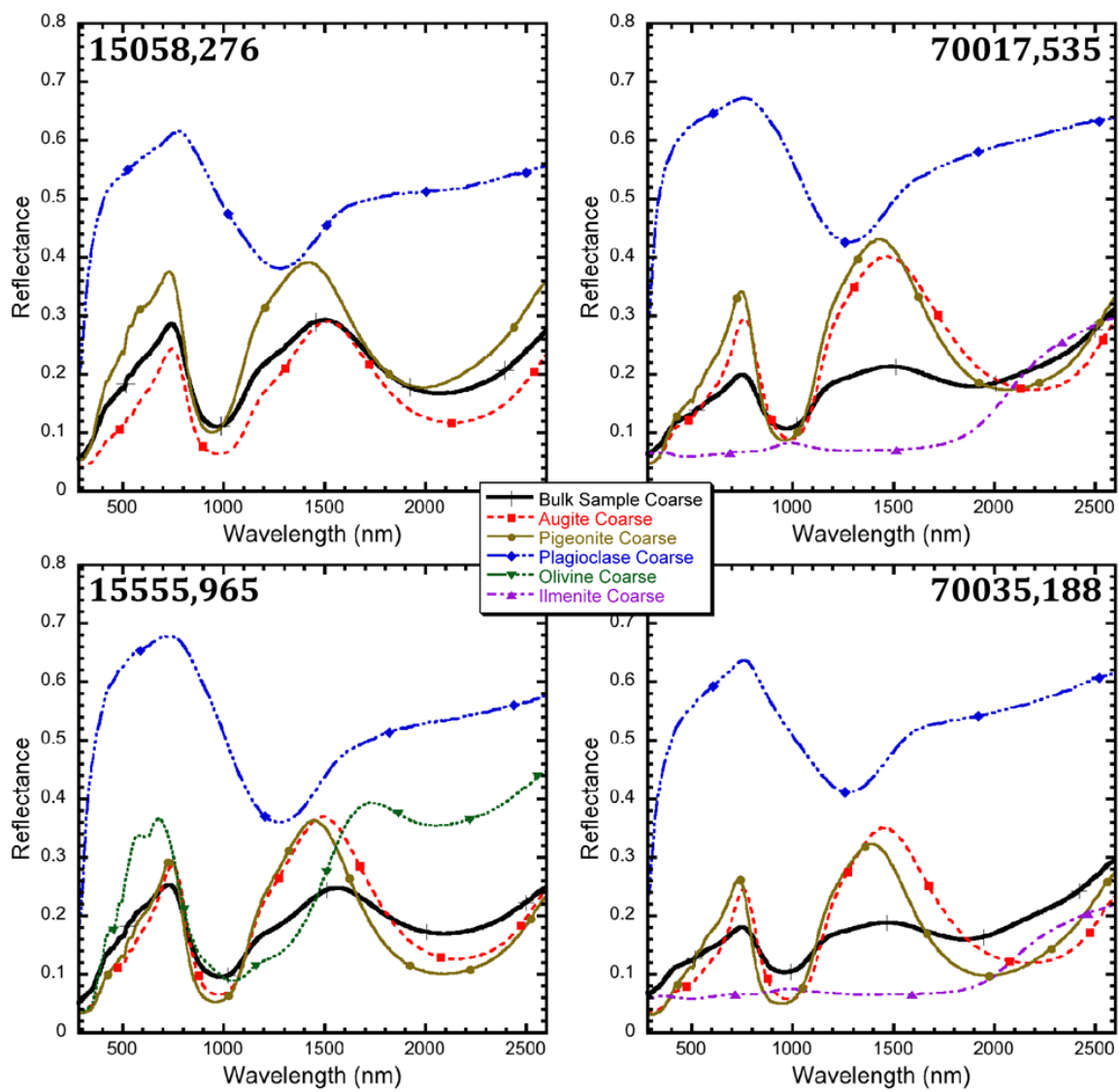


Figure 6.

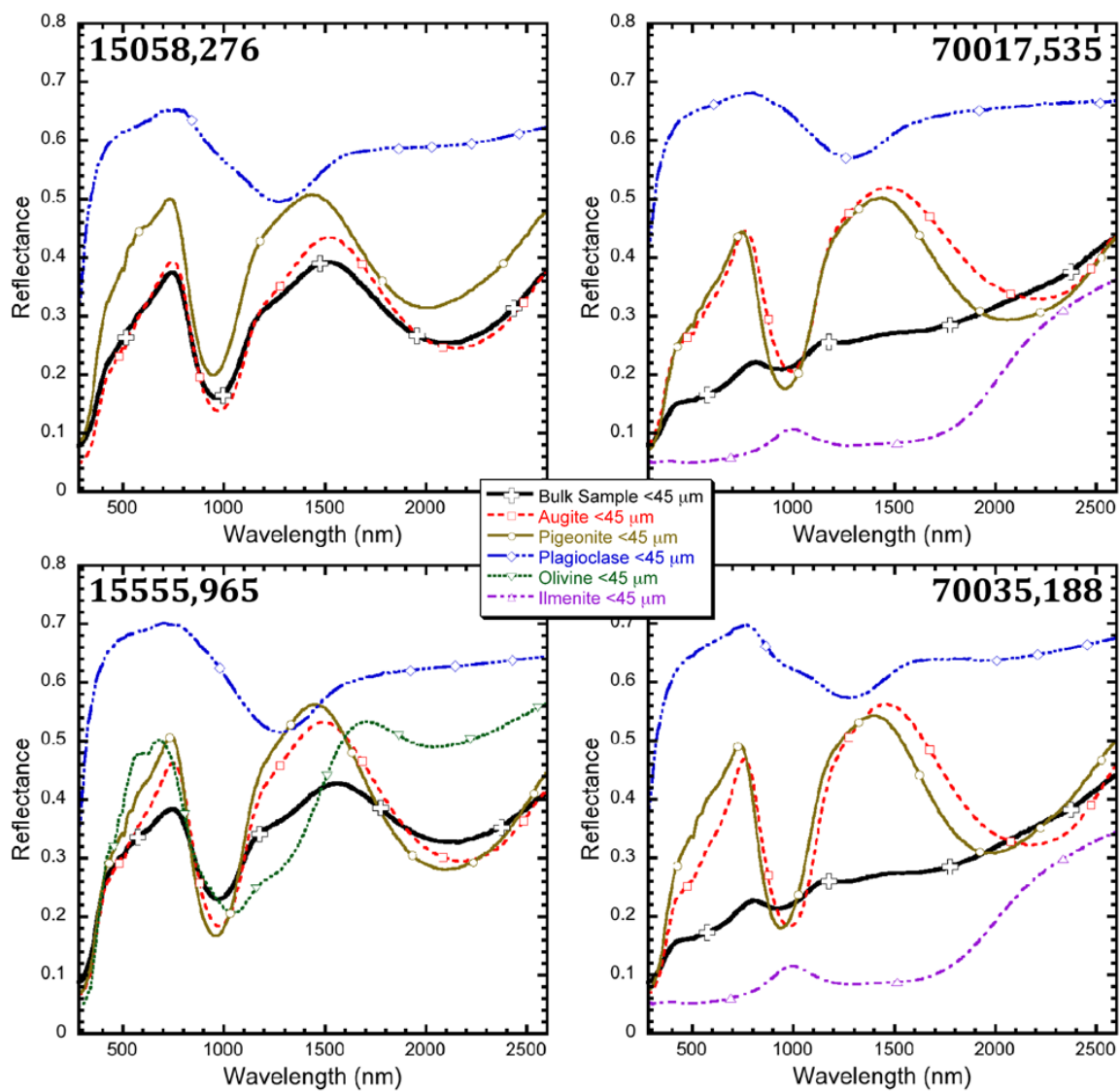


Figure 7.

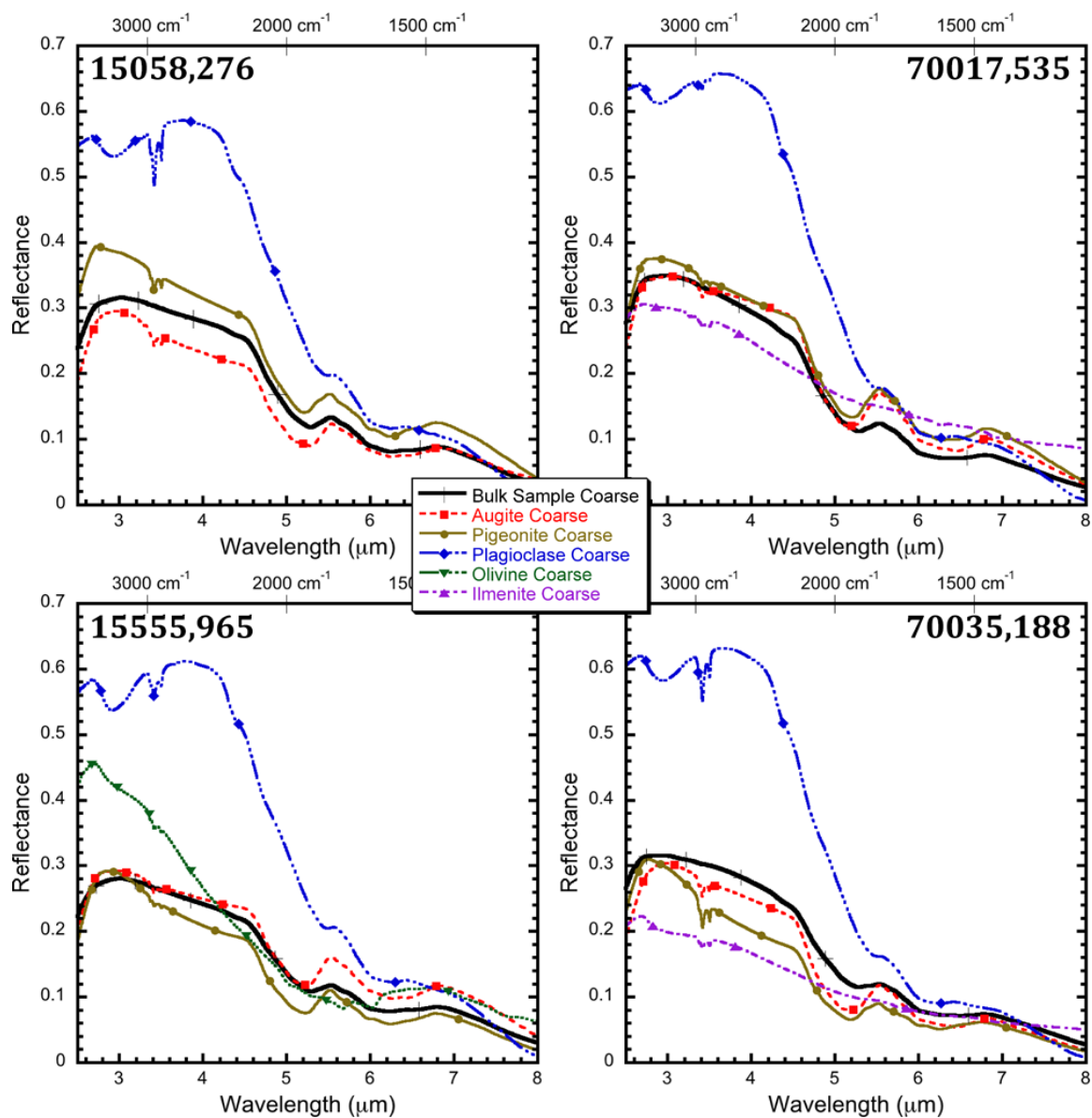


Figure 8.

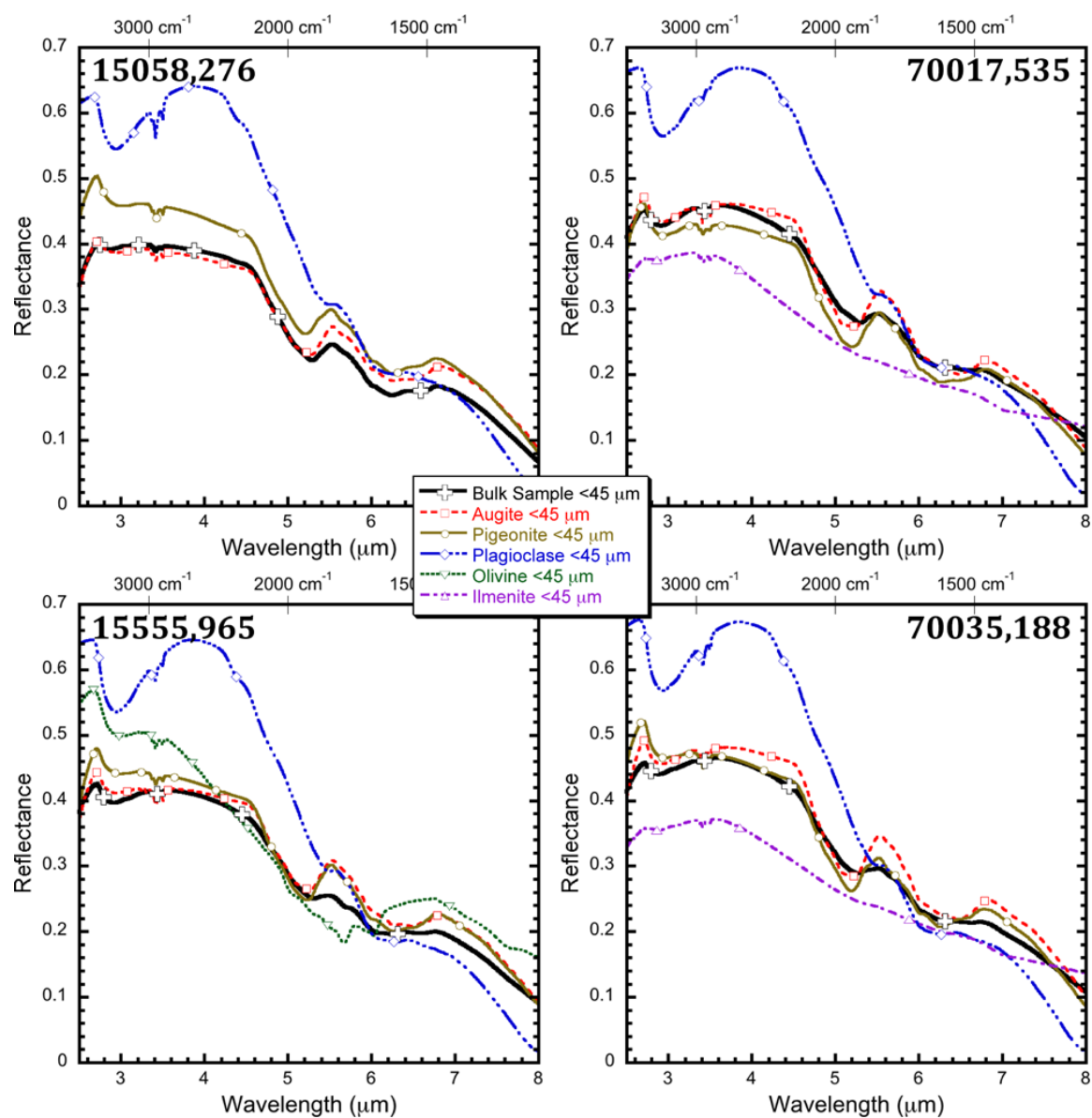


Figure 9.

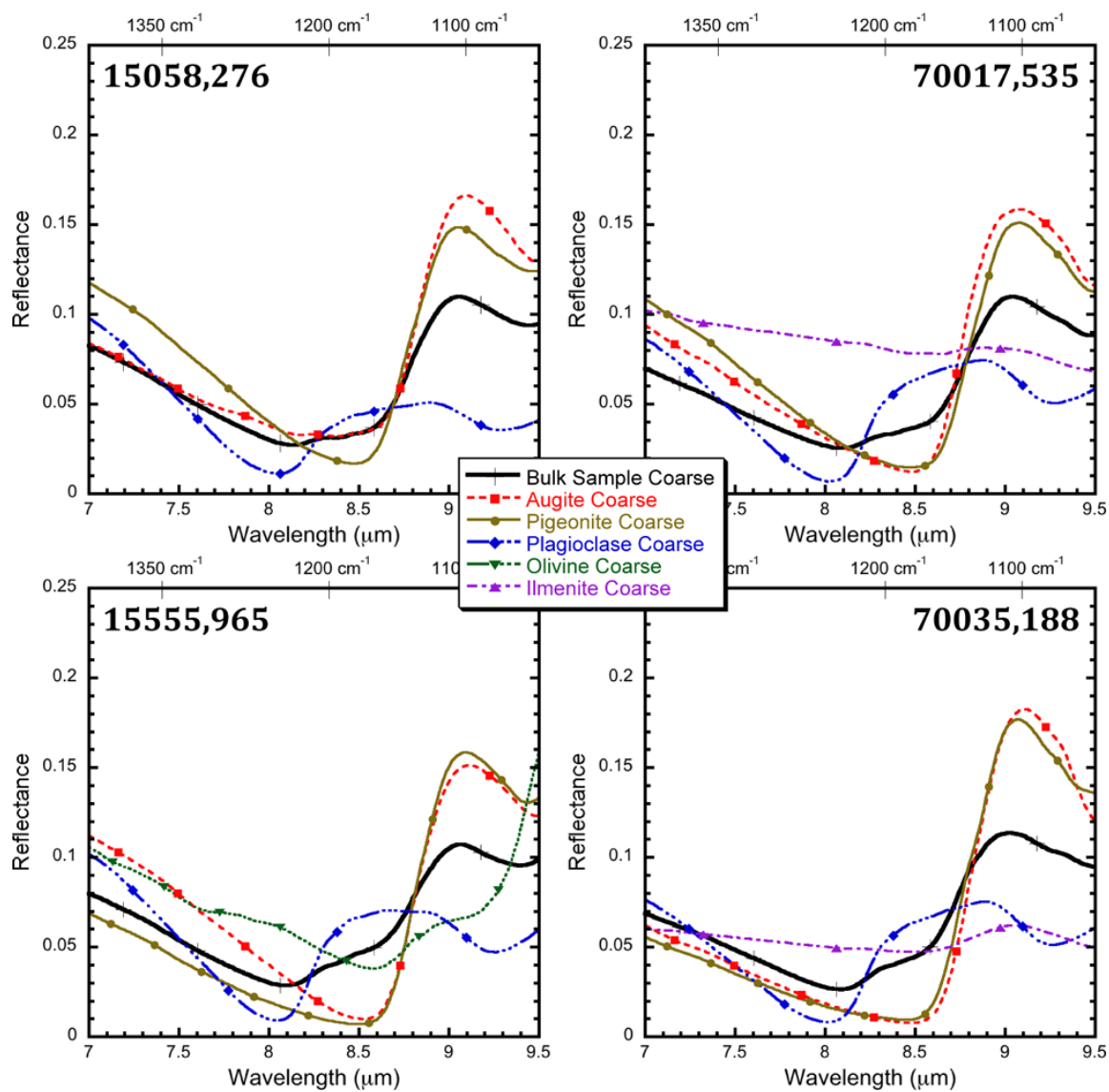


Figure 10.

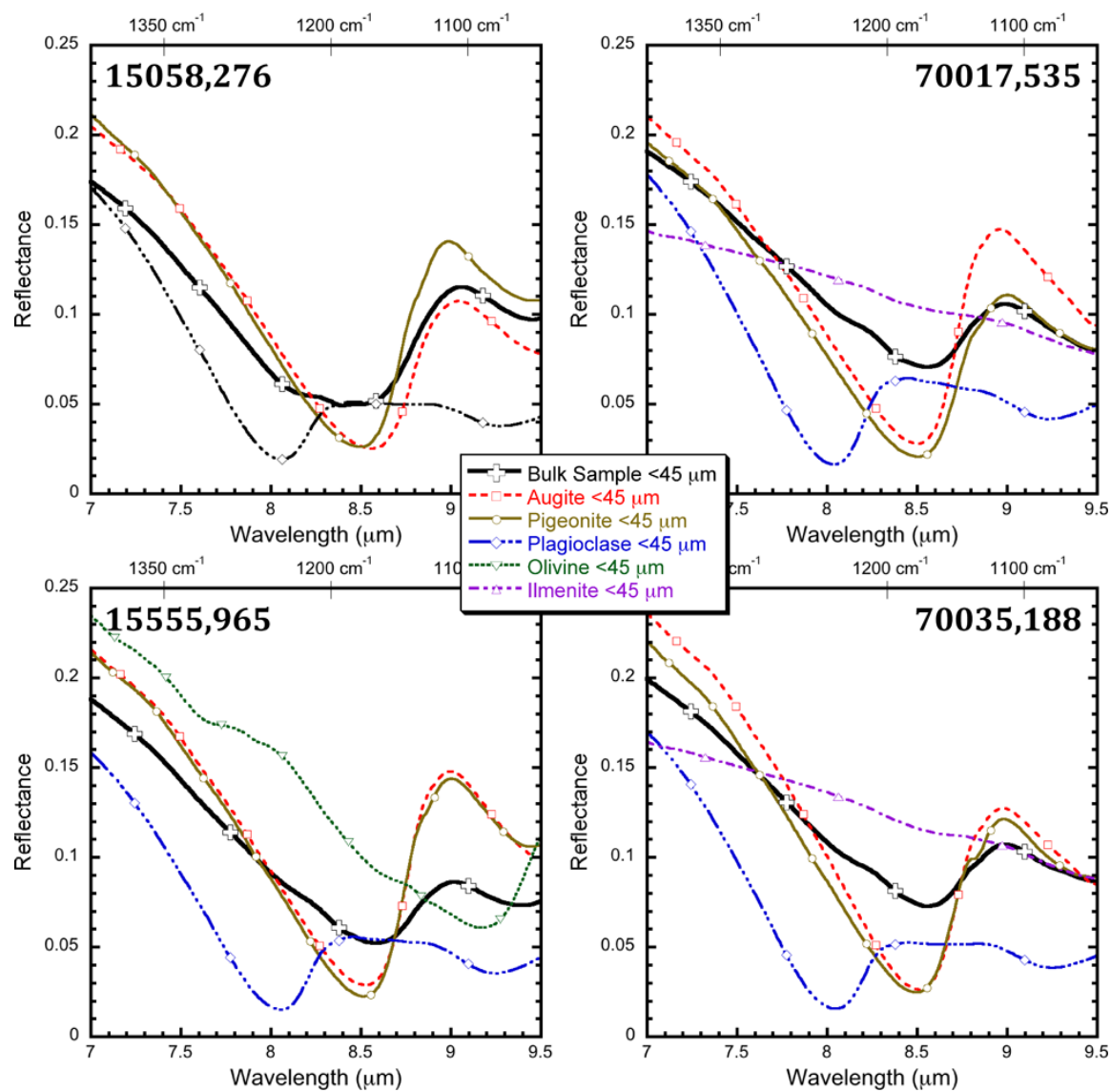


Figure 11.

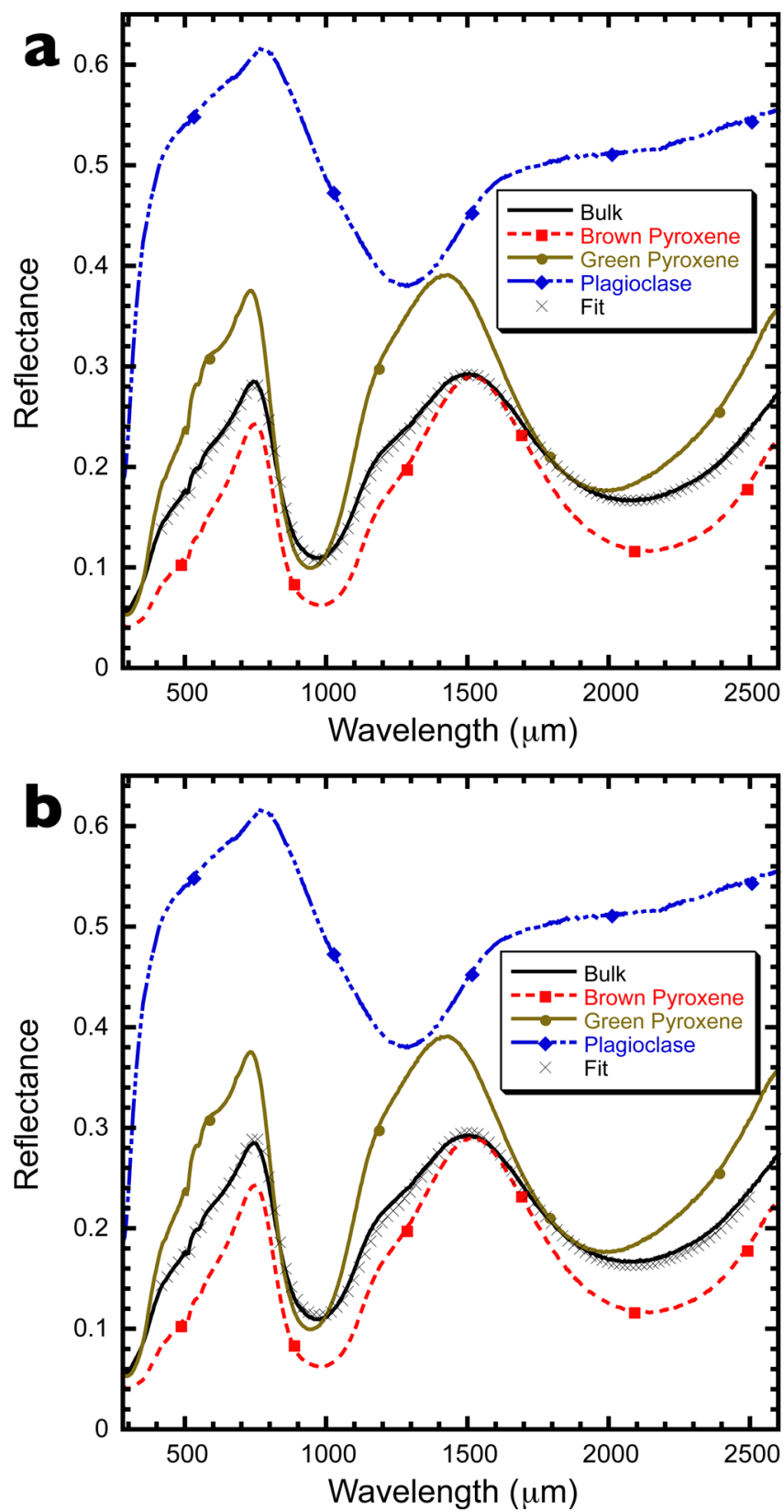


Figure 12.

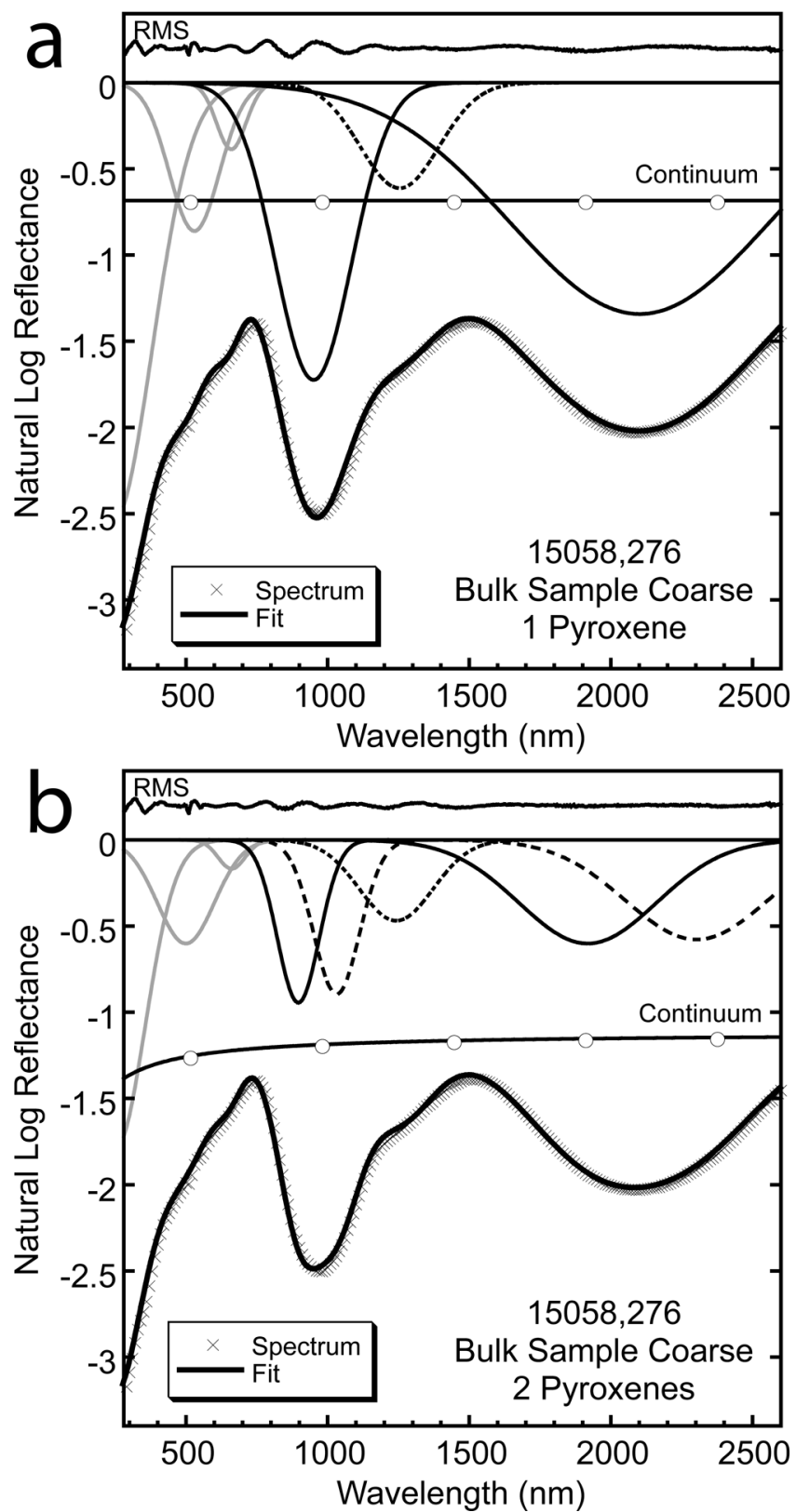


Figure 13.

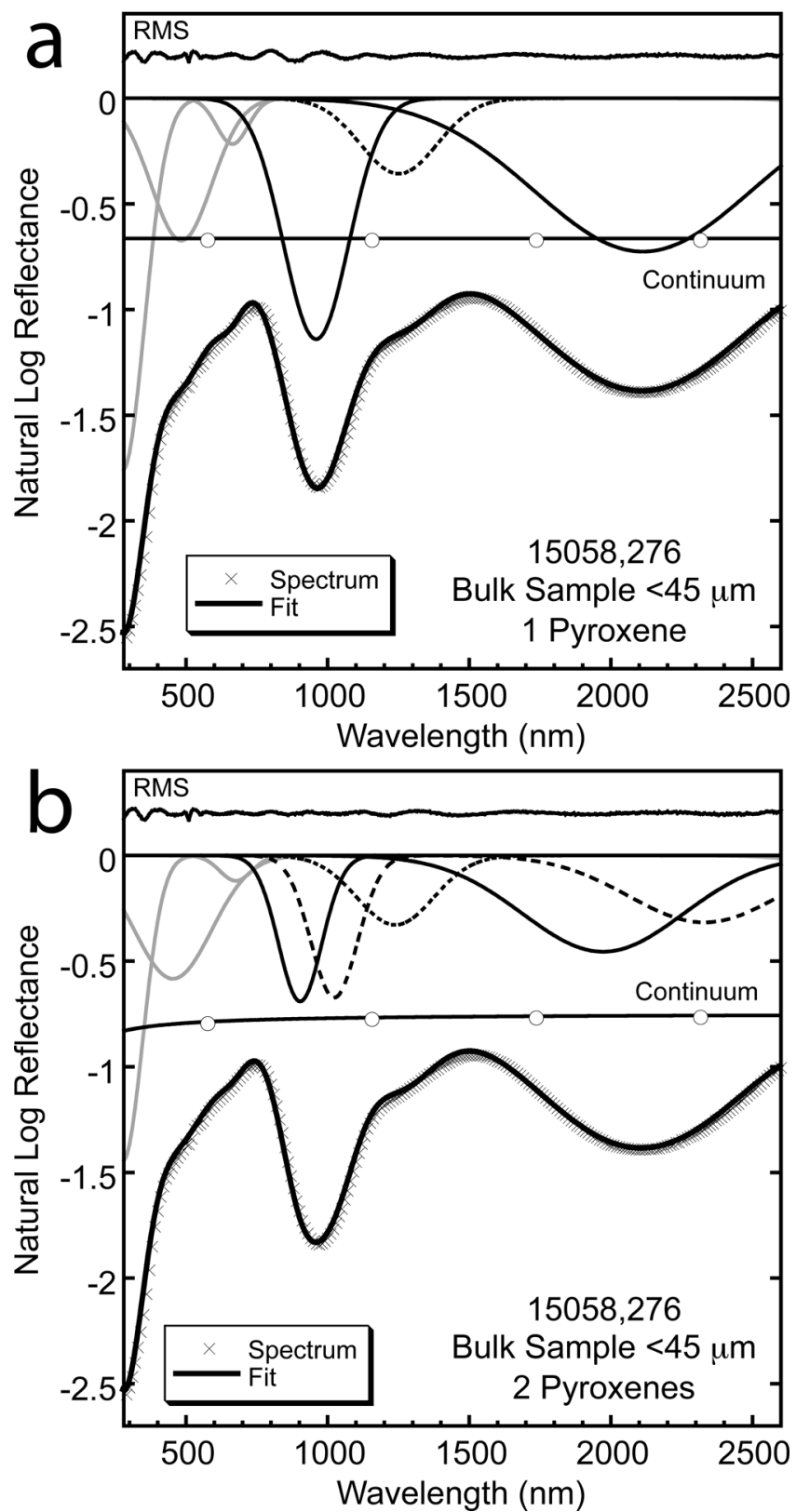


Figure 14.

CHAPTER 2: Reflectance Properties of Ilmenite and Ilmenite-Rich Mare Basalts and Soils: Implications for Remote Detection

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Abstract

A systematic statistical analysis of the correlation between ilmenite abundance and visible to near-infrared spectral parameters is presented for a suite of lunar sample reflectance spectra. The spectra analyzed include the mare basalt soil samples studied by the Lunar Soil Characterization Consortium [*Pieters*, 1998; *Pieters et al.*, 2000a; LSCC; *Taylor et al.*, 2001] and the mare basalt samples evaluated by the Lunar Rock and Mineral Characterization Consortium [LRMCC; *Isaacson et al.*, 2010]. Spectral ratios were calculated across visible to near-infrared wavelengths (0.35 – 2.6 μm), and the degree of correlation between spectral ratios and ilmenite abundance was calculated for all ratios. For lunar soils, a similar correlation analysis was performed between spectral parameters and soil maturity as measured by I_s/FeO in order to isolate more effectively the spectral signature of ilmenite. Analyses were performed independently for the two types of samples, and a comparative analysis of the results was undertaken. Those parameters most highly correlated with ilmenite abundance were identified for each sample suite, as were parameters common to the results for both types of samples. Such parameters represent a logical starting point for parameterizations of ilmenite abundance from hyperspectral reflectance data covering visible to near-infrared wavelengths. However, the results also confirm that the two types of samples analyzed (rocks and soils) are fundamentally different and must be treated as such; efforts to analyze them with a single approach must be undertaken with extreme caution.

1 Introduction

The presence of abundant ilmenite (FeTiO_3) in lunar mare basalts is one of the major properties that distinguish some lunar basalts from other basalts in the solar system [Papike *et al.*, 1976; *Basaltic Volcanism Study Project*, 1981; McSween, 1985; Neal and Taylor, 1992; Papike *et al.*, 1998; Shearer *et al.*, 2006]. Lunar basalts are classified primarily by their TiO_2 content. While additional subclassifications are made based on other chemical or mineralogical properties such as K content, the very low titanium (VLT), low titanium (LT), and high titanium (HT) scheme is the first level of characterization of mare basalts. While not the only TiO_2 -bearing phase, ilmenite is by far the dominant phase in determining the bulk TiO_2 of a basalt. Some HT basalts can contain up to ~35 modal % opaques, of which the dominant phase is largely ilmenite (other opaques such as spinels and armalcolite are minor in comparison to ilmenite) [Papike *et al.*, 1976; Neal and Taylor, 1992].

Ilmenite is a clue to the source region of mare basalts and the evolution of that source region over time. As one of the last phases to crystallize in abundance from the hypothesized lunar magma ocean [Nyquist and Shih, 1992; Hess and Parmentier, 1995], ilmenite would initially have been concentrated near the top of the magma ocean-derived cumulate pile. It has been proposed that the gravitational instability created by such an arrangement led to massive overturn of the cumulate pile, sequestering ilmenite and other associated incompatible element-rich cumulates deeper into the lunar interior, where they mixed with more primitive cumulates to form mare basalt sources [e.g., Ringwood and Kesson, 1976; Ryder, 1991; Spera, 1992; Hess and Parmentier, 1995; Shearer *et al.*, 1996]. While the exact mechanism of incorporation of Ti-rich materials into mare basalt

sources is the subject of some debate, the process likely occurred at depth, as incorporation of Ti-rich materials into mare basalts at shallow depths is difficult to explain [Ringwood and Kesson, 1976; Shearer *et al.*, 1996]. Mare basalt compositions are diverse, reflecting either heterogeneity in the basalt source regions or varying levels assimilation of magma ocean cumulates by melts from the primitive interior [e.g., Neal and Taylor, 1992; Shearer *et al.*, 2006]. Some of the youngest and oldest basalts on the Moon are rich in Ti [Charette *et al.*, 1974; Pieters, 1978; Lucey *et al.*, 2000; Gillis *et al.*, 2003; Hiesinger *et al.*, 2003; Prettyman *et al.*, 2006; Hiesinger *et al.*, 2010], indicating a lack of a simple chemical evolution in the mare basalt source region. The uncertainty over the role of ilmenite in the thermal and chemical evolution of the Moon has continued to drive interest in reliable estimates of ilmenite abundance beyond regions directly sampled by human and robotic exploration.

Efforts to map ilmenite across the lunar surface historically have relied on an empirical correlation between bulk soil TiO_2 abundance and a ratio between reflectance values in ultraviolet and visible (UV-Vis) wavelengths [e.g., Charette *et al.*, 1974; Pieters, 1978; Johnson *et al.*, 1991; Lucey *et al.*, 2000; Gillis *et al.*, 2003]. This relationship is correlated with TiO_2 largely because of the opaque, spectrally neutral nature of ilmenite-rich materials [e.g., Charette *et al.*, 1974; Pieters, 1978; Johnson *et al.*, 1991; Lucey *et al.*, 2000; Gillis *et al.*, 2003; Cloutis *et al.*, 2008]. While TiO_2 is highly correlated with ilmenite abundance in lunar basalts, the lunar surface is dominated by lunar soil. Accurate modal abundance data is extremely challenging (if not impossible) to obtain for lunar soils, while bulk chemical composition is a much easier measurement to make. Thus, the necessary data to perform direct correlations with ilmenite abundance

were not available to previous investigators in sufficient volume to enable direct parameterization of ilmenite abundance. Because of this lack of mineral abundance data, these previous studies relied on the empirical correlation between the UV-Vis ratio and bulk TiO₂ abundance. An example of the UV-VIS ratio (using Clementine UVVIS multispectral reflectance data) is provided in Figure 1. The opaque, spectrally neutral properties of ilmenite-rich high-Ti soils across visible wavelengths has led other investigators to hypothesize that ilmenite may be a component in the Mercurian surface [e.g., *Denevi et al.*, 2009; *Riner et al.*, 2009].

While ilmenite is dark and spectrally neutral across the visible, longer wavelength reflectance studies reveal that ilmenite is quite spectrally complex [e.g., *Nash and Conel*, 1974; *Riner et al.*, 2009; *Isaacson et al.*, 2010]. The general spectral properties of ilmenite include a relative increase in reflectance near 1 μm and an upturn in reflectance in the NIR ($>1.7 \mu\text{m}$), although the physical properties of the ilmenite (i.e. particle size) and the optical properties of host materials can affect ilmenite's optical properties substantially. The lunar ilmenites examined by Isaacson et al. [2010] are broadly similar to the synthetic ilmenite examined by Riner et al. [2009], but differ from their synthetic counterpart in their long wavelength features; the lunar ilmenites exhibit a “rollover” in the long wavelength reflectance tail, whereas the synthetic ilmenites exhibit constantly increasing reflectance with wavelength. Ilmenite has dramatic effects on reflectance spectra, including muted 1 and 2 μm absorption features, reddened continuum slopes, and decreased albedos. These properties illustrate some of the confounding issues in dealing with ilmenite, as these effects are similar to those of the nanophase iron responsible for the optical properties of mature lunar soils [e.g., *Pieters et al.*, 2000b; *Hapke*, 2001;

Noble et al., 2001; *Taylor et al.*, 2001; *Taylor et al.*, 2010]. Additionally, the upturn in reflectance at long wavelengths can mimic the effect of thermally emitted radiation [e.g., *Clark*, 1979; *Clark et al.*, 2009]. Ilmenite clearly exhibits additional spectral features beyond a flat, low-reflectance spectrum across visible wavelengths, though its spectral properties and effects on spectra of basalts are complex. The increased wavelength coverage of modern orbital spectrometers should enable these features to be detected through remote sensing. In this paper, we conduct a detailed investigation of the spectral properties of ilmenite and ilmenite-rich mare basalts and suggest possible avenues in which ilmenite might be detected directly with remotely-sensed datasets.

2 Background: Ilmenite Spectroscopy

The spectral properties of ilmenite are less well-characterized than those of olivine and pyroxene. Previous research on ilmenite spectroscopy and in particular remote detection has focused on its opaque character and prominent relative “blue” (negative) continuum slope across visible wavelengths. This “blue” slope is the basis of the traditional approach to mapping TiO_2 on the Moon with the UV-Vis ratio [e.g., *Charette et al.*, 1974]. This opaque, “blue” character has been attributed largely to Ti^{4+} -O [*Loeffler et al.*, 1974] and Fe^{2+} - Ti^{4+} [*Loeffler et al.*, 1975] charge transfer (CT) absorptions. The observed spectral properties of opaque minerals such as ilmenite are extremely complex, and are highly dependent on a number of physical properties of the mineral in question as well as its host material. Variables such as particle size of the opaque mineral, particle size of the host material, and the opacity of the host material have significant effects on the reflectance properties of the opaque-bearing material. The review of ilmenite’s spectral properties presented here is a general introduction based on

results presented in the literature, but does not address all of the important effects of the variables mentioned above. The spectroscopy of opaque phases like ilmenite is an area of ongoing research, and our understanding of the effects of these variables is continually evolving as more diverse samples are examined [e.g., *Riner et al.*, 2009; *Tompkins and Pieters*, 2009; *Isaacson et al.*, 2010].

Crystallographic sites in the ilmenite structure are octahedrally-coordinated and populated by Fe^{2+} and Ti^{4+} cations according to stoichiometry [e.g., *Cloutis et al.*, 2008]. Ilmenite forms a solid solution with hematite (Fe_2O_3), and terrestrial ilmenites commonly occur in association with hematite and contain some Fe^{3+} [*Waychunas*, 1991]. However, lunar ilmenites should not contain Fe^{3+} due to the reducing lunar environment, and are typically nearly pure stoichiometric FeTiO_3 [*El Goresy et al.*, 1971; *Taylor et al.*, 1971; *El Goresy*, 1976]. Features in the UV wavelengths ($\sim 250 - 300$ nm) have been attributed to Fe^{2+} -O and Ti^{4+} -O charge transfer absorptions, and a stronger absorption near 500-600 nm has been attributed to a Fe^{2+} - Ti^{4+} CT absorption, although a Ti^{3+} - Ti^{4+} CT may also be partially responsible [*Loeffler et al.*, 1975]. Similar features near ~ 600 nm are also observed in Ti-bearing pyroxenes [e.g., *Isaacson et al.*, 2010], and are attributable to the Fe^{2+} - Ti^{4+} CT, although other transitions such as Ti^{3+} - Ti^{4+} CT and a spin-allowed CF transition in Ti^{3+} are also possible [*Loeffler et al.*, 1975; *Burns et al.*, 1976]. The relative strengths of these absorptions may explain the “blue” slope of ilmenite in the UV [*Strens and Wood*, 1979; *Cloutis et al.*, 2008].

An absorption beyond $1\ \mu\text{m}$ has been attributed to a crystal-field transition in Fe^{2+} [*Loeffler et al.*, 1975; *Strens and Wood*, 1979], although this is not well-characterized. The Fe^{2+} -bearing crystallographic sites in the ilmenite structure are asymmetric, having

roughly the same degree of distortion as the orthopyroxene M1 site [Lindsley, 1976; Smyth and Bish, 1988], which indicates that such transitions are a possible explanation for the feature. Clearly, a more complete characterization of the crystal field stabilization energy [e.g., Burns, 1993] for this transition is required. More recent analyses of ilmenite extended observations into the near-infrared and noted a prominent increase in reflectance around 1 μm and another beyond $\sim 1.5 \mu\text{m}$ [Riner *et al.*, 2009; Isaacson *et al.*, 2010]. The character of ilmenite reflectance spectra is understood in general, but has not received the breadth of focused study devoted to analyses of the mafic silicates, and thus many specifics of the reflectance properties of ilmenite and related Fe-Ti oxides are poorly understood.

3 Methods

3.1 Samples and Limitations

The data we will use to evaluate systematically the spectral effects of ilmenite include the spectral datasets of the Lunar Soil Characterization Consortium [LSCC; Taylor *et al.*, 2001; Taylor *et al.*, 2010] and the Lunar Rock and Mineral Characterization Consortium [Isaacson *et al.*, 2010]. Example spectra from this combined dataset are illustrated in Figure 2 (LRMCC) and Figure 3 (LSCC). The LSCC and LRMCC performed detailed mineralogy/petrography and spectroscopy analyses, obtaining careful bulk composition and modal abundance data for the soils (LSCC), rocks (LRMCC), and their components. The LRMCC also conducted similar analyses of mineral separates of the bulk basalt samples.

The LSCC modal mineralogy results were determined through an automated point counting procedure with digital X-ray images of lunar soil grain mounts. The phases

were determined based on specified chemical thresholds (e.g., ilmenite is classified by its abundance of Ti and Fe relative to Si). While the LSCC was careful to use good criteria to classify agglutinitic glasses, it is possible that very Ti-rich glasses could be falsely classified as ilmenites. Such Ti-rich glasses would have very different optical properties from ilmenite. Thus, the modal abundance data for ilmenite in the lunar soils must be considered to have at least some level of error.

Despite the thorough nature of the LRMCC and LSCC studies, the available data with which to quantify the spectral effects of ilmenite is limited. Critical properties such as sample texture (in the case of basalts) and soil maturity at constant ilmenite abundances (as well as ilmenite abundance at constant maturity) cannot be well constrained with this dataset. Additionally, the LRMCC samples are compositionally quite similar apart from ilmenite abundance; a more robust input dataset ideally would have diversity in texture and composition. The ilmenite in the LRMCC basalt samples typically occurs as intergrowths with pyroxene, as illustrated by Figure 4. The incomplete nature of the dataset is illustrated by the thin section images presented in Figure 5, which illustrate the range of sample textures in the Apollo 17 very high titanium textural sequence identified by Papike et al [1976]. The LRMCC samples were selected specifically for their coarse-grained nature to facilitate mineral separations, so they represent only one “endmember” in sample texture. Ilmenite intergrown with other phases represents a very different scattering regime than a physical mixture such as the basalt-ilmenite mixtures. The reader is thus reminded that the conclusions of this study should not be considered a comprehensive evaluation of the spectral properties of ilmenite; a substantially more diverse dataset would be required for such an evaluation.

The general effects of ilmenite on spectra of lunar mare basalts are illustrated by the spectra plotted in Figure 6. The low-Ti and high-Ti are compositionally similar apart from the abundant ilmenite in 70017. To first order, the differences between the 15058 and 70017 spectra can be attributed to ilmenite. The general effects described in the introduction are readily apparent: weakened 1 and 2 μm absorptions, decreased albedo, and enhanced continuum slope into the near-infrared. The goal of this work is to quantify these effects, and to identify the critical wavelength regions in which basalt spectra show the most prominent effects of ilmenite.

3.2 Modal Abundance Data

As context for the analysis of the role of ilmenite in the reflectance spectra of the LSCC and LRMCC samples, we present the modal abundance data reported by the two consortia [Taylor *et al.*, 2001; Isaacson *et al.*, 2010]. Additionally, to establish which other compositional parameters are variable in the samples and to verify that the LRMCC samples are compositionally similar apart from ilmenite abundance, we report ilmenite-normalized modal abundance (INMA) data. INMA data are calculated by summing the modal abundance data other than ilmenite, and deriving a scaling factor to normalize the (Total – Ilmenite) value to 100%. The modal abundances of non-ilmenite phases are then multiplied by this scaling factor to produce INMA. Modal abundance and INMA data for the LRMCC samples are reported in Tables 1 and 2. For simplicity, we described those modal abundance values reported as <0.1 by Isaacson *et al.* [2010] as “trace” (tr.). These “trace” abundances should not be disregarded, as even volumetrically minor phases can have substantial effects on reflectance spectra, as discussed by Isaacson and Pieters

[2010]. Modal abundance and INMA data for the LSCC samples are presented in Tables 3-6 (separated into low-Ti and high-Ti samples).

3.3 Spectral Parameters and Correlations

We created a series of spectral parameters covering the visible to near-infrared, over the wavelength region common to both LSCC and LRMCC spectra (0.35 μm to 2.6 μm). For the purposes of this project, we define “spectral parameters” as ratios of reflectance values at distinct wavelengths (spectral ratios). Parameters were created by calculating ratios of the reflectance value of each input spectrum at two distinct wavelengths over the full wavelength range, sampled in 0.025 μm (25 nm) increments. LSCC and LRMCC spectra were analyzed separately. These parameters were regressed with the modal abundance of ilmenite for each sample.

The degree of correlation for each parameter was estimated through the use of the Spearman coefficient (LRMCC spectra) and the Pearson coefficient (LSCC spectra). The Pearson coefficient (technically referred to as the Pearson product-moment correlation coefficient) is a statistical measure of the correlation between two variables assuming a linear relationship. It is defined as the covariance of the variables divided by the product of the variables’ standard deviations. The Spearman coefficient (technically referred to as the Spearman rank correlation coefficient) is a related measure, and effectively represents a Pearson coefficient between the ranks of the variables. The Spearman coefficient determines the correlation between the variables assuming a monotonic relationship, as compared to the Spearman coefficient which assumes a linear relationship [e.g., *Myers and Well*, 2003; *Miller and Miller*, 2004]. The Spearman coefficient was chosen as it is suitable for nonlinear correlations, and we have no reason to expect linear

relationships over nonlinear relationships. However, the LRMCC samples effectively exhibit only two abundances of ilmenite, and the Spearman coefficient is unable to produce reliable results for the spacing of the LRMCC abundance data. The Pearson coefficient is slightly more capable of handling this situation, but any correlation approach based on such limited input data must be treated with some skepticism. Specifically, the Pearson coefficient is quite high (near ± 1) for many parameters, as the LRMCC data present something similar to a “two point line” regression.

The level at which the correlation coefficient is statistically significant (statistically separable from the null hypothesis with a correlation coefficient of 0) is strongly dependent on the number of input values (N). At the 90% confidence level, a conservative estimate of this statistically significant cutoff threshold is 0.93 (~ 0.9) for the LRMCC spectra (N=4) and 0.32 (~ 0.3) for the LSCC spectra (N=27), assuming a normal distribution. If the LRMCC and LSCC results are combined (N=31), the threshold is 0.30. Only correlation coefficients above these thresholds can be considered statistically significant.

The parameters were arranged in a 2-D matrix for display, with wavelength on the X and Y axes. The denominator of the ratio was plotted on the Y axis, and the numerator of the ratio on the X axis. The degree of correlation (correlation coefficient) was plotted in color, with extreme colors relating to values near ± 1 . Thus, each “pixel” in these figures corresponds to a specific parameter or spectral ratio. The upper and lower “halves” (opposite sides of the diagonal) are inversely related, as the two sides represent the inverse of the same ratios. This arrangement is illustrated schematically in Figure 7, and was developed by Pieters et al. [2002]. We refer to such figures as “ratio correlation

maps”. Two versions of the ratio correlation maps will be presented. The first version shows correlation for all parameters, regardless of whether the correlation coefficient is statistically significant, as discussed above. The second version shows results only for those parameters exhibiting a correlation coefficient above the statistically significant cutoff threshold defined above.

Correlations between spectral parameters and ilmenite abundance were conducted for LRMCC and LSCC spectra separately, and the most highly correlated wavelength regions identified for each suite. Note that for the LSCC spectra, we did not analyze the bulk sample (<45 μm) spectra, as the LSCC reported modal abundances for the grain size separates only [Taylor *et al.*, 2001]. Because the spectral effects of ilmenite can mimic the effect of maturity, the most useful parameters are those correlated with ilmenite but not correlated with maturity as measured by I_s/FeO . Thus, we also performed correlations with I_s/FeO , a proxy for soil maturity [Housley *et al.*, 1975; Morris, 1976; 1978]. We used the I_s/FeO values reported by the LSCC for the specific grain size separates [Taylor *et al.*, 2001]. Parameters highly correlated with ilmenite but not with I_s/FeO were identified using thresholds for correlation coefficients for ilmenite vs. coefficients for I_s/FeO .

After completing the independent correlation analyses for the LRMCC and LSCC spectra, we performed an initial comparison of the results by identifying parameters that are highly correlated with ilmenite (and not with I_s/FeO in the case of the LSCC spectra) for both sample suites. Parameters identified in this analysis would represent the most logical initial elements of a full parameterization for ilmenite abundance for diverse lunar materials. To identify these parameters, we used a similar technique as was applied to

isolate the correlation with ilmenite from the correlation with I_s/FeO for the LSCC spectra (the use of thresholds). Thresholds were defined for correlation coefficients between ilmenite abundance and spectral parameters for the LRMCC spectra, and for ilmenite abundance vs. spectral parameters as well as I_s/FeO vs. spectral parameters for the LSCC spectra.

Finally, we performed a correlation analysis between spectral parameters and ilmenite abundance in which the LRMCC and LSCC spectra were combined into a single input dataset of 31 spectra (4 LRMCC, 27 LSCC). The Spearman correlation coefficient was used for these analyses. We do not generate reports optimized parameters using correlation coefficient thresholds as in the individual analyses of the LRMCC and LSCC spectra. As discussed below, this exercise reinforces that lunar soils and rocks are fundamentally different in their spectral properties, and that they cannot be grouped together easily in such analyses.

4 Results

The results of the correlation analyses are presented in Figures 8-10. These figures use the scheme illustrated in Figure 7, in which the numerator of the spectral ratio in question is on the x axis and the denominator on the y axis. Each pixel on one side of the diagonal thus corresponds to a unique ratio, and pixels with reversed row, column coordinates (e.g. 5, 13 vs. 13, 5) represent the inverse of the same ratio. Colors correspond to the correlation coefficient between the parameter values for the set of spectra and the ilmenite abundance or I_s/FeO of the sample, depending on the figure. Extreme values (colors close to red and blue) indicate higher correlation, with positive values indicating a positive relationship and negative values indicating an inverse

relationship. We highlight both positive and negative correlations, as both indicate correlation between parameter and ilmenite or I_s/FeO , with the trend line slope's sign being the only difference.

4.1 LRMCC Correlations

Figure 8 presents the correlation analysis between spectral ratios and ilmenite abundance for the LRMCC basalt samples. The upper figure presents the results for all parameters, while the lower figure presents results only for parameters with correlation coefficients above the statistically significant threshold of 0.9 discussed above, as discussed in the methods section. The input spectral dataset for this figure was the series of bulk sample spectra at both grain sizes ($<125\ \mu\text{m}$ and $<45\ \mu\text{m}$). Note that many parameters are either highly correlated or highly anti-correlated with ilmenite abundance. This reflects the relative simplicity of this dataset; the samples are compositionally quite similar, with the major difference being the abundance of ilmenite. Thus, most differences between the spectra will be related to ilmenite abundance, producing high degrees of correlation. The parameters most highly correlated with ilmenite (Pearson correlation coefficients > 0.99) are reported in Table 7. These parameters are taken only from the upper half of the ratio correlation map ($y > x$), so the inverse pair of each parameter is not reported.

4.2 LSCC Correlations

The ratio correlation maps between ilmenite abundance and spectral ratios for the LSCC spectra are shown in Figure 9, again with the upper plot showing results for all parameters and the lower plot showing only statistically significant results. The input dataset for this figure was all LSCC spectra for which ilmenite abundance data were

available for the corresponding sample. In practice, this means that bulk sample spectra (<45 μm) were excluded, as modal abundance results were reported by the LSCC only for the grain size separates [Taylor *et al.*, 2001]. Considerably more variation in correlation is observed in this map, reflecting the more complex nature of the soil samples. Multiple parameters vary highly between the samples, only one of which is ilmenite abundance. Thus, far fewer parameters are strongly correlated or anti-correlated with ilmenite relative to the LRMCC results.

The spectral parameters for the LSCC spectra were correlated with maturity (I_s/FeO) in addition to ilmenite abundance. The ratio correlation maps for this analysis are shown in Figure 10. As in Figures 8 and 9, the upper figure presents results for all parameters, while the lower figure presents only statistically significant results. Many regions are highly correlated or anti-correlated with maturity, although significant regions of this ratio correlation map show intermediate values, suggesting that parameters exist that are not highly correlated with soil maturity. Qualitatively, this map appears different than the ilmenite ratio correlation map in Figure 9, suggesting that parameters can be identified that are correlated with ilmenite but not with maturity.

The best parameters from the LSCC analyses were determined through the use of thresholds, in which all parameters below a certain ilmenite correlation coefficient value and above a certain I_s/FeO correlation coefficient threshold were rejected. This scheme is illustrated graphically in Figure 11, a scatterplot of ilmenite correlation coefficient vs. I_s/FeO correlation coefficient. The points in this scatterplot correspond to “pixels” from the upper halves (so as not to duplicate parameters with their inverses) of the ratio correlation maps in Figure 9 and 10. In other words, the “Y” coordinate in Figure 11

corresponds to the pixel values in Figure 9, and the “X” coordinate in Figure 11 corresponds to the pixel values in Figure 10. The colors correspond to progressively more “strict” thresholds on the correlation coefficients for ilmenite abundance and I_s/FeO . The parameters correlated highly with ilmenite abundance and not with maturity are presented in Tables 8 and 9. Table 8 reports parameters with less restrictive thresholds (orange points in Figure 11), and Table 9 reports parameters with more restrictive thresholds (red points in Figure 11).

4.3 LRMCC-LSCC Combined Analysis

The results of the initial comparative analysis of the LRMCC and LSCC results are presented in Figure 12, a plot of ilmenite correlation coefficients for both LRMCC and LSCC spectra. The results for all spectral parameters are plotted in light gray open circles, and subsets based on various threshold values are plotted in various other colors and markers, as defined in the figure caption. Note that the subclasses become progressively more restrictive, meaning that successive subclasses are subsets of preceding subclasses. The parameters identified in these various subclasses are reported in Tables 10-13.

The results of the combined LRMCC and LSCC correlation analysis are presented in a ratio correlation map in Figure 13. Essentially all parameters analyzed fall below the statistically significant threshold of 0.3 identified above. Other than a few parameters sensitive to UV-Vis slope (lower left of the ratio correlation map shown in Figure 13), no parameters exhibit statistically significant correlations with ilmenite abundance.

5 Discussion

While the spectra illustrated in Figures 3 and 5 show that ilmenite has dramatic and complex spectral properties, such an assessment is fundamentally qualitative. The results presented in Figure 8-10 represent an attempt to quantify these spectral properties by identifying spectral parameters most sensitive to the abundance of ilmenite in a basalt or basaltic soil. We employed an approach where all spectral ratios (at a specified wavelength interval of 0.025 μm or 25 nm) were regressed with the compositional or maturity parameter (ilmenite abundance or I_s/FeO , and a display scheme in which the results of all correlation analyses can be seen at once as a spectral ratio “map”, as demonstrated by Figure 7. The ratio correlation maps shown in Figures 8 – 10 are presented in two versions, as discussed in the Methods section. The discussion presented here focuses largely on the plots showing results for all parameters (upper plots in Figures 8 – 10). While some of the results discussed fall below the cutoff threshold and are absent from the lower plots in Figures 8-10, they do show relative trends in the strength of correlations, and thus are still useful indicators of the spectral effects of ilmenite on basalts. However, such results (parameters) should not be used to quantify or parameterize the abundance of ilmenite based on vis/NIR reflectance spectroscopy, as quantitatively, they are statistically insignificant.

5.1 LRMCC

The ratio correlation maps for ilmenite abundance vs. spectral ratios for the LRMCC basalt samples (Figure 8) appear quite simple, as most spectral parameters are either highly correlated or anti-correlated with ilmenite abundance (few parameters have correlation coefficients near 0). This simplicity is primarily a result of the relative

simplicity and uniformity of the basalt samples as well as the small number of samples; apart from ilmenite, few parameters vary between the samples (see the INMA results presented in Table 2). The simplicity of the correlation results and limited variation of the LRMCC samples are not surprising, because the LRMCC samples were chosen to be similar in composition and texture, as the primary goal of the LRMCC was to characterize the samples in detail and to generate high-quality mineral separates from the samples [Isaacson *et al.*, 2010], which is extremely difficult for finer-grained samples. Additionally, as the LRMCC samples effectively have only two ilmenite abundances, unless all spectral ratios have nearly the same value, the correlation coefficient will generally be either strongly positive or strongly negative due to the limited input dataset. As illustrated in Figure 5, mare basalt texture can vary widely, as can the composition of the basalts [e.g., Papike *et al.*, 1976; Neal and Taylor, 1992]. A more complete database of basalt textures and compositions would likely yield a more robust set of spectral parameters most uniquely sensitive to ilmenite over other properties of the samples.

Despite the limitations, we can make some observations based on Figure 8. First, the ratios in the UV and UV-Vis are highly correlated with ilmenite abundance, as expected based on previous efforts to map ilmenite based on the UV-Vis ratio (see discussion in Introduction). Second, ratios of wavelengths in the UV to wavelengths near 1.5 μm are highly correlated with ilmenite. This match is a corollary of the UV-Vis correlation, because wavelengths near 1.5 μm tend to be highly correlated with visible albedo in samples dominated by pyroxene absorptions, as 1.5 μm sits between the two major pyroxene ferrous absorption features. Ratios of wavelengths in the UV to the longest wavelengths covered in this map (2.6 μm) are anti-correlated with ilmenite

abundance. This observation reflects the long wavelength “upturn” observed in spectra of the ilmenites and ilmenite-rich samples (e.g. Figure 2, 6); as this upturn becomes more pronounced, ratios of UV wavelengths to long wavelengths will decrease. This anti-correlation becomes more prominent with numerators of $\sim 0.4\text{--}0.6\ \mu\text{m}$. The enhanced correlation relative to numerators farther into the UV is due to the small “upturn” in reflectance in ilmenite spectra in the UV. Note, however, that this upturn is not consistent among all ilmenite samples, and is likely dependent on grain size, texture, and composition. Ratios of wavelengths near $1.5\ \mu\text{m}$ to long wavelengths ($\sim 2.6\ \mu\text{m}$) are also anti-correlated with ilmenite abundance. This anti-correlation is again linked to the long-wavelength upturn caused by ilmenite.

Somewhat surprisingly, the correlation between parameters sensitive to the strength of the ferrous absorption features and ilmenite abundance is less pronounced than the correlation between parameters sensitive to continuum slope (i.e. “upturns” in reflectance) and ilmenite abundance. For example, ratios of wavelengths near $1\ \mu\text{m}$ to wavelengths near $1.5\ \mu\text{m}$ show only modest correlation with ilmenite abundance. The positive correlation is due to ilmenite causing the strength of the absorption to diminish, as these parameters are ratios of wavelengths within the absorption feature ($1\ \mu\text{m}$) to wavelengths outside of the absorption feature ($1.5\ \mu\text{m}$). The correlation is moderate for the standard Clementine UVVIS $750\ \text{nm} / 950\ \text{nm}$ ratio [e.g., *Lucey et al.*, 2000]. The correlation becomes stronger if the numerator wavelength is dropped to a lower value (e.g. $\sim 550\ \text{nm}$). This observation may be due to the additional weak, broad feature in the visible wavelength region observed in the ilmenite-rich samples (heavy black lines in Figure 6), also noted by Isaacson et al. [2010]. Strong correlations, however, are

observed between ratios of wavelengths near 1.2 μm and wavelengths near 1.55 μm . This correlation is likely due to the tendency of ilmenite to mute the rise in reflectance between the 1 and 2 μm pyroxene absorptions. The coarse-grained sample spectra plotted in Figure 6 demonstrate this effect, as the spectrum of ilmenite-poor 15058 spectrum rises to much higher reflectance values and has a much steeper local “slope” relative to the spectrum of ilmenite-rich 70017. The effect of ilmenite on the 2 μm pyroxene absorption is more difficult to isolate in the ratio correlation map than the effect on the 1 μm absorption. This difficulty is largely because ratios sensitive to the long-wavelength upturn are also those that would be sensitive to the strength of the 2 μm absorption. To first order, the long wavelength upturn produces similar effects on ratios as would a weakened 2 μm absorption, and is correlated with the same sign (i.e., ratios sensitive to these properties are anti-correlated with ilmenite abundance), as discussed above in the context of the long-wavelength upturn (ratios of $\sim 1.5 \mu\text{m}$ to $\sim 2.6 \mu\text{m}$).

The parameters most highly correlated with ilmenite abundance for the LRMCC spectra (Person correlation coefficient >0.99) are reported in Table 7. Most of these parameters are ratios of wavelengths near $\sim 1700 \text{ nm}$ to longer wavelengths. This observation suggests that for the LRMCC spectra, the dominant effect of ilmenite is the long-wavelength upturn.

5.2 LSCC

The ratio correlation maps for ilmenite and the LSCC spectra, illustrated in Figure 9, are significantly more complex, with more subtle structure, than the ratio correlation map for the LRMCC spectra. The most prominent difference between Figures 8 and 9 is the smaller abundance of parameters with correlation coefficients near ± 1 in Figure 9.

The smaller number of parameters with high correlation coefficients (positive or negative) reflects the complexity of lunar soils relative to lunar rocks, especially a compositionally and texturally similar suite such as that analyzed by the LRMCC. However, we can identify a number of parameters that show significant correlation with ilmenite abundance. Unsurprisingly, one of the most highly correlated parameters is a ratio of the UV ($\sim 0.4 \mu\text{m}$) to the visible ($0.6\text{-}0.7 \mu\text{m}$), most likely due to the tendency of ilmenite to “flatten” reflectance spectra across this wavelength region. A similar correlation is observed with ratios of wavelengths in the UV to wavelengths near $1.5 \mu\text{m}$. This correlation was also observed for the LRMCC samples, and is discussed above.

Unlike the LRMCC spectra, the LSCC spectra exhibit a positive correlation between ilmenite abundance and ratios between the UV and long wavelengths ($\sim 2.5 \mu\text{m}$). This positive correlation suggests that the effect of the long wavelength upturn observed in the LRMCC spectra is not observed dominantly in the LSCC spectra, and that the flattening of the spectrum in the UV is the dominant factor in these parameters rather than the long-wavelength upturn. The lack of a zone of enhanced correlation for numerators near $0.4\text{-}0.6 \mu\text{m}$ and denominators near $2.6 \mu\text{m}$ suggests that the UV “upturn” noted in the LRMCC spectra is not a factor in the LSCC spectra. Parameters sensitive to the long wavelength continuum slope of the spectra (e.g. $\sim 1.6 / \sim 2.1 \mu\text{m}$) do show anti-correlation with ilmenite abundance, as in the LRMCC spectra. However, the cause of this anti-correlation is likely due more to muting of the $2 \mu\text{m}$ absorption rather than the pronounced reflectance upturn noted in the LRMCC spectra. The reasoning for this conclusion is that the anti-correlation becomes less prominent as the denominator moves to longer wavelengths (up in the y dimension on the map, i.e. out of the $2 \mu\text{m}$ absorption).

As in the LRMCC spectra, a correlation between the slopes of the spectra just short of the reflectance high between the two pyroxene absorption features (e.g. $\sim 1.2 \mu\text{m}$ / $\sim 1.35 \mu\text{m}$) is positively correlated with ilmenite abundance.

The LSCC spectra exhibit prominent correlations between parameters sensitive to the strength of the $1 \mu\text{m}$ absorption feature and ilmenite abundance, which was less true for the LRMCC spectra. As discussed above, they also exhibit a fairly moderate anti-correlation between ilmenite abundance and the strength of the $2 \mu\text{m}$ absorption feature. The strength of the $1 \mu\text{m}$ absorption feature is captured by ratios of wavelengths near $0.9\text{--}1.0 \mu\text{m}$ to longer wavelengths ($\sim 1.1\text{--}1.5 \mu\text{m}$). The correlations between ilmenite abundance and parameters sensitive to the ferrous absorption band strength are stronger than the correlations observed with parameters sensitive to continuum slope (e.g. UV-Vis, UV-NIR ($\sim 1.5 \mu\text{m}$)). This is opposite to the results for the LRMCC spectra, in which parameters sensitive to continuum slope exhibited the highest correlation with ilmenite abundance. Both ilmenite abundance and soil maturity (I_s/FeO) influence the band strength and continuum properties of lunar sample spectra. These results suggest that in the case of lunar soils, ilmenite abundance is more highly correlated with the strength of the absorption features, whereas it is more correlated with continuum slope in the LRMCC spectra. In other words, sample maturity (I_s/FeO) appears to have a proportionally stronger effect on continuum slope relative to absorption feature strength for lunar soil spectra, as the correlation between ilmenite abundance and continuum slope parameters is weaker than the correlation between ilmenite abundance and band strength parameters, opposite to the results observed for the LRMCC spectra.

The ratio correlation maps for I_s/FeO for the soil spectra are illustrated in Figure 10. As expected, I_s/FeO is highly correlated with continuum slope, as exhibited most prominently by ratios in the UV-Vis to longer wavelengths (the prominent blue region on the left side of the ratio correlation map). I_s/FeO is also positively correlated with ratios sensitive to the strength of the 1 μm absorption feature, specifically those in which the numerator is in the absorption (e.g. $\sim 1 \mu\text{m}$) and the denominator is beyond the absorption (e.g. $\sim 1.2 \mu\text{m}$). The correlation with slope at wavelengths shorter than the reflectance high between the pyroxene absorptions ($\sim 1.6 \mu\text{m}$) is not observed, as the spectral effect of nanophase iron in this region is generally to impart a fairly linear continuum slope; it does not produce the pronounced wavelength-dependent “flattening” effects apparent in spectra of ilmenite-rich materials. A strong anti-correlation with I_s/FeO is observed for ratios of $\sim 1.5 \mu\text{m}$ to $\sim 1.6\text{-}1.7 \mu\text{m}$. This anti-correlation is likely linked to the strength of the 2 μm absorption feature, as was the case for the ilmenite correlation discussed above. The positive correlation between wavelengths near $\sim 2.4 \mu\text{m}$ and wavelengths closer to $2.6 \mu\text{m}$ is likely linked to the strength of the 2 μm absorption as well, as stronger 2 μm absorptions in less mature soils (lower I_s/FeO values) would lead to a steeper local continuum slope and lower values of these ratios, and thus a positive correlation with I_s/FeO .

For the LSCC spectra, many parameters are highly correlated with both ilmenite abundance and I_s/FeO . The most useful parameters for isolating the spectral effects of ilmenite, however, are those that are highly correlated with ilmenite abundance (correlation coefficients near ± 1) and neither correlated nor anti-correlated with I_s/FeO (correlation coefficients near 0). Figure 11 illustrates our method for selecting such

parameters. The construction of Figure 11 is described in the methods section. Briefly, Figure 11 plots the correlation coefficients for parameters and ilmenite abundance (Y) and parameters vs. I_s/FeO (X) on the two axes. Figure 11 can be thought of as a combination of Figures 9 and 10, in which the pixel values of each figure are plotted on one axis in Figure 11. The colors correspond to increasingly restrictive thresholds for the correlation coefficients of parameters vs. ilmenite abundance and parameters vs. I_s/FeO . The identified parameters for the two most restrictive subsets are reported in Tables 8 and 9. These parameters are those most highly correlated with ilmenite abundance while being relatively un-correlated with I_s/FeO , and thus are the parameters most useful for an empirical parameterization of ilmenite abundance based on reflectance spectra of lunar soils. Most of these parameters are sensitive largely to the strength of the 1 μm band, consistent with our observation that in the case of soil spectra, ilmenite abundance is more highly correlated with ferrous absorption band strength rather than continuum slope or a long-wavelength upturn as in the LRMCC spectra.

5.3 Comparison of LRMCC and LSCC results

Figures 8-10 represent fairly independent analyses of two suites of spectra. However, if one seeks to parameterize ilmenite based on reflectance spectra in a manner applicable to diverse lunar materials, it is important to identify parameters sensitive to ilmenite abundance in both rocks and soils. We do not attempt such a parameterization here, but as our analyses have identified the top parameters in the distinct datasets, the necessary data are compiled to perform a comparative analysis and identify those parameters most correlated with ilmenite (and not with I_s/FeO in the case of soils). The results of this comparison are presented in Figure 12, a scatterplot similar to the one

shown in Figure 11. However, unlike Figure 11, both axes in Figure 12 represent correlation coefficients with ilmenite. The two axes represent the two datasets. The parameters selected were identified by thresholds for correlation coefficients, as described in the Methods section. The parameters identified by the various subsets plotted in Figure 12 are reported in Tables 10-13. The parameters are largely ratios of wavelengths in the 1 μm ferrous absorption band to wavelengths near $\sim 1.5 \mu\text{m}$. This observation indicates that while the long wavelength upturn may be the dominant effect of ilmenite in the LRMCC spectra, the stronger correlation with ilmenite of parameters sensitive to the 1 μm absorption strength in the LSCC spectra dominates overall when the datasets are analyzed concurrently. Those parameters that are highly correlated with ilmenite (and not correlated with I_s/FeO for soil spectra) in both the LSCC spectra and the LRMCC spectra represent the most ideal parameters upon which to initiate attempts to develop a common ilmenite parameter.

The results presented in Figure 13 suggest that despite the identification of parameters highly correlated with ilmenite abundance common to both the LRMCC and LSCC datasets, analysis of rocks and soils with a single approach is an extreme challenge. When they are grouped into a common analysis in which parameters are calculated on a common “scale”, as is done in Figure 13, the fundamental differences between rocks and soils become apparent. While it is not a new conclusion to suggest that rocks and soils cannot be grouped in this way for spectroscopic analysis, these results suggest that extreme caution must be used in applying the optimized parameters to the detection and mapping of ilmenite with remotely-sensed lunar reflectance spectroscopy data. Figure 13 shows that rocks and soils likely will require unique approaches to

determining ilmenite abundance with reflectance spectra, and that a single parameterization suitable and accurate for both rocks and soils will be difficult (if not impossible) to define.

6 Conclusions

We have conducted a systematic analysis of the statistical correlation between spectral ratios (spectral parameters) and ilmenite abundance in a suite of lunar sample spectra, both immature (mare basalts) and mature (mare soils). The compositions of these samples span a range of ilmenite contents, both for soils and basalts. We have identified those parameters most highly correlated with ilmenite abundance for both sample suites. In the course of our analysis of the soil spectra, we have identified parameters correlated with ilmenite abundance and not with I_s/FeO (maturity) by performing a similar correlation analysis between spectral parameters and I_s/FeO . We have also performed a comparative analysis of the results of the independent examinations of the LRMCC (basalts) and LSCC (soils) spectra. By defining thresholds for both sample suites, we have identified a set of parameters highly correlated with ilmenite abundance in both sample suites, the size of which varies with the threshold criteria applied. These results represent a quantification of the effect of ilmenite on spectra of lunar samples as represented by our input dataset. While the general effects can be seen visually in reflectance spectra for immature, ilmenite-rich materials (e.g. Figure 6), our work has quantified the effect by identifying which parameters are most highly affected by ilmenite abundance, if we assume that the correlation between parameters and ilmenite abundance is largely a product of ilmenite abundance. The parameters identified by our work will be particularly useful in analysis of spectra in

which the spectral effects of ilmenite are less obvious than in the examples shown in Figure 6, both in the case of immature materials with less abundant ilmenite and especially in the case of lunar soils, in which few spectral effects are obvious through visual analysis of reflectance spectra. However, we have also demonstrated that lunar rocks and soils have fundamentally different spectral reflectance properties, and that they likely will need to be analyzed separately; a single parameterization of ilmenite abundance based on our results that is applicable to both rocks and soils will be extremely difficult (if not impossible) to formulate.

Our results are limited, however, by the input data. The LRMCC and LSCC sample suites were carefully selected based on a set of criteria relevant to the particular project. In the case of the LSCC, one of the major goals was to establish a well-characterized suite of soil samples spanning a range of maturities for the various major compositional suites (e.g. TiO_2 content for basaltic soils). The LRMCC samples were selected for their coarse-grained texture and to be representative of low-Ti and high-Ti samples. Neither suite was selected specifically for the purpose of quantifying the effect of ilmenite on reflectance spectra. In both cases, the diversity of the input data limits the conclusions we can draw. A more ideal sample suite would include, for soils, a range of ilmenite abundances at each maturity level. In the case of the basalts, a suite in which sample texture and composition (both ilmenite abundance and abundance of other mineral components) were more varied would improve the robustness of our conclusions, as it would enable us to identify more reliably those parameters that are most highly correlated with ilmenite abundance. Our analysis of the LRMCC spectra confirms that in the case of texturally and compositionally homogeneous (apart from ilmenite abundance)

samples, many spectral parameters are highly correlated with ilmenite. A more diverse sample suite would enable the isolation of those parameters that truly capture the effect of ilmenite abundance. However, despite the limitations of the available data for such studies, we have quantitatively characterized the complex effects of ilmenite on reflectance spectra of lunar materials, as well as identified a series of spectral parameters that would be most suitable for potential parameterization of ilmenite abundance from reflectance spectra.

7 References

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Table 1. Modal abundance data for LRMCC samples from Isaacson et al. [2010]

Phase	15058	15555	70017	70035
Olivine	0.1	11.8	1.5	1.2
Orthopyroxene	3.7	0.3	0.0	0.0
Pigeonite	25.6	32.4	17.7	20.2
Augite	16.7	18.6	34.2	27.7
Fe-pyroxene	17.1	5.4	0.6	1.1
Plagioclase	30.1	27.3	25.7	30.1
Tridymite	3.5	0.8	1.6	0.9
Ilmenite	1.4	1.3	17.3	17.4
Chromite	tr.	0.4	0.0	0.0
Ulvöspinel	0.9	1.0	0.3	0.3
Armalcolite	0.0	0.0	0.1	0.1
Rutile	0.0	0.0	tr.	0.0
Troilite/Metal	0.2	0.2	0.3	0.4
K-rich glass	0.5	0.4	0.6	0.6
Phosphates	0.1	0.1	0.1	tr.
Total	99.9	100.0	100.0	100.0
Total No Ilmenite	98.5	98.7	82.7	82.6
Scale Factor	1.02	1.01	1.21	1.21

Table 2. Ilmenite-normalized modal abundance (INMA) data for LRMCC samples

Phase	15058	15555	70017	70035
Olivine	0.1	12.0	1.8	1.5
Orthopyroxene	3.8	0.3	0.0	0.0
Pigeonite	26.0	32.8	21.4	24.5
Augite	17.0	18.8	41.4	33.5
Fe-pyroxene	17.4	5.5	0.7	1.3
Plagioclase	30.6	27.7	31.1	36.4
Tridymite	3.6	0.8	1.9	1.1
Ilmenite	0.0	0.0	0.0	0.0
Chromite	tr.	0.4	0.0	0.0
Ulvöspinel	0.9	1.0	0.4	0.4
Armalcolite	0.0	0.0	0.1	0.1
Rutile	0.0	0.0	tr.	0.0
Troilite/Metal	0.2	0.2	0.4	0.5
K-rich glass	0.5	0.4	0.7	0.7
Phosphates	0.1	0.1	0.1	tr.
Total	100.0	100.0	100.0	100.0
Total Pyroxene, INMA	64.1	57.4	63.5	59.3
Total OPX+Pig., INMA	29.7	33.1	21.4	24.5
Total Augite + Fe-Px, INMA	34.3	24.3	42.1	34.9

Table 3. Modal abundance data for low-Ti LSCC samples from Taylor et al. [2001]

	12030			12001			15071			15041		
	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm
Ilmenite	2.6	3.2	3	2.6	1.8	1.6	1.9	1.8	1.2	1.2	0.8	0.7
Plagioclase	15.3	14	18	13.4	13.9	15.6	18.1	19.4	19.8	15.5	16.2	18
Pyroxene	33.8	21.4	15.3	19.9	17.9	13.5	22.1	16.7	10.9	22.5	17	5.3
Olivine	4.3	3.7	2.5	3.4	4.2	2.2	3.9	2.8	1.9	3.3	2.4	0.6
Agglutinitic Glass	39.4	49.8	55	56.2	56.8	61.9	47.6	49.2	59.7	51.3	56.7	70.4
Volcanic Glass	1.2	1.5	1.6	1.5	1.3	1.9	4	4.1	3.6	2.3	2.6	1.9
Others	3.4	6.4	4.6	3	3.8	3.3	2.4	6	2.9	3.9	4.3	3.2
Total	100	100	100	100	100	100	100	100	100	100	100	100
Is/FeO	12	17	32	51	67	115	49	80	159	66	92	161
Total No Ilmenite	97.4	96.8	97	97.4	98.2	98.4	98.1	98.2	98.8	98.8	99.2	99.3
Scale Factor	1.027	1.033	1.031	1.027	1.018	1.016	1.019	1.018	1.012	1.012	1.008	1.007

Table 4. INMA data for low-Ti LSCC samples

	12030			12001			15071			15041		
	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm
Ilmenite	0	0	0	0	0	0	0	0	0	0	0	0
Plagioclase	15.7	14.5	18.6	13.8	14.2	15.9	18.5	19.8	20.0	15.7	16.3	18.1
Pyroxene	34.7	22.1	15.8	20.4	18.3	13.7	22.5	17.0	11.0	22.8	17.1	5.3
Olivine	4.4	3.8	2.6	3.5	4.3	2.2	4.0	2.9	1.9	3.3	2.4	0.6
Agglutinitic Glass	40.5	51.4	56.7	57.7	58.0	62.9	48.5	50.1	60.4	51.9	57.2	70.8
Volcanic Glass	1.2	1.5	1.6	1.5	1.3	1.9	4.1	4.2	3.6	2.3	2.6	1.9
Others	3.5	6.6	4.7	3.1	3.9	3.4	2.4	6.1	2.9	3.9	4.3	3.2
Total	100	100	100	100	100	100	100	100	100	100	100	100
Is/FeO	12	17	32	51	67	115	49	80	159	66	92	161

Table 5. Modal abundance data for high-Ti LSCC samples from Taylor et al. [2001]

	10084			71061			71501			70181			79221		
	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm
Ilmenite	6.4	5.2	5	10.4	9.7	7.6	12.3	9.7	7.6	8.9	6.7	3.4	7.3	6	5.2
Plagioclase	16.8	17.1	17.4	13.9	15.2	18.1	16.5	19.8	20	16.9	18.3	18.5	16.9	16	18.6
Pyroxene	16	12.2	8.4	20.8	12.5	8.3	21.3	13.7	8.8	15.7	8.5	4.6	13.5	9.7	3.6
Olivine	1.4	1.1	0.9	3.9	4.5	3.8	3.6	3.4	3.2	3.6	3.8	3.2	4.8	3.4	2.2
Agglutinitic Glass	53.9	57	62.6	31.4	37.9	45.4	38.3	44.8	53.1	43.4	51.7	58.3	46.5	54.3	61.5
Volcanic Glass	3.4	2.9	3.7	18.9	18.8	15.7	6.7	7.5	5.9	10.1	9.2	10.3	10.9	9.2	8
Others	2.1	4.5	2	0.7	1.3	1.1	1.3	1.1	1.5	1.3	1.8	1.7	0.1	1.4	0.8
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Is/FeO	67	87	145	9	14	28	28	50	88	53	63	104	57	78	169
Total No Ilmenite	93.6	94.8	95	89.6	90.3	92.4	87.7	90.3	92.4	91.1	93.3	96.6	92.7	94	94.8
Scale Factor	1.068	1.055	1.053	1.116	1.107	1.082	1.140	1.107	1.082	1.098	1.072	1.035	1.079	1.064	1.055

Table 6. INMA data for high-Ti LSCC samples

	10084			71061			71501			70181			79221		
	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm	20-45 μm	10-20 μm	<10 μm
Ilmenite	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Plagioclase	17.9	18.0	18.3	15.5	16.9	19.6	18.8	21.9	21.6	18.6	19.6	19.2	18.2	17.0	19.6
Pyroxene	17.1	12.9	8.8	23.2	13.9	9.0	24.3	15.2	9.5	17.3	9.1	4.8	14.6	10.3	3.8
Olivine	1.5	1.2	0.9	4.4	5.0	4.1	4.1	3.8	3.5	4.0	4.1	3.3	5.2	3.6	2.3
Agglutinitic Glass	57.6	60.1	65.9	35.0	42.0	49.1	43.7	49.6	57.4	47.7	55.4	60.4	50.2	57.8	64.9
Volcanic Glass	3.6	3.1	3.9	21.1	20.8	17.0	7.6	8.3	6.4	11.1	9.9	10.7	11.8	9.8	8.4
Others	2.2	4.7	2.1	0.8	1.4	1.2	1.5	1.2	1.6	1.4	1.9	1.8	0.1	1.5	0.8
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Is/FeO	67	87	145	9	14	28	28	50	88	53	63	104	57	78	169

Table 7. Optimized parameters for LRMCC spectra (Pearson coefficient for ilmenite correlation > 0.99)

Parameter	LRMCC Ilmenite Pearson	LSCC Ilmenite Spearman	LSCC I _s /FeO Spearman
1700 / 2475	0.9963	0.3581	0.1780
1650 / 2525	0.9963	0.3474	0.1231
1675 / 2500	0.9958	0.2951	0.1249
1650 / 2550	0.9956	0.3058	0.1163
1675 / 2525	0.9955	0.3697	0.1640
1625 / 2550	0.9955	0.3281	0.1221
1700 / 2450	0.9955	0.3281	0.1685
1600 / 2600	0.9953	0.3492	0.1716
1725 / 2425	0.9953	0.3037	0.2107
1675 / 2475	0.9953	0.2869	0.1154
1650 / 2500	0.9953	0.2863	0.1063
1725 / 2450	0.9951	0.3318	0.2247
1750 / 2400	0.9948	0.3013	0.1869
1750 / 2425	0.9948	0.2505	0.2009
1600 / 2575	0.9947	0.3798	0.1505
1700 / 2500	0.9946	0.3397	0.2073
1625 / 2525	0.9946	0.3288	0.1127
1625 / 2600	0.9945	0.3602	0.1884
1600 / 2550	0.9945	0.3281	0.1240
1625 / 2575	0.9944	0.3724	0.1530
1575 / 2600	0.9943	0.3660	0.1673
1725 / 2475	0.9942	0.3266	0.2171
1775 / 2350	0.9941	0.2799	0.1017
1700 / 2425	0.9940	0.3116	0.1786
1750 / 2375	0.9940	0.2857	0.0779
1775 / 2375	0.9939	0.2716	0.1224
1725 / 2400	0.9937	0.3349	0.1508
1575 / 2575	0.9935	0.3792	0.1466
1650 / 2475	0.9932	0.3376	0.1081
1650 / 2575	0.9931	0.3749	0.1585
1750 / 2350	0.9931	0.3006	0.0284
1775 / 2400	0.9930	0.2887	0.2272
1675 / 2450	0.9928	0.2939	0.1108
1800 / 2350	0.9928	0.2741	0.1698
1825 / 2300	0.9928	0.2200	0.1005
1800 / 2325	0.9927	0.3028	0.1624
1650 / 2600	0.9926	0.3669	0.2250
1800 / 2300	0.9926	0.3098	0.1002
1675 / 2550	0.9925	0.3721	0.2058
1700 / 2525	0.9924	0.3938	0.2070
1625 / 2500	0.9924	0.2722	0.1002

1575 / 2550	0.9923	0.3046	0.1179
1775 / 2325	0.9923	0.3031	0.1096
1750 / 2450	0.9923	0.2734	0.2244
1825 / 2275	0.9922	0.2371	0.0195
1600 / 2525	0.9920	0.3379	0.1188
1550 / 2600	0.9919	0.3379	0.1444
1825 / 2250	0.9918	0.2310	0.0302
1775 / 2425	0.9913	0.2686	0.2501
1700 / 2400	0.9912	0.3364	0.1111
1725 / 2375	0.9911	0.3138	0.0821
1800 / 2375	0.9911	0.2793	0.2125
1800 / 2275	0.9910	0.3584	0.0247
1825 / 2325	0.9909	0.2185	0.1780
1550 / 2575	0.9908	0.3288	0.1142
1775 / 2300	0.9906	0.2918	0.0360
1825 / 2225	0.9904	0.3239	0.0021
1750 / 2325	0.9903	0.3138	0.0711
1850 / 2225	0.9900	0.2573	0.0079
1850 / 2250	0.9900	0.1470	0.0580

Table 8. Optimized parameters for LSCC Spectra, Spearman coefficient (ilmenite correlation > 0.6, Is/FeO correlation <0.4)

Parameter	Ilmenite Correlation	I _s /FeO Correlation	Difference
925 / 1050	0.814	0.235	0.579
950 / 1000	0.811	0.330	0.481
950 / 1025	0.800	0.167	0.632
875 / 1225	0.768	0.395	0.374
975 / 1000	0.767	0.193	0.574
925 / 1075	0.765	0.133	0.632
900 / 1100	0.756	0.222	0.535
875 / 1350	0.751	0.386	0.364
875 / 1375	0.749	0.384	0.365
875 / 1325	0.747	0.397	0.350
950 / 1050	0.727	0.042	0.685
875 / 1400	0.718	0.370	0.348
875 / 1500	0.709	0.373	0.336
975 / 1025	0.708	0.050	0.658
900 / 1125	0.708	0.165	0.542
875 / 1525	0.704	0.362	0.341
875 / 1425	0.701	0.333	0.368
875 / 1450	0.699	0.348	0.351
1225 / 1325	0.690	0.369	0.322
900 / 1375	0.689	0.161	0.529
875 / 1475	0.689	0.337	0.351
1200 / 1325	0.687	0.362	0.325
900 / 1275	0.675	0.143	0.532
900 / 1350	0.674	0.147	0.527
900 / 1325	0.667	0.132	0.536
900 / 1300	0.661	0.127	0.534
900 / 1500	0.661	0.154	0.507
900 / 1675	0.657	0.323	0.334
350 / 600	0.657	0.394	0.262
900 / 1250	0.651	0.122	0.529
950 / 1075	0.650	0.113	0.537
900 / 1700	0.649	0.383	0.266
900 / 1550	0.647	0.170	0.477
900 / 1650	0.646	0.260	0.386
900 / 1400	0.643	0.120	0.523
350 / 575	0.643	0.348	0.295
900 / 1625	0.642	0.231	0.411
1200 / 1300	0.641	0.395	0.246
1200 / 1350	0.640	0.341	0.299
350 / 550	0.639	0.340	0.299
900 / 1575	0.639	0.175	0.465
400 / 425	0.639	0.352	0.286

1250 / 1275	0.639	0.252	0.386
1200 / 1375	0.637	0.330	0.308
1175 / 1325	0.637	0.335	0.302
1150 / 1325	0.635	0.284	0.351
900 / 1525	0.635	0.126	0.509
1175 / 1350	0.634	0.343	0.291
1175 / 1275	0.633	0.375	0.259
1250 / 1325	0.632	0.229	0.403
900 / 1150	0.631	0.042	0.589
900 / 1450	0.629	0.089	0.540
925 / 1100	0.626	0.047	0.579
900 / 1225	0.625	0.085	0.541
1175 / 1375	0.625	0.304	0.321
1225 / 1350	0.623	0.319	0.304
900 / 1425	0.623	0.086	0.537
1225 / 1375	0.619	0.274	0.345
900 / 1600	0.617	0.179	0.438
900 / 1175	0.617	0.038	0.578
900 / 1475	0.613	0.093	0.520
1250 / 1300	0.611	0.270	0.341
900 / 1200	0.610	0.060	0.551
1950 / 2000	0.607	0.034	0.574
375 / 450	0.605	0.364	0.241
350 / 525	0.600	0.290	0.310

Table 9. Optimized parameters for LSCC Spectra, Spearman coefficient (ilmenite correlation > 0.7, Is/FeO correlation <0.3)

Parameter	Ilmenite Correlation	I _s /FeO Correlation	Difference
925 / 1050	0.814	0.235	0.579
950 / 1025	0.800	0.167	0.632
975 / 1000	0.767	0.193	0.574
925 / 1075	0.765	0.133	0.632
900 / 1100	0.756	0.222	0.535
950 / 1050	0.727	0.042	0.685
975 / 1025	0.708	0.050	0.658
900 / 1125	0.708	0.165	0.542

Table 10. Optimized parameters for LRMCC and LSCC spectra (LRMCC Ilmenite correlation > 0.5, LSCC Ilmenite correlation > 0.5, LSCC Is/FeO correlation < 0.5)

Parameter	LRMCC Ilmenite Pearson	LSCC Ilmenite Spearman	LSCC Is/FeO Spearman
1950 / 2000	0.9854	0.6074	0.0336
1950 / 1975	0.9732	0.5527	0.0275
350 / 475	0.9724	0.5157	0.1893
1800 / 2100	0.9715	0.5032	0.1301
350 / 500	0.9692	0.5631	0.2302
1800 / 2075	0.9667	0.5145	0.1285
2025 / 2050	0.9653	0.5710	0.0763
375 / 425	0.9632	0.5347	0.2315
2025 / 2075	0.9626	0.5573	0.1408
375 / 450	0.9588	0.6049	0.3640
1725 / 2150	0.9586	0.5057	0.1340
1775 / 2075	0.9582	0.5047	0.1450
350 / 525	0.9551	0.6004	0.2904
1725 / 2125	0.9549	0.5005	0.1472
1750 / 2075	0.9520	0.5286	0.1640
1700 / 2150	0.9507	0.5047	0.1606
1725 / 2100	0.9483	0.5133	0.2089
1700 / 2125	0.9466	0.5063	0.1661
375 / 475	0.9453	0.6493	0.4827
350 / 550	0.9453	0.6395	0.3405
1725 / 2075	0.9419	0.5215	0.1954
1700 / 2100	0.9398	0.5316	0.1820
1800 / 1975	0.9375	0.5185	0.2348
350 / 800	0.9323	0.5414	0.4889
400 / 425	0.9311	0.6386	0.3521
350 / 575	0.9297	0.6428	0.3478
350 / 600	0.9217	0.6566	0.3942
1800 / 1925	0.9181	0.5194	0.2366
350 / 625	0.9135	0.6627	0.4281
350 / 650	0.9079	0.6554	0.4586
1225 / 1575	0.9000	0.5252	0.3783
350 / 675	0.8970	0.6538	0.4415
350 / 775	0.8913	0.5466	0.4470
1200 / 1600	0.8911	0.5102	0.3979
1200 / 1575	0.8901	0.5212	0.3582
1225 / 1525	0.8886	0.5273	0.2629
350 / 700	0.8867	0.6379	0.4467
1200 / 1550	0.8828	0.5225	0.3490
1225 / 1500	0.8822	0.5292	0.2318
1800 / 1850	0.8790	0.5545	0.2217
350 / 725	0.8755	0.6040	0.4318

350 / 750	0.8732	0.5995	0.4440
1200 / 1525	0.8732	0.5350	0.2605
1175 / 1550	0.8701	0.5188	0.3289
1200 / 1500	0.8653	0.5518	0.2849
1175 / 1525	0.8595	0.5316	0.2889
1200 / 1475	0.8538	0.5179	0.2299
1175 / 1500	0.8508	0.5496	0.2864
1800 / 1825	0.8466	0.5209	0.2461
1225 / 1425	0.8450	0.5087	0.2198
1200 / 1450	0.8412	0.5377	0.2290
1175 / 1475	0.8384	0.5304	0.2473
1275 / 1375	0.8307	0.5237	0.1206
1225 / 1400	0.8300	0.5438	0.2672
1175 / 1450	0.8253	0.5273	0.2357
1150 / 1500	0.8249	0.5163	0.2269
1200 / 1425	0.8231	0.5307	0.2531
1225 / 1375	0.8159	0.6190	0.2742
1250 / 1375	0.8133	0.5765	0.1643
1225 / 1350	0.8096	0.6230	0.3194
1275 / 1325	0.8084	0.5558	0.1380
1175 / 1425	0.8072	0.5277	0.2516
1250 / 1350	0.8062	0.5998	0.1976
1200 / 1400	0.8053	0.5521	0.2660
950 / 1725	0.7963	0.5005	0.0382
950 / 1700	0.7944	0.5066	0.0101
1225 / 1325	0.7919	0.6902	0.3685
925 / 1725	0.7900	0.5857	0.1921
925 / 1750	0.7893	0.5854	0.2385
925 / 1700	0.7892	0.5857	0.1340
1175 / 1400	0.7888	0.5383	0.2794
1225 / 1300	0.7884	0.6422	0.4745
1200 / 1375	0.7881	0.6373	0.3298
1725 / 1750	0.7864	0.5053	0.2186
1250 / 1325	0.7839	0.6318	0.2287
900 / 1700	0.7834	0.6486	0.3829
925 / 1675	0.7828	0.5955	0.1105
900 / 1725	0.7823	0.6104	0.4272
925 / 1650	0.7808	0.5429	0.0315
1150 / 1425	0.7801	0.5011	0.2101
925 / 1775	0.7796	0.5490	0.3032
900 / 1750	0.7795	0.5967	0.4586
900 / 1675	0.7775	0.6569	0.3234
1250 / 1300	0.7769	0.6114	0.2702
1200 / 1350	0.7767	0.6401	0.3411
900 / 1650	0.7760	0.6459	0.2598

925 / 1625	0.7760	0.5512	0.0296
925 / 1800	0.7742	0.5332	0.3359
900 / 1625	0.7716	0.6419	0.2305
1175 / 1375	0.7714	0.6245	0.3038
1225 / 1275	0.7693	0.6548	0.4919
925 / 1600	0.7662	0.5408	0.0073
875 / 1650	0.7660	0.6257	0.4852
900 / 1775	0.7645	0.5671	0.4751
875 / 1625	0.7628	0.6312	0.4583
1150 / 1400	0.7612	0.5280	0.2431
925 / 1575	0.7611	0.5472	0.0064
900 / 1600	0.7610	0.6172	0.1789
1175 / 1350	0.7586	0.6343	0.3432
925 / 1825	0.7575	0.5121	0.3768
900 / 1575	0.7553	0.6395	0.1750
1200 / 1325	0.7542	0.6865	0.3618
900 / 1800	0.7531	0.5429	0.4797
875 / 1600	0.7512	0.6535	0.4510
925 / 1550	0.7509	0.5356	0.0140
875 / 1575	0.7450	0.6884	0.4156
900 / 1550	0.7441	0.6474	0.1704
1150 / 1375	0.7434	0.5970	0.2754
925 / 1525	0.7413	0.5399	0.0159
1200 / 1300	0.7407	0.6407	0.3945
1175 / 1325	0.7366	0.6370	0.3347
900 / 1525	0.7335	0.6346	0.1258
1250 / 1275	0.7333	0.6386	0.2522
875 / 1550	0.7323	0.6902	0.4000
925 / 1500	0.7320	0.5307	0.0342
1150 / 1350	0.7293	0.5836	0.2608
900 / 1825	0.7241	0.5500	0.4950
900 / 1500	0.7227	0.6606	0.1539
1175 / 1300	0.7219	0.6431	0.4003
875 / 1525	0.7197	0.7036	0.3624
1125 / 1375	0.7138	0.5108	0.1325
1200 / 1275	0.7117	0.6746	0.4122
900 / 1475	0.7093	0.6129	0.0928
1150 / 1325	0.7080	0.6349	0.2840
875 / 1500	0.7065	0.7088	0.3725
1175 / 1275	0.6970	0.6334	0.3747
900 / 1450	0.6951	0.6291	0.0892
925 / 1425	0.6942	0.5011	0.0769
1150 / 1300	0.6928	0.5787	0.3105
875 / 1475	0.6899	0.6887	0.3374
1125 / 1325	0.6804	0.5225	0.1594

900 / 1425	0.6788	0.6230	0.0861
925 / 1400	0.6783	0.5093	0.0629
1175 / 1250	0.6777	0.5506	0.4351
875 / 1450	0.6717	0.6987	0.3481
1150 / 1275	0.6710	0.5863	0.3008
925 / 1375	0.6644	0.5390	0.0605
900 / 1400	0.6600	0.6434	0.1203
900 / 1850	0.6597	0.5420	0.4904
925 / 1350	0.6532	0.5356	0.0403
875 / 1425	0.6505	0.7006	0.3328
900 / 1375	0.6433	0.6893	0.1606
925 / 1325	0.6399	0.5362	0.0550
900 / 1350	0.6293	0.6743	0.1472
925 / 1300	0.6292	0.5448	0.0385
875 / 1400	0.6258	0.7180	0.3698
1000 / 1025	0.6223	0.5579	0.1447
925 / 1275	0.6183	0.5335	0.0586
900 / 1325	0.6125	0.6673	0.1316
925 / 1250	0.6089	0.5231	0.0650
950 / 1100	0.6060	0.5102	0.2516
875 / 1375	0.6029	0.7489	0.3835
900 / 1300	0.5984	0.6615	0.1273
900 / 1275	0.5838	0.6749	0.1429
875 / 1350	0.5824	0.7507	0.3863
925 / 1150	0.5764	0.5072	0.1649
900 / 1875	0.5727	0.5374	0.4855
900 / 1250	0.5703	0.6508	0.1215
925 / 1125	0.5636	0.5435	0.1444
875 / 1325	0.5575	0.7467	0.3969
900 / 1225	0.5544	0.6254	0.0846
975 / 1050	0.5496	0.5796	0.1331
900 / 1200	0.5481	0.6104	0.0595
950 / 1075	0.5413	0.6505	0.1130
875 / 1300	0.5351	0.7342	0.4339
900 / 1175	0.5300	0.6166	0.0382
925 / 1100	0.5193	0.6263	0.0470
875 / 1275	0.5112	0.7666	0.4574
900 / 1150	0.5017	0.6309	0.0415

Table 11. Optimized parameters for LRMCC and LSCC spectra (LRMCC Ilmenite correlation > 0.6, LSCC Ilmenite correlation > 0.5, LSCC Is/FeO correlation < 0.4)

Parameter	LRMCC Ilmenite Pearson	LSCC Ilmenite Spearman	LSCC Is/FeO Spearman
1950 / 2000	0.9854	0.6074	0.0336
1950 / 1975	0.9732	0.5527	0.0275
350 / 475	0.9724	0.5157	0.1893
1800 / 2100	0.9715	0.5032	0.1301
350 / 500	0.9692	0.5631	0.2302
1800 / 2075	0.9667	0.5145	0.1285
2025 / 2050	0.9653	0.5710	0.0763
375 / 425	0.9632	0.5347	0.2315
2025 / 2075	0.9626	0.5573	0.1408
375 / 450	0.9588	0.6049	0.3640
1725 / 2150	0.9586	0.5057	0.1340
1775 / 2075	0.9582	0.5047	0.1450
350 / 525	0.9551	0.6004	0.2904
1725 / 2125	0.9549	0.5005	0.1472
1750 / 2075	0.9520	0.5286	0.1640
1700 / 2150	0.9507	0.5047	0.1606
1725 / 2100	0.9483	0.5133	0.2089
1700 / 2125	0.9466	0.5063	0.1661
350 / 550	0.9453	0.6395	0.3405
1725 / 2075	0.9419	0.5215	0.1954
1700 / 2100	0.9398	0.5316	0.1820
1800 / 1975	0.9375	0.5185	0.2348
400 / 425	0.9311	0.6386	0.3521
350 / 575	0.9297	0.6428	0.3478
350 / 600	0.9217	0.6566	0.3942
1800 / 1925	0.9181	0.5194	0.2366
1225 / 1575	0.9000	0.5252	0.3783
1200 / 1600	0.8911	0.5102	0.3979
1200 / 1575	0.8901	0.5212	0.3582
1225 / 1525	0.8886	0.5273	0.2629
1200 / 1550	0.8828	0.5225	0.3490
1225 / 1500	0.8822	0.5292	0.2318
1800 / 1850	0.8790	0.5545	0.2217
1200 / 1525	0.8732	0.5350	0.2605
1175 / 1550	0.8701	0.5188	0.3289
1200 / 1500	0.8653	0.5518	0.2849
1175 / 1525	0.8595	0.5316	0.2889
1200 / 1475	0.8538	0.5179	0.2299
1175 / 1500	0.8508	0.5496	0.2864
1800 / 1825	0.8466	0.5209	0.2461

1225 / 1425	0.8450	0.5087	0.2198
1200 / 1450	0.8412	0.5377	0.2290
1175 / 1475	0.8384	0.5304	0.2473
1275 / 1375	0.8307	0.5237	0.1206
1225 / 1400	0.8300	0.5438	0.2672
1175 / 1450	0.8253	0.5273	0.2357
1150 / 1500	0.8249	0.5163	0.2269
1200 / 1425	0.8231	0.5307	0.2531
1225 / 1375	0.8159	0.6190	0.2742
1250 / 1375	0.8133	0.5765	0.1643
1225 / 1350	0.8096	0.6230	0.3194
1275 / 1325	0.8084	0.5558	0.1380
1175 / 1425	0.8072	0.5277	0.2516
1250 / 1350	0.8062	0.5998	0.1976
1200 / 1400	0.8053	0.5521	0.2660
950 / 1725	0.7963	0.5005	0.0382
950 / 1700	0.7944	0.5066	0.0101
1225 / 1325	0.7919	0.6902	0.3685
925 / 1725	0.7900	0.5857	0.1921
925 / 1750	0.7893	0.5854	0.2385
925 / 1700	0.7892	0.5857	0.1340
1175 / 1400	0.7888	0.5383	0.2794
1200 / 1375	0.7881	0.6373	0.3298
1725 / 1750	0.7864	0.5053	0.2186
1250 / 1325	0.7839	0.6318	0.2287
900 / 1700	0.7834	0.6486	0.3829
925 / 1675	0.7828	0.5955	0.1105
925 / 1650	0.7808	0.5429	0.0315
1150 / 1425	0.7801	0.5011	0.2101
925 / 1775	0.7796	0.5490	0.3032
900 / 1675	0.7775	0.6569	0.3234
1250 / 1300	0.7769	0.6114	0.2702
1200 / 1350	0.7767	0.6401	0.3411
900 / 1650	0.7760	0.6459	0.2598
925 / 1625	0.7760	0.5512	0.0296
925 / 1800	0.7742	0.5332	0.3359
900 / 1625	0.7716	0.6419	0.2305
1175 / 1375	0.7714	0.6245	0.3038
925 / 1600	0.7662	0.5408	0.0073
1150 / 1400	0.7612	0.5280	0.2431
925 / 1575	0.7611	0.5472	0.0064
900 / 1600	0.7610	0.6172	0.1789
1175 / 1350	0.7586	0.6343	0.3432
925 / 1825	0.7575	0.5121	0.3768
900 / 1575	0.7553	0.6395	0.1750

1200 / 1325	0.7542	0.6865	0.3618
925 / 1550	0.7509	0.5356	0.0140
900 / 1550	0.7441	0.6474	0.1704
1150 / 1375	0.7434	0.5970	0.2754
925 / 1525	0.7413	0.5399	0.0159
1200 / 1300	0.7407	0.6407	0.3945
1175 / 1325	0.7366	0.6370	0.3347
900 / 1525	0.7335	0.6346	0.1258
1250 / 1275	0.7333	0.6386	0.2522
925 / 1500	0.7320	0.5307	0.0342
1150 / 1350	0.7293	0.5836	0.2608
900 / 1500	0.7227	0.6606	0.1539
875 / 1525	0.7197	0.7036	0.3624
1125 / 1375	0.7138	0.5108	0.1325
900 / 1475	0.7093	0.6129	0.0928
1150 / 1325	0.7080	0.6349	0.2840
875 / 1500	0.7065	0.7088	0.3725
1175 / 1275	0.6970	0.6334	0.3747
900 / 1450	0.6951	0.6291	0.0892
925 / 1425	0.6942	0.5011	0.0769
1150 / 1300	0.6928	0.5787	0.3105
875 / 1475	0.6899	0.6887	0.3374
1125 / 1325	0.6804	0.5225	0.1594
900 / 1425	0.6788	0.6230	0.0861
925 / 1400	0.6783	0.5093	0.0629
875 / 1450	0.6717	0.6987	0.3481
1150 / 1275	0.6710	0.5863	0.3008
925 / 1375	0.6644	0.5390	0.0605
900 / 1400	0.6600	0.6434	0.1203
925 / 1350	0.6532	0.5356	0.0403
875 / 1425	0.6505	0.7006	0.3328
900 / 1375	0.6433	0.6893	0.1606
925 / 1325	0.6399	0.5362	0.0550
900 / 1350	0.6293	0.6743	0.1472
925 / 1300	0.6292	0.5448	0.0385
875 / 1400	0.6258	0.7180	0.3698
1000 / 1025	0.6223	0.5579	0.1447
925 / 1275	0.6183	0.5335	0.0586
900 / 1325	0.6125	0.6673	0.1316
925 / 1250	0.6089	0.5231	0.0650
950 / 1100	0.6060	0.5102	0.2516
875 / 1375	0.6029	0.7489	0.3835

Table 12. Optimized parameters for LRMCC and LSCC spectra (LRMCC Ilmenite correlation > 0.6, LSCC Ilmenite correlation > 0.6, LSCC Is/FeO correlation < 0.4)

Parameter	LRMCC Ilmenite Pearson	LSCC Ilmenite Spearman	LSCC Is/FeO Spearman
1950 / 2000	0.9854	0.6074	0.0336
375 / 450	0.9588	0.6049	0.3640
350 / 525	0.9551	0.6004	0.2904
350 / 550	0.9453	0.6395	0.3405
400 / 425	0.9311	0.6386	0.3521
350 / 575	0.9297	0.6428	0.3478
350 / 600	0.9217	0.6566	0.3942
1225 / 1375	0.8159	0.6190	0.2742
1225 / 1350	0.8096	0.6230	0.3194
1225 / 1325	0.7919	0.6902	0.3685
1200 / 1375	0.7881	0.6373	0.3298
1250 / 1325	0.7839	0.6318	0.2287
900 / 1700	0.7834	0.6486	0.3829
900 / 1675	0.7775	0.6569	0.3234
1250 / 1300	0.7769	0.6114	0.2702
1200 / 1350	0.7767	0.6401	0.3411
900 / 1650	0.7760	0.6459	0.2598
900 / 1625	0.7716	0.6419	0.2305
1175 / 1375	0.7714	0.6245	0.3038
900 / 1600	0.7610	0.6172	0.1789
1175 / 1350	0.7586	0.6343	0.3432
900 / 1575	0.7553	0.6395	0.1750
1200 / 1325	0.7542	0.6865	0.3618
900 / 1550	0.7441	0.6474	0.1704
1200 / 1300	0.7407	0.6407	0.3945
1175 / 1325	0.7366	0.6370	0.3347
900 / 1525	0.7335	0.6346	0.1258
1250 / 1275	0.7333	0.6386	0.2522
900 / 1500	0.7227	0.6606	0.1539
875 / 1525	0.7197	0.7036	0.3624
900 / 1475	0.7093	0.6129	0.0928
1150 / 1325	0.7080	0.6349	0.2840
875 / 1500	0.7065	0.7088	0.3725
1175 / 1275	0.6970	0.6334	0.3747
900 / 1450	0.6951	0.6291	0.0892
875 / 1475	0.6899	0.6887	0.3374
900 / 1425	0.6788	0.6230	0.0861
875 / 1450	0.6717	0.6987	0.3481
900 / 1400	0.6600	0.6434	0.1203
875 / 1425	0.6505	0.7006	0.3328
900 / 1375	0.6433	0.6893	0.1606

900 / 1350	0.6293	0.6743	0.1472
875 / 1400	0.6258	0.7180	0.3698
900 / 1325	0.6125	0.6673	0.1316
875 / 1375	0.6029	0.7489	0.3835

Table 13. Optimized parameters for LRMCC and LSCC spectra (LRMCC Ilmenite correlation > 0.7, LSCC Ilmenite correlation > 0.6, LSCC Is/FeO correlation < 0.3)

Parameter	LRMCC Ilmenite Pearson	LSCC Ilmenite Spearman	LSCC Is/FeO Spearman
1950 / 2000	0.9854	0.6074	0.0336
1250 / 1325	0.7839	0.6318	0.2287
900 / 1625	0.7716	0.6419	0.2305
900 / 1600	0.7610	0.6172	0.1789
900 / 1575	0.7553	0.6395	0.1750
900 / 1550	0.7441	0.6474	0.1704
900 / 1525	0.7335	0.6346	0.1258
900 / 1500	0.7227	0.6606	0.1539
900 / 1475	0.7093	0.6129	0.0928

Figure Captions

Figure 1. Clementine UV-Vis ratio image for the Tranquilitatis/Southern Serenitatis region of the Moon. The image is a ratio of the 415 and 750 nm Clementine UVVIS bands. The high-Ti basalts of Tranquilitatis have high UV-Vis ratios. This is an example of the techniques traditionally used to map TiO_2 abundance across the lunar surface.

Figure 2. Selected spectra measured by the LRMCC [Isaacson *et al.*, 2010] used as input data for the present study. We have plotted the coarse and fine-particle separates measured by the LRMCC, but have only included bulk samples (and ilmenite separates for the high-Ti samples). Details on the samples and measurements are provided by Isaacson *et al.* [2010].

Figure 3. Example LSCC spectra used as inputs for the present study. We plot all size separates for three mature soil samples, with offsets as indicated. Note that the bulk samples ($<45\ \mu\text{m}$) were excluded from our analyses, as the LSCC reported modal abundance results only for the grain size separates [Taylor *et al.*, 2001].

Figure 4. Thin section image of mare basalt sample 70017,535 analyzed by Isaacson *et al.* [2010]. This image was acquired with cross-polarized transmitted light. Note the complex intergrowth of ilmenite with the large pyroxene grain, which exhibits sector zoning between augite and pigeonite.

Figure 5. Thin section images of the Apollo 17 very high titanium textural sequence identified by Papike *et al.* [1976]. The LRMCC samples (70017 & 70035) are the most coarse-grained of these samples, and represent only one endmember of the textural variability of mare basalt samples. The range of textures evident in even these example thin section images indicates that the LRMCC samples do not represent fully the range of scattering regimes possible in basalt samples, and thus conclusions about the range of possible effects of ilmenite on reflectance spectra of lunar rocks based on these samples will be limited. Note the variable scales of these images, as indicated by the scale bars, which have a constant width of 1 mm. The scanned thin section images were obtained from the digital petrographic thin section collection hosted by Arizona State University (<http://ser.sese.asu.edu/DPSC/>). The images used are: ap1703_12_02, ap1702_08_07, ap1704_09_01, ap1704_12_09, ap1704_09_14, ap1703_13_01, ap1702_01_01.

Figure 6. Selected spectra from Figure 2. The effects of ilmenite on reflectance spectra of basalts are more clearly visible when ilmenite-rich bulk samples (heavy black lines) are plotted on the same axes as ilmenite-poor bulk samples (heavy grey lines) along with spectra of ilmenite separates. The bulk samples (black and grey) are compositionally similar apart from ilmenite abundance, so the large-scale differences between the samples can be largely attributed to ilmenite, to first order. Note the weakened 1 and $2\ \mu\text{m}$ absorptions in the high-Ti bulk sample, and the distortion of the absorption features, particularly the $2\ \mu\text{m}$ absorption due to the long wavelength upturn caused by ilmenite.

Figure 7. Schematic illustration of the construction of ratio correlation maps (Figures 8-10). Each pixel in the map (denoted by squares in this figure) refers to the ratio of the wavelength on the x axis (numerator) to the ratio of the wavelength on the y axis (denominator). The pixel value is the correlation coefficient (Spearman/Pearson) between that particular parameter (ratio) and material property abundance for whichever input dataset is being analyzed (LRMCC ilmenite abundance in Figure 8, LSCC ilmenite abundance in Figure 9, LSCC I_s/FeO in Figure 10). Note that the maps are “symmetric”, as ratios on opposite sides of the diagonal are merely inverses.

Figure 8. Ratio correlation maps for spectral parameters vs. ilmenite abundance for the LRMCC spectra (both grain sizes). Pixel values are the Pearson correlation coefficient between spectral parameter and ilmenite abundance, mapped onto a color ramp between -1 and 1 as indicated by the color scale bar. The upper plot shows results for all parameters, while the lower plot shows the same results but with parameters whose correlation coefficients fall below the statistically significant threshold masked in grey.

Figure 9. Ratio correlation map for spectral parameters vs. ilmenite abundance for the LSCC spectra (excluding bulk samples i.e. $<45\ \mu\text{m}$). As in Figure 8, pixel values are the correlation coefficient mapped onto a -1 to 1 color ramp as indicated by the scale bar. The correlation coefficient used for the LSCC samples is the Spearman coefficient (see discussion in the text). As in Figure 8, the upper plot presents results for all parameters, while the lower plot masks out parameters with correlation coefficients falling below the statistically significant threshold.

Figure 10. Ratio correlation map for spectral parameters vs. maturity (I_s/FeO) for the LSCC spectra, again excluding bulk samples. Pixel values are the Spearman correlation coefficient, with the colors scaled between ± 1 as indicated by the scale bar. Again, the upper plot shows results for all parameters, while the lower plot masks out parameters whose correlation coefficient falls below the statistically significant threshold.

Figure 11. Scatterplot of correlation coefficients for parameters vs. ilmenite abundance (Y) and parameters vs. maturity (I_s/FeO) (X). This scatterplot illustrates the thresholding process used to select parameters that are highly correlated with ilmenite abundance and not with I_s/FeO . This figure plots the absolute value of the correlation coefficients, as the sign of the correlation is not important for our analyses. The various subsets identified correspond to increasingly restrictive thresholds. The legend text entries refer to the thresholds used for each correlation coefficient (in absolute value). Each succeeding subset is a subset of the previous subset. In other words, the red class is a subset of the orange class, which is a subset of the blue class, which is a subset of the “All” class.

Figure 12. Scatterplot of ilmenite correlation coefficients (absolute values) for LRMCC and LSCC samples. This illustrates graphically the thresholding process used to identify the parameters most highly correlated with ilmenite and not with I_s/FeO in both the LRMCC and the LSCC spectra. The legend entries refer to the thresholds applied, in the following order: minimum ilmenite correlation coefficient for LSCC, maximum I_s/FeO correlation coefficient for LSCC, minimum ilmenite correlation coefficient for LRMCC.

As in Figure 10, each succeeding subclass is a subset of previous subclasses. We do not show a third I_s/FeO axis on this plot, but it is one of the criteria used for selecting the parameters grouped into the various subclasses. The I_s/FeO criteria is why some parameters that fall in the upper right on this plot (high correlation coefficients with ilmenite in both sets of spectra) are not grouped into one of the subclasses; those parameters do not meet the maximum I_s/FeO threshold criterion.

Figure 13. Ratio correlation map for spectral parameters vs. ilmenite abundance for LRMCC and LSCC spectra (excluding bulk samples as in Figures 9 and 10) analyzed as a single input dataset. Pixel values represent the Spearman correlation coefficient mapped onto a -1 to 1 color ramp as indicated by the scale bar. The low values (both positive and negative) of the correlation coefficients reflect the fundamental differences between lunar rocks and soils.

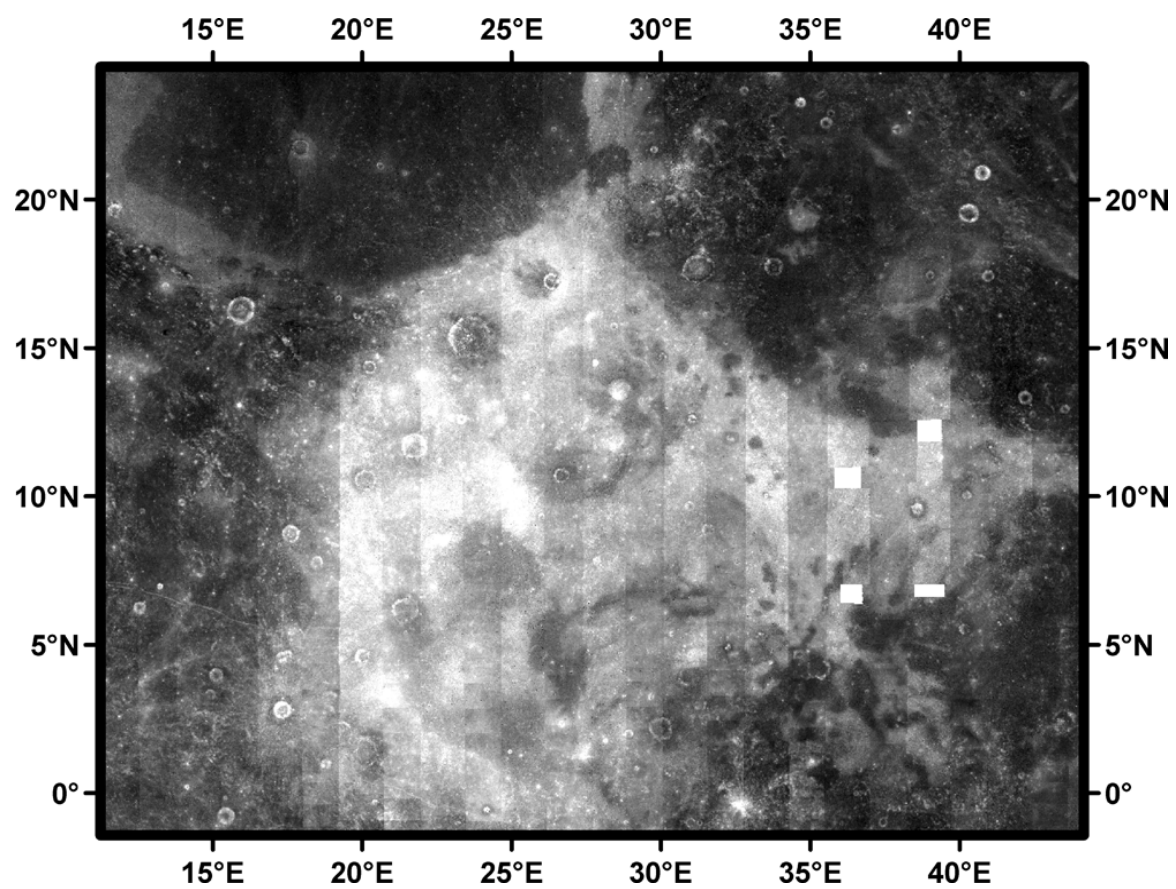


Figure 1.

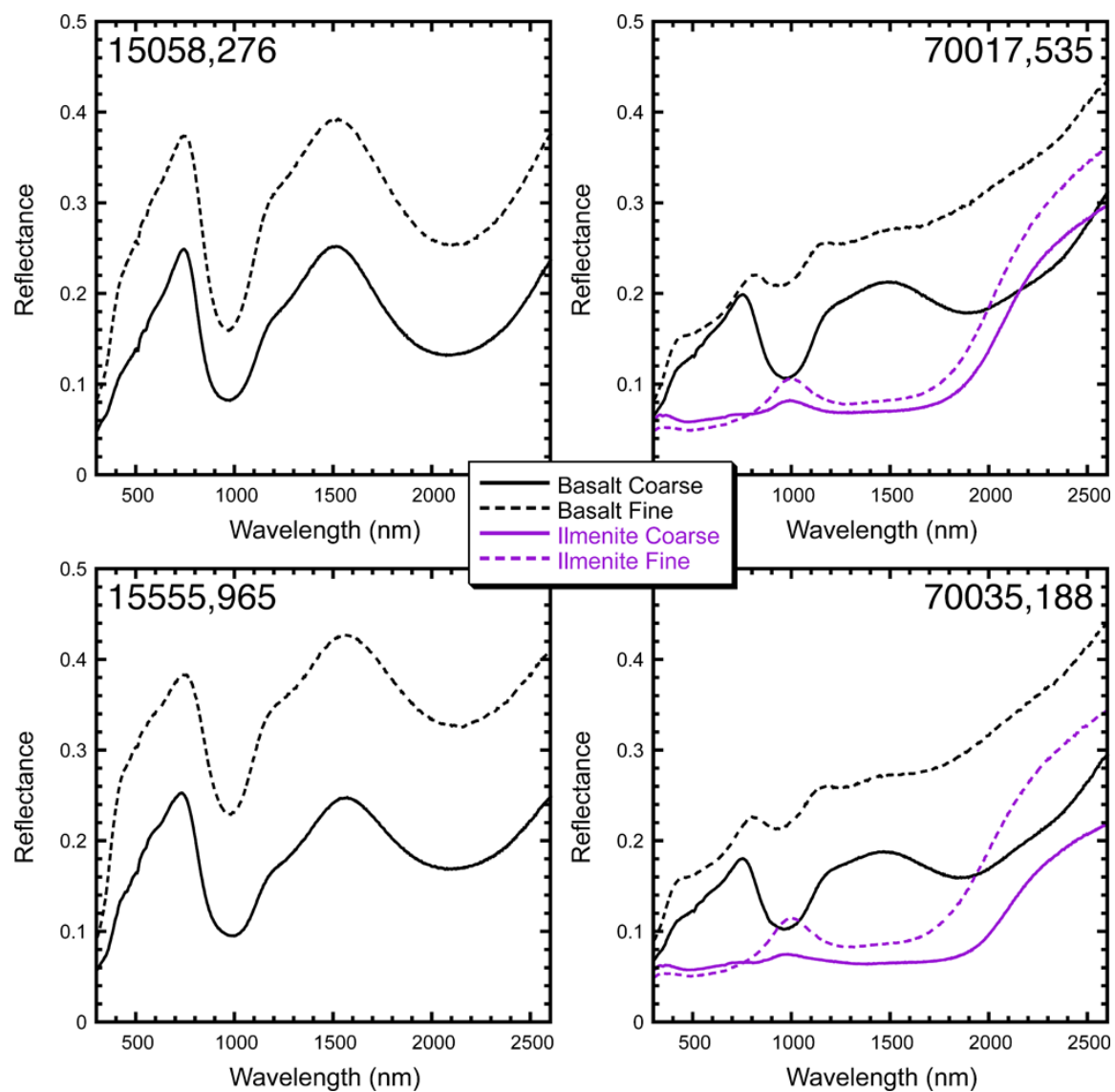


Figure 2.

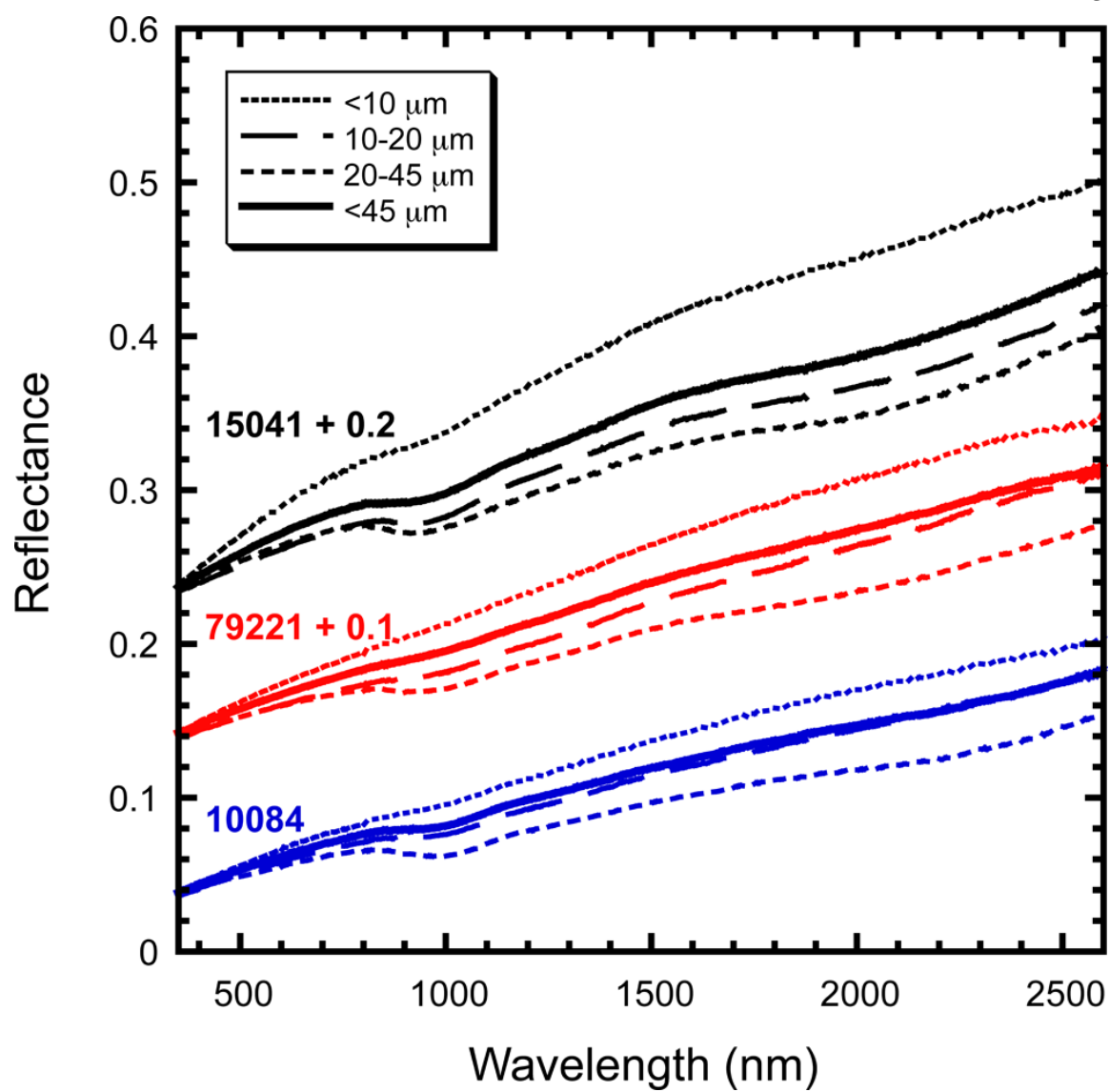


Figure 3.

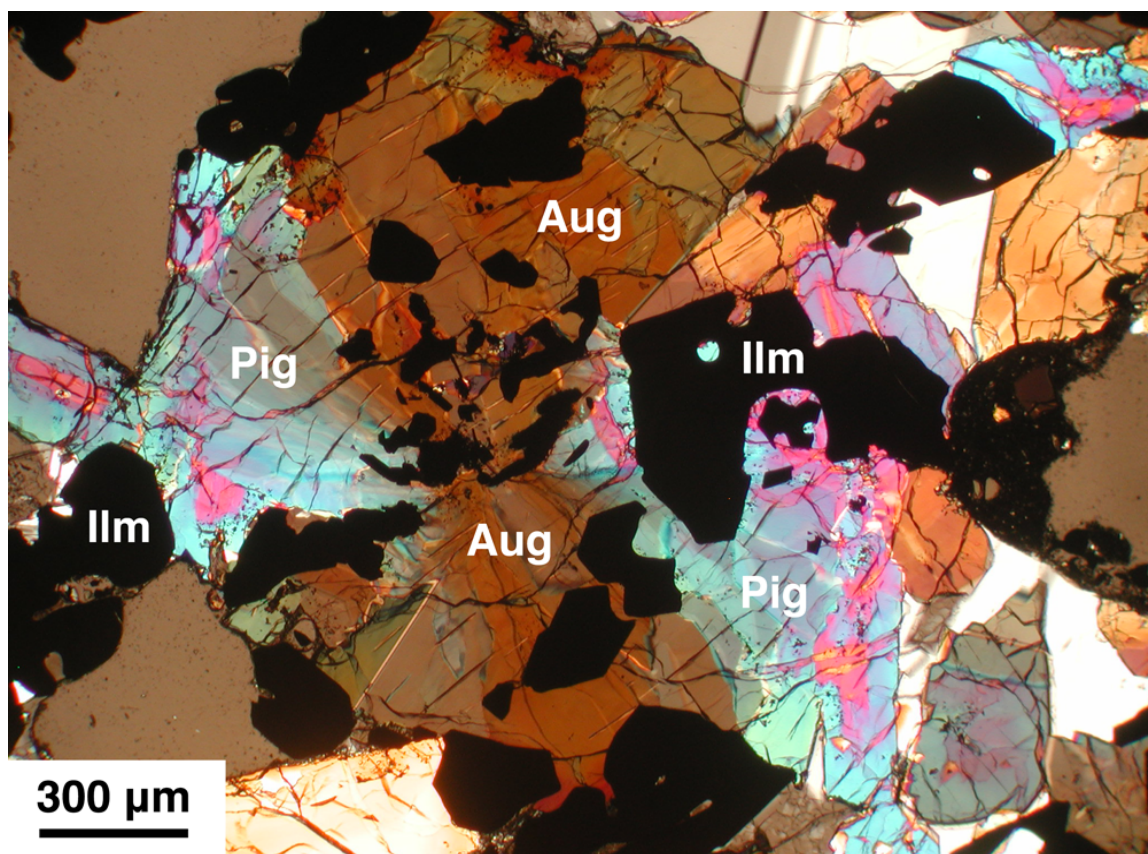


Figure 4.

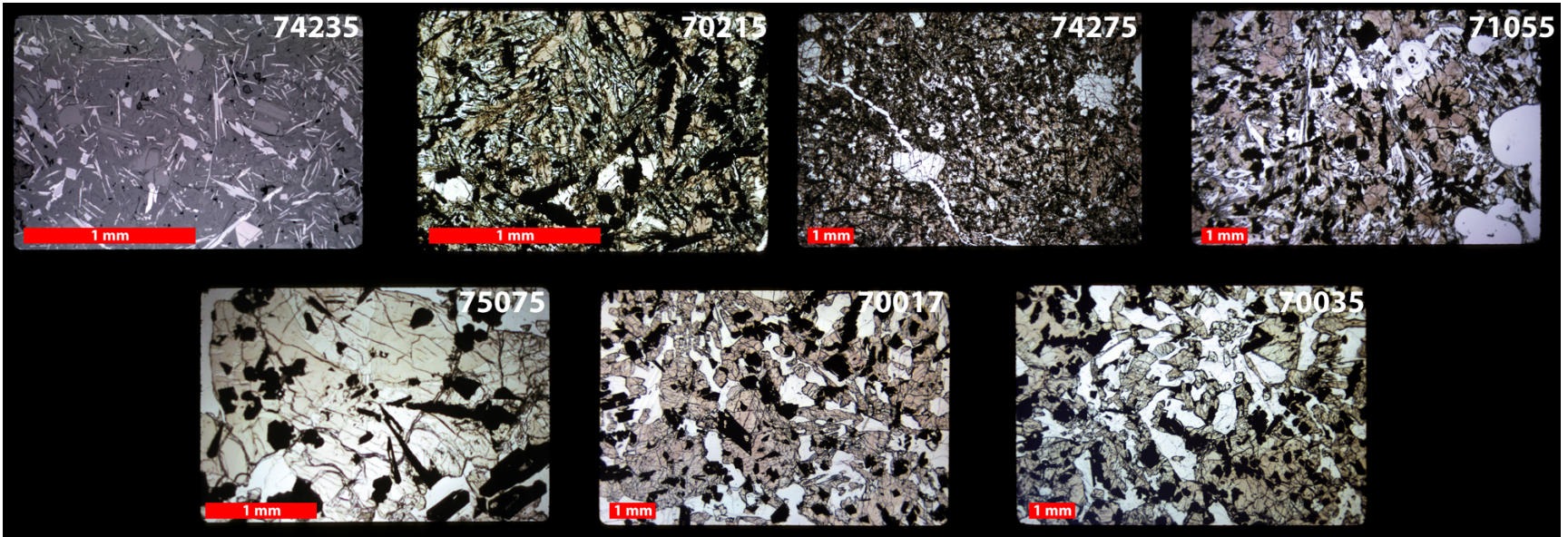


Figure 5.

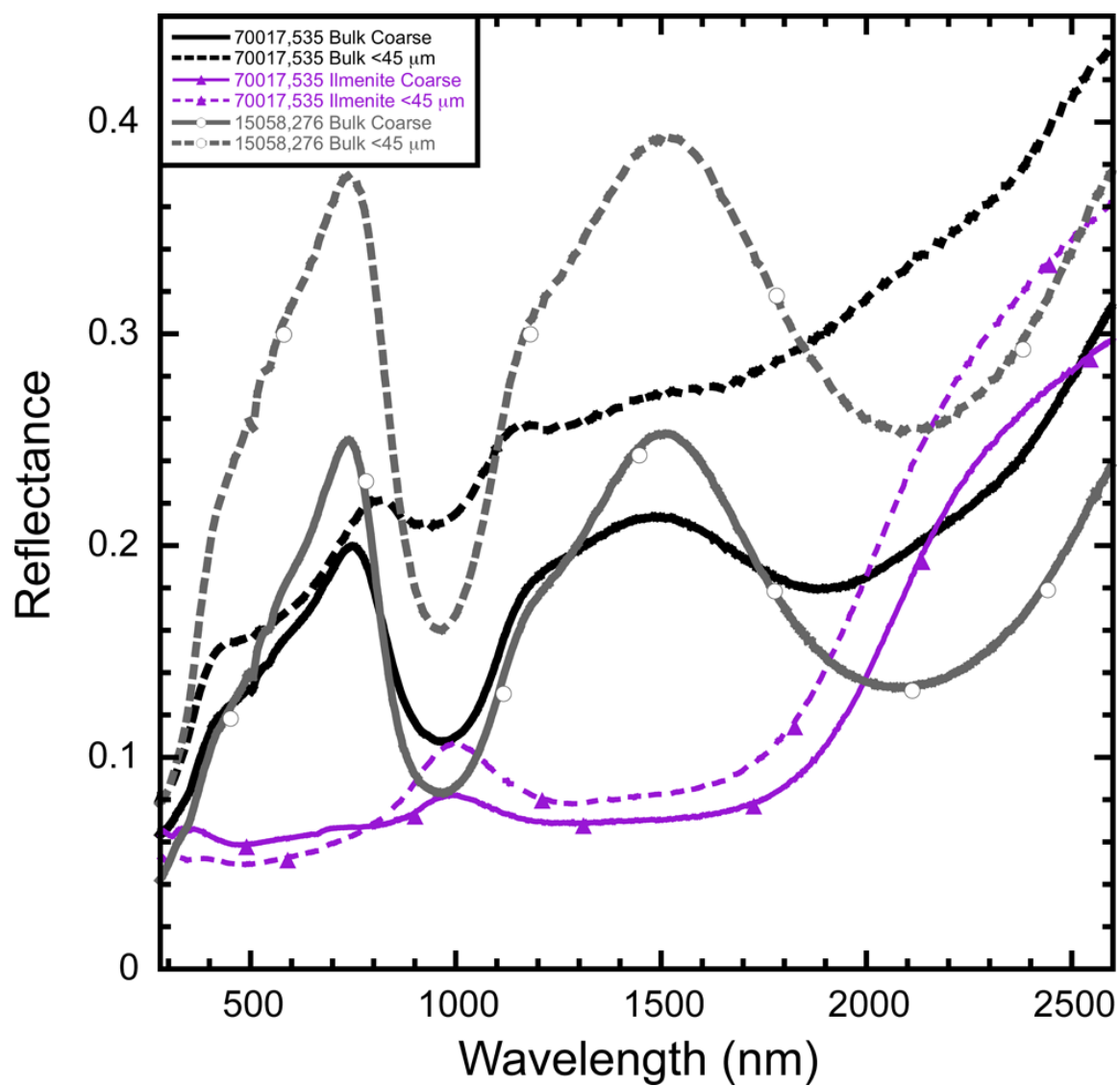


Figure 6.

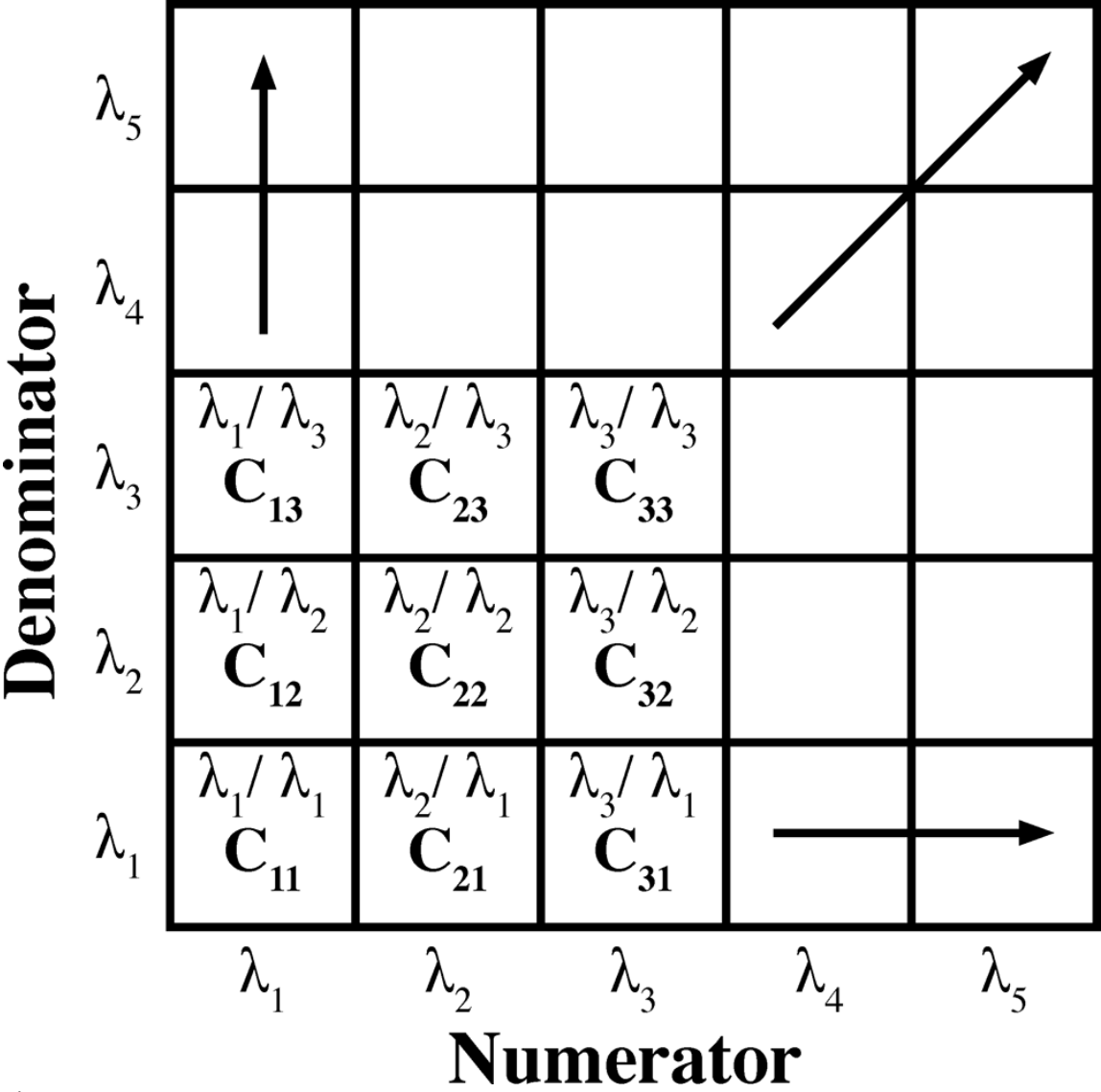


Figure 7.

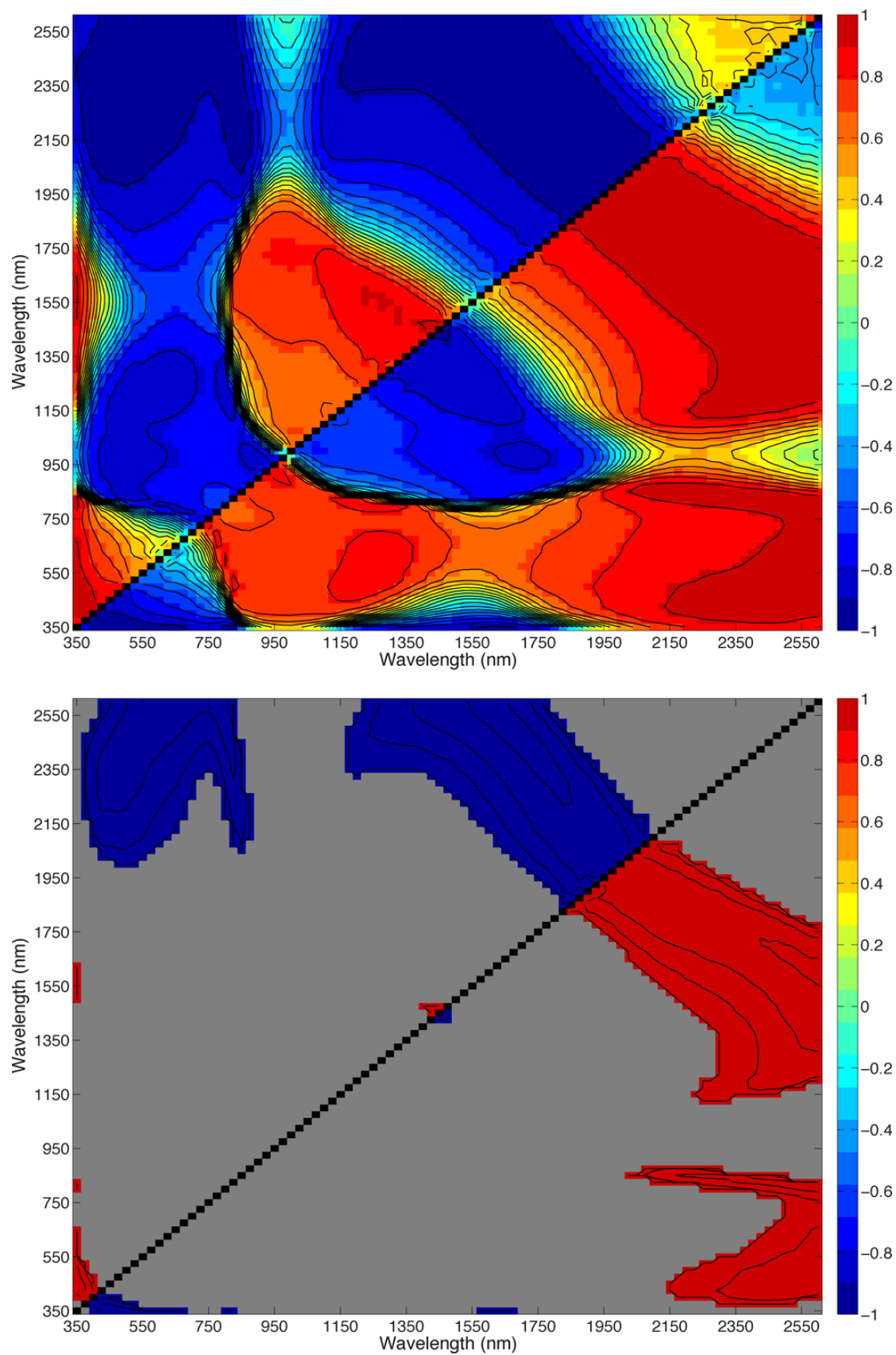


Figure 8.

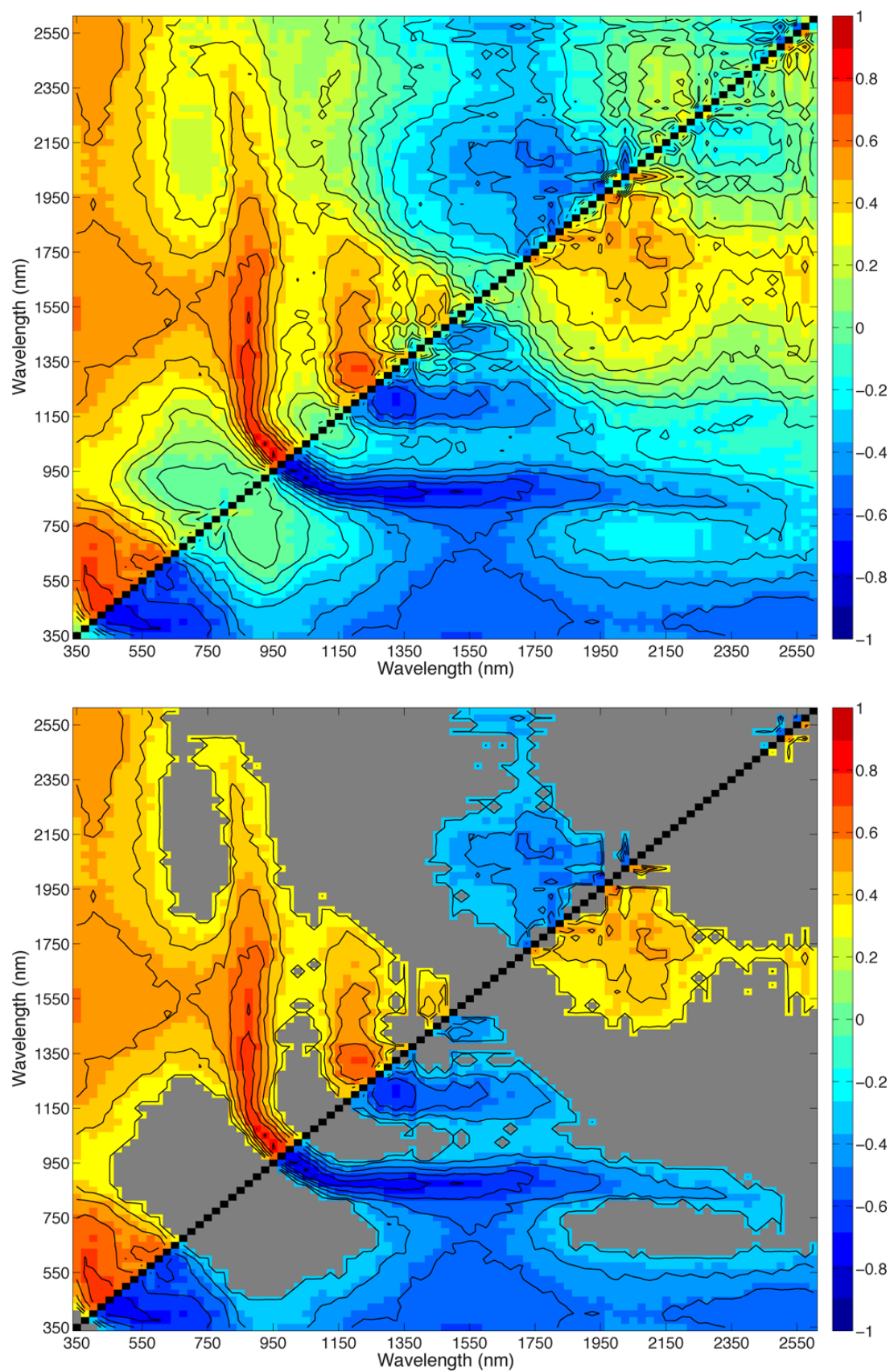


Figure 9.

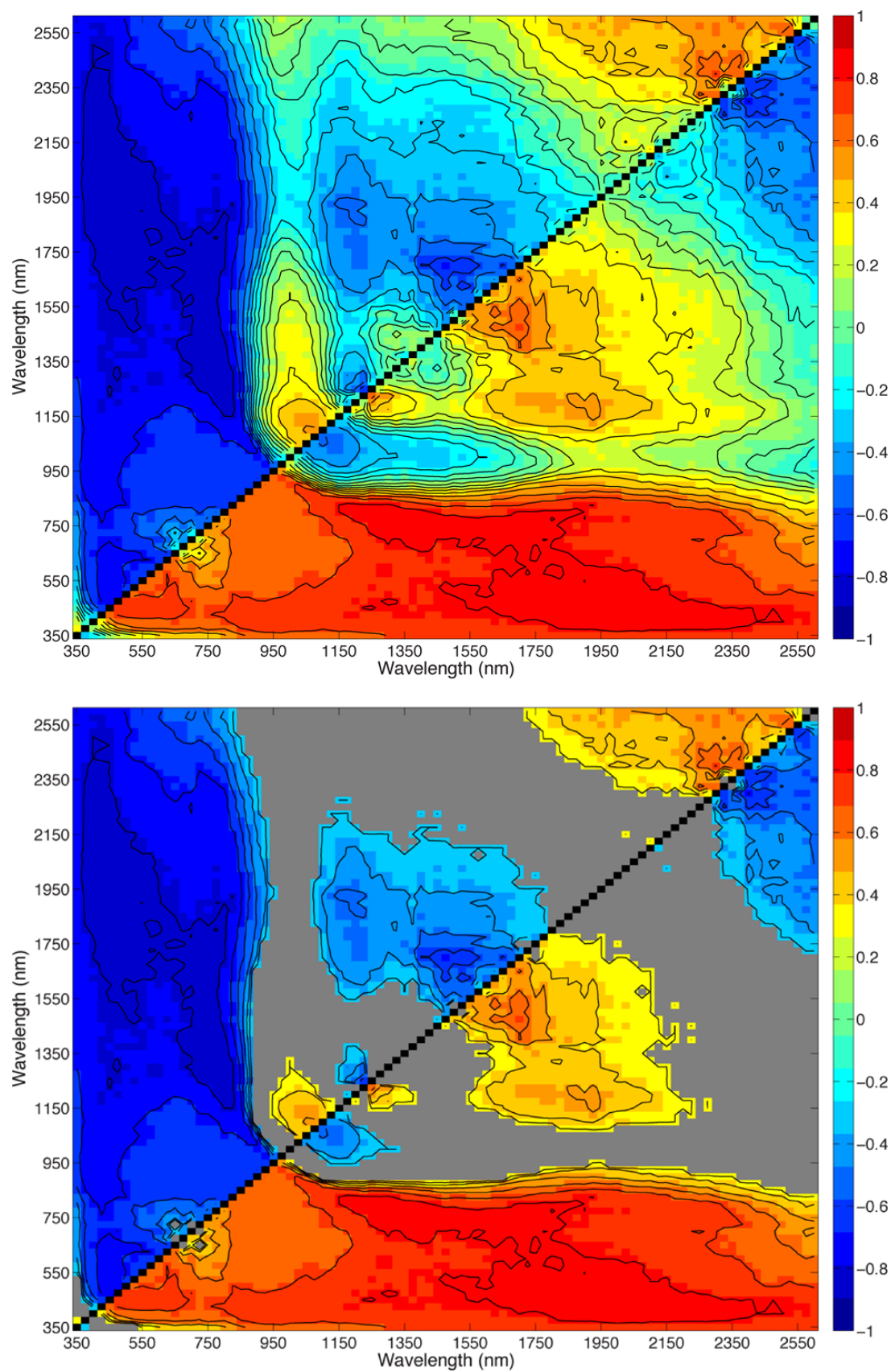


Figure 10.

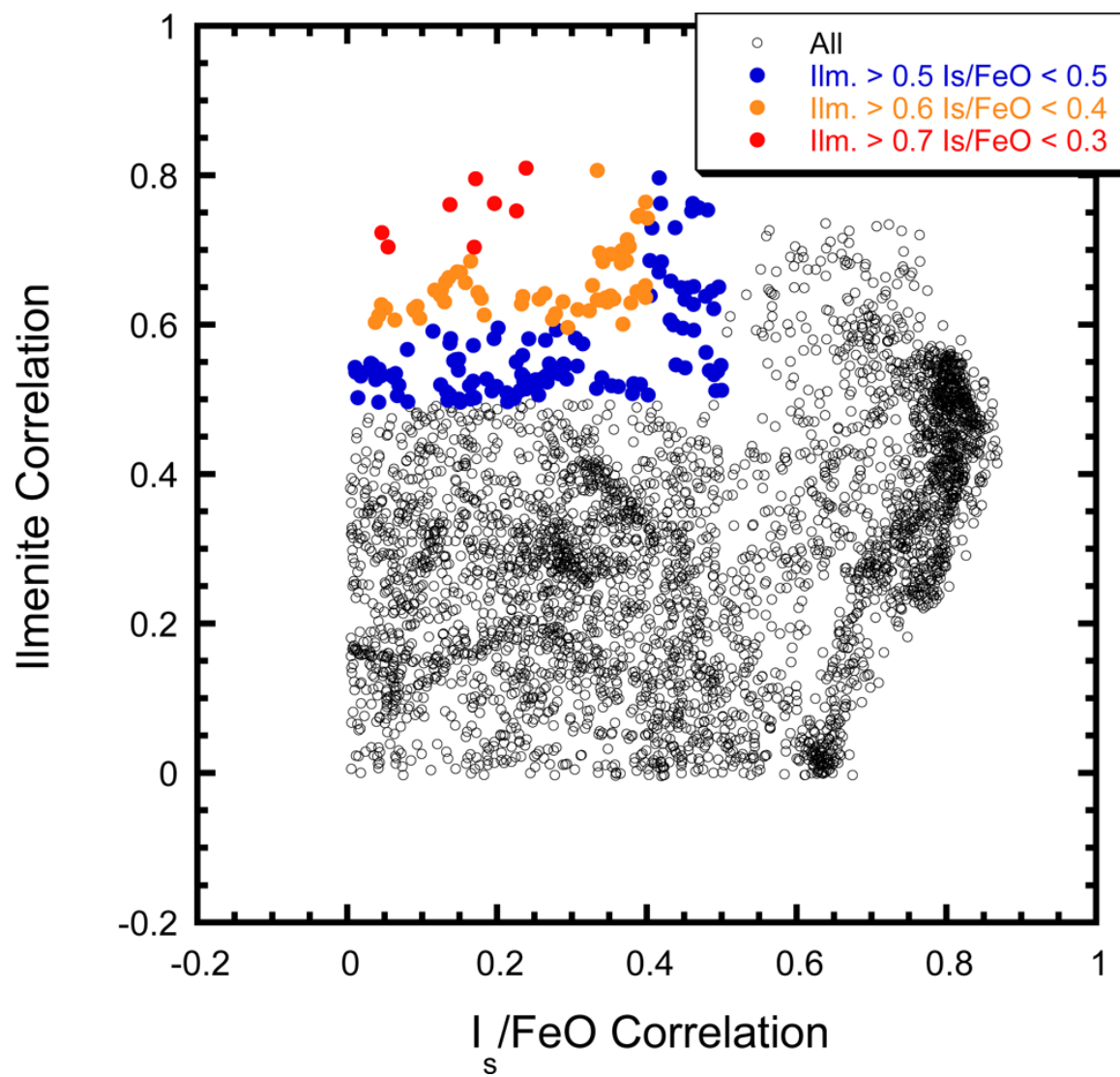


Figure 11.

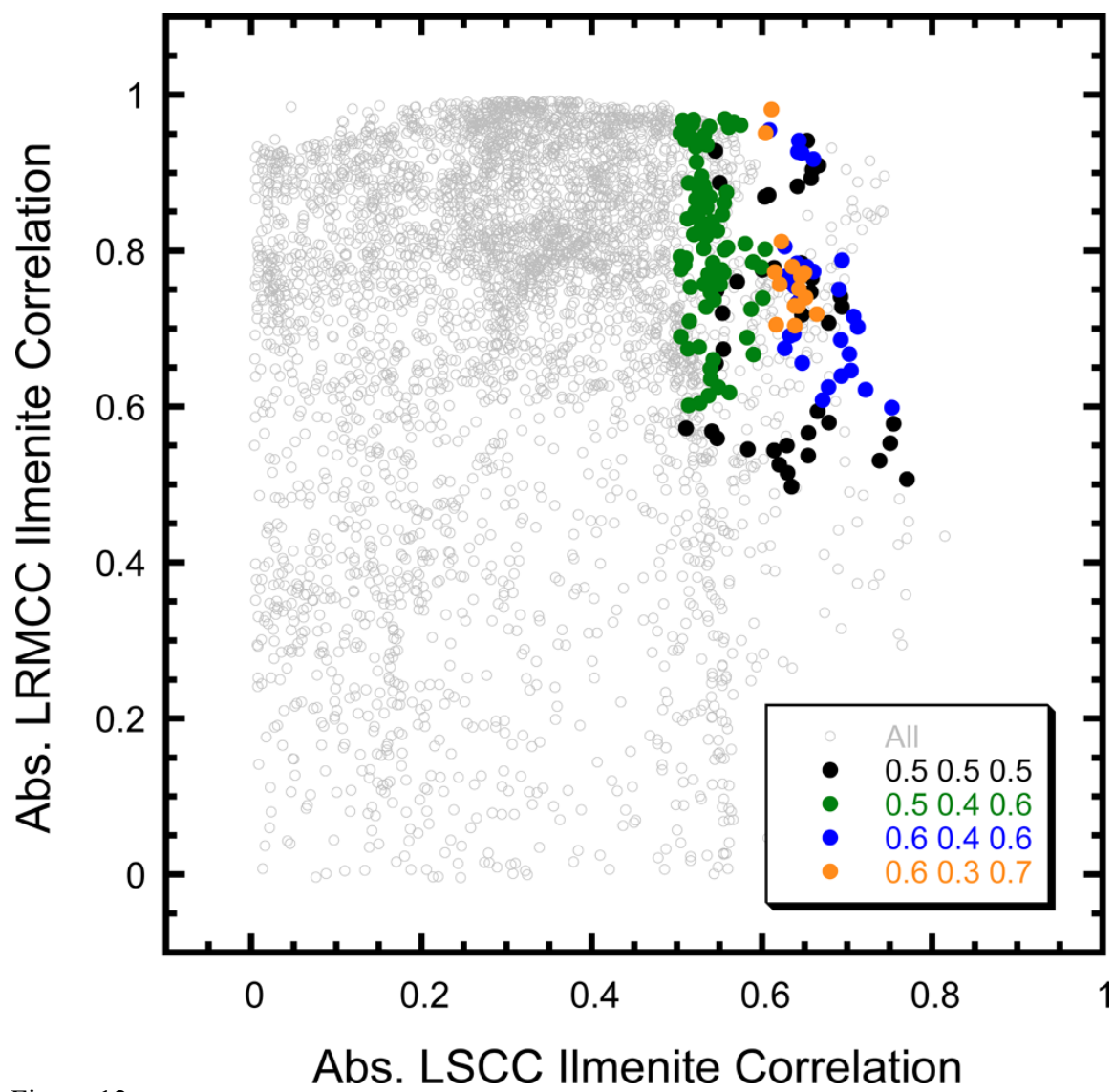


Figure 12.

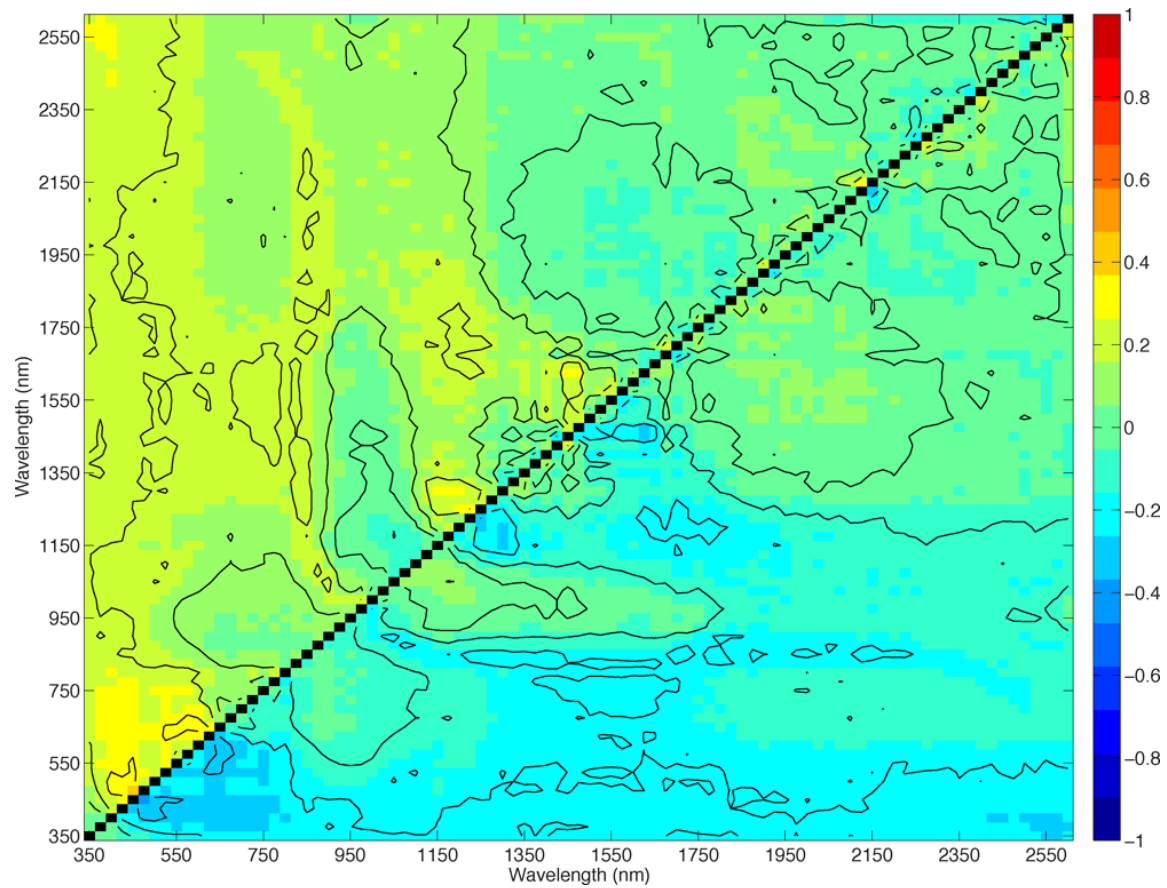


Figure 13.

CHAPTER 3: Deconvolution of Lunar Olivine Reflectance Spectra: Implications for Remote Compositional Assessment

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Abstract

Lunar olivines typically contain inclusions of Cr-spinel (chromite) that influence their measured optical properties. These altered optical properties complicate modeled predictions of olivine composition from reflectance spectra. Approaches developed for inclusion-free terrestrial olivine spectra must be modified to be applied to chromite-bearing lunar olivine spectra. We present a revised approach for predicting the compositions of chromite-bearing lunar olivines using the Modified Gaussian Model (MGM). The results of this revised approach for lunar olivines are consistent with previous results for terrestrial olivine reflectance spectra, and successfully predict the olivine's composition. These results are an important step in compositional assessment of remotely-sensed olivine spectra, and are essential to ongoing investigations of that topic. Our results are based on a limited set of available lunar olivine separates, and would be strengthened by the inclusion of additional compositions.

1 Introduction

The thermal and chemical evolution of planetary bodies is a major guiding theme in planetary science and exploration. Planetary bodies cool in a number of ways, including magma ocean processes, density stratification (differentiation), internal convection, and volcanism. These processes affect the chemical evolution of planetary bodies, as the composition and mineralogy of zones within the bodies evolve as thermal evolution progresses. Rocks contain distinct records of the thermal history of a planetary body, as their mineralogy and mineral composition are products of the processes that produced and/or altered them. Olivine in particular is a very important mineral with which to interpret the petrologic evolution of igneous rocks, as it is commonly the first mineral to crystallize from typical mafic magmas (BVSP, 1981). In the case of a primary magma, the olivine's composition indicates the degree of evolution of the mantle source of the magma from which the olivine crystallized. Generally speaking, highly forsteritic (high Mg' (Mg/Mg+Fe)) olivine is indicative of a primitive source, whereas more fayalitic (low Mg') olivine is indicative of a more evolved source (BVSP, 1981). The composition of lunar olivine is an indicator used to determine if a rock is from a particular lithologic suite (Hess, 1994; Papike et al., 1998; Warner et al., 1976; Warren and Wasson, 1977).

1.1 Olivine Reflectance Properties

Olivine has a distinctive signature in visible to near-infrared (VNIR) reflectance spectra. Typical olivine spectra have a broad, composite absorption feature near 1050 nm caused by electronic transitions in Fe^{2+} ions located in distorted octahedral crystal lattice sites [Burns, 1970; Burns et al., 1972; Burns, 1974; Burns, 1993]. An example is

illustrated in Figure 1, which shows a spectrum of San Carlos olivine ($\sim\text{Fo}_{90}$), a common laboratory standard sample. The three absorptions that comprise the composite feature are labeled with the Fe^{2+} -bearing crystallographic site responsible for the specific absorption. Visible to near-infrared reflectance spectroscopy is sensitive to olivine composition, because these three absorption features shift as a function of the olivine's Mg' [Burns, 1970; King and Ridley, 1987; Sunshine and Pieters, 1998]. When individual absorption bands are deconvolved with quantitative techniques such as the Modified Gaussian Model (MGM) [Sunshine *et al.*, 1990], spectra of olivine can be used to estimate the olivine's composition by inverting the MGM-derived band parameters to solve for composition as a function of band position [Sunshine and Pieters, 1998].

1.2 Chromite Inclusions in Lunar Olivines

Reflectance spectra of typical lunar olivines differ from those of terrestrial and synthetic olivine (Isaacson and Pieters, 2008; Isaacson *et al.*, 2010). Lunar olivines contain small but significant abundances of fine Cr-spinel inclusions (e.g., Dymek *et al.*, 1975). Spinel has strong absorption features beyond ~ 1600 nm (Cloutis *et al.*, 2004), a wavelength region where typical olivines are bright and featureless. A laboratory reflectance spectrum of a typical Cr-spinel (chromite) is shown in Figure 1. Olivine is a relatively transparent mineral, therefore strongly absorbing, opaque inclusions such as spinels have dramatic effects on olivine reflectance spectra, even in trace amounts. Lunar olivine spectra are not featureless beyond the principal composite crystal-field ferrous absorption. Instead, lunar olivine spectra drop in reflectance across this region due to the chromite inclusions. The differences between lunar olivine and terrestrial olivine spectra have prominent effects on the deconvolution of the spectra with approaches such as the

MGM. The presence of the strong long-wavelength absorptions in lunar olivine spectra requires the inclusion of absorptions into the model that interfere with fits to the primary olivine crystal-field ferrous absorptions. The result of these complications is that the standard approach developed for spectra of terrestrial olivine (Sunshine and Pieters, 1998) is unable to estimate the composition of lunar olivine samples with any accuracy (Isaacson and Pieters, 2008). A revised, systematic approach for lunar olivine is required if the richness of information available from global analyses of remotely-sensed spectra of lunar olivine is to be harvested. The advent of global hyperspectral lunar datasets (Mall et al., 2009; Matsunaga et al., 1999; Pieters et al., 2009) is now enabling such remote compositional analyses, so this revised approach is an important element of ongoing research of lunar olivine composition through remote sensing.

2 Background: MGM Fits of Olivine Spectra

2.1 Traditional Approach

The MGM is an inverse model that performs deconvolutions of a spectrum into a set of absorptions superimposed onto a continuum slope. Mathematically, the absorptions are defined by Gaussian distributions in average bond length of the site and cation of interest, and in the model are expressed as three parameters for each absorption: band center, band width, and band strength. The continuum slope is defined by a set of polynomial coefficients, which act as additional model parameters. The model adjusts the various models parameters to minimize, in a least squares sense, the sum of the squares of the residuals. It is important to remember that models such as the MGM seek to minimize the error of a fit without regard for whether the resulting model parameters are consistent with the structure of the mineral or mixture in question. The reader is referred to the work

of Sunshine et al. (1990) for additional background on the MGM, approach, and underlying mathematics. For laboratory spectra of terrestrial olivines, a flat continuum slope is commonly used, and the offset (y intercept value) of the continuum is allowed to vary freely in the optimization routine. The MGM initial parameters are defined by three absorptions near 1000 nm for the principal olivine feature, and two absorptions at shorter wavelengths to account for absorptions in the visible to near-ultraviolet. The result of such a fit performed on the San Carlos olivine spectrum shown in Figure 1 is illustrated in Figure 2a. MGM results for this and all other fits shown or described in this paper are provided in Table 1. Intensities are reported as natural log reflectance; band centers and widths (FWHM) are reported in nm. As expected, the model parameters derived from this fit (absorption band center, width, and strength) are consistent with the trends derived by Sunshine and Pieters (1998). The RMS error across the visible wavelengths does not affect the critical 1000 nm region of the fit, and is a result of simplifying the fit across this region.

2.2 Inadequacy of Traditional Approach for Lunar Olivine spectra

Also illustrated in Figure 2 (Figure 2b) is an example result from application of the approach described above to a spectrum of chromite-bearing lunar olivine. The lunar olivine sample illustrated in Figure 2b (separated from dunite sample 72415) is very similar in Mg' to the San Carlos olivine illustrated in Figure 2a (Fo₈₈ for 72415, Fo₉₀ for San Carlos). Thus, the band centers and band widths of the three principal absorption features should be nearly identical between the spectra. Absolute band strength varies as a function of grain size and other textural properties of a sample. The prominent absorption near 2000 nm in these olivine spectra is attributed to the chromite inclusions, and an

additional absorption is added to account for this feature. The modeled fit plotted in figure 2b is unrealistic for many reasons, including the RMS error, relative band positions, and relative band strengths. Specifically, the band positions are inconsistent with results for the San Carlos olivine, especially for the M1-1 band, and the central M2 absorption is modeled as the strongest absorption, a result completely inconsistent with previous analyses of olivine spectra (Burns, 1970; Sunshine and Pieters, 1998). Clearly, the standard approach developed for terrestrial samples returns substantially different results when applied to spectra of chromite-bearing lunar olivines, even when an additional band is included in the fit in an attempt to account for the spinel feature.

The poor fit is caused primarily by two factors, both related to the spinel absorptions: the spinel absorption severely reduces the overall reflectance at long wavelengths (>1500 nm) and also introduces another feature that the model attempts to include in minimizing the error in the fit. The traditional approach relies on a bright, flat region beyond 1500 nm on which the flat continuum slope is based (the fit in Figure 2a is an excellent example, as the reflectance at wavelengths >1500 nm is much higher than the reflectance maximum at wavelengths below the 1000 nm absorption feature, near ~ 700 nm). The spectrum in Figure 2b has nearly identical maximum reflectance values at wavelengths above and below the 1000 nm absorption, so a flat continuum slope cannot come to rest on a high value as in Figure 2a. The continuum slope intersects the spectrum in Figure 2b, which creates problems when fitting the first M1 olivine absorption in particular. Additionally, the absorption added to account for the spinel feature expands to such extreme widths that it expands into the 1000 nm, and interferes with the fit in this

critical wavelength region. Generally, this approach does not produce acceptable results for lunar olivine reflectance spectra.

3 Methods: Revised MGM approach for lunar olivine

MGM deconvolutions of remotely-sensed lunar olivine spectra will be complicated largely by two factors: the chromite absorptions discussed above, and the variable continuum slopes common to remotely-sensed spectra of planetary surfaces. The original approach developed by Sunshine & Pieters (1998) and the revised approach presented here rely on flat continuum slopes, which are likely to be unrealistic for remotely-sensed spectra. This paper addresses the complications resulting from chromite absorptions. Treatment of complications due to continuum slope is the focus of ongoing work.

3.1 Wavelength Range

We have revised the deconvolution approach outlined above to account for the complications due to chromite absorptions in laboratory spectra of lunar olivines. The modification includes two fundamental steps: truncate the spectrum and enforce a flat continuum slope. In this approach, spectra of lunar olivines are fit between wavelengths of 600 and 1750 nm. Wavelengths shorter than 600 nm do not contribute to the compositional analysis method discussed here. The 600 nm cutoff was chosen to allow full modeling of the first M1 olivine band; a longer cutoff wavelength would run the risk of eliminating some data needed to constrain that band fully. The 1750 nm cutoff was chosen as a compromise between avoiding the bulk of the spinel feature and fully capturing the long wavelength M1 olivine band. In addition to the three principal olivine

absorptions, two additional absorptions are included in the revised modeling approach to account for the residual spectral structure at short and long wavelengths.

3.2 Continuum Slope

The choice of continuum slope has significant effects on band strength and width as well as band position, and systematic results rely on a systematic selection of continuum slope. For consistency, we use flat continuum slopes, which are appropriate for laboratory spectra. The flat continuum slope can be modeled with a variety of offset values. We have experimented with a variety of offsets, and have found that increasing the offset value such that the initial continuum slope lies well above the spectrum being deconvolved produces results most consistent with the terrestrial trends. If the initial continuum slope has an offset value that is too low, the three principal absorptions are not given enough freedom to “move” and do not converge on physically reasonable results. In an extreme case, the continuum slope can even intersect the spectrum, producing especially poor results. In our experience, it is better to err on the side of a continuum offset that is too large rather than too small. The chosen offset will affect the absolute strengths of the absorption features, but will not affect the relative band strengths. However, excessive offset values could introduce errors by allowing broadening of the two bands added to the three principal olivine absorptions in the model fits.

The results of applying this revised MGM approach for lunar olivine are illustrated in Figure 3. The three principal olivine absorptions are plotted in black, and the two additional absorptions discussed above are plotted in grey. The three lunar olivine spectra evaluated and plotted in Figure 3 are: 72415 (~Fo₈₈), Figure 3a; 76535 (~Fo₈₇), Figure 3b; 15555 (~Fo₄₈), Figure 3c. All lunar olivines were measured with a particle size of <125

μm . While band centers are the principal basis of the compositional assessment, a fit is not considered satisfactory if the relative band strengths of the three olivine absorptions are not consistent with known trends (Burns, 1970; Sunshine and Pieters, 1998). The results in Figure 3 suggest that the modifications introduced to deal with the long-wavelength spinel absorptions are functioning appropriately.

3.3 Model Initial Conditions

Three distinct starting points were tested for MGM deconvolutions of the lunar olivine spectra. Reasonable model parameters for Mg-rich ($\sim\text{Fo}_{90}$), Fe-rich ($\sim\text{Fo}_{45}$) and intermediate ($\sim\text{Fo}_{70}$) compositions were chosen based on the Sunshine & Pieters results (1998). This approach was taken to evaluate the sensitivity of the approach to the initial model parameters in the ideal case of laboratory spectra and to optimize the starting conditions for our fits. This is an important consideration, because the nonlinear MGM must be given a reasonable starting point. Model parameters for our three starting conditions are provided in Table 2. As in Table 1, intensities are given in natural log reflectance, and band centers and widths (FWHM) are given in nm.

4 Results: Consistency with compositional trends

Shown in Figure 4 are the compositions of lunar olivines analyzed in this study plotted against the MGM-derived actual band centers (range brackets) and compared with the results of Sunshine and Pieters (1998) (open symbols) and the trends derived by the Sunshine and Pieters (1998) study of terrestrial olivine (dotted lines). The range brackets indicate the spread in band centers obtained from the different starting points for the MGM fits. In viewing the MGM results in Table 1, it is apparent that the Fe-rich starting point

actually produces the most Mg-rich compositional predictions, especially for 72415. This is likely a result of the higher initial band width for the M1-2 band in this scenario, giving this fit slightly more freedom and producing a more Mg-rich result, which is more consistent with the actual olivine composition. The result for the Fe-rich starting point applied to the 15555 olivine is nearly identical to results derived from the other starting points for this spectrum, and all converge to reasonable parameters for this olivine's composition ($\sim\text{Fo}_{48}$).

The trends in lunar olivine band centers are reasonably consistent with those determined for terrestrial olivines by Sunshine & Pieters (1998). Based on the small sample size of the dataset (effectively 2 compositions of olivine), any assessment of systematic deviations from previously-established trends must be regarded with some amount of skepticism. Generally, it appears that fits to the basalt olivine spectrum ($\sim\text{Fo}_{48}$) produce band centers for the M2 absorption that are offset to short wavelengths relative to the Sunshine & Pieters (1998) results. However, the deviation from the trend lines is not substantially larger than observed in some of the scatter in the Sunshine & Pieters (1998) results. Further analysis of deviations between results of the revised approach for lunar olivine and the results for terrestrial olivine spectra (Sunshine and Pieters, 1998) will require more data points for lunar olivine (i.e., additional lunar olivine compositions) such that a true regression can be performed rather than fitting a two point line. The consistency between our results and the terrestrial trends suggests that a similar approach to compositional prediction as that employed for terrestrial olivine spectra may be employed for lunar olivine spectra. However, the robustness of the compositional predictions would be improved by complementing our work with additional lunar olivine compositions.

5 Discussion: Compositional predictions from lunar olivine reflectance spectra

MGM deconvolutions of olivine spectra can be used to predict the composition of the olivine based on the trends in band positions previously established. We demonstrate with our approach that the trends in band centers for lunar olivine spectra are consistent with those demonstrated for terrestrial olivine spectra. However, these lunar trends are based on only a few data points, so we chose to use the trends developed from the suite of terrestrial olivines to evaluate the robustness of our results for compositional prediction. The use of the terrestrial olivine trend lines is acceptable because our deconvolution approach for lunar olivine provides results consistent with results for deconvolutions of terrestrial olivines with the traditional approach. We evaluate our results by treating our lunar olivine spectra as “unknowns” and predicting their composition from the fit results.

The compositional prediction method is based on minimization of the deviations in band centers from the established trends for all three absorption features simultaneously. Trend line equations are defined for each individual absorption band, and the unknown (Fo#) is parameterized in terms of the band center wavelength for each individual absorption (each linear trend line is defined by band center as a function of Fo#). The deviation of the band center wavelengths from the trend lines for each absorption is minimized by varying the Fo# (minimize the differences between actual and trend line-derived band centers, which are parameterized as a function of Fo#). The Fo# giving the minimum deviation from the three trend lines simultaneously is the predicted composition. This approach minimizes the effect of a deviation of a single absorption from the trends by weighting all three absorptions equally.

Figure 5 demonstrates the results of “predicting” the composition for our lunar olivine spectra, as it plots the range of “predicted” composition when treating the spectrum as an unknown against the actual composition determined by independent elemental analysis techniques. The range in predicted compositions reflects the range in band centers resulting from the varied model starting points. The results generally fall within a range of 5-10% (5-10 Fo# range), indicating a very good accuracy of the predictions. Additionally, because we have used the trends derived for terrestrial olivine spectra to “predict” the composition of lunar olivines deconvolved with our revised approach, the very good agreement between predicted and measured compositions demonstrates both the accuracy of the prediction method for lunar olivine spectra and the consistency between results for the fitting procedures devised for lunar and terrestrial olivine spectra.

6 Conclusions

The common chromite inclusions in lunar olivines have dramatic effects on the reflectance spectra of lunar olivines between 1600 and 2600 nm. Approaches to deconvolving olivine spectra developed for terrestrial olivines are based on a full wavelength range (<600 nm to 2600 nm) and do not produce satisfactory results for lunar olivines. A new method for deconvolving lunar olivine spectra based solely on the reflectance between 600 and 1750 nm is successful at reproducing the expected trends in individual absorption band position. Because these trends are the basis of predicting the composition of an “unknown” olivine measured with reflectance spectroscopy, this revised approach for lunar olivine spectra is a vital component of predictions of lunar olivine composition from remotely-sensed spectra.

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Table 1. Results of MGM fits

Fo#	Info	Figure	M1-1 Center	M1-1 FWHM	M1-1 Intensity	M2 Center	M2 FWHM	M2 Intensity	M1-2 Center	M1-2 FWHM	M1-2 Intensity	Fo# Pred.
90	San Carlos	2a	836.1	231.1	-0.2042	1032.3	178.4	-0.2602	1210.8	426.1	-0.3471	91.5
88	72415	2b	859.9	167.7	-0.2212	1029.5	170.6	-0.4024	1203.0	350.2	-0.4126	85.7
88	72415 Mg- Rich	4, 5	844.1	227.9	-0.3707	1036.7	180.3	-0.4456	1218.3	321.5	-0.6585	82.9
88	72415 Int.	3a, 4, 5	844.1	227.9	-0.3706	1036.7	180.3	-0.4455	1218.2	457.5	-0.6585	83.0
88	72415 Fe- Rich	4, 5	843.2	227.5	-0.3462	1036.9	175.7	-0.4127	1209.4	478.6	-0.6659	88.0
87	76535 Mg- Rich	4, 5	848.9	229.7	-0.4903	1035.3	185.7	-0.4954	1223.1	460.8	-0.7733	78.6
87	76535 Int.	3b, 4, 5	848.9	229.7	-0.4902	1035.3	185.7	-0.4953	1223.1	460.8	-0.7733	78.6
87	76535 Fe- Rich	4, 5	849.0	229.2	-0.4671	1035.3	180.7	-0.4599	1215.1	479.2	-0.7814	82.8
48	15555 Mg- Rich	4, 5	869.9	234.3	-0.981	1045.0	202.3	-0.7459	1255.3	501.5	-1.4066	49.6
48	15555 Int.	3c, 4, 5	869.8	234.3	-0.981	1045.0	202.5	-0.7469	1255.4	501.3	-1.4065	49.6
48	15555 Fe- Rich	4, 5	870.9	233.6	-0.9483	1045.5	197.2	-0.6926	1249.2	520.0	-1.4162	52.2

Table 2. MGM starting parameters

Band, Parameter \ Starting Fit	Mg-Rich ($\sim\text{Fo}_{90}$)	Intermediate ($\sim\text{Fo}_{70}$)	Fe-Rich ($\sim\text{Fo}_{45}$)
Short, Center	630	630	630
Short, Width	115	115	115
Short, Intensity	-0.02	-0.02	-0.02
M1-1, Center	840	855	880
M1-1, Width	228	228	228
M1-1, Intensity	-0.2	-0.2	-0.2
M2, Center	1036	1038	1055
M2, Width	176	176	176
M2, Intensity	-0.225	-0.225	-0.225
M1-2, Center	1210	1232	1255
M1-2, Width	424	424	460
M1-2, Intensity	-0.275	-0.275	-0.275
Long, Center	1650	1650	1650
Long, Width	250	250	250
Long, Intensity	-0.0125	-0.0125	-0.0125
Continuum Offset (C0)	Variable	Variable	Variable
Continuum Slope (C1)	1E-10	1E-10	1E-10

Figure Captions

Figure 1. Bidirectional reflectance spectra of terrestrial olivine and chromite. San Carlos olivine ($\sim\text{Fo}_{90}$) is labeled with the specific Fe^{2+} -bearing site causing each of the component absorptions. The chromite spectrum is described by Cloutis et al. [2004], sample C105.

Figure 2. Example MGM fits to olivine spectra using the standard approach described by Sunshine & Pieters [1998]. (a) Fit to San Carlos olivine ($\sim\text{Fo}_{90}$) spectrum shown in Figure 1. This is an example of a high-quality fit. (b) Fit to spectrum of lunar olivine separated from 72415 ($\sim\text{Fo}_{88}$). The effect of the chromite inclusions is seen in the reduced reflectance and the absorption feature beyond 1500 nm. Even when adding an absorption to account for the chromite absorption, an unsatisfactory fit is produced, as evidenced by the RMS error and inconsistent band properties of the three olivine absorptions as compared to the San Carlos olivine fit in (a).

Figure 3. Revised approach for MGM deconvolution of chromite-bearing lunar olivine reflectance spectra. Grey areas indicate wavelengths excluded from MGM deconvolutions in our approach. The three lunar olivine spectra analyzed in this study are shown with example MGM fits using our approach. All olivine spectra illustrated in this figure were measured with a particle size of $<125\ \mu\text{m}$ (a) 72415 ($\sim\text{Fo}_{88}$). (b) 76535 ($\sim\text{Fo}_{87}$). (c) 15555 ($\sim\text{Fo}_{48}$).

Figure 4. Results of MGM deconvolutions of lunar olivine reflectance spectra as compared to results from Sunshine & Pieters [1998] for terrestrial olivine spectra. The actual Fo# of the olivines studied is plotted against the MGM-derived band centers. Range brackets represent the range of band center results produced from the three different starting points. Specific absorptions are labeled (M1-1, M2, M1-2).

Figure 5. Predicted Fo# vs. actual Fo# for lunar olivine spectra. Predicted Fo#'s are the result of treating the lunar olivines as unknowns, and “predicting” their compositions using the method outlined in the text. Range brackets illustrate the range of predicted compositions from the three starting points. These predictions should be considered a “best case scenario” for compositional predictions from lunar olivine reflectance spectra, and are accurate to within 5-10%.

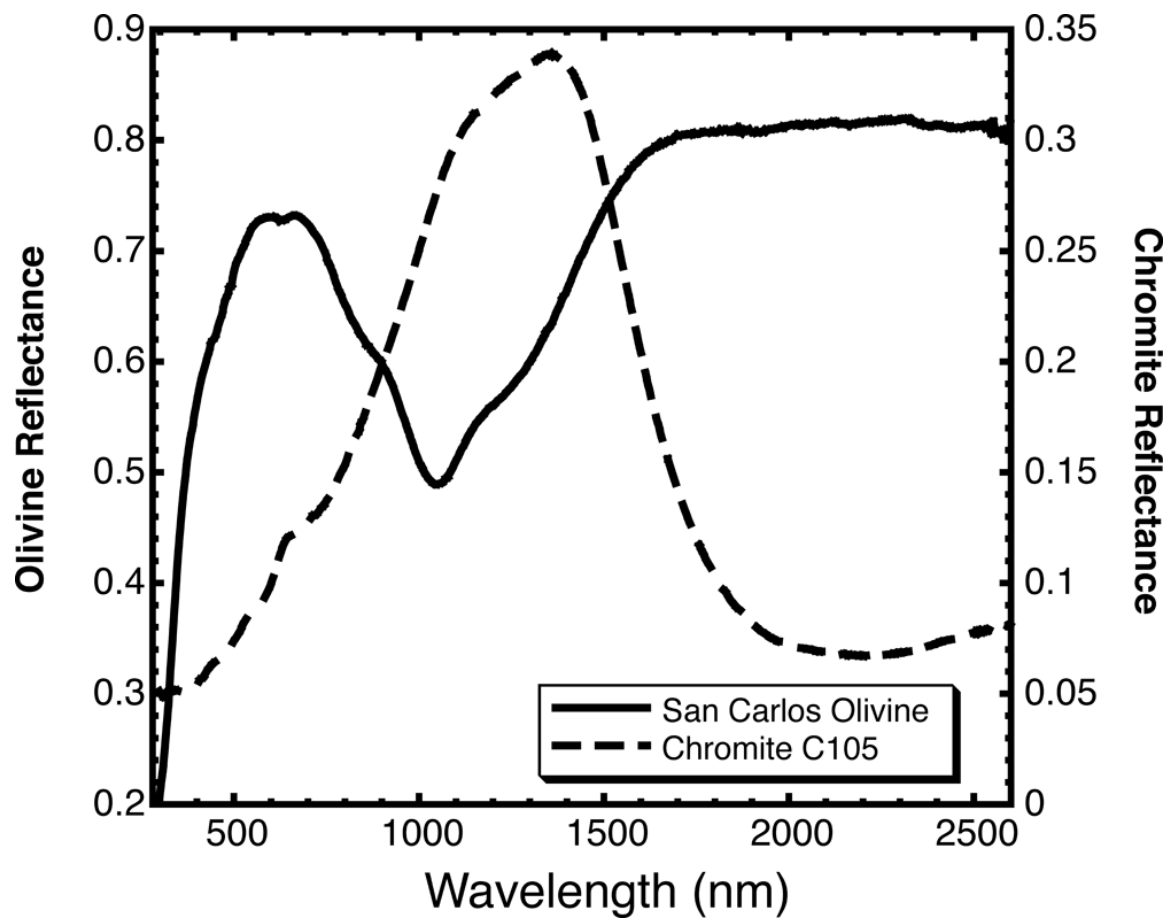


Figure 1.

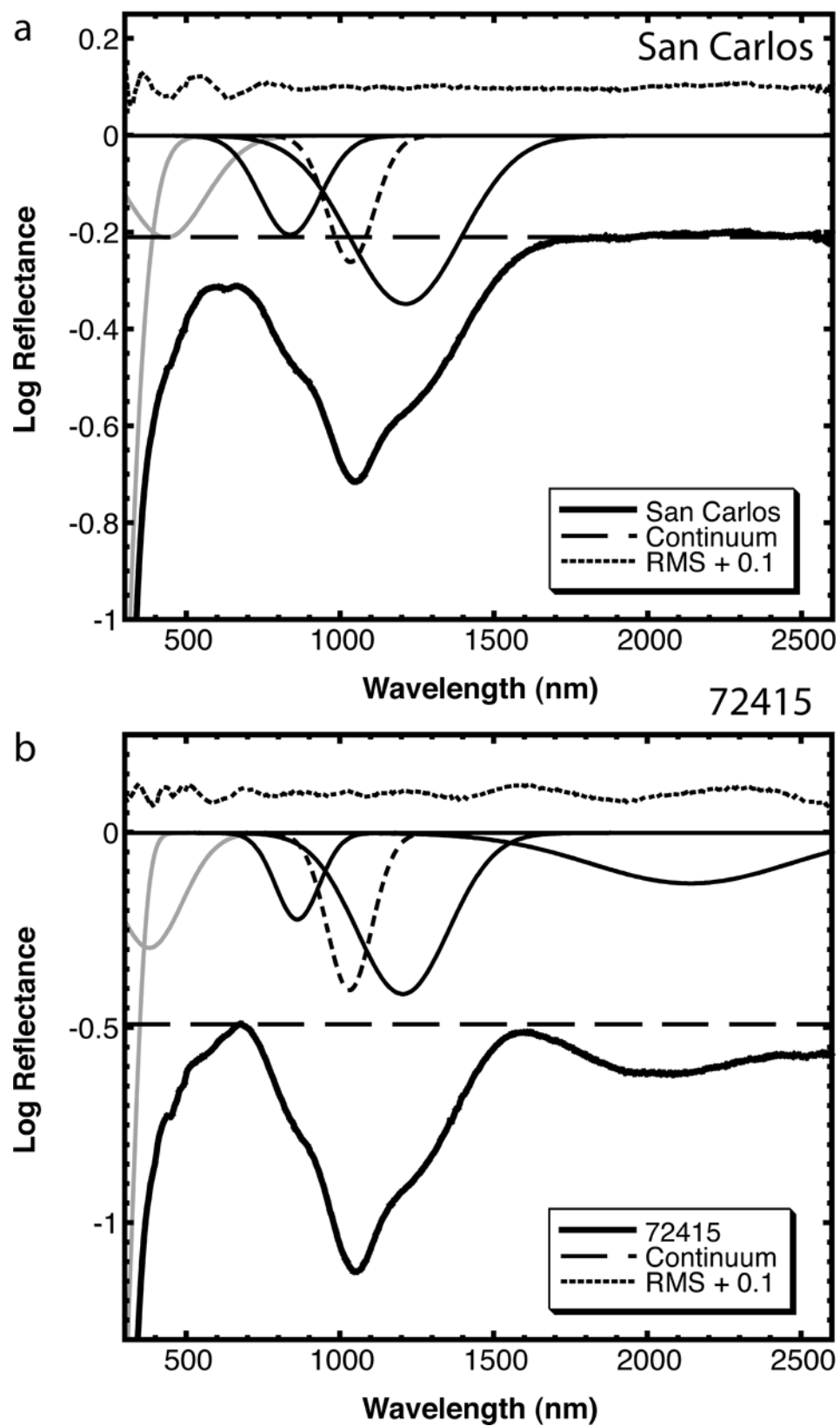


Figure 2.

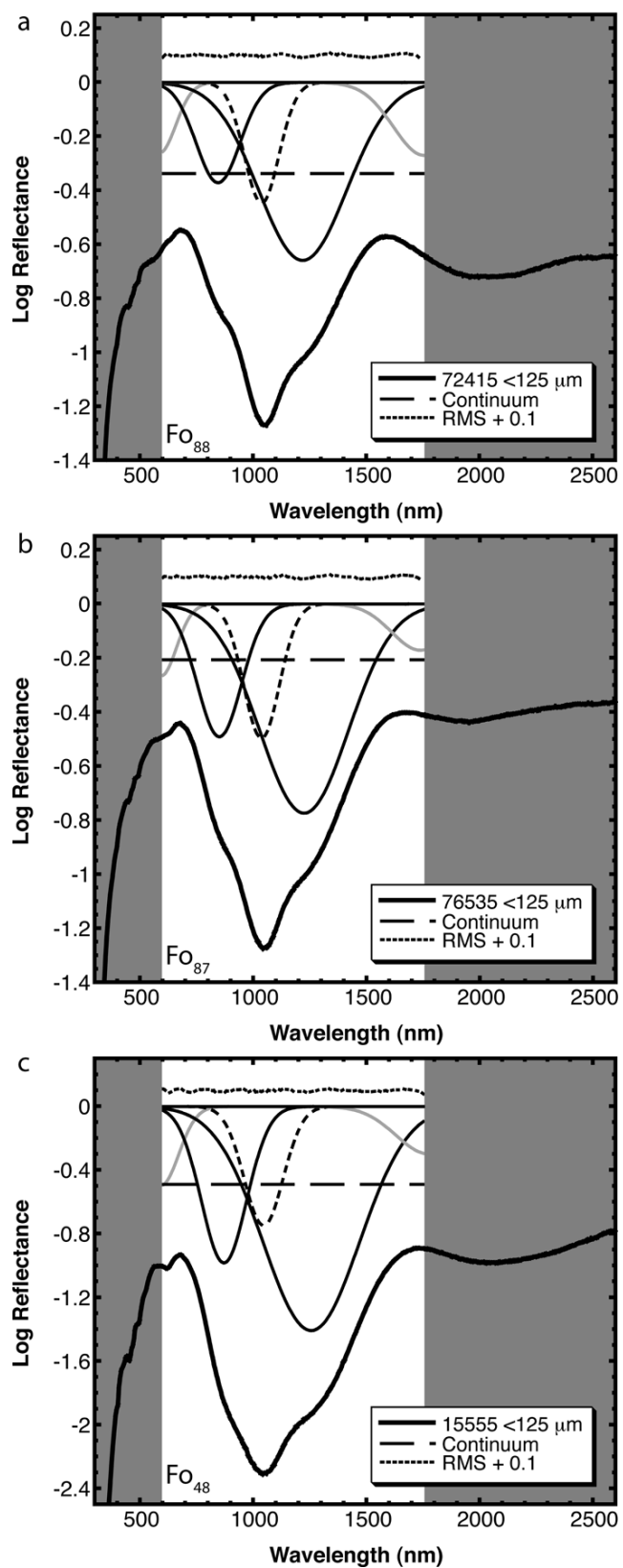


Figure 3.

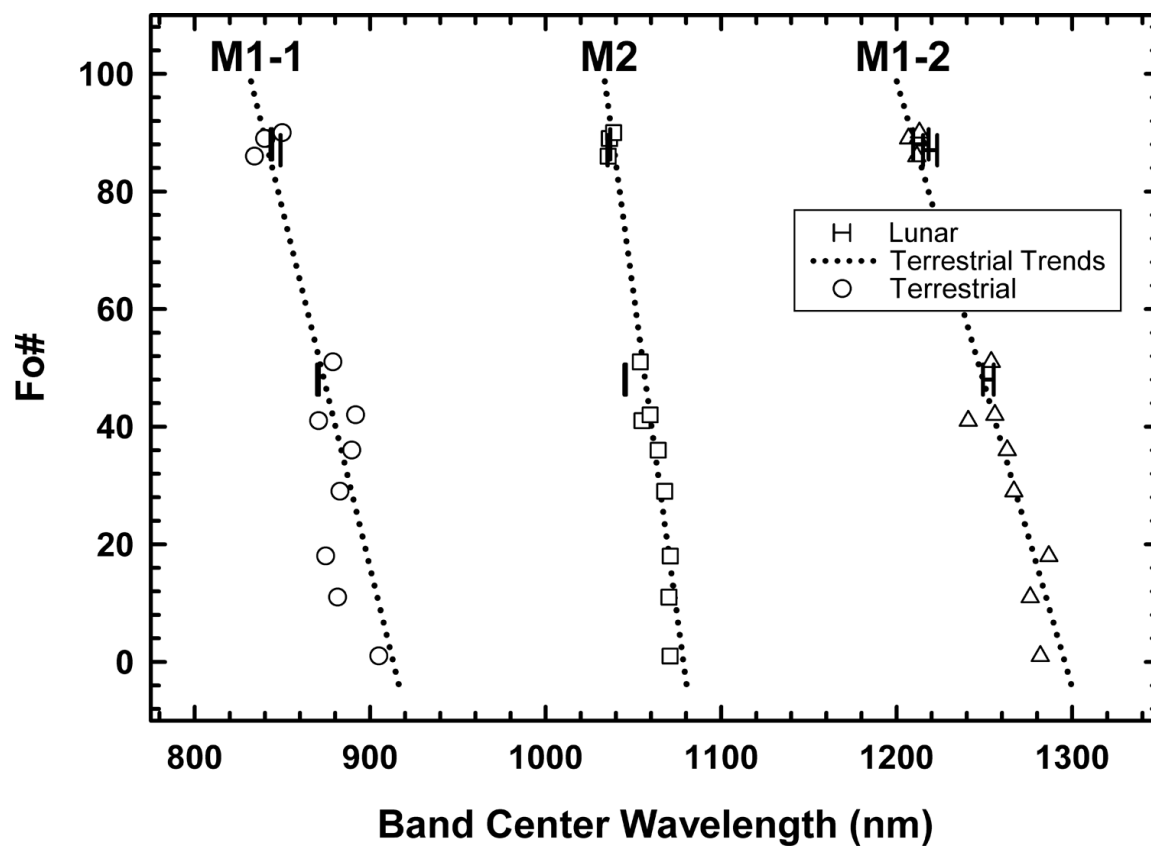


Figure 4.

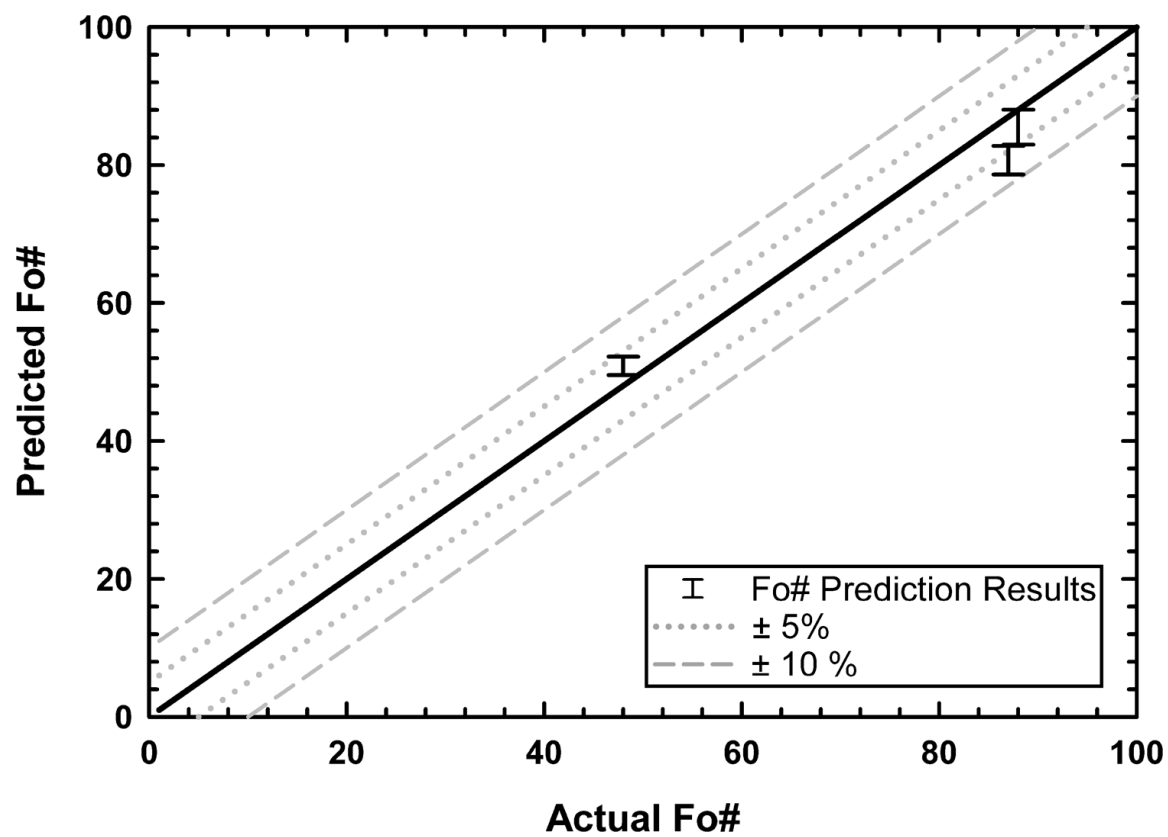


Figure 5.

CHAPTER 4: Remote Compositional Analysis of Lunar Olivine-Rich Lithologies with Moon Mineralogy Mapper (M³) Spectra

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Abstract

We build on the work of Isaacson and Pieters [2010] to develop a systematic approach for deconvolution of remotely-sensed lunar olivine-rich visible to near-infrared (VNIR) reflectance spectra with the Modified Gaussian Model (MGM). Whereas the Isaacson and Pieters [2010] work focused only on complications due to chromite inclusions in lunar olivines, we develop an approach for addressing the prominent continuum slopes common to remotely-sensed spectra of planetary surfaces. We have validated our approach only for the lunar case, where “red” continuum slopes are the norm, although there is no fundamental reason the approach should not work for spectra of other planetary surfaces such as Mars. The approach is based on removing a local continuum slope determined using tangent points on either side of the composite olivine ferrous absorption feature near 1000 nm. By applying the approach to a suite of laboratory spectra, we have developed a correction for the apparent shift in MGM-derived band position introduced by performing the continuum removal. The corrected MGM-derived band positions are then used to estimate the olivine’s composition using the approach of Isaacson and Pieters [2010]. Initial application of these techniques to olivine-rich spectra collected from the lunar farside by the Moon Mineralogy Mapper (M^3) predict compositions less magnesian than olivines in Mg-suite rocks, more magnesian than typical olivines in mare basalts, and consistent with olivines found in feldspathic lunar meteorites.

1 Introduction

The mineralogy and mineral composition of planetary samples contain a rich record of the thermal and chemical evolution of the planetary body. The processes responsible for the cooling of planetary bodies include magma ocean formation and solidification, differentiation (density stratification) and overturn, large-scale convection, and volcanic activity. These processes all produce distinct signatures in the mineral assemblages and mineral compositions produced across a range of depths and across the body's surface. While the record can be complex, the composition and mineralogy of planetary samples represent one of the most powerful tools available for unraveling the geologic history of a planetary body. While samples are the most powerful tool, remote sensing, such as with visible to near-infrared (VNIR) reflectance spectroscopy, offers a number of advantages. These advantages include global coverage (if conducted from orbit) and the ability to analyze composition without returned samples, although such remote measurements are greatly strengthened by the context and ground truth provided by returned samples [e.g., *Pieters*, 1999].

Olivine in particular is a useful mineral with which to evaluate the geologic evolution of igneous planetary bodies such as the Moon. Olivine is typically the first mineral to crystallize from a mafic magma, and its composition is indicative of the composition and degree of evolution of the source region in the case of a primary magma [BVSP, 1981]. Generally, forsteritic (high Mg' ($\text{Mg}/\text{Mg}+\text{Fe}$)) olivine is indicative of a primitive source, and more fayalitic (low Mg') olivine is indicative of a more evolved source [BVSP, 1981]. Additionally, olivine has a distinctive signature in VNIR reflectance spectra, and this signature is compositionally dependent, meaning that

remotely-sensed VNIR reflectance spectra are sensitive to both the presence and composition of olivine on planetary surfaces [Burns, 1970; King and Ridley, 1987; Sunshine and Pieters, 1998; Dyar *et al.*, 2009]. Typical olivine spectra have a broad, composite absorption feature centered near 1050 nm. These absorptions are caused by electronic transitions in Fe^{2+} ions located in distorted octahedral crystallographic sites. The central absorption is caused by Fe^{2+} in the M2 site, while the two exterior absorptions are caused by Fe^{2+} in the M1 site [Burns, 1970; Burns *et al.*, 1972; Burns, 1974; Burns, 1993]. An example olivine spectrum is plotted in Figure 1, which shows the spectrum of San Carlos olivine ($\sim\text{Fo}_{90}$), a common laboratory standard due to its composition and relative purity. The three component absorptions that produce the composite absorption feature are labeled with the Fe^{2+} -bearing crystallographic site responsible for the component absorption.

The composite absorption feature in olivine reflectance spectra is sensitive to the composition of the olivine. Specifically, the positions of the three component absorptions are a function of the olivine's Mg' , and shift in regular, well-characterized ways with changing Mg' [Sunshine and Pieters, 1998]. When olivine spectra are deconvolved with quantitative techniques such as the Modified Gaussian Model (MGM), the MGM-derived band parameters of the individual component absorptions can be used to estimate the olivine's composition [Sunshine *et al.*, 1990; Sunshine and Pieters, 1998]. As demonstrated by previous work, these MGM-derived parameters can be inverted to solve for olivine composition as a function of band position [Sunshine and Pieters, 1998; Isaacson and Pieters, 2010]. The relative strengths, and to a lesser extent, widths of the

three component absorptions also shift with changing olivine Mg', although this trend is less useful for compositional analysis.

Compositional analysis of lunar olivines is complicated by the presence of inclusions of Cr-spinel, which causes absorptions beyond ~1600 nm [Cloutis *et al.*, 2004; Isaacson and Pieters, 2010]. Inclusion-free olivine spectra are bright and featureless across this wavelength region, a property which was used to define a standard approach to deconvolutions of olivine spectra [Sunshine and Pieters, 1998]. The absorptions due to Cr-spinel inclusions, common across lunar olivines, cause the results of MGM deconvolutions of lunar olivine spectra to be inconsistent with deconvolutions of terrestrial olivine spectra of similar composition [Isaacson and Pieters, 2010]. Because the terrestrial olivine spectra deconvolutions are the basis of the trends used for compositional predictions, Cr-spinel-bearing lunar olivines require a modified approach to MGM deconvolutions. Such a modified approach has been developed by Isaacson and Pieters [2010], and involves truncating the olivine spectra to focus only on the 1000 nm region, as well as enforcing a flat (slope value of 0) continuum slope. This approach was able to reproduce the trends determined through analysis of terrestrial spectra lacking Cr-spinel absorptions (S&P) to within ~5-10% accuracy.

The study by Isaacson and Pieters [2010] identified two major complications in compositional analyses of lunar olivines with remotely-sensed VNIR reflectance spectra: the long wavelength absorptions caused by Cr-spinel inclusions and the effect of continuum slopes common to remotely-sensed spectra of planetary surfaces. The Isaacson and Pieters [2010] study addressed the former complication, but explicitly did not address the latter, limiting their analyses to laboratory reflectance spectra in which

flat continuum slopes are appropriate. In this study, we extend the Isaacson and Pieters [2010] approach to address the effect of continuum slopes. We propose a method for standardizing the continuum slope used to deconvolve remotely-sensed olivine spectra, and evaluate the effect of this method on the trends in MGM-derived band position developed for terrestrial olivine spectra and reproduced in chromite-bearing lunar olivine spectra.

2 Methods

2.1 *Variable Continuum Slopes: Continuum Removal*

Continuum slopes in remotely-sensed spectra are highly variable, being influenced by surface texture, grain size, viewing geometry, and alteration such as through the process of space weathering. On the Moon, continuum slopes are predominantly affected by the presence of vapor-deposited nanophase iron-bearing rims on grains of lunar soil [e.g., *Hapke*, 2001; *Taylor et al.*, 2001; *Noble et al.*, 2005; *Taylor et al.*, 2010]. The optical effects of this nanophase iron are complex, but one of the major effects is an increase in the slope of the continuum (i.e., “red” continuum slopes). This effect becomes more pronounced with increasing degree of weathering leading to the deposition of more nanophase iron on grain rims [e.g., *Pieters et al.*, 2000; *Noble et al.*, 2001]. Even relatively immature materials on the Moon exhibit fairly pronounced continuum slopes. Thus, flat continuum slopes such as those used in previous systematic treatments of olivine reflectance spectra will not be practical for the majority of remotely-sensed spectra collected of the lunar surface.

The ubiquitous but variable nature of continuum slopes in remotely-sensed VNIR reflectance spectra of planetary surfaces is a major complication in quantitative analysis

of diagnostic absorption features present in those spectra. While the MGM can model continuum slopes with polynomial functions of varying orders, a systematic approach is required if producing systematic results for remotely-sensed spectra is the goal. Such a treatment is required to place analyses of lunar olivines into the context of previous work that is the basis of the trends that drive the compositional prediction approach. We employ the approach developed by Isaacson and Pieters [2010] (truncating spectra and enforcing flat continuum slopes), but we include additional steps to address spectra for which flat continuum slopes are not practical.

Our approach to dealing with continuum slopes is to “remove” the continuum slope prior to conducting MGM fits. We acknowledge that other approaches to addressing the effect of the continuum slope may be possible, although direct comparisons to laboratory results for terrestrial olivines may not be possible if other approaches are employed. Alternative approaches for dealing with the continuum slope may well be developed, but would likely require a re-analysis (or at least a re-calibration of the trends) of laboratory olivine spectra in light of the new deconvolution approach.

The continuum slope to be removed is determined by fitting a local continuum over the principle olivine absorption feature. This local continuum slope is determined by tangent points on the short and long wavelength side of the absorption. Our method is to pick the “high reflectance” points on either side of the absorption as the tangent points. In our experience, the long-wavelength inflection point typically falls near ~ 1700 nm, while the short-wavelength inflection point is more variable. This is generally true for spectra of Cr-spinel-free olivine and remotely-sensed lunar olivine spectra, but not true for laboratory spectra exhibiting significant Cr-spinel absorptions, for which a shorter

wavelength must be chosen for the long-wavelength tangent point. We attempted continuum removal with continuum slope tangent points optimized for each spectrum as well as with fixed tangent points for all spectra. We also evaluated various combinations of fixed and optimized tangent points (e.g. optimized short wavelength point, fixed long wavelength point for all spectra). While the differences are generally slight, we found that the best, most consistent results were produced with short wavelength tangent points optimized for each spectra and fixed long wavelength tangent points at 1700 nm. After performing the continuum removal based on these local continuum slopes, MGM fits are conducted as described by Isaacson and Pieters [2010]. As in the Isaacson and Pieters [2010] approach, in fitting a particular spectrum, multiple starting points are used to ensure that a “global” optimum fit is achieved. We employ the standard starting points presented by Isaacson and Pieters [2010], varying only the offset of the continuum slope in the starting models to a more reasonable value for continuum-removed spectra, which intersect 0 in log reflectance space.

2.2 Effect of Continuum Removal: Laboratory Spectra

We also evaluate the effect of the continuum removal process on the results of MGM fits to olivine spectra. This evaluation is necessary to determine if the results of fits to continuum-removed spectra are directly comparable to results of fits done without continuum removal. Such consistency is essential for compositional predictions based on the results of the fits, because the trend lines used for the predictions were developed from fits done without any continuum removal. Our procedure for evaluating the effect of continuum removal is to perform continuum removal on a series of laboratory spectra using the method described above. An example of the continuum removal process is

shown in Figure 2 for the spectrum of San Carlos olivine shown in Figure 1. A series of standard fits (based on the starting fits described by Isaacson and Pieters [2010], as discussed above) were then performed on the continuum-removed spectra as well as the original spectra, varying only the initial continuum offset to be appropriate for each case, as discussed above. As described above, the tangent points for definition of the local continuum slope were optimized individually for the short wavelength point and fixed at 1700 nm for the long wavelength point.

2.2.1 Band Shift

After performing the described series of fits, the MGM-derived band centers of the continuum-removed and original spectra (from the same fits) were then compared, and the differences between continuum-removed band centers and non-continuum-removed band centers were defined as a “band shift”:

$$Shift_n = \lambda_{CR,n} - \lambda_{O,n} \quad (1)$$

In (1), n refers to the specific absorption (Gaussian), CR refers to the continuum-removed spectrum, and O refers to the original (non-continuum-removed) spectrum. Positive band shift values indicate that the apparent band positions shift to longer wavelengths after continuum removal. Note that this does not indicate that the bands move physically ; the positions of the absorptions are controlled by mineral physics as described by crystal field theory [e.g., *Burns*, 1970; *Burns*, 1993]. The shift is an apparent shift induced by the continuum removal process.

The spectra included in these analyses included the San Carlos olivine spectrum shown in Figure 1 (RELAB San Carlos a.k.a. RSC), a spectrum of an olivine separate from lunar sample 72415 (~Fo₈₈) (both RSC and 72415 were studied by Isaacson and

Pieters [2010]), and spectra of a series of San Carlos olivines subjected to pulsed laser irradiation of varying intensity in an attempt to simulate the space weathering process [Yamada *et al.*, 1999; Sasaki *et al.*, 2002; Sasaki *et al.*, 2003]. This suite of laboratory spectra will be referred to as the “evaluation suite”. The irradiated San Carlos (ISC) spectra are particularly useful for this evaluation because they exhibit a range of continuum slopes in spectra of an olivine of constant composition, and analysis by Hiroi and Sasaki [2001] suggests that the absorption bands do not move with increased irradiation. Thus, any band shift detected by our analyses can be attributed to continuum removal. This suite of spectra is plotted in Figure 3.

2.2.2 Band Shift Correction

After calculating band shift values for the three component olivine absorptions across the suite of spectra, the band shift results were evaluated in the context of the continuum slopes removed from each of the spectra. This was done by plotting the band shift results for each component absorption vs. the continuum slopes removed from the spectra. Trend lines were fit to the band shift vs. continuum slope results in a least squares sense, and were fit separately for each component absorption. This produced a distinct trend line for each component absorption. The trend line fits were constrained to pass through the origin, as no band shift can be observed for spectra from which no continuum slope is removed. The trend lines were calculated based only on the ISC results, as they provide a self-consistent suite in which the only variable is degree of irradiation. The 72415 and RSC results are generally consistent with the ISC results, but potentially add additional complexity because of the differences between these samples/spectra and those of the ISC suite. To avoid these complexities, the 72415 and

RSC results were excluded from the trend line fits. In other words, the ISC spectra represent the best opportunity to capture systematic trends in apparent band position based on the effect of continuum slope and continuum removal. From the calculated trend lines, corrections to the MGM-derived band centers produced from fits to continuum-removed spectra were defined. Put simply, the band shift correction (BSC) for a spectrum m and component absorption n is calculated as:

$$BSC_{m,n} = TLS_n * LCS_m \quad (2)$$

TLS refers to the slope of the trend line fit to the band shift results for the ISC spectra for absorption n . LCS is the slope of the local continuum for spectrum m (tangent on either side of the olivine absorption, as was done to remove the continuum from the evaluation suite laboratory spectra). Corrected band positions are determined by applying this band shift correction for each component absorption. The corrected band centers are used to predict the composition of the olivine using the methods described by Isaacson and Pieters [2010].

2.3 Application to M^3 Spectra

These procedures (continuum removal, MGM fits, band shift correction, compositional prediction) were applied to a suite of olivine-dominated reflectance spectra collected by the Moon Mineralogy Mapper (M^3) in its low-resolution mode of 140 m/pixel spatial resolution and 20-40 nm spectral resolution. A description of the M^3 instrument and data is provided by Pieters et al. [2009], and a condensed version can be found in Appendix B. Here, we focus on a suite of olivine-dominated spectra extracted from the region around the Moscoviense basin. Olivine-rich areas were highlighted by using a ratio of the integrated band strengths at 1000 and 2000 nm. In our formulation

(1000 nm / 2000 nm), spectra with strong 1000 nm features and weak 2000 nm features, such as olivine, will have high values in this ratio parameter. This approach is highlighted in Figure 4, which shows this ratio parameter mapped in color overlaid on a M^3 albedo band for context. Areas showing up in “hot” colors in this scheme will tend to be olivine-rich. A number of spectra were extracted, although only the “best” (most pure olivine signature) were selected for MGM fitting. The band shift correction was applied based on the results of the ISC subset of the evaluation suite. The absolute correction is derived for each spectrum based on its continuum slope (LCS in equation (2)) and the results of the evaluation suite analyses (TLS in equation (2)).

3 Results

3.1 Laboratory Spectra

3.1.1 MGM Fits

The selected tangent points and the slope of the local continuum removed from the laboratory spectra are provided in Table 1. The significant chromite absorption in the 72415 olivine spectrum necessitated an alternate long wavelength tangent point, while a standard long wavelength tangent point was used for all other spectra. The continuum removal process for these spectra, based on the values provided in Table 1, is illustrated in Figure 5. Example fits to the evaluation suite are illustrated in Figure 6. Full results of the MGM analyses of the evaluation suite, both original and continuum-removed based on the parameters in Table 1, are reported in Tables 2 (original) and 3 (continuum-removed). The multiple entries for each spectrum refer to the various starting points for the MGM. As discussed above, a range of initial parameters were evaluated, although

only those parameters that were the most logical and consistent with the evaluation suite spectra are reported here. Band centers for both sets are compared directly in Table 4, with continuum removal parameters from Table 1 provided for reference.

3.1.2 Band Shift and Band Shift Correction

Table 5 reports band shift values obtained by comparing the fits of continuum-removed evaluation suite spectra to fits of non-continuum-removed evaluation spectra. The band shift values reported in Table 5 are plotted against the slope of the local continuum removed in Figure 7. This plot is the basis of the band shift correction, as the band shift correction for any analyzed spectrum can be determined for each component absorption by solving for band shift (Y) based on the continuum slope removed from that spectrum (X). The trend lines shown on this plot were calculated from the ISC spectra only, as discussed in the Methods section. The slopes of the trend lines plotted in Figure 7 are reported in Table 6. Because these trend lines are constrained to pass through the origin, offset values are not reported.

3.2 M^3 Spectra

3.2.1 MGM Fits

Examples of M^3 spectra collected from olivine-rich areas, as highlighted by Figure 4, are plotted in Figure 8. The numbering scheme for the spectra in this figure and in subsequent tables refers to the original suite extracted, of which only a subset was evaluated with the MGM deconvolutions, explaining the discontinuous numbering. Example fits to these spectra are illustrated in Figure 9. It should be noted that more spectra were evaluated than are shown in Figures 8 and 9, but the spectra shown in those

figures are representative of the suite. The slopes removed from the M^3 spectra prior to performing the MGM fits are reported in Table 7. The full results of the MGM fits to the M^3 spectra are reported in Table 8. As was done with the laboratory spectra, a range of starting points for the deconvolutions were employed. We report only the results from the intermediate starting point, as it allows more freedom for the fit to converge on the best result.

3.2.2 Band Shift Corrections and Predicted Compositions

The calculated band shift values for these spectra, based on the continuum slope removed as reported in Table 7, are reported in Table 9, as are the corrected band positions. The predicted compositions (Mg') from the MGM fits to these spectra, both original and from the band shift corrections, are also reported in Table 9. The results of the compositional predictions are shown in Figure 10, in which the predicted compositions are plotted on the Y axis and the MGM-derived band positions for the three component absorptions are plotted on the X axis. Open symbols refer to the original fits, and filled symbols refer to the band shift corrected results.

4 Discussion

4.1 Effect of Continuum Removal: Laboratory Spectra

4.1.1 MGM Fits

Examples of fits to the original and continuum-removed spectra are shown in Figure 6, and full results of the MGM fits are reported in Tables 2 and 3. While a wide range of initial MGM parameters were used to capture the systematics fully, we report only those starting points most consistent with the compositions of the laboratory spectra

analyzed, as it minimizes uncertainty about the effect of starting point on derived band centers for the two cases and allows the effect of continuum removal to be isolated more thoroughly. Before discussing band center results, note the effect of continuum removal on relative band strengths. This is particularly apparent in the 15 mJ spectrum, which exhibits a fairly pronounced local continuum slope. Prior to continuum removal, the M1-1 band is disproportionately strong based on relative band strengths determined for terrestrial olivine spectra [*Sunshine and Pieters, 1998*]. This result is due to the use of as a flat continuum slope in the deconvolution, which necessitates a stronger band to account for the sloped nature of the spectrum. Continuum removal causes the band strengths to be more consistent with the anticipated trends from laboratory analyses. While difficult to see in plots such as Figure 6, systematic differences in the MGM-derived band positions are observed between fits to continuum-removed and fits to non-continuum-removed spectra. The results presented in Tables 2 and 3 are condensed in Table 4, which reports only band centers for the three principal absorptions and the slope of the local continuum removed.

4.1.2 Band Shifts

By comparing the band centers for fits to continuum-removed and non-continuum-removed spectra, a “band shift” is determined, as reported in Table 5. Band shift, as described in the methods, is defined as the continuum-removed band center minus the band center for the original spectrum. A general trend of increasing band shifts with increasing local continuum slope was observed, suggesting that the continuum-removal process causes an apparent shift in band position that becomes more severe with increased slope of the local continuum removed from the spectrum. We are not

suggesting that the physical absorption bands actually move based on continuum slope; absorption features are linked to electronic transitions in cations in crystallographic sites, and their position in wavelength space is linked to the crystal structure of the mineral. However, the continuum removal process apparently causes the bands to appear shifted to longer wavelengths, and thus a correction is required in order to compare continuum-removed results to laboratory results obtained using flat continuum slopes and no continuum removal.

Our band shift results for the evaluation suite are illustrated in Figure 7. Symbols refer to the three component absorptions as indicated by the legend in the upper left. Colors refer to the spectrum in the evaluation suite, as indicated by the labels in the lower right. While we limited our analyses to spectra with positive (“red”) continuum slopes that dominate lunar VNIR reflectance spectra, the 72415 spectrum does exhibit a minor negative slope and does fall near the trend lines derived for the ISC spectra, suggesting that our approach could be applied to spectra with negative (“blue”) continuum slopes as well. While the fits are not ideal, particularly for the M1-1 band, the overall trends are clearly of increasing band shift with increased continuum slope. Even this conclusion shows that if the continuum-removal approach is applied to remotely-sensed spectra, the band shift effect must be considered if direct comparisons to laboratory results (necessary for compositional predictions in our approach) are to be made. The scatter in the M1-1 results are somewhat concerning, but this band does tend to show the most scatter even in terrestrial olivine spectra, which suggests that the scatter observed in our results may not be entirely due to our approach [Sunshine and Pieters, 1998]. The slopes of these trend

lines are reported in Table 6, and are the basis of the band shift correction (they are the *TLS* variable in equation (2)).

4.2 Application to M^3 spectra

4.2.1 MGM Fits

We performed continuum removal to the M^3 spectra with the same method used for the laboratory spectra. Because the basis of the band shift correction is the continuum slope removed from a spectrum, the values of the local continuum slopes were recorded, as reported in Table 7. The results of MGM deconvolutions to these spectra are reported in Table 8, with only the results of the intermediate starting point reported, as discussed in the Results section. Example fits, based on the same example M^3 spectra shown in Figure 8, are shown in Figure 9. Immediately apparent is the higher level of “noise” in the M^3 spectra relative to laboratory spectra, as evidenced by the high-frequency variation in the input spectra (black X’s). Also apparent is the reduced spectral sampling of M^3 across this wavelength region (20 nm). These factors combine to produce noisier fits, as indicated by the dotted pink RMS error line. Relative to fits to the continuum-removed laboratory spectra, higher continuum offsets were used for fits to the M^3 spectra. We experimented with a range of offset values, and found that for these spectra, a higher offset value allowed the individual Gaussians more freedom to move and converge on the appropriate fit result. Note also the apparent errors in the fit at extreme short and especially long wavelengths. This is a byproduct of the high continuum offset and the use of only one Gaussian to model the outer wavelengths. This is inconsequential to the MGM results for the three principal olivine absorptions. The angularity of the Gaussians

(and consequentially of the spectral fit) is a product of the reduced spectral sampling of the M^3 spectra in comparison to the laboratory spectra (5 nm).

4.2.2 Band Shifts, Predicted Compositions, and Precautions

The products of the MGM fits to the M^3 spectra are provided in Table 9, which lists the band shift values derived from the local continuum slopes of the M^3 spectra and the slopes of the trend lines in Figure 7. Table 9 also lists the corrected band center values (after applying the band shift correction) for each of the three principal olivine absorptions for M^3 spectra. The results of the compositional predictions are also reported. While formal “error bars” are not reported for the compositional predictions, the predictions should not be interpreted with the degree of precision they are reported. A procedure for quantifying the error in such predictions has not been defined explicitly. Future work on this subject will likely focus on deconvolutions of laboratory spectra with reduced spectral sampling and various levels of random noise introduced. For the results presented here, while errors for the predictions cannot be quantified, their precision is surely significantly greater than their accuracy. In other words, the compositional prediction equation yields a value assuming that the input band centers are known absolutely (no errors are incorporated in the prediction). A number of factors, such as spectral sampling and noise, ensure that this is not the case, particularly with the reduced spectral resolution of the M^3 data. Even in the ideal case of MGM deconvolutions of laboratory olivine reflectance spectra, compositional predictions with this approach can be accurate only to within ~5-10% (5-10 range of Fo#) [Sunshine and Pieters, 1998; Isaacson and Pieters, 2010], and the accuracy of these predictions based on M^3 spectra is

surely degraded substantially from that 5-10% level of accuracy. Thus, our reported compositions should be viewed and interpreted as approximate solutions.

Despite the caveats regarding over-interpretation of the predicted compositions, the compositions predicted from the M^3 spectra generally are consistent with compositions of olivines analyzed in lunar samples. The olivine compositions predicted from fits to the M^3 spectra appear to be less Mg-rich than those of Mg-suite rocks (typically near $\sim\text{Fo}_{90}$ or slightly below) [e.g., *Dymek et al.*, 1975], but more Mg-rich than the average of olivines found in mare basalts. Olivines in mare basalts can cover a wide range of compositions, from $\sim\text{Fo}_{80}$ to Fo_0 , but are generally more iron-rich than Mg-suite olivines [1976]. Our predicted compositions are consistent, however, with olivines found in feldspathic lunar meteorites such as ALHA81005 (although the compositions are also consistent with the most Mg-rich olivines found in mare basalts). While the feldspathic breccias contain a wide variety of phases, olivines with compositions of Fo_{65} - Fo_{80} (and occasionally lower) are common [e.g., *Kurat and Brandstatter*, 1983; *Isacson et al.*, 2009]. Furthermore, ALHA81005 likely originated from the farside feldspathic highlands, based on its overall feldspathic composition and low abundance of KREEP [e.g., *Kallemeyn and Warren*, 1983; *Pieters et al.*, 1983], making the correlation between olivine compositions more robust. Note that we do not suggest that our results indicate a probable source region for ALHA81005. We merely point out the similarity in olivine compositions as a consistency check for our methods.

4.3 Mixtures

Currently, our approach is applicable only to spectra in which olivine is the dominant phase (i.e., no other ferrous absorptions in the 1000 nm region). This rules out

compositional analyses of pyroxene-olivine mixtures. Olivine-plagioclase mixtures can be analyzed, especially if the plagioclase is in its shocked form (maskelynite) and lacks its typical feature near 1300 nm [e.g., *Bell and Mao*, 1973; *Adams and Goullaud*, 1978; *Pieters*, 1996]. Crystalline, Fe-bearing plagioclase does exhibit absorptions near 1300 nm, and if such absorption features were detectable in the olivine-plagioclase mixture spectrum, that spectrum could not be analyzed with our present approach. However, the plagioclase absorption feature does tend to get masked by other mafic absorptions such as those of olivine and pyroxene [e.g., *Isaacson et al.*, 2010], meaning that olivine-plagioclase mixtures generally can be analyzed with our approach except in rare cases where the plagioclase absorption feature persists.

Our approach could in theory be applied to spectra of mixtures such as olivine-pyroxene. The complications lie in determining the properties of the olivine absorptions in the presence of additional absorptions near 1000 nm. As discussed above, the MGM seeks a mathematically-optimized solution, without regard for whether or not the fit is physically reasonable (consistent with the mineralogy of the material represented by the input spectrum). Each Gaussian is based on three model parameters (position, strength, and width), so the presence of additional absorption features substantially increases the number of free parameters in the model, and reduces the likelihood of obtaining a unique and physically reasonable fit. However, if a method were available to constrain the model parameters appropriately and allow the olivine absorptions to be deconvolved properly, our approach could certainly be used to predict the composition of the olivine. For example, the 2000 nm pyroxene absorption feature could be used to help constrain the Gaussian(s) used to model the pyroxene 1000 nm absorption feature, as the properties

of the pyroxene absorption features are related [e.g., *Adams*, 1974; *Hazen et al.*, 1978; *Cloutis et al.*, 1986; *Klima*, 2008]. In the case of lunar olivine, however, this approach would in turn be complicated by the presence of the chromite absorptions near 2000 nm.

5 Conclusions

We have demonstrated an approach for dealing with the multitude of complications in remotely-sensed lunar olivine reflectance spectra not present in laboratory spectra of terrestrial olivine. Our work builds on the work of Isaacson and Pieters, which addressed the implications of the chromite inclusions common to lunar olivines. The present study has demonstrated a systematic approach for addressing variable continuum slopes common to remotely-sensed spectra of planetary surfaces. Using a suite of laboratory spectra, we have demonstrated that the continuum removal process causes a systematic shift in apparent MGM-derived band position that must be corrected in order to make direct comparisons with trends in terrestrial olivine spectra. This is a vital correction, as these trends are the basis of compositional predictions from MGM deconvolutions of olivine spectra. Our evaluation was limited to spectra with positive continuum slopes, although there is no physical reason that the approach could not be applied to spectra with negative (“blue”) continuum slopes.

The reduced spectral sampling and lower signal to noise ratio of the M^3 spectra relative to typical laboratory spectra affect the accuracy of compositional predictions. We cannot quantify the degree to which the accuracy of the predictions based on M^3 spectra is degraded relative to predictions based on laboratory spectra, but suggest potential methods by which this degradation could be estimated. However, our analyses of a suite of olivines from near the northwest rim of the Moscoviense basin on the lunar

farside indicate that the composition of the olivines is less magnesian than olivines from Mg-suite rocks in the Apollo collection, somewhat more magnesian than the average composition of mare basalt olivines (but not inconsistent with some of the more Mg-rich olivines found in mare basalts), and consistent with olivines found in feldspathic lunar meteorites such as ALHA81005. This approach is applicable to remotely-sensed spectra of the lunar surface dominated by olivine (spectra of mixtures will require additional constraints). Furthermore, the techniques demonstrated and validated here are also applicable to reflectance spectra collected from other planetary surfaces such as Mars.

6 References

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Table 1. Local continuum slope parameters for evaluation suite spectra

Sample ¹	Tan. λ Short	Tan. λ Long	Slope ²
RSC	665	1700	7.03
72415	680	1590	-1.48
ISC 0	580	1700	5.42
ISC 1	580	1700	4.24
ISC 15	700	1700	20.0
ISC 30	730	1700	28.7

¹RSC = RELAB San Carlos, 72415 = 72415 Olivine, ISC = Irradiated San Carlos (numbers refer to pulse laser intensity, higher indicating greater degree of irradiation).

²Slope * 1E5. Units: Reflectance/ λ , λ in nm.

Table 2. MGM Results for Fits to the Evaluation Suite Spectra Without Continuum Removal

Spectrum	St. Point	M1-1 Ctr. ¹	M1-1 FWHM ²	M1-1 Intensity ³	M2 Center	M2 FWHM	M2 Intensity	M1-2 Center	M1-2 FWHM	M1-2 Intensity
RSC	Mg High	841.6	228.5	-0.219	1034.5	177.1	-0.264	1213.8	426.5	-0.356
	Int. High	842.0	228.6	-0.220	1034.7	177.3	-0.265	1214.4	425.9	-0.356
	Mg Low	840.9	228.1	-0.203	1034.0	176.1	-0.254	1208.8	424.2	-0.341
	Int. Low	841.6	228.2	-0.206	1034.3	176.2	-0.256	1210.0	423.6	-0.343
72415	Mg High	862.0	225.1	-0.293	1040.1	171.4	-0.403	1209.8	422.1	-0.545
	Int. High	862.1	225.1	-0.294	1040.1	171.5	-0.404	1209.9	421.8	-0.545
	Mg Low	862.5	225.0	-0.293	1040.2	171.2	-0.403	1209.8	421.0	-0.543
	Int. Low	862.6	225.0	-0.293	1040.2	171.3	-0.404	1210.0	420.6	-0.543
ISC 0 mJ	Mg High	847.6	228.4	-0.209	1046.0	177.7	-0.257	1244.7	428.0	-0.354
	Int. High	847.9	228.6	-0.210	1046.1	177.8	-0.258	1245.2	427.4	-0.355
	Mg Low	847.9	228.2	-0.204	1046.0	176.9	-0.254	1243.5	426.7	-0.349
	Int. Low	848.1	228.3	-0.205	1046.1	177.0	-0.255	1244.1	426.1	-0.350

ISC 1 mJ	Mg High	850.5	228.5	-0.208	1046.1	177.9	-0.260	1242.2	428.7	-0.371
	Int. High	850.8	228.6	-0.209	1046.2	178.0	-0.261	1242.6	428.1	-0.372
	Mg Low	850.8	228.3	-0.204	1046.1	177.2	-0.258	1241.4	427.4	-0.367
	Int. Low	851.0	228.4	-0.205	1046.2	177.3	-0.259	1241.9	426.8	-0.367
ISC 15 mJ	Mg High	843.1	230.0	-0.303	1043.9	181.5	-0.291	1234.5	435.0	-0.411
	Int. High	843.4	230.1	-0.303	1044.0	181.6	-0.292	1234.8	434.3	-0.411
	Mg Low	841.3	229.8	-0.290	1043.4	181.0	-0.282	1230.8	434.6	-0.397
	Int. Low	841.6	229.9	-0.291	1043.6	181.1	-0.283	1231.3	433.9	-0.397
ISC 30 mJ	Mg High	843.1	231.1	-0.356	1042.8	184.1	-0.309	1229.1	438.4	-0.420
	Int. High	843.3	231.3	-0.355	1042.9	184.2	-0.309	1229.3	437.7	-0.419
	Mg Low	840.9	230.9	-0.344	1042.2	183.3	-0.298	1224.3	437.3	-0.404
	Int. Low	841.1	231.0	-0.344	1042.3	183.4	-0.299	1224.6	436.6	-0.403

¹Band Centers reported in nm

²FWHM values in nm

³Intensity reported as natural log reflectance

Table 3. MGM results for fits to the evaluation suite spectra after continuum removal

Spectrum	St. Point	M1-1 Ctr. ¹	M1-1 FWHM ²	M1-1 Intensity ³	M2 Center	M2 FWHM	M2 Intensity	M1-2 Center	M1-2 FWHM	M1-2 Intensity
RSC	Mg High	858.1	227.6	-0.169	1038.6	175.9	-0.244	1220.6	424.7	-0.333
	Int. High	858.1	227.7	-0.170	1038.7	176.0	-0.245	1221.1	424.2	-0.333
	Mg Low	859.5	227.4	-0.166	1038.8	175.4	-0.241	1219.2	423.6	-0.329
	Int. Low	859.6	227.5	-0.166	1038.8	175.5	-0.242	1219.8	423.0	-0.329
72415	Mg High	859.4	225.7	-0.302	1039.3	171.6	-0.407	1207.8	419.4	-0.546
	Int. High	859.4	225.7	-0.302	1039.3	171.6	-0.407	1208.0	419.0	-0.545
	Mg Low	860.3	225.4	-0.301	1039.4	171.1	-0.407	1207.9	416.8	-0.543
	Int. Low	860.4	225.5	-0.302	1039.5	171.1	-0.407	1208.0	416.4	-0.542
ISC 0 mJ	Mg High	856.6	228.2	-0.181	1048.5	177.7	-0.247	1250.2	427.7	-0.348
	Int. High	856.7	228.3	-0.182	1048.6	177.8	-0.248	1250.6	427.1	-0.348
	Mg Low	857.6	227.9	-0.179	1048.6	176.5	-0.245	1249.7	426.2	-0.345
	Int. Low	857.7	228.0	-0.180	1048.8	176.7	-0.246	1250.1	425.5	-0.345

ISC 1 mJ	Mg High	857.8	228.3	-0.185	1048.0	177.7	-0.251	1246.0	428.2	-0.364
	Int. High	858.0	228.4	-0.186	1048.1	177.9	-0.252	1246.5	427.7	-0.364
	Mg Low	858.8	227.9	-0.184	1048.2	176.6	-0.250	1245.8	426.4	-0.362
	Int. Low	859.0	228.1	-0.184	1048.3	176.7	-0.251	1246.2	425.9	-0.362
ISC 15 mJ	Mg High	862.7	227.8	-0.141	1049.8	176.3	-0.230	1246.0	425.1	-0.330
	Int. High	862.6	227.9	-0.142	1049.8	176.4	-0.231	1246.6	424.5	-0.331
	Mg Low	864.6	227.7	-0.136	1050.0	175.9	-0.226	1244.6	424.8	-0.325
	Int. Low	864.7	227.7	-0.137	1050.1	175.9	-0.227	1245.1	424.0	-0.326
ISC 30 mJ	Mg High	858.2	227.7	-0.110	1049.7	175.8	-0.213	1245.2	423.0	-0.287
	Int. High	858.0	227.7	-0.112	1049.8	175.9	-0.215	1246.1	422.4	-0.288
	Mg Low	860.7	227.6	-0.101	1049.8	175.7	-0.205	1241.4	423.8	-0.280
	Int. Low	861.1	227.7	-0.102	1049.9	175.6	-0.206	1242.0	422.9	-0.280

¹Band Centers reported in nm

²FWHM values in nm

³Intensity reported as natural log reflectance

Table 4. Comparison of MGM-derived band centers for evaluation suite spectra, with and without continuum removal (CR = continuum-removed)

Spectrum	Fit	M-1 Ctr.	M2 Ctr.	M1-2 Ctr.	M1-1 Ctr. CR	M2 Ctr. CR	M1-2 Ctr. CR	Cont. Slope ¹	Cont. Intercept
RSC	Mg High	841.6	1034.5	1213.8	858.10	1038.6	1220.6	7.03	0.685
	Int. High	842.0	1034.7	1214.4	858.1	1038.7	1221.1	7.03	0.685
	Mg Low	840.9	1034.0	1208.8	859.5	1038.8	1219.2	7.03	0.685
	Int. Low	841.6	1034.3	1210.0	859.6	1038.8	1219.8	7.03	0.685
72415	Mg High	862.0	1040.1	1209.8	859.4	1039.3	1207.8	-1.48	0.587
	Int. High	862.1	1040.1	1209.9	859.4	1039.3	1208.0	-1.48	0.587
	Mg Low	862.5	1040.1	1209.8	860.3	1039.4	1207.9	-1.48	0.587
	Int. Low	862.6	1040.2	1210.0	860.4	1039.5	1208.0	-1.48	0.58
ISC 0 mJ	Mg High	847.6	1046.0	1244.7	856.6	1048.5	1250.2	5.42	0.843
	Int. High	847.9	1046.1	1245.2	856.7	1048.6	1250.6	5.42	0.843
	Mg Low	847.9	1046.0	1243.5	857.6	1048.6	1249.7	5.42	0.843
	Int. Low	848.1	1046.0	1244.1	857.7	1048.8	1250.1	5.42	0.843
ISC 1 mJ	Mg High	850.5	1046.1	1242.2	857.8	1048.0	1246.0	4.24	0.848
	Int. High	850.8	1046.2	1242.6	858.0	1048.1	1246.5	4.24	0.848
	Mg Low	850.8	1046.1	1241.4	858.81	1048.2	1245.8	4.24	0.848
	Int. Low	851.0	1046.2	1241.9	859.0	1048.3	1246.2	4.24	0.848
ISC 15 mJ	Mg High	843.1	1043.9	1234.5	862.7	1049.8	1246.0	20.0	0.516
	Int. High	843.4	1044.0	1234.8	862.6	1049.8	1246.6	20.0	0.516
	Mg Low	841.3	1043.4	1230.8	864.6	1050.0	1244.6	20.0	0.516
	Int. Low	841.6	1043.6	1231.3	864.7	1050.1	1245.1	20.0	0.516

ISC 30 mJ	Mg High	843.1	1042.8	1229.1	858.2	1049.7	1245.2	28.7	0.341
	Int. High	843.3	1042.9	1229.3	858.0	1049.8	1246.1	28.7	0.341
	Mg Low	840.9	1042.2	1224.3	860.7	1049.8	1241.4	28.7	0.341
	Int. Low	841.1	1042.3	1224.6	861.1	1049.9	1242.0	28.7	0.341

¹Slope * 1E5. Units: Reflectance/ λ , λ in nm.

Table 5. Band Shift Results for Evaluation Suite Spectra

Spectrum	St. Pt. ¹	M-1 Shift	M2 Shift	M1-2 Shift	Cont. Slope ²	Cont. Intercept
RSC	Mg High	16.54	4.06	6.81	7.03	0.685
	Int. High	16.14	3.94	6.72	7.03	0.685
	Mg Low	18.64	4.80	10.44	7.03	0.685
	Int. Low	17.95	4.48	9.71	7.03	0.685
72415	Mg High	-2.67	-0.79	-1.93	-1.48	0.587
	Int. High	-2.65	-0.79	-1.95	-1.48	0.587
	Mg Low	-2.21	-0.72	-1.86	-1.48	0.587
	Int. Low	-2.18	-0.72	-1.94	-1.48	0.58
ISC 0 mJ	Mg High	8.96	2.48	5.49	5.42	0.843
	Int. High	8.77	2.43	5.44	5.42	0.843
	Mg Low	9.66	2.69	6.18	5.42	0.843
	Int. Low	9.60	2.66	5.96	5.42	0.843
ISC 1 mJ	Mg High	7.37	1.97	3.85	4.24	0.848
	Int. High	7.21	1.93	3.82	4.24	0.848
	Mg Low	7.94	2.12	4.37	4.24	0.848
	Int. Low	7.91	2.11	4.25	4.24	0.848
ISC 15 mJ	Mg High	19.55	5.84	11.53	20.0	0.516
	Int. High	19.19	5.78	11.81	20.0	0.516
	Mg Low	23.26	6.59	13.78	20.0	0.516
	Int. Low	23.03	6.55	13.77	20.0	0.516
ISC 30 mJ	Mg High	15.07	6.87	16.09	28.7	0.341
	Int. High	14.73	6.83	16.80	28.7	0.341
	Mg Low	19.82	7.62	17.09	28.7	0.341
	Int. Low	19.99	7.68	17.45	28.7	0.341

¹Starting point for MGM fit. Mg/Int. refers to band positions (Mg-rich, Intermediate) following the Isaacson and Pieters approach. High/Low refers to initial continuum offset.

²Slope * 1E5. Units: Reflectance/ λ , λ in nm.

Table 6. Slopes of Trend Lines in Band Shift vs. Continuum Slope Plot (Figure 7)

Band	Band Shift Trend Slope ¹ (ISC Constrained)
M1-1	79221.4
M2	27880.3
M1-2	61897.9

¹Slope value assumes band shifts are in units of nm, and local continuum slopes are in units of reflectance / nm.

Table 7. Local Continuum Slopes removed from M³ Spectra Prior to MGM Fits

Spectrum	Continuum Slope ¹	Continuum Offset
9	9.80E-05	0.317
12	8.80E-05	0.248
16	1.57E-04	0.238
17	1.36E-04	0.298
18	1.29E-04	0.353
21	1.04E-04	0.169
22	9.40E-05	0.147
23	1.06E-04	0.146
24	8.10E-05	0.166
25	1.27E-04	0.137

¹Slope value assumes band shifts are in units of nm, and local continuum slopes are in units of reflectance / nm.

Table 8. MGM Results for Continuum-Removed M³ Spectra

Spectrum	M1-1 Ctr. ¹	M1-1 FWHM ²	M1-1 Intensity ³	M2 Center	M2 FWHM	M2 Intensity	M1-2 Center	M1-2 FWHM	M1-2 Intensity
9	853.6	228.1	-0.154	1033.9	176.0	-0.132	1256.5	424.7	-0.261
12	864.0	228.0	-0.153	1032.9	176.1	-0.135	1247.2	424.4	-0.266
16	868.7	228.0	-0.128	1028.6	176.1	-0.117	1247.6	424.3	-0.235
17	867.1	228.0	-0.165	1033.6	176.1	-0.123	1240.8	424.3	-0.236
18	855.1	228.1	-0.151	1033.2	176.0	-0.106	1245.7	424.4	-0.237
21	854.4	228.1	-0.133	1033.7	176.0	-0.114	1248.6	424.3	-0.225
22	855.0	228.1	-0.132	1031.0	176.0	-0.114	1245.0	424.3	-0.210
23	855.3	228.1	-0.120	1033.2	176.0	-0.106	1247.6	424.3	-0.206
24	858.7	228.1	-0.160	1035.1	176.0	-0.115	1242.5	424.3	-0.214
25	857.6	228.1	-0.122	1030.0	176.0	-0.084	1241.6	424.2	-0.165

¹Band Centers reported in nm²FWHM values in nm³Intensity reported as natural log reflectance

Table 9. Band Shift Corrections and Predicted Olivine Compositions for Evaluated M³ Spectra

Spectrum	Cont. Slope ¹	M1-1 Shift	Corr. M1-1 Ctr.	M2 Shift	Corr. M2 Ctr.	M1-2 Shift	Corr. M1-2 Ctr.	Corrected Comp. ²
9	9.80E-05	7.8	845.9	2.7	1031.2	6.1	1250.4	66.3
12	8.80E-05	7.0	857.1	2.5	1030.5	5.4	1241.8	66.0
16	1.57E-04	12.4	856.2	4.4	1024.2	9.7	1237.9	70.1
17	1.36E-04	10.8	856.3	3.8	1029.9	8.4	1232.4	71.5
18	1.29E-04	10.2	844.9	3.6	1029.6	8.0	1237.7	73.9
21	1.04E-04	8.2	846.1	2.9	1030.8	6.4	1242.2	70.7
22	9.40E-05	7.4	847.5	2.6	1028.3	5.8	1239.2	72.3
23	1.06E-04	8.4	846.9	3.0	1030.3	6.6	1241.0	71.1
24	8.10E-05	6.4	852.3	2.3	1032.9	5.0	1237.5	69.9
25	1.27E-04	10.1	847.5	3.5	1026.4	7.9	1233.7	75.6

¹Continuum slopes are in units of reflectance / nm.

²The precision of the compositional prediction is much higher than its accuracy, as there is uncertainty in the MGM band positions but the prediction equations treat the band positions as absolutely certain. Composition is reported as Fo# ($Mg^{\circ} = Mg/(Mg+Fe)$).

Figure Captions

Figure 1. Bidirectional reflectance spectrum of San Carlos olivine ($\sim\text{Fo}_{90}$). The component absorptions that comprise the composite olivine 1000 nm absorption feature are labeled with the Fe^{2+} -bearing site responsible for the component absorption. Note the bright, featureless nature of the spectrum beyond ~ 1500 nm.

Figure 2. Demonstration of the continuum removal process using a local continuum slope tangent on either side of the principal absorption feature, with the long wavelength point fixed at 1700 nm and the short wavelength point variable depending on the spectrum. The short wavelength tangent point for this spectrum is at 665 nm, as indicated in Table 1. The thin line is the original spectrum, the dashed line the local continuum slope, and the heavy line the continuum-removed spectrum. The long wavelength slope in the continuum-removed spectrum is negative because the continuum slope is steeper than the original spectrum in this wavelength region.

Figure 3. Laboratory reflectance spectra used to evaluate the effect of the continuum removal process on the MGM-derived band parameters (“evaluation suite”). (a) RELAB San Carlos (RSC) and 72415 olivine. Data from Isaacson and Pieters [2010]. (b) Weathered San Carlos (ISC) spectra subjected to varying degrees of laser energy as labeled in the lower left. Data from Yamada et al. [1999].

Figure 4. Integrated band depth ratio image for small crater northwest of Mare Moscoviense. Color overlay is a ratio of the integrated band depths (IBD) over the 1000 and 2000 nm ferrous absorption features. High values indicate spectra with strong 1000 nm and weak 2000 nm absorptions, suggestive of olivine-rich lithologies. This map was used as a guide to select the olivine-dominated reflectance spectra analyzed in this study. The base image is a single M^3 band near 3000 nm that is sensitive to morphology. Image is ~ 40 km across.

Figure 5. Continuum removal process for the evaluation suite presented in Figure 3. The line style scheme is the same as in Figure 3, and the color scheme is as labeled in the lower left of each sub-figure. The arrangement of samples between top and bottom is the same as in Figure 3. Note the range of continuum slopes exhibited by these spectra, including the slightly negative slope of 72415. The tangent points are as indicated in Table 1.

Figure 6. Example MGM fits to selected spectra from the evaluation suite (Figures 3 and 5). Original spectra are on the top, and continuum-removed on the bottom, labeled with “CR”. The left side shows the San Carlos RELAB (S.C.R.) spectra, and the right side shows the ISC 15 mJ spectra. Note the differing continuum slopes between S.C.R. and ISC 15 mJ prior to continuum removal, leading to a disparity in relative band strengths that is resolved after continuum removal. These fits were all produced from the same MGM starting point, with only the continuum offset adjusted.

Figure 7. Band shift values calculated by comparing fits of continuum-removed spectra to fits of the original spectra using the same starting points. Symbol styles indicate the component absorption, as indicated in the upper left, while colors indicate the spectrum, as labeled in the lower right. Trend lines were calculated from the ISC spectra only and are constrained to pass through the origin. RSC band shift values are plotted in open symbols, as they were excluded from the trend line fits. The trend line fits are discussed more thoroughly in the text. The trend lines are labeled with open versions of the symbols used to indicate the component absorption, and are plotted in grey. The slopes of these trend lines are the basis of the band shift correction.

Figure 8. Example M^3 spectra collected from the region illustrated in Figure 4. These do not make up the full suite of spectra analyzed, but are representative of the suite. The numbering of the spectra refers to the full suite, explaining the non-sequential numbering. The spectra have been truncated at 2600 nm to enable direct comparison with laboratory spectra.

Figure 9. Example MGM fits to continuum-removed M^3 spectra. The examples shown are fits to the same spectra shown in Figure 8 after applying our continuum removal approach. The same color scheme is used as in Figure 6. The angular nature of the Gaussians is a product of the reduced spectral sampling of M^3 relative to laboratory data. The higher offset values as compared to fits to the evaluation suite spectra are discussed in the text. The increased “noise” in the fit is a product of the reduced spectral sampling and increased noise of the M^3 data relative to laboratory spectra. The poor fits of these spectra at long wavelengths are a product of higher continuum offsets and modeling the long wavelength region with only one Gaussian, and are inconsequential to the results for the critical component absorptions of the 1000 nm feature.

Figure 10. MGM-derived band positions and predicted compositions for the M^3 spectra analyzed in this study. Open symbols are the original MGM-derived results (Table 8), and filled symbols are the results after applying the band shift corrections indicated in Table 9. There is some deviation from the trends developed for terrestrial olivines [Sunshine and Pieters, 1998], most notably for the central M2 absorption, but the overall agreement is quite good. The results for the M^3 spectra cluster within a fairly narrow compositional range, providing a measure of self-verification through self-consistency. Although error bars are not shown and the error is not quantified, these compositional predictions should be treated as approximate, as discussed in the text.

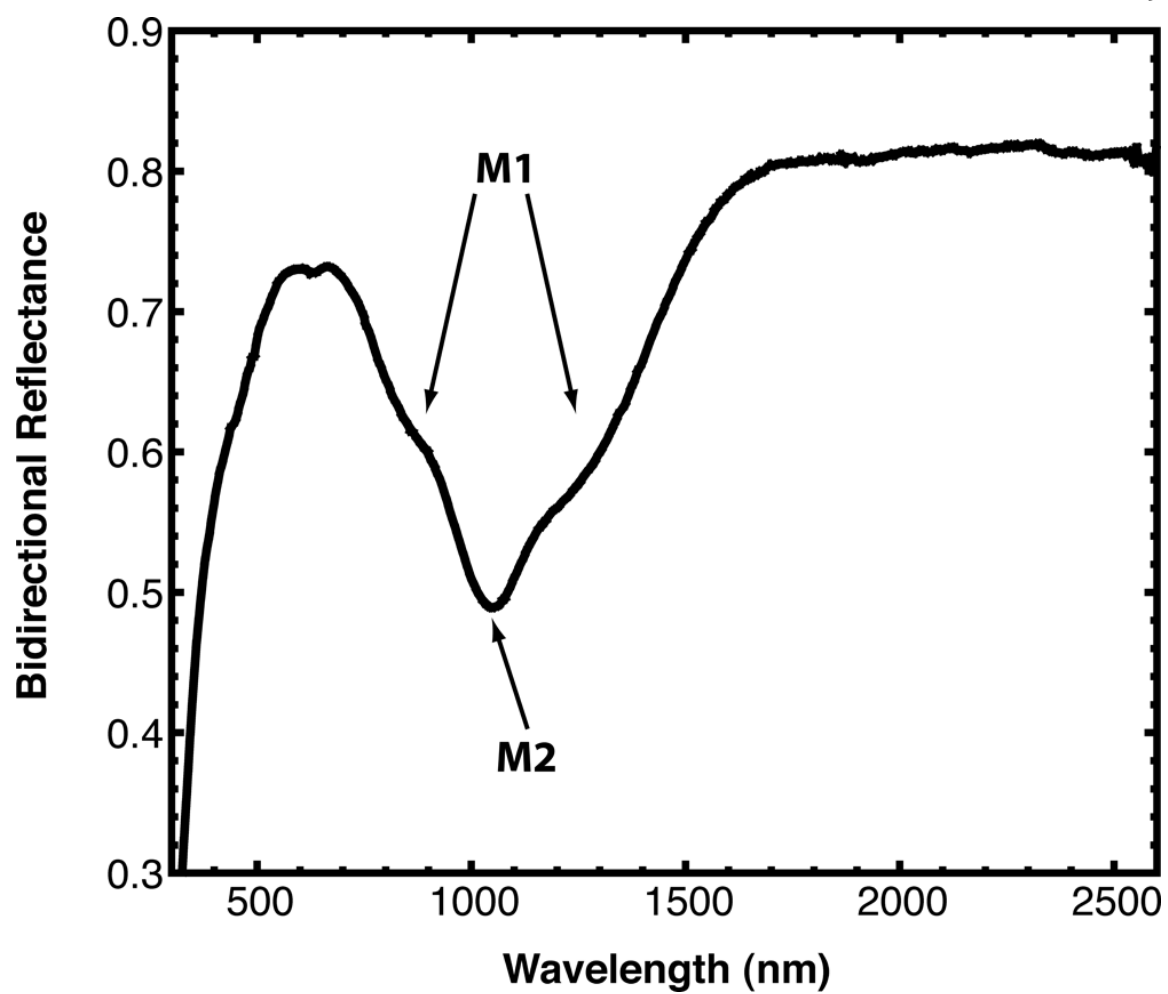


Figure 1.

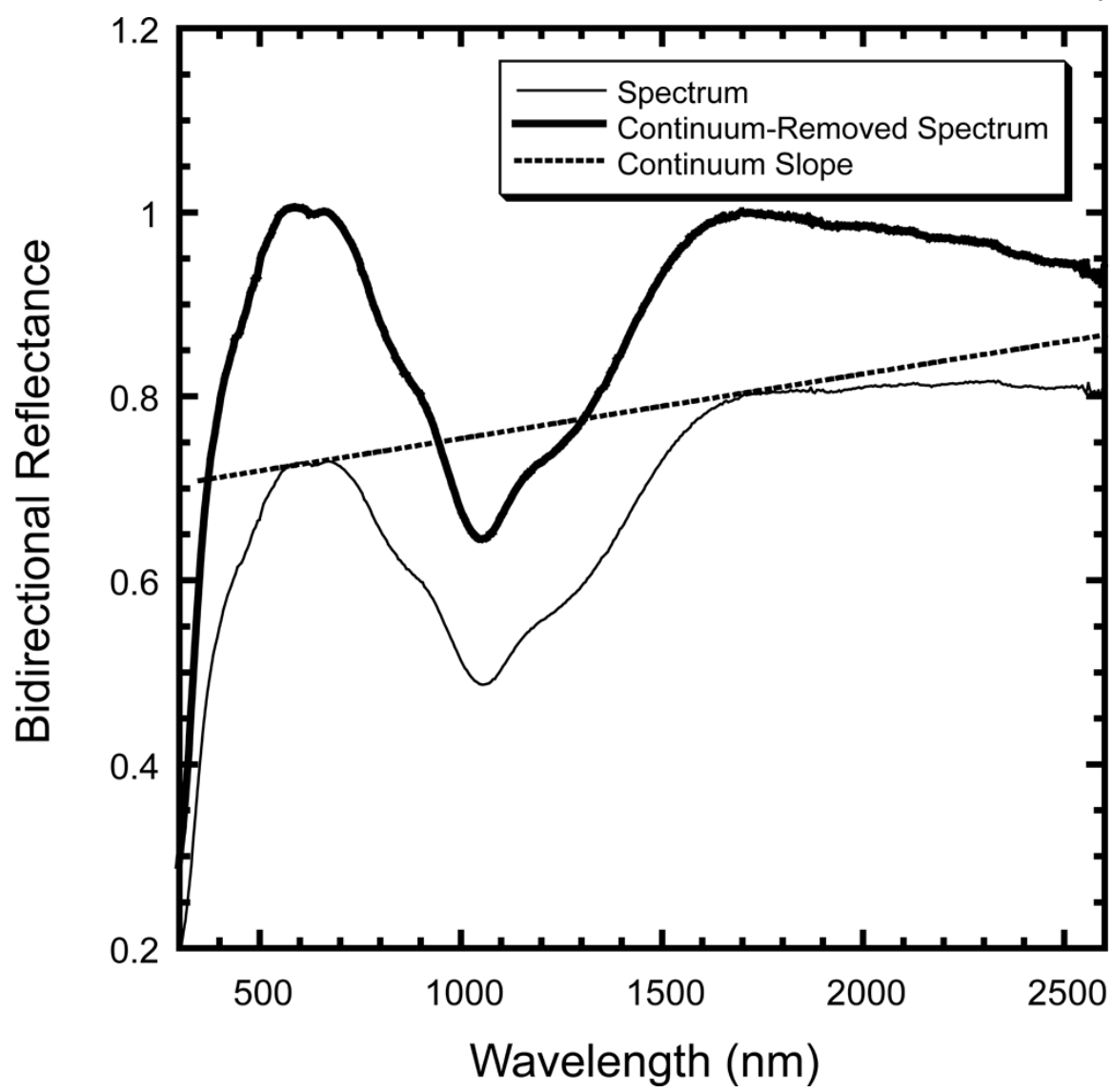


Figure 2.

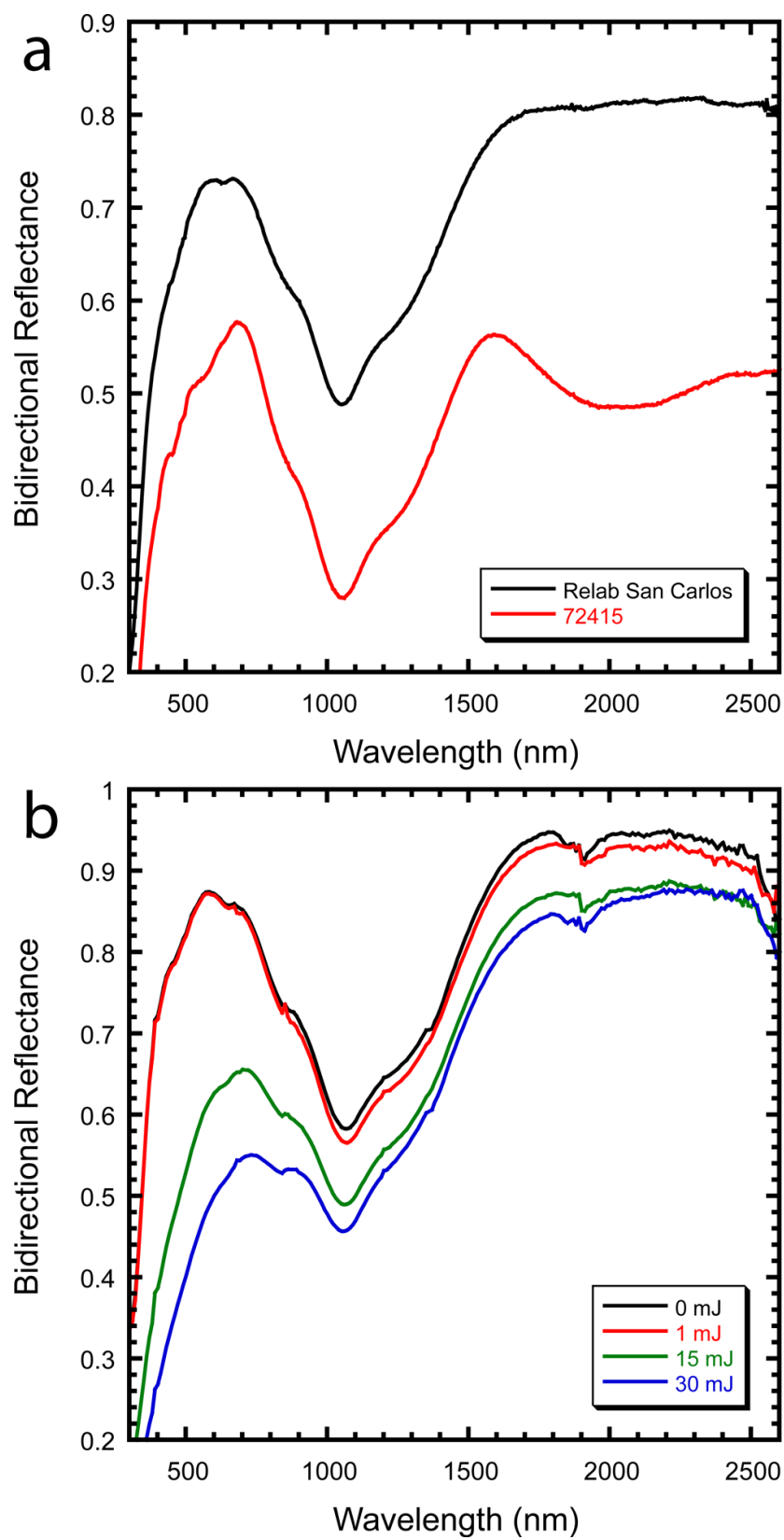


Figure 3.

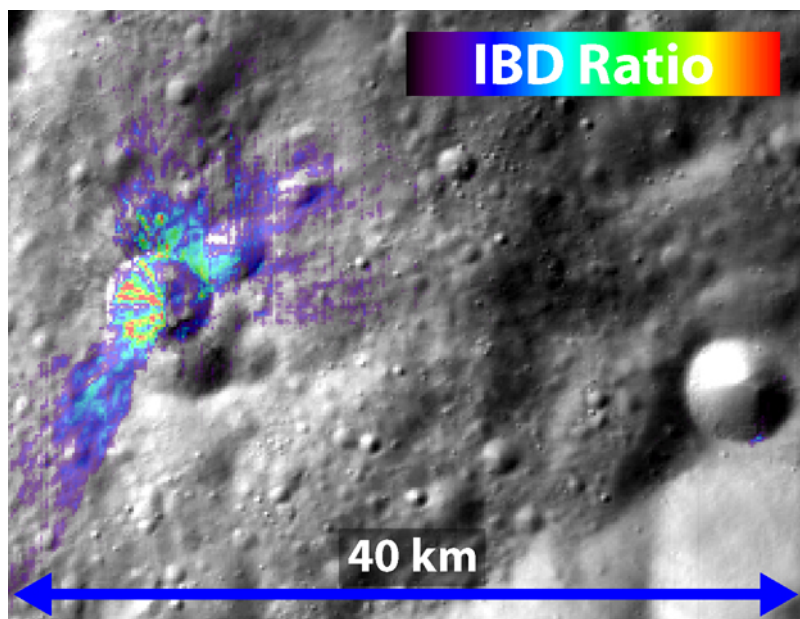


Figure 4.

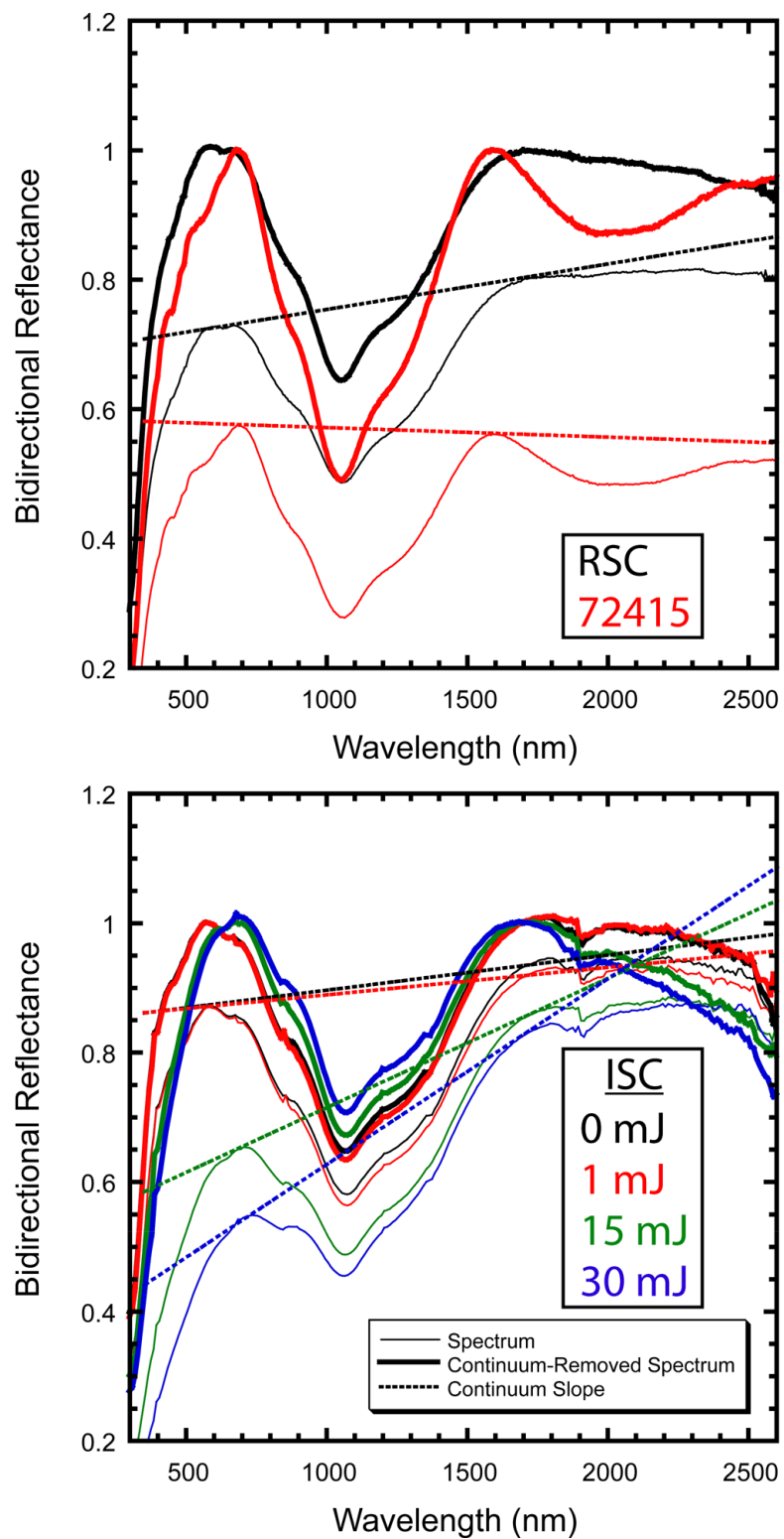


Figure 5.

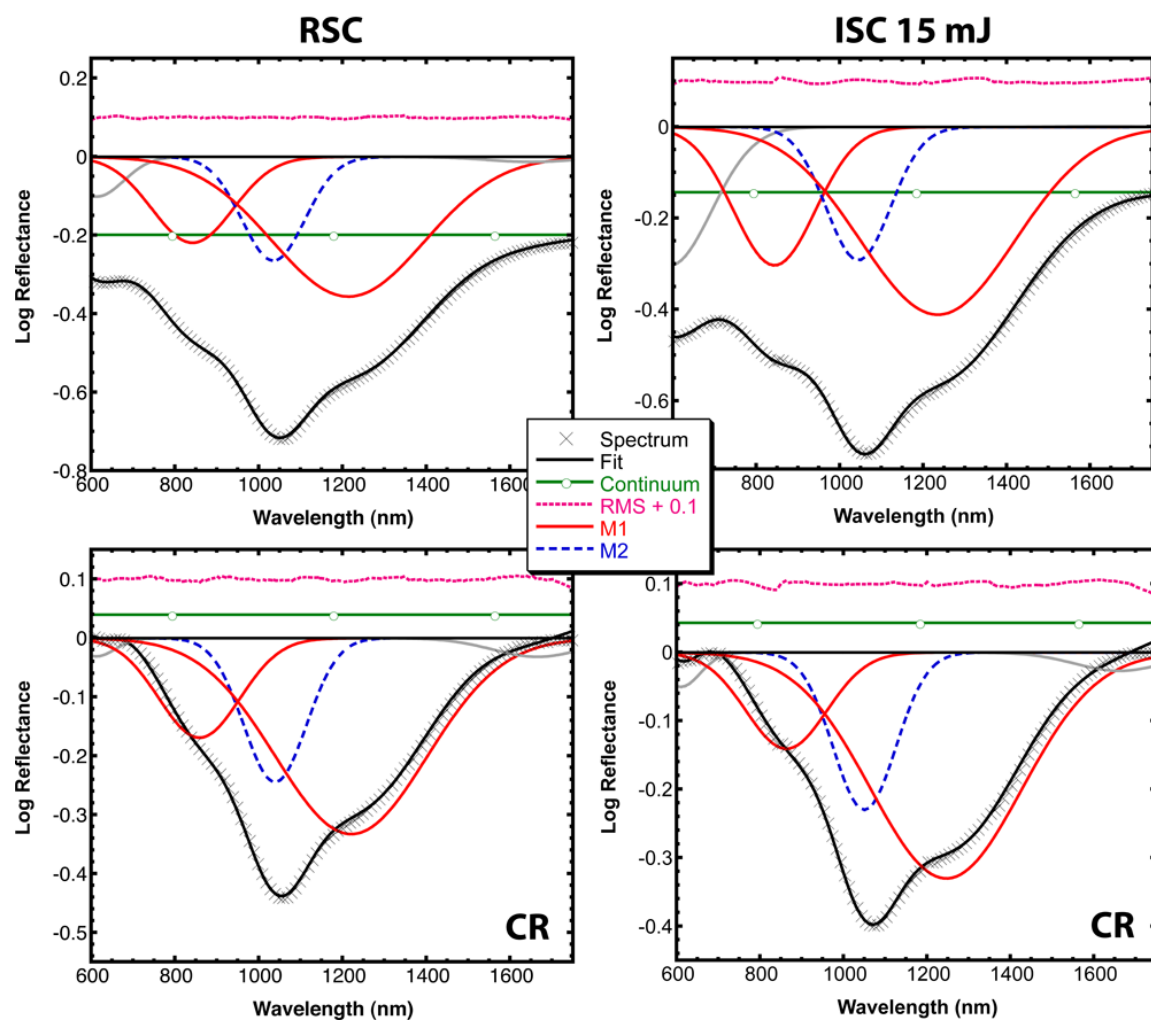


Figure 6.

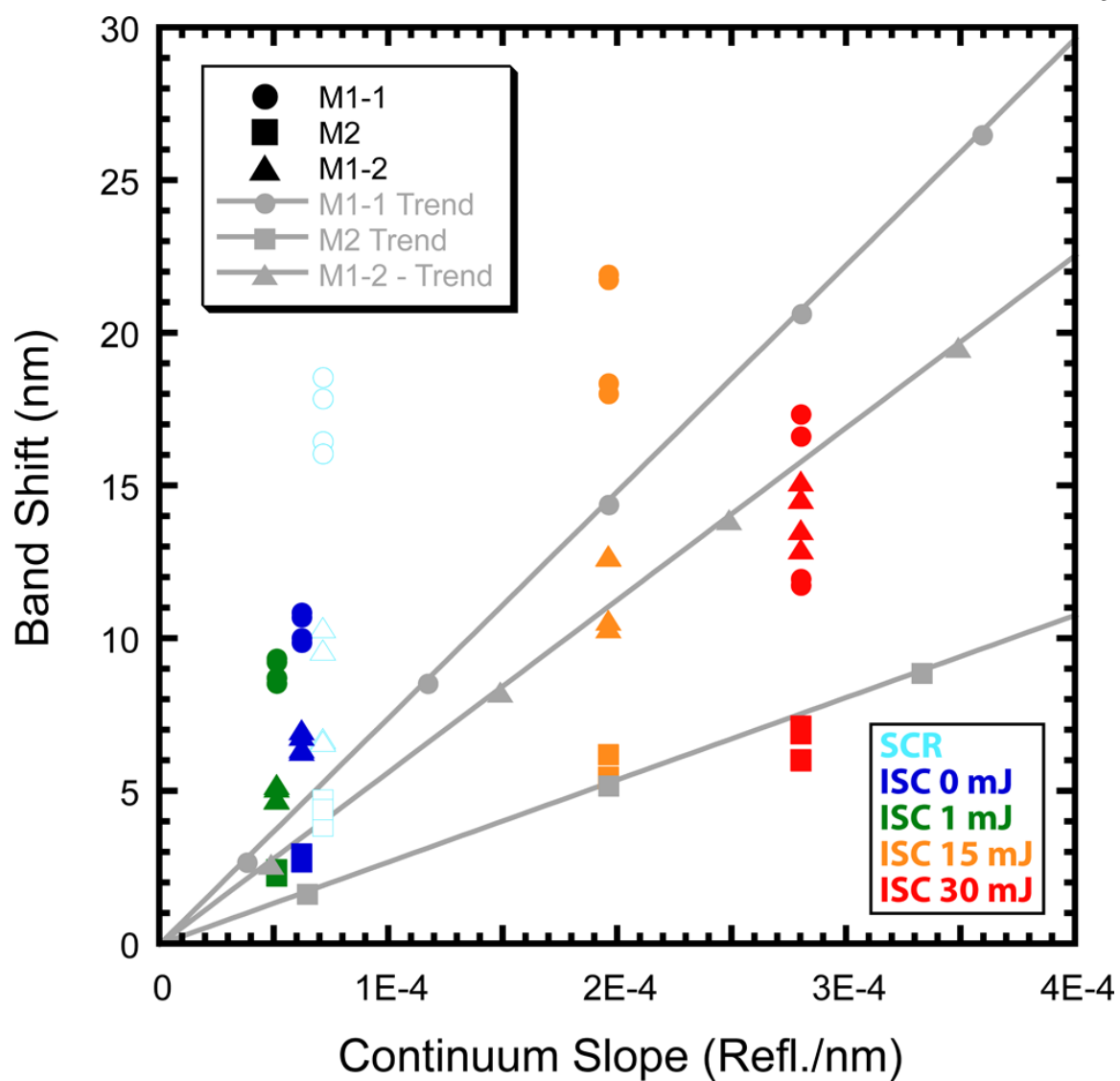


Figure 7.

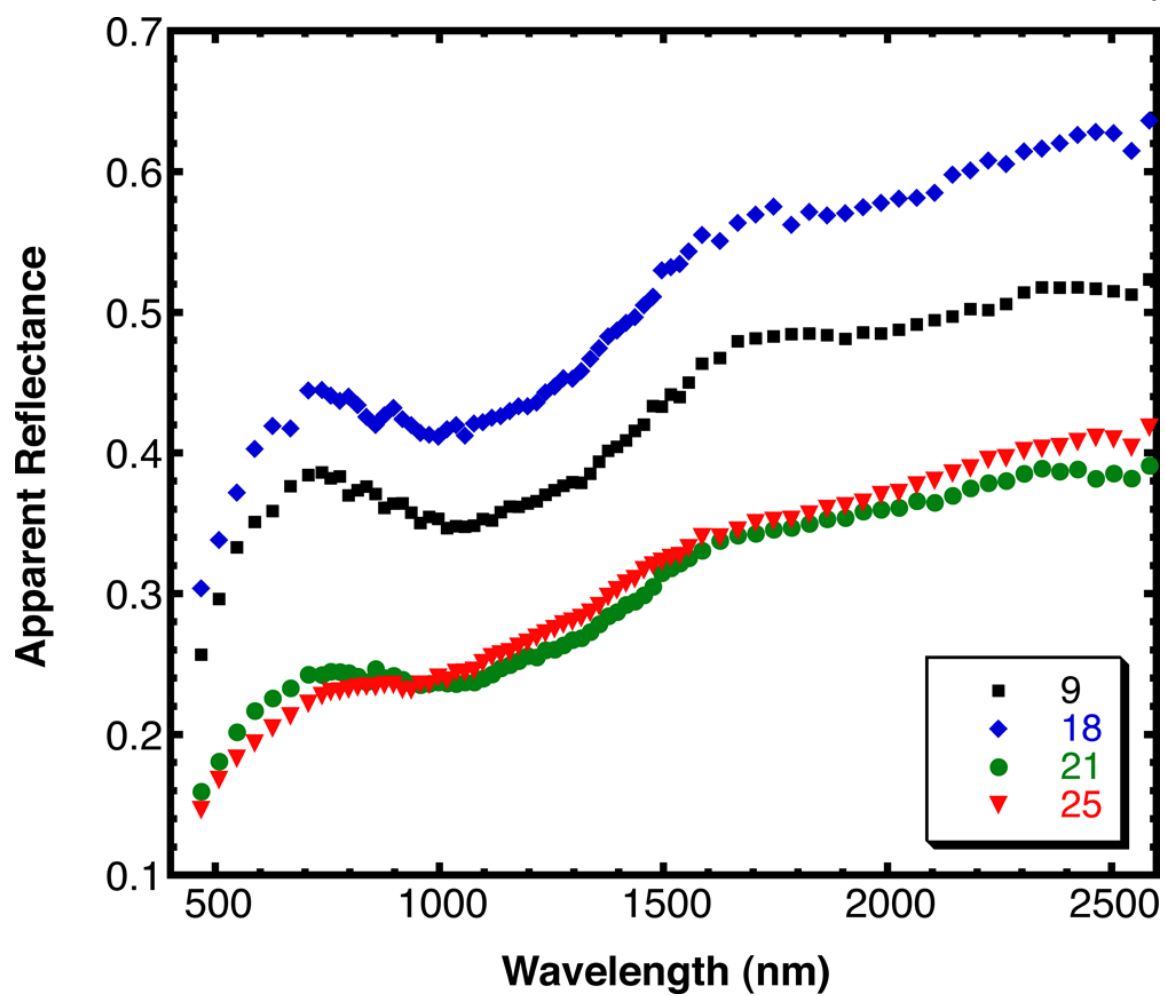


Figure 8.

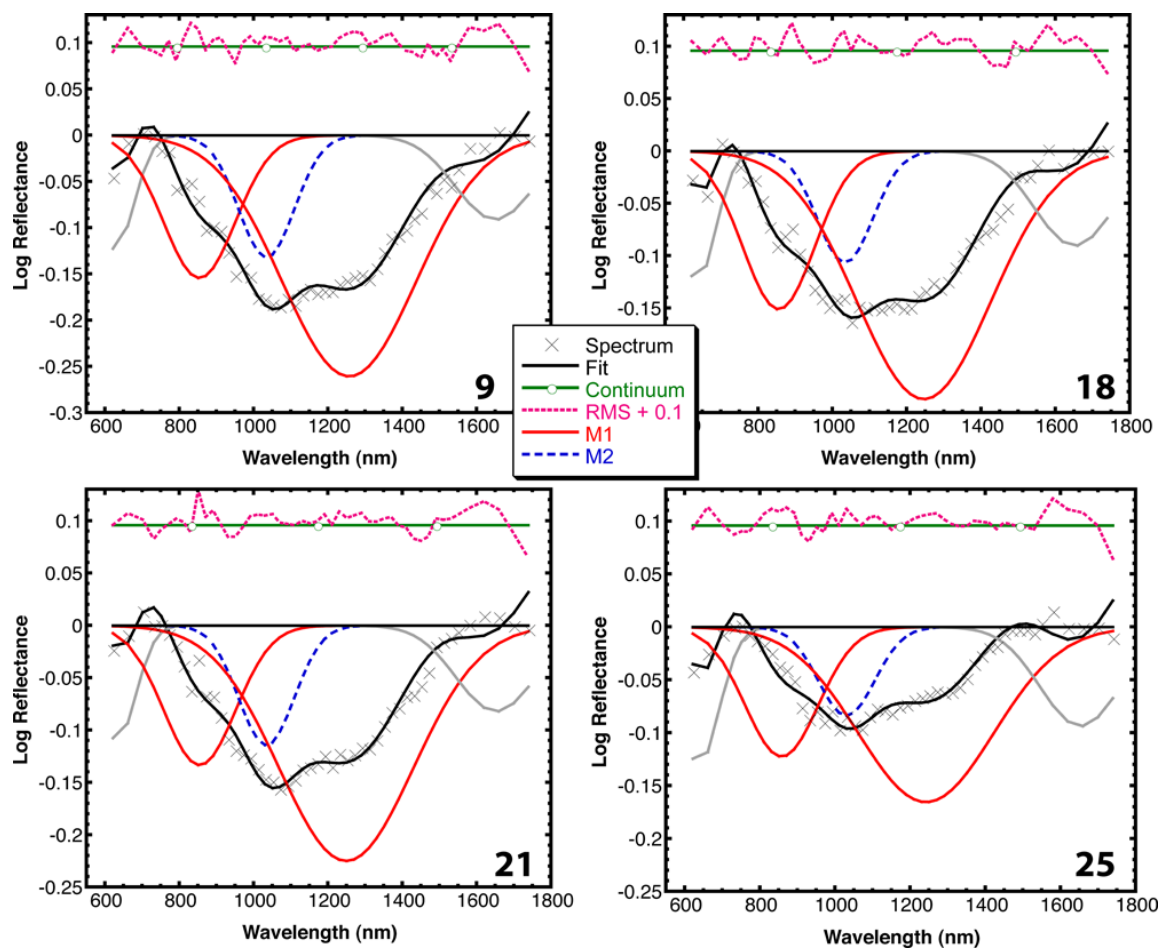


Figure 9.

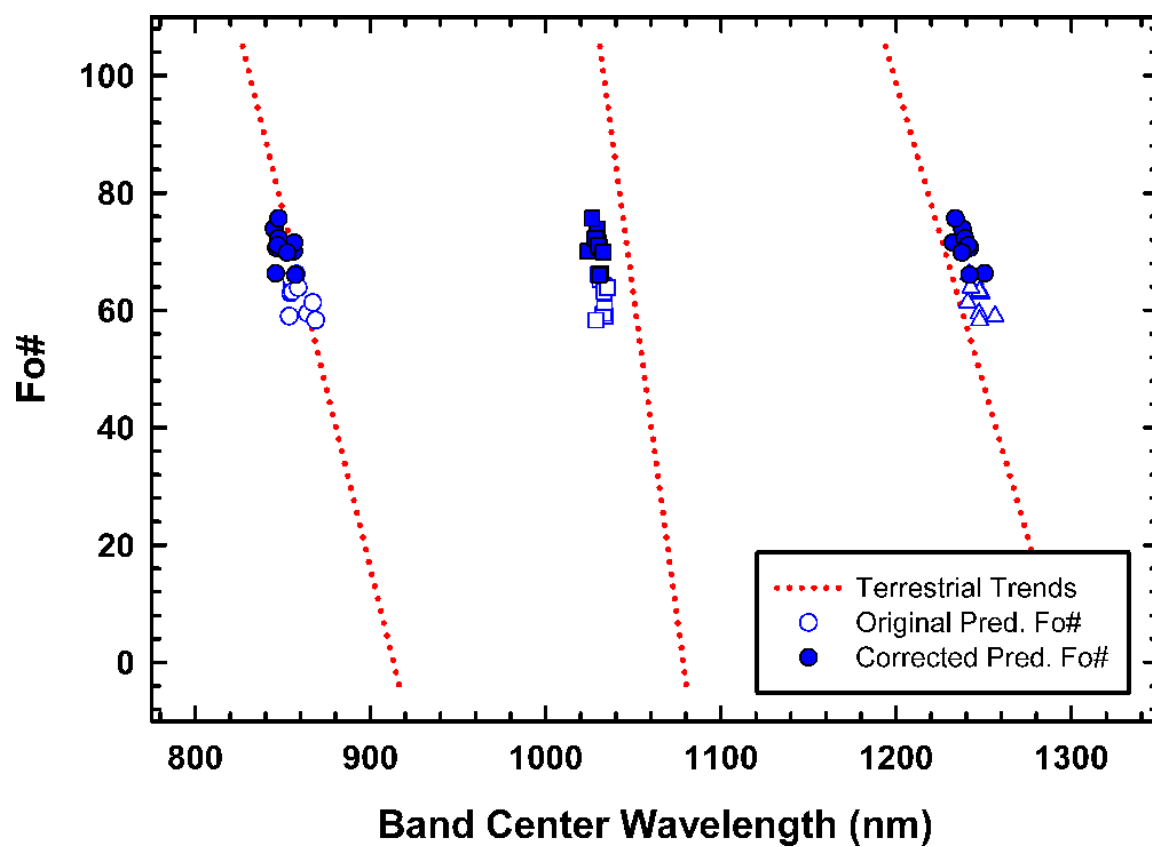


Figure 10.

CHAPTER 5: Spectroscopy of Lunar Meteorites: Expanded Ground Truth Through Diverse Sampling of the Lunar Crust

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Abstract

Data collected after the Apollo missions were complete suggest that the Apollo samples were all collected from an anomalous geochemical province of the lunar surface, and thus that the Apollo samples may present an incomplete view of global lunar geology. Lunar meteorites represent a more stochastic sampling of the lunar crust, and offer the opportunity for a refined, global view of lunar geologic evolution. However, the meteorites suffer from the lack of known geologic context as is available for the Apollo samples collected by astronauts. Modern remote-sensing missions have returned global compositional data from the Moon at high spatial resolution. Among these new datasets, the highest spatial resolution is provided by data returned by optical instruments such as reflectance spectrometers, which rely in large part on ground truth to perform compositional assessments. Textural, compositional, and reflectance spectroscopy analyses are performed on a suite of lunar meteorite samples, and present first results of efforts to measure the individual components of these samples. Such measurements, along with quantitative analyses of the reflectance spectra, provide valuable new ground truth data for lunar science and establish the groundwork needed to constrain the geologic context of these valuable samples with modern remotely-sensed datasets.

1 Introduction

Understanding the evolution of planets is fundamental to understanding the early evolution of the solar system. Of particular interest is the evolution of rocky bodies, as they preserve a record that may be suggestive of the early evolution of the Earth. The Moon is an excellent natural laboratory for studying the evolution of rocky solar system bodies, as it holds a preserved record of its early evolution. The Moon is believed to have undergone significant early thermal and chemical evolution through the cooling of a global magma ocean [Wood *et al.*, 1970b; Wood *et al.*, 1970a; Solomon, 1977; Warren, 1985; Hess and Parmentier, 1995], massive basin-forming impacts [Wilhelms *et al.*, 1987; Spudis, 1993], and concurrent and subsequent volcanic activity [e.g., Head, 1976; Head and Wilson, 1992; Hiesinger *et al.*, 2003]. Furthermore, the study of lunar evolution has a major advantage over the study of other rocky bodies in that it is the only solar system body from which we have returned samples with documented locations.

1.1 Apollo Samples, KREEP, Mg-Suite

The Apollo samples have shaped the canonical view of the lunar crust, which holds that the crust is composed of the ancient feldspathic highlands and younger volcanic basalts. The feldspathic highlands were produced by plagioclase flotation in a crystallizing magma ocean [e.g., Wood *et al.*, 1970a; Warren, 1985], or possibly post-magma ocean overturn and melting [e.g., Hess and Parmentier, 1995; Longhi, 2003]. More recent volcanic units (mare basalts) were produced by melting in a mantle source region. Mare basalts in the sample collection are compositionally diverse, indicating that their source regions are heterogeneous or that melts from the primitive interior

assimilated varying degrees of magma ocean cumulates[e.g., *Wood et al.*, 1970a; *Warren*, 1985; *Hess and Parmentier*, 1995; *Shearer et al.*, 2006]. In addition, a third component termed KREEP, named for its enrichment in potassium, incompatible rare earth elements, and phosphorus, was identified in the Apollo samples. This component was present to at least some degree in samples collected at all Apollo sites. It was hypothesized that the KREEP component derived from a residual liquid (urKREEP) from the crystallization of a global lunar magma ocean (LMO) [*Warren*, 1985; 1988]. KREEP is most commonly found associated with mafic impact melt breccias, which are typically associated with basin-forming impacts thought to expose and melt materials from depth. These circumstances (mafic materials associated with KREEP melted and excavated from depth by giant impacts) contributed to the paradigm that the crust was characterized by increasing content of mafic, KREEP-rich materials with depth [*Ryder and Wood*, 1977], a conclusion consistent with results from crustal thickness modeling [*Wieczorek and Zuber*, 2001]. The ubiquity of KREEP in the sample collection and its presumed association with late-stage magma ocean materials, as well as its apparent occurrence at depth led to the assumption of a global KREEP layer at the base of the lunar crust [e.g., *Warren*, 1985; 1988]. The petrologic reasoning is sound but based on the assumption that the KREEP-rich layer occurs globally, which the Apollo collection samples do little to dispute.

Furthermore, detailed analysis of the Apollo samples identified a suite of mafic rocks (gabbro-norites, norites, troctolites, and dunites) characterized by extremely high Mg^* ($Mg/Mg+Fe$) for rocks crystallizing from an evolving magma source. This suite of mafic materials is known as the Apollo magnesian (Mg) suite. The Apollo Mg suite is

thought to have been produced by intrusions of KREEP-rich materials into and mixing with feldspathic highlands materials [Longhi, 1980; Warren, 1988; Papike *et al.*, 1996; Shearer and Papike, 2005]. This suite of rocks offers significant insight into early volcanic and petrologic processes on the Moon.

1.2 Limitations of the Apollo Samples

Global geochemical data collected from lunar orbit after the Apollo samples were returned suggest that the Apollo samples may not be representative of the entire lunar surface. Data produced by the gamma ray and neutron spectrometers on the Lunar Prospector spacecraft [Feldman *et al.*, 1999] as well as Apollo gamma ray data [Metzger *et al.*, 1973], in particular thorium abundance data, show that the Apollo samples all come from within or near a relatively small region on the lunar nearside marked by elevated Th abundance, as illustrated in Figure 1 [Haskin, 1998; Haskin *et al.*, 1998; Haskin *et al.*, 2000; Lawrence *et al.*, 2000]. This region has been termed the Procellarum KREEP Terrance (PKT) by Jolliff *et al.* [2000], and appears to be unique [e.g., Jolliff *et al.*, 2000; Korotev, 2005; Warren, 2005; Warren *et al.*, 2005]. Samples from all Apollo sites contain a KREEP component, which is taken as evidence for the existence of a global KREEP-rich layer at the base of the lunar crust [e.g., Ryder and Wood, 1977; Warren, 1988; Shearer and Papike, 1999]. However, the anomalous source region of the Apollo samples suggests that the KREEP layer may not be a global phenomenon and may be restricted to the PKT [Korotev, 2000]. The anomalous nature of the source region of the Apollo samples suggests that they present an incomplete picture of the lunar crust and its formation. The anomaly calls into question a fundamental assumption upon which our understanding of lunar crustal evolution is based [Korotev *et al.*, 2003a].

1.3 Stochastic Sampling of the Lunar Crust and Need For Geologic Context

Impacts on planetary surfaces are a stochastic process. As lunar meteorites should represent a random sampling of the lunar crust, it is logical to consider the information they provide when forming a comprehensive understanding of lunar geology. While the meteorites' mineralogy and bulk composition are generally similar to that of the Apollo samples, many exhibit important geochemical differences, and the minerals may have different compositional trends [Korotev, 2005]. The feldspathic lunar meteorites are particularly deserving of study, as they can contribute to a broader understanding of lunar crustal evolution. An example of a problem to which study of the feldspathic lunar meteorites is highly relevant is the nature of the Apollo highlands magnesian suite. The feldspathic lunar meteorites often contain a suite of Mg-rich materials that appear to be chemically and genetically distinct from the Apollo magnesian suite [Korotev *et al.*, 2003a; Korotev, 2005]. Specifically, the meteoritic magnesian materials are more feldspathic (have higher Al_2O_3 content), are not associated with a KREEP component, and cannot be produced by any combination of materials in the Apollo collection [Korotev *et al.*, 2003a; Warren *et al.*, 2005]. The combination of these properties suggests that the feldspathic meteorites come from regions unrelated to the Apollo 16 site, and that the Apollo 16 samples are not fully representative of the diversity of the global feldspathic highlands. It also appears that the lunar crust must harbor at least two magnesian suites. One of the suites is strongly represented in the Apollo collection, and is associated with a KREEP-rich materials (the Apollo Mg-suite). The other (KREEP-poor) suite is more strongly associated with the feldspathic meteorites, and is associated with the Feldspathic Highlands Terrane, distinct from the KREEP-rich

PKT [Korotev *et al.*, 2003a; Warren *et al.*, 2005]. The feldspathic lunar meteorites generally show no association with KREEP, which supports the argument that the hypothesized global KREEP layer at the base of the lunar crust in fact may be restricted to the PKT [Korotev *et al.*, 2003a; Korotev, 2005].

Lunar meteorites are a valuable additional source of lunar material that can provide invaluable “ground truth” data to guide future lunar exploration, especially if that data is from “new” materials that are distinct from the Apollo collection. The compositional data returned by optical instruments such as reflectance spectrometers offer the highest spatial resolution of any compositional remote sensing technique currently in use. Use of such datasets is greatly strengthened by ground truth data for compositional assessments [e.g., Pieters, 1999], and the lunar meteorites provide can valuable new ground truth data. Additionally, laboratory reflectance spectra of meteorite samples provide a valuable “spectral library” to guide future lunar exploration with new lunar spectroscopic datasets [e.g., Matsunaga *et al.*, 1999; e.g., Sugihara *et al.*, 2004; Haruyama *et al.*, 2008; Ohtake *et al.*, 2008; Mall *et al.*, 2009; Pieters *et al.*, 2009]. The lunar meteorites also represent additional samples of the lunar crust that can broaden our understanding of lunar geology based on study of samples returned by the Apollo and Luna missions. However, information provided by the feldspathic lunar meteorites is somewhat limited by the unknown geologic context of the samples. By characterizing systematically the meteorite samples and their components with laboratory reflectance spectroscopy, the groundwork will be laid for evaluating the geologic context of these important samples with remotely-sensed data.

2 Samples and Methods

Six samples were allocated by the Meteorite Working Group from the NASA Antarctic meteorite section. They were provided in chip form, and include two feldspathic breccias, two unbrecciated basalts, and two basaltic breccias. Summary information for these samples is provided in Table 1, as well as abbreviations for each sample name. Polished thin sections were also provided for the feldspathic breccia samples (QUE/ALH).

2.1 Petrography and Mineral Composition Analyses

Prior to reflectance spectroscopy measurements, we conducted compositional analyses of our samples. In some cases, lunar meteorite stones can be quite heterogeneous, so it is advantageous to perform compositional analyses of a particular subsample rather than rely on previous analyses in the published literature. We prepared a set of grain mounts of small fragments of the basaltic samples, and used the provided thin sections to characterize the feldspathic breccia samples. While this approach means that the subsamples of the feldspathic breccias we were allocated were not analyzed specifically, these samples are highly valuable, and this approach was deemed preferable to losing sample mass in creating new thin sections for these samples.

The petrography and mineral compositions of our chip samples were characterized using a combination of optical microscopy, backscattered electron imagery (scanning electron microscopy, SEM), and electron microprobe analysis using the Cameca SX-100 at the University of Tennessee. Operating conditions for the microprobe were as follows: 15 keV accelerating voltage, 20 nA beam current, and 2 μm beam diameter. For analyses of plagioclase/maskelynite and some glass phases, the beam was

de-focused to a 5 μm diameter and the current reduced to 10 nA to minimize loss of volatile elements such as K and Na. Modal mineralogy was not measured, but previous studies have documented the mineralogy of these stones [e.g., *Simon et al.*, 1983; *Delaney*, 1989; *Warren and Kallemeyn*, 1989; *Takeda et al.*, 1992; *Bischoff*, 1996; *Richter et al.*, 2005; *Zeigler et al.*, 2005; *Anand et al.*, 2006; *Joy et al.*, 2006; *Joy et al.*, 2008; *Liu et al.*, 2009].

2.2 Reflectance Spectroscopy: Chip Samples

Following geochemical analyses, the samples were analyzed with reflectance spectroscopy in the RELAB at Brown University. All measurements were carried out in bidirectional reflectance (BDR, 0.28 μm – 2.6 μm) and in biconical reflectance by FT-IR (~1 μm - ~50 μm). FT-IR measurements were connected with BDR measurements by scaling FT-IR measurements to the BDR measurements at a common wavelength. Samples were first analyzed as chip samples. Chip samples are not ideal to measure with reflectance spectroscopy for a variety of reasons. First, they are difficult to measure consistently, as targeting the same portion of the sample with the varying measurement techniques is a logistical challenge. This difficulty means that there is an implicit assumption in connecting FT-IR spectra with BDR spectra: one must assume that the same spot was analyzed with each technique. In fact it was not possible to connect all chip sample spectra in this way, likely due to differences in the spots analyzed. The second problem with chip samples is common to reflectance measurements of non-particulate samples. Non-particulate samples are much harder for photons to penetrate, so it is difficult to make quality reflectance measurements. This is especially challenging for glassy breccia samples such as the feldspathic breccias (ALH and QUE) and to a

lesser extent the basaltic fragmental breccias (EET87 and EET96). Measurement of chip samples typically causes reflectance spectra to have a significant negative (“blue”) continuum slopes [e.g., *Yon and Pieters*, 1988].

2.3 Preliminary Analysis of Stone Components: MIL05035 Case Study

Analysis of the individual components of the meteorite stones in addition to analysis of the bulk chip samples is preferred for the reasons outlined above. Additionally, in the case of the breccia samples, analysis of the chip sample amalgamates a number of diverse components into one composite measurement. This measurement characterizes the bulk properties of the meteorite sample, but does not allow characterization of the diverse mineral and lithic clasts that make up the sample. These clasts can be quite diverse, and each may provide useful constraints if analyzed individually. Furthermore, the clasts may not be related to one another other than by their having been formed into a breccia by repeated bombardment and lateral transport across the lunar surface and then ejected as a meteoroid and delivered to Earth as a brecciated meteorite. Highly diverse lithologies may be grouped into a meteorite sample, also true of breccia samples in the Apollo collection. An example of this phenomenon is the occurrence of mare basalt materials in samples collected at the Apollo 16 site [*Korotev*, 1997; *Petro and Pieters*, 2006], over 200 km from the nearest *in situ* mare basalt. As the insight to be gained from analysis of meteorite breccia samples is often gained primarily from analysis of specific clasts, the desired geologic context for the meteorite samples is really the geologic context for the component clasts in the case of breccia samples. Thus, the clasts must be characterized individually rather than only as a

component of the bulk samples. Separation of the samples into their component clasts and mineral phases is underway.

2.3.1 Separations and Measurements

We have performed preliminary separations for MIL05035 by hand picking under a binocular microscope. The procedure for performing mineral separates involves crushing samples to coarse particulates (~125 – 250 μm). Pure grains/clasts are separated, and mixed grains/clasts crushed to finer particle size for separation as pure grains/clasts. This procedure is documented with digital imaging. After separation, separates were crushed and sieved to a particle size of <125 μm for measurement. Reflectance spectra of the separates have been acquired in BDR and with FT-IR. Analyses of particulate bulk samples are planned but have not been completed. Separation and analysis of the separates as well as particulate bulk samples are planned for the remaining samples.

2.3.2 Quantitative Deconvolutions

After analysis of the components in MIL05035, quantitative deconvolutions were performed with the Modified Gaussian Model (MGM) [*Sunshine et al.*, 1990]. The MGM fits a spectrum with a predefined number of Gaussians superimposed onto a continuum slope. More details of the MGM are provided by Sunshine et al. [1990]. The pyroxene separate spectrum was analyzed first, and the result of that deconvolution used as the input to deconvolution of the bulk chip sample spectrum. Fits were attempted using single Gaussians for the 1 and 2 μm pyroxene absorptions, but did these fits did not produce acceptable results. Two Gaussians each for the 1 and 2 μm absorptions were

used, in addition to one Gaussian for the 1.2 μm feature. For the pyroxene separate spectrum, a linear polynomial in energy was used for the continuum slope, with slope and offset allowed to vary freely. For the chip sample spectrum, the continuum slope was found manually and was locked, with only the offset allowed to vary freely. The results of these deconvolutions were compared to previously established trends with pyroxene composition in the 1 and 2 μm absorption band positions [Adams, 1974; Hazen *et al.*, 1978; Cloutis and Gaffey, 1991]. Such MGM deconvolutions will be applied to reflectance spectra of particulate bulk samples and individual stone components and separates.

3 Results

3.1 Petrography/Mineral Composition

3.1.1 Texture

Example backscattered electron (SEM) images of each grain mount/thin section are presented in Figure 2. These images give a general overview of the texture of each meteorite sample. Backscattered electron images are primarily indicative of the average atomic number (z value) of the target material; higher average atomic number elements reflect more electrons, producing a “brighter” image. In the case of our samples, plagioclase grains and glasses will appear darkest, followed by Mg-rich pyroxene, Ca/Fe rich pyroxene (Fe “brighter” than Ca), and olivine (Fe-rich brighter than Mg-rich), although the distinction between Mg-rich olivine and denser Ca/Fe-rich pyroxene can be non-unique depending on the context. Oxide minerals (e.g. ilmenite, spinel, armalcolite), sulfides (e.g. troilite), and reduced metals appear the brightest. The complex nature of

the feldspathic breccias is apparent; they are composed of a diverse mix of large mineral fragments and lithic clasts, smaller fragments, melt, glassy matrix, and minor occurrences of fusion crust. Pyroxene grains typically exhibit prominent exsolution lamellae. The unbrecciated basalts are quite coarse-grained, exhibiting large pyroxene and plagioclase grains with volumetrically minor fayalitic olivine. The pyroxenes exhibit prominent compositional zoning, especially in the case of LAP (see detail below). The basaltic fragmental breccias are complex, but less complex than the feldspathic breccias. The EET samples are paired, so they exhibit similar compositions and textures [*Lindstrom et al.*, 1999; *Mikouchi*, 1999; *Nishiizumi et al.*, 1999; *Warren and Ulff-Møller*, 1999; *Korotev et al.*, 2003b; *Korotev et al.*, 2009]. Prominent, coarse exsolution features are observed in the large pyroxene grains (see discussion below), as well as abundant, glassy matrix material, particularly apparent in the EET87 image.

3.1.2 Mineral Compositions

The compositions of major mineral phases (pyroxene, olivine, and plagioclase/maskelynite) as determined by electron microprobe analysis are presented in Figure 3. The feldspathic breccias exhibit diverse pyroxene compositions, and exhibit abundant low-Ca compositions that are absent from the basaltic samples. Olivine compositions are diverse, but significant clustering is observed near ~Fo80. Plagioclase compositions are very Ca-rich, typical for feldspathic lunar samples [e.g., *Papike et al.*, 1998]. Pyroxenes in LAP are diverse, but lack the low-Ca compositions seen in the feldspathic breccias. LAP pyroxenes extend to pyroxferroite compositions. These can be seen in Figure 2, in the “bright” Fe-rich rims on the large pyroxene grains. The fayalite compositions observed in LAP can be seen in the mottled “bright” regions in the LAP

portion of Figure 2. These fayalites are associated with a K-rich glass phase and are found in regions with late-stage mesostasis, indicating that they were among the last phases to crystallize from the melt [Anand *et al.*, 2006]. Plagioclase compositions are less Ca-rich in LAP and MIL, consistent with other mare basalts. Despite their brecciated nature, the EET samples exhibit narrower compositional ranges than pyroxenes in LAP and MIL. Plagioclase compositions in the EET samples are more Ca-rich than those in LAP/MIL, but less Ca-rich than those in ALH/QUE. Olivine compositions are <Fo60, consistent with but not diagnostic of mare basalt olivine compositions [e.g., Papike *et al.*, 1976; Neal and Taylor, 1992].

3.1.3 Pyroxene Exsolution/Zoning

Examples of pyroxene exsolution and zoning are presented in Figure 4. SEM images are presented along with pyroxene quadrilaterals showing compositions measured in profiles across pyroxene grains. Note that the SEM images do not necessarily show all profiles plotted in the quadrilaterals; rather, they show example profiles. The light blue shaded regions correspond to the outlines drawn in Figure 3, and indicate the full range of pyroxene compositions measured in the sample. Colors correspond between profiles in the images and the quadrilaterals. Pyroxenes in LAP and MIL exhibit compositional zoning, particularly in the case of LAP. Pyroxenes in ALH, QUE, and the EET samples exhibit prominent exsolution features. These situations must be considered in interpreting reflectance spectra, as zoned pyroxenes vs. exsolved pyroxenes present different conditions for interactions with photons.

3.2 Reflectance Spectra

3.2.1 Chip Samples

Bidirectional reflectance spectra of the chip samples are illustrated in Figure 5. The blue continuum slope caused by measurement of chip samples is apparent in several of these spectra, most notably the feldspathic breccias. Mid-infrared spectra are plotted in Figure 6. The prominent reflectance minimum near 8 μm is the Christiansen feature (CF). The Christiansen feature is a reflectance minimum (and emission maximum). Its wavelength position is controlled by the position of the fundamental Si-O vibrational absorption feature, and is sensitive to sample composition (generally, it moves to shorter wavelengths with decreasing SiO_2 content) [e.g., *Salisbury and Walter*, 1989; *Salisbury*, 1993]. The feature near 3 μm is caused by water (not surprising in “find” meteorite samples that have substantial residence times on Earth prior to collection; this water is predominantly terrestrial contamination). Weak features near 3.4 μm are attributed to the C-H stretch in organic hydrocarbons, and are also likely to be due to terrestrial contamination, as the samples were not exposed to any organics during preparation.

3.2.2 MIL05035 Components

Bidirectional reflectance spectra of the components of MIL05035 are plotted in Figure 7. Note that the “maskelynite” spectrum exhibits apparent pyroxene absorptions; this sample is likely contaminated by pyroxene. Maskelynite lacks strong absorptions and is quite transparent, so even fairly minor levels of contamination by a strongly absorbing phase such as pyroxene can have dramatic effects on its reflectance spectrum.

A spectrum of a Fe-rich plagioclase separate exhibiting a prominent 1.3 μm absorption feature is plotted for comparison [Isaacson *et al.*, 2010].

Mid-infrared spectra of these same separates are plotted in Figure 8. More diversity is apparent in the position of the CF. As expected, the pyroxene exhibits a longer-wavelength CF. Note the weak absorption near $\sim 4.4 \mu\text{m}$ in the 70017 plagioclase spectrum. While weak, this feature is diagnostic of plagioclase [e.g., Isaacson *et al.*, 2010]. This feature is also observed in some of the chip sample spectra (e.g. ALH).

Deconvolutions of the MIL05035 pyroxene and bulk chip spectra are presented in Figure 9. Minor disagreement between the fit and the spectrum of the pyroxene separate can be observed, particularly near 1.2 μm and near 2.0 μm . This spectrum was measured of a fairly coarse-particle separate, so band saturation is a possibility. Deconvolutions will be attempted on spectra of samples with smaller particle sizes once such spectra are available. Slightly more substantial disagreement is observed between the fit and input spectrum of the bulk chip sample, in the same wavelength regions (1.2 and 2.0 μm). The 2 μm pyroxene absorption appears somewhat bowl-shaped, perhaps indicating some limitations of measurement as a chip sample. However, the quality of the fit is excellent considering the spectrum was measured under far-from-ideal conditions. Results of the MGM deconvolutions of the MIL05035 pyroxene and chip sample spectra are presented in Table 2. The results of these deconvolutions are compared to established trends in absorption feature position [Adams, 1974; Hazen *et al.*, 1978; Cloutis and Gaffey, 1991] in Figure 10. Each absorption is plotted as a single point, with the pyroxene separate absorptions in filled symbols and the bulk chip absorptions in open symbols. The short-

wavelength absorption is designated “LCP” for low-Ca pyroxene, and the long-wavelength absorption is designated “HCP” for high-Ca pyroxene.

4 Discussion

While limited in number, our suite of lunar meteorite samples exhibits significant diversity. This diversity extends from texture to chemical composition, mineralogy, and reflectance properties. Thus, while not representative of the full suite of lunar meteorites (which numbers well over 100 at last count), this suite is indicative of the utility of lunar meteorites to lunar science.

4.1 Textural and Compositional Diversity

Texturally, these samples exhibit a range of properties. The feldspathic breccias are complex, exhibiting texture at all magnifications up to the limit of the backscattered electron imagery (acquired with the electron microprobe at the University of Tennessee in its scanning electron microscope mode). Large clasts are present, as are fragments and grains of individual minerals. However, abundant small fragments and breccias make up the composite feldspathic breccia samples. The complex history of these samples is evident from their texture; numerous components, many already combined into breccias, were combined to produce the final composite breccia samples. The complex texture of these samples indicates the degree to which spectroscopic measurements of the bulk sample are limited. Not only are such samples challenging to measure, measurement of the bulk sample groups highly diverse and distinct components into a single measurement that is not necessarily representative of the specific components of interest.

4.1.1 Textural Effects on Reflectance Spectra

The unbrecciated basalts texturally are quite simple relative to the feldspathic breccias. They exhibit large mineral grains, dominantly pyroxene and plagioclase (maskelynite in the case of MIL). Pyroxene grains are prominently zoned, particularly in the case of LAP. Olivines are volumetrically minor and quite iron-rich. The unbrecciated samples do not contain distinct lithic clasts with diverse histories, so measuring their individual components is less critical than in the case of the breccia samples, particularly the feldspathic breccias. This is not to say that such measurements are not important, as they are. The less complex nature of the basalt samples (LAP and MIL) suggests that they are more appropriate for measurement as bulk samples (as chips), as photons can interact more easily with the mineral grains without complications from the multitude of other phases and glassy matrix present in the breccias. This easier photon interaction is apparent from the reflectance spectra, as LAP and MIL exhibit prominent absorption features while the breccia samples exhibit more complex and lower “quality” spectra.

The basaltic breccias are something of a textural “midpoint” between LAP/MIL and the feldspathic breccias. They exhibit abundant glassy matrix and small clasts, but do not have the same textural complexity at all scales. They also exhibit prominent large pyroxene grains, which are far less common in ALH/QUE. The large pyroxene grain size affects the reflectance spectroscopy results, as the EET samples do exhibit more prominent absorptions than ALH/QUE, but exhibit negative slopes and less prominent absorptions relative to LAP/MIL. Lithic clasts are less common in these samples than in

the feldspathic breccias, so analysis of the individual components in these samples will likely focus on the pyroxene grains.

4.1.2 Pyroxene Exsolution/Zoning

Pyroxenes in all six samples typically exhibit prominent compositional zoning (LAP and to a lesser extent, MIL) or exsolution (ALH, QUE, EET87, EET96). Zoning and exsolution are illustrated in Figure 4, which shows examples from each sample as well as example compositional profiles along pyroxene grains.

In the zoned pyroxenes (LAP, MIL), the profile compositions represent true trends. In the case of LAP, the more Mg-rich and Ca-poor compositions are found toward the interiors of pyroxene grains, and compositions evolve first toward high-Fe contents (right on the quadrilateral) and then toward high-Fe, high-Ca compositions (up the right axis of the quadrilateral). This trend is particularly apparent in the profile illustrated in green. In the case of MIL pyroxenes, core-to-rim zoning is less apparent. Across the profiles in the quadrilateral, there is an evolution from Mg-rich to Ca-rich, but the trend apparently is not associated with grain cores or rims. As discussed above, not all profiles plotted on the quadrilaterals are illustrated in the SEM images. The images provide representative examples of zoning/exsolution, and the compositional results (quadrilaterals) provide broader context.

The large grain size and zoned nature of the pyroxenes in LAP and MIL also suggest an important note of caution in interpreting reflectance spectra of crushed samples. The outer surface of pyroxene grains in the chip samples (in LAP) is predominantly Fe- and Ca-rich. After crushing and sieving, which involves breaking grains, this will no longer be the case, and we must assume that the compositional zoning

becomes more mixed as various “depths” in the mineral grains become exposed at the newly created surfaces. Photons still traverse mineral grains, but the compositions encountered on these traverses will be affected by the crushing process. The effect will likely be less strong in MIL, which exhibits zoning in pyroxene grains but does not exhibit prominent trends in core-to-rim profiles.

In the case of exsolved pyroxenes, which are abundant in the breccia samples (ALH/QUE and the EET samples), the compositional profiles indicate the range of compositions found across a pyroxene grain but do not generally reflect any particular core-to-rim trend. The extremes of a compositional transect generally reflect the two exsolved “endmember” compositions, and the spread between the extremes likely reflects “mixed” compositions in which components of each endmember were captured by an individual point analysis. Examples of this effect can be seen clearly in the QUE section of Figure 4. The white profile, corresponding to the open symbols on the quadrilateral, is across a pyroxene with remarkably coarse exsolution features. Clear differentiation is observed between the compositional endmembers; the dark, Mg-rich endmember vs. the bright, Ca-rich endmembers stand out clearly on the quadrilateral and in the image. However, the red profile on the quadrilateral (not shown in the backscattered electron image as it was taken on a different pyroxene grain) exhibits two endmembers but prominent mixing of compositions in the intermediate analyses. This phenomenon also causes the more regular “spread” observed in profiles across pyroxenes with finer-scale exsolution features, such as the examples for ALH and the EET samples. Prominent exsolution, most notable in the QUE sample, must be considered in interpreting

reflectance spectra of these pyroxenes, as photons interacting with the grains are effectively sensing two distinct pyroxene compositions.

4.2 Reflectance Spectra

4.2.1 Chip Sample Spectral Diversity

As suggested in the preceding sections, chip samples are not ideal for reflectance spectroscopy measurements. Measurement of chip surfaces (rather than particulate) leads to challenges in obtaining quality reflectance spectra, as proportionally more photons are reflected specularly rather than internally scattered after interacting with mineral grains. Additionally, such measurements tend to impart prominent negative (“blue”) continuum slopes, which is certainly observed in our results, as illustrated in Figure 5. The slopes are most prominent for the feldspathic breccia sample spectra, moderately apparent for the basaltic breccia spectra, and not readily apparent (but still present, as indicated by the relative reflectance values around the prominent 1 and 2 μm absorption features) in the unbrecciated basalt spectra. This relative detectability of the spectral slope consistent with the sample textures, as the feldspathic breccias exhibit the most complex and “welded” texture, followed by the intermediate nature of the basaltic breccias and the unbrecciated basalts with large mineral grains and lack of abundant matrix materials. QUE in particular has abundant glassy matrix, and the chip sample is clearly quite difficult for photons to interact with in the visible to near-infrared wavelength region, as it exhibits very few notable absorptions and essentially only exhibits the blue continuum slope, apart from the weak short-wavelength (likely charge transfer) absorption. ALH exhibits weak, fairly short-wavelength 1 and 2 μm absorptions, likely indicative of a low-

Ca pyroxene composition. Pyroxenes in ALH span a wide range, but in this bulk chip sample spectrum, the low-Ca component appears to dominate.

The basalts and basaltic breccia samples exhibit longer-wavelength 1 and 2 μm pyroxene absorptions, consistent with the more Ca- and Fe-rich pyroxene compositions found in those samples. LAP appears to exhibit slightly longer-wavelength absorptions than the other three, most notable in the 2 μm absorption. These longer-wavelength absorption features are consistent with the measured compositions given in Figure 3, as LAP exhibits more Ca- and Fe-rich compositions than MIL and the basaltic breccias. However, those Ca- and Fe-rich compositions are restricted to grain rims; the central parts of the LAP pyroxene grains have compositions generally comparable to pyroxenes in MIL. Figure 3 is somewhat deceptive, as it indicates the range of pyroxene compositions found in a sample, but not necessarily the relative abundance of the various compositions. Nevertheless, these observations suggest that in the case of LAP, the grain exteriors are contributing disproportionately to the spectrum, as the grain interiors are compositionally similar to MIL pyroxenes but the LAP spectrum exhibits longer-wavelength absorption bands.

All of these spectra exhibit 1.2 μm absorption features, although the strength is variable between the spectra. EET96 in particular appears to exhibit a prominent 1.2 μm absorption, but this may be a product of the measurement conditions. Note that the spectrum of EET at wavelengths below the 1 μm absorption is flattened quite substantially, likely due to the measurement of a chip sample causing specular reflectance. A similar effect may occur between the 1 and 2 μm absorptions, mimicking a strong 1.2 μm absorption. Similar effects are observed in EET87, but less prominently.

The 1 and 2 μm features are proportionally weaker in EET96 and EET87, and as in the case of the “flattening”, this absorption “weakening” is more pronounced in EET96. It is tempting to attribute these observations to physical differences between the samples (abundance of matrix material or some other physical property), but such conclusions cannot be drawn from measurements of irregular surfaces. Variable sample surface orientation and texture can have significant effects on relative features between spectra, so such analyses must wait until measurements of these samples in particulate form have been acquired.

4.2.2 Chip Sample Diagnostic Mid-Infrared Features

In the mid-infrared, the effect of measurement as chip samples rather than particulate samples becomes less prominent. The wavelength range covered by Figure 6 is still largely in the volume scattering regime in which photons interact primarily with the interiors of samples rather than being scattered primarily by their surfaces. Reflectance spectra across this wavelength range tend to decrease in reflectance even in particulate form, so the “blue” continuum slope is not obviously apparent. The measurement of chip samples does cause absorption features to be quite weak relative to comparable measurements of particulate samples, as was observed in the near-infrared. Absorptions due to pyroxene between 5 and 7 μm are apparent, most notably in LAP and MIL. Weak absorptions due to crystalline plagioclase near 4.2 μm can be observed in some spectra, such as ALH and possibly LAP. While QUE is quite feldspathic, it is a difficult sample for photons to interact with, as observed in the near-infrared, and it exhibits few diagnostic features in this wavelength range as well. MIL has abundant maskelynite, the shocked, vitrified form of plagioclase. However, the feature near 4.2

μm is a result of crystalline plagioclase, and thus it is not observed in the spectrum of MIL. All spectra exhibit CF's near $8 \mu\text{m}$, although the unbrecciated basalts appear to exhibit slightly longer-wavelength CF's. Measurement of these samples as particulates will improve the detectability of features in this wavelength region.

4.2.3 MIL05035 Components

We have begun the process of deconstructing these samples into their components, and present the results for MIL05035 as a case study. The spectra collected of the MIL05035 separates, presented in Figure 7 along with the bulk chip sample spectrum, illustrate the difficulties and benefits of deconstructing the samples in this manner. To first order, the chip sample spectrum follows the pyroxene spectrum. This is unsurprising in a sample largely dominated by pyroxene and maskelynite; the pyroxene should be the optically dominant phase. Some differences can be observed, including the strength of the absorption features, which is likely a product of measurement as a particulate. The $2 \mu\text{m}$ pyroxene absorption in the chip spectrum appears to be a bit asymmetric relative to the pyroxene spectrum, perhaps due to the zoned nature of the pyroxene grains causing some compositions to “appear” in different proportions in the pyroxene separate relative to the chip sample. However, some artifact of the viewing geometry is more likely to blame. The “maskelynite” exhibits significant pyroxene contamination, as evidenced by the 1 and $2 \mu\text{m}$ pyroxene absorptions. Some important differences are apparent, including the broadened “flattened” region around $1.2 \mu\text{m}$ relative to the pyroxene spectrum and the longer wavelength reflectance maximum between the 1 and $2 \mu\text{m}$ absorptions relative to the pyroxene spectrum. Maskelynite tends to exhibit weak, broad absorption features similar to those in Fe-bearing glasses

[*Bell and Mao, 1973; Adams and Goullaud, 1978; Pieters, 1996*]. This broadened “flattened” region in the MIL “maskelynite” spectrum may be due to some residual spectral signature of the maskelynite features, although this is quite difficult to quantify in the presence of substantial pyroxene contamination. For comparison, a spectrum of a Fe-bearing (~0.35 wt.% FeO) plagioclase is also plotted. This spectrum was measured by Isaacson et al. [2010]. The diagnostic plagioclase 1.3 μm absorption feature is apparent. This absorption feature is a possible cause of the broadened “flattened” region in the MIL “maskelynite” spectrum, although maskelynite is not likely to retain a prominent 1.3 μm absorption after vitrification.

4.2.4 MIL05035 Mid-Infrared Constraints

The mid-infrared results (Figure 8) confirm that the maskelynite lacks diagnostic plagioclase absorptions. The 70017 plagioclase spectrum exhibits the weak, diagnostic feature at ~4.4 μm , while the MIL “maskelynite” spectrum does not. The maskelynite spectrum does exhibit a short-wavelength CF, consistent with its feldspathic composition. The MIL “maskelynite” exhibits a CF at slightly longer wavelength than the 70017 plagioclase, consistent with small amounts of pyroxene contamination. The pyroxene separate spectrum exhibits prominent absorption features that are only weakly apparent in the chip sample spectrum. The pyroxene features between 5 and 7 μm are readily apparent, as is the longer-wavelength CF. The chip sample CF falls between the pyroxene and maskelynite CF, as expected.

4.2.5 MIL05035 Component Deconvolutions

Deconvolutions are an excellent method for making quantitative assessments and comparisons between absorption features in reflectance spectra. Furthermore, whether these spectra are to be used as ground truth or as baselines in the attempt to constrain the geologic context of the meteorite sample, variations in spectral features on the Moon are generally quite subtle. Diagnostic differences between spectra and the physical properties of absorption features (strength, width, and position) can be extremely difficult to detect with the unaided eye. Properties of absorption features thus must be quantified.

Our chosen deconvolution method is the MGM, which determines the diagnostic physical properties for each absorption band. We attempted to fit the pyroxene spectrum with a single Gaussian each for the 1 and 2 μm absorptions, and were unable to obtain satisfactory fits in which the properties of the 1 and 2 μm Gaussians are consistent with previously-established trends in deconvolution of pyroxene reflectance spectra [e.g., *Klima*, 2008]. This indicates that more than one composition of pyroxene is evident in the spectrum, likely due to the zoned nature of the pyroxenes in MIL. The results of deconvolutions with two Gaussians each for the 1 and 2 μm pyroxene absorptions are shown in Figure 9. The relative band strengths of the low-Ca and high-Ca components are consistent, a requirement for a “good” fit. The results of deconvolutions of the chip spectrum are generally consistent with those of the pyroxene separate spectrum. This suggests that for simple samples such as MIL (pyroxene dominates the spectrum), measurement and deconvolution of the bulk sample may be sufficient. Recall that this “bulk sample” spectrum was measured as a chip rather than a particulate, so conclusions drawn from this deconvolution must be seen as preliminary.

The results of these deconvolutions are compared to previously established trends in pyroxene 1 and 2 μm band positions in Figure 10. Our results, for both the pyroxene separate and the bulk chip sample, both low-Ca and high-Ca pyroxenes, fall toward the long wavelength ends of the data clouds for the 2 μm band. The LCP Gaussians fall toward the short-wavelength edge of the cloud for 1 μm band, whereas the HCP Gaussians fall slightly toward the long-wavelength side of the data cloud for the 1 μm band. The HCP Gaussians for the pyroxene and chip spectra differ more than the LCP Gaussians. These deviations may be due to slightly incorrect FWHM values for the MGM-derived Gaussians; if the bands are too narrow or too wide, the derived band centers can be misleading. We have compared our MGM results to previously published results for synthetic pyroxenes [*Klima et al.*, 2007] and found our results to be consistent with the range of MGM-derived parameters obtained by that study. However, it should be noted that that study only addressed synthetic Ca-free pyroxenes, while the pyroxenes in MIL contain significant Ca. Ca^{2+} is a larger cation than Fe^{2+} , and can cause the absorptions due to Fe^{2+} in the M1 and M2 site to occur at slightly different wavelengths, potentially leading to broader modeled absorption bands for the 1 μm band. However, this effect should largely be accounted for by the use of two Gaussians for each of the 1 and 2 μm absorptions. We do find that the chip sample 1 μm LCP Gaussian has a slightly higher FWHM than the pyroxene separate spectrum 1 μm LCP Gaussian. The difference in FWHM values may explain why the 1 μm LCP Gaussians for the chip sample and pyroxene separate spectra vary slightly in Figure 10. The chip sample 2 μm Gaussians are substantially wider than the pyroxene separate 2 μm Gaussians, and are somewhat beyond the range found by Klima et al. [2007], although we must again bear in

mind the caveat that the compositions of the Klima et al. [2007] pyroxenes do not match the MIL pyroxenes. These inconsistencies may point to a limitation in deconvolution of chip sample spectra, and may be a result of the slightly “asymmetric” nature of the chip sample spectrum’s 2 μm absorption that was noted above. Nevertheless, incorrect FWHM results, possibly due to measurement of the bulk sample as a chip rather than as a particulate, are a possible explanation for the fairly short wavelength modeled positions of the 1 μm LCP Gaussians and/or the disagreement between the HCP Gaussians of the pyroxene/chip spectra.

Despite some minor inconsistencies, these sorts of quantitative assessments of spectra collected of the meteorite samples and their components are important for maximizing the value of analyses of the meteorite samples. Qualitative assessments are not sufficient, as the spectral diversity of the lunar surface is fairly subtle. Whether these results are applied as ground truth or as baselines to search for the samples’ geologic context, these quantified results can be applied directly to comparable results obtained from analyses of remotely-sensed data.

5 Summary & Conclusions

The lunar meteorite collection presents a highly diverse sampling of the lunar crust, almost certainly including regions far from those sampled by the Apollo and Luna programs. While our small subset of the full lunar meteorite collection does not span the diverse range of samples found in the full collection, it does demonstrate the highly diverse nature of the collection. We have conducted textural and compositional analyses using SEM and electron microprobe. These analyses provide invaluable context for interpreting the reflectance spectra collected of the chip samples and being collected of

the individual components of those chip samples. The chip sample spectra are valuable, but suffer from limitations in the ability to collect high-quality reflectance spectra of slab and chip samples. Furthermore, the chip samples are collections of diverse components, particularly in the case of the breccia samples and especially so for the feldspathic breccias. Not only are the chip samples difficult to measure, a bulk sample spectrum would not be sufficient for these samples even if measured of a particulate sample. Separation of these samples into their components is underway, and results for MIL05035 are presented as an example of the value of such work. Quantitative deconvolutions of the pyroxene separate spectra from MIL05035 and the MIL05035 chip sample spectrum are presented. These results exemplify the sort of data needed to harness the full value of the lunar meteorite samples as ground truth or as constraints for determining the geologic context of the meteorite samples with remotely-sensed hyperspectral reflectance data.

6 References

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Table 1. Lunar Meteorite Sample Details

Sample No.	Parent Subsample No.	Type	Allocated Mass (mg)	Abbreviated Name
ALHA81005,97	24	Anorthositic regolith breccia	304	ALH
QUE93069,58	0	Anorthositic regolith breccia	315	QUE
LAP02205,63	55	Unbrecciated basalt	319	LAP
MIL05035,43	25	Unbrecciated basalt	331	MIL
EET87521,87	11	Basaltic fragmental breccia	312	EET87
EET96008,47	17	Basaltic fragmental breccia	320	EET96

Table 2. Results of MGM Deconvolutions of MIL05035 Pyroxene Separate and Chip Sample Spectra

Absorption	Parameter	Px. Sep. Value	Chip Value
LCP 1 1 μm	Center ¹	904.62	902.62
	FWHM ²	182.11	196.62
	Intensity ³	-0.959	-0.7699
HCP 1 μm	Center	1027.7	1038.5
	FWHM	189.93	190.68
	Intensity	-0.7962	-0.7117
1.2 μm	Center	1224.2	1226.7
	FWHM	283.95	279.24
	Intensity	-0.3096	-0.3922
LCP 2 2 μm	Center	1949.2	1934.1
	FWHM	598.08	681.37
	Intensity	-0.6223	-0.5375
HCP 2 μm	Center	2345.1	2364.2
	FWHM	587.61	628.2
	Intensity	-0.4379	-0.4572
Continuum	Offset	0.647	1.56
	Slope	-4.45E-06	-1.99E-05

¹Band centers reported in nm

²Full width at half maximum values reported in nm

³Intensity values reported as natural log reflectance

Figure Captions

Figure 1. Global Lunar prospector Th map [Lawrence *et al.*, 2000]. Blue shades indicate low values, and reds indicate high values, with a maximum of ~13 ppm. Apollo landing sites are indicated with squares, and Luna sample return sites with circles. Note the elevated Th abundances for all Apollo sample collection sites. The region of enhanced Th concentration on the nearside has been termed the Procellarum KREEP Terrane (PKT) by Jolliff *et al.* [2000].

Figure 2. Example backscattered electron images for grain mounts (basalts and basaltic breccias) and thin sections (feldspathic breccias) of our lunar meteorite samples. The “brightness” of regions in such images is controlled by the average atomic number of the mineral or phase. Dense phases such as oxides, sulfides, and metals appear bright, whereas relatively low-density phases such as Mg-rich pyroxene and plagioclase appear dark. Note the complex, brecciated nature of the feldspathic breccias, the coarse crystalline nature of the unbrecciated basalts, and the intermediate texture of the basaltic breccias.

Figure 3. Compositions of pyroxene, olivine, and plagioclase analyzed in our lunar meteorite samples.

Figure 4. Examples of zoning and/or exsolution exhibited by pyroxenes in our lunar meteorite samples. One example image is given for each sample. Colored lines indicate compositional profiles collected across a grain, and refer to colored symbols on the associated pyroxene quadrilaterals. All profiles shown on the quadrilaterals are not shown in the images, unless they could all be represented in a single backscattered electron image (LAP). For samples other than LAP, only example images are shown. Note the prominent compositional zoning in the unbrecciated basalts, and the core-to-rim trend from Mg-rich, Ca-poor pyroxenes to Fe-rich and then Fe-rich and Ca-rich in LAP pyroxenes. Prominent exsolution is exhibited in the breccia samples. Note in particular the broad exsolution features exhibited by the pyroxene grain from QUE (compositions in the quadrilateral for the example shown in the image are indicated by arrows).

Figure 5. Bidirectional reflectance spectra of lunar meteorite chip samples. Measurement as chip samples imparts a substantial negative (“blue”) continuum slope, and causes a significant portion of incident photons to be reflected specularly rather than scattered internally by mineral grains. This situation tends to produce poor reflectance spectra. The quality of these reflectance spectra is in inverse proportion to their degree of brecciation and textural complexity; the unbrecciated basalts exhibit the “best” spectra with the most prominent, diagnostic absorptions, and the feldspathic breccias exhibit spectra with the weakest diagnostic absorptions and most ambiguous spectral features.

Figure 6. Mid-infrared reflectance spectra of the meteorite chip samples. Color and line styles are identical to Figure 5. Note the slightly longer-wavelength position of the Christiansen Feature (CF) for the unbrecciated basalts, and the general muting of spectral

features (due to measurement as chips rather than particulate samples). Some samples exhibit weak features near $4.2\ \mu\text{m}$ that are diagnostic of crystalline plagioclase (e.g. ALH, and possibly LAP).

Figure 7. Bidirectional reflectance spectra of separated components of MIL05035 along with the spectrum of the chip sample plotted in Figure 5 and 6. Also plotted is a spectrum of a pure, crystalline iron-bearing plagioclase studied by Isaacson et al. [2010] that exhibits the characteristic plagioclase $1.3\ \mu\text{m}$ absorption feature. The chip sample spectrum is quite similar to the pyroxene spectrum, not surprising in a sample containing primarily pyroxene and maskelynite. The “maskelynite” spectrum exhibits absorption features at $1\ \mu\text{m}$, $1.2\ \mu\text{m}$, and $2\ \mu\text{m}$ due to contamination from pyroxene. However, it exhibits a longer-wavelength reflectance “high” between the 1 and $2\ \mu\text{m}$ absorption feature, perhaps an effect of residual spectral structure due to the maskelynite.

Figure 8. Mid-infrared reflectance spectra of MIL05035 components, chip, and 70017 plagioclase (vis/NIR spectra in Figure 7). Pyroxene features are much more prominent in the pyroxene spectrum than in the chip spectrum. Note the $4.2\ \mu\text{m}$ feature present in the 70017 plagioclase spectrum and its absence to the vitrified MIL05035 maskelynite spectrum. The pyroxene separate spectrum exhibits a long-wavelength CF, and the plagioclase/maskelynite spectra exhibit shorter-wavelength CF's. The chip sample CF falls between the pyroxene and maskelynite CF's.

Figure 9. MGM deconvolutions of the pyroxene separate and chip sample spectra shown in Figure 7. The results of the pyroxene separate spectrum deconvolution (a) were used as inputs to the chip spectrum deconvolution (b). The derived MGM parameters are presented in Table 2.

Figure 10. Comparison of MGM-derived band centers with previously-established trends in band centers. Results for the pyroxene separate spectrum are plotted in filled symbols, and for the chip spectrum in open symbols. Note the slight spread between the LCP absorptions, and the slightly more substantial spread between the HCP absorptions. Some explanations for these observations are proposed in the text. Previous data are from Adams (JBA) [1974], Hazen et al. (RMH) [1978], and Cloutis and Gaffey (EAC) [1991].

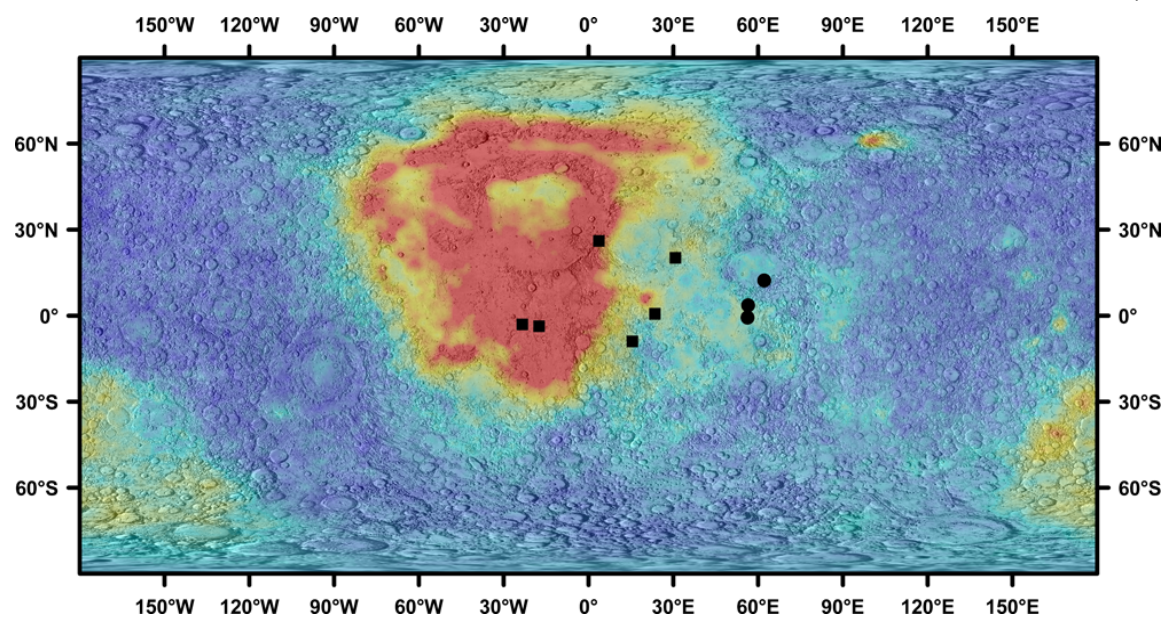


Figure 1.

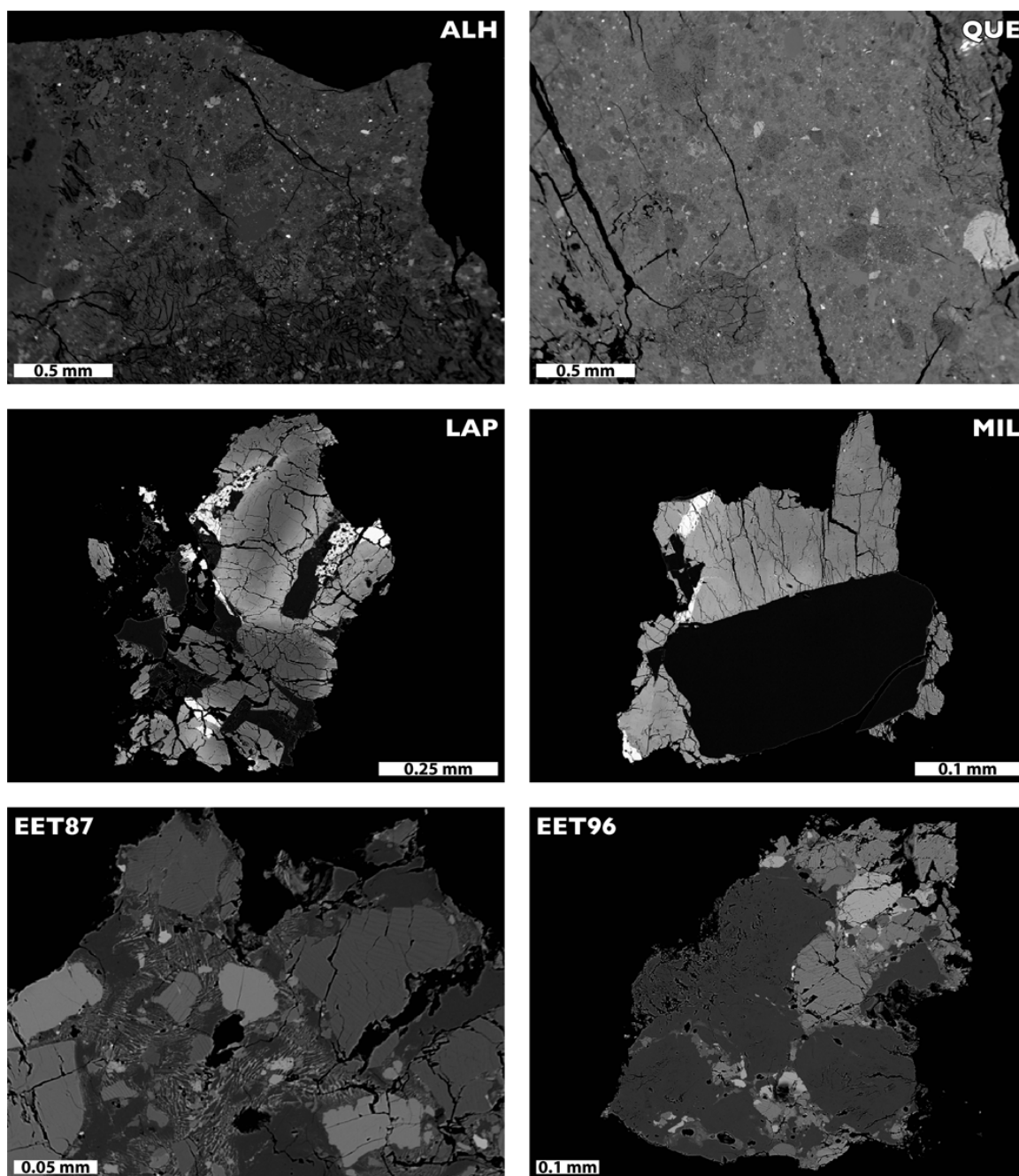


Figure 2.

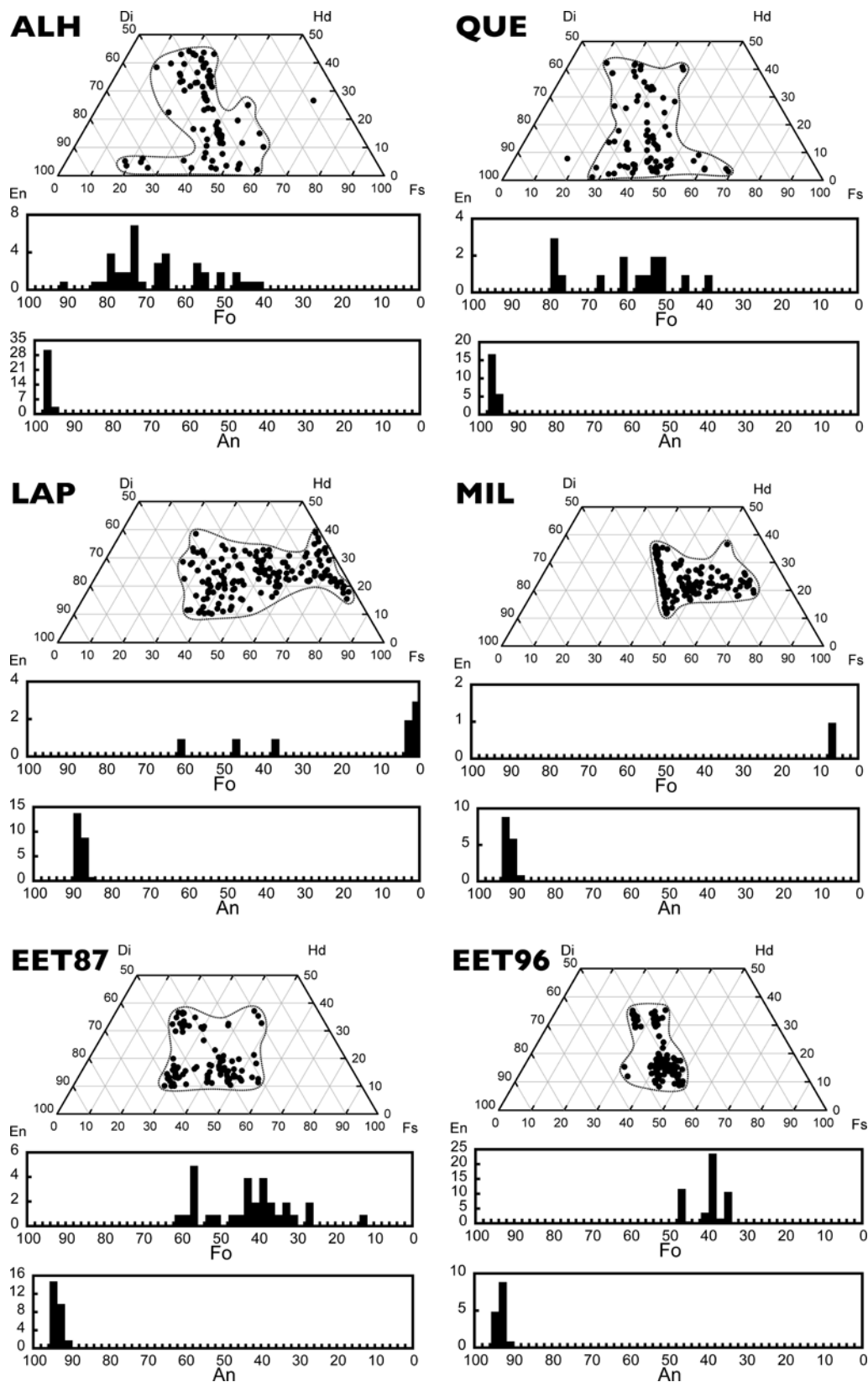


Figure 3.

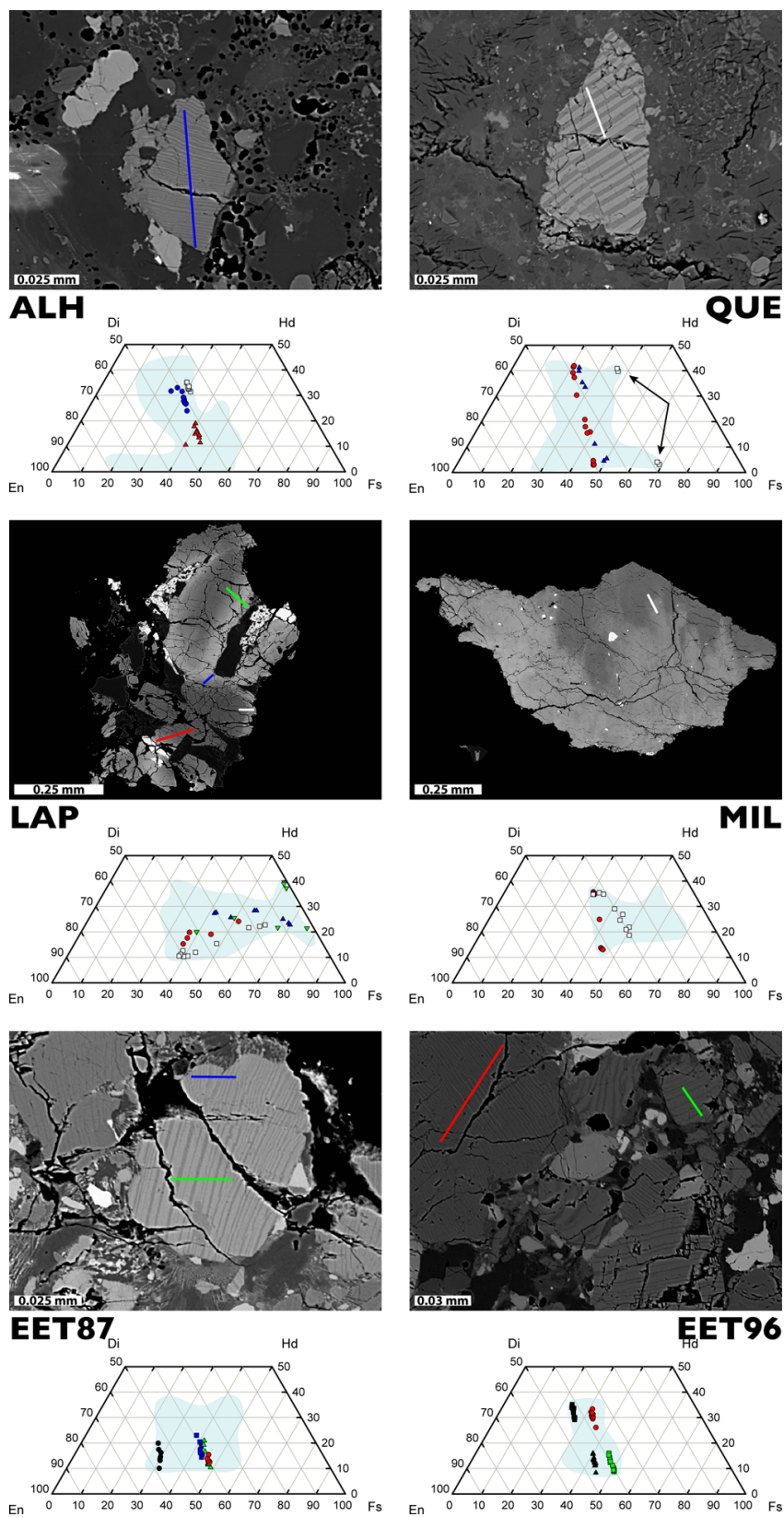


Figure 4.

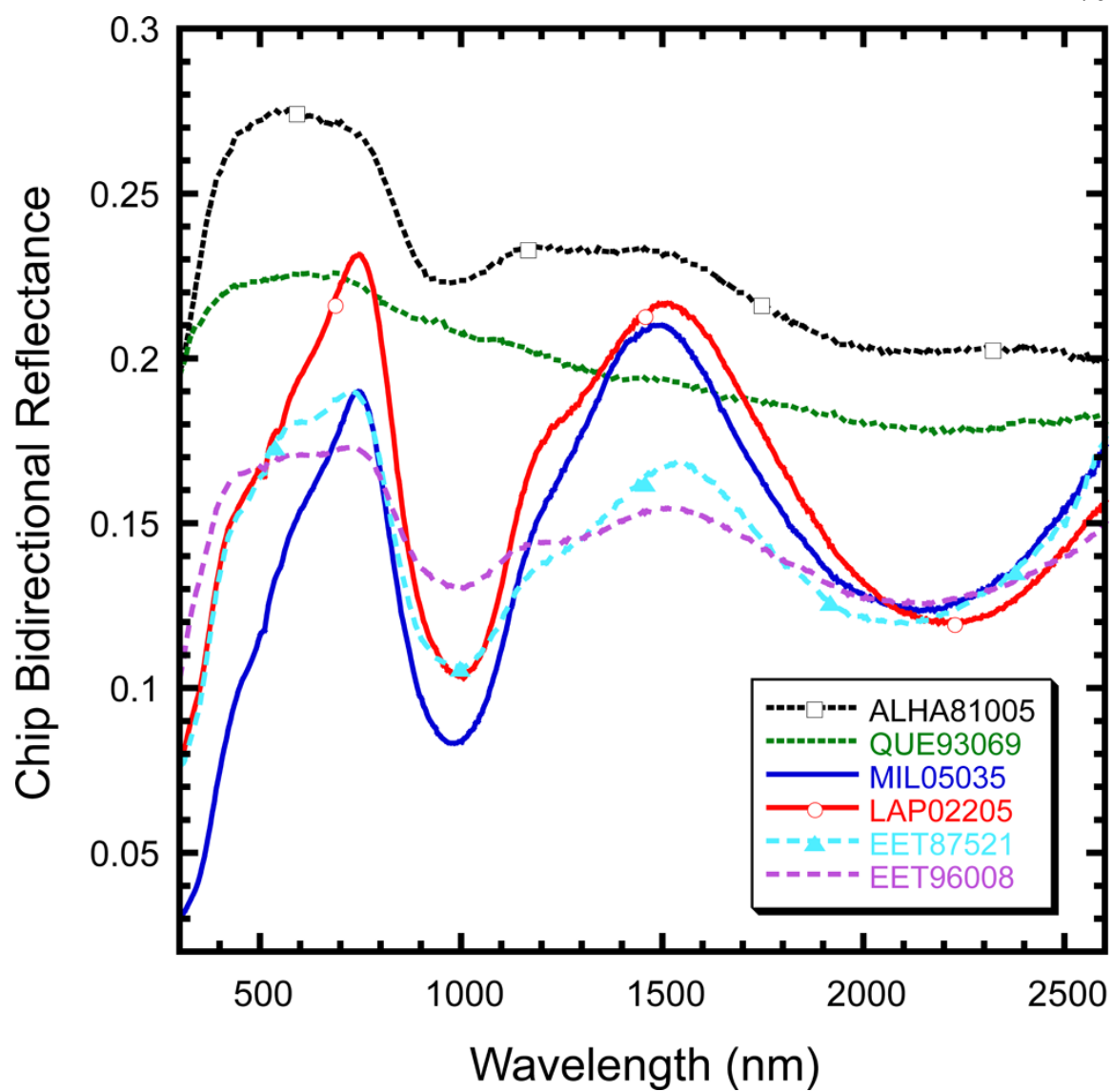


Figure 5.

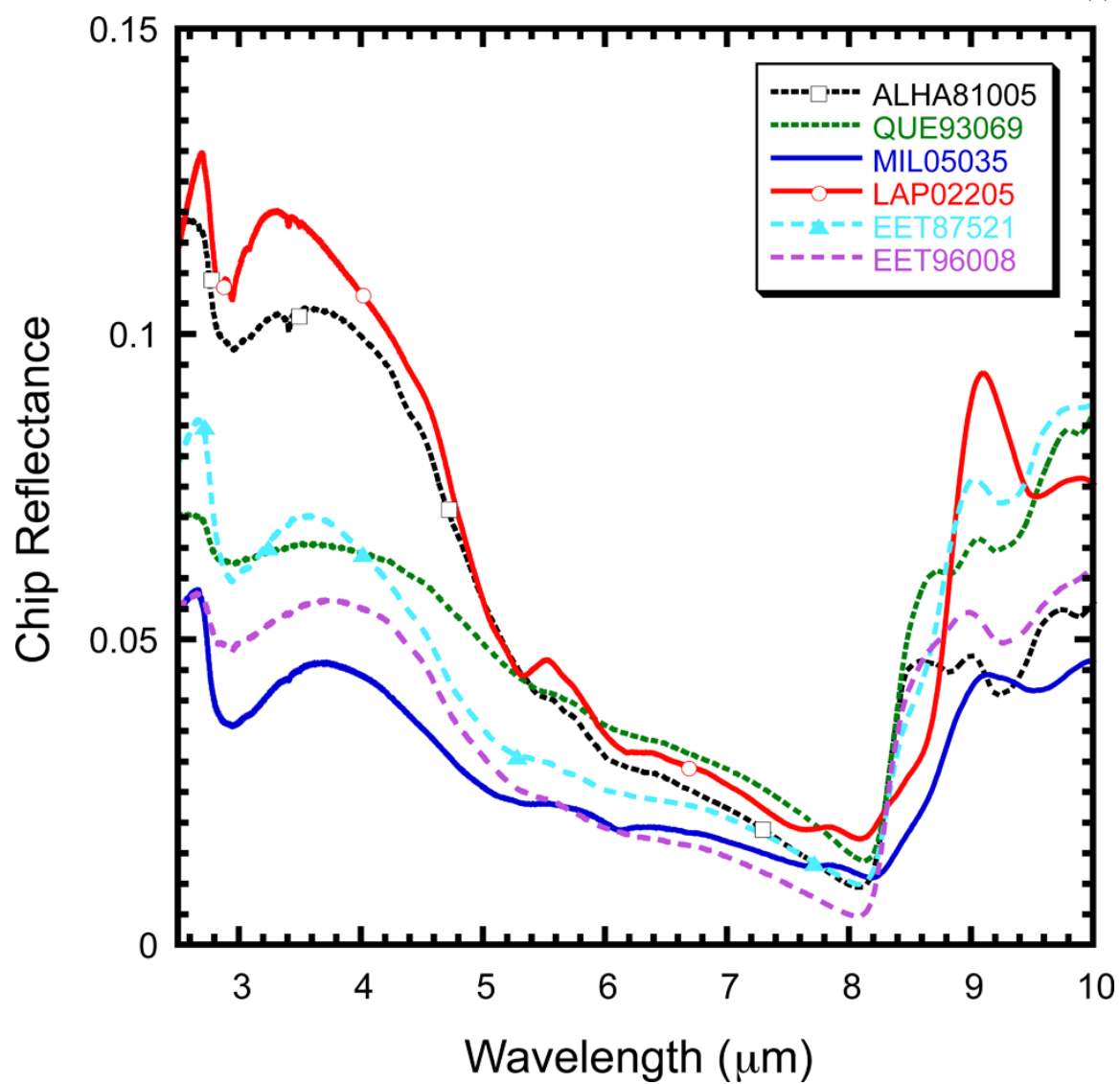


Figure 6.

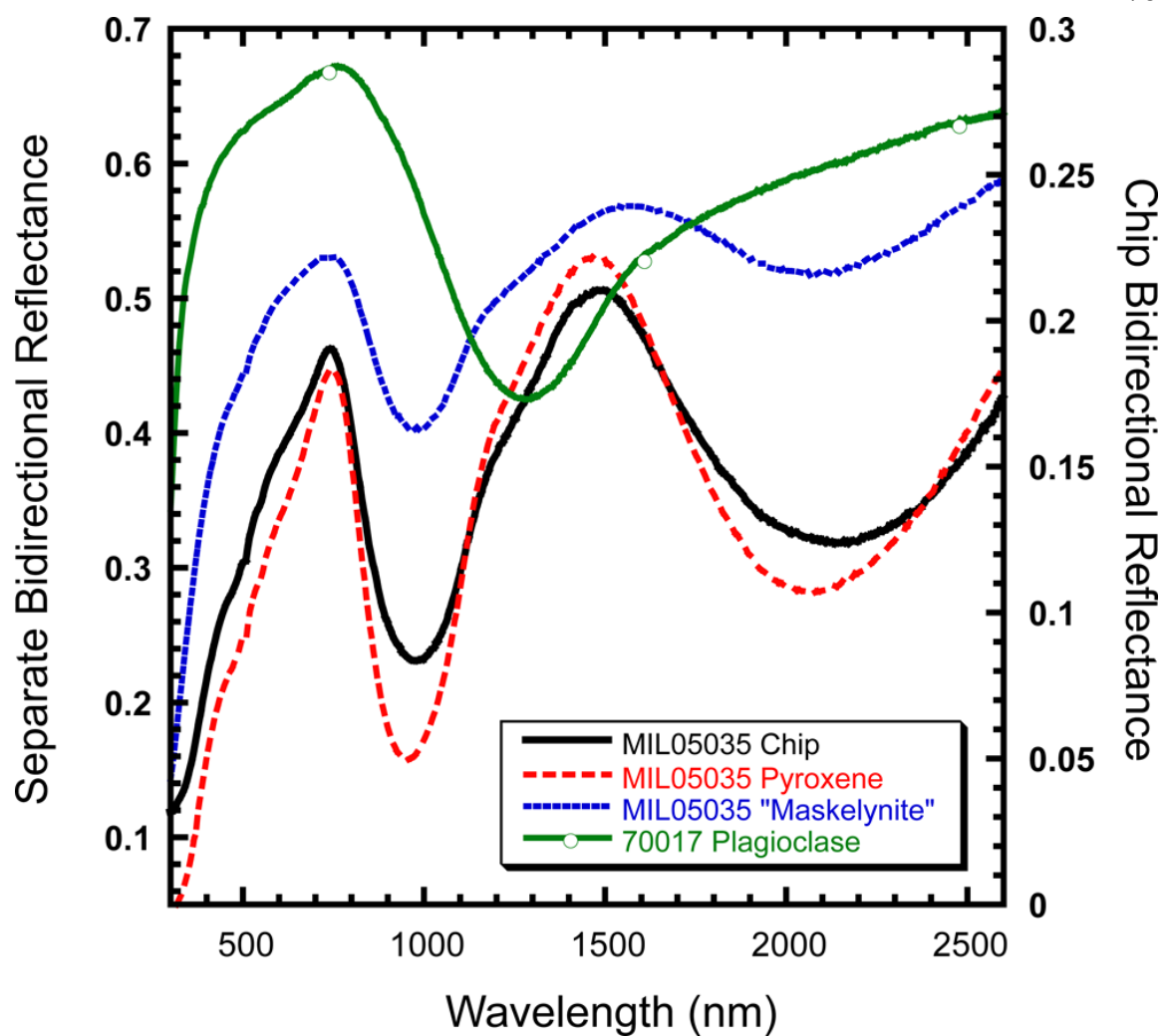


Figure 7.

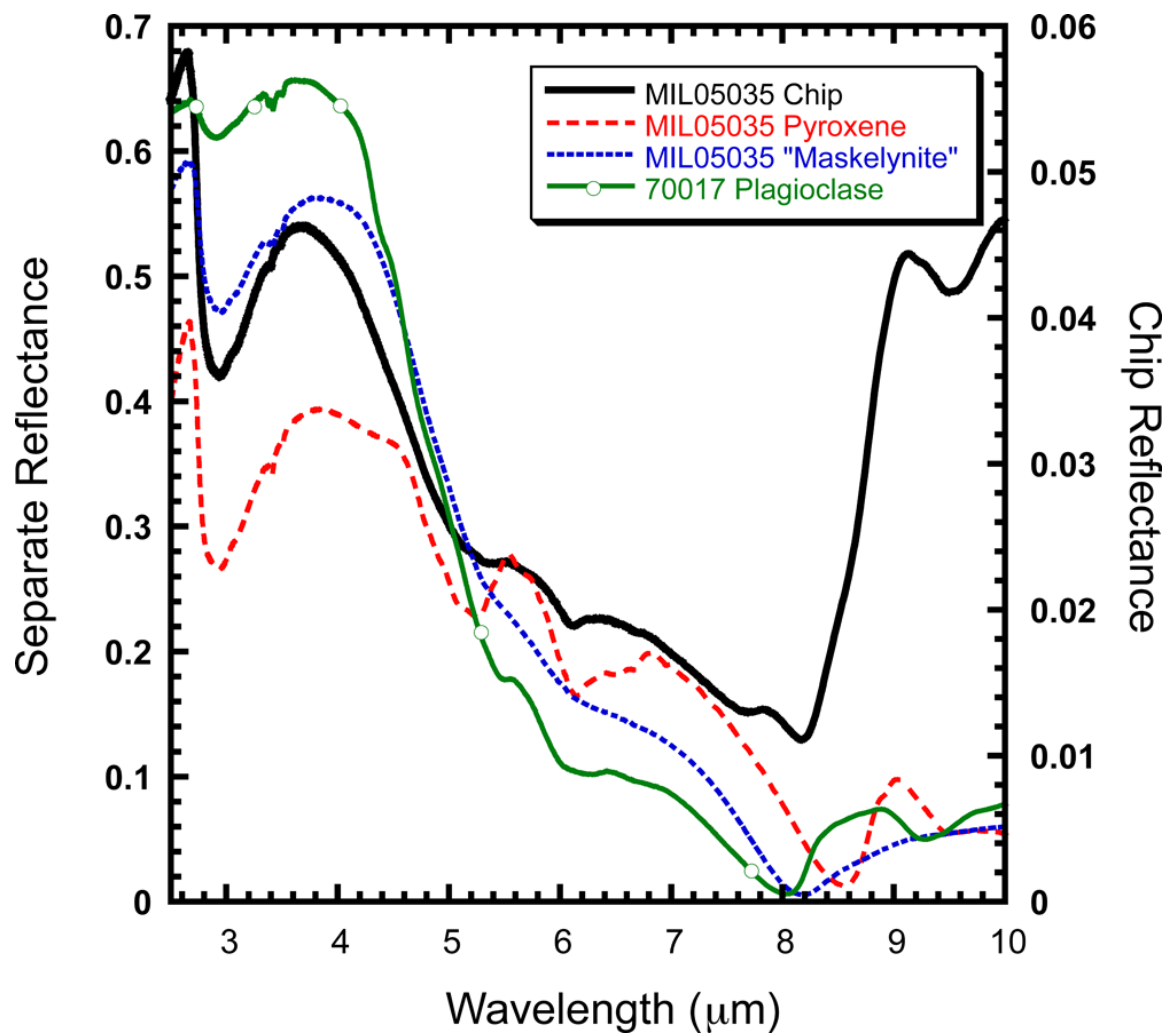


Figure 8.

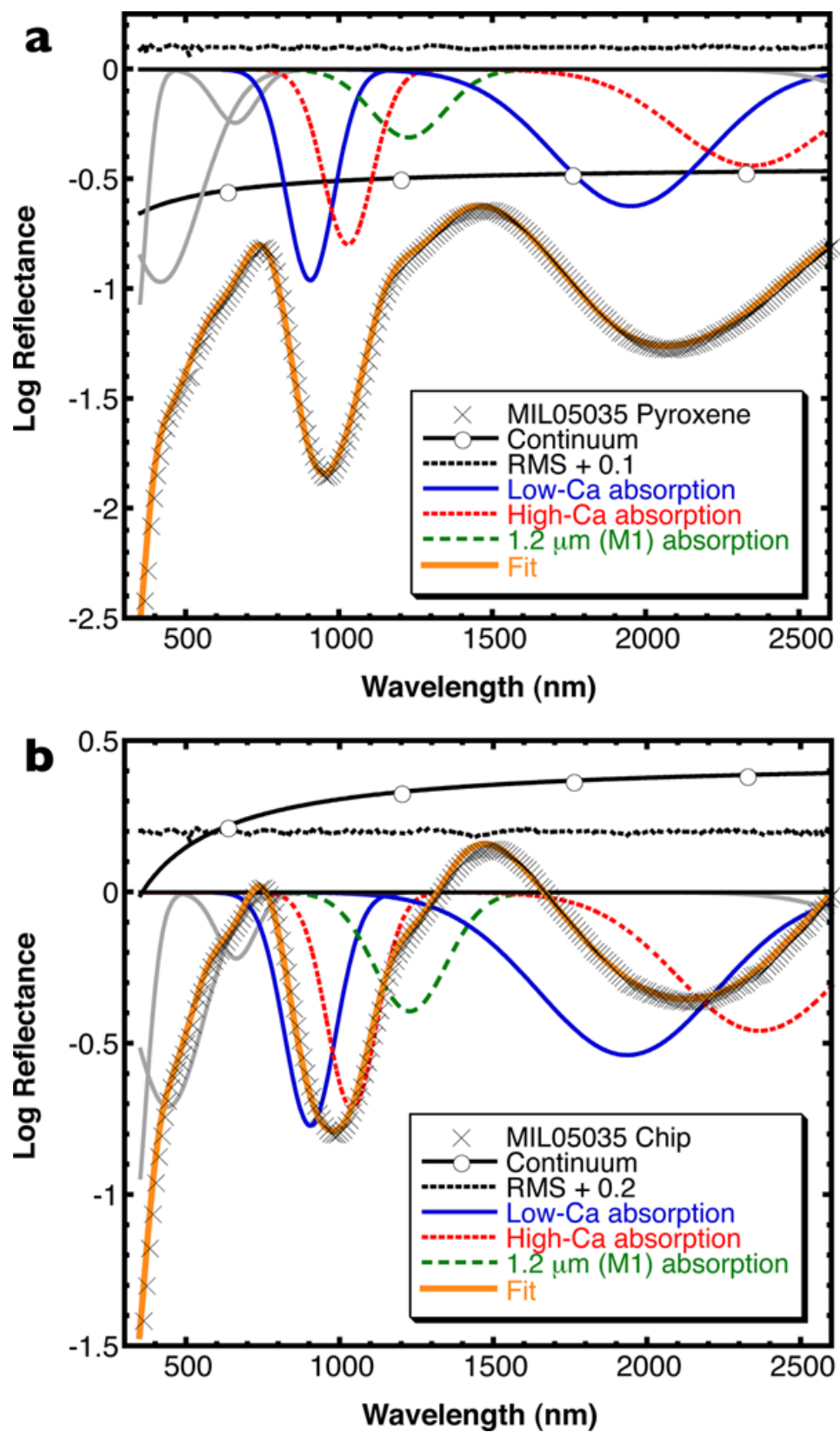


Figure 9.

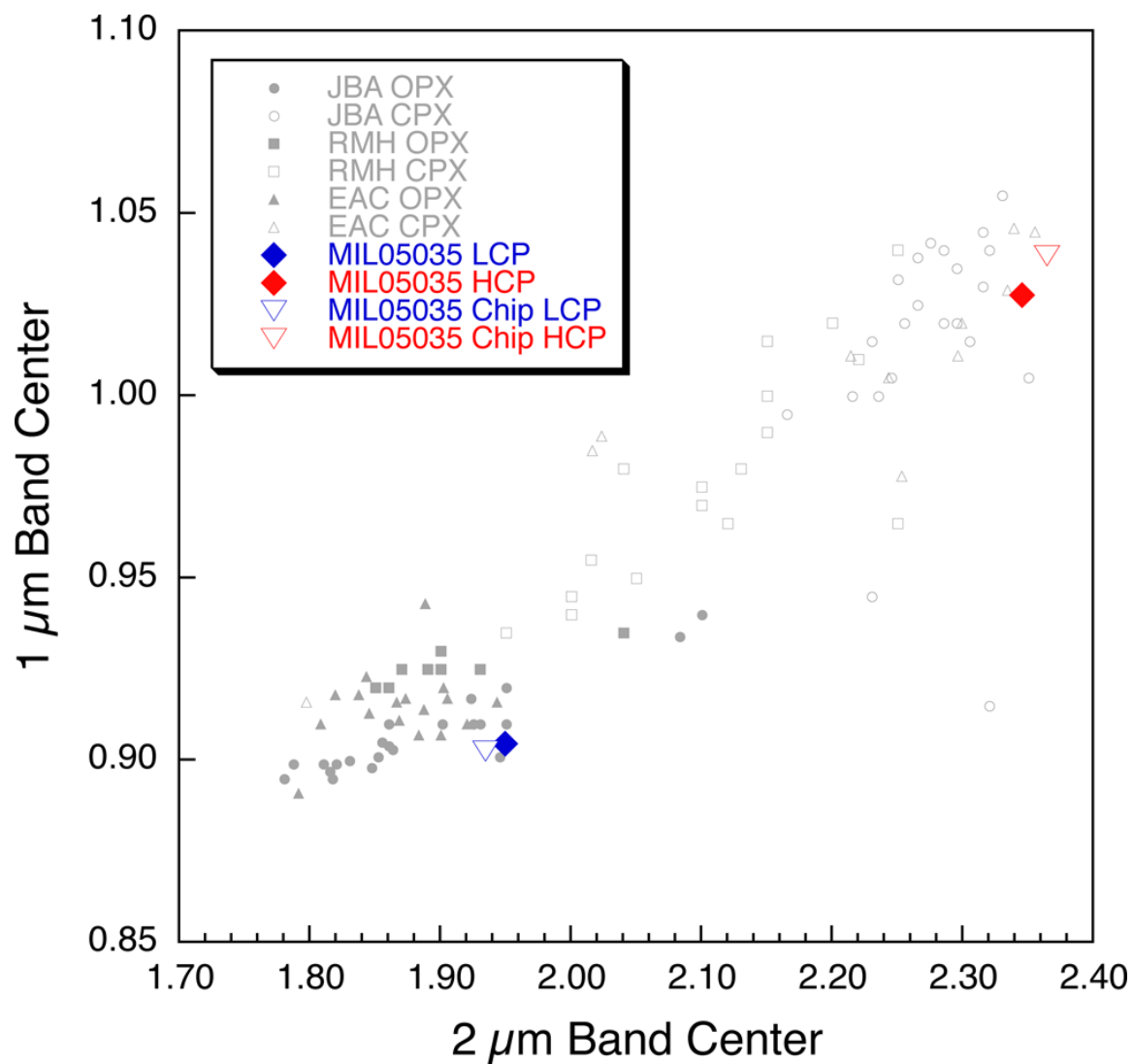


Figure 10.

CHAPTER 6: Investigation of the Water Content of Lunar Soil with Laboratory Reflectance Spectroscopy: First Results

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Abstract

Reflectance spectra of lunar soils measured in terrestrial laboratories always exhibit absorption features near 3 μm . These features near 3 μm are diagnostic of H_2O and OH. These absorption features are typically attributed to adsorbed terrestrial water, the logic being that lunar soil is dry and hydrophilic and water adsorbs onto the soil grains upon their exposure to the terrestrial atmosphere. We performed heating experiments designed to remove loosely-held adsorbed water on lunar soil sample 15041, collecting reflectance spectra before and after heating runs. The 3 μm absorption was observed to weaken following heating runs relative to pre-heating measurements. However, despite heating the soil sample to a maximum of $\sim 400^\circ\text{C}$ for 1 hour, significant absorption features remained in reflectance spectra collected immediately following the heating runs. We conclude that while some adsorbed water was driven off by the heating experiments, substantial water/OH remained on or in the sample, and that a source other than terrestrial water may be responsible for the 3 μm absorption feature observed in laboratory spectra of lunar soil samples.

1 Introduction

The search for water on the Moon has long been a goal in lunar science. From the first suggestion that permanently shadowed regions at the lunar poles might harbor volatiles in cold traps [Urey, 1952; Watson *et al.*, 1961a] to the current era of exploration with various remote sensing experiments specifically devoted to the search for water [e.g., Colaprete *et al.*, 2009; Spudis *et al.*, 2009], the topic has been something of a “holy grail” in lunar science. Historically, the accepted paradigm holds that the Moon is completely dry, having lost most of its volatiles during the giant impact that produced the Moon [e.g., Hartmann and Davis, 1975; Cameron and Ward, 1976; Pahlevan and Stevenson, 2007], although recent results are beginning to suggest that the Moon may be less dry than previously thought [Saal *et al.*, 2008; Clark, 2009; McCubbin *et al.*, 2009; Pieters *et al.*, 2009; Sunshine *et al.*, 2009].

When lunar samples were returned by the Apollo and Luna programs in the 1960's and 1970's, trace signatures of water were detected in lunar soils, but these detections were attributed to terrestrial contamination from the Earth's atmosphere [e.g., Epstein and Taylor, 1974]. The contamination assumption is rooted in the instability of water in the equatorial regions of the lunar surface where the samples were collected. This instability led to the assumption that the samples were dry when collected on the Moon, but were instantly coated with small amounts of adsorbed terrestrial water when exposed to the terrestrial atmosphere because of the extremely hydrophilic nature of the soils [e.g., Holmes *et al.*, 1973; Epstein and Taylor, 1974; Gammage and Holmes, 1977]. Experiments were conducted soon after the return of the lunar samples in which soils were heated to very high temperatures, in some cases up to 1400°C, as well as crushed in

an attempt to determine their volatile content. A number of gases were released from the samples, including H₂O [Gibson and Johnson, 1971; Gibson and Moore, 1972; Muller, 1972; Simoneit *et al.*, 1973; Gibson and Andrawes, 1978; Graham *et al.*, 1979]. However, these experiments could not distinguish between terrestrial contamination and native lunar water because of the common isotopic ratios between the Moon and Earth and the extreme difficulty of estimating pristine lunar D/H ratios [Epstein and Taylor, 1971; 1974]. Nevertheless, some workers suggested that a significant portion of the water released from the soils was produced while the soils were on the lunar surface [e.g., Gibson and Johnson, 1971].

Lunar soils measured in reflectance spectroscopy laboratories have the same “problem” with water. Absorption features near 3 μm are always observed in laboratory spectra of lunar soils [e.g., Pieters, 1998; Pieters and Taylor, 1998], and such features are diagnostic of water or hydroxyl. The precise shape and position of the 3 μm absorption is variable and often diagnostic of specific phases [e.g., Farmer, 1974]. This variability of features near 3 μm is illustrated by Figure 1, which is modified from Pieters *et al.* [2009]. For the purposes of this discussion, the various phases responsible for the absorption near 3 μm will be referred to generally as “water”, and the absorption near 3 μm as the “3 μm feature”. The 3 μm features in lunar soil reflectance spectra have traditionally been attributed to adsorbed terrestrial water, and they are persistent. The features weaken after samples are kept in a purged environment (dry and free of CO₂) for several days, but are not completely eliminated [Pieters, 1998; Pieters and Taylor, 1998]. This suggests that the water is not merely loosely bound to the soils, but is bonded more substantially to the soil grains. We have undertaken experiments in an attempt to measure reflectance

spectra of lunar soil from which this adsorbed water has been removed to the greatest extent possible. Our experiments involve heating a lunar soil sample to temperatures well above the boiling point of water (up to $\sim 400^{\circ}\text{C}$) in an attempt to drive off adsorbed water and measure the reflectance spectra of lunar soil free from this adsorbed water.

2 Methods

We chose to work with mare basalt soil sample 15041,210, which was previously analyzed as part of the Lunar Soil Characterization Consortium [Taylor *et al.*, 2001]. It is a mature mare basalt sample ($I_s/\text{FeO}=94$), and has a grain size range of 20-45 μm . Its spectrum, measured before any heating experiments, is plotted in Figure 2. This spectrum exhibits the typical features observed in lunar soils (weak 1 and 2 μm pyroxene absorptions, dark overall albedo, and reddened continuum slope) [Pieters, 1978; Pieters *et al.*, 2000; Hapke, 2001; Noble *et al.*, 2001; Taylor *et al.*, 2001]. However, this spectrum also exhibits a weak feature near 3 μm . Other features commonly associated with hydration, such as 1.4 and 1.9 μm absorptions, typically are not observed in reflectance spectra of lunar soils, and are not observed in the 15041 spectrum in Figure 2. We conducted our experiments with a small sample mass (~ 350 mg).

2.1 Heating Procedures

Our experimental procedure was based on the approach of Milliken and Mustard [2005] and involved heating the sample in air. All heating experiments and reflectance spectroscopy measurements were conducted in the RELAB at Brown University. Prior to any heating experiments, the sample, contained in an aluminum dish, was weighed and then left overnight in the spectrometer chamber, which is under constant dry air purge

with air filtered for H₂O and CO₂. The purged dry air is produced by a Parker Balston model 74-5041NA FT-IR Purge Gas Generator. This apparatus produces air with extremely low water (~1.5 ppmv) and CO₂ (<1 ppmv) contents. Spectra of the sample were collected following the overnight ‘purge’ prior to conducting heating experiments (labeled ‘purged’ in the plots shown below). The sample was contained in an aluminum dish, and was heated in one-hour increments.

2.2 Reflectance Measurements

We measured the sample’s reflectance spectrum by FT-IR immediately following a heating increment. A reasonable estimate for the delay between removing the sample from the furnace following the one-hour heating increment and collecting the post-heating spectrum is 5-10 seconds. While it is possible that some re-adsorption could occur over this timeframe, we believe that the soil sample was sufficiently hot and has sufficiently high specific heat to make this a relatively minor concern. Following the reflectance measurement, the sample was allowed to cool in the purged spectrometer for a period of two hours, and then subjected to another heating run where the temperature was increased by 50°C relative to the previous run. Heating runs were conducted with a minimum temperature of 200°C and a maximum temperature of 400°C. Heating experiments were conducted in several “batches”, and the minimum and maximum temperature varied between batches. Batch 1 covered temperatures of 200°-300°C, and batch 2 temperatures of 250°-400°C. The timescale of water re-adsorption was determined by a “re-adsorption” experiment in which the sample was measured repeatedly as the sample cooled over the two hour period following the initial post-heating reflectance measurement.

As the measurements following heating require opening the spectrometer chamber to load the sample and do not allow sufficient time for the purged environment to be re-established following the introduction of ambient laboratory air, the reflectance measurements have strong absorptions from atmospheric water and CO₂. The absorptions from atmospheric water occur at shorter wavelengths than the features at 3 μm caused by the water in or on the lunar soil, so they do not prevent analysis of that feature. They occur on the short wavelength “wing” of that 3 μm absorption feature, however, and they complicate evaluation of the maximum reflectance value of this wing. One of the principal methods for analyzing the strength of the water absorption feature is to calculate a band depth, which involves computing a continuum slope over the absorption feature. Thus, the atmospheric absorptions, which obscure the short wavelength wing of the absorption, prevent accurate determination of the continuum slope. We were forced to develop a procedure to correct for this atmospheric water.

2.3 Atmospheric Correction Procedure

Our approach involved collecting a number of spectra with an empty spectrometer chamber other than the brushed gold reference standard. A background or reference spectrum was acquired in a purged environment using the reference standard of the FT-IR spectrometer. The chamber was then opened and allowed to reach ambient conditions. After closing the chamber, a series of spectra were collected as the chamber returned to the purged conditions. The result is a series of spectra of decreasing amounts of laboratory air in the spectrometer’s path length, which we call “re-equilibration” spectra. These spectra are flat and have reflectance values near unity outside of the atmospheric absorption windows, but exhibit strong absorptions in those windows.

Examples of such spectra are shown in Figure 3. The spectra shown in Figure 2 have been scaled at 2.4 μm to avoid offset errors due to the inability to collect proper backgrounds over the course of the run. The spectra have reflectance values near unity outside the atmospheric absorptions because the target of the spectrometer is the calibration reference standard. The strengths of these absorptions decrease with increasing time, as the concentrations of H_2O and CO_2 in the chamber decrease. We compared the strength of the atmospheric absorptions in our “heated soil” spectra to those in the suite of re-equilibration spectra, and selected the re-equilibration spectrum whose atmospheric absorption strengths most closely matched those of a “heated soil” spectrum. We then “removed” the atmospheric absorptions from the soil spectrum by dividing the soil spectrum by the selected re-equilibration spectrum. This approach is sufficient to remove the atmospheric absorptions such that a reasonable continuum slope could be fit over the 3 μm absorption feature.

2.4 Band Area Calculations

We quantified the strength of the 3 μm absorption by calculating a band area or “integrated band depth”. This was accomplished by first fitting a continuum slope over the 3 μm feature. The spectra were first scaled at 2.4 μm . This wavelength was selected so that spectra are scaled to a wavelength just short of the principal water absorption feature. A continuum was then fit between 2.7 μm and the maximum reflectance value beyond the 3 μm region, typically at around 4.2 μm . Because the 2.7 μm wavelength lies in the atmospheric absorption region, residual errors from the atmospheric correction can impart significant bias to the band area calculation, particularly for the weak water bands observed in lunar soils. To avoid this bias, we selected a ‘standard’ reflectance value for

the 2.7 μm wavelength from which to calculate this continuum slope for all spectra. The standard value was obtained from the ‘purged’ spectrum measured in one of the heating batches. This approach means that errors in absolute albedo between measurements, which are possible due to subtle geometry effects, may bias the band area calculation. However, our choice to scale all spectra to a standard wavelength mitigates this concern, and this process reduces the much larger source of error imparted by residual atmospheric absorption bands. The integrated band depth for the 3 μm feature was then calculated by summing the total offset between continuum slope and spectrum between 2.7 and 3.3 μm . This procedure was performed for each heated soil spectrum collected during this study.

We acknowledge that our experimental procedure is not the ideal method for dehydrating hydrophilic samples by heating. An ideal procedure would involve heating the samples under vacuum, and collecting spectra continuously as the sample is heated. However, such a procedure was not possible within the scope of this study.

3 Results

The results of the heating experiments are presented in plots of scaled reflectance. Data are presented in plots focused on the 3 μm region, with results presented separately for each of the three “batches” of heating experiments. Spectra collected during the heating experiment batches are plotted in Figure 4, with batches 1 and 2 illustrated in Figure 4a and 4b. The “purged” spectra were collected after leaving the sample in the purged spectrometer chamber overnight, but prior to heating experiments for a given batch. The various “heated” spectra are labeled with the temperature at which the sample was heated for a one-hour increment, and were collected as quickly as possible after transferring the sample from furnace to spectrometer chamber.

The results of the “re-adsorption” measurements are presented in Figure 5, a plot of band area versus time after removal from furnace. This plot illustrates the band area calculated for each spectrum collected during the re-adsorption measurements, using the method described above.

4 Discussion

4.1 *Persistence of 3 μm Absorption*

All spectra plotted in Figure 4 exhibit features near 3 μm , indicating that some amount of water remained in or on the sample when it was measured following each heating step. The water bands generally became weaker as the sample was heated to progressively higher temperatures, perhaps indicating that the heating process was driving off increasing amounts of water at higher temperatures. However, even heating the samples to well above the boiling point of water does not drive the water content of the samples below the detection limit with this technique, which typically ranges from a few to a few tens of ppm [e.g., *Rossmann*, 2006]. It is possible that some water could be re-adsorbing onto the sample in the brief time between heating and measurement, and thus that the actual amount of water driven off of the sample by heating is greater than indicated by these results. However, the data presented in Figure 5 suggests that this is not a dominant effect, as significant increases in band strength begin to occur only at ~ 10 minutes after removal from the furnace. Also evident in Figure 5 is an initial increase, after the ~ 10 minutes previously mentioned, in band strength (likely due to residual atmospheric water introduced by breaking the purge in the spectrometer chamber) followed by a gradual decrease in band strength as the purged environment is re-established. These “re-adsorption” experiments were done under a purged environment,

so it is possible that the re-adsorption timescale could be shorter under ambient conditions.

We acknowledge that such experiments as those illustrated in Figure 5 cannot capture the critical time period immediately after heating and during measurement (~30 seconds), but the delay between removal from the furnace/measurement and dramatic increase in band area suggests that re-adsorption on such short timescales is not a dominant factor. Our experiments are limited by being conducted under ambient conditions; more robust conclusions could be obtained by conducting the heating experiments and spectroscopic measurements under vacuum. Such work has recently been undertaken by Zent et al. [2010] and Hibbitts et al. [2010].

4.2 Volatile Release from Lunar Soils

The nature of the bond between water molecules and the lunar soil grains is unclear. It was thought initially that water from the terrestrial atmosphere would adhere to soil grains through the relatively weak process of physical adsorption. However, were physical adsorption solely responsible for the water observed spectroscopically in the lunar samples, heating experiments such as those performed here would likely be able to drive off most if not all of the water. Thus, the water observed in the samples after heating to relatively extreme temperatures is at least partially bonded through chemisorption (characterized by strong ionic/covalent bonding), which is a much stronger process than physical adsorption or physisorption (characterized by the weaker van der Waals force) [Gibson and Johnson, 1971; Holmes et al., 1973; Gammage and Holmes, 1977; Graham et al., 1979; Fubini et al., 1989]. Indeed, early experimental work with lunar soils seemed to suggest that the soils were particularly hydrophilic due to the

network of fine pores and fractures in the samples, which produced an increase in specific surface area. This property could be altered only by annealing these small-scale “defects” at high temperature ($>700^{\circ}\text{C}$) [Fuller *et al.*, 1971; Gibson and Moore, 1972; Holmes *et al.*, 1973; Gammage and Holmes, 1977]. However, the fact that the water absorption features in our spectra were observed to weaken with increasing heating temperature suggests some success at dehydrating the sample, perhaps indicating that at least some of the water is attached to the soil sample through adsorption [e.g., Simoneit *et al.*, 1973].

4.3 Source of Water in Lunar Soil

Our experiments cannot rule out the possibility that at least some component of the water causing the absorptions near $3\text{ }\mu\text{m}$ observed in this study is of lunar origin. It has long been hypothesized that the lunar poles may harbor deposits of water-rich materials in permanently-shadowed regions [Urey, 1952; Watson *et al.*, 1961a; Watson *et al.*, 1961b; Arnold, 1979; Taylor *et al.*, 1995; Nozette *et al.*, 1996; Feldman *et al.*, 1998; Feldman *et al.*, 2001; Nozette *et al.*, 2001; Cocks *et al.*, 2002; Crider and Vondrak, 2002; Campbell *et al.*, 2003]. Furthermore, recent discoveries suggest the presence of widely distributed surficial water or hydroxyl on the Moon [Clark, 2009; Pieters *et al.*, 2009; Sunshine *et al.*, 2009], and potential local occurrences of significantly more abundant water near the poles [Colaprete *et al.*, 2010; Spudis *et al.*, 2010]. The lunar sample collection contains little evidence of hydrated phases or other chemical or mineralogical signs of lunar water. Nevertheless, numerous hypotheses have been proposed for the generation and retention of water on the lunar surface [e.g., Urey, 1952; Arnold, 1979; Crider and Vondrak, 2000; Feldman *et al.*, 2001; Crider and Vondrak, 2002; Ong *et al.*,

2006; Saal *et al.*, 2008], and the recent detection of small amounts of water broadly distributed across the Moon's surface has re-ignited investigation of the process or processes responsible for producing lunar water. In light of the difficulty of removing the water from our soil sample despite aggressive heating experiments and the plausibility of native lunar water on the lunar surface, we must conclude that some component of the water causing the 3 μm absorptions observed in this study is potentially of lunar origin.

5 Conclusions

We have conducted experiments to dehydrate a lunar soil sample. Dehydration was conducted by hour-long heating runs in a furnace, covering temperatures from 150°C – 400°C. Water content was assessed by collecting reflectance spectra across the diagnostic 3 μm H₂O absorption feature. Absorptions due to water were observed even after heating the soil sample to 400°C. We interpret our results to indicate that water in the lunar samples is not retained merely by simple adsorption; some combination of adsorption and chemisorption is indicated. Furthermore, our results cannot rule out the possibility that some of the water observed in lunar soils is of lunar rather than terrestrial origin.

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Figure Captions

Figure 1. Model reflectance spectra water, OH, and water ice exhibiting absorption features in the 3 μm (3000 nm) region. Spectra were modeled as thin surface layers of water, OH, and ice (with abundance equivalent to ~ 1000 ppm and a 100 μm path length) on several analog substrates. The differing band positions of the “3 μm feature” of OH, water, and water ice are apparent from this figure. Modified from Pieters et al. [2009].

Figure 2. Reflectance spectrum of lunar soil sample used in our heating experiments, 15041,210. This spectrum was measured prior to heating experiments, and was created by splicing (at 2.55 μm) measurements by the bidirectional reflectance spectrometer ($i=30^\circ$, $e=0^\circ$) and biconical FT-IR spectrometers in the RELAB at Brown University. The spectrum exhibits properties typical of mature mare soils: weak pyroxene absorptions, low albedo, and “red” continuum slope. The absorption near 3 μm is attributed to water.

Figure 3. Example atmospheric “re-equilibration” spectra plotted as scaled reflectance. Spectra were scaled at 2.4 μm to avoid offsets due to the inability to take proper background spectra throughout the course of the re-equilibration experiment. The strength of the atmospheric absorption bands decreases with time. Spectra are labeled by the number of minutes elapsed since the start of the re-equilibration experiment. Spectra such as these were used to perform an atmospheric correction on the spectra collected of the lunar soil sample immediately after a heating run, as described in the text.

Figure 4. Portions of FT-IR spectra collected immediately following heating runs. Spectra are colored according to the temperature of the heating runs. The strength of the water absorption near 3 μm is observed to decrease with increased heating temperature. (a) and (b) represent distinct “batches” (batches 1 and 2, respectively) of heating runs and spectroscopic measurements. Spectra have been scaled to their values at 2.4 μm and corrected for atmospheric absorptions, as discussed in the text.

Figure 5. Band area of the 3 μm absorption plotted against time following removal from the furnace for a re-adsorption experiment sequence. Band area is calculated by summing (over the 2.7 μm to 3.3 μm region) the band depth relative to a local continuum slope over the absorption. Because band depth is dimensionless (it is effectively a ratio of reflectance values), our summed (integrated) band area is also dimensionless. The spectra analyzed to produce the band area data shown here were collected following the 300°C heating run in the first batch (part (a) in Figure 3). Band area is observed to increase following removal from the furnace, but not for at least 10 minutes. The initial increase in band area is followed by a more gradual decrease, as discussed in the text. These results suggest that re-adsorption of water between removal of the sample from the furnace and spectroscopic measurement (~ 5 -10 seconds) is not a predominant concern for our experiments, although the effect must still be considered.

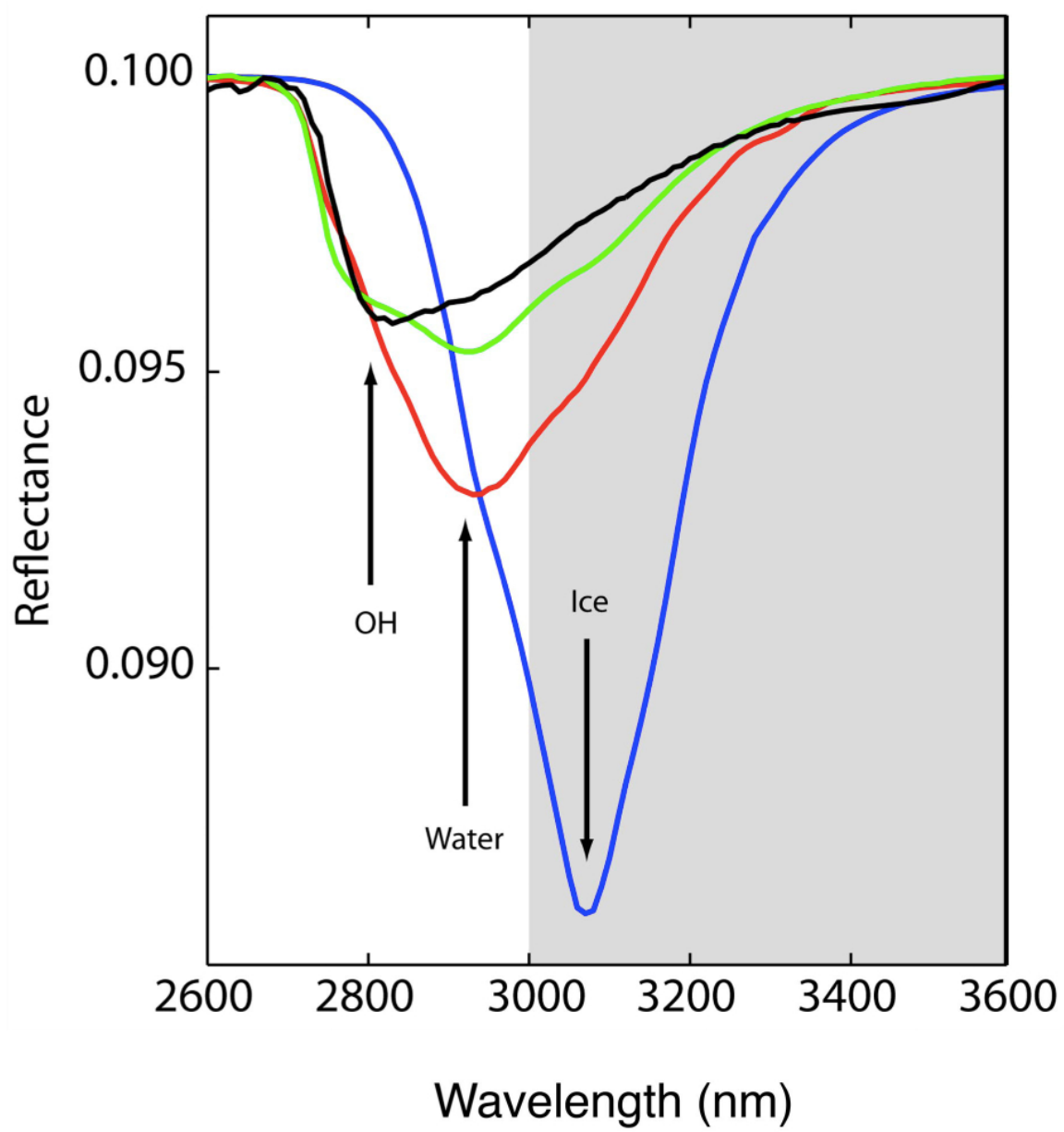


Figure 1.

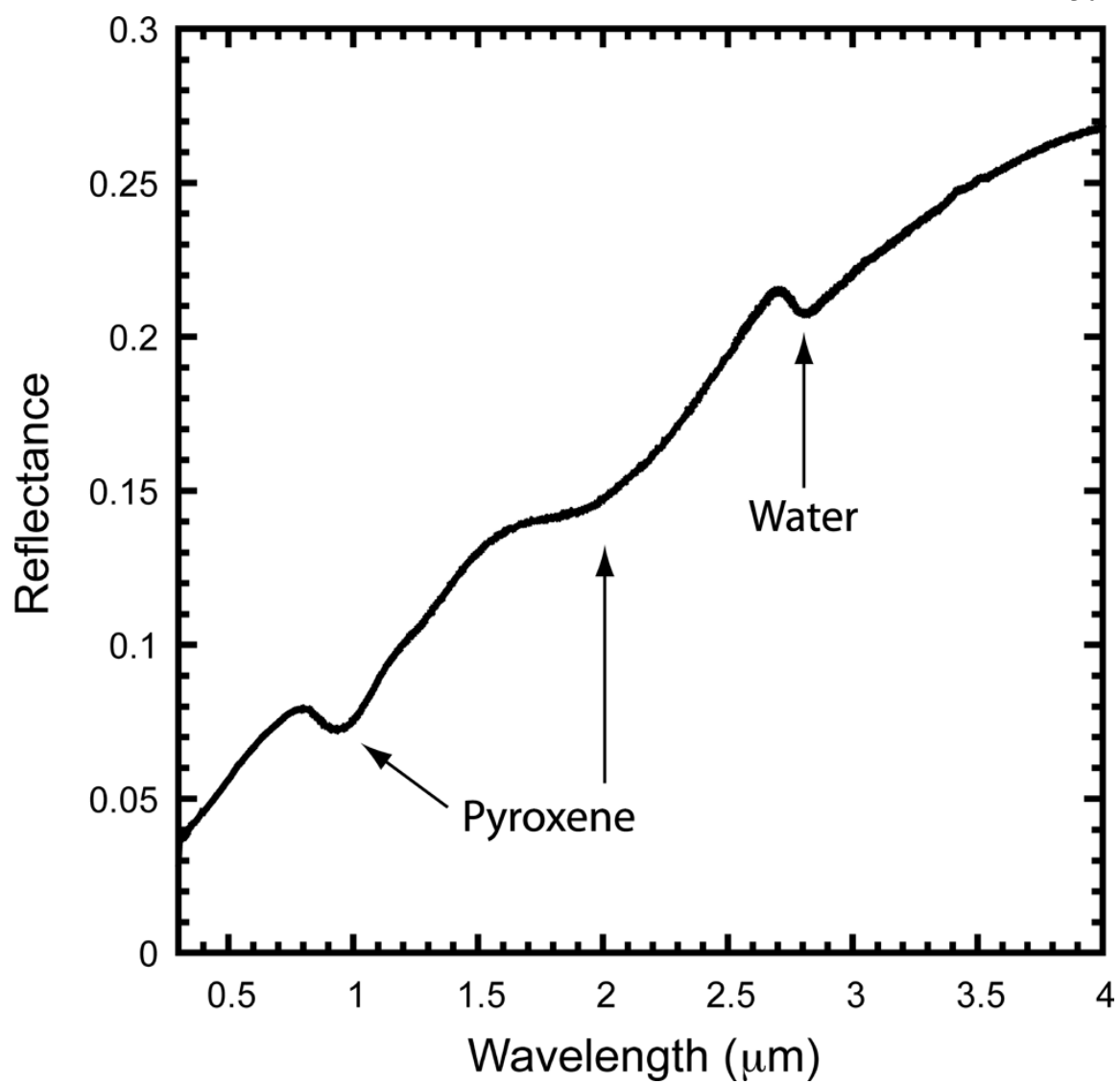


Figure 2.

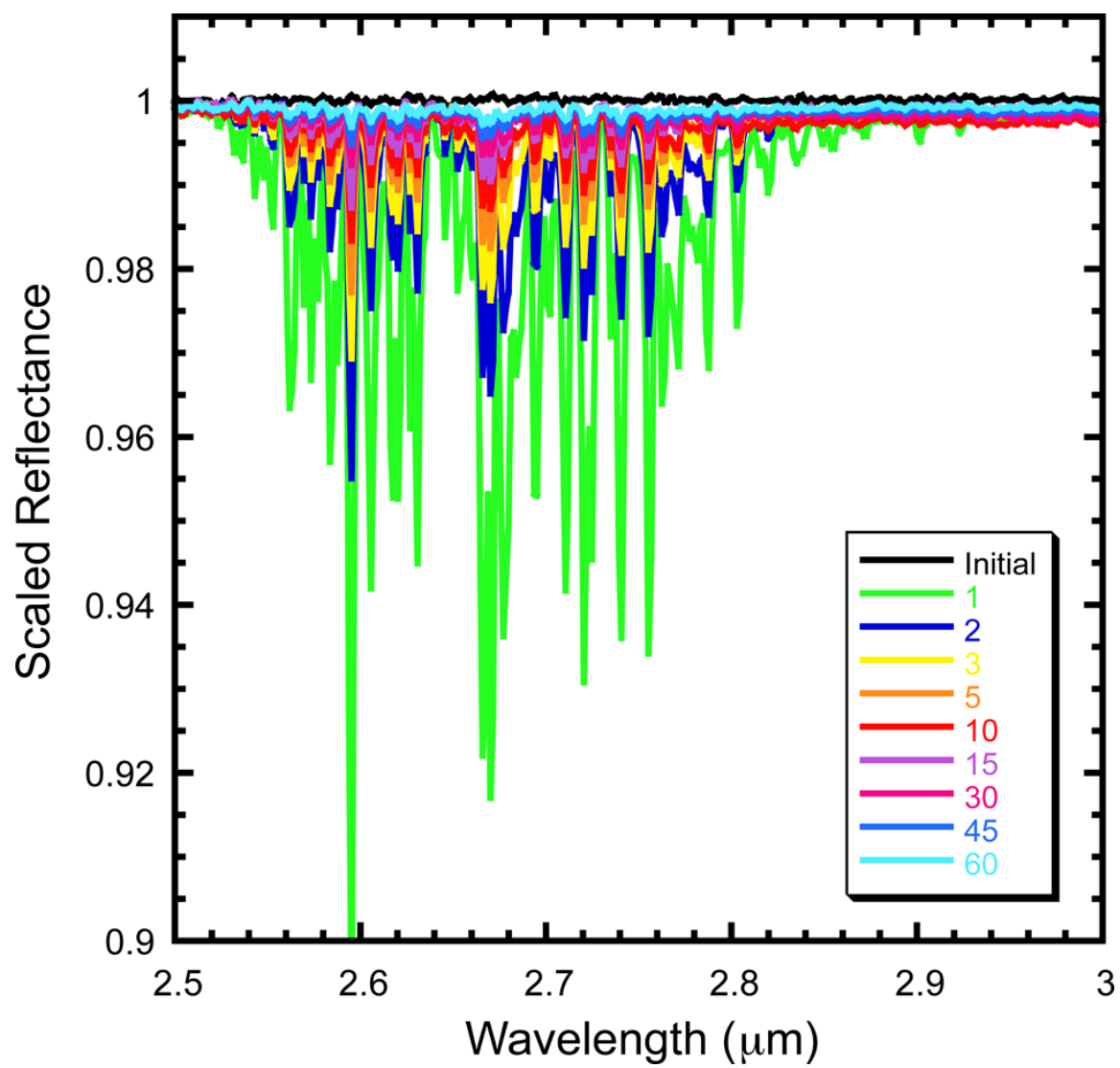


Figure 3.

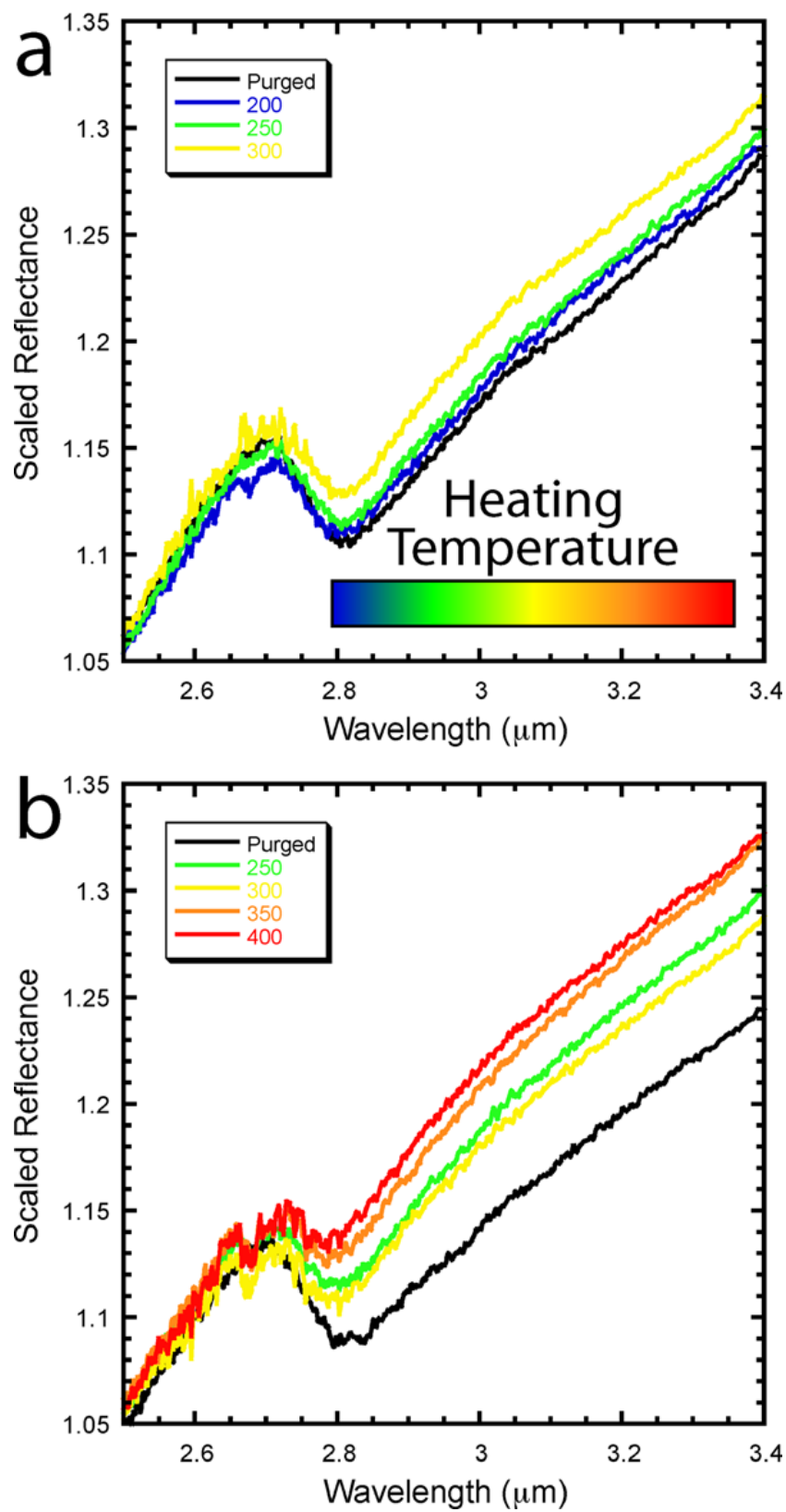


Figure 4.

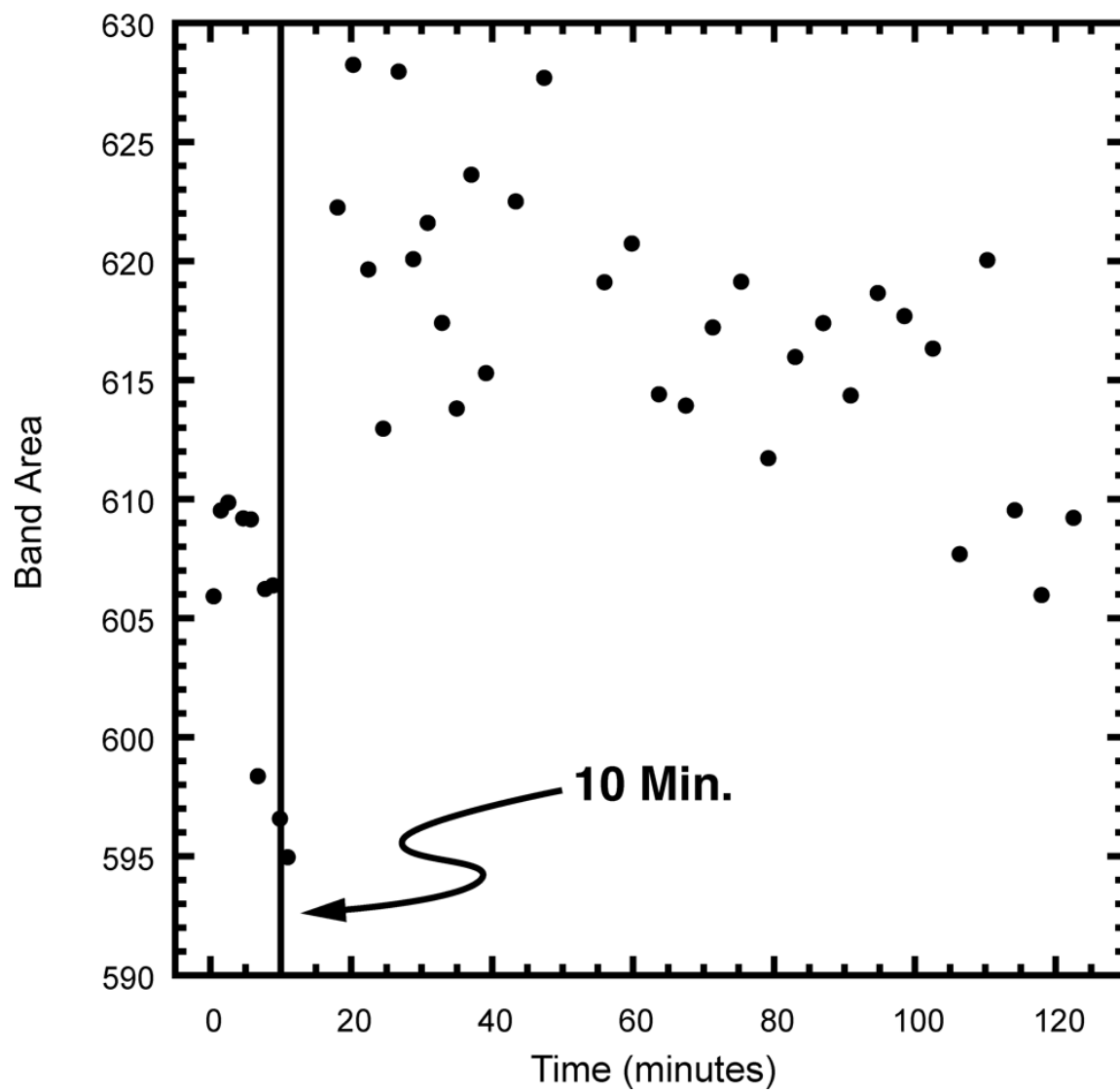


Figure 5.

CHAPTER 7: Synthesis and Final Remarks

Peter J. Isaacson

1 Summary of Major Conclusions

Analyses of the variety of lunar samples presented in the previous six chapters have described the importance of working with real lunar samples. Analogues are certainly valuable, but the unique conditions on the Moon produce samples whose properties cannot be replicated in terrestrial or synthetic analogues. The impact of the differences between lunar samples and terrestrial or synthetic analogues is variable, but in some cases is quite substantial.

One of the most important differences between lunar samples and analogues in the context of reflectance spectroscopy is the oxidation state of cations, particularly iron and titanium. The Moon is an extremely reducing environment, and the oxidized form of iron is essentially absent from the sample collection (nearly all iron in lunar materials exists as Fe^{2+} or as reduced iron metal, often in combination with each other) [Papike *et al.*, 1998]. Iron is responsible for the vast majority of the absorption features exhibited by common lunar minerals in the visible to near-infrared, and the different oxidation states of iron exhibit vastly different absorption properties [Burns, 1993]. In all cases presented in the preceding chapters, the lunar samples exhibit compositional and spectral properties that make them unique (e.g. visible wavelength absorptions in Ti-rich pyroxenes and basalts, long wavelength “rollover” in ilmenite spectra, chromite inclusions in olivine). It is possible, even probable, that with sufficient effort, appropriate analogues for these samples could be identified in the terrestrial sample collection. However, I would argue that these analogues could not be identified without already knowing the distinguishing properties of the lunar samples. The lunar samples discussed

in chapters 1 and 2 are excellent examples of the importance of using lunar materials as ground truth. These samples represent the best test for mixing models that seek to determine surface composition through hyperspectral remote sensing of the lunar surface, and the complexities discussed here and in chapters 1 and 2 show why they are superior to and cannot be replaced easily with terrestrial analogues.

The properties that make lunar samples unique and important also present complexities. Chapters 3 and 4 address one of these complexities in analyzing the effect of chromite inclusions on deconvolutions of lunar olivine reflectance spectra. Chapter 4 examines the prominent continuum slopes common to spectra of the lunar and other planetary surfaces, but the treatment in Chapter 4 is limited to a very specific case. The problem of how to address the continuum slope of remotely-sensed spectra represents an important area of ongoing research, and in my opinion is a problem that will limit large-scale comparative types of studies using quantitative deconvolutions until a satisfactory, all-inclusive solution is discovered.

Lunar sample ground truth is not limited to samples collected decades ago. Continued examination of samples collected by the Apollo and Luna programs is vital and continues to lead to extraordinary advances in lunar science. However, the lunar meteorites represent an additional suite of lunar samples that is still evolving (albeit at a fairly slow rate). The lunar meteorites add important diversity to the lunar sample collection, as many of them apparently come from regions distinct from the unique geochemical region from which the Apollo samples were collected [e.g., *Korotev, 2005*]. With the continued discovery of new lunar meteorite samples, their value will only continue to grow, as more and more samples unique from those collected by the Apollo

and Luna programs are found. We have the capabilities to begin to narrow down the geologic context of these samples, as argued in Chapter 5. If analyzed correctly, the lunar meteorite collection can and should be considered on par with the Apollo samples, and will continue to expand our understanding of lunar geology.

2 Outstanding Issues

2.1 Ilmenite: Sample Limitations

One of the most obvious outstanding issues resulting from this work concerns the treatment of ilmenite in chapter 2. The LRMCC samples were selected based on a specific set of criteria, namely obtaining two low-Ti and two high-Ti samples and having sufficiently coarse grain size to allow mineral separation by hand picking. The samples were not selected to be the optimal basis for evaluating the effect of ilmenite on spectra of lunar basalts. They represent two important endmembers, but as suggested in chapter 2, additional samples are required to perform statistically significant correlations between ilmenite abundance and spectral parameters. Samples with more widely varying ilmenite contents are a critical piece currently absent from this work. Additionally, chapter 2 suggests that variable sample texture is another area in which additional sample diversity is required, because the results of Chapters 1 and 2 as well as previous research suggest that the spectral signature of ilmenite is highly dependent on grain size and the texture of its host material [e.g., *Riner et al.*, 2009; *Tompkins and Pieters*, 2009]. Chapter 2 presents examples of samples with variable texture that would contribute valuable diversity to the results presented here.

2.2 Olivine: Continuum Slope

Chapter 4 proposes a method for addressing the effect of the lunar continuum slope in the case of olivine-dominated spectra. This approach produces results consistent with previously-established trends, but is heavily based on the olivine-specific case and not necessarily applicable to general quantitative deconvolutions of remotely-sensed spectra of planetary surfaces. This specialization limits the degree to which deconvolution results can be cross-compared even between studies of the same planetary body that employ different approaches, much less between planetary bodies that exhibit variable continuum slope properties. While this problem is not a new conclusion of the work presented here, our work is an additional example of the need for a common approach to dealing with the continuum slope aspect of spectral deconvolutions based on the Modified Gaussian Model (MGM). This limitation will hinder large-scale application of the MGM to produce results comparable between diverse studies until a general solution is developed, in my opinion.

2.3 Meteorites: Stone Components and Geologic Context

The results presented in Chapter 5 provide a tantalizing glimpse of the potential of the lunar meteorite collection. Clearly, an additional examination of the samples discussed in Chapter 5 is warranted, as the specific components of these stones have yet to be analyzed beyond the preliminary work with MIL05305. Analysis of particulate samples, both of the bulk samples and of the specific components, is clearly warranted, as measurement in chip form does not produce satisfactory results, particularly for the breccia samples. The position of the absorption features in the resulting spectra must then be quantified, as was done for the MIL05035 example. Once that groundwork has

been completed, the results can be compared with results from remotely-sensed data to begin to constrain the geologic context of these samples.

3 Applications

While the focus of this work is lunar-centric, study of lunar samples has applications beyond study of the Moon.

3.1 Spectral Mixing Models

The results presented in Chapter 1 represent, to my knowledge at this writing, some of the best-available samples and reflectance spectra upon which to test and develop models for nonlinear spectral unmixing. Spectral unmixing efforts typically select analogue mineral spectra as endmembers to unmix a spectrum of unknown mineralogy and composition [e.g., *Johnson et al.*, 1992; *Adams et al.*, 1993; *Clark*, 1995; *Clark et al.*, 2003]. As I have discussed throughout this work, real samples, in particular lunar samples, exhibit important differences from terrestrial or synthetic analogue counterparts. Thus, spectral unmixing models have a number of automatic “outs”, or free parameters to which poor fitting results can be attributed. In fits of known bulk samples using analogue mineral endmember spectra, poor fits can be attributed to a number of factors, many of which relate to the differences between the chosen endmembers and the actual endmembers present in the sample being analyzed. The LRMCC samples eliminated many of these unknowns, so the number of free parameters to which poor results can be attributed is reduced dramatically. Chapter 1 presents example mixture modeling for one of the samples, and while the results are good, they are not perfect. The samples are as perfect as we’ve yet obtained against which to test mixture models. The

inability of mixture models to reproduce the physical properties of the input rock sample suggests that for perfect samples, the mixture models are imperfect. Application of diverse spectral unmixing methods to these samples and spectra is a priority, as these samples present a Darwinian test for spectral unmixing; they will identify those models that perform best, and will likely suggest avenues for improvement. I caution that these samples do not represent the only test for mixture models; they will only identify those mixture models that perform best for materials dominated by crystal field absorptions. They are less relevant to models and materials involving sharper vibrational absorption features such as those exhibited by alteration minerals such as sulfates and phyllosilicates [e.g., *Bibring et al.*, 2005].

3.2 Ilmenite Parameterization

As discussed in Chapter 2, traditional approaches to mapping ilmenite (in actuality, TiO_2) abundance on the lunar surface have focused on the ultraviolet and visible wavelengths. We have characterized the spectral features of ilmenite and ilmenite-rich basalts, and identified a number of additional wavelength regions in which the effect of ilmenite is particularly apparent (e.g., the 1.2 - 1.3 μm and 1.7 μm regions in addition to the principal pyroxene absorption regions near 1 and 2 μm). With the onset of high-quality datasets that collect spectra of the global lunar surface across a much broader wavelength range than previously available, these additional wavelength regions can be incorporated into improved approaches to detecting ilmenite and potentially mapping its abundance across the lunar surface. A new approach that utilizes ilmenite signatures across broader wavelength coverage would represent a substantial improvement over previous approaches, which (out of necessity) relied on an empirical

correlation between TiO_2 content and the UV-Vis ratio, rather than relying on features directly attributable to ilmenite. The laboratory basis for such an approach is limited by the available samples, as discussed under “Outstanding Issues”. However, the approach outlined in Chapter 2 represents a potential basis for improved detection and mapping of ilmenite on the Moon with new global hyperspectral coverage with instruments such as the Moon Mineralogy Mapper and SIR-2 on Chandrayaan-1 and the Spectral Profiler on SELENE/KAGUYA [Matsunaga *et al.*, 1999; Mall *et al.*, 2009; Pieters *et al.*, 2009].

3.3 Olivine

The modification to the MGM deconvolution approach for lunar olivine was motivated by the chromite inclusions common to lunar olivine that alter the olivine’s reflectance properties. It is primarily a lunar problem in that lunar olivines commonly exhibit the properties that require this modified approach. However, the modified approach is certainly applicable to any olivine spectrum exhibiting features due to Cr-spinel inclusions. The methods proposed in Chapter 4 are more broadly applicable to remotely-sensed spectra of olivine-rich materials. Continuum slopes are common to remotely-sensed spectra of planetary surfaces [e.g., Pieters, 1986; Vilas, 1988; Fischer and Pieters, 1993; Gaffey *et al.*, 1993; Pieters and McFadden, 1994; Blewett *et al.*, 1997]. Chapter 4 suggests that a common approach to addressing the continuum slope is required to enable compositional predictions based on previously-established trends, and proposes a method to address the effect of the continuum slope in the case of olivine-dominated reflectance spectra. In principle, this method is applicable to any olivine-dominated reflectance spectrum that exhibits a prominent continuum slope. This approach thus has wide-ranging applications for predicting olivine composition on a

range of planetary bodies. As modern spectrometers are flown to more and more rocky solar system bodies, we will likely encounter new opportunities to apply these techniques to predict olivine composition.

4 Final Thoughts

The current era of planetary exploration is rich, with high-quality spectroscopy datasets being collected from many solar system bodies. As the quality of instruments and the data they produce continue to improve, the importance of reliable ground truth measurements will only grow. Ever increasing dataset quality, in spectral resolution, coverage, signal level, and spatial resolution, will enable researchers to focus on more and more specific aspects of spectral reflectance, magnifying the effect of the deviations between analogues and true ground truth if data are not interpreted in the proper context. Lunar science is thus at an enormous advantage to other fields in planetary science, as other fields lack the sample basis for constraining remote sensing measurements beyond the small meteorite collections, valuable as those samples are. The lunar sample collection continues to underlie enormous advances in lunar science and will continue to provide a cornerstone for new directions through remote sensing with ever-improving datasets.

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APPENDIX A: Petrography of Samples Analyzed by The Lunar Rock and Mineral Characterization Consortium

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1 Mineral Composition

Mineral compositions determined by EMP analysis of the thin sections and prepared mineral separates are presented in the following sections.

1.1 Thin Section Analysis

The paired thin sections accompanying the basalt slab samples were analyzed to determine the mineralogy and petrography of the four basalt samples. The compositional ranges of the mineral phases present were determined by electron microprobe analysis, and the modal mineralogy was determined using the FeatureScan Phase Distribution software package of an Oxford instrument energy dispersive spectrometer interfaced to the microprobe. A detailed description of this technique is provided by Taylor et al. (1996). The geochemical data and mineral compositional ranges determined for the thin section samples are presented in tables A1-A4.

1.2 Mineral Separate Analysis

The slab samples were used to prepare controlled mineral separates for reflectance spectroscopy analyses. The composition of these samples was determined by electron microprobe analysis of grain mounts prepared from small subsets of the mineral separates. The geochemical data and compositional ranges of the prepared mineral separates are presented in tables A5-A8. Mineral separates are consistent with the compositions measured for the thin sections.

2 Pyroxene Zoning and Crystallization History

The pyroxenes from all four samples exhibit prominent compositional zoning. Two examples are shown in Figure A1, one each from the Apollo 15 and 17 samples. The Apollo 17 sample pyroxenes exhibit sector zoning, so a clean straight A-B traverse from rim to core to rim is quite difficult to achieve. For this reason, the Apollo 17 traverse is labeled by core and rim, rather than A to B. In addition to the traverses, photomicrographs of the grains analyzed are shown. Images were acquired with plane-polarized transmitted light.

Based on the observed compositional zoning in pyroxene grains, the Apollo 15 pyroxenes range from low-Ca, high-Mg compositions in grain cores to low-Mg augites toward grain rims, with Fe enrichment toward grain rims. 15555 appears to exhibit two evolutionary trends in pyroxene crystallization: pigeonite cores trending to augites and ferro-augites or following a low-Ca trend toward Fe-rich pigeonite compositions. In both cases, grains become increasingly Fe-rich toward the rims, consistent with previous analyses [e.g., *Bence and Papike*, 1972; *Brown et al.*, 1972; *Gay et al.*, 1972; *Juan et al.*, 1972; *Longhi et al.*, 1972; *Ryder*, 1985].

The Apollo 17 pyroxenes show slightly different pyroxene crystallization sequences. The pyroxenes tend to be zoned from augite cores to Mg-rich pigeonite rims. The rims exhibit Fe enrichment, as in the Apollo 15 pyroxenes. Both types of pyroxene become Fe-enriched with the evolution of the crystallization. While pyroxene zoning is somewhat irregular, the overall trend from augite to pigeonite with very late Fe enrichment is clear and consistent with previous analyses [e.g., *Papike et al.*, 1974; *Brown et al.*, 1975; *Hill et al.*, 2006]. Pigeonites and sub-calcic augites frequently rim

olivines, indicating that they formed by resorption of the olivine [Brown *et al.*, 1975; Neal and Taylor, 1992]. The petrographic results suggest that the samples were relatively slow to cool [Brown *et al.*, 1975]. Additionally, the high-Ca augites tend to be titaniferous, as illustrated by Figure 4. This suggests that ilmenite and augite co-precipitated as the system became Ti-rich [Papike *et al.*, 1974]. This is confirmed by a plot of $Mg' (Mg/Mg+Fe)$ for augite vs. ilmenite, illustrated in Figure A2, which shows that both minerals became simultaneously Fe-rich during crystallization, showing that the minerals were in equilibrium. The presence of microcrystalline ilmenite in the augite separate, possibly causing the observed absorption features in the visible, is thus not surprising. These petrographic results suggest that these titaniferous pyroxenes and ilmenites co-precipitated in a slow, stable cooling path. Augites become more Ti-poor as Ca content decreases (Figure 4), perhaps indicating a trend in Ti content with increasing degree of crystallization, as pyroxenes progress from the augite cores to pigeonite rims.

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Table A1. Compositional Data for 15058,248

	Fe- Px¹	Aug²	Pig³	Opx⁴	Ol⁵	Pl⁶	Ilm⁷	Usp⁸	Cr- Usp⁹	Chr¹⁰
SiO₂	47.0	51.1	52.6	53.8	30.0	45.6	0.03	0.05	0.04	0.04
TiO₂	1.02	0.79	0.35	0.28			52.1	33.2	27.6	2.94
Al₂O₃	1.02	2.73	1.33	1.04	0.04	33.3	0.08	1.69	3.08	12.4
V₂O₃								0.19	0.37	1.08
Cr₂O₃	0.05	0.95	0.77	0.84	0.03			1.32	11.06	50.3
MgO	1.24	14.8	21.2	25.2	2.31	0.19	0.08	0.09	1.27	6.19
CaO	12.9	16.3	4.80	2.39	0.61	18.6		<0.03		
MnO	0.39	0.23	0.33	0.25	0.64		0.28	0.27	0.30	0.22
FeO	37.1	13.7	19.1	16.8	66.6	0.57	47.3	63.1	56.4	27.3
Na₂O	0.05	<0.03	<0.03	<0.03		0.92				
K₂O						0.05				
Total	100.7	100.6	100.4	100.6	100.2	99.3	99.9	99.9	100.1	100.4

¹Pyroxferroite, ²Augite, ³Pigeonite, ⁴Orthopyroxene, ⁵Olivine, ⁶Plagioclase, ⁷Ilmenite,
⁸Ulvöspinel, ⁹Chromium Ulvöspinel, ¹⁰Chromite

Table A2. Compositional Data for 15555,971

	Pig	Aug	Ol1¹¹	Ol2¹²	Pl	Ilm	Usp1	Usp2	Chr¹³	Chr¹⁴
SiO₂	53.4	47.2	30.5	35.7	45.8	0.03	0.22	0.08	0.07	0.12
TiO₂	0.34	1.39	---	---	---	51.9	29.7	20.8	4.23	3.94
Al₂O₃	0.85	1.59	0.04	<0.03	33.7	0.1	2.69	5.81	13.3	12
V₂O₃	---	---	---	---	---	---	---	---	0.99	1.07
Cr₂O₃	0.58	0.22	<0.03	0.27	---	0.36	7.39	22.4	44.2	47.1
MgO	21.9	3.42	3.84	26.3	0.2	0.29	0.55	2.83	1.42	4.96
CaO	3.64	17.5	0.56	0.32	18.6	0.03	0.09	0.19	0.03	0.03
MnO	0.35	0.33	0.68	0.36	---	0.34	0.36	0.23	0.24	0.25
FeO	19.6	28.5	64.6	37.5	0.55	45.8	58.3	46.1	35.7	29.7
Na₂O	<0.03	0.05	---	---	0.84	--	---	---	---	---
K₂O	---	---	---	---	<0.03	---	---	---	---	---
Total	100.6	100.3	100.1	100.5	99.7	98.8	99.7	99.1	100.2	99.1

¹³Mg-poor Chromite¹⁴Mg-rich Chromite

Table A3. Compositional Data for 70017,541

	Aug	Pig	Ol	Pl	Ilm	Cr-Usp	Arm¹⁵
SiO₂	47.4	53.1	37.5	46.6	0.24	0.31	0.26
TiO₂	3.56	0.78	0.10	---	54.4	18.9	71.0
Al₂O₃	4.50	0.99	---	33	0.03	6.35	2.00
Cr₂O₃	1.02	0.29	0.11	---	0.99	26.7	1.22
MgO	14.4	23.4	34.9	0.33	6.12	4.88	5.29
CaO	19.8	3.84	0.18	17.6	0.16	0.01	0.48
MnO	0.19	0.38	0.30	---	0.36	0.34	0.08
FeO	8.02	17.4	27.7	0.33	37.7	40.4	18.6
Na₂O	0.09	<0.03	---	1.36	---	---	---
K₂O	---	---	---	0.03	---	---	---
Total	99	100.2	100.8	99.3	100	97.9	98.9

¹⁵ Armalcolite

Table A4. Compositional Data for 70035,193

	Pig	Aug	Ol	Pl	Ilm	Cr- Usp	Arm
SiO₂	52.9	48.2	36.0	46.6	<0.03	0.25	0.08
TiO₂	0.83	3.51	0.06		54.2	21.4	72.9
Al₂O₃	1.02	4.13		32.89	0.02	6.91	1.91
V₂O₃						0.41	
Cr₂O₃	0.38	0.89	0.18		0.74	21.65	1.99
FeO	17.3	8.25	33.6	0.34	39.6	44.3	14.6
MnO	0.35	0.16	0.38		0.36	0.31	0.07
MgO	23.3	14.6	29.5	0.21	4.55	4.03	7.83
CaO	3.74	19.8	0.29	17.7	0.04	0.21	0.28
Na₂O	<0.03	0.10		1.40			
K₂O				0.07			
Total	99.8	99.7	100.0	99.2	99.5	99.4	99.6

Table A5. Compositional Data for Mineral Separates from 15058,276

	15058		
	Pyroxene		Plagioclase
	Green	Brown	
N	45	45	50
SiO₂	53.0 (11)	49.1 (15)	46.3 (99)
TiO₂	0.30 (12)	0.84 (24)	---
Al₂O₃	1.14 (39)	1.48 (52)	33.4 (91)
Cr₂O₃	0.80 (9)	0.45 (30)	---
MgO	22.7 (21)	10.9 (45)	0.17 (10)
CaO	3.44 (11)	10.5 (25)	18.0 (56)
MnO	0.31 (3)	0.38 (6)	---
FeO	18.1 (13)	26.0 (64)	0.61 (11)
Na₂O	0.01 (1)	0.03 (1)	1.05 (22)
K₂O	---	---	0.05 (4)
Total	99.9	99.6	99.7

Table A6. Compositional Data for Mineral Separates from 15555,965

	15555			
	Pyroxene		Olivine	Plagioclase
	Light Brown	Reddish-Brown		
N	47	49	37	42
SiO ₂	51.0 (10)	48.3 (11)	34.2 (22)	45.8 (59)
TiO ₂	0.61 (20)	1.15 (21)	---	---
Al ₂ O ₃	1.35 (48)	1.52 (31)	0.03 (6)	33.2 (66)
Cr ₂ O ₃	0.55 (16)	0.29 (15)	0.14 (8)	---
MgO	18.3 (20)	11.0 (28)	22.4 (82)	0.24 (4)
CaO	6.80(24)	10.8 (23)	0.37 (9)	18.1 (38)
MnO	0.35 (5)	0.38 (5)	0.40 (9)	---
FeO	20.3 (26)	25.4 (41)	42.0 (99)	0.51 (7)
Na ₂ O	0.03 (1)	0.03 (2)	---	0.98 (16)
K ₂ O	---	---	---	0.03 (2)
Total	99.28	98.87	99.6	98.8

Table A7. Compositional Data for Mineral Separates from 70017,535

	70017			
	Pyroxene		Plagioclase	Ilmenite
	Light Brown	Dark Brown		
N	33	58	37	20
SiO ₂	51.2 (96)	49.2 (11)	46.8 (81)	0.03 (3)
TiO ₂	1.07 (34)	2.07 (77)	---	53.7 (15)
Al ₂ O ₃	1.21 (45)	2.47 (11)	32.7 (65)	0.21 (11)
Cr ₂ O ₃	0.36 (9)	0.58 (22)	---	1.04 (11)
MgO	19.7 (32)	14.8 (14)	0.20 (2)	3.06 (13)
CaO	6.17 (20)	15.2 (24)	17.3 (47)	0.03 (1)
MnO	0.37 (6)	0.30 (6)	---	0.38 (4)
FeO	20.1 (34)	14.5 (43)	0.36 (7)	41.4 (17)
Na ₂ O	0.03 (2)	0.08 (2)	1.43 (15)	---
K ₂ O	---	---	0.06 (2)	---
Total	100.2	99.2	98.9	99.8

Table A8. Compositional Data for Mineral Separates from 70035,188

	70035			
	Pyroxene		Plagioclase	Ilmenite
	Light Brown	Dark Brown		
N	50	50	25	25
SiO ₂	51.4 (10)	49.5 (12)	46.9 (72)	0.09
TiO ₂	1.11 (47)	1.94 (64)	---	54.0
Al ₂ O ₃	1.39 (60)	2.46 (89)	33.0 (47)	0.05
Cr ₂ O ₃	0.42 (11)	0.61 (17)	---	0.80
MgO	20.9 (23)	16.3 (20)	0.24 (3)	3.37
CaO	6.19 (36)	14.0 (38)	17.3 (35)	---
MnO	0.32 (4)	0.27 (6)	---	0.37
FeO	17.5 (24)	13.6 (38)	0.35 (6)	41.4
Na ₂ O	0.03 (2)	0.07 (2)	1.47 (18)	---
K ₂ O	---	---	0.06 (2)	---
Total	99.3	98.8	99.3	100.0

Figure Captions

Figure A1. Examples of pyroxene zoning in LRMCC Apollo 15 (left) and Apollo 17 (right) basalt samples. Pyroxene quads (top) are labeled with zoning trends from “core” to “rim” along profiles from A to B as indicated on the plane-polarized transmitted light microscope images (bottom). Pyroxenes in the two Apollo 17 samples exhibit sector zoning, so clear identification of “core” and “rim” is difficult to define precisely as in the example from an Apollo 15 pyroxene (left).

Figure A2. Mg' for ilmenites vs. augites in 70035. The high degree of correlation indicates that the two minerals are in equilibrium and co-precipitated during crystallization.

Figure A1.

Figure A2.

APPENDIX B: Description of the Moon Mineralogy Mapper (M³) Instrument and Data Products

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Summarized from Pieters et al. [2009].

1 M³ on Chandrayaan-1

The Moon Mineralogy Mapper (M³) was an imaging spectrometer covering the visible to near-infrared wavelengths. The M³ was a guest instrument on Chandrayaan-1, which was the first lunar mission of the Indian Space Research Organization (ISRO). The M³ was selected in February 2005 as a NASA Discovery Program Mission of Opportunity following a NASA peer-review. The M³ complemented the strong Chandrayaan-1 suite of payloads, which included several guest payloads from NASA and ESA as well as a number of ISRO-supplied payloads [Goswami and Annadurai, 2009].

2 M³ Instrument and Data Characteristics

The M³ was a passively cooled, pushbroom grating imaging spectrometer. The M³ collected reflectance data simultaneously across 600 illuminated cross-track spatial elements and 260 spectral elements. The M³ field of view (FOV) is 24°. From the nominal 100 km polar orbit of Chandrayaan-1, the cross-track coverage of the M³ is ~40 km, and the full spatial resolution of the M³ data is ~70 m/pixel. At full spectral resolution, M³ collected reflectance spectra at 10 nm resolution from 430 – 3000 nm. The M³ had a low-resolution mode, in which both spatial resolution and spectral resolution were reduced by onboard averaging. Much of the M³ data were collected in this low-resolution mode, which had a spatial resolution of ~140 m/pixel, 85 spectral bands over the 430 – 3000 nm range, and a spectral resolution of 20-40 nm, depending on the wavelength. At equatorial latitudes, the M³ data exhibited a high signal-to-noise ratio (>400) in its full resolution mode. For a direct comparison of the M³ imaging modes, the

reader is referred to Table 1 of Pieters et al. [2009]. The M³ was engineered to have extremely high spatial and spectral uniformity, which ensures that spectral data are co-registered without difficult and imperfect corrections, and simplifies the calibration process enormously. Additionally, the M³ covered its broad spectral range with a single detector, eliminating the need to splice various wavelength regions to produce full reflectance spectra. For more detail on the M³ design and data products, the reader is referred to the pre-launch overview of Pieters et al. [2009]. This publication is part of a special issue of the journal *Current Science* that contains pre-launch publications describing the various payloads on Chandrayaan-1.

3 References

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