

Infrared Reflectance Spectroscopy of Meteorites, Analogs, and Returned
Samples: Advances in Context, Connections, and Characterization

by

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Peer-Reviewed Publications (*yet to be published)

1. **C. D. Schultz**, R. E. Milliken, J. S. Boesenberg, I. Kerraouch “The many faces of Aguas Zarcas: Investigating spectral heterogeneity and brecciation across multiple spatial scales”, *Meteoritics & Planetary Science* (in review).
2. D. S. Lauretta, H. C. Connolly, et al. “Asteroid (101955) Bennu in the laboratory: Properties of the sample collected by OSIRIS-REx”, *Meteorites & Planetary Science* (2024).
3. T. Hiroi, R. E. Milliken, K. M. Robertson, **C. D. Schultz**, K. Amano, et al. “Evidence of Global Weathering by Solar Wind on the CI1 Chondrite Asteroid 162173”, *Icarus* (2023).
4. **C. D. Schultz**, B. A. Anzures, R. E. Milliken, T. Hiroi “Assessing the Spatial Variability of the ~3 μm OH/H₂O Absorption Feature in CM2 Carbonaceous Chondrites,” *Meteoritics & Planetary Science* (2023).
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6. B. A. Anzures, **C. D. Schultz**, R. E. Milliken, T. Hiroi “Assessing Effects of Particle Size on Water Content Estimates of Carbonaceous Chondrites and their Parent Bodies,” (in prep.).
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8. C. Avdellidou, A. Di Donna, **C. D. Schultz**, B. Harthong, M. Price, R. Peyroux, D. T. Britt, M. Cole, M. Delbo “Very Weak Carbonaceous Asteroid Simulants I: Mechanical Properties and Response to Hypervelocity Impacts,” *Icarus* (2020)
9. P. T. Metzger, D. T. Britt, S. D. Covey, K. M. Cannon, **C. D. Schultz**, K. D. Grossman, J. G. Mantovani, R. P. Mueller. “Measuring the Fidelity of Asteroid Regolith and Cobble Simulants,” *Icarus* (2018).
10. D. T. Britt, **C. D. Schultz**, P. T. Metzger (2018) Thermal Cycling and the Strength of Primitive Asteroids. Proceedings of the ASCE Earth and Space 2018 Conference.

Abstracts

1. C. D. Schultz, R. E. Milliken (2024) The Curious Case of the Missing Mantle: How Carbonaceous Chondrites May Confound the Spectral Identification of Partially Differentiated Asteroids. *55th Lunar and Planetary Science Conference*, Abstract # 1005
2. C. D. Schultz, R. E. Milliken, T. Hiroi, H. H. Kaplan, V. E. Hamilton, E. A. Cloutis, D. M. Applin, H. C. Connolly, D. S. Lauretta (2024) Insights From Returned Bennu Samples Into the Spectral Detection of Carbonates and Organics by OSIRIS-REx. *55th Lunar and Planetary Science Conference*, Abstract # 1129
3. R. E. Milliken, T. Hiroi, C. D. Schultz, V. E. Hamilton, H. H. Kaplan, E. A. Cloutis, D. M. Applin, H. C. Connolly, D. S. Lauretta (2024) Reflectance Spectra of Bennu Samples in the 3 Micrometer Region: Initial Results from RELAB and Implications for Remote Sensing of Primitive Asteroids. *55th Lunar and Planetary Science Conference*, Abstract # 1573
4. T. Hiroi, R. E. Milliken, C. D. Schultz, H. H. Kaplan, V. E. Hamilton, E. A. Cloutis, D. M. Applin, D. N. DellaGiustina, H. C. Connolly, D. S. Lauretta (2024) Bidirectional Visible-NIR Reflectance Spectrum of an Aggregate Sample Returned by NASA’s OSIRIS-REx Mission Indicating Possible Space Weathering on Asteroid 101955 Bennu.

5. K. Ishimaru, D. S. Lauretta, H. C. Connolly, A. J. Ryan, R. L. Ballouz, R. J. Macke, C. D. Schultz, J. Aebbersold, and E. H. Blumenfeld (2024) Morphological Comparison Between Returned Sample Particles and Boulders of Asteroid Bennu. *55th Lunar and Planetary Science Conference*, Abstract # 1907
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10. Anzures B. A., Schultz C. D., Milliken R. E., Hiroi T. (2020) Assessing Effects of Particle Size on Water Content Estimates on Carbonaceous Chondrites and Their Parent Bodies. *52nd Lunar and Planetary Science Conference*, (submitted)
11. Schultz C. D., Anzures B. A., Milliken R. E., Hiroi T. (2020) Assessing the Spatial Variability of the $\sim 3\ \mu\text{m}$ OH/H₂O Absorption Feature in CM2 Carbonaceous Chondrites. *51st Lunar and Planetary Science Conference*, Abstract #2303
12. Peppin M., Schultz C. D., Britt D. T., Metzger P. T., Landsman Z., Cannon K. M. (2019) Developing a Standard Method to Test Rheology of Regolith Simulants. *2019 AGU Fall Meeting*, P31C-3469
13. Schultz C. D., Landsman Z. A., Rivkin A. S., Britt D. T., Stockstill-Cahill K. R. (2019) Evolution of $3\ \mu\text{m}$ Feature in Volatile-Rich Asteroid Regolith Simulant. *Asteroid Science in the Age of Hayabusa2 and OSIRIS-REx*.
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15. Britt D.T., Schultz C.D. and Covey S. (2018) UCF/DSI Asteroid Regolith Simulants. (2018) *ASCE Earth and Space Conference*.
16. Britt D.T., Schultz C. and Metzger P. Thermal Cycling and the Strength of Primitive Asteroids. (2018) *ASCE Earth and Space Conference*.
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19. Schultz C.D. and Britt D.T. (2018) Mechanical properties of CI carbonaceous asteroid regolith simulant. *49th Lunar and Planetary Science Conference*, (LPI Contrib. No. 1366)

20. Miyamoto H.; Britt D.T. and 18 Co-authors (2018) Phobos Environment Model and Regolith Simulant for MMX Mission. *49th Lunar and Planetary Science Conference*, (LPI Contrib. No. 1882)
21. Britt D.T., Covey S., and Schultz C (2017) University of Central Florida / Deep Space Industries Asteroid Regolith Simulants. *DPS annual meeting*.
22. Macke R.J., Britt D.T., Schultz C., and Consolmagno G.J. (2017) Low-Temperature Heat Capacity and Thermal Cycling of CI simulant Material. *80th Annual Meeting of the Meteoritical Society*, (LPI Contrib. No. 1987)
23. Schultz C. and Britt D.T. (2017) Structural and Mechanical Properties of Properties of Asteroid Regolith Simulant. *4th SSERVI Exploration Science Forum*.
24. Schultz C., Donoghue J.F., Parbus B., and Sanchez G.A. (2017) Reconstruction of Paleostorm History Using Geochemical Proxies in Coastal Lake Sediments. *University of Central Florida Undergraduate Research Symposium*.
25. Schultz C., Britt D.T., and Whizin A. (2017) Structural and Mechanical Properties of Properties of Thermal Cycled Asteroid Regolith Simulant. *University of Central Florida Undergraduate Research Symposium*.

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Acknowledgements

Growing up in central Florida made it extremely easy to fall in love with space and exploration. NASA's Kennedy Space Center, the launch port from where all space shuttles launched, was ~50 miles east. From the Panera, which was the highest point in my hometown, Clermont, I had a perfect unobstructed view east towards The Cape. From there I viewed countless shuttle launches, which to me looked like small suns rising from the horizon and into oblivion. Night launches were the most dramatic and spectacular! And though I can't remember exactly when it happened, it was sometime during this period that I fell in love with the human endeavor that is space exploration. It was the thrill of discovery and learning, the aspiration to know the unknown and to probe the deepest and most fundamental questions core to our existence. Most importantly, it was the fact that space exploration is a community endeavor that inspired me to pursue it. It's an endeavor that aspires to bring out the best in us, to find shared purpose and belonging. For no matter where we venture and what we may discover, it was we humans, together, that did it.

The privilege I've enjoyed of pursuing a PhD here at Brown, to begin my own journey into space, has been nothing short of a dream come true. And to countless folks I am indebted and eternally grateful for preparing me for and providing me with this magnificent opportunity.

To Dan Britt, my first advisor at the University of Central Florida, I am immensely grateful. As a mechanical engineering undergraduate in desperate search of space-related research experiences, Dan was the first person to take me in and provide me with

opportunities to get involved. But beyond the job, it was the countless hours of conversations we had together, the professional networking opportunities that he provided, and the unwavering professional and personal support that without which, I would not be writing this Acknowledgements section. Thank you, Dan, for all your support.

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enthusiastic support. You have been an amazing mentor and such a joy to work with. Thank you for sharing with me your passion for teaching and laboratory work. I'd similarly like to thank Takahiro Hiroi, whom I've had the immense fortune of befriending and learning more about meteorite and asteroid spectroscopy than I could have ever hoped for. You've made me a better scientist for it. To Joseph Boesenberg, you are a treasure of this department, and I have so enjoyed your friendship and our endless conversations on meteorite petrology. My sincerest thanks go to you for the countless hours you've spent mentoring and teaching me the joys of meteoritics. To Gerrit Budde, your friendship and mentorship over these last few years is sincerely appreciative. I am so lucky I was able to learn from you during this time. To Jack Mustard, the only other person besides Ralph that has been on my committee since the beginning, your infectious enthusiasm for spectroscopy and hard-won wisdom that you've shared have been like a light house in stormy seas, helping to steady me and set me on the right path.

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What truly makes DEEPS the amazing place that it is, is the vibrant, welcoming, and wonderful cast of fellow graduate students. To Seb and Kierra, I love you guys and I'm so grateful to have been your lab mate throughout these last few years. You both have made

coming in to work such a fun experience and something that I look forward to every day. A very special shoutout goes to my D&D families, the Interstellar and Rag Tag Crews. To Beau, Janie, Fiona, Joanna, Matt, Tyler, and Gabby, thank you for making me a part of so many weird and wonderful adventures. D&D nights with you all were some of the best moments of my time in Providence. To my own lab group, Melly, Katya, and Meg, I was so lucky to be able to do this thing with you all. To Melly, you are one of the strongest, tenacious, yet utterly kind and generous people I've ever met. You have been a constant source of companionship and support through the best of times and the most challenging of times. I'm so grateful to have gone through this with you. To Katya, Joao Sr. and Joao Jr., I am so glad you all made the choice to come to Rhode Island! You were instant family, and our weekend board game and family dinners have been a constant source of laughter and joy. Thank you guys so much for your friendship. To Rachel, Mike, Hannah, and Brendan, some of the more senior members of the Milliken lab, your support in the early years made the transition to Brown such a more pleasant experience. I'm so grateful of the time we shared and the support, guidance, and mentorship you all provided early on. I only wish we had more time together! To the rest of the DEEPS graduate students, you all are the best. If I listed the names of everyone whose friendship has made a positive impact on my time here, then I would be listing the entire grad student roster over the last five years. Please know that each of you has made my time here so much more enjoyable because you were a part of it.

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of companionship throughout all of these years. I'm so lucky to have you as my sister. To Kristen, Louie, and Petey, I am immensely thankful to have had your support and companionship. You all made COVID so much less terrible than it could have been. To Jan and Fenix, I love you guys so much and I'm so grateful for all the wonderful memories we've shared together, from Jazz Fest and climbing nights to board games and cookouts, time with you has been the best. Y por último a Lina, has enriquecido mi vida de maneras inconmensurables. Su amor, amabilidad, y apoyo me han hecho una persona mejor y más feliz. Gracias michiki.

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Preface

“We shall not cease from exploration, and the end of all our exploring will be to arrive where we started and know the place for the first time.”

–T.S. Eliot

If the solar system were a bakery, then the stunning variety of planets and moons would be the cakes and pastries, each with its own unique flavor and charm. And these planets and moons, just like the baked goods, are the end products of assembly, processing, heating, and cooling, though on a much grander scale and guided solely by physics and chemistry. By analogy, the leftover crumbs and scattered ingredients are the meteorites, asteroids, and comets that litter our solar system today. Like the lingering unincorporated crumbs, these bodies represent the battered and leftover remnants from a bygone era of planetary formation. They are the building blocks of planets and moons. Recorded in their chemistry, mineralogy, and physical properties are the conditions that led to the formation and evolution of the solar system itself. One of the key endeavors of the study of planetary science is not only to understand the conditions and processes that resulted in our solar

system but also to uncover the fundamental processes that may govern planetary formation and evolution in planetary systems throughout the universe. Once considered to be the varmints of the skies, the humble asteroids and their meteoritic progeny hold these clues and the hope for a deeper understanding of our origins.

0.1 Background

On New Year's Day, 1801, Giuseppe Piazzi, an Italian priest, mathematician, and astronomer discovered the first asteroid, (1) Ceres. However, it was William Herschel in 1802 who coined the term 'asteroid', derived from the Greek *asteroeides*, meaning "star-like". Today, more than 200 years later, over one million small bodies have been discovered. These include populations of asteroids, comets, centaurs and minor planets with orbits stretching from Venus to the edge of the solar system. Most, however, reside between Mars and Jupiter, in a region known as the Main Asteroid Belt.

The primary means by which we've come to discover and know these bodies is by remote observations via telescope. It is only within the last few decades that spacecrafts began to visit these small bodies, providing humanity with the first up-close view of these small and enigmatic worlds. Early telescopic measurements of asteroid included only their apparent brightness as well as their positions in space and time. Bobrovnikoff (1929) and Recht (1935) were among the first to attempt to photographically measure the colors of asteroids. However, they had little success due to the faintness and subtle color differences—a challenge that continues to present significant difficulties to this day. Increasing numbers

of asteroid observations at more colors in visible light and at near-infrared wavelengths led to the establishment of the first taxonomic schemes that broadly classified these bodies as being either carbonaceous (carbon-rich) or siliceous (silicate-rich). Landmark papers by Chapman et al. (1975), Bowell et al. (1978), and Tholen et al. (1984) established and organized a simple taxonomic lettering scheme based on asteroids reflectance using as many as 25 medium-band filters covering wavelength ranges from 0.3 to 1.1 μm that grouped asteroids into a few broad classes. The increased spectral resolution of these observations allowed astronomers to begin inferring finer compositional details of these bodies. This included the ability to discriminate between minerals like olivine and pyroxene.

After decades of advancement in sensor and spectrometer design, we have now cataloged over 1.3 million asteroids in our solar and have made spectral measurements of thousands of them. Most of these spectral measurements are acquired at even higher spectral resolutions and at wavelengths extending into the mid- and far-IR, enabling more robust detections of even more types of minerals and other phases (e.g., DeMeo et al., 2015).

Meteorites, once thought to have interstellar origins, were only relatively recently understood to originate from within our solar system. The Příbram meteorite, which fell in former Czechoslovakia in 1959, was the first meteorite to have its trajectory, impact position, and orbit determined based on bolide photographs (Ceplecha, 1961), thus giving it a solar system provenance. Since the 1970's and 1980's, both dynamical (Wetherill, 1985; Wisdom, 1987; Greenberg and Nolan, 1989) and spectral (McCord et al., 1970; McCord and Gaffey, 1974; Chapman, 1976; Bell et al., 1989a; Pieters et al., 1976; Pieters, 1984;

McFadden et al., 1984; Wetherill and Chapman, 1988; Cruikshank et al., 1991) arguments have been put forth linking most meteorites to asteroidal parent bodies. Today this link is robustly established, though the HEDs (Howardites, Eucrites, and Diogenites) and Almahatta Sitta meteorites are the only group of meteorites to be confidently linked to specific asteroidal parent bodies (4 Vesta and 2008 TC3, respectively).

Carbonaceous chondrites, a carbon-rich class of meteorites, are among the most enigmatic and important solar system materials available for study. As chondrites, they are known for the sub-millimeter silicate inclusions called chondrules, that indicates the primitive nature of these materials and gives them their name. Carbonaceous (C) chondrites are also among the most organic and volatile-rich materials meteorites, suggesting their origins in the outer solar system where low temperatures allowed these phases to remain stable and accrete into growing planetesimals.

The action of water in the outer solar system at low to moderate temperatures, termed aqueous alteration or fluid-assisted metamorphism, respectively, modified the primary mineralogical and textural characteristics of pristine solar system materials. Periods of gravitational and dynamical instability among the giant planets caused the migration of these water-rich bodies to the inner solar system (Walsh et al., 2011; Levison et al., 2011), laying the foundation for the current distribution of small bodies we observe today. As a byproduct, these models of planet and asteroid migration offer a compelling framework for understanding the delivery of a significant fraction of Earth's water and volatile inventory (e.g., Morbidelli et al., 2000; Alexander et al., 2012; Marty, 2012). While classic models suggest the Earth is built from as much as ~15% carbonaceous chondrite-like material (e.g.,

Wanke, 1981), modern isotopic studies predict that the bulk silicate Earth inherited as much as ~30–60% of its Mo isotopes in a late-stage accretion of carbonaceous bodies from the carbonaceous chondrite reservoir (Budde et al., 2019).

Other groups of meteorites, like the irons and stony achondrites, offer important insights into the growth and thermal metamorphism of early forming planetesimals. Iron meteorites and pallasites, most of which are thought to sample the cores and core-mantle boundaries of disrupted planetesimals, appear to originate from over 60 distinct parent bodies and provide the only way for us to directly measure the interiors of planetesimals (Wasson, 1995; Burbine et al., 2002). Asteroid (4) Vesta and the HED meteorites offer a glimpse into one of the only surviving planetesimals in our solar system, and one of the few that is known to have melted and differentiated. As a result, these bodies, along with other achondrites like them, provide important constraints that serve as benchmarks for models of melt segregation, differentiation, and magma ocean generation in planetesimals (Elkins-Tanton et al., 2013).

0.2 Motivations

While the study of asteroids and meteorites has undoubtedly transformed our understanding of the birth and evolution of our solar system, answers to fundamental questions continue to elude us. Some of the major outstanding questions today that motivated the work of this dissertation include: (1) Were asteroids responsible for the delivery of water and organic molecules to early Earth, thus seeding the conditions for life

to emerge? (2) Where and how much water is distributed throughout the asteroid belt and does it only occur in C-type bodies? (3) How do planetesimals grow and evolve and what is the solution to the missing mantle conundrum? (4) What was the nature of the starting material of Earth and the other planets and what were the conditions of the early solar system? (5) How did planetesimals form and what was the primordial compositional gradient of the solar system?

The study of meteorites will undoubtedly continue to provide invaluable insights, but their lack of geologic context remains a significant limitation in fully answer these questions. The answer to many of these fundamental questions will likely come from the remote spectral analysis of large populations of asteroids and asteroid families. Observations of these bodies expanded into mid-infrared wavelengths by the James Webb Space Telescope will yield even more detailed information on the composition and evolution of these bodies. Therefore, the development and refinement of frameworks for the proper interpretation of these spectra will be critical to advancing our understanding.

Motivated by these compelling questions and many others, we are living in a golden age of asteroid exploration. Within my time in graduate school, I have had the privilege of witnessing and being a part of the exploration and sample return of asteroids (162173) Ryugu and (101955) Bennu by the JAXA-led Hayabusa2 mission and the NASA-led OSIRIS-REx mission. Indeed, an entire chapter in this dissertation is dedicated to the analysis of pristine grains of regolith returned from asteroid Bennu. The years 2021 to 2022 alone saw the launch of three dedicated asteroid missions. Launched in 2021, the Lucy mission has already made its first close fly-by of asteroid (152830) Dinkinesh and its surprise binary

satellite Selam. Also launched in the same year, the DART mission made its terminal observations of asteroid Dimorphos, a satellite of the asteroid (65803) Didymos, thus demonstrating humanities first attempts to deflect an asteroid. And as I write this, the Psyche spacecraft is at 2.23 AU enroute for a 2029 encounter with asteroid (16) Psyche, one of the strangest small bodies in the asteroid belt. And with the myriad of asteroid-observing ground- and space-based telescopes, including the James Webb Space Telescope that entered service in 2022, the next two decades hold the promise of many new discoveries.

The study of asteroids and meteorites are highly complementary, with discoveries in each one advancing our understanding of the other. Together, they represent some of the most accessible bodies planetary scientists can study. Indeed, meteorites are one of the only types of extraterrestrial materials that are abundantly supplied to Earth and can be studied in a laboratory. And while dedicated and opportunistic spacecraft missions have allowed the detailed characterization of nearly a score of asteroids to date, the primary way we have for understanding them is remote sensing. As such, the robust spectroscopic characterization of meteorites and other analog materials in the laboratory creates an important framework that can be used to accurately interpret remote sensing observations of asteroids and other small bodies.

0.3 Overview of Dissertation

In the broadest terms, the goal of the work contained within this dissertation is twofold: (1) to address compelling and outstanding questions related to the origin and

evolution of small bodies, and (2) to advance new understandings and frameworks for accurately contextualizing and interpreting observations of asteroids.

In Chapter 1, I set out to answer the question: what is the spatial variability of the $\sim 3\ \mu\text{m}$ OH/H₂O feature in CM2 carbonaceous chondrites? While presented as a seemingly esoteric question, the $\sim 3\ \mu\text{m}$ OH/H₂O spectral absorption feature is a key indicator of the hydration state and degree of aqueous alteration of both asteroids and meteorites. Laboratory work has shown that the strength, shape, and position of this feature is highly correlated to the abundance and speciation of hydrated minerals present in C chondrites. However, virtually all this work has been performed on powdered meteorites and mineral analogs, which by their nature are homogenized mixtures that have lost all spatial and textural petrographic information. To resolve this, I mapped at high spatial resolution the infrared reflectance spectra of six polished and intact CM2 chondrite chips, thus allowing us to understand how this hydration feature varies spatially and how its correlated with the petrography and texture of the meteorites. Supplementing these analyses are XRD measurements used to derive the bulk modal mineralogy of each of these samples.

Chapter 2 picks up where Chapter 1 leaves off, by asking the nature next question of how brecciation affects spectral interpretations of carbonaceous meteorites and asteroids. Brecciation is an important feature of many C chondrites, whereby diverse lithologies of the same or sometimes genetically unrelated materials are mixed together from the collisional evolution of the meteorite parent bodies. This begs the question: do these lithologies exhibit distinct spectral signatures? And if so, how are these convolved to produce a bulk spectrum of the entire sample? We know that meteorites and their asteroidal progenitors are complex

mixtures of diverse components, but what does a disk-integrated spectrum actually tell us about the body? To answer this question, I analyzed the spectral and petrographic properties of the Aguas Zarcas meteorite, a nearly pristine CM2 chondrite that has been found to exhibit at least five distinct lithologies that can all confidently be attributed to a single meteorite fall. A novel aspect of this study was the coordinated analysis of high-spatial resolution μ FTIR spectral mapping with elemental mapping via electron probe microanalysis (EPMA). Additionally, I applied software nominally developed for the analysis of spectral images cubes to these nine-element EPMA maps to investigate the history of this meteorite in a new way. I quantitatively investigated the petrographic relationship between the diverse Aguas Zarcas lithologies to elucidate aspects of the metamorphic pathways that took place on the Aguas Zarcas parent body.

In Chapter 3, I turned my attention to a longstanding issue in the study of asteroids and meteorites termed the missing mantle conundrum. Despite the abundant evidence indicating that planetesimals reached temperatures that allowed for differentiation and melt segregation, the apparent scarcity of olivine- and pyroxene-rich mantle material in meteorite collections and remote sensing data of asteroids has been a long-standing mystery. I proposed and tested the hypothesis that differentiated olivine- and pyroxene-rich asteroid interiors are present in the main asteroid belt, but their diagnostic spectral signatures are effectively masked by dark, chondritic materials mixed and incorporated through the natural collisional evolution of these bodies. I measured and analyzed the visible and infrared spectral features of mixtures of CM2 and CV3 meteorites with synthetic mantle analogs to determine the spectral detection thresholds of the mantle analog materials. In other words,

I quantitatively assessed how much mantle material is needed to be spectrally detected when mixed with dark primitive chondritic material.

The highlight of my graduate school experience was the privilege I had of investigating pristine samples of asteroid (101955) Bennu that were just recently returned to Earth by the OSIRIS-REx spacecraft and mission team. This work is contained within 4th Chapter of this dissertation. Serving as a member of OSIRIS-REx sample analysis team provided me the opportunity to be among the first people to study these incredible samples. As previously discussed, one of the greatest challenges in the study of meteorites is the lack of provenance and geologic context, thus introducing a fundamental limitation to our interpretations. Returned samples of asteroid Bennu are sourced from Hokioi crater, thought to be one of the youngest and reddest features on the surface of Bennu. This history of provenance provides us with the unparalleled ability to link interpretations gleaned from sample analysis to processes operating on a known feature of a known body, a feat that is only achieved with sample return. In coordination with the rest of the sample spectroscopy team, I analyzed the particle-to-particle spectral heterogeneity of a ~20 mg bulk aggregate sample of Bennu. The goal of this analysis was to investigate the prevalence and compositional diversity of phyllosilicates, carbonates, and organics within the sample to understand the parent body and space weathering processes that have modified Hokioi crater, Bennu, and its parent body.

In the final chapter, Chapter 5, I synthesize these works to present the highlights of our findings and the new frameworks that will be used to contextualize and interpret future observations of small bodies.

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Chapter 1 | Assessing the Spatial Variability of the $\sim 3\ \mu\text{m}$ OH/H₂O

Absorption Feature in CM2 Carbonaceous Chondrites

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1.1 Abstract

H₂O and OH are readily detected in hydrated minerals in CM chondrites via reflectance spectroscopy due to their characteristic vibration absorptions at infrared wavelengths. Previous spectroscopic work on bulk powdered CM chondrites has shown that spectral parameters, like the wavelength position of the ' $3\ \mu\text{m}$ absorption feature', vary systematically with the extent to which the samples have been aqueously altered. However, it is yet unclear how these spectral features may vary across an intact meteorite chip when measured at spatial scales smaller than that of the individual components of the meteorite.

Here we explore the spatial variability of this spectral feature and others on intact CM2 chips which, unlike powders, retain their petrologic and textural characteristics. We also model the modal mineralogy of the bulk meteorite powders and correlate this with key

spectral features, demonstrating that μ FTIR mapping provides a powerful, rapid, and non-destructive technique for assessing compositional diversity and variations in water-rock interactions in chondritic planetary materials.

In all CM2 chondrites studied here, we find that variations in the position, shape, and strength of the 3 μ m absorption feature reveal a single chondrite can exhibit as much spectral variation as the entire suite of CM2 chondrites. The observed variations in the position and shape of the 3 μ m feature within individual CM2 chondrite chips suggests a range of alteration products (e.g., Mg-rich to Fe-rich phyllosilicates) are present and record sub-mm scale variations in the amount and/or chemistry of the altering fluids. The samples having experienced the most progressive aqueous alteration show the least amount of variability in features like the 3 μ m absorption band minimum position, whereas the least altered samples exhibit the most variability. We also find that the bulk spectral signatures in the least altered samples appear to be biased towards the spectral signatures of clasts versus matrix. By extension, asteroid reflectance spectra exhibiting 3 μ m absorption features consistent with those measured here may be interpreted in a similar framework in which the spectrum of what may appear to be the least altered asteroids represent an average that belies the true diversity of mineralogy and chemistry of the body.

1.2 Introduction

Reflectance spectra of primitive C-complex asteroids have been found to exhibit absorption features diagnostic of water in the form of hydrated minerals and ices (e.g., Feierberg et al., 1981; Lebofsky et al., 1981; Rivkin and Emery, 2010; Campins et al., 2010; Takir and Emery, 2012; Rivkin et al., 2015; Hamilton et al., 2019; Kitazato et al., 2019). Specifically, symmetric and asymmetric stretching modes of metal-OH and H₂O and the first overtone of the H₂O bending mode give rise to a series of vibrational absorptions in the ~2.7–4 μ m wavelength region. The overlapping nature of these OH/H₂O absorptions can produce a broad and complex ‘hydration’ feature commonly referred to as the “3 μ m feature”. Despite the complex overlapping nature of the individual vibration modes, the shape, strength, symmetry, and the wavelength position of the absorption band minimum of the 3 μ m hydration feature can be used to infer the composition of hydrated materials and, by extension, provide insight into the nature of volatiles and aqueous processes on primitive asteroids.

Carbonaceous (C) chondrites, which are the most hydrated and volatile-rich of all meteorites, are thought to be genetically related to the C-complex asteroids (e.g., Gaffey et al., 1993; Pieters and McFadden, 1994; Hiroi et al., 2001; Kanno et al., 2003). The CM group of chondrites are regolith and impact breccias (Bischoff 2006) that span petrologic types 1–2 (Zolensky et al., 1997) and thus represent a range of alteration histories. Observed in these meteorites are both hydrous and anhydrous minerals (phyllosilicates, magnetite, carbonates, and various other Fe,Mg-oxides and silicates) that are products of relatively low-temperature aqueous alteration reactions (Brearley, 2006; Zolensky et al., 2008). Phyllosilicates (e.g., Fe,Mg-serpentine and smectites) tend to be the volumetrically

dominant product of aqueous alteration and give rise to one or more infrared active vibration features in the 2.7–4 μm wavelength range. The exact wavelength position of cation-OH absorptions in reflectance spectra of C chondrites depends on the octahedral cation composition of their phyllosilicates (Takir et al., 2013, 2019; Beck et al., 2010, 2014; Bishop et al., 2007; Osawa et al., 2001; Sato et al., 1997). As an example, systematic spectroscopic investigations of bulk CM chondrite powders reveal a transition in the position of the 3 μm absorption band minimum from longer (2.76–2.80 μm) to shorter (2.71–2.72 μm) wavelengths that accompanies a transition from a mineralogy dominated by Fe-rich serpentines to one dominated by Mg-rich serpentines (Takir et al., 2013). An inverse relationship between Fe-rich and Mg-rich serpentines was also observed by Howard et al., (2009, 2011) and was suggested to be linked to progressive aqueous alteration that resulted in an overall increase in the abundance of phyllosilicates relative to anhydrous silicates.

These spectral variations, and the potential diagnostic capacity of the 3 μm feature to estimate the cation composition of phyllosilicates and the degree of aqueous alteration in general, has inspired workers to propose taxonomic schemes to classify meteorites and asteroids based on the wavelength position and shape of the 3 μm hydration feature (Takir and Emery, 2012; Takir et al., 2013; Garenne et al., 2014; Beck et al., 2010). The utility of coordinated compositional and spectral analyses of C chondrites is that it provides a means to contextualize spectra (primarily ground-based telescopes) of primitive C-complex asteroids and infer their composition and degree of hydration based on data of their closest meteorite spectral analogs (Takir et al., 2015).

However, the spectroscopic measurements acquired in the majority of previous studies were performed on aliquots of bulk powdered meteorites, which by their nature are homogenized mixtures that have lost all spatial and textural petrologic information. Consequently, spectra collected on these powders represent some kind of average spectrum of the material in which the spectrally dominant component(s) may not be the volumetrically dominant component(s). Indeed, studies by Hamilton et al., (2020) and Hanna et al., (2020) demonstrated that microscopic spectral analyses of intact meteorite chips enable the study of individual components and phases that would otherwise be diluted and/or homogenized by powdering the samples. Recent petrologic studies have also investigated the brecciated nature of carbonaceous meteorites and have shown that a single CM chondrite can contain lithologies representing a range of petrologic types, from 2.0–2.9 (Lentfort et al., 2021), and thus record a range in degree/type of aqueous alteration on the parent body.

In this context, it is currently unclear how the shape, strength, and position of the 3 μm absorption feature may vary across an intact meteorite chip when measured at spatial scales smaller than that of the individual components of the meteorite and the extent to which features in spectra of bulk powder samples may bias our interpretation of aqueous alteration processes on C chondrite parent bodies. With these observations in mind, the primary goals of this study are twofold. First, we wish to assess the sub-mm spatial heterogeneity of the 3 μm absorption feature within individual CM2 chondrites to see if they span the range of CM2 chondrites as a whole, with a focus on the chondrite matrix. Second, we wish to determine the extent to which bulk spectroscopic measurements might ‘smear

out' or destroy important information in the 3 μm region that is below the spatial scale of individual components or, conversely, assess the degree to which bulk spectroscopic measurements are truly representative of a CM2 chondrite chip.

We measured and evaluated near-IR (NIR) to mid-IR (MIR) ($\sim 1\text{-}16\ \mu\text{m}$) spectral reflectance maps of individual CM2 chondrite chips at sub-millimeter scales. The CM2 group of C chondrites are ideal for this study because they exhibit significant compositional diversity as well as spectral diversity in the 3 μm wavelength range (Zolensky et al., 1997; Hiroi et al., 2021). In addition to characterizing the shape, strength, and position of the 3 μm absorption feature, we also analyzed additional NIR and MIR spectral features that have been found to be diagnostic of mineralogy and degree of alteration (e.g., NIR spectral slope, Christiansen feature position, position of Si-O stretch feature). An important component of this work is also to relate the spectral features observed in the NIR and MIR wavelength region to the composition of these samples, e.g., the abundance of hydrous versus anhydrous phases. Powder X-ray diffraction (XRD) patterns were collected for splits of each sample to provide compositional and mineralogical context for the spectral data.

1.3 Methodology

1.3.1 Sample selection and preparation

Seven CM2 chondrites (Table 1) were analyzed in this study and were selected from a suite of 44 C chondrite chips from the United States Antarctic meteorite collection previously investigated and discussed by Hiroi et al. (2021). The selected meteorites were

chosen to sample a range of 3 μm band shapes and positions (Fig. 1) that may reflect (1) variable and/or progressive degrees of aqueous alteration on the meteorite parent body and/or (2) varying degrees of terrestrial alteration. From this suite we selected the following five meteorites for both spectroscopic and XRD analysis: Allan Hills (ALH) 84031, ALH 84048 (paired to ALH 84031), Elephant Moraine (EET) 83326, EET 83389, and Queen Alexandra Range (QUE) 97077. A sixth sample, Meteorite Hills (MET) 00639, was also selected for spectroscopic analysis but swapped with MET 00630 (paired to MET 00639) for XRD analysis to avoid destruction of the limited amount of MET 00639. Although ALH 84048 is paired to ALH 84031, it was selected for this study because it exhibits spectral features distinct from ALH 84031. For a brief review of the mineralogy, petrology, and spectral properties of these samples reported by previous authors, please see the Supplemental Text.

The CM2 chondrites were first fractured using a chip-splitter to produce a smaller intact chip approximately 5 mm in size. The flattest surface was then polished using 15- μm diamond grit embedded plastic lapping film to produce a smooth surface with an area approximately 2 mm by 2 mm. The lightly polished chips were then mounted on a brass tube using Crystalbond™ for ease of handling and to mount for spectral measurements. High-resolution photomicrographs of the polished surfaces of these meteorites were then captured using an Olympus BS51 polarizing petrographic microscope mounted with an Olympus DP72 high-resolution camera

1.3.2 Microscope Fourier Transform Infrared (FTIR) spectroscopy

IR reflectance spectra of the polished meteorite chips were measured from ~1–16 μm using a Bruker LUMOS microscope FTIR spectrometer (hereafter referred to as μFTIR) with 4 cm^{-1} spectral resolution under purged dry-air conditions (dewpoint of -70°C) with an MCT detector at Brown University. A gold mirror reflectance standard was used as a spectral reference and was re-measured after every 25th spot. A rasterized map consisting of several hundred spot measurements of sizes of $125\text{ }\mu\text{m}$ by $125\text{ }\mu\text{m}$ was acquired for each meteorite across the polished surface. The reflectance spectrum for each spot was an average of 300 scans.

“Bulk” IR spectra with larger spot sizes on the order of a few mm in diameter were measured from $0.8\text{--}25\text{ }\mu\text{m}$ using a Nicolet NEXUS 870 FTIR with a 4 cm^{-1} spectral resolution in the NASA RELAB facility at Brown University. A diffuse gold reflectance standard was used as a spectral reference. Near-IR (NIR) spectra ($0.8\text{--}5\text{ }\mu\text{m}$) were collected using a CaF_2 beamsplitter and white light source, whereas mid-IR (MIR) spectra ($1.5\text{--}25\text{ }\mu\text{m}$) were collected using a KBr beamsplitter and IR (globar) source. All FTIR spectra were acquired using a DTGS detector. The NIR and MIR spectra were spliced together at a wavelength of $\sim 2.52\text{ }\mu\text{m}$ to provide a single continuous “bulk” reflectance spectrum for each meteorite chip.

1.3.3 X-ray diffraction (XRD)

Separate aliquots of six of the seven CM2 chondrites were powdered using an agate mortar and pestle and sieved to a particle size range of $25\text{--}45\text{ }\mu\text{m}$. Powder X-ray diffraction analyses of these samples were performed on a Bruker benchtop D2 Phaser X-ray

diffractometer. The configuration of the instrument included a Cu K α tube, 0.6 mm divergence slit, 0.3 mm anti-scatter shield, 2 θ Soller slit, Ni-filter, and lynxeye detector. Each analysis was performed from 5–90° 2 θ with a step size of 0.02° and a time step of 18 seconds.

To determine the bulk modal mineralogy of each sample, Rietveld refinement (Rietveld, 1969) was performed using the Topas software (version 4.1). The fundamental parameters approach (Cheary and Coelho, 1992) was used to model the measured XRD diffraction patterns of each meteorite. Fundamental instrument parameters were used to calculate the instrumental contribution to peak profiles and specimen-related crystallite size and strain broadening. The diffraction pattern background was modeled using a third- to fifth-order Chebyshev polynomial. A scaling factor, systematic specimen displacement error, and a spherical harmonics preferred-orientation correction were also used in the modeling.

Structure files representing the main known mineralogical constituents of CM2 chondrites were used in the Rietveld refinements (see Supplementary Data for structure files) and include a variety of phyllosilicates, olivines, pyroxenes, sulfides, sulfates, carbonates, feldspars, and common Fe-,Mg-oxide minerals. The phyllosilicate contribution was modeled using a combination of antigorite, chrysotile, lizardite, cronstedtite, and smectite-group structure files. Small sample amounts did not allow for detailed phyllosilicate treatments (e.g., clay size separation, glycolation, etc.), thus only total modeled phyllosilicate abundance is reported for each sample. Occupancy refinements for olivine and orthopyroxene include both Fe²⁺ and Mg²⁺ cations to account for variable cation

compositions such that the total occupancy value represents the Fe-Mg ratio for the entire cell. Unit-cell parameters, along with crystal size and strain, were also refined for each structure file.

1.3.4 Spectral band parameter analysis

Several key spectral band parameters were calculated to investigate the variability of the 3 μm absorption feature and various other spectral features at NIR and MIR wavelengths. To eliminate weak high-frequency noise within our data, each reflectance spectrum was smoothed by applying a Gaussian filter with a standard deviation of 2. For the study of the 3 μm region, each spectrum was first truncated to $\sim 2.5\text{--}5\text{ }\mu\text{m}$ and then normalized by performing a continuum removal procedure. The spectral continuum was calculated by applying an upper convex hull (e.g., Kaplan and Milliken, 2018) across each reflectance spectrum. The convex hull is the smallest convex polygon that encloses all points within a set. In this case, only the edges of the polygon above the reflectance spectrum and between the bounding wavelengths were used to create a continuum. This continuum-creation method was favored over the traditional approach of manually defining the bounding points of a linear-fit continuum across the absorption feature for each spectrum because it was found to be more accurate and rapid for the unique attributes of the thousands of spectral evaluated in this study. Each spectrum was then divided by its spectral continuum to produce a continuum-removed reflectance spectrum. Band parameter calculations at MIR wavelengths were carried out on spectra that were truncated from $\sim 6\text{--}16\text{ }\mu\text{m}$ and smoothed

but not continuum-removed, as features appear as peaks rather than absorptions for MIR spectra of non-particulate materials.

To fully characterize the variability of the 3 μm absorption feature, we calculated the wavelength position of the absorption band minimum, the full width at half maximum (FWHM), and the degree of asymmetry. We also calculated the wavelength position of the Christian feature (CF) and the wavelength position of the reflectance maximum of the Si-O stretch feature between $\sim 9\text{-}12\ \mu\text{m}$.

The wavelength position of the 3 μm absorption band minimum (B_{min}) is defined as the wavelength corresponding to the absolute reflectance minimum of the absorption feature. The full width at half max ($FWHM$) is the width (in micrometers) of the absorption feature at the point in reflectance equal to one-half the band depth of the absorption:

$$FWHM = B_{longward} - B_{shortward}$$

Here, $B_{longward}$ and $B_{shortward}$ are the bounding wavelength positions on the longward and shortward side of the absorption band, respectively. Band depth, which is an intermediate calculation for determining $FWHM$, is given by:

$$B_{depth} = \frac{R_{continuum} - R_{min}}{R_{continuum}}$$

Here, R_{min} is the reflectance value at the position of the band minimum and $R_{continuum}$ is the calculated reflectance value of the spectral continuum at the same wavelength.

Related to *FWHM*, we calculate the degree of ‘asymmetry’ of the 3 μm feature as a measure of how asymmetrical the shape of the absorption band is. This can provide insight into the relative contributions of OH and H₂O absorptions for the complex 3 μm feature and is calculated by:

$$\text{Deg. of asymm.} = \frac{B_{\text{longward}} - B_{\text{min}}}{B_{\text{min}} - B_{\text{shortward}}}$$

A degree of asymmetry value of unity would imply a perfectly symmetrical absorption band, whereas a value $\gg 1$ would indicate an absorption band that is highly skewed towards longer wavelengths (thus exhibiting a checkmark-like shape).

The Christiansen Feature position is calculated as the wavelength position of the reflectance minimum in the $\sim 8 \mu\text{m}$ region, where the real component of the complex index of refraction is equal to that of the surrounding medium (air in our case), which results in a reflectance minimum (emission maximum).

In silicate minerals, prominent Si-O stretching vibrations occur in the $\sim 10\text{--}13 \mu\text{m}$ wavelength region, and in C chondrites this feature is commonly the result of a convolution of tetrahedral Si-O vibrations in phyllosilicates and the fundamental Si-O stretching vibration in olivine (e.g, Salisbury et al., 1992; McAdams et al., 2015). Here we calculate the wavelength position of the MIR reflectance maximum (Si-O stretch) as the wavelength corresponding to the absolute maximum reflectance in $10\text{--}13 \mu\text{m}$ region.

As a word of caution, the relationships between spectral parameters in the 3 μm and MIR regions with mineralogy must be carefully interpreted, especially when extrapolating

these relationships to asteroid spectra. Though the spectra presented here were measured in a dry-air environment, it has been demonstrated that the 3 μm absorption feature can undergo dramatic changes in shape when measured under more asteroid-like conditions, i.e., hard vacuum and desiccation from heating (e.g., Takir et al., 2013, 2019; Garrene et al., 2016; Beck et al., 2010). For meteorite samples, asteroid-like conditions serve to reduce the spectral contributions from terrestrial absorbed water and in some cases structural water associated with certain terrestrial alteration products (e.g., sulfates and oxy-hydroxides). Specifically, vacuum dehydration reduces the depth of absorptions attributed to the H_2O stretching mode and bending overtone near 2.8–3.1 μm . This is also commonly accompanied by an increase in the asymmetry of the 3 μm absorption feature, i.e., an increase in the slope on the longer wavelength edge of the 3 μm feature.

Such spectral changes can influence the absolute values of spectral parameters derived for the 3 μm region. However, because all previous experiments investigating the relationship between vacuum dehydration and spectral shape have been performed on powdered meteorites, the extent to which such changes occur for intact meteorite chips is currently unclear. Powdered samples have a much higher surface area for terrestrial water to be physically absorbed, thus it is not unreasonable to expect that the 3 μm absorption feature observed for a chip would be much less influenced by this type of terrestrial contamination. This is supported by Figure 1, where spectra of the intact chips exhibit much weaker features in the 3 μm region compared with the powdered versions, consistent with less surface-adsorbed H_2O . All samples (chips) examined in this study were prepared and measured under identical conditions, thus differences and similarities in spectra are robust

in a relative sense, but absolute values are presumably different compared with powdered samples. Variations in the strength and shape of the 3 μm region as it relates to water content and particle size was recently explored by Anzures (2021), and additional studies that explore and quantify these relationships for meteorite chips are worthy of future investigation but beyond the scope of this paper.

1.4 Results

1.4.1 XRD

The bulk powder XRD patterns were used to model the abundances of a variety of minerals that commonly occur as major and minor components in CM2 chondrites. Figure 2 summarizes these results for each meteorite by grouping the individual minerals modeled into larger families of minerals including phyllosilicates, olivines, pyroxenes, feldspars, sulfides, iron oxides, magnesium oxides, sulfates, and metal. Overall, the modeled XRD patterns from the Rietveld refinement fit the measured patterns well, with Rwp values that ranged from 0.810–1.994. Observed in all measured patterns was a systematic increase in the background intensity from $\sim 10\text{--}25^\circ 2\theta$. While the precise cause of this is unknown, it is likely attributable to increasing X-ray fluorescence associated with the Cu X-rays and Fe absorption edge. An example of the Rietveld refinement model with the measured pattern for MET 00639 is shown in Figure 3. The XRD patterns and modeled fits for the remaining five meteorites are shown in Supplementary Figure 1.

In our modeled fits, a combination of phyllosilicates, olivine, and pyroxene made up 80–90 wt.% of each sample. Phyllosilicate abundances ranged from 28.93 wt.% for EET 83226 to 87.44 wt.% for ALH 84031. Minor components of these samples include sulfides, iron and magnesium oxides, sulfates, refractory feldspars, and iron-nickel metal. Analytical uncertainties were on the order of 5–10 % of measured values. Misfits in the model (e.g., at $\sim 21^\circ 2\theta$) are generally attributed to the serpentine phase and could be due to improperly modeling the preferred orientation effects, degree of crystallinity or specific polytype.

The successful modeling of the phyllosilicate component of each XRD pattern required an assemblage of several structure files representing a range of phyllosilicate species commonly found in CM2 chondrites. Major phyllosilicate species tended to include antigorite, greenalite, chrysotile, and to a lesser extent cronstedtite and lizardite. Smectite-group clay minerals including montmorillonite and nontronite also yielded an improved fit for several meteorite patterns. Olivine compositions were determined by allowing for variable occupancies of Fe and Mg in the M1 and M2 crystal sites. Compositions ranged from Fo₂₇ to Fo₉₉ and appeared to be positively correlated with the increasing abundance of bulk phyllosilicates in the sample. Pyroxenes were favored to be Mg-rich orthopyroxene assemblages with lesser amounts of diopside, augite, and pigeonite. Several meteorites (e.g., EET 83226) were found to have secondary minerals interpreted to be the products of terrestrial weathering, in some instances in abundances as high as 12 wt.%. These include iron oxides such as goethite and hydrous forms of CaSO₄ (e.g., gypsum, CaSO₄·2H₂O) and MgSO₄ (e.g., starkeyite and hexahydrite, MgSO₄·4H₂O and MgSO₄·6H₂O, respectively). The

latter are of particular note because hydrous Mg sulfates can exhibit very strong absorptions in the 3 μm region even when present in small abundances and with low hydration states (e.g., Milliken and Mustard, 2005).

1.4.2 NIR and MIR reflectance spectroscopy

Bulk FTIR spectra as well as the continuum-removed 3- μm region of each meteorite for both the chip and powdered aliquots are presented in Figure 1. The μFTIR reflectance spectra are presented in their entirety in Supplementary Figure 2. For comparison, reference spectra of mineral phases commonly found in CM2 chondrites, including phyllosilicates, mafic silicates, and terrestrial alteration products (e.g., Fe-oxides), are presented in Supplementary Figure 3.

Collectively, the shapes, strengths, and wavelength positions of absorptions in the 3 μm wavelength region were found to be quite variable among the six CM2 chondrites, suggesting the chosen samples do indeed represent a range of composition and alteration histories – terrestrial alteration included in this context. Significant spectral variability was also observed *within* individual chondrites. As an example, a selection of spatially referenced individual reflectance spectra for ALH 84048 and QUE 97077 representing their spectral diversity are plotted in Figure 4. These spectra show a remarkable diversity in the shape, strength, and position of diagnostic absorption features in both the 3 μm - and MIR-region that tend to be correlated with the presence of clasts and inclusions. However, spectral diversity is also seen *within* the matrix despite the appearance of petrologic homogeneity.

The wavelength position of the 3 μm band reflectance minimum (absorption maximum) was chosen as the primary spectral feature of interest because it has been previously proposed as a proxy for degree of aqueous alteration. Focusing on this parameter also allows us to contextualize our results within the results and taxonomic framework proposed by Takir et al. (2013), where band minimum position was proposed to be linked to petrologic type (degree of aqueous alteration). To quantify the spatial variability of the 3 μm band minimum for each meteorite within our dataset, we calculated median, interquartile range (*IQR*), and statistical outlier statistics for each meteorite. A box and whisker plot representing these statistics is shown in Figure 5.

Given the 25th and 75th percentiles (*Q1* and *Q3*, respectively), the *IQR* (*Q3* – *Q1*) can be measured and gives a useful metric for the dispersion or variability of a dataset. The *IQR* for each meteorite was found to be: ALH 84031 = 0.00153 μm , ALH 84048 = 0.00153 μm , EET 83326 = 0.03021 μm , EET 83389 = 0.01917 μm , MET 00630 = 0.00303, QUE 97077 = 0.01543 μm . From these data, a dichotomy is evident between the chondrites that appear spectrally “homogeneous” (ALH 84031, ALH 84048, and MET 00630) and those that appear spectrally “heterogeneous” (EET 83226, EET 83389, and QUE 97077) in the 3 μm wavelength region. The *IQR* values for the spectrally heterogeneous group were systematically an order of magnitude larger than those for the spectrally homogeneous group. In light of this finding, for the remainder of this paper we divide and discuss the samples in terms of the spectrally homogeneous and spectrally heterogeneous groups.

1.4.3 Spectrally homogeneous meteorites: ALH 84031, ALH 84048, and MET 00630

ALH 84031

The range of 3 μm band minimum positions calculated from the μFTIR reflectance spectra of ALH 84031 (Supplementary Figure 2a) was found to be quite uniform and exhibited the lowest variation among all chondrites discussed here. Including outliers, these values ranged from 2.719–2.761 μm . By virtue of the band minimum position and its narrowness, which are consistent with Mg-OH, the minerals most likely giving rise to this feature are Mg-rich serpentines (e.g., antigorite, lizardite, or chrysotile). Most spectra exhibit a concave curvature on the longward side of this OH absorption feature that give it a checkmark-like shape. The 3 μm feature in the corresponding ‘bulk’ reflectance spectrum (acquired via FTIR) is weaker (smaller band depth value) but is largely consistent with the shape and position observed in the μFTIR spectra.

MIR μFTIR spectra (Supplementary Figure 2b) also appear to be uniform in shape and feature a prominent reflectance peak near ~ 10 μm attributable to Si-O stretching vibrations in phyllosilicates. The wavelength position of the MIR reflectance maximum ranges from 9.825–11.395 μm , with peak positions at longer wavelengths tending to be positively correlated with 3 μm band positions. Additional MIR features include a peak centered at ~ 7 μm that is consistent with carbonates and two peaks centered near 9 μm and 11.5 μm that are likely part of the broader Si-O stretch feature. The MIR μFTIR spectra of ALH 84031 appear to be most consistent with predominantly Mg-rich serpentine group minerals (e.g., lizardite, Supplementary Figure 3b) with a few localized occurrences of carbonates. The bulk FTIR spectrum of the same region is much lower in reflectance and exhibits a broad but more subdued reflectance peak at ~ 10 μm and 16 μm consistent with those seen in the

μFTIR data. However, absent in the bulk spectrum is the carbonate feature at ~7 μm and the additional features near ~9 μm and ~11.5 μm.

ALH 84048

The μFTIR spectra of ALH 84048 (Supplementary Figure 2c) exhibited two distinct types of 3 μm absorption features: a narrow and deep feature with a reflectance minimum near 2.71 μm consistent with Mg-OH in Mg-rich phyllosilicates, and a much weaker 3 μm feature centered at longer wavelengths that exhibits multiple distinct absorptions near 2.8 and 2.9 μm and that tends to occur with MIR features consistent with olivine and/or orthopyroxene (Figure 4, spectrum 237; Supplementary Figure 3b). In aggregate, the 3 μm band minimum positions observed in the μFTIR spectra range from 2.710–2.795 μm. The shape of the 3 μm bands from ~2.75 – 3.5 μm were commonly convex and only slightly deeper but less narrow than those observed for ALH 84031. The 3 μm band observed in the bulk FTIR spectrum (black spectrum in Figure 4b) exhibited a wavelength position of 2.178 μm and was largely consistent in shape and strength with the μFTIR spectra. Similar to ALH 84031, spectral analogues include Mg-rich serpentine-group minerals with occurrences of incompletely altered mafic silicates (e.g., olivine).

The MIR μFTIR spectra of ALH 84048 (Supplementary Figure 2d) are generally similar to those measured for ALH 84031, but with slightly lower reflectance values and a wider range in spectral contrast. The MIR region is dominated by a prominent reflectance peak ranging in position from ~9.9–10.5 μm and a broader peak centered near 16 μm. Strong reflectance peaks were also observed in many of the μFTIR spectra near ~7 μm, which is

consistent with carbonates, and at $\sim 9\ \mu\text{m}$ and $\sim 11.5\ \mu\text{m}$ that are consistent with a phyllosilicate Si-O stretching feature. Several spectra also exhibited features with multiple peaks that appear consistent with larger (but localized) zones of mafic silicates, likely in the form of incompletely altered clasts. As presented in Figure 4b, these features (e.g., spot 237) overlap with what may be a relic clast (e.g., CAI or chondrule) that has been strongly altered to form serpentine and carbonate. The bulk FTIR spectrum of ALH 84048 also exhibits a prominent peak at $\sim 10.5\ \mu\text{m}$ and $\sim 16\ \mu\text{m}$ but lacks the well-defined features observed at ~ 7 , ~ 9 , and $\sim 11.5\ \mu\text{m}$ in the μFTIR spectra.

MET 00630

The $3\ \mu\text{m}$ band minimum positions observed in MET 00630 were highly consistent, ranging from $2.71\text{--}2.72\ \mu\text{m}$ and with only several outliers observed to have positions from $2.74\text{--}2.90\ \mu\text{m}$ (Figure 5 and Supplementary Figure 2i). The strength and shape of these features were highly uniform and extremely narrow, with the short wavelength portion of the band being convex and the long wavelength portion being much steeper. Band depths ranged from $\sim 0.10\text{--}0.20$. The $3\ \mu\text{m}$ feature observed in the bulk FTIR spectrum was shallower but still consistent with the strength, shape, and position of the individual μFTIR spectra. Of the samples studied, MET 00630 exhibited the shortest average wavelength position ($\sim 2.71\ \mu\text{m}$) for the $3\ \mu\text{m}$ ‘hydration’ feature. This position and shape is consistent with a Mg-rich phyllosilicate mineralogy (e.g., Mg-rich serpentine, Supplementary Figure 3a) and extensive aqueous alteration.

The μ FTIR MIR spectra (Supplementary Figure 2j) can be divided into two categories based on the general shape of the Si-O feature and the number of observed reflectance peaks. The first type exhibits two broad and nearly symmetrical peaks at $\sim 10.2\ \mu\text{m}$ and $\sim 16\ \mu\text{m}$, consistent with the Mg-rich serpentine similar to what was observed in ALH 84031 and ALH 84048. The second type exhibits a Si-O stretch feature with multiple resolvable peaks near $9.6\ \mu\text{m}$, $10.5\ \mu\text{m}$, and $11\ \mu\text{m}$ that appears to be most consistent with olivine. Several spectra of the second type appear to correlate with $3\ \mu\text{m}$ band minimum positions at relatively longer wavelengths. A minor peak at $6.5\ \mu\text{m}$, consistent with carbonate, is also observed in several spectra. The FTIR bulk spectrum is most consistent with the first type (phyllosilicate-like spectrum) at MIR wavelengths but is much darker and exhibits significantly reduced spectral contrast. There is no clear evidence for any olivine- or carbonate-like features in the bulk MIR spectrum.

1.4.4 Spectrally heterogeneous meteorites: EET 83226, EET 83389, and QUE 97077

EET 83226

The μ FTIR spectra of EET 83226 exhibited the most spectral diversity of all meteorites investigated in both the $3\ \mu\text{m}$ and MIR region (Supplementary Figure 2e and 2f). The wavelength positions of the $3\ \mu\text{m}$ band minima varied from $\sim 2.77\ \mu\text{m}$ to $2.97\ \mu\text{m}$, with outliers as short as $2.71\ \mu\text{m}$. Band minimum positions associated with the 25th and 75th percentiles were located at $2.85\ \mu\text{m}$ and $2.89\ \mu\text{m}$, respectively. The shape of the $3\ \mu\text{m}$ feature in virtually all μ FTIR was observed to be convex, rounded, and more symmetrical with band depths ranging from ~ 0.10 – 0.60 . Based solely on the shapes and positions of the

features observed, Fe-rich phyllosilicates (e.g., cronstedtite, Supplementary Figure 3a) and Mg-sulfates appear to be the most consistent spectral analogue. A visual inspection of EET 83226 suggests significant terrestrial weathering. A common product of this reaction is the formation of Fe-oxy-hydroxides (e.g., goethite, limonite, and ferrihydrite), which may be present and contributing to the broad 3 μm features centered at longer wavelengths (Supplementary Figure 3a).

MIR μFTIR spectra of EET 83226 exhibit a remarkable diversity in shape, strength, and position of features. A number of spectra feature prominent peaks at ~ 11 μm and 16 μm with smaller shoulders at 10 μm and 12 μm that are consistent with the presence of Mg,Fe-phyllosilicates. Dominating this region, though, are multi-peak features more consistent with the presence of olivine and pyroxene. The shape and strength of MIR features appear highly correlated with the 3 μm band minimum position. The more subdued features are correlated with 3 μm band minima at longer wavelengths (~ 2.90 – 3.00 μm) whereas the relatively stronger features with higher spectral contrast are linked to 3 μm band minima at shorter wavelengths (~ 2.80 – 2.85 μm). The bulk FTIR spectrum features a broad Si-O stretch feature with weak but resolvable peaks near 9.4 μm , 9.9 μm , 10.5 μm , and 11.5 μm that likely represents the convolution of a variety of phases present in this sample.

EET 83389

The μFTIR spectra of EET 83389 (Supplementary Figure 2g) showed a modest range in the wavelength position of the 3 μm band minimum with most values ranging from 2.76 μm to 2.81 μm , but it showed the most variance in band depth, with values ranging from

~0.15–0.90. The slope of the longward edge of the 3 μm absorption feature is influenced by the strength of an additional feature superimposed at 3.1 μm that causes the shape of the broader feature to vary from slightly convex to slightly concave. In aggregate, these features appear to be most consistent with the presence of either Mg,Fe-phyllsilicates, terrestrial alteration products like goethite, or both (Supplementary Figure 3). The 3 μm band of the bulk FTIR spectrum is positioned at 2.791 μm and is more consistent with the sharper and slightly concave spectra seen in Mg-rich phyllosilicate minerals.

The MIR μFTIR spectra of EET 83389 (Supplementary Figure 2h) show an impressive diversity in the shape and strength of features but can be sorted into three types of spectra. The first type features a prominent phyllosilicate-like reflectance peak near 10.5–11.0 μm with several smaller shoulders occurring near 9–10 μm and 12 μm . The second type shows a similarly broad but less prominent feature center closer to 10 μm with two shoulders near 9.0 μm and 11.5 μm . The third type is a multi-peak feature more consistent with the presence of olivine and has reflectance peaks positioned at 9.0 μm , 10 μm , 10.4 μm , 10.8 μm , 11.1 μm , and 11.6 μm . The type of feature does not appear to be strongly correlated with the 3 μm band minimum wavelength position. The bulk FTIR spectrum exhibits a broad Si-O stretch feature with weak but resolvable reflectance peaks at 9.0 μm , 9.9 μm , 10.4 μm , and 11.4 μm that is most consistent with a convolution of type two and type three spectra representing areal mixtures of phyllosilicates and olivine.

QUE 97077

The 3 μm absorption features observed in the μFTIR spectra of QUE 97077 (Supplementary Figure 2k) range in wavelength position from 2.719 μm to 2.816 μm and can be sorted into two distinct types based on the shape and number of features present. The first type is characterized by band minimum positions located near 2.76 μm and a shape consistent with Mg,Fe-serpentine. In many of these spectra, two distinct absorptions can be resolved at ~ 2.72 μm and 2.76 μm , for which the latter corresponds to the lowest reflectance value and thus the absolute band minimum position of the entire feature. The second set of spectra are similar but exhibit additional absorptions near ~ 2.82 μm and 3.0 μm . Many of these spectra also show additional features at 3.37 μm and 3.48 μm . This suite of features is most consistent with the presence of Mg-rich phyllosilicates and carbonates, where the local abundance of each controls the relative strength of the absorptions. The bulk FTIR spectrum is most consistent with the first type of spectra where two distinct absorptions at 2.72 and 2.76 μm are resolvable and observed.

The MIR μFTIR spectra of QUE 97077 (Supplementary Figure 2l) are rather uniform but can be sorted into at least two types. The first type exhibits a prominent and broad reflectance peak centered near 10 μm with three minor superimposed peaks occurring at ~ 9.7 μm , 10.2 μm , and 10.5 μm . This Si-O stretch feature is consistent with the presence of Mg,Fe-phyllosilicates and minor amounts of olivine. Several spectra also show a reflectance peak at 7 μm that is consistent with carbonate. The second type exhibit a broad multi-peak feature with peak positions at 9.8 μm , 10.2 μm , 10.6 μm , 11.2 μm and 12.0 μm consistent with the presence of olivine. The bulk FTIR spectrum is brighter but most consistent with the first type of spectrum.

1.5 Discussion

The seven CM2 chondrites investigated in this study (two of which are paired: MET 00630 and MET 00639) are diverse in their texture, mineralogy, and spectral features. Petrographically, these meteorites exhibit a variety of clasts set in fine-grained matrix that appear to be modified by various degrees of alteration. Some of this alteration is presumably due to fluid-rock interactions on the asteroid parent body, but in other cases it is the result of alteration by terrestrial weathering in the Antarctic environment. Spectroscopic and XRD analyses of the sample set has revealed two fundamental observations: (1) meteorites in both spectral groups, but especially the spectrally heterogeneous group, exhibit significant diversity in the 3 μm and longer MIR wavelength region as measured by the wavelength position, shape, and strength of diagnostic absorptions, and (2) FTIR spectra acquired at larger spatial scales of the “bulk” meteorite chips and of bulk powders do not always capture the same range of features found in the μFTIR spectra. Clasts and even separate regions within the matrix of the least aqueously altered chondrites exhibit distinct and important spectral features and characteristics that are lost or overrepresented in spectra acquired over larger spatial scales or when the meteorite is powdered. In addition, certain components, such as hydrous sulfate salts, have an influence on the 3 μm region that is disproportionate to their abundance in the bulk sample. Consequently, bulk NIR-MIR spectra for some CM2 meteorites are highly biased towards specific components that may

not be representative of the extent and range of aqueous alteration on the meteorite parent body, and we discuss these issues in detail below.

1.5.1 Spectral variability in the NIR and 3 μm Wavelength Region

The wavelength position of the reflectance minimum (absorption maximum) in the $\sim 3 \mu\text{m}$ region has been suggested to be a useful indicator of the degree of aqueous alteration in C chondrites (Bates et al., 2020; Takir et al., 2013; Beck et al., 2010). In order to reduce spectral effects of terrestrially adsorbed H_2O , Takir et al., (2013) evaluated reflectance spectra of bulk powder C chondrite samples measured under vacuum and proposed a taxonomic classification scheme by which CM2 chondrites can be assigned into one of three groups based on the $3 \mu\text{m}$ wavelength position. In this framework, chondrites in Group 1 exhibit band minimum positions between $2.76 \mu\text{m}$ and $2.80 \mu\text{m}$, host Fe-rich serpentine, and are among the least altered of the samples studied. Chondrites in Groups 2 and 3 are more extensively altered as their mineralogy evolves from Fe-rich to Mg-rich serpentine, and their spectra exhibit band positions at $2.72 \mu\text{m}$ and $2.71 \mu\text{m}$, respectively.

Presented in Figure 5 is the spread in $3 \mu\text{m}$ band positions for the six meteorites, with the three Groups of Takir et al. (2013) labeled and shown in gray for comparison. For the most altered (highest phyllosilicate abundance) and spectrally homogeneous meteorites in our sample suite, the majority of the spectra exhibit $3 \mu\text{m}$ features that fall into either Group 2 or Group 3. The wavelength positions of the band minima for the μFTIR spectra are also largely consistent with the position calculated from the corresponding bulk FTIR spectra (shown as stars in Figure 5). In contrast, the majority of μFTIR spectra for EET 83389 and

QUE 97077 exhibit 3 μm band minima with positions that fall within Group 1. The 3 μm position for the bulk FTIR spectrum of EET 83389 is within the range observed for the μFTIR data, but for QUE 97077 the position observed for the bulk FTIR spectrum is noticeably shifted to shorter wavelengths (2.72 μm) and falls within the Group 2 designation. Sample EET 83226 is distinct in that its μFTIR spectra exhibit band minimum positions at significantly longer wavelengths, from 2.81 to 2.93 μm , that fall outside of all three taxonomic groups as defined by Takir et al. (2013). The position observed in the bulk FTIR spectrum of this sample is on the long wavelength edge of this range. When considering *all* spectral measurements for each sample (e.g., the “outliers” in Figure 5), we find that the variability in the 3 μm band for each chondrite spans at least two, if not all three, of the taxonomic groups.

These results further demonstrate that bulk spectral measurements are not always entirely representative of the range in mineralogy and chemistry of aqueous alteration products when observed at much finer spatial scales. To further highlight this point, in Figure 6 we present the spatially resolved distribution of 3 μm band positions for each meteorite, where differences in the position of this feature can be matched to specific textures and the presence of clasts versus matrix. Interestingly, variations in the position of the 3 μm band minimum are observed even in some of the most altered meteorites that have very high phyllosilicate abundances, and these spectral variations do not always appear to correlate with obvious textural features at this scale. That is, the matrix in the highly altered and spectrally homogeneous chondrites exhibits variations in the 3 μm band position that may be linked to small scale variations in phyllosilicate mineralogy/chemistry. However, only

so much textural information can be gleaned from the visible photomicrographs used in this study, and ongoing work is focused on higher resolution imaging and elemental mapping of these and similar samples to better understand what drives spectral variability within the matrix.

In contrast, for the spectrally heterogeneous meteorites it can be observed that differences in the 3 μm band position can be linked to the distribution of clasts, where altered chondrules and other clasts tend to yield spectra with band minima positioned at longer wavelengths. To better understand these trends we categorized the μFTIR spectra of EET 83389 into two groups. The first group consists of spectra associated with the chondrite matrix and the second group are spectra associated with obvious clasts (i.e., chondrules, CAIs, AOAs, etc.). Statistics for the band positions of these two groups are shown in Figure 7. Spectra associated with the matrix exhibit a narrow range of 3 μm band minima centered at $\sim 2.78 \mu\text{m}$ (IQR ranges from ~ 2.774 – $2.80 \mu\text{m}$). Most band positions range from ~ 2.765 – $2.785 \mu\text{m}$ with some outliers extending to $2.81 \mu\text{m}$. Spectra of the clasts exhibit 3 μm band minima with a longer average wavelength position of $\sim 2.85 \mu\text{m}$ and with values spanning a much wider range (2.765 – $2.825 \mu\text{m}$, outliers extending to $2.895 \mu\text{m}$). When comparing these values to the statistics calculated for the total set of spectra (matrix and clasts), it can be seen that the total set nearly mirrors the spread in data for the clasts. This implies that for EET 83389, hydrous phases associated with the clasts and not the matrix have a strong influence on the bulk spectral properties. Similar characteristics likely explain the long wavelength positions observed for EET 83226 and QUE 97077, which also contain numerous light-toned clasts.

In Figure 8 we present all other spectral parameters calculated for both the μ FTIR spectra and the bulk FTIR spectra as plotted against the 3 μ m band minimum position. The FWHM and asymmetry parameters are used to provide information related to the shape of the complex 3 μ m feature, and the FWHM exhibits the strongest positive correlation with the 3 μ m band minimum position (Figure 8a). FWHM values calculated from bulk FTIR spectra fall centrally within the range of those from the μ FTIR spectra, suggesting this spectral characteristic is repeatable across these different spatial scales. The range of values observed for these samples, and the relationship in band position and width, is largely consistent with previous studies of bulk samples (e.g., Takir et al., 2013; Bates et al., 2020). The positive trend can be attributed to the competing spectral contributions of OH⁻ and H₂O. For OH-bearing samples, the addition of H₂O, whether adsorbed to surfaces or associated with hydrous minerals, will give rise to absorptions in the ~2.8 – 3.5 μ m wavelength region. This will broaden the overall shape of the 3 μ m band, yielding larger FWHM values, and with increasing H₂O it can result in the maximum absorption point coinciding with an H₂O stretching vibration mode at longer wavelengths of ~2.8-2.95 μ m compared with the OH vibration mode at shorter wavelengths of ~2.7-2.8 μ m.

However, by itself the FWHM value does not necessarily provide information on the relative contribution of OH versus H₂O, as both species can give rise to rather symmetrical absorptions. Expanding on the description above for a sample with both OH and H₂O, the continued addition of H₂O is expected to produce an initial increase and subsequent decrease in the overall asymmetry of the 3 μ m feature. As an example, consider a C chondrite sample that contains only serpentine and no smectite (or contains smectite but

with no interlayer H₂O). Its reflectance spectrum could exhibit only a very narrow and somewhat symmetrical absorption centered at ~2.7-2.8 μm . If the sample were to then gain H₂O, it would result in additional and partially overlapping absorptions in the ~2.7 – 3.5 μm region that would produce a more asymmetrical shape for the 3 μm region as a whole. Indeed, the bulk spectrum for MET 00630 in Figure 3a exhibits a narrow OH feature at ~2.71 μm whereas the bulk spectrum for ALH 84048 also exhibits a clear OH feature but with additional absorptions in the 2.8-3.5 μm region consistent with the presence of more H₂O. The continued addition of H₂O would result in the latter absorptions becoming even stronger, potentially masking the distinct OH feature and resulting in a very broad, strong, and ultimately more symmetrical absorption centered near ~2.9-3.1 μm that adopts spectral characteristics similar to bulk liquid water (i.e., higher degrees of hydrogen bonding). The bulk FTIR spectrum for sample EET 83226 in Figure 3b provides an example of this endmember. When coupled with other spectral parameters, a measure of the asymmetry can act as a useful proxy for assessing the relative contributions of OH and H₂O to the 3 μm hydration feature.

In this study, we define the degree of asymmetry as a measure of the skewness in shape of the 3 μm absorption feature, where a value of 1 indicates a perfectly symmetrical band and a value of $\gg 1$ indicates a band that is highly skewed towards longer wavelengths. For our samples, a non-linear negative correlation emerges between the degree of asymmetry and the wavelength position of the 3 μm feature (Figure 8b). Chondrites with 3 μm bands positioned at longer wavelengths have values closer to 1 (higher symmetry) and indicate H₂O is a dominant spectral contributor. In contrast, samples whose spectra exhibit

3 μm bands positioned at shorter wavelengths exhibit asymmetry values as high as 22; this indicates the presence of OH is still discernable in the spectra and that the spectral contribution of H_2O is quite variable.

When the asymmetry parameter is combined with the 3 μm wavelength position, it is easy to visualize the spectral dichotomy in the μFTIR meteorite spectra and distinguish spectrally homogeneous (shorter wavelength position, more highly skewed) from spectrally heterogeneous (longer wavelength position, more symmetrical) samples. In this parameter space (Figure 8c) the two EET samples are clearly different from the other four. As described above, individual μFTIR spectra that exhibit long wavelength positions in these samples generally correspond to the brighter clasts. The XRD data reveal that these two samples also contain significant amounts (~6-12 %) of hydrous sulfate salts (Figure 4). We conclude that for spectra of the EET samples, features in the 3 μm region are dominated by the presence of hydrated sulfates that are the result of terrestrial weathering. Although the observed spectral characteristics at 3 μm are indicative of high hydration states, these two samples are the least aqueously altered of the group (in terms of parent body processes) when considering their lower phyllosilicate abundances. The μFTIR and bulk spectra for the EET samples are dominated by the bright, terrestrially altered, sulfate-bearing clasts with little evidence for phyllosilicate-bearing matrix in the 3 μm wavelength region.

The asymmetry values calculated for the bulk FTIR spectra of the other (non-EET) samples are also largely consistent with their μFTIR counterparts, except for QUE 97077 which plots outside of the cloud of points calculated from its μFTIR spectra (Figure 8c). The bulk spectrum for QUE 97077 is most similar to the bulk spectra of the two ALH samples,

both in terms of shape and minimum wavelength position (Figures 3, 5, 8). However, individual μ FTIR spectra for the QUE sample exhibit a range in parameter values that fall between the homogeneous ALH/MET samples and the heterogeneous EET samples. The bulk spectrum for QUE 97077 is most similar in shape and strength to the bulk spectrum for ALH 84048, but the former contains roughly twice as much hydrated sulfate as the latter. As with the EET samples, it is likely that terrestrially formed hydrous sulfates associated with the bright clasts in the QUE sample (see Figure 6) exhibit a strong influence on the characteristics of the 3 μ m band in various μ FTIR spectra for this sample. But unlike the EET samples, the hydrated sulfates are not dominating the bulk spectral properties of the QUE sample. The bulk spectrum and its associated spectral parameter values are still indicative of an Mg-phyllosilicate-rich, highly aqueously altered C chondrite; the presence of terrestrial alteration phases are only evident in the 3 μ m region for the spatially-resolved μ FTIR data. The degree to which the presence of hydrous sulfates do or do not influence the bulk properties of the 3 μ m region may be due to the absolute abundance of the sulfates, their hydration state, the specific type of sulfate (e.g., Ca- versus Mg-sulfates), or a combination of these factors. The observation that the two EET samples contain highly hydrated Mg-sulfates suggests the nature of the sulfate material and its stable form at the time of measurement play an important role, particularly in terms of influencing the wavelength position of the 3 μ m band minimum.

Band depth values of the 3 μ m feature are moderately variable for most of the meteorites and exhibit a weak positive correlation with the wavelength position of the 3 μ m band minimum (Figure 8e). Because all spectra were acquired from an intact lightly polished

surface and under identical viewing geometry, differences in spectral contrast due to particulate/grain size effects should be negligible. Instead, band depth should be modulated primarily by the presence of highly absorbing species and the abundance of optically active phases within each measurement spot. The ALH 84031 and ALH 84048 samples, which have similar mineralogy and similar abundance of total phyllosilicates, exhibit very similar band depth values. Interestingly, spectra for MET 00630, which has a similar total abundance of phyllosilicates, exhibits systematically lower band depth values. This suggests either a decoupling between band depth and phyllosilicate abundance or a higher abundance of strongly absorbing phases in MET that subdue the OH feature. QUE 97077, which has a lower total abundance of phyllosilicates, exhibits 3 μm band depth values that overlap with those of MET 00630 and are sometimes much higher, further suggesting a decoupling of phyllosilicate abundance and OH absorption strength. Band depths calculated from bulk FTIR spectra are generally consistent with those calculated from the μFTIR spectra for all meteorites, once again with the exception of QUE 97077 (Figure 8c).

An additional feature measured at NIR wavelengths was the SWIR continuum slope (Figure 8f), i.e., the ratio of reflectance values at 2.4 μm and 1.7 μm . Values of the slope range from negative (0.8) to positive (1.3) for the samples studied here, and a negative correlation is apparent between the SWIR slope and 3 μm band minimum for the μFTIR data. When treated collectively, the very weak negative correlation that emerges in the μFTIR data appears to disagree with the bulk trends observed by Bates et al., (2020) where a weak positive correlation was reported. While estimation of silicate species and degree of aqueous alteration based spectral slope and other features not uniquely related to

absorptions is tenuous at best, the point we make here is that the spectral and band parameter variability observed within individual chondrites can be significant, and diagnostic features are not always observable in spectra acquired over large spots or of bulk samples.

1.5.2 Spectral Variability in the MIR wavelength region

The volumetrically dominant product of aqueous alteration in C chondrites are phyllosilicates, and the strongest features for identification of phyllosilicates at MIR wavelengths result from (Si,Al,Fe)O vibrations in the tetrahedral sheet (Michalski et al., 2006). In reflectance spectra of phyllosilicates, reflectance peaks (reststrahlen bands) in the 8–11 μm region were found to depend on the Al and Fe substitutions for Si and the influence of octahedral Al and Fe cations on the tetrahedral SiO bonds (Bishop et al., 2008; Farmer and Palmieri, 1975; Lyon and Tuddenham, 1960). Michalski et al., (2006) also noted that these SiO₄ vibrations are non-unique and must be coupled with other features for accurate mineral identification. More specifically, the Al³⁺ tetrahedral sheet substitutions and dioctahedral versus trioctahedral crystal structures have competing effects on the exact positions of the feature, which must be disentangled for proper silicate identification.

Spectra of C chondrites have previously been shown to exhibit intense and sharp absorptions near ~10 μm that result from an Si-O asymmetric stretching vibration (Osawa et al., 2005). In a bulk reflectance spectrum, or a spectrum acquired for a bulk C chondrite powder (e.g., Figure 3), this feature is a convolution of distinct silicates, where each mineral has a unique and specific spectral feature dictated by its chemical composition and crystal

structure (Dyar et al, 2009; Bishop et al., 2008; Duke and Stephens, 1964; Tarte, 1963). Given the complex and very fine-grained nature of C chondrite matrix, this aspect is likely still true even at the 50-150 μm spot size measured here for MIR wavelengths (Supplementary Figure 2). Beck et al., (2010, 2014) measured transmission spectra for a variety of CM chondrites and found significant spectral variability in the 10 μm region that they attributed to varying degrees of aqueous alteration. Specifically, they observed a continuum between a saponite-like 10 μm feature for the most heavily altered samples to an 11.2 μm feature for the most olivine-rich samples. They suggested these observations could be due to the presence of disordered, amorphous, and poorly crystalline silicates that are known to exhibit unstructured bands with peaks near ~ 10 μm . In another study, McAdam et al., (2015) measured the reflectance spectra of a suite of bulk CM chondrite powders and found a correlation between the peak position of the 10 μm feature and the mineralogy (abundance of phyllosilicates) of each meteorite. Specifically, some CM chondrites were interpreted to be less aqueously altered due to the presence of more olivine, which causes a prominent reflectance peak at longer wavelengths (~ 12.3 μm). In contrast, highly aqueously altered meteorites contained more Mg-rich phyllosilicates and their MIR spectra exhibited peaks at shorter wavelengths (~ 11.4 μm). These findings suggested that the position of the reflectance peak at MIR wavelengths may be a useful proxy for assessing the degree of aqueous alteration in C chondrites.

If the 3 μm and MIR taxonomic frameworks put forth by Takir et al., (2013) and McAdam et al., (2015), respectively, do indeed correlate with degree of aqueous alteration, then one would expect the 3 μm band minimum position and 10 μm reflectance peak

position to be somewhat correlated with one another. Figure 8b shows these two parameters plotted against one another for our μ FTIR and bulk FTIR chip spectra. A qualitative assessment shows that there is no discernible trend in these data for spectra of the meteorite chips examined here. Furthermore, specific wavelength positions of the 10 μ m SiO stretch reflectance peak overlap with one another and range from $\sim$ 9.7 μ m to 11.5 μ m (but tend to cluster between 10–11 μ m). In other words, each of the meteorites studied here exhibits a range of 10 μ m peak positions regardless of its degree of alteration or position of the 3 μ m band. We do not observe the reflectance peaks positioned at longer wavelengths ($\sim$ 12.3 μ m) that were observed in McAdam et al., (2015). Instead, the wavelength position of the SiO stretch feature is more consistent with those observed in the transmission spectra of Beck et al., (2010, 2014). This may be a result of differences in the physical properties of the samples being measured (i.e., particulates in McAdam et al., 2015, versus thin sections of Beck et al., 2014, versus optically thick chips in this study). This is supported by comparing the various MIR spectra of each sample as presented in Figure 1, where it can be observed that spectra of the bulk powders exhibit reflectance peaks at longer wavelengths than the corresponding bulk spectra of the intact chips.

A possible explanation for the variability in the position of the SiO stretch feature observed within each CM chondrite is that the SiO stretch is more sensitive to variations in cation chemistry and its effects on the silicate crystal structure compared with the octahedral metal-OH vibration that commonly gives rise to the strongest phyllosilicate-related absorption in the 3 μ m region. This is further supported by the μ FTIR spectra of QUE 97077 (Figure 4), where spectra from spots 137, 152, and 276 have virtually identical 3 μ m

absorption features centered at the same wavelength position yet exhibit three very different SiO stretch features at MIR wavelengths. The MIR feature for spot 152 appears to be much more consistent with olivine, whereas spots 137 and 276 appear more consistent with phyllosilicates, albeit with different shapes and peak positions. The spectrum at spot 276 also shows features consistent with carbonates. This variability in MIR features, which must be linked to differences in mineralogy within the measurement spot, is observed even though the corresponding 3 μm features are virtually indistinguishable. Petrographically, all of these spots appear to be associated with the chondrite matrix. These results suggest the MIR region may be more sensitive than the 3 μm region in determining the relative abundance of phyllosilicate versus primary mafic silicates at small spatial scales.

An additional feature worth discussing is the wavelength position of the Christiansen Feature (CF), which corresponds to a reflectance minimum (emissivity maximum) in the ~8-9 μm region, and which has been found to correlate with Si abundance in silicates (Salisbury, 1993). Bishop et al., (2008) studied this feature for several groups of phyllosilicates and found a shift in position of the CF to shorter wavelengths with increasing silica content. However, it's noted that the position of the CF does not correlate linearly with Si and appears to depend on the amount of Al, Fe, and Mg present in the tetrahedral layers of these phyllosilicates. Bates et al., (2020) studied the CF in CM and CI chondrites and found the wavelength position and shape to vary with the chemistry of the phyllosilicates and degree of aqueous alteration. They observed CF positions to occur at shorter wavelengths when Mg-serpentine abundance increased above the Fe-serpentine abundance, which also preceded a shift in the 3 μm absorption feature to shorter

wavelengths. In our data, the CF positions exhibit an extremely weak negative correlation to the position of the 3 μm absorption band minimum (Figure 8d). The majority of CF positions cluster between 8–9 μm . Like the MIR SiO peak position, isolating a single chondrite shows that it can exhibit CF positions that span the entire range of values observed for all chondrites measured in this study. CF positions calculated from the bulk FTIR spectra are largely consistent with those calculated from the μFTIR spectra. Interestingly, the samples with the largest range in CF position values are those with the highest phyllosilicate abundance and which are most spectrally homogenous in the 3 μm wavelength region. In contrast, the spectrally heterogeneous EET samples exhibit a narrower range in CF positions, and there is no obvious evidence for the presence of sulfates in most of the MIR data.

1.5.3 Implications for Observed Spectral Variability

It is significant that such spectral heterogeneity is observed in the shape, strength, and position of the 3 μm absorption band both between different CM2 chondrites as well as within individual samples. However, mineralogic heterogeneity has long been known to occur within individual CM2 chondrites through either inferred, direct, or indirect spectroscopic, chemical, and petrographic measurements. To first order, CM2 chondrites are genomict regolith breccias (Bischoff, 2006) and are petrologically heterogeneous at the mm- to cm-scale. CM2 chondrites like Nogoya and Cold Bokkeveld, for example, have been found to consist of brecciated lithic clasts that appear to represent different stages of aqueous alteration and thus range between petrologic types 1 and 2 (Zolensky et al., 1997;

Metzler, 1995). CM chondrites may also differ texturally from sample to sample by hosting variable ratios of matrix to primary accretionary lithic clasts.

In VIS-NIR-MIR spectral studies, it is reasonable and intuitive to presume that a measured reflectance spectrum is influenced by the relative amounts of the components of the meteorite within the measured volume. Cloutis et al., (2011b) noted that duplicate VIS-NIR spectra of CM chondrite powders exhibited differences in a variety of measured band parameters, including spectral slope and the shape and strength of absorptions attributed to phyllosilicates, but determining the specific drivers of that heterogeneity were beyond the scope of that study. Cloutis et al. (2011b) demonstrated that simply emptying and repacking the same small aliquot of a sample produced only minor deviations in overall reflectance and little to no variation in diagnostic absorptions. Those authors concluded that petrologic heterogeneities in CMs become more evident in reflectance spectra beyond the scale of the amount of sample used, which was typically < 1–2 grams. It is also important to note that when measuring and comparing reflectance spectra of bulk powders, as the case for many previous spectral studies of CM chondrites, the particle size distributions of particulate samples can influence spectral parameters such as slope, albedo, and band strength.

The results of this study provide direct evidence of spectral diversity at the sub-mm scale as it relates to clast and matrix components. While brecciation does play a significant role at larger spatial scales, we observe that sub-mm spectral heterogeneity is largely driven by the differences in individual chondrite clasts and local variations in mineralogy within both clasts and matrix. Anhydrous precursory phases in primitive chondrites show a diversity in chemistry and mineralogy (e.g., Bland et al., 2007). Alteration of these phases

by means of restricted and chemically diverse fluid flow (Bland et al., 2009, 2005; Corrigan et al., 1997) on the meteorite parent body would alter these components at different rates and to different degrees of completion, thus resulting in the precipitation of different mineral phases that should result in a menagerie of mineral types (Hanowsky and Brearley, 2001). Variations in the position and shape of the 3 μm feature within individual CM2 chondrite chips suggests a range of alteration products (e.g., Mg-rich to Fe-rich phyllosilicates) are present, and variations in phyllosilicate mineralogy may record sub-mm scale variations in the amount and/or chemistry of the altering fluids. As such, μFTIR mapping is a useful rapid and non-destructive technique for assessing variations in water-rock interactions within and between asteroid parent bodies as well as identifying areas in C chondrites that are contaminated by hydrous terrestrial alteration products (e.g., sulfate salts).

1.5.4 Correlations Between Spectral Features and Phyllosilicate Abundance

Presented in Figure 9 are the key spectral parameters plotted against the total abundance of phyllosilicates estimated from the XRD patterns. We note that bulk phyllosilicate abundance calculated for MET 00639 is plotted with the spectral parameters calculated for MET 00630, its paired counterpart. From these data, several interesting trends emerge.

In the framework of Howard et al. (2011), total phyllosilicate abundance is a useful proxy for the total extent of aqueous alteration. Interestingly, two clear negative correlations emerge from our data to show that with the increasing total abundance of phyllosilicates (1) the position of the 3 μm band minimum appears to shift to shorter wavelengths, and (2) the

overall variability of the position tends to decrease (Figure 9a). The first observation agrees well with the general framework of Takir et al., (2013), where they observed 3 μm band positions at shorter wavelengths with increasing degrees of alteration. The second observation suggests the least altered meteorites (based on lower phyllosilicate abundance) display much more variability in the position of the 3 μm band. However, as discussed above, the spectral characteristics of the ‘less’ altered meteorites are significantly influenced in the 3 μm region by the presence of hydrous sulfates from terrestrial weathering. Similar negative trends with increasing phyllosilicate abundance are also observed for FWHM and band depth values (Figures 9b and 9d).

The position of the MIR reflectance peak shows an extremely weak negative correlation with increasing phyllosilicate abundance (Figure 9c), with median values ranging from $\sim 10.5 \mu\text{m}$ to $10.3 \mu\text{m}$. This is in contrast with the more dramatic shifts observed in McAdam et al., (2015) who reported a range of $12.3\text{--}11.4 \mu\text{m}$. Our data do exhibit a positive correlation between the position of the CF and increasing phyllosilicate abundance, although the most altered meteorites exhibit distinct bimodal distributions in this parameter (Figure 9e). Lastly, SWIR slope values exhibit no clear correlation with the abundance of phyllosilicates (Figure 9f).

1.5.5 Spectral heterogeneity at different spatial scales

An important aspect of this study is the comparison of reflectance spectra measured at spot sizes below and above the size of individual chondrite clasts as measured by the

μ FTIR and FTIR, respectively. It is observed in both the 3 μ m and MIR region that the bulk FTIR spectra, while typically consistent with the majority of the μ FTIR spectra, did not always capture or reveal the diversity of spectral features and shapes found in the μ FTIR spectra. For example, the bulk FTIR MIR spectrum of MET 00630 (Supplementary Figure 2j) shows an SiO stretch feature typical of a phyllosilicate-dominated mineralogy, which is consistent with the XRD measurements on its paired sample MET 00639. However, in the μ FTIR spectra we can observe at least several dozen spectra consistent with local occurrences of olivine and perhaps other mafic silicates that are not apparent in the bulk FTIR spectrum. Even for MIR spectra that appear much more homogeneous, e.g., ALH 84031 (Supplementary Figure 2b), the bulk FTIR spectrum cannot capture the range of reflectance peak positions observed for the SiO stretch feature.

To further investigate the spatial scales at which spectral diversity may be lost or smeared out in CM chondrites, we performed a Monte Carlo simulation on the hundreds of μ FTIR spectra collected for each meteorite, where nominal spot sizes for the original spectra were 125 μ m x 125 μ m. Assuming linear checkerboard mixing, we averaged together multiple spots to resample the spot measurement size to 250 μ m x 250 μ m, 500 μ m x 500 μ m, 1 mm x 1 mm, and 2 mm x 2 mm (when applicable). These spots were then randomly sampled from the entire population 1000 times, from which we then calculated the 3 μ m absorption band position for each averaged spectrum. It should be noted that linear mixing may not be the best method for averaging spectra due to nonlinear multiple scattering effects that are present when measuring larger regions. However, this method will at least allow some perspective on how spectral diversity changes at different spatial scales.

Captured in Figure 10 are box-and-whisker plots that show the summary statistics of the 3 μm band positions resulting from the 1000 resampled spectra for each meteorite. The positions calculated on the 125 μm x 125 μm spots are virtually identical to those shown in Fig. 4 simply because these are randomly sampling the original individual spots. At resampled spot sizes of 250 μm x 250 μm there is only a slight reduction in spectral diversity that is marked by a loss of some of the most extreme outliers. Stepping up to resampled spot sizes of 500 μm x 500 μm shows a significant reduction in the spread of 3 μm band positions for virtually all meteorites as the interquartile ranges, whiskers, and outliers begin to converge around the median values. In some cases, as with the spectrally homogeneous samples ALH 84031 and ALH 84048, more than 99% of their 3 μm band minima fully converged onto a single representative value. This trend of convergence continues up to spot sizes of 1000 μm x 1000 μm and 2000 μm x 2000 μm , where eventually all 1000 calculated 3 μm band positions converge onto a single median value. The value each meteorite converges to is extremely close to the 3 μm band minimum calculated from the bulk FTIR spectra as shown in Figure 10 by the solid-colored lines. In most cases, the discrepancy between the 3 μm band minimum calculated from the resampled spectra and the bulk FTIR spectra is no more than 0.01 μm . At the extreme, the discrepancy between the convergence value and “bulk” FTIR of QUE 97077 is ~ 0.06 μm .

From these results we highlight two aspects. First, the reduction in spectral diversity is most pronounced in the progression of resampled spot sizes from 250 μm x 250 μm to 500 μm x 500 μm . The scale of this spatial transition seems to coincide with the maximum sizes of individual components in these meteorites. This may point to a regime where

measured photons may not be from individual components but rather from a mixture of chondritic components, e.g. matrix *and* chondrules. Second, the assumption of linear checkboard mixing, while not necessarily capturing the complex reality of absorption and scattering in fine-grained components, does a decent job at producing a spatially resampled spectrum for which the 3 μm band positions are similar to those measured for inherently larger spots by the benchtop FTIR. These interpretations imply that a spot size of $< 250 \mu\text{m}$ (and likely much smaller) is necessary to characterize variations in the position, shape, and strength of diagnostic absorption features in CM chondrites, including the 3 μm feature. Coordinated analyses between elemental mapping techniques (e.g., electron probe microanalysis) and even higher resolution spectral mapping are required to further investigate that scale and causes of spectral heterogeneity that may be found within the individual components of chondritic meteorites (e.g., matrix, chondrules, etc.).

1.6 Conclusion

Variations in the position, shape, and strength of the 3 μm absorption feature reveal that a single chondrite can exhibit as much spectral variation as the entire suite of CM2 chondrites. In the taxonomic framework proposed by Takir et al., (2013), the majority of spectra measured via microscope-FTIR are consistent with corresponding bulk FTIR spectra and fall into a single taxonomic group. However, when considering all spectra from a given sample, each meteorite exhibited 3 μm band minima that spanned two to three of the taxonomic groups. The 6–13 μm MIR wavelength region also exhibits diversity in the shape,

strength, and position of diagnostic features that are consistent with the presence of phyllosilicates, mafic silicates (e.g., olivine and pyroxene), and carbonate. The MIR spectral features are loosely correlated with changes in the shape, strength, and position of the 3 μm absorption feature, but variation in the latter does not always correlate to strength of phyllosilicate features in the MIR region. A spectral parameter designed to assess the degree of asymmetry in the 3 μm region yields further evidence for spectral variability within individual chondrites that rivals the variability present within the entire group of CM2 chondrites. When coupled with the 3 μm band minimum position, this parameter may allow for new methods of classification for the 3 μm hydration feature and the relative spectral contributions of OH and H₂O to C chondrite and asteroid reflectance spectra. Further studies that integrate spatially resolved measurements of these spectral parameters with coordinated petrologic and mineralogic identification are necessary to better establish these relationships and quantify the influence of terrestrial weathering products.

In both bulk and spatially resolved (μFTIR) spectra, the position of the 3 μm band minimum shifts to shorter wavelengths with increasing total abundance of phyllosilicates, generally consistent with the framework proposed by Takir et al., (2013). Considering the total abundance of phyllosilicates as a proxy for the degree of aqueous alteration within a chondrite, we find that the most altered chondrites tend to have 3 μm band minima at shorter wavelengths ($\sim 2.71\text{--}2.72\ \mu\text{m}$) and exhibit much less variability in band position than spectra of the less altered and more spectrally heterogeneous chondrites.

The spectral variability and differences between matrix and clast components within individual chondrites is typically not revealed by bulk FTIR spectra of intact chips for

measurement spot sizes larger than the individual meteorite components. The same conclusion can likely be drawn when comparing microscope FTIR spectra to measurements conducted on powdered meteorites, as all spatial heterogeneity will be lost, and spectral features will be homogenized. By extension, asteroids exhibiting 3 μm absorption features in their reflectance spectra consistent with those measured here may be interpreted in a similar framework in which the spectrum of the least altered asteroids represents an average that belies the true diversity of mineralogy and chemistry of the body. Confounding the interpretation of hydration features in lab spectra is our observation that some of the lesser altered CM2s contain hydrous Mg-sulfate, presumably of terrestrial origin, that dominates the 3 μm region in a manner disproportionate to its abundance relative to phyllosilicates. This highlights the importance of independent verification of sample mineralogy to properly link spectral features/variations to degree of aqueous alteration and thus parent body processes.

These results should be an important consideration for researchers conducting laboratory spectroscopy experiments on highly valued samples from asteroid sample return missions. To comprehensively analyze and understand the spatial and spectral relationships likely present within these samples, we recommend similar measurements be made on these samples prior to any destructive preparation methods spectroscopists traditionally employ. In short, μFTIR techniques have the power to nondestructively reveal interesting and important spectral and mineralogic relationships found within intact samples that traditional methods fail to capture.

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1.8 Supplementary Text

Meteorite Literature

The seven meteorites selected in this study were a subset of the C chondrites investigated by Hiroi et al. (2021) and sample the diversity of strength, shape, and position of 3 μm absorption features seen among all CM chondrites in that study. The spectral, elemental, mineralogic, and isotopic characteristics of several of these samples were also investigated by previous researchers and are briefly summarized below and in Supplementary Table 1.

Both ALH 84031 and ALH 84048 are CM2 chondrites and have an assigned weathering grade of Ae (Schwarz et al., 1985, 1986). ALH 84031 was found to have a light brown polygonally fractured fusion crust with minor evaporite deposits formed on its exterior. Fayalite mol % of ALH 84031 ranges from 0–2 mol %. Both have been determined to have affinities to the ALH 83100 pairing group.

EET 83226 is currently listed as an ungrouped C2 chondrite but in the past was assigned as a CM2 chondrite. It has an assigned weathering grade of A/B, and a fayalite and ferrosilite mol % range of 0.5–69 and 0.6–10, respectively (Schwarz et al., 1985). EET 83226 is among the most well studied meteorites selected in this work. In a study of C and O isotopic ratios of carbonates in carbonaceous and ordinary chondrites, Grady et al., (1988) found EET 83226 to have among the lowest $\delta^{13}\text{C}$ values (+2.9 ‰) in their, which was interpreted to possibly mean that the sample may have been affected by terrestrial weathering, which was contradictory to its low weathering grade. Also noting the observation by Gibson et al. (1987) that EET 83226 has an unusually low total of carbon abundance for a CM2 chondrite, Grady et al. (1988) suggested that rather than terrestrial weathering, EET 838226 was instead misclassified as a CM2 chondrite. Klock et al. (1989) measured fine-grained, opaque matrix particles of EET 83226 via energy-dispersive analysis and reported representative compositions of matrix olivine and pyroxene grains. In a coordinated elemental, petrologic, and petrographic study of bulk samples and thin sections of EET 83226 Abreu et al. (2018) found that this sample appeared to have a closer affinity to CV-CK chondrites. The corrected mean chondrule diameter was found to be 156 μm ($n = 809$), which is most consistent with chondrule diameters reported for CO chondrites. The texture of their samples were highly porous with a heterogeneous distribution of tochilinite and framboidal magnetite. EDS X-ray elemental maps also revealed a complex mineralogy of framboidal magnetites, Ca-sulfates, tochilinite-cronstedtite intergrowth-like materials, and forsteritic olivine. Unlike previous studies that had linked EET 83226 to CM chondrites, Abreu et al. (2018) suggest a possible

relationship to the CV-CK clan and possibly with the CO chondrites. In a spectral study of the 3 μm hydration feature, Takir et al. (2019) found the 3 μm absorption feature of EET 83226 to be consistent with CM chondrites. The broad nature of this absorption feature and its position at 2.83 μm suggests a composition of Fe-serpentine and a history of only minor aqueous alteration. More recently, in a multi-faceted study including SEM, LA-ICP-MS, and Raman Spectroscopy, Yesiltas et al. (2022) found EET 83226 to be clastic and highly porous with a largely anhydrous mineralogy, large chondrules with 30–100 μm thick fine-grained rims, metal phases that include Fe-Ni, FeS, and chromite, and extensive olivine zoning where Fe/(Fe + Mg) ratios can differ by as much as 45 wt %. Their results suggest EET 83226 may be an anomalous CO3 chondrite.

EET 83389 is classified as a CM2 chondrite with an A/B weathering grade and fayalite and ferrosilite mol % values of 0.2–37 and 1–13, respectively (Score et al., 1987). These authors note a clastic nature observable in the bulk sample and numerous chondrules and irregular granular aggregates in thin sections. Nickel-iron is present in trace amounts and olivine grains are close to forsterite. In a study of the visible and near-infrared characteristics of EET 83389, Cloutis et al. (2011) note a strong red slope, which may be attributable to terrestrial weathering in some cases. They also observe an absorption band near 2.32 μm that is most consistent with Mg-bearing serpentine group phyllosilicates.

MET 00630 and MET 00639 are both CM2 chondrites with a weathering grade of A and are paired to one another (McBride et al., 2003). The fayalite and ferrosilite mol % of MET 00630 and MET 00639 are 0–2, 2–7 and 0–41, 2–6, respectively. The visible and near-infrared reflectance spectrum of MET 00639 was measured by Cloutis et al. (2011)

and was found to have a relatively flat and featureless spectrum with a strong dip in reflectance shortward of 0.4 μm . Also on MET 00639, Takir et al. (2013) provided a more detailed petrographic study on the abundance of different phases and found abundant matrix phyllosilicates, ≤ 0.02 vol% metallic Fe-Ni, mafic silicate phenocrysts in chondrules having experienced 85–99 vol % alteration, 2–5 vol % large PCP clumps with an FeO/SiO₂ ratio of 0.89, sulfides occurring as pentlandite and pyrrhotite, and Ca-rich and complex carbonates. Taking a multi-instrument coordinated approach, Davidson et al. (2020) found that MET 00639 was likely moderately heated and highly aqueously altered. The 3 μm absorption feature in the IR spectrum of MET 00639 resembles a CM1 chondrite, yet the strength of the feature is weak, possibly indicating dehydration from heating. The bulk mineralogy of the sample was found to be ~83 vol.% phyllosilicates and ~12 vol.% anhydrous silicates with lower overall Fe-cronstedtite XRD peaks than typical CM chondrites, which could reflect a difference in crystallinity due to partial dehydration. Chondrules are both FeO-rich and FeO-poor and are predominantly <500 μm in diameter and commonly possess fine-grained rims. Iron metal is rare (<0.5 vol.%) and Ni-poor (<7 wt.% Ni).

Lastly, QUE 97077 is a CM2 chondrite with a weathering grade of A/B and fayalite and ferrosilite mol % values of 1–35 and 0–1, respectively (McBride et al., 2000). These authors also note thin sections consisting of a few small chondrules (up to 0.5 mm), rare metals and sulfides, and a matrix that predominantly consists of Fe-rich serpentine. Cloutis et al. (2011) observed absorption features centered near 0.7, 0.9–0.95 and 1.1–1.12 μm in the reflectance spectrum of QUE 97077, which appeared to be most consistent with

serpentine group minerals and/or mixed-valence serpentine group minerals. Investigating the infrared reflectance spectrum of QUE 97077, Duan et al. (2022) observed aliphatic CH₃ absorption bands at 3.38 and 3.48 μm and an aliphatic CH₂ absorption band at 3.41.

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1.10 Figures and Tables

Table 1: Classification, weathering grade, and mineral compositions of meteorites used in this study as reported by the Meteoritic Bulletin.

Meteorite Name	Classification	Weathering Grade	Mineral Composition		Source of Classification
			Fayalite (mol%)	Ferrosilite (mol%)	
ALH 84031	CM2	Ae	0–2	n.d.	Schwarz et al., (1985)
ALH 84048	CM2	Ae	n.d.	n.d.	Schwarz et al., (1986)
EET 83226	C2-ung	A/B	0.5–69	0.6–10	Schwarz et al., (1985)
EET 83389	CM2	A/B	0.2–37	1–13	Score et al. (1987)
MET 00630	CM2	A	0–2	2–7	McBride et al. 2003)
MET 00639	CM2	A	0–41	2–6	McBride et al. (2003)
QUE 97077	CM2	A/B	1–35	0–1	McBride et al. (2000)

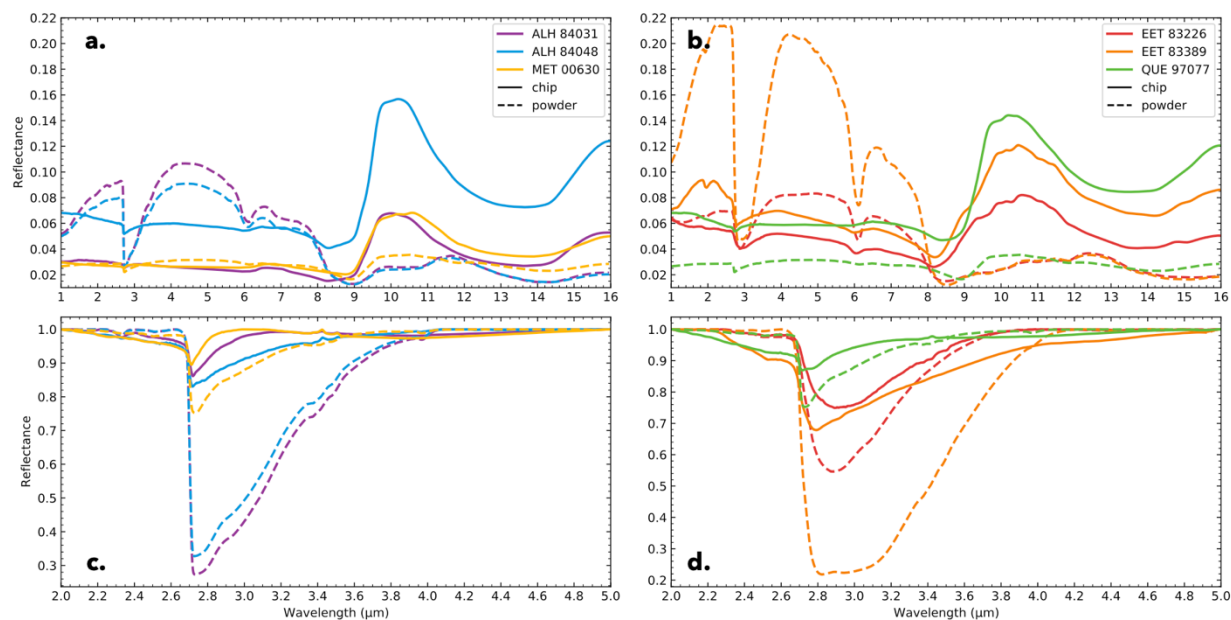


Figure 1: Bulk infrared spectra of both chip and < 25 μm powder aliquots of ALH 84031, ALH 84048, EET 83226, EET 83389, MET 0630, and QUE 97077 was acquired using the Nicolet NEXUS 870 FTIR spectrometer. Panels (a) and (b) shows the entire infrared spectrum acquired. Panels (c) and (d) shows the 3 μm region of the same spectra but with continua-removed. Measurement spot sizes were on the order of a few mm.

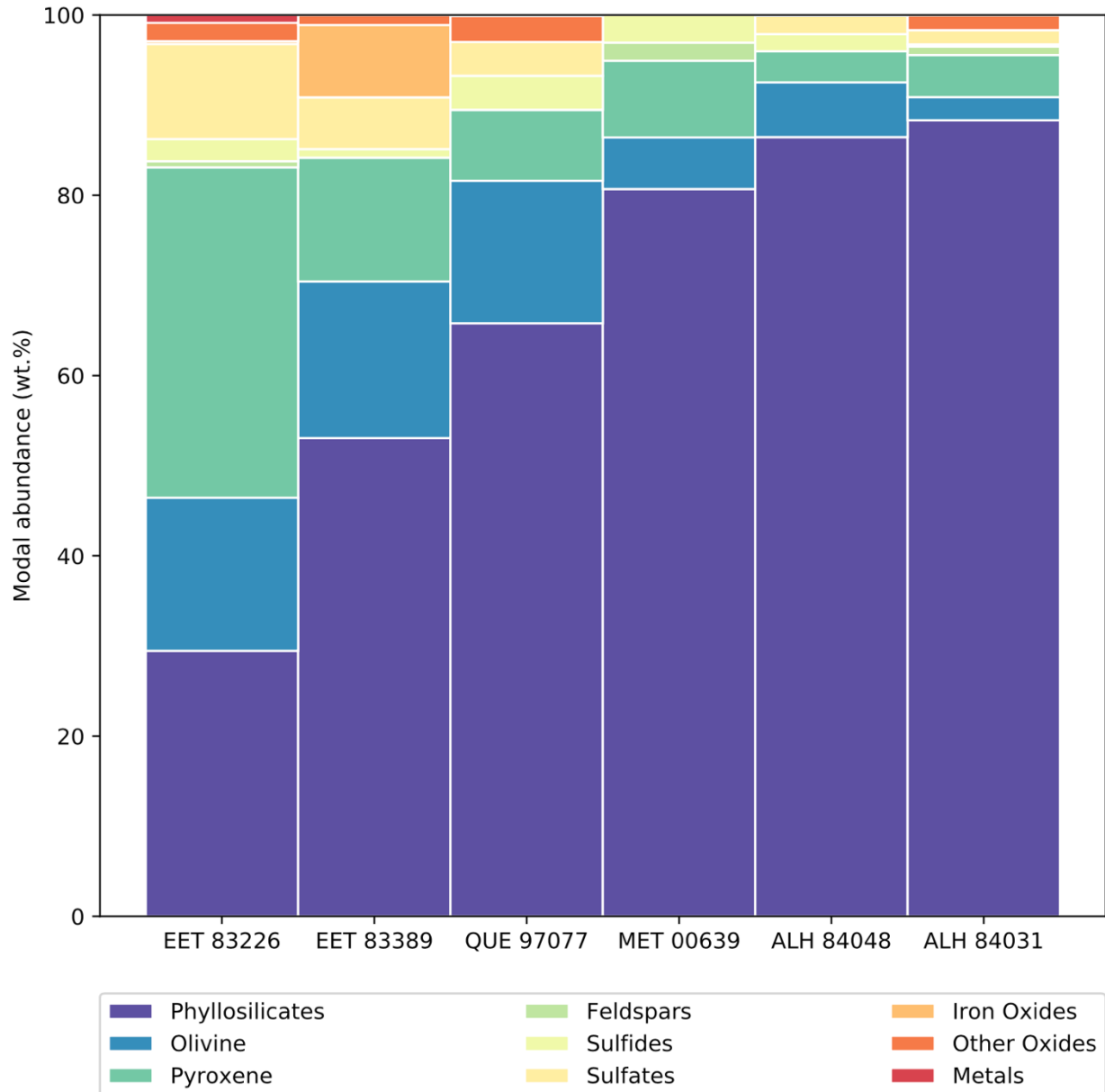


Figure 2: Modal mineral abundances of the major and minor CM2 chondrite components. The specific minerals used in Rietveld refinement modeling were grouped into one of ten “families” of minerals. Included in the phyllosilicate family are antigorite, lizardite, chrysotile, cronstedtite, montmorillonite, and nontronite.

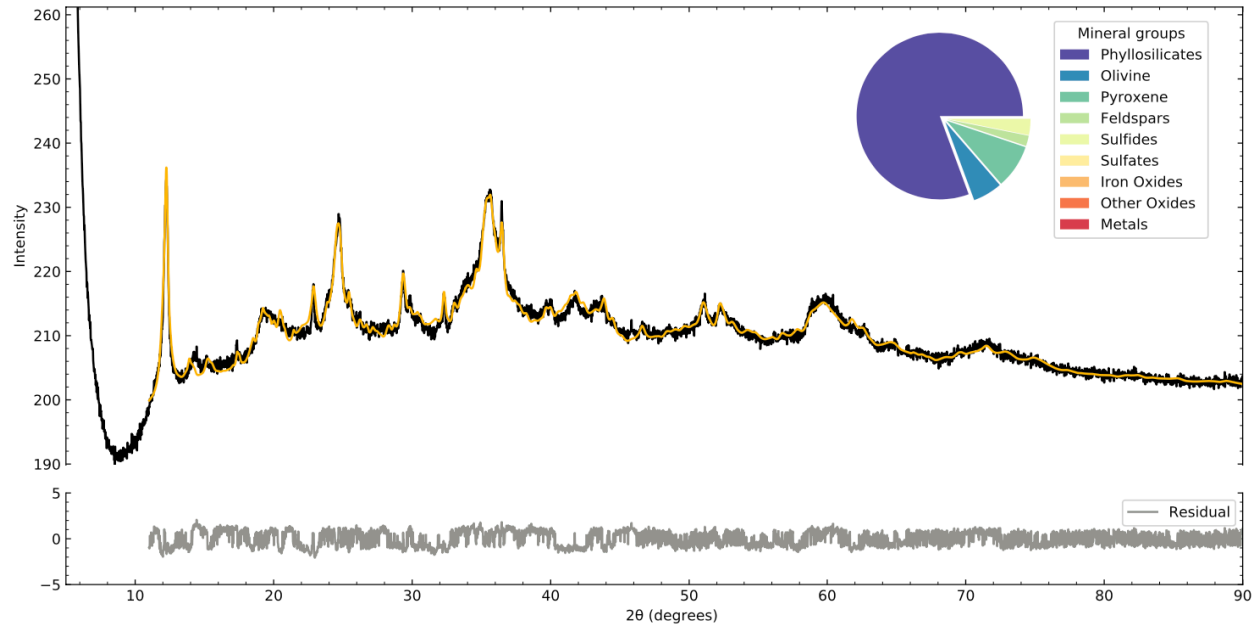


Figure 3: The measured XRD pattern and the Rietveld refinement modeled fit are shown for meteorite MET 00630 along with bulk mineral abundances determined from the Rietveld refinement model. The residual, shown in the bottom subpanel, ranges between -2.031 to 2.079. Colored sticks above the XRD and Rietveld pattern indicate the approximate 2θ positions of the major mineral constituents.

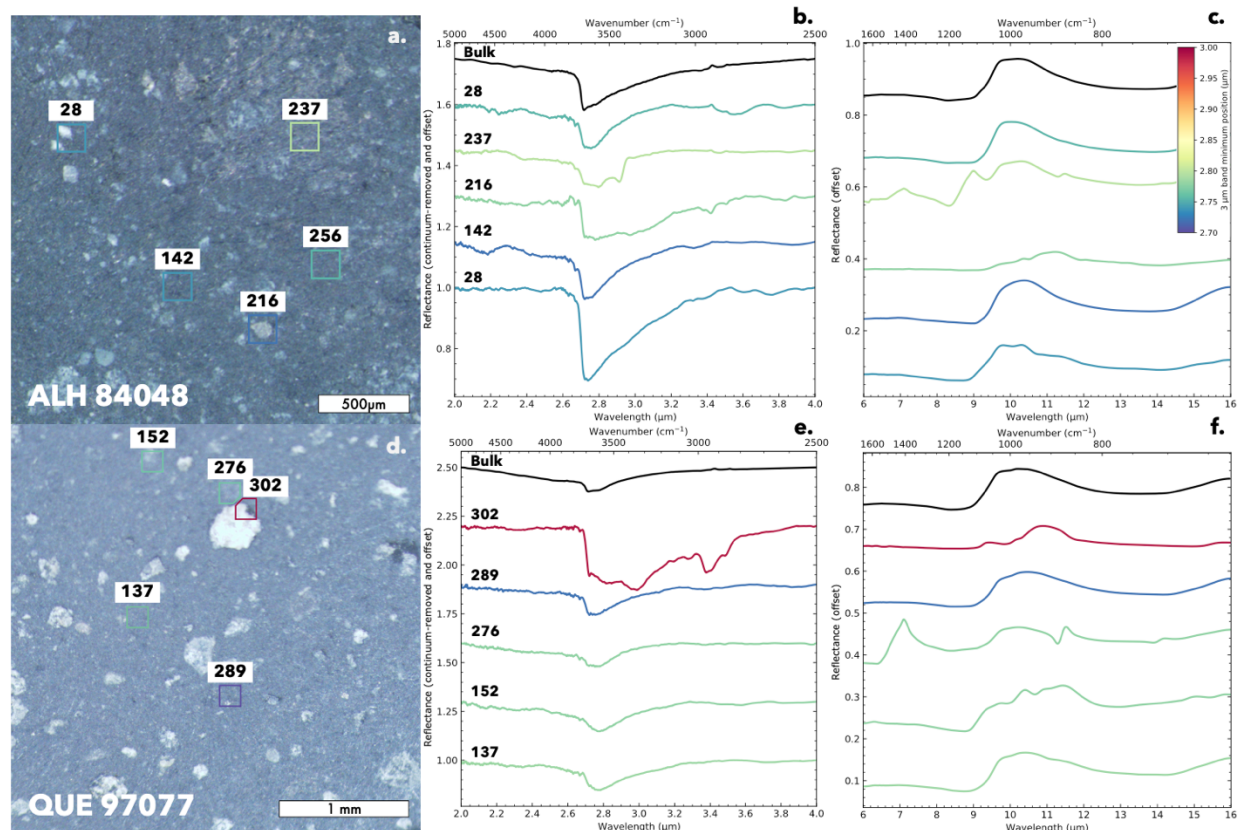


Figure 4: Selected microscope-FTIR spectra for meteorites ALH 84048 and QUE 97077 show the diversity in shape, strength, and band minimum position of the continuum-removed 3 μm absorption feature (subpanels b. and e.). The corresponding MIR region spectra (subpanels c. and f.) are also presented along with the spatially referenced measurement locations (subpanels a. and d.). The color for each spectrum and measurement bounding box corresponds to the 3 μm band minimum position of each μFTIR spectrum. The bulk FTIR spectrum is plotted in black. Measurement spot sizes were 125 μm by 125 μm . All spectra are offset for clarity.

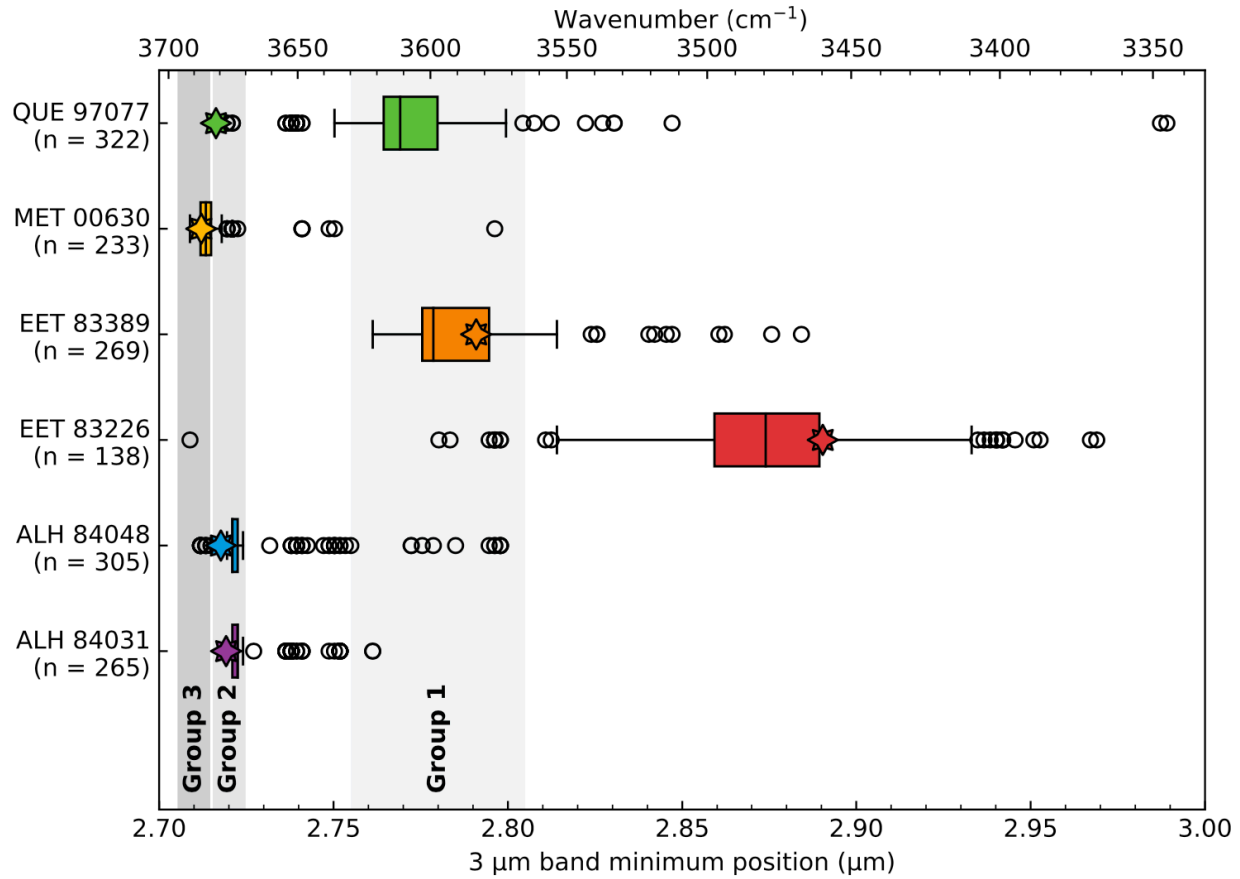


Figure 5: Summary statistics including the medians, interquartile ranges, and outliers were calculated on the 3 μm band minimum positions for each meteorite and are plotted as box-and-whisker plots. The 3 μm band minimum position calculated from the bulk FTIR spectrum is shown as a colored star. Given the IQR, or the interquartile range ($Q3 - Q1$), outliers are determined as values that are either greater than $Q3 + IQR \times 1.5$ or less than $Q1 - IQR \times 1.5$. Groups 1, 2, and 3 correspond to the wavelength range used to classify CM2 chondrites based on their 3 μm absorption band minimum positions from Takir et al., (2013).

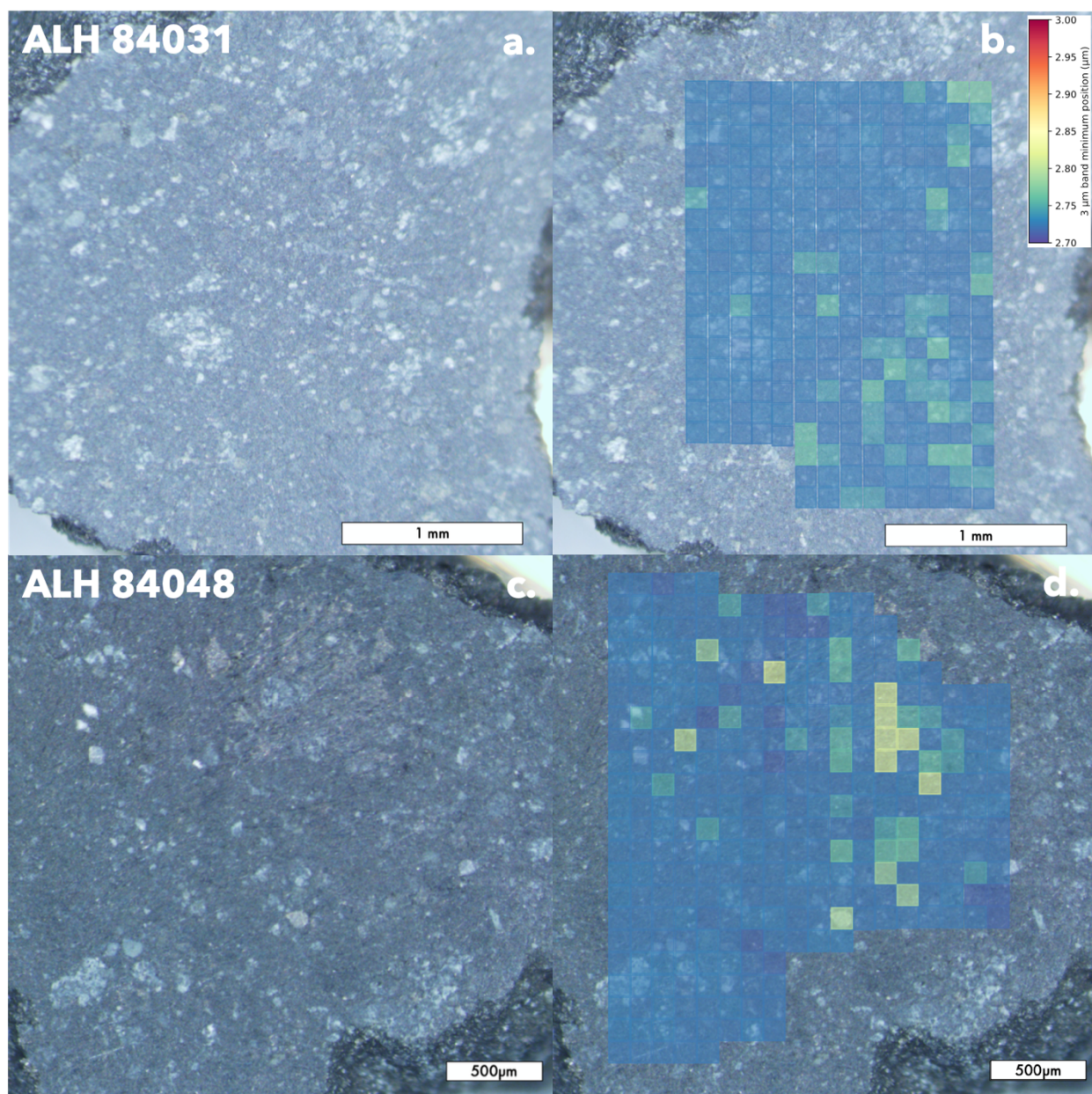


Figure 6: Pictomicrograph images of (a.) ALH 84031, (c.) ALH 84048, (e.) EET 83226, (g.) EET 83389, (i.) MET 00630, and (k.) QUE (97077). Also shown are the corresponding spectral maps generated from the 3 μm band minimum positions calculated from the μFTIR spectra of each meteorite. The differences in color correspond to the band minimum position calculated from each spectrum.

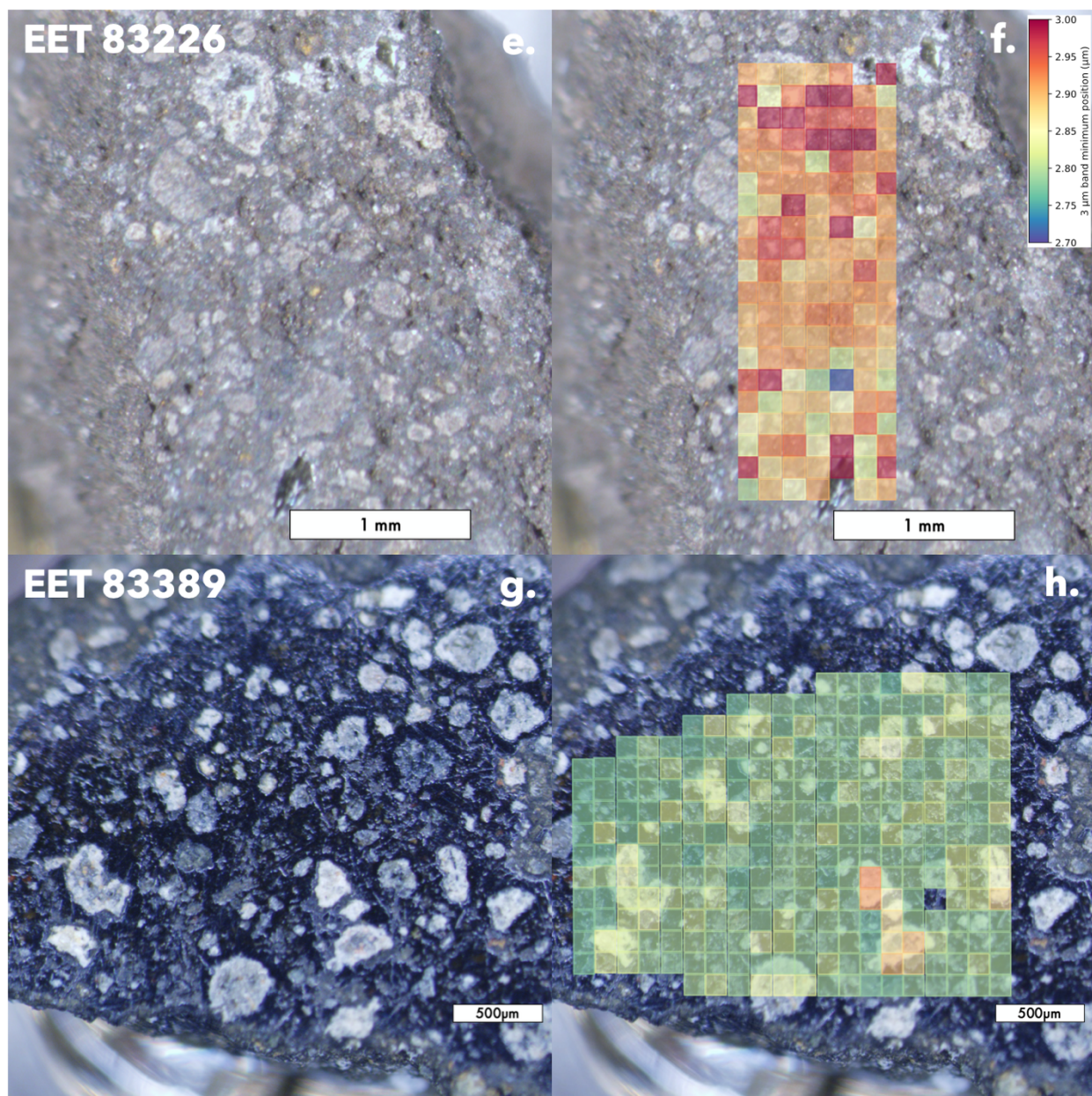


Figure 6 (continued): Pictomicrograph images of (a.) ALH 84031, (c.) ALH 84048, (e.) EET 83226, (g.) EET 83389, (i.) MET 00630, and (k.) QUE (97077). Also shown are the corresponding spectral maps generated from the 3 μm band minimum positions calculated from the μFTIR spectra of each meteorite. The differences in color correspond to the band minimum position calculated from each spectrum.

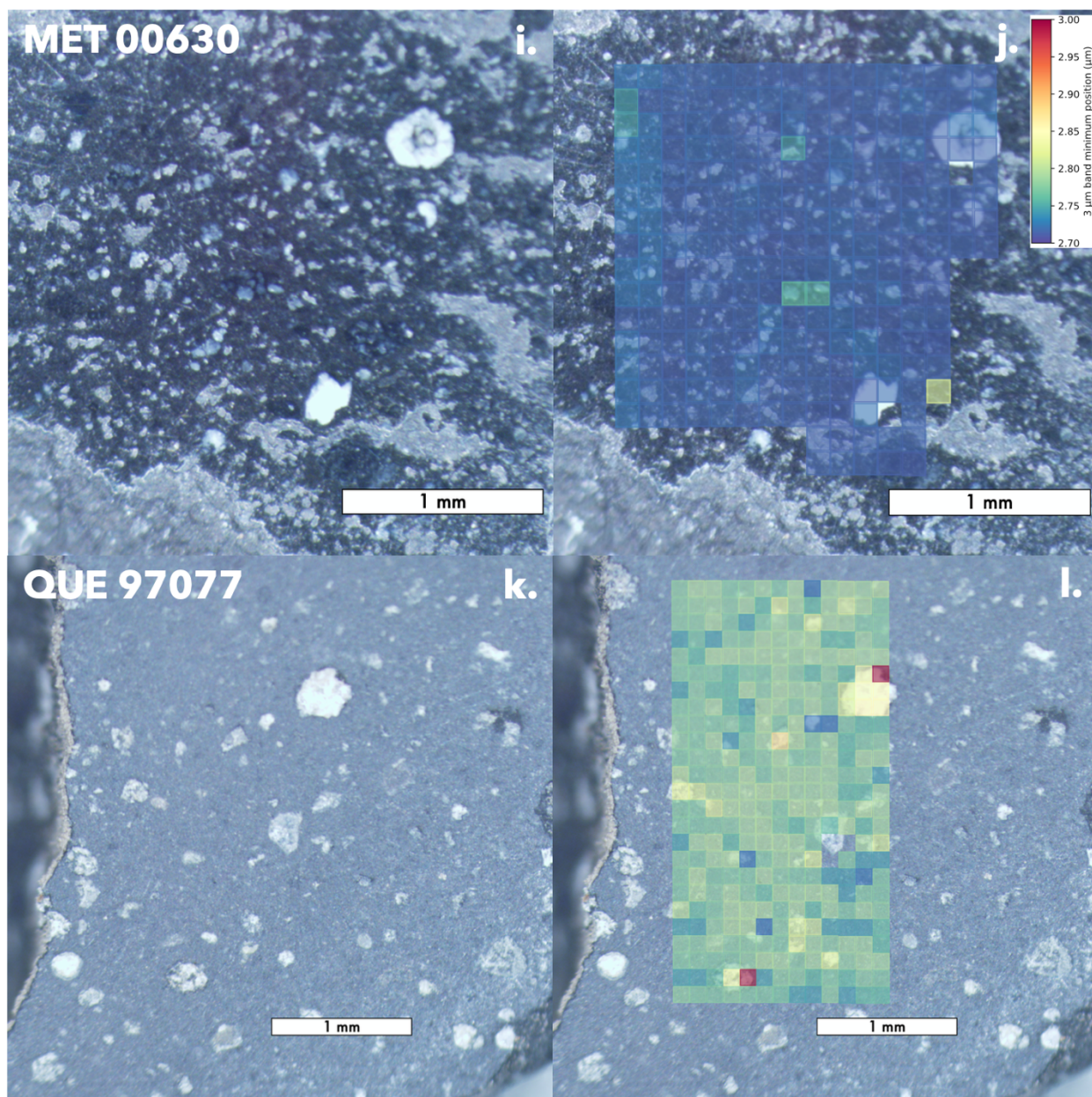


Figure 6 (continued): Pictomicrograph images of (a.) ALH 84031, (c.) ALH 84048, (e.) EET 83226, (g.) EET 83389, (i.) MET 00630, and (k.) QUE (97077). Also shown are the corresponding spectral maps generated from the 3 μm band minimum positions calculated from the μFTIR spectra of each meteorite. The differences in color correspond to the band minimum position calculated from each spectrum.

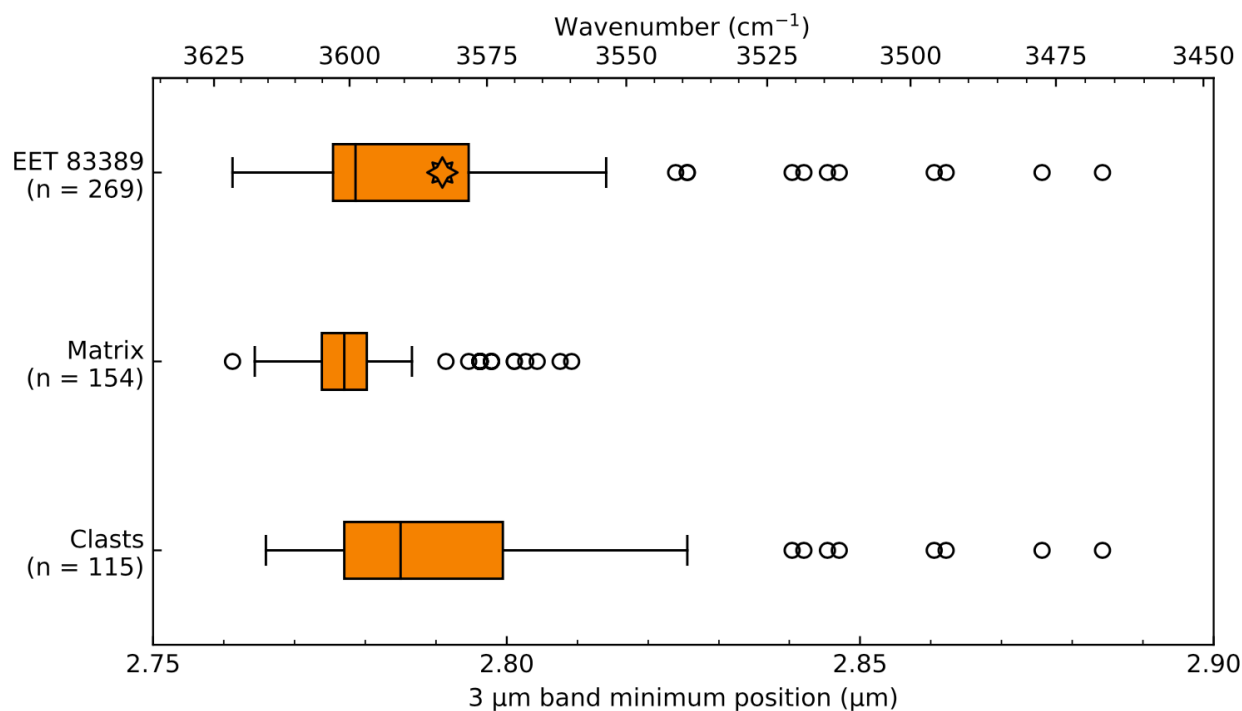


Figure 7: The summary statistics of the 3 μm band minimum for EET 83389, previously shown in Figure 5, were isolated and compared to the statistics calculated from the spectra of the individual components of this meteorite. Specifically, the μFTIR were regrouped based on whether they corresponded to the chondrite matrix or a clast. The same summary statistics were calculated for these two subgroups and are also presented. Summary statistics include the medians, interquartile ranges, and outliers.

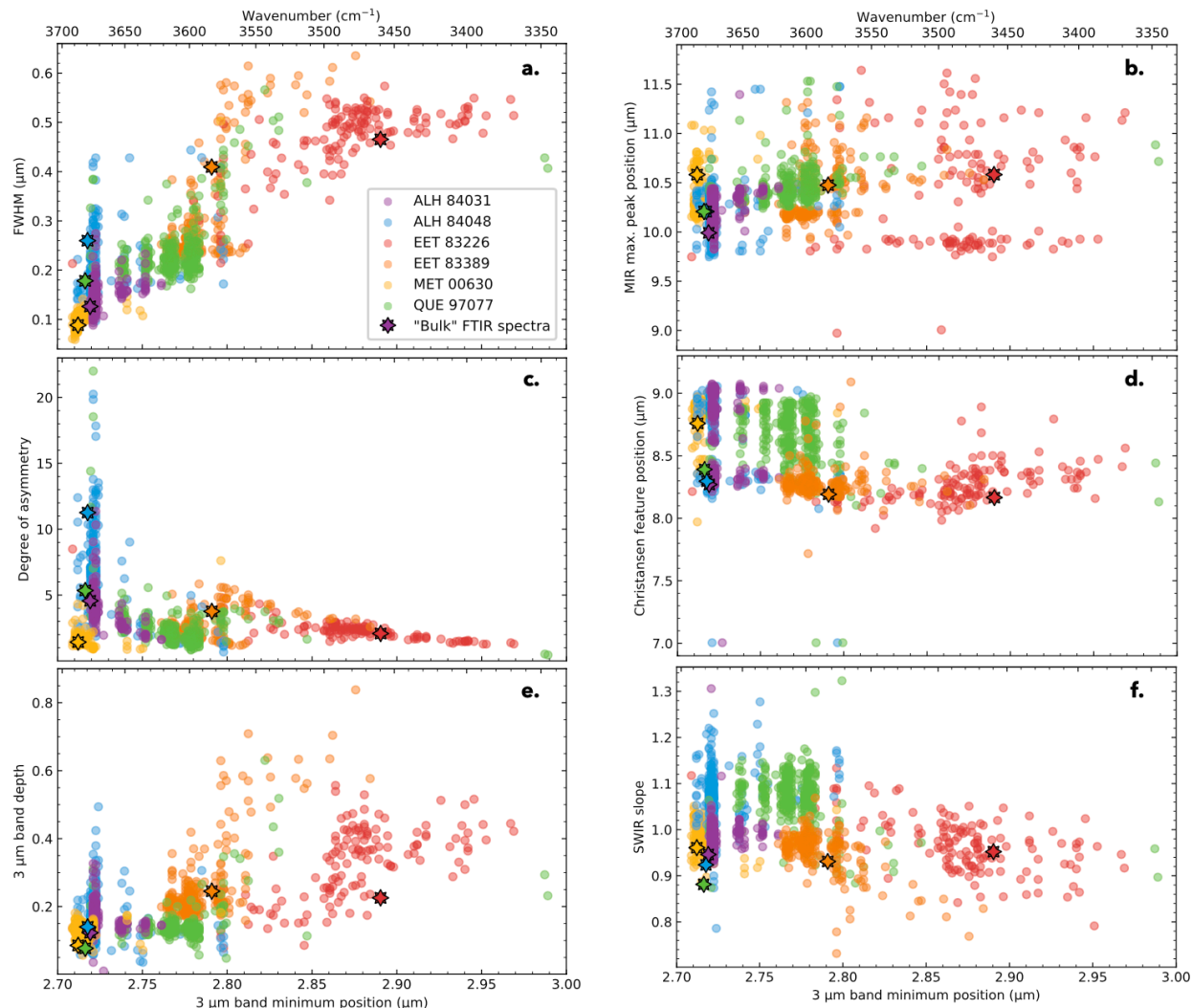


Figure 8: Key spectral parameters were calculated from the μ FTIR spectra (colored circles) and bulk FTIR spectrum (colored stars) and plotted together here. All are plotted as a function of the wavelength position of the 3 μ m band minimum and include (a.) FWHM, (b.) wavelength position of the MIR SiO stretch feature, (c.) degree of asymmetry, (d.) the wavelength position of the Christiansen Feature, (e.) the 3 μ m band depth, and (f.) the SWIR continuum slope.

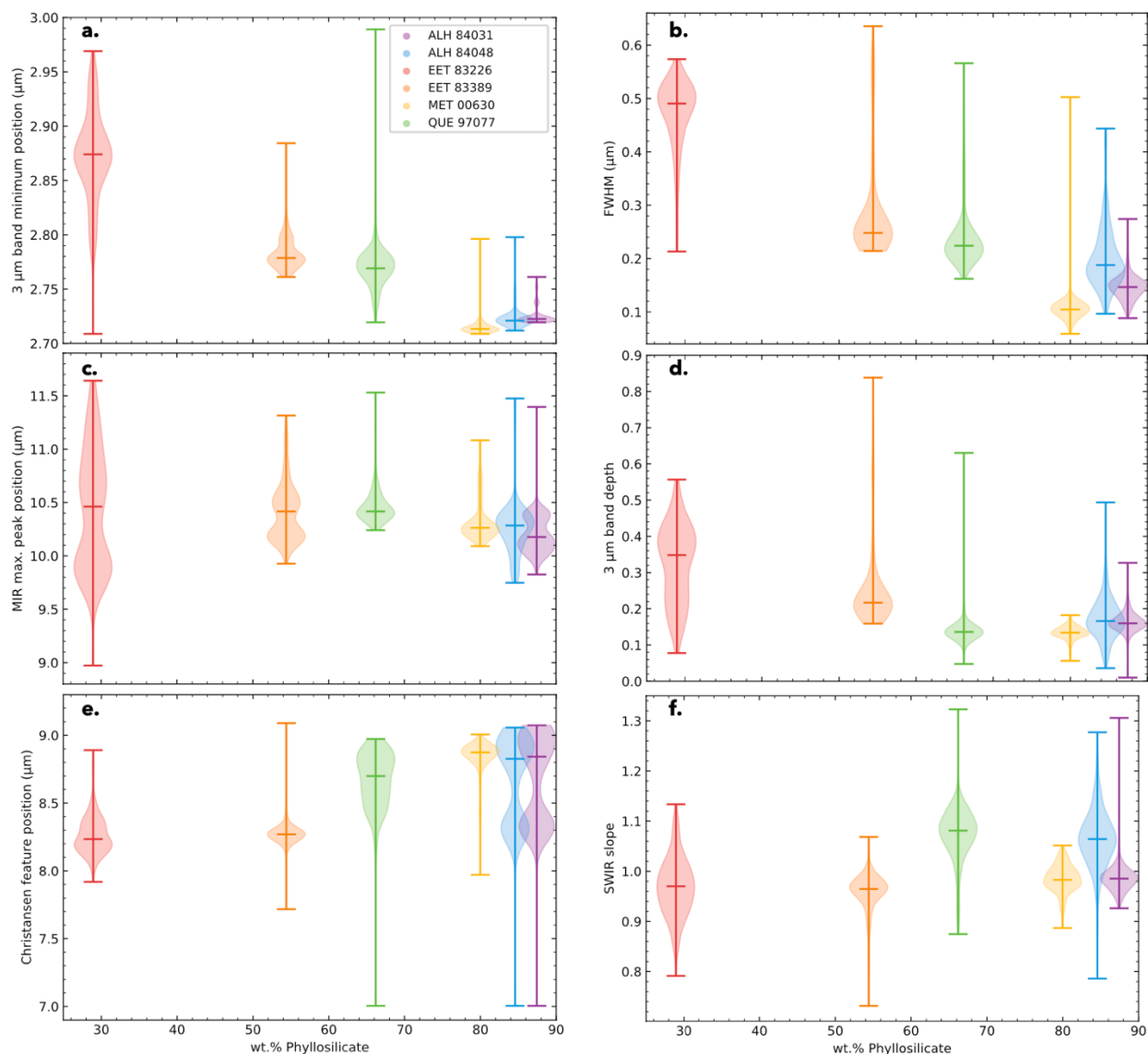


Figure 9: Violin plots showing the relative distribution of spectral parameters calculated from the μFTIR spectra of each meteorite are plotted as a function of the total bulk abundance of phyllosilicates measured for sample. Dashes indicate median values and extrema. Spectral parameters include (a.) wavelength position of the 3 μm absorption band minimum, (b.) FWHM, (c.) wavelength position of the MIR SiO stretch feature, (d.) 3 μm band depth, (e.) the wavelength position of the Christiansen Feature, and (f.) the SWIR continuum slope.

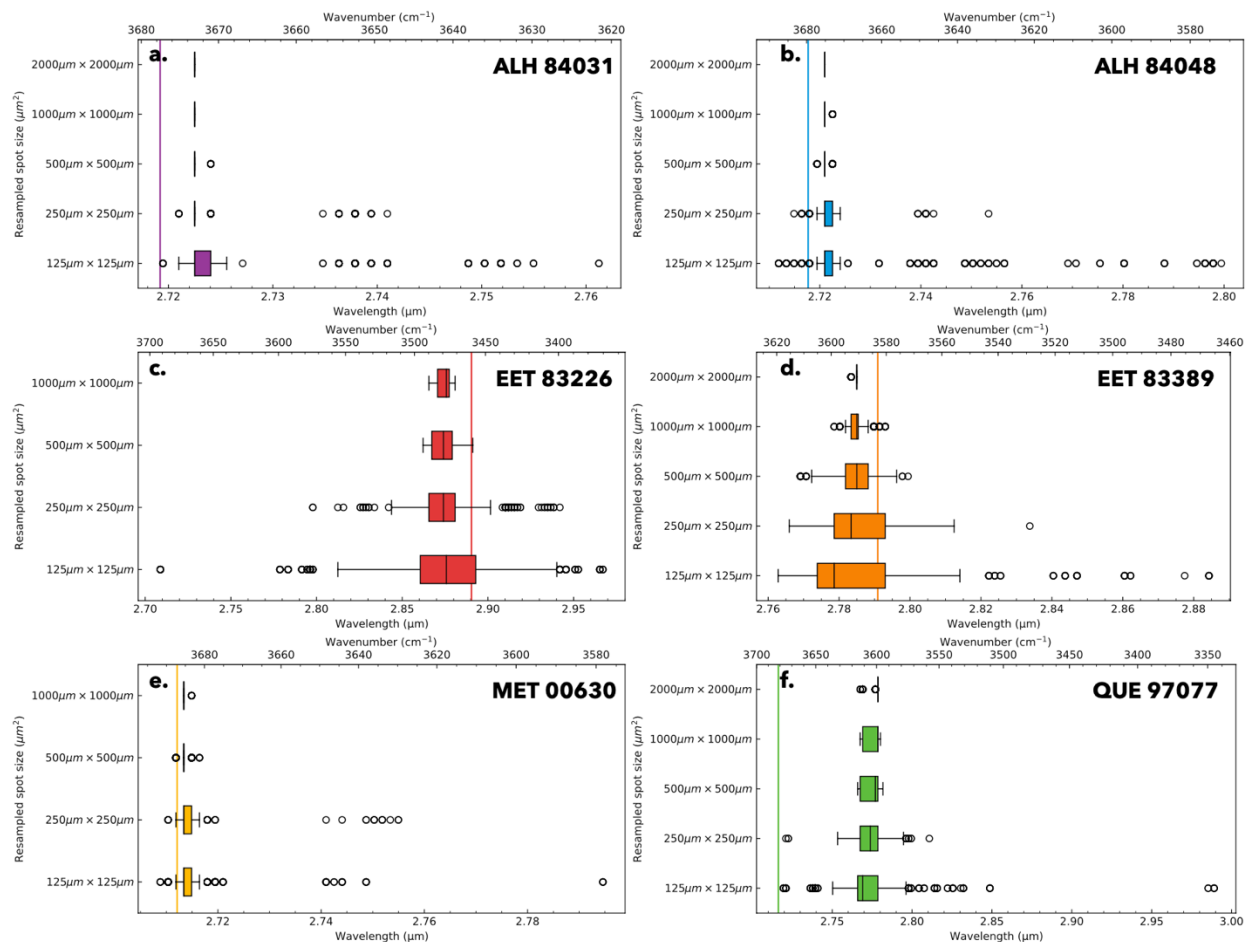
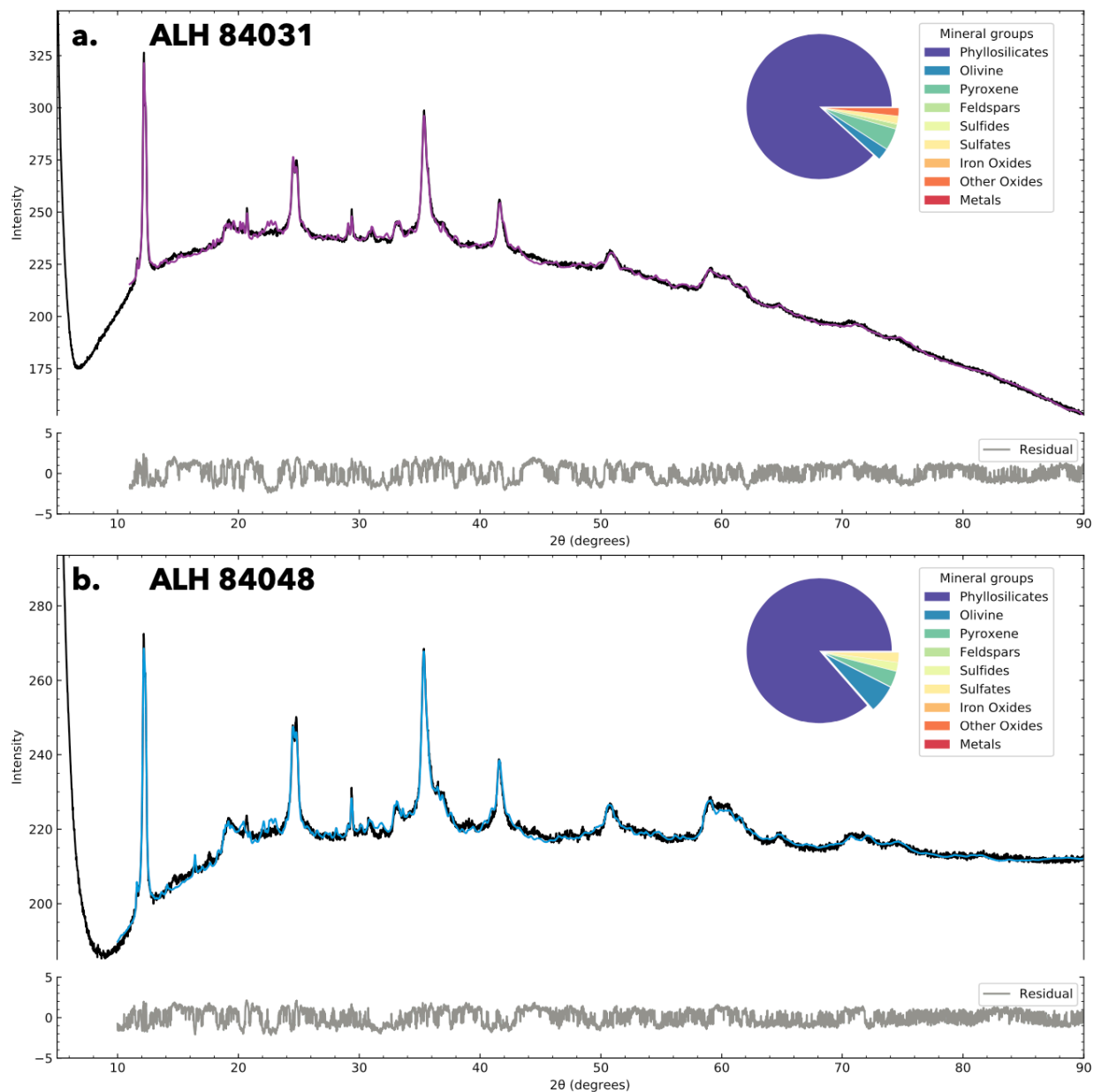
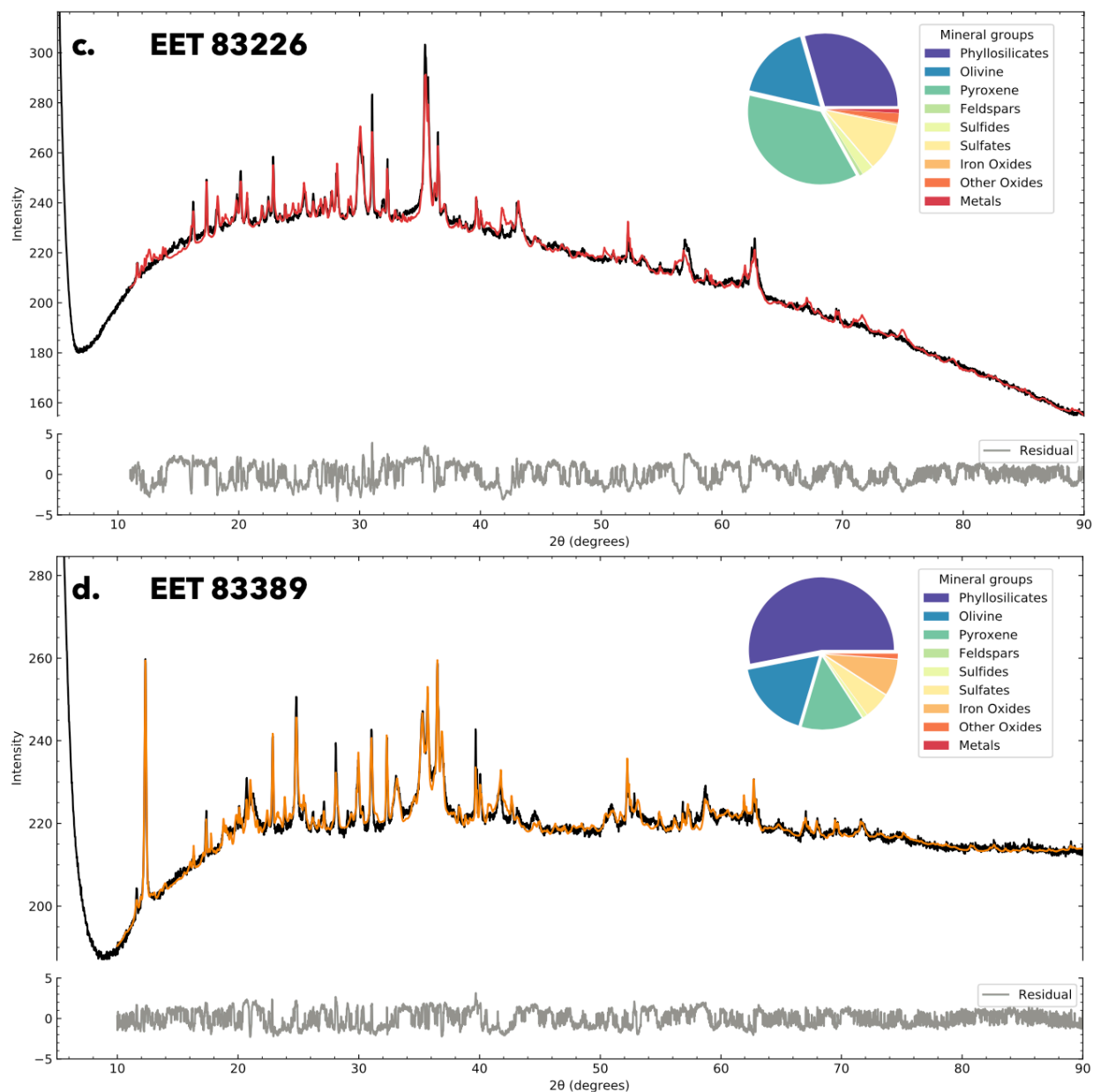


Figure 10: The distribution of 3 μm band minimum positions after resampling measurement spot sizes for meteorites ALH 84031 (a), ALH 84048 (b), EET 83226 (c), EET 83389 (d), MET 00630 (e), and QUE 97077 (f). Measurement spot sizes were resampled by linearly averaging together multiple individual μFTIR spectra spots. The 3 μm absorption band position was then calculated on the averaged spectra representing the resampled spot size. This was then repeated 1000 times for each meteorite to produce the Box-and-Whisker plots shown above. The y-axis labels correspond to the width x length dimensions in microns of the synthetically resampled measurement spot size. X-axis labels correspond to the wavelength position of the 3 μm absorption band minimum position. Colored boxes represent the IQR. Outliers are considered as being $Q1 - 1.5 \times IQR$ or $Q3 + 1.5 \times IQR$. The solid vertical line represents the 3 μm absorption band minimum position calculated from the “bulk” FTIR spectrum.

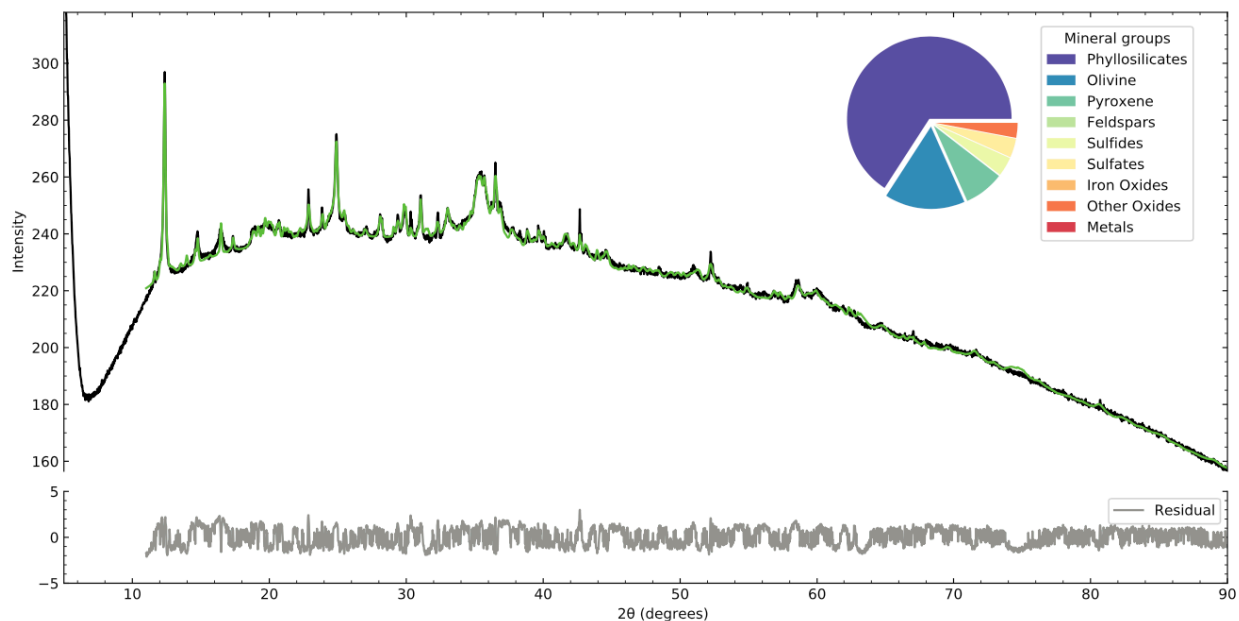
Supporting Information



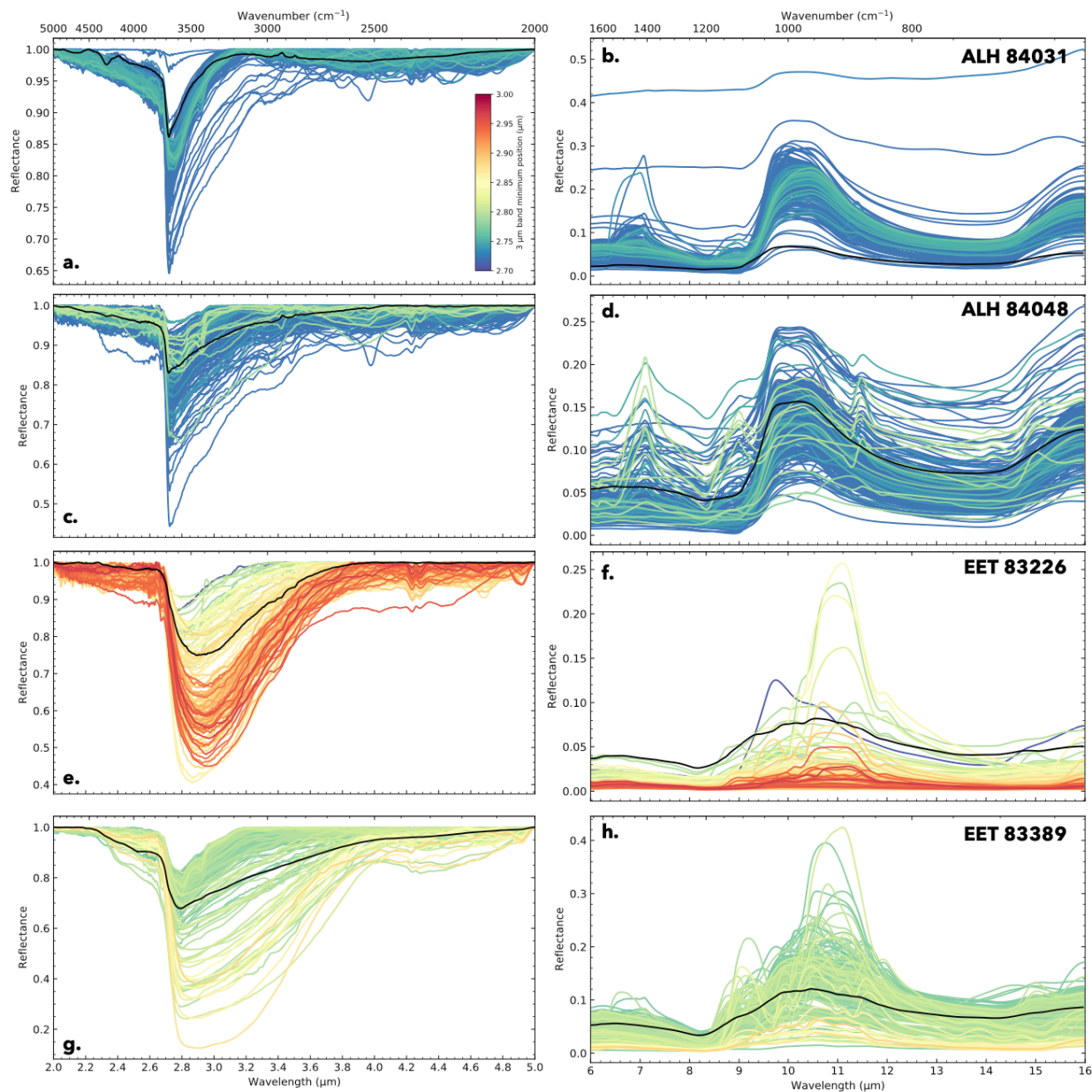
Supplementary Figure 1: The measured XRD pattern and the Rietveld refinement modeled fit are shown for (a.) ALH 84031, (b.) ALH 84048, (c.) EET 83226, (d.) EET 83389, and (e.) QUE 97077 along with bulk mineral abundances determined from the goodness of model fit. Residuals from the difference between the modeled fit and the measured XRD pattern are shown in the bottom subpanels.



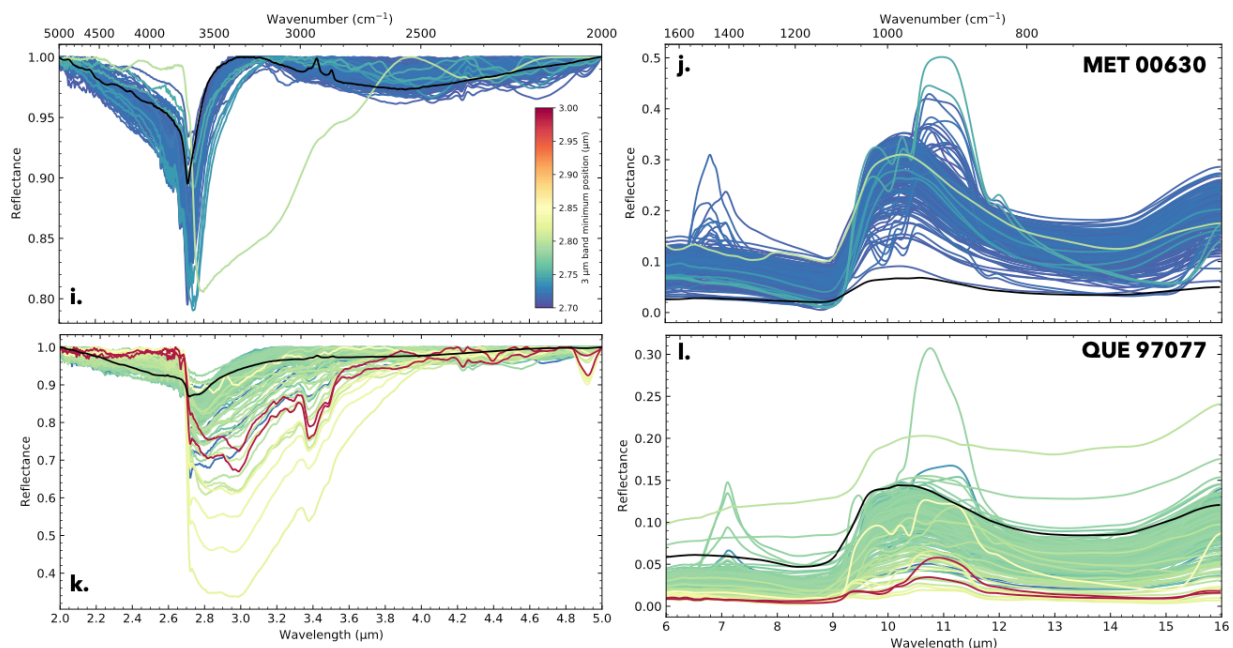
Supplementary Figure 1 (continued): The measured XRD pattern and the Rietveld refinement modeled fit are shown for (a.) ALH 84031, (b.) ALH 84048, (c.) EET 83226, (d.) EET 83389, and (e.) QUE 97077 along with bulk mineral abundances determined from the goodness of model fit. Residuals from the difference between the modeled fit and the measured XRD pattern are shown in the bottom subpanels.



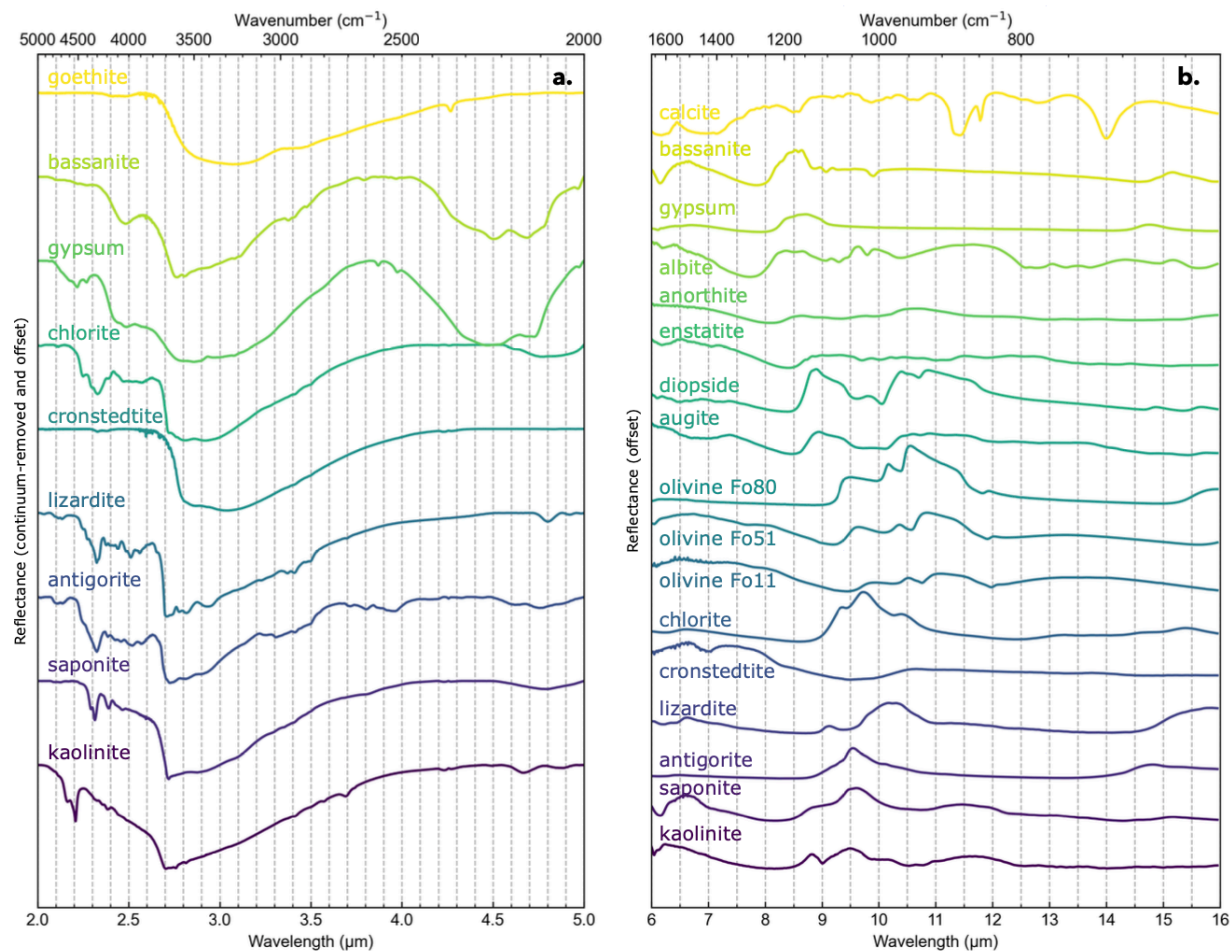
Supplementary Figure 1 (continued): The measured XRD pattern and the Rietveld refinement modeled fit are shown for (a.) ALH 84031, (b.) ALH 84048, (c.) EET 83226, (d.) EET 83389, and (e.) QUE 97077 along with bulk mineral abundances determined from the goodness of model fit. Residuals from the difference between the modeled fit and the measured XRD pattern are shown in the bottom subpanels.



Supplementary Figure 2: All μ FTIR and bulk FTIR spectra collected for meteorites ALH 84031, ALH 84048, EET 83226, EET 83389, MET 00630, and QUE 97077. Subpanels (a.), (c.), (e.), (g.), (i.), and (k.) show the continuum-removed 3 μ m absorption from 2.0 to 5.0 μ m. Subpanels (b.), (d.), (f.), (h.), (j.), and (l.) show the corresponding MIR spectral region from 6.0 to 16 μ m. In all subpanels, the color of each spectrum corresponds to the 3 μ m band minimum position of each spectrum, save for the bulk FTIR spectrum, which is plotted in black.



Supplementary Figure 2 (continued): All μ FTIR and bulk FTIR spectra collected for meteorites ALH 84031, ALH 84048, EET 83226, EET 83389, MET 00630, and QUE 97077. Subpanels (a.), (c.), (e.), (g.), (i.), and (k.) show the continuum-removed 3 μ m absorption from 2.0 to 5.0 μ m. Subpanels (b.), (d.), (f.), (h.), (j.), and (l.) show the corresponding MIR spectral region from 6.0 to 16 μ m. In all subpanels, the color of each spectrum corresponds to the 3 μ m band minimum position of each spectrum, save for the bulk FTIR spectrum, which is plotted in black.



Supplementary Figure 3: Representative spectra of the 3 μm (a.) and mid-IR wavelength region (b.) acquired from the USGS Spectral Library (Kokaly et al., 2017) of compositionally relevant mineral phases commonly found in CM2 chondrites. Included are Fe,Mg-rich phyllosilicates, mafic silicates, and terrestrial alteration products (e.g., goethite and gypsum). All spectra acquired were measured from powdered aliquots of the coarsest size fraction available in the library, which provides a limitation on the usefulness of comparison to the polished whole-rock samples used in this study.

Data S1: Provided in the supporting text is a brief literature review highlighting the mineralogy and petrology of the samples studied here as described by previous investigators.

Chapter 2 | Near- and Mid-Infrared Spectral Diversity in the Aguas Zarcas Carbonaceous Chondrite and Implications for Inferring Aqueous Processes on Primitive Asteroids Using Remote Sensing

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2.1 Abstract

Mighei-like (CM) carbonaceous chondrites are complex brecciated meteorites that exhibit significant chemical, mineralogic, and petrographic diversity both between and within individual samples. As most reflectance spectroscopy studies of carbonaceous chondrites are performed on bulk powders, important questions remain about the true spectral diversity of these complex breccias and the degree to which lab-based meteorite spectra can be reliably related to remotely acquired spectra of primitive asteroids. The Aguas Zarcas meteorite is a unique CM chondrite in that it has been found to exhibit at least five chemically and isotopically distinct lithologies that are all associated with a single Fall event (Kerraouch et al., 2021, 2022). Here we describe a coordinated petrographic and

spectroscopic study to further investigate the thermochemical and collisional history of the Aguas Zarcas parent body and to better understand how to interpret remotely acquired spectra of primitive asteroids. Four intact sections of the Aguas Zarcas meteorite, which together represent at least three to four distinct lithologies, were analyzed using microscope FTIR (μ FTIR) spectroscopy and electron probe microanalysis (EPMA) elemental mapping. Our study found significant variations in spectral features, particularly in the mid-infrared (MIR) wavelength region, that can be linked to petrographic diversity between lithologies. The relative abundance of matrix ranges from 55 vol.% in a metal-rich lithology to ~90 vol.% in a CM1/2 lithology. The relative abundance of matrix phyllosilicates and pyroxene appears to have the strongest influence on the shape, position, and strength of MIR spectral features. Linear spectral unmixing models as a method for compositional interpretation showed varying accuracy when compared to EPMA-based estimates, with integrated μ FTIR spectral maps showing better results compared to unmixing of bulk (larger spot size) FTIR spectra. A notable discovery in two sections of the Aguas Zarcas meteorite was the presence of carbonate veins along the boundary of chemically and petrographically separate lithologies, which provide important constraints on the nature and timing of pre- and post-brecciation aqueous alteration.

2.2 Introduction

Integrated petrographic and spectroscopic studies of carbonaceous (C) chondrites, commonly assumed to be derived from C-complex asteroids, offer a framework based on

direct compositional information that can aid in interpreting remotely acquired spectra of primitive asteroids. Many C chondrites, particularly those in the CM group, are complex breccias characterized by a diverse range of components at various spatial scales. These components, which include compositionally and texturally distinct lithologies, offer critical insights into the thermochemical and collisional evolution of their parent bodies (Bischoff et al., 2006). Recent petrologic analyses by Lentfort et al., (2021) demonstrated that any single CM chondrite can exhibit several lithologies that span a range of petrologic types (as defined by Rubin et al., 2007, hereafter referred to as the Rubin scale). This indicates the parent bodies of these chondrites may not have experienced uniform processing. Instead, they likely contained regions that experienced varying degrees and/or conditions of aqueous alteration. When compared with the results of spectral reflectance studies by Takir et al. (2013, 2015, 2019) and others, it is implied that these chemically distinct lithologies should exhibit distinct spectral signatures. However, despite these known complexities, most spectroscopic studies of meteorites have only been performed on bulk powders. This preparation method homogenizes the samples, and thereby erasing important petrologic context and spatial heterogeneity. Consequently, many questions remain about the true diversity of spectral properties for C chondrites and, by extension, how to accurately link lab-based meteorite spectra to remotely acquired spectra of asteroids, including complex carbonaceous rubble piles such as Ryugu and Bennu (Kitazato et al., 2019; Hamilton et al., 2019).

To better understand these issues, we present coordinated petrographic and spectroscopic analyses of several intact (non-powdered) samples of the Aguas Zarcas

meteorite. This meteorite fall, with a total collected mass exceeding 27 kg (Gattacceca et al., 2020), has been classified within the CM group of carbonaceous chondrites. The diverse Aguas Zarcas meteorite showcases the extent to which a single carbonaceous meteorite can exhibit brecciation and lithologic heterogeneity. Recent studies by Kerraouch et al., (2021, 2022) has shown that this meteorite exhibits at least five petrographically distinct lithologies. Unlike the CM chondrites in general, which are complex and compositionally diverse breccias (Lentfort et al., 2021), the samples of the Aguas Zarcas meteorite studied here are all associated with the same Fall. This allows for an in-depth examination of the compositional, petrographic, and spectroscopic heterogeneity present within a single meteorite parent body. While CM chondrites are generally assumed to share some genetic heritage, they are not all associated with the same delivery event, making it difficult to determine a priori precisely how many parent bodies they may represent. In contrast, the Aguas Zarcas meteorite has a more direct application to our understanding of how spectroscopic signatures of different lithologies may be convolved when analyzing disk averaged or spatially resolved spectra of individual asteroids, including rubble piles such as Ryugu and Bennu that host brecciated materials.

In this study, we present elemental and spectral reflectance data for several lithologies in the Aguas Zarcas meteorite and discuss their range of petrographic and mineralogical attributes. Our primary objective is to assess how the compositional and lithologic heterogeneity of this meteorite is (or is not) manifest in spectra acquired at different spatial scales and, by extension, possible parent body scales. We seek to address the following questions: (1) Do the different lithologies of the Aguas Zarcas meteorite have

distinct spectral properties? For brecciated samples, how does the average spectrum of each lithology compare to the bulk spectrum of a given sample? (2) Can the bulk spectrum of a heterogeneous sample be modeled via simple linear “checkerboard” mixing using the spectral endmembers of the individual components? Or are bulk sample spectra strongly biased towards one lithology? (3) Do the position/shape/strength of the 3 μm OH/H₂O absorption feature vary with increasing matrix (e.g., phyllosilicate) abundance and/or matrix composition in a systematic way? (4) How might these results affect our interpretations of remotely acquired spectra of primitive C-type asteroids? Might some components be systematically over- or under-estimated based on spectral interpretations? The coordinated petrographic-spectroscopic study of the Aguas Zarcas meteorite presented here is a first step in understanding the nature of how brecciation in C chondrites relates to spectral properties at near/mid-infrared wavelengths. These results provide a point of comparison for ongoing and future analyses of samples returned from near-Earth asteroids Ryugu and Bennu (Watanabe et al., 2019; Lauretta et al., 2019; Nakamura et al., 2022).

2.3 Methods

2.3.1 Analytical Methods

Four samples from the Aguas Zarcas meteorite were cut, mounted in epoxy, and polished. One sample, provided by Imene Kerraouch and prepared at the Institute für Planetologie at the University of Münster in Germany was a fresh-cut and newly analyzed section (UM-1). Two other samples (PL19149 and PL19145), also prepared that the

University of Muenster, were previously analyzed by Kerraouch et al. (2021, 2022) and are hereafter referred to as UM-2 and UM-3, respectively. Another sample (Field-1), provided by Philipp Heck at the Field Museum in Chicago, was analyzed by Villalon et al., (2020). Rasterized elemental oxide maps of the major elements Mg, Fe, Si, S, Ca, Al, P, Ni, and Na were acquired via a Cameca electron microprobe at Brown University set to 15 kV running at 50 nA. Step sizes between measurement points were 5 μm and the dwell time for each measurement was set to 70 ms. Total elemental counts typically summed to <100 wt.% (save for occurrences of Fe,Ni-metal, which summed to >100 wt.%) because of the significant porosity of these samples relative to the mineral endmembers to which the microprobe spectrometers were calibrated. False-color overview images based on the EPMA data are presented in Figures 1 and 2.

Rasterized spectral maps with 70–140 μm spot sizes were acquired via a Bruker LUMOS Microscope FTIR (μFTIR) equipped with an MCT detector. Bulk spectra with spot sizes on the order of the entire samples (see Figure 1 for sizes) were collected on a Nicolet Nexus 870 benchtop FTIR equipped with a Pike AutoDiff reflectance accessory. Spectral resolution for both spectral datasets was 4 cm^{-1} and the spectral range examined in this study is 1.7–16 μm . All spectra were acquired relative to a diffuse gold reflectance standard. In this paper we refer to the ~1.7 - 4 μm wavelength range as the near-IR (NIR) and longer wavelengths as the mid-IR (MIR) regions.

2.3.2 Mineral and component quantification

The apparent areal abundances of distinct phases and components were quantified using nine-element EPMA maps. Endmember phases were first identified based on their distinct elemental compositions. Using the IDL/ENVI image analysis software, regions of interest (ROIs) were defined for each major endmember phase (e.g., chondrule olivine, matrix phyllosilicates, sulfides, etc.). These ROIs were then used as inputs for a Maximum Likelihood supervised classification algorithm with the probability threshold set to 0.10. Given this parameter, the algorithm classifies every pixel within the selected region as either one of the classes (belonging to one of the endmember input ROIs) or unclassified. All nine elements, unnormalized, were utilized for classification.

In general, 80–90% of all pixels were able to be classified as one of 5–9 distinct compositional endmembers for the four samples studied here. It is expected that ~10–20% of the pixels may be marked “unclassified” due to the spatial resolution of the EPMA data (~5–6 μm) relative to the finer scale of true compositional heterogeneity in the samples. The unclassified pixels were either of mixed composition (due to overlapping phases) that did not fit within any one endmember composition or were minor phases that were not accounted for as endmember inputs. The relative abundance of all classified pixels was normalized to produce percent areal abundance values for each phase that sum to 100 percent for each sample.

2.3.3 Spectral Analysis and Modeling

Determining spectral endmembers

Due to the dimensions of the spectral map regions, many reflectance spectra were acquired over the epoxy in which the samples were mounted. To identify and isolate pixels dominated by epoxy, all spectra were passed through a KMeans clustering algorithm set to identify a variable number of clusters. Epoxy spectra were readily identified as a distinct cluster by this process, but some regions of the meteorite that had naturally low reflectance were also initially grouped into this cluster. These were successfully separated by allowing the algorithm to identify more clusters, but at the expense of retaining some pixels at the boundaries of the samples that contain some epoxy. We erred on a more conservative approach and sacrificed approximately 5–15 pixels (spectra) per map in order to ensure all spectra were epoxy-free. We then removed the epoxy-contaminated spectra from the dataset. Table 1 reports the total number of remaining spectra analyzed as well as the size of each spectral footprint (pixel) for each map.

The KMeans clustering algorithm was then rerun on the epoxy-free spectral dataset to identify possible spectral endmembers, with the hope that such spectral endmembers would correspond to distinct phases/compositions. To find the optimum number of clusters ($n_clusters$), we ran an optimization routine that calculated the silhouette scores and inertial value scores for $n_cluster$ values that ranged from 2 to 30. Increasing the number of clusters produced additional groups with fewer members that appeared to capture distinct spectral endmembers, but the differences between some endmembers were marginal and cluster membership was often on the order of $< 1\%$ of the total number of all pixels.

Based on these results, the KMeans clustering algorithm was ultimately run on the epoxy-free spectral maps using an $n_clusters$ value of 8–12 to identify a somewhat

parsimonious but relatively distinct set of spectral endmembers within each spectral map. In all cases, at least half of the spectral endmembers identified by this method were not independent but could instead be described as linear mixtures of other clusters. This is a natural outcome of our spectral mapping analysis, where most pixels, being on the order of 70–140 μm in size, typically span two or three components of the meteorite (e.g., matrix and chondrule). Compared with the EPMA data, the result is a smaller number of pixels that cover a single phase/component of the meteorite. Nevertheless, several of the returned clusters did capture distinct and independent spectral endmembers, and these subsets were identified as the final set of endmember spectra that best represent each sample, and these were used as inputs in the spectral models discussed below. The correlation between these independent spectral endmembers and distinct phases/components were also verified by comparing the final spectral clustering maps with the corresponding EPMA elemental maps for each sample.

Spectral modeling: component endmembers

To determine the total percent contribution of each spectral endmember within a full spectral map for a given sample, every μFTIR spectrum (pixel) was modeled as a linear combination of the spectral endmembers identified for that sample. The spectral endmembers and the spectrum to be modeled were used as inputs into Scipy's linear least-square solver (`scipy.optimize.lsqr_linear`). Here, $\mathbf{A}$ is an m -by- n matrix of the spectral endmembers and $\mathbf{b}$ is the target vector of the spectrum to be modeled, and the solver seeks to minimize $\|\mathbf{Ax} - \mathbf{b}\|_2$, where $\mathbf{x}$ is a vector containing the weights corresponding to each spectrum

which is subject to the lower and upper bounds: $lower\ bound \leq x \leq upper\ bound$. In this case, the lower bounds were set to 0 and the upper bounds were set as positive infinity. This routine returns the vector $\mathbf{x}$, which are the numerical weights corresponding to each endmember spectrum. These weights were then normalized to 100 for each pixel such that they describe the percent spectral contribution of each endmember used to model each target (pixel) spectrum. We stress that these results represent fractions of the *spectral* contribution of each endmember to the modeled spectrum, which may or may not be similar to the actual volume or mass fraction of the mineral phases in each pixel or for the overall meteorite. This distinction is relevant to the discussion below, where phase abundances from the spectral models are compared with those from the EPMA maps. The modeled spectra for individual pixels were ultimately very similar to the measured spectra (i.e., spectral fits had low RMSE values). As such, averaging all of the modeled μ FTIR spectra for a given section yielded a spectrum very similar to a simple average of all the directly measured μ FTIR spectra for that section.

The percent spectral contribution of each endmember for each pixel was then summed and divided by the total number of pixels in each map, thus yielding an estimate of the total percent contribution of each spectral endmember for each full sample. These results – which are based on the spatially resolved μ FTIR maps – were taken to represent the ‘actual’ percent spectral contribution of each endmember in each sample and were compared with phase abundances from EPMA maps. These ‘actual’ percent spectral contribution values were also used as weighting coefficients for a forward linear spectral model that used the corresponding endmember spectra as inputs. For each sample, the

spectrum produced from the forward model was compared with the measured bulk FTIR spectrum. In reality, although this final spectrum is from a forward model, the input weighting coefficients result from the inverse model of each μ FTIR spectrum, as described above. Therefore, we refer to these versions of bulk modeled spectra as “ μ FTIR inverse models”. They are compared with the directly measured bulk FTIR spectra, which represent a measurement spot size on the order of several millimeters, spanning the bulk of each sample. Each directly measured bulk FTIR spectrum was itself modeled inversely (linear unmixing) using the same μ FTIR spectral endmembers as inputs and solving for spectral abundances (weighting coefficients). We refer to these spectral fits and associated modeled spectral abundances as “FTIR inverse model” results. These are compared with the pixel-level spectral abundances and the EPMA-derived abundances for each component.

Spectral modeling: lithologic endmembers

For the meteorites that showed clear evidence for brecciation at scales larger than that of the individual components, we also modeled the bulk FTIR spectra as percent spectral contribution of each lithology. This was done to assess the degree to which a given lithology – rather than individual components – may or may not contribute to the bulk spectral characteristics. In this scenario, the average spectrum for each lithology was calculated by averaging together all spectra (pixels) belonging to each lithology. The ‘actual’ percent spectral contribution of each lithology was determined to be equal to the areal percentage of each lithology, which was determined by dividing the number of pixels belonging to each lithology over the total number of pixels in the μ FTIR map. This areal

contribution was assumed to be related and proportional to the volumetric contribution sampled by the bulk FTIR measurement. These lithologic spectral endmembers (averages) were then used in an identical way as described above to linearly unmix the bulk reflectance spectrum to determine the ‘modeled’ percent spectral contribution of each lithology.

2.4 Results

2.4.1 Petrography and elemental analysis

The four Aguas Zarcas sections analyzed here are all regolith breccias that span a wide range of petrographic properties and appear to represent at least three or possibly four distinct lithologies (Figure 1 and Figure 2). Two of the sections analyzed (UM-2 and UM-3) were impact breccias consisting of two distinct lithologies demarcated by clear chemical and petrographic boundaries. The other two sections appear to consist of a single (but differing) lithology. The sections UM-2 and UM-3 were previously classified by Kerraouch et al., (2021, 2022) as hosting both CM1/2 and CM-like lithologies, based on petrographic, mineralogical, and isotopic properties. In this same scheme, we classify the UM-1 section as belonging to the Met-1 lithology, based on its relatively high abundance of metal, low matrix fraction, large chondrule abundance, and the presence of accretionary rims. We also tentatively classify the Field-1 section as belonging to the CM1/2 lithology based on its relatively high abundance of matrix, its relatively lower abundance of chondrules, the presence of accretionary rims, and its notably low metal abundance. However, the chemistry of its matrix appears notably more S-rich than the other CM1/2 lithologies studied

here (Supplementary Figure 1). Table 2 provides a detailed overview of the relative abundance of matrix, chondrules, and major mineral groups for each lithology. For a more detailed review of the chemistry, mineralogy, and isotopic characteristics of these lithologies, we refer the reader to Kerraouch et al., (2021, 2022). In the proceeding text we summarize the results and highlight major findings of the sections studied here.

Aguas Zarcas – UM-1 (Met-1)

The Met-1 lithology of the Aguas Zarcas meteorite was first identified as a unique lithology by Kerraouch et al. (2021) who reported the anomalously high abundance of Fe-Ni metal given its classification as a CM chondrite. The UM-1 section, corresponding to the Met-1 lithology and analyzed in this study, contains approximately 2 vol.% Fe-Ni metal, predominantly as kamacite. This metal is distributed as metallic blebs both throughout the matrix and within some chondrules, with sizes ranging from a few micrometers to ~200 μm . Some pre-terrestrial alteration is observed for several of these grains. Pentlandite and pyrrhotite are the other dominant opaque phases and make up approximately 0.5 vol.% of the sample. Chondrules make up approximately 26 vol.% of the sample and are predominantly composed of variable amounts of forsterite, enstatite, and a lesser abundant phase with a composition consistent with diopside. Fayalite-rich and zoned olivine chondrules and lithic fragments are also present in lesser amounts, and an altered Fe-rich barred olivine chondrule is also present. Matrix and fine-grained rims make up ~69 vol.% of the sample. Fine-grained rims are present around many of the chondrules and other lithic fragments and appear to be consistent with an Fe-bearing but Mg-rich phyllosilicate. The

matrix appears to be composed of this same phase as well as a more Fe- and S-rich component that is chemically consistent with cronstedtite-tochilinite-intergrowths (TCIs) Supplementary Figure 1. Using the most Mg-rich and Fe-rich matrix components as endmembers for our supervised classification algorithm, we attempted to quantify the ratio of Mg-phylllosilicate to Fe-phylllosilicate ($\text{MgO} / (\text{MgO} + \text{FeO})$) in the matrix and calculated a value of 0.727. This should be interpreted as only a rough estimate, as most matrix crystallites are much smaller than the electron beam used to generate our EPMA maps. Consequently, the Mg, Fe, and Si chemistries of these phyllosilicates lie along a continuum ranging from Mg-rich to Fe-rich. This sample also has the highest abundance of CAls (~1.6 vol.%) and carbonates (0.88 vol.%; Figure 2) measured across all Aguas Zarcas samples and lithologies studied here.

Figure 3 presents an $\text{MgO-FeO-SiO}_2+\text{Al}_2\text{O}_3$ ternary diagram that shows the compositional variation of the phases discussed here relative to measured and ideal mineral standards. For these data to be projected in ternary space, the oxide wt.% values used for the vertices were first normalized to sum to 100 wt.%. However, the classification of the pixels was based on the unnormalized, full nine-element EPMA maps. The normalization results in an apparent overlap in ternary space between the Mg-rich and Fe-rich phyllosilicate phases. Though some pixels may appear to have overlapping $\text{MgO-FeO-SiO}_2 + \text{Al}_2\text{O}_3$ chemistries, they often have distinct differences in other elements and in oxide totals (which can be linked to differences in microporosity). As an example, a major distinction in the “Mg-rich” and “Fe-rich” matrix phyllosilicate phases are increased sulfur abundances in the latter, consistent with the interpretation of TCIs and possibly sub-micron pyrrhotite

grains for this phase (e.g., Supplementary Figure 1). These aspects also apply to the other studied sections that appear to have overlapping phyllosilicate chemistries in the ternary plots (e.g., the Field-1 sample).

Aguas Zarcas – Field-1

The Aguas Zarcas Field-1 sample has a much higher volumetric abundance of matrix (~88 vol.%) compared to its abundance of chondrules and other lithic fragments (~11 vol.%). Chondrules and lithic fragments are predominantly forsteritic olivine with lesser amounts of enstatite. Sizes vary from several tens of micrometers to ~700 μm . Ca-rich carbonates and rare sulfide grains make up <1 vol.% of the sample. The matrix appears to be composed of two fine-grained phases consistent with an Mg-rich and Fe-rich phyllosilicate. The Fe-rich phyllosilicate is the most abundant matrix phase and appears most consistent with TCI-like compositions. Fine-grained-rims and fine-grained-fragments (FGFs) are exclusively composed of the more Mg-rich variety. Many FGFs appear to be edges of fine-grained-rims that were isolated from the sectioning of the sample and now show up as distinct fragment due to the 2D view of the sample. The ratio of Mg-phyllosilicate to Fe-phyllosilicate ($\text{MgO} / (\text{MgO} + \text{FeO})$) in the matrix is ~0.48. The two phases do not appear to be randomly distributed throughout the matrix, but rather the Fe-rich phase appears to exhibit a sponge-like texture. Fe-Ni metal is absent and CAI-fragments (several micrometers in size) are rare. The high abundance of matrix and presence of FGRs and chondrules suggests a CM1/2 classification in the scheme proposed by Kerraouch et al., (2022). However, the matrix appears to be more Fe- and S-rich than the other CM1/2

lithologies studied here, which may constitute its distinction as a separate lithology. Nevertheless, for consistency with previous conventions we classify it as a CM1/2 lithology.

Aguas Zarcas – UM-2 (PL19149)

The UM-2 section shows evidence for genomict brecciation, where two very clear lithologies are present and demarcated both chemically and petrographically. The first lithology (UM-2 CM1/2, Lithology 1 in Figure 1) exhibits 5.6 vol.% chondrules present as lithic clasts that are composed entirely of forsteritic olivine. Sulfides including pentlandite and pyrrhotite are distributed throughout the matrix and occur at 1.3 vol.%. Ca-rich carbonate grains are abundant and scattered throughout the matrix at 0.7 vol.% (Figure 2). CAls are present but rare at only ~0.4 vol.%. The matrix compromises 92.1 vol.% of this lithology and is composed of clearly distinguishable Mg-rich and Fe-rich phyllosilicate endmembers consistent with mixed composition serpentine and TCI. The Mg-serpentine-like phase is among the most Mg-rich phyllosilicate phases present in the samples studied here and is the dominant matrix component, with a Mg- to Fe-phyllosilicate ratio of 0.51. Fine-grained-rims are absent in this lithology. The high abundance of matrix of this lithology is consistent with the C1 classification of Kerraouch et al., (2022) but the presence of minor amounts of chondrule fragments, carbonates, and CAls rules this out. Instead, this lithology is classified as CM1/2.

The second lithology (UM-2 CM, Lithology 2 in Figure 1) has a much higher abundance of chondrules and lithic fragments (24.5 vol.%) predominantly composed of forsteritic olivine and somewhat lesser amounts of low-Ca pyroxene. Abundant sulfides and

a few metal grains are present in the matrix at levels of 3.9 vol.% with a few co-occurring with chondrule fragments. The matrix makes up 70.9 vol.% of this lithology and is composed of equal amounts of an Mg-rich and Fe-rich phyllosilicate phase. The compositions of these two phyllosilicate endmembers are markedly more Fe-rich than those in the CM1/2 Lithology (Figure 3). Carbonate grains up to several tens of micrometers in size are also present at 0.46 vol.%. The petrographic features of Lithology 2 appear to be most consistent with the CM classification given by Kerraouch et al., (2022), though the sulfide abundances are unusually high.

Carbonate veining is a defining feature of the UM-2 sample. Nearly pure calcite that has a composition similar to the carbonate fragments found throughout the rest of the sample appears to have precipitated along fractures that demarcate the boundary between the two lithologies (Figure 2b). This suggests aqueous alteration and precipitation of carbonate may have post-dated the brecciation event that brought these two lithologies together, as discussed in more detail below.

Aguas Zarcas – UM-3 (PL19145)

The UM-3 (pl19145) section of Aguas Zarcas is also a genomict breccia consisting of at least two distinct lithologies (Figure 1). The dominant lithology, Lithology 1 classified as CM1/2 (Kerraouch et al., 2022; previously as C1/2 in Kerraouch et al., 2021), contains abundant matrix (83.5 vol.%) dominated by an Fe-rich phase and a second S- and Mg-enriched phase. The increased sulfur in the latter may indicate the presence of tochilinite, TCIs, alongside Mg-rich phyllosilicates. For simplicity, we refer to these various matrix

phases collectively as “phyllosilicates”, while recognizing that strictly speaking the S and some of the Mg/Fe may not be in a phyllosilicate mineral. The average Mg# of the “phyllosilicate” matrix material is 0.44. Relic chondrule olivine and pyroxene are present (15 vol.%) with many chondrules exhibiting textures of progressive aqueous alteration. A large (~650 μm diameter) pseudomorphic chondrule appears to have been completely altered, save for a small relic olivine grain in the center. Relic enstatite grains also appear to be associated with another pseudomorphic chondrule that has been progressively altered. Sulfide grains several tens of micrometers in size are distributed throughout the matrix (0.8 vol.%) with rare tiny blebs of metal. Ca-rich carbonate grains are abundant (0.7 vol.%) throughout the matrix and are often embedded within and around CAI-diopside-like clasts.

The second lithology is designated as a CM-like lithology (Lithology 2), though its chemistry is somewhat more complicated than the previous sections and lithologies studied here. It has the lowest abundance of matrix (55.1 vol.%) that appears to be dominated entirely by an Fe-rich phyllosilicate phase consistent with TCIs (Figure 3). Mg-phyllosilicates, if present, are much less common in this lithology compared to all others. The entire lithology also appears to be enriched in the mobile elements Na and S. No clearly defined chondrules are present, though this lithology has the highest abundance of lithic fragments of olivine and pyroxene (38.7 vol.%). High-Ca pyroxene is also abundant, as are sulfides (~6 vol.%). Carbonate grains are present but in lower relative proportion (0.24 vol.%). Like the UM-2 section, Ca-rich carbonate veining is also present within this sample. A single carbonate vein ~250 μm long and a few tens of micrometers wide demarcates part of the boundary separating one lithology from the other (Figure 2b). This suggests the

aqueous alteration event that led to carbonate precipitation post-dated the brecciation event that joined these two lithologies together.

2.4.2 Overview of μ FTIR and 'bulk' FTIR NIR and MIR Reflectance Spectra

For a first order comparison between the overall spectral signatures of these sections and their dominant lithologies, we present in Figure 4 the bulk FTIR reflectance spectra in both the $\sim 3\ \mu\text{m}$ (NIR) and MIR wavelength regions. Reflectance spectra of the individual lithologies of UM-2 and UM-3 are also presented and were generated by averaging all of the μ FTIR spectra acquired for each lithology, as described above.

The strength, shape, and reflectance minimum wavelength position of the $3\ \mu\text{m}$ absorption feature, which is a convolution of the OH stretch and H_2O symmetric and asymmetric stretching and overtone bending vibrational modes, exhibits a moderate amount of variation between samples. The wavelength positions of the band minimum for this feature varies from $2.708\ \mu\text{m}$ for the Field-1 section to $2.720\ \mu\text{m}$ for the CM lithologies in the UM-2 and UM-3 sections. All sections, save for UM-1 (Met-1 lithology), also appear to have a superposed absorption centered between $2.75\text{--}2.78\ \mu\text{m}$. This gives rise to a wider and more convex shape to the long wavelength edge of the $3\ \mu\text{m}$ feature, and it is consistent with the presence of H_2O -bearing phases such as smectites. The sharper, narrower feature seen in the UM-1 spectrum may be due to either a lower abundance of Fe-rich phyllosilicate or a lack of other H_2O -bearing phases in this sample. All samples also exhibit absorptions of varying intensities at ~ 3.36 and $3.40\ \mu\text{m}$ ascribed to aliphatic organic compounds (e.g.,

Kaplan et al., 2019). Though carbonates also exhibit diagnostic features at these wavelengths (Bishop et al., 2021), the lack of additional carbonate features in the bulk spectra at 3.8–4 μm and 6.4 μm makes their attribution to these shorter wavelength features unlikely.

The MIR FTIR spectra of the bulk samples and lithologies exhibit two to three distinct spectral types that vary as an expression of the SiO stretching mode and metal-OH bending mode. Spectra for the Field-1 section, UM-2 bulk, UM-2 Lith 1 (CM1/2), UM-3 bulk, and UM-3 Lith 1 (CM1/2) can be characterized as exhibiting a typical phyllosilicate-like feature with two distinct reflectance peaks at ~ 9.8 and ~ 10.2 μm . This is consistent with the EPMA data that indicate a high matrix (phyllosilicate) abundance in these lithologies. In contrast, average spectra of the Met-1 lithology (UM-1 section) and CM lithology (Lithology 2) of the UM-2 section show a broader feature with five to seven reflectance peaks positioned at approximately 9.92, 10.19, 10.46, 10.81, 11.06, 11.46, and 11.95 μm . These broad, multi-peak features are consistent with features typical of pyroxene and olivine. The spectrum for the CM lithology (Lithology 2) of the UM-3 section is similar but with a much more pronounced reflectance peak at 11.45 μm . These spectral features are consistent with the higher abundance of primary (unaltered) silicates in these lithologies as shown by the EPMA data.

2.4.3 Modeling ‘Bulk’ Spectral Properties & Comparison to EPMA Mineralogy

As noted above, several hundred IR reflectance spectra were acquired for each rasterized spectral map of the samples. Measurement spot sizes were on the order of 70–

140 μm , which in most cases allows the identification of at least some spectrally pure endmembers throughout each section. However, at this scale the majority of spectra for each sample are more consistent with a combination of two or more of these spectral endmembers (e.g., olivine and phyllosilicate). This is a consequence of the fine scale heterogeneity in the samples and multiple phases commonly being present within any given μFTIR spot. Nonetheless, it was possible to extract examples of what appear to be pure spectral endmembers associated with the major phases (i.e., phyllosilicate matrix, olivine, etc.). The MIR wavelength region was found to have the most spectral diversity and exhibits the most diagnostic features associated with each phase. As a consequence, the MIR range was used to identify the spectral endmembers for all sections. These endmember spectra were then used to examine variations in the corresponding 3 μm ‘hydration’ region.

The spectral endmembers for each sample are presented in panels a and b of Figures 5-8 for the different wavelength regions, along with modeled spectral fits in panel c. As described in the Methods section, the μFTIR spectral endmembers were used as inputs to the pixel-scale linear unmixing, and the resulting spatial maps of the spectral contribution of each endmember are presented in Figures 9-12 for each sample. A representative RMSE map showing the goodness of spectral fit is presented in Supplemental Figure 2. As described above, the individual spectral contributions for each pixel were combined to produce an estimate of the total spectral abundance of each of the phases for each sample as a whole. These μFTIR inverse model estimates of spectral abundance are presented in panel d in Figures 5-8 and were used as the weighting coefficients to model the bulk spectral properties. The same spectral endmembers were used to inversely model the bulk FTIR

spectrum. The resulting spectral abundances from those FTIR inverse models are also presented in panel c of Figures 5-8, alongside the modal abundances derived from the EPMA elemental maps. We now present spectral modeling results for each section.

UM-1(Met-1)

The UM-1 section, corresponding to the Met-1 lithology, exhibits at least four distinct spectral endmembers in the MIR that are associated with Fe,Ni-metal blebs, chondrule olivine (forsterite), chondrule pyroxene (enstatite), and matrix phyllosilicates (**Figure 5a-b**). Two compositionally distinct matrix phyllosilicate endmembers, an Mg-rich and Fe-rich phase, were identified in the elemental maps but varied on spatial scales of only a few tens of micrometers. Because of the 70 μm spot size of each μFTIR spectrum for this sample, obtaining a pure spectrum of either phase was untenable. As a result, the μFTIR matrix phyllosilicate spectrum is likely an average of these chemically distinct phases.

The endmember matrix phyllosilicate spectrum exhibits a broad reflectance peak in the MIR roughly centered near $\sim 10\ \mu\text{m}$, with two weaker peaks superimposed at $\sim 9.92\ \mu\text{m}$ and $10.19\ \mu\text{m}$ and a weak, narrow feature near $\sim 11.44\ \mu\text{m}$. The latter seems to align well with a weak feature seen in the bulk FTIR reflectance spectrum of this sample, and this may be due to pyroxene. In the $3\ \mu\text{m}$ region we observe a deep and broad absorption centered near $2.72\ \mu\text{m}$ with a broad shoulder centered near $\sim 2.9\ \mu\text{m}$. The position of the band minimum is most consistent with an Mg-rich serpentine-like phase. However, the roughly 10 nm difference in the position of the band minimum in the matrix phyllosilicate spectrum

compared to the band minimum observed in the bulk spectrum would place these two spectra into separate groups if using the framework of Takir et al., (2013).

The reflectance spectrum associated with Fe,Ni-metal in the MIR region is bright (reflectance of ~90%), relatively flat, and featureless. In the 3 μm region (2.5–4.0 μm) this spectrum is also featureless but exhibits a strong red slope, rising from about 10% to 16% reflectance over this wavelength region.

Forsterite was the most abundant olivine phase present in this section, with some lithic fragments being several hundreds of micrometers wide. The MIR spectrum associated with this phase produced a well-defined SiO-stretch feature characteristic of Mg-rich olivine (Hamilton, 2010). A sharp and well-defined reflectance peak is centered near 10.75 μm with smaller features superimposed at 10.18 μm and 11.96 μm . A strong reflectance peak is also present at 9.48 μm . Of these, only the minor feature at 10.18 μm appears to align with one of the features in the bulk spectrum. In the 3 μm region, the olivine spectral endmember exhibits a very weak OH absorption feature centered near ~2.73 μm .

Low-Ca pyroxene was another dominant phase observed in the elemental maps, and the MIR spectrum of this phase includes a broad multi-peak SiO vibration feature. Reflectance peaks are observed at ~9.24, 9.90, 10.48, 10.82, 11.10, and 11.54 μm . The wavelength positions of these peaks line up extremely well with the various weak features observed in the bulk spectrum. Similar to forsterite, in the 3 μm wavelength region we observe a very weak absorption centered near 2.73 μm . This feature does not match the hydration absorption in the bulk FTIR spectrum, which is centered near 2.71 μm .

In terms of spectral fit, there is generally excellent agreement between the FTIR inverse and measured bulk FTIR spectrum (Figure 5c). The μ FTIR-modeled spectrum also shows some agreement with the bulk FTIR spectrum in regard to overall shape and wavelength position of various MIR features, with the exception that the position of the reflectance maximum is shifted to longer wavelengths and the reflectance level is ~5% lower. The latter is because some of the input μ FTIR spectral endmembers are generally darker than the bulk FTIR spectrum, an attribute that is accounted for in the inverse FTIR model but that cannot be accommodated in the μ FTIR model (because spectral abundances are pre-defined).

In general, the pixel-scale μ FTIR spectral modeling results (Figure 5d) are consistent with the elemental maps in that metal, olivine, pyroxene, and matrix/phylllosilicate appear to be spatially correlated to these phases as identified in the EPMA maps (see Figure 9). For both inverse models (bulk FTIR and μ FTIR) there is extremely good agreement in the results for the total spectral contribution of the matrix phylllosilicate (~68.5 vol.%), and this compares remarkably well with the 68.88 vol.% matrix calculated from the elemental microprobe map. The actual vs modeled abundance of all other endmembers are not in as good agreement but differ by only a few percent. The bulk FTIR modeled abundance of Fe,Ni-metal (~8.0 vol.%) predicts a slightly stronger contribution compared with the ~4.1 vol.% μ FTIR-modeled amount. These are both overpredictions when compared to the 1.94 vol.% estimated from EPMA. Both spectral models predicted abundances of pyroxene (21.0 and 17.5 vol.%, respectively) that are overpredictions compared to the 14.72 vol.% total pyroxene estimated from EPMA. However, there is excellent agreement between the μ FTIR

modeled spectral (~9.9 vol.%) and EPMA-estimated (10.05 vol.%) abundance of olivine in the sample. In contrast, the abundance of olivine from modeling the bulk FTIR spectrum was ~2% - a clear underestimation. This suggests that olivine is spectrally detectable in the higher spatial resolution μ FTIR data but that it is spectrally masked – and thus its abundance is difficult to determine - based on a bulk spectral measurement, even when present at ~10%.

In summary, the μ FTIR, pixel-scale estimates of spectral abundance of the four distinct phases provides decent matches to the phase abundances observed in the elemental maps, and these spectral abundances can reproduce the spectral shape of the bulk sample to a certain degree, but there remains a mismatch in overall reflectance level and wavelength position of the reflectance maximum. The albedo mismatch is resolved in the inverse model of the bulk spectrum because those results include more spectral contribution of the metal, but this appears to be at the expense of olivine. The bulk FTIR spectrum is different enough from a simple weighted average of the μ FTIR spectra to suggest that the former is not a simple linear combination of the latter. The general shape of the bulk FTIR spectrum can be reproduced by a linear model (Figure 5c), but the relative abundances of the non-phylllosilicate components are inaccurate (Figure 5d). Despite these drawbacks, both spectral models correctly predict the total amount of matrix phylllosilicate (and thus the total amount of non-phylllosilicate components). Both spectral models also highlight the important presence of metal in this lithology, but it is overestimated by a factor of ~2-4 compared with the EPMA data.

Field-1 (CM1/2)

Spectral endmembers for this sample include two phyllosilicate-rich matrix and two olivine-like endmembers (Figure 6a-b). The lack of spectral heterogeneity in this sample is generally consistent with mineralogy of the sample determined from EPMA mapping. Specifically, the high abundance of matrix (87.84 vol.%), the relatively low abundance of pyroxene (< 5 vol.%) and the low abundance of opaque phases all suggest there should be relatively little spectral variability. The larger pixel scale (140 μm) for this map, done to map the entirety of this larger section, also resulted in fewer spectral measurements capturing pure endmember phases. Only the most abundant phases (matrix phyllosilicate and chondrule olivine) were readily identifiable in the μFTIR data. The EPMA maps show compositional heterogeneity within the matrix of the sample that is suggestive of Fe-rich and Mg-rich phyllosilicate endmembers (see Figure 3), but we are not confident the larger μFTIR spot sizes were able to acquire spectra that clearly distinguish these two phases. Nevertheless, the two different matrix phyllosilicate and two different olivine spectral endmembers that were independently identified in the μFTIR data presumably do, at some level, represent real compositional heterogeneity within this sample.

Reflectance spectra of the two matrix phyllosilicate endmembers exhibit similar overall shapes in the MIR: a broad reflectance peak centered near $\sim 10\ \mu\text{m}$ with a minor peak superimposed near $10.15\ \mu\text{m}$. The primary difference between the two spectral endmembers is their overall reflectance level, and the inclusion of both endmembers translated to better results in spectral modeling with lower mapped RMSE values. The shape and position of these features, especially the endmember labeled Matrix Phyllosilicate 1,

are extremely consistent with the measured bulk FTIR spectrum in the MIR region (Figure 6b). Absorptions in the 3 μm region were also similar for each matrix endmember. This includes a band minimum position near 2.72 μm , which is slightly longer than the 2.708 μm position measured in the bulk FTIR spectrum, and a broad absorption shoulder centered between 2.90–2.95 μm .

The two olivine-like endmember spectra are roughly similar in shape but differ in the specific positions of their spectral features. MIR spectra of the endmember labeled Chondrule Olivine is most consistent with a moderately high Mg content, with a prominent reflectance peak centered at 10.74 μm , a shoulder at ~ 11.1 μm , and several minor peaks centered at 9.39, 10.13, and 11.92 μm . The positions of these features are consistent with an olivine composition of $\sim\text{Fo70}$ (Hamilton, 2010). The second olivine-like endmember spectrum, labeled Olivine + Pyroxene, also has a main peak centered near 10.59 μm with subordinate features at 9.59, 10.16, and 11.91 μm , but with an additional weak feature at 9.88 μm and shoulders centered near ~ 11.15 and 11.38 μm . These additional features are likely due to minor amounts of pyroxene. The position of the reflectance maximum is consistent with an olivine of higher Mg content, $\sim\text{Fo90}$. Near-IR spectra of both the Chondrule Olivine and Olivine + Pyroxene endmembers feature minor but prevalent 3 μm absorptions centered at 2.73 and 2.74 μm , respectively.

Pixel-level spectral modeling yields endmember abundance maps that are generally correlated with the petrographic features of the section as seen in EPMA maps (Figure 10). RMSE values of spectral fits for each pixel generally ranged from 0.01–0.03, with only a few values higher than 0.07. Neither the inverse FTIR or μFTIR models yield good spectral fits

compared with the measured bulk FTIR spectrum, though the former yields a spectrum with a roughly similar overall shape (Figure 6c). However, there is a mismatch in reflectance value, typically of a few percent, that varies with wavelength. The μ FTIR modeled spectrum exhibits weak reflectance peaks associated with pyroxene and olivine, phases which are indeed present in the sample, but these peaks are not as distinct in the measured bulk FTIR spectrum.

When summing the non-matrix olivine/olivine + pyroxene endmembers, the μ FTIR modeling indicates ~6% spectral contribution for these phases, which is approximately half the EPMA-estimated olivine abundance of 11.0 vol.% (Figure 6d). Similarly, combining the two matrix phyllosilicate endmembers produces an estimate of 94% spectral contribution of total matrix phyllosilicate, which is higher than the 89.0 vol.% determined from EPMA-based estimations. Inverse modeling of the bulk FTIR spectrum performed even poorer, estimating 100% spectral contribution of matrix phyllosilicate phases.

In summary, the measured bulk spectrum is clearly dominated by the spectral properties of the phyllosilicate-rich matrix, with little spectral evidence for presence of olivine or pyroxene. Whether using the μ FTIR-derived spectral abundances or the full inverse model of the bulk FTIR spectrum, there is an underestimation of olivine compared with EPMA-based values. Despite somewhat poor spectral fits, the spectral models correctly predict a very high abundance of phyllosilicate-rich matrix, but because these features dominate the bulk spectral properties it is an overestimation and the ~11% olivine is not properly recognized.

UM-2 (pl19149)

This section, which hosts both a CM1/2 and a CM-like lithology, was found to have four distinct spectral endmembers that correspond to an Fe,Mg-matrix phyllosilicate, an Fe- and S-rich matrix component, Mg-rich olivine, and Fe-rich olivine (Figure 7a-b). The μ FTIR spot size of 70 μ m allowed the identification of spectrally pure endmembers. Yet, as with previous measurements, the scale of spatial variation of the Mg-rich and Fe-rich phyllosilicate components of either lithology was smaller than the measurement footprint. The two matrix components identified in the μ FTIR spectra correspond to the compositionally distinct matrices of the two lithologies, but they are still an average (bulk) representation of the compositional heterogeneity that EPMA data demonstrate exists at finer spatial scales. Interestingly, although carbonate is present throughout the sample in the form of vein fill and small masses, it was not identified as a distinct spectral endmember, an observation that we discuss in more detail below.

The first matrix spectral endmember from the CM1/2 lithology (UM-2, Lithology 1) features a broad phyllosilicate-like reflectance peak in the MIR with two resolvable superimposed peaks centered near 9.80 and 10.26 μ m (Figure 7b). These are roughly consistent with the similar structure and position of the reflectance peaks at $\sim$ 9.75 and $\sim$ 10.21 μ m in the bulk FTIR spectrum. The 3 μ m absorption feature of this lithology shows a narrow absorption centered at $\sim$ 2.72 μ m that is flanked by a broader absorption centered near 2.78 μ m (Figure 7a). The reflectance minimum of the absorption observed here is slightly longward compared with the 2.706 μ m band minimum observed for the bulk FTIR spectrum, though the broader $\sim$ 2.78 μ m absorptions are generally more consistent.

The second matrix spectral endmember is associated with the CM lithology (UM-2, Lithology 2) and is broadly similar but with some clear differences from the matrix spectrum described for the CM1/2 lithology (Lithology 1). Rather than a clear dual-peaked spectrum, the main MIR feature appears as broader reflectance peak centered near $\sim 10.4 \mu\text{m}$ with multiple minor peaks superposed at 9.95, 10.23, 10.42, 11.13, and 11.46 μm (Figure 7b). The positions of these minor peaks are similar to the MIR reflectance peaks of the pyroxene spectrum observed in the Met-1 lithology (sample UM-1). While no discrete endmember pyroxene spectrum was observed in the μFTIR spectral map for the CM lithology of this section, the presence of these pyroxene features in the 'matrix' spectral endmember is consistent with the distinct presence of pyroxene estimated from EPMA-mapping (9.24 vol.% low-Ca pyroxene). As such, this spectrum is likely an average of the matrix and smaller grains of pyroxene that are present within each spectral footprint. The $3 \mu\text{m}$ absorption of the CM-like lithology is generally consistent in position with that of the bulk FTIR spectrum but less consistent in overall shape. We observe a band minimum centered near $\sim 2.71 \mu\text{m}$ with a broad longward absorption centered near $\sim 2.77 \mu\text{m}$. Unlike the sharp and distinct OH absorption seen in the bulk FTIR spectrum and matrix CM1/2 lithology spectrum, the OH absorption in the CM lithology matrix spectrum is only marginally stronger than the broad $2.77 \text{ H}_2\text{O}$ absorption it superposes.

The two olivine endmember spectra appear to represent somewhat different compositions within the solid solution series. The first, labeled Olivine 1, features a multi-peak MIR feature with two prominent reflectance peaks centered at 10.17 and 10.50 μm , and minor peaks superimposed at 9.83, 11.07, 11.40, and 11.92 μm . The position of these

features suggests an olivine composition of >Fo90 (Hamilton, 2010). The locations of these areas (Figure 11) are consistent with the EPMA-generated elemental maps, which show nearly pure fragments of forsterite grains located in these same areas. The second olivine spectral endmember, Olivine 2, exhibits a prominent and broad reflectance peak with a maximum at 11.06 μm and additional superimposed minor peaks at 9.29, 10.13, and 11.94 μm . These positions are also consistent with an Mg-rich olivine composition but possibly with more Fe than Olivine 1 (Hamilton, 2010). The shape of the primary peak is also odd for olivine in that it is asymmetrical towards the longer wavelength edge, suggesting this endmember may have an additional component. This would be consistent with the elemental maps, which at the same locations show Mg-rich forsterite with potentially overlapping matrix and/or sulfide grains. Nevertheless, the spectrum identified is clearly a distinct spectral endmember in the μFTIR spectral map and is referred to as a primarily “olivine” endmember in the spectral modeling.

Similar to the previous section, inverse modeling of the bulk FTIR spectrum performed quite poorly, estimating 100% of the Lithology 2 matrix endmember component, despite this being the volumetrically smaller of the two lithologies (Figure 7c-d). This poor fit is further seen in the μFTIR -based modeling of the spectrum, which shows a general broad reflectance peak centered near $\sim 10.4 \mu\text{m}$ but is too dark and fails to match subtle, important features of the bulk measured spectrum associated with lithic components (Figure 7c). A better spectral fit might be obtained by including an additional spectral endmember in the inverse models that would artificially adjust the overall reflectance level and/or spectral

contrast, but this does not appear to have a physical basis in terms of observed spectral endmembers for this sample.

Based on pixel-scale abundances, the μ FTIR model of the entire UM-2 section predicted approximately 56.5% spectral contribution of the first matrix endmember (Lithology 1), and approximately 39.3% for the second matrix endmember (Lithology 2) (Figure 7d). These seem to be under- and over-estimations, respectively, compared to the 60.1 and 24.6 vol.% estimated from EPMA-mapping results when considering the abundance of each matrix type for the sample as a whole (i.e., accounting for the different areas of each lithology). Combining both olivine endmembers, the total estimated spectral contribution was 4.2%, which is an underestimation compared with the 12.2 total vol.% olivine estimated from EPMA-mapping for the sample as a whole.

In summary, although spectral modeling indicates phyllosilicate-rich matrix is dominant in Lithology 1 and important in Lithology 2, neither model could not accurately account for the abundance of olivine, despite the identification of two olivine spectral endmembers. In addition, subtle spectral evidence of pyroxene is present in the matrix endmember for Lithology 2, consistent with its higher abundance in that lithology, but the spectral models do not accurately capture the ~12% abundance of olivine and pyroxene in this sample as a whole. These results are perhaps not surprising when considering that the bulk FTIR spectrum is clearly dominated by phyllosilicate features with only weak features attributable to other silicates. Finally, carbonate is not identified as a distinct spectral endmember, despite its presence throughout the sample, and there is no clear evidence for its presence in the bulk FTIR spectrum or model results.

UM-3 (pl19145)

The UM-3 section also exhibited two distinct lithologies, a CM1/2 and a CM-like lithology, that host at least five distinct spectral endmembers that can be linked to compositional differences (Figure 8a-b).

As in previous measurements, the scale of spatial variation between the Mg-rich versus Fe-rich phyllosilicate in the CM1/2 lithology (Lithology 1) is smaller than the spectral footprint, which results in a bulk averaged spectrum for the matrix spectral endmember. This spectrum is similar in the MIR to the matrix spectrum observed in CM1/2 lithology of UM-2, with two distinct reflectance peaks at ~9.80 and ~10.25 μm that partially overlap to make up a single broad feature. The features are highly consistent with the shape and peak positions observed in the 'bulk' FTIR spectrum. Similarly, the position and shape of the 3 μm absorption feature of the same spectrum is also consistent with the 'bulk' FTIR spectrum. Specifically, there exists a narrow absorption near 2.71 μm with a broader superimposed absorption centered roughly near 2.77 μm .

The spectrum of the matrix component of the CM-like lithology is entirely different in shape and features in the MIR region compared with the CM1/2 lithology. There is a broad multi-peaked feature spanning ~9–13 μm with a single prominent reflectance peak at 11.42 μm , and smaller superposed peaks centered at 9.20, 9.91, 10.38, and 12.02 μm . There is significant compositional diversity within the matrix of this lithology, so it is unlikely that this spectrum represents a single phase. The 3 μm region is also different for the matrix in this lithology. We do not observe the same type of narrow 3 μm absorption that was

characteristic of spectra for other matrix/phylosilicate endmembers, but instead observe a broad and shallow absorption centered near $\sim 2.8 \mu\text{m}$ that could be consistent with a cronstedtite composition. Compositionally, this matrix is most consistent with an Fe-rich serpentine and/or TCI-like phase (see description above), and this lithology also has numerous olivine/pyroxene grains.

We also included a third phyllosilicate-like spectral endmember that is associated with an altered clast in the CM1/2 lithology (see Figure 12 for location). Similar to the matrix phyllosilicate endmember observed for this lithology, its spectrum exhibits a double-peak feature in the MIR with reflectance peaks centered near 9.82 and $10.39 \mu\text{m}$, though the slope between these features is negative whereas the slope between the same features in the matrix spectrum and the bulk FTIR spectrum is positive. The $3 \mu\text{m}$ absorption feature for spectra of this clast shows a single deep and narrow absorption centered at $2.71 \mu\text{m}$ and lacks the broader feature at $\sim 2.8 \mu\text{m}$ that is typically associated with the other phyllosilicate-like spectral endmembers. This indicates the phase is dominated by OH with little H_2O , which along with the band position is consistent with Mg-serpentine.

Two mafic spectral endmembers were identified that correspond to pyroxene and an Mg-rich olivine. The MIR region for the olivine shows a prominent reflectance peak at $10.48 \mu\text{m}$ with several additional peaks at 9.74 , 10.12 , and $11.96 \mu\text{m}$, consistent with an olivine composition of $>\text{Fo}90$ (Hamilton, 2010). This feature is also most similar in shape to the forsteritic olivine spectrum observed in UM-2. In the $3 \mu\text{m}$ region, the olivine spectral endmember exhibits a shallow asymmetric absorption with a reflectance minimum positioned at $2.71 \mu\text{m}$. The pyroxene endmember spectrum exhibits a broad feature with

reflectance peaks located at 9.04, 9.58, 9.88, 10.42, 10.81, 11.13, and 11.40 μm . The 3 μm absorption feature observed for this spectrum is nearly identical to that of the olivine spectrum, with a shallow asymmetric feature with a minimum at 2.71 μm .

The μFTIR modeled spectrum generally has the same shape and features at ~ 9.9 and ~ 10.3 μm as in the bulk FTIR spectrum, but with additional features at longer wavelengths that are attributable to the various minor peaks in the CM Lithology 2 matrix spectrum (Figure 8c). The μFTIR spectral fits predict 77.4 vol.% of Lithology 1 CM1/2 matrix phyllosilicate, 15.5 vol.% Lithology 2 CM matrix phyllosilicate, 2.0 vol.% olivine, 4.3 vol.% altered clast, and 0.8 vol.% pyroxene (Figure 8d). This compares to EPMA-based estimations of 72.1 vol.% Lithology 1 matrix phyllosilicate, 7.5 vol.% Lithology 2 matrix phyllosilicate, 10.0 vol.% olivine, 2.2 vol.% altered clast, and 3.7 vol.% pyroxene. Though the spectral estimation of the first matrix phyllosilicate endmember compares favorably, the remaining endmembers are off on their predictions by a factor of two to four. Considering matrix phyllosilicate and altered components separately from mafics, we get an overall prediction of ~ 97 vol.% matrix/altered components and ~ 3 vol.% mafics, which compares with the 83.5 vol.% and 15.0 vol.% predicted from EPMA mapping. Even when considering all alteration components, the fraction of apparently unaltered material remains underestimated, particularly olivine.

Similar to sample UM-2, inverse modeling of the FTIR bulk spectrum predicted 100 vol.% matrix and altered endmembers, which was divided between ~ 44.5 vol.% CM1/2 matrix phyllosilicate, 28.9 vol.% CM matrix phyllosilicate, and ~ 26.7 vol.% altered clast. The lack of olivine/pyroxene in this model is perhaps not surprising given the lack of

diagnostic features associated with those phases in the bulk FTIR spectrum. The overall shape of the inverse FTIR spectral fit is very similar to the μ FTIR model spectrum (Figure 8c), though the spectral contrast is somewhat enhanced and the reflectance level is better matched to the measured FTIR spectrum.

In summary, both the μ FTIR and FTIR spectral models underestimate the abundance of olivine+pyroxene in this sample, even when including a third and spectrally distinct alteration component. A main difference in the two models is attributable to this altered clast – the inverse FTIR model predicts a significant spectral contribution from this endmember, but this is not observed in the individual pixel-scale μ FTIR data. This suggests that the altered clast might have an influence on bulk spectral properties that is disproportionate to its actual volumetric abundance.

2.4.4 Lithologic Spectral Modeling of Bulk FTIR Spectra

The UM-2 and UM-3 sections exhibited clear brecciation at the scale of the sample (Figure 2b), and we also evaluated the degree to which average spectral properties of each lithology could be used to model the bulk spectral properties of these samples. The average spectrum for each lithology was calculated by averaging the individual μ FTIR spectra within the boundaries of that lithology. The lithologic spectral averages were then used to inversely model the sample's bulk FTIR spectrum.

For section UM-2, the CM1/2 lithology is more consistent with the bulk spectrum in terms of the overall shape of the 3 μ m absorption feature (Figure 13a). However, the band minimum position of the bulk spectrum (2.706 μ m) is slightly better matched by the UM-2

CM-like lithology (2.711 μm) rather than the position of the CM1/2 lithology (2.721 μm). The CM1/2 lithology also provided a better match to the shape and position of SiO feature at MIR wavelengths, whereas the average spectrum of the UM-2 CM lithology exhibits additional peaks in this region compared with the bulk spectrum (Figure 13b). Inverse modeling of the MIR region of the bulk spectrum predicts 28.8 vol.% of the UM-2 CM1/2 lithology and 71.2 vol.% of the UM-2 CM-like lithology, compared to the actual values of 61.0 vol.% and 39 vol.%. Similarly, modeling the 3 μm region resulted in an estimated 100 vol.% contribution of UM-2 Lithology 2 (Figure 7c-d). However, the spectral fits are quite poor, and this is driven largely by differences in spectral slope, spectral contrast, and absolute reflectance level between the measured bulk FTIR spectrum and the μFTIR spectral endmembers used as model inputs.

Qualitatively, the spectral shape of the phyllosilicate-dominated CM1/2 (Lithology 1) is clearly a better match to the bulk FTIR spectrum of the UM-2 sample, particularly at MIR wavelengths. Including ad hoc spectral endmembers such as lines of different slope and albedo that could adjust spectral contrast, slope, and reflectance level in the model would likely result in better spectral fits, but our primary intent here is to test the degree to which the known and directly observed spectral endmembers can reproduce the bulk spectral properties. In the case of UM-2, it is clear that the μFTIR data as measured cannot be linearly combined to accurately reproduce the bulk spectral properties. A cursory comparison of the lithology and bulk spectra shows that the latter has only very weak features that are diagnostic of the less-altered CM lithology. This is consistent with the other spectral modeling results for this sample: though the CM lithology is ~39% of the sample

and contains olivine and pyroxene, the spectral evidence for this distinct lithology and its unaltered constituents is rather weak. The bulk spectral properties are dominated by the more heavily altered CM1/2 lithology.

Similar results were obtained for section UM-3 – the CM1/2 lithology was most consistent with the bulk spectrum in both the shape and position of the 3 μm absorption feature and the MIR SiO stretch feature (Figure 14). As with UM-2, the MIR spectrum of the CM-like lithology in UM-3 is dissimilar to the dual-peak feature seen in the bulk MIR spectrum. Linear unmixing of the MIR bulk spectrum using the spectra of these two lithologies produced somewhat better results than the previous sample, but spectral fits are still rather poor, for similar reasons as noted above. Estimated abundances were 70.3 vol.% and 29.7 vol.% for the CM1/2 and CM lithologies, respectively, compared to the actual abundance of 81.1 vol.% and 18.9 vol.%. As with UM-2, linear unmixing of the 3 μm absorption region produced a poor spectral fit. The model also estimates 100 vol.% of the CM lithology, a clear overestimation that is again driven by the large differences in spectral slope between the bulk FTIR and μFTIR endmember spectra. As with UM-2, the bulk spectrum for UM-3 is clearly dominated by the spectral properties of the more altered lithology (CM1/2) with little evidence of the distinct CM lithology and its higher abundance of unaltered components.

2.5 Discussion

2.5.1 Brecciation and Implications for Variable Degrees of Aqueous Alteration

The four AZ sections studied here are primitive, accretionary breccias with two sections (UM-2 and UM-3) also showing evidence for genomic brecciation. At least three distinct lithologies (Met-1, CM1/2, and CM) appear to be represented by the six primary clasts identified among the four sections. As a group, the primary clasts span a range of petrographic and chemical characteristics, including differing abundances of phyllosilicate-rich matrix, mafic components (e.g., chondrules and olivine/pyroxene fragments), carbonate grains/veins, and variable ratios of Mg-rich to Fe-rich matrix phyllosilicate (Figure 15 and Figure 16).

The most pronounced trend observed among these features is a negative linear correlation between the percent abundance of matrix and percent abundance of olivine and pyroxene – grouped as ‘mafic component’ here – found in chondrules and lithic fragments (Figure 15a). This trend is consistent with the commonly held view that matrix phyllosilicates form at the expense of chondrules and lithic fragments with increasing degree of aqueous alteration (e.g., Browning et al., 1996). Based on the abundance of matrix phyllosilicates, the samples studied here span petrologic subtypes from ~2.0–2.7 in the scheme of Rubin et al. (2007), or ~1.1–1.8 in the scheme of Howard et al. (2015). Assuming that matrix and phyllosilicate abundance is a reliable indicator of the degree of aqueous alteration (Howard et al., 2009, 2011, 2015), the samples studied here span an impressive range of degree of aqueous alteration for a single meteorite. This observation is consistent with chemical and isotopic data presented by Kerraouch et al. (2022), which suggest that

these lithologies formed in different locations on the parent body and/or under very different conditions.

If it is assumed the different sections (and components therein) originated from a single parent body whose initial distribution of chondrules and matrix was homogeneous, then the range in matrix phyllosilicate abundance would imply significant spatial variability in the degree and style of aqueous alteration within that parent body. Alternatively, the different primary clasts and lithologies may have originally formed on a heterogeneous parent body or on multiple parent bodies prior to being incorporated into the current breccia. In this scenario, the linear trend in Figure 15a may simply represent the fact that chondrules and matrix typically account for 95 vol.% of carbonaceous chondrites, i.e. they are largely a binary system. Regardless of these scenarios, the range in abundance of matrix phyllosilicate is consistent with a range in degree of aqueous alteration that is now preserved in a single (albeit brecciated) meteorite. Positive correlations are observed between total matrix abundance and proportion of Mg phyllosilicate (Figure 15b), as well as between total matrix abundance and percent abundance of carbonates (Figure 15c), though the metal-rich lithology of UM-1 is somewhat of an outlier in both cases.

A transition in cation chemistry from Fe-rich to Mg-rich matrix phyllosilicates has been observed among many CM group carbonaceous chondrites (e.g., King et al., 2017) and has been linked to progressive aqueous alteration. In this framework, amorphous silicates, metals, and sulfides are first dissolved and converted into Fe-cronstedtite and tochilinite. This is followed later by the serpentinization of refractory coarse-grained inclusions that then gave way to the production of Mg-rich phyllosilicates. It is notable that

this trend is observed here within a single meteorite. If all lithologies and primary clasts of the AZ meteorite derive from a single primary parent body, then it suggests lateral and/or vertical variations in degree of aqueous alteration on that body. This heterogeneous style of alteration would be in contrast to observations and models that predict asteroid-scale homogeneity for some C chondrite parent bodies (e.g., Bland & Travis, 2017). Alternatively, if the different AZ lithologies are instead sourced from different parent bodies that were mixed and joined through collisional evolution, this indicates they had distinct evolutionary pathways that represented a range in degree and style of aqueous alteration.

Interestingly, the Met-1 lithology in sample UM-1 clearly deviates from the trends described above, which may result from it having a distinct heritage and starting composition compared with the other CM-related lithologies. In a comprehensive study of the chemistry, mineralogy, and isotopic characteristics of these and other AZ samples, Kerraouch et al. (2022) found all samples exhibited some level of affinity to the CM chondrite group. However, the Met-1 lithology exhibited chemical, petrographic, and isotopic characteristics that may warrant classification as an ungrouped carbonaceous chondrite material, which suggests a distinct or at least more complicated petrogenesis. We also observe a negative linear correlation between the percent abundance of Mg-phyllosilicates and the percent abundance of mafic components, with Met-1 again showing deviation. This trend is in agreement with the notion that Mg-rich phyllosilicates like Mg-serpentine are the products of aqueous alteration of olivine and pyroxene in chondrules and other lithic fragments.

To explore this relationship in more detail, the percent abundance of olivine, low-Ca pyroxene, and high-Ca pyroxene are plotted against the percent abundance of matrix in Figure 16. All three mafic components exhibit a negative trend with increasing matrix, with olivine abundance decreasing from ~14 vol.% to ~6 vol.% and a similar trend for low-Ca pyroxene, which decreases from ~10 vol.% to ~0 vol.%. The strongest trend is between the total pyroxene (low-Ca + high-Ca pyroxene) and matrix abundance, in which the former decreases from ~26 vol.% to ~0 vol.% over a range of ~55-95 vol.% matrix (Figure 16d). Over this range of matrix abundance, the amount of pyroxene is reduced twice as much as that of olivine, suggesting much of the phyllosilicate-rich matrix may have formed at the expense of pyroxene (assuming all clasts originally had similar olivine and pyroxene abundances). This is in contrast to laboratory experiments that have found forsterite and fayalite to have much higher dissolution rates than enstatite and diopside (e.g., Brantley and Olsen, 2014 and references therein), but the surface areas of different primary phases may have been quite different. Some studies exploring weathering rates in natural terrestrial systems have found that minerals like clinopyroxene and plagioclase weather more rapidly than olivine (Wasklewicz et al., 1993), but these seem to be the exception. Experimental studies show that the most favorable fluid conditions for the preferential dissolution of pyroxenes in systems of forsterite, enstatite, and diopside tend to be near neutral to slightly acidic pH and at temperatures of 25–70°C (Oelkers, 1999). This is further supported by numerical models, which show under asteroid-relevant conditions, Fe-rich metal, low-ca pyroxene, diopside, and feldspars can alter faster than forsterite (Zolotov and Mironenko, 2008).

These observations are in decent agreement with previous studies of aqueous alteration in CM chondrites, whose geologic history and variability are complex to say the least (e.g., Suttle et al., 2021). In general, olivine and pyroxene are progressively replaced by Fe- and then Mg-rich alteration products, and the lithologies studied here may represent different points along this continuum. Important for this study, from a spectroscopy viewpoint, is that anhydrous silicates are still present in some of the AZ lithologies at abundances of ~10% and higher, yet spectral evidence of those phases is weak to absent in most of the bulk spectra. This is discussed in more detail below.

To further investigate systematic changes in the chemistry of olivine with progressive dissolution and aqueous alteration, we plot the probability density function of MgO# in all grains that exhibit olivine-like chemistries (Figure 17). Using total matrix abundance as a proxy for degree of aqueous alteration, we observe no obvious trend between extent of alteration and the distribution of olivine MgO# in each lithology (Figure 17). There is also no obvious correlation between the distribution of MgO# in olivine grains as a function of the abundance of Mg-rich phyllosilicates. Possible explanations for the lack of trends in olivine composition and phyllosilicate composition are the heterogeneous distribution of precursor anhydrous phases within the original material(s) and/or the limited number of sections studied. For example, if Fe-rich olivine grains were dominant at a local scale or within a given clast, then even after extensive alteration any remaining olivine grains would still be Fe-rich. This may be reflected in the chemistry of the CM1/2 lithologies in UM-2 and UM-3, where the olivine chemistry appears to be more strongly dominated by FeO relative to the other samples. This is intriguing given that these are the more altered lithologies and

fayalite is expected to alter faster, which should skew compositions of residual olivine towards forsterite. However, we stress that the EPMA measurements that these analyses are based on are presumed to be olivine, but the accuracy of these mineralogical assignments are tied to how well our supervised classification algorithm was able to cluster pixels that were (chemically) similar to known olivine grains in the sample. To that end, it is possible that nanometer-scale alteration phases could be present within these “olivine” grains, thus skewing the results and interpretations of olivine chemistries. The detection of such phases, however, remains beyond scope of the methods used in this study. Nevertheless, in general, the chemistry observed in olivine grains appears uncorrelated to matrix formation and instead is likely related more to the starting composition of the precursory phases and complex interactions between olivine and other phases present like pyroxene (e.g., Huang et al., 2017a, 2017b).

Carbonate grains in the matrix and intimately associated within CAIs were studied in detail by Kerraouch et al. (2021, 2022) where they interpreted the carbonates in different lithologies to have a similar origin, i.e., precipitated from the same or chemically identical fluids. Though we do not have isotopic data, the nearly identical chemistry for the various carbonates observed in the present sections is consistent with this interpretation. In addition to carbonate grains, we also observe the presence of Ca-rich carbonate veins that demarcate the boundary between the CM1/2 and CM lithologies in the UM-2 and UM-3 sections (Figure 2b). This previously unreported veining has interesting implications for the timing of aqueous alteration. First, the presence of the veins along the clast boundaries implies the aqueous alteration responsible for the precipitation of the carbonate veins (and plausibly

the carbonate grains) must have occurred after the brecciation event that joined these lithologies together. When considering the two lithologies in both sections are different petrologic subtypes indicative of different degrees of aqueous alteration, this presents two possibilities.

The first possibility is that there was a single episode of aqueous alteration that postdated the brecciation event and that was responsible for the precipitation of the carbonate veins and the alteration of precursory anhydrous phases that produced phyllosilicates in the matrix. If the two lithologies, which are only mm apart, did indeed experience the same history of aqueous alteration (e.g., similar amount and composition of fluid), this implies that each lithology exhibited a different initial chemistry, porosity, permeability, and/or ratios of matrix, chondrule, and CAI components.

The second possibility is that there were at least two episodes of aqueous alteration – a pre-brecciation episode for each lithology that was responsible for significant alteration (e.g., matrix phyllosilicate formation), followed by at least one post-brecciation alteration event that was responsible for the precipitation of the carbonate veins and grains. This scenario does not require that the starting lithologies be heterogeneous and instead allows for the possibility of a homogeneous parent body that experienced pre-brecciation aqueous alteration that was spatially variable, a notion that is supported by isotope data presented by Kerraouch et al. (2022). While we cannot directly evaluate the likelihood of either scenario at present, future investigations that include isotopic analysis of carbonate veins and carbonate grains dispersed through the matrix and intimately associated with the CAIs in each lithology are warranted.

2.5.2 Efficacy of spectral proxies and band parameters as indicators of alteration

A primary goal of this study was to identify whether or not different lithologies of the Aguas Zarcas meteorite exhibit distinct spectral signatures and, if so, which components drive that spectral diversity. We also explore how spectra of different lithologies compare to bulk (large spot size) spectra that integrate over multiple lithologies. Given the petrographic context provided above, we can broadly assess the utility of the bulk spectral data as a qualitative means to identify mineralogy and possible differences in phyllosilicate/matrix chemistry and degree of aqueous alteration.

The MIR Region

Qualitatively, the bulk spectra of the four different sections are strikingly similar in overall shape, with the exception that the MIR spectrum for the UM-1 sample also exhibits weak pyroxene/olivine features (Figure 4). In that sense, the sample with the lowest abundance of matrix phyllosilicate components is correctly recognized as spectrally distinct. However, the MIR spectral differences of the other samples are more similar, and there is no unique correlation between band positions and abundance of matrix. This is even clearer when considering the average spectra of the different lithologies in the UM-2 and UM-3 samples. Spectra for those CM1/2 lithologies are nearly identical, despite their different abundances of matrix material (see Figure 4). However, the spectral averages for

the less altered and more mafic-rich CM lithologies are clearly different and more similar to the spectrum of the less altered Met-1 lithology.

All lithologies identified in the samples studied here are dominated by matrix phyllosilicates (~55–90 vol.%), which is confirmed spectrally in both the μ FTIR and FTIR data in the 9–13 μ m region by a broad SiO stretch reflectance peak. Lithologies that have ~15 vol.% or less of mafic components exhibit a dual-peak SiO stretch feature attributable to matrix phyllosilicates, whereas spectra for lithologies with ~24 vol.% or more mafic component exhibit additional weak features attributable to pyroxene that are superposed on the broader matrix phyllosilicate peak. Although olivine spectral features are observed in some individual μ FTIR spectra, in no average MIR spectrum do we see clear features that can confidently be attributed to olivine, despite it being present in abundances of ~5–15 vol.% in the sample suite. If we subtract the olivine abundance from the overall mafic abundance, then the amount of pyroxene necessary to have an observable effect on average spectra in the MIR region is 5–10 vol.%. Additionally, we notice an increase in the strength of a reflectance peak near 11.45 μ m with increasing total pyroxene abundance (~10–26 vol.%), which we tentatively attribute to pyroxene. These observations suggest that olivine has the potential to be significantly underestimated based on qualitative spectral analysis alone, even when present by as much as 15 vol.% (and perhaps more), whereas pyroxene may be identifiable when present at ~5 vol.% in C chondrites and their parent bodies. However, these features are superposed on a broader and stronger phyllosilicate feature, and such weak features may not be recognizable in lower signal-to-noise telescopic or spacecraft data.

Together, the results presented here demonstrate that although different degrees of alteration in different clasts/lithologies can be broadly recognized using MIR data, when several lithologies are present in a single observation it is the more altered lithologies that dominate. The peak position of phyllosilicate features at MIR wavelengths does not vary uniquely and consistently in wavelength as a function of degree of aqueous alteration (abundance of phyllosilicate matrix).

The 3 μm “Hydration” Region

The strength, shape, and position of the 3 μm feature has been extensively studied as a potential proxy for phyllosilicate abundance and cation chemistry (Takir et al., 2013, 2019; Beck et al., 2010, 2014; Bishop et al., 2008; Osawa et al., 2001; Sato et al., 1997). Specifically, 7 Å phyllosilicate minerals like serpentine, which are the dominant matrix component in CM chondrites (Brealey, 2006), exhibit a narrow metal-OH vibrational absorption near 2.7 μm that shifts to longer wavelengths (2.71 $\rightarrow$ 2.76 μm) as the dominant octahedral cation changes from Mg to Fe (e.g., Bishop et al., 2008). When combined with independent observations that the matrix composition of CM chondrites transitions from Fe-serpentine to Mg-serpentine with progressive aqueous alteration (Howard et al., 2009, 2011), this has led to the suggestion that the position of this metal-OH absorption may be a useful proxy for degree of alteration in C chondrites and primitive asteroids.

Previous high spatial resolution spectral measurements of CM2 chips have shown that samples with 3 μm band positions centered at longer wavelengths tend to exhibit a more heterogeneous distribution and higher abundance of non-matrix phases (Schultz et al.,

2023). Plots in Figure 18 compare the wavelength position and depth of the 3 μm absorption feature with various compositional properties of each lithology. Of these, we see a rough negative correlation with the wavelength position of the 3 μm absorption band minimum and the total abundance of matrix. Similarly, we see a rough positive correlation between the 3 μm band depth and total abundance of matrix. Specifically, lithologies with matrix abundances on the order of ~60 vol.% exhibit average spectra with 3 μm band minimums positioned near 2.72 μm whereas the lithologies with matrix abundances at >80–90 vol.% exhibit positions centered near 2.71 μm .

This trend in band position with increasing matrix abundance is consistent with previous observations in other C chondrites, (e.g., Beck et al., 2010; Takir et al., 2013; Bates et al., 2019). However, studies of other meteorites of similar petrologic subtypes to the least altered lithologies studied in these AZ samples have been shown to exhibit 3 μm absorption features with minima at substantially longer wavelengths (~2.74–2.78 μm) than observed here (Takir et al., 2013, 2019; Schultz et al., 2023). That is, when combining our data with that of previous studies of C chondrites (e.g., Takir et al., 2013, 2019), we find that the ~3 μm band positions can span a relatively wide range for a given petrologic subtype. We also observe no correlation between position of the 3 μm band minimum and the total abundance of either the Mg-rich phyllosilicate phase or the Fe-rich phyllosilicate phase alone, though it does correlate roughly to total phyllosilicate abundance. While easy to measure, these results suggest the wavelength position of the metal-OH band minimum in the 3 μm region may not provide a robust method for assessing the relative differences in degree of alteration within or between C chondrites and their parent bodies.

Similar results are seen when considering the overall shape of the 3 μm hydration feature. Broad and strong H_2O absorptions are observed for samples with the most (UM-2 CM1/2 lithology) and least (UM-3 CM lithology) amount of matrix phyllosilicate, and some samples with intermediate abundances have 3 μm regions dominated by OH with minimal H_2O . This is particularly noteworthy because the AZ meteorite was collected shortly after its fall and has not been subjected to alteration in the open terrestrial environment to the same degree as most other meteorites. We suggest that the observed variation in the 3 μm region is driven more by the relative proportions of serpentine (OH, no structural H_2O) and Mg-smectite (e.g., saponite, OH and interlayer H_2O). The proportions of these phases may be variable between altered clasts/lithologies and may not have evolved in one direction with increased aqueous alteration and phyllosilicate production. In this scenario, phyllosilicates in the Met-1 lithology of the UM-1 sample would be expected to be dominated by serpentine, whereas lithologies whose spectra have broader 3 μm features may have higher proportions of smectite such as saponite.

The position, shape, and strength of the complex 3 μm hydration feature do not appear to be a robust indicator of total matrix phyllosilicate abundance, and important information in this spectral region is clearly lost when measuring bulk powders of complex carbonaceous chondrite breccias. Alternatively, and given the complexity of Aguas Zarcas, these results may simply highlight the odd nature of this particular brecciated meteorite compared with previously reported trends for bulk powdered CM chondrites as a whole. Regardless, this demonstrates that without *a priori* knowledge of the petrography and group affinity of a given sample, relying on these spectral proxies for accurate remote

compositional analysis of similar brecciated and complex (e.g., rubble pile) asteroids may be complicated.

2.5.3 Predicting phase abundances using linear spectral unmixing models

An additional objective of this study was to evaluate the efficacy of linear spectral unmixing models for compositional analysis using both the 3 μm and MIR wavelength regions. We assume that the EPMA-based estimates of matrix (phyllosilicate), olivine, and pyroxene abundances for all lithologies are the ‘correct’ modal values and compare abundance estimates from the linear spectral models against these values. The bar charts in Figures 5-8 show that pixel-level modeling produced better overall results, with phase estimation errors typically on the order < 10 vol.%. This demonstrates that with higher spatial resolution spectral data it is possible to obtain decent estimates of phase abundances in aqueously altered C chondrites. Though it remains challenging to identify different phases within the extremely fine-grained matrix, it is possible to accurately estimate the total abundance of matrix within and between samples. On the other hand, inverse models of bulk FTIR spectra performed systematically worse, errors typically on the order of a few to tens of vol.%. The estimated phyllosilicate abundance showed the most error, due to the model selecting one matrix endmember in favor of another. Errors for total matrix contribution for the sections with multiple matrix phyllosilicate endmembers were on the order of $\sim 11\text{--}15$ vol.%. Of all three major phases considered, only olivine was systematically under-estimated by $6\text{--}12$ vol.% by all modeling techniques, though bulk spectrum modeling tended to produce slightly higher errors.

Inverse modeling from the μ FTIR spectra based on the 3 μ m region performed similarly well to the MIR-region modeling, with errors typically less than ~ 5 vol.% (Figure 12b). This result was surprising considering that the mafic silicates studied here do not have any diagnostic absorption features in this wavelength regime. Nevertheless, their 3 μ m absorption features, which are likely attributed to the presence of minor alteration products resulting from incipient aqueous alteration, are characteristic enough for the different components to allow for moderately good estimations. In contrast, estimations based on unmixing of the 3 μ m region for the *bulk* spectra gave poor results, with errors ranging from ~ 10 –90 vol.%.

Modeling of the bulk FTIR spectra may be considered most analogous to the task of linearly unmixing telescopic point-source spectra of asteroids. It is important to note that even though a linear unmixing model may be able to reproduce the measured spectrum of an object (meteorite or asteroid), the associated spectral fractions may not be equivalent to the actual modal abundances of different phases. As shown here, in the case of modeling phase abundances in carbonaceous chondrites, the large errors in inferred phase abundances could easily lead to the broad misclassification of C chondrite group affinity and metamorphic subtype, which by analogy would lead to a similar misclassification of asteroid taxonomy. It is also notable that the multiple Aguas Zarcas lithologies studied here each exhibited distinct spectral features in both the 3 μ m and mid-IR region, which again by analogy would imply that a single spectral shape may not be representative of a given primitive body within a taxonomic class and, likewise, objects with different spectral shapes may actually have similar compositions and histories.

Our pixel-level modeling was performed on spectra with a spatial footprint roughly on the order of the size of the macroscopic inclusions found within the AZ samples (chondrules, metal blebs, CAIs, etc.) and would be most analogous to high-resolution imaging spectrometers like the μ OMEGA instrument (Bibring et al., 2017) or CIVA instrument (Bibring et al., 2007). Modal abundance estimations using this method would be expected to return more accurate results with deviations from true abundances ranging from a few to 10 vol.%. Again, using C chondrites as an analog, predictions of taxonomic group affinity would be improved but precise identification of petrologic subtype (e.g., Rubin et al., 2007; Howard et al., 2015) would warrant caution.

The systematic underestimation of olivine by the MIR linear mixing model also has important implications for the interpretation of both the spectra and the processes that modified C chondrites and their parent bodies. It is expected that planetesimals were quite heterogeneous as a group but also within an individual body (Weiss and Elkins-Tanton, 2013). Olivine is expected to be the volumetrically dominant mantle product produced from the partial to complete melting of chondritic planetesimals (Elkins-Tanton et al., 2013). Using MIR linear mixing models to estimate the abundance of this key phase may lead to underpredictions of olivine abundance for primitive bodies, which in turn limits our ability to test planetesimal formation models by direct detection of olivine mantle material.

The two phases which appear to have the strongest control on the shape and position of the mid-IR spectral feature are matrix phyllosilicates and pyroxene. The fine-grained matrix phyllosilicates found within Aguas Zarcas and other CM chondrites are expected to be secondary phases produced from the dissolution of primary anhydrous phases, namely

olivine and pyroxene, via aqueous alteration. The results presented here further confirm that pyroxene and olivine are primary phases consumed by progressive aqueous alteration. Therefore, the ability to determine the relative abundance of matrix phyllosilicates to pyroxene should be seen as a useful proxy for estimating the extent to which a C chondrite or their asteroid parent bodies have been modified by progressive aqueous alteration.

There are several considerations to explain the differences in efficacy of bulk spectral modeling compared with pixel-level modeling. First, the bulk spectrum and the μ FTIR endmember spectra used for modeling were acquired with two different spectrometers operating at two different spatial scales, with one being an order of magnitude larger than the other. Spectral effects like brightening, darkening, or artificial wavelength-dependent slopes may be induced due to differences in viewing geometry and multiply scattered light being captured at these two spatial scales. Indeed, in the 3 μ m region we observe that the bulk FTIR spectra systematically have a 'bluer' slope than the μ FTIR spectra, which typically have a neutral to red slope. These slope effects are enough to force simple linear models to favor endmembers that, while having a better fit to the slope, do not fit the shape and position of the complex 3 μ m OH/H₂O absorption. A combination of performing continuum-removal to negate the effects of slope on the spectrum and/or narrowing the wavelength region used for the model may produce more accurate estimations. Similarly in the MIR, we note that the overall brightness of the bulk spectrum tends to be slightly brighter than the μ FTIR spectrum over the same range. This may have led to overestimation of phases like metal, which were flat in this region but much brighter. This endmember could act to produce an overall brighter spectrum. Considering this, more accurate results in the MIR

may be achieved by incorporating an artificial flat spectrum as a spectral endmember. This would have the effect of providing a means for the overall brightness of the model to be adjusted without having to incorporate unphysical amounts of true spectral endmembers. Results would then be normalized to only the true spectral endmembers.

Despite the wide range of variations that could be applied in spectral models, the gross differences observed between the pixel-scale μ FTIR and bulk FTIR data indicate endmember spectra of individual components cannot be linearly summed in their known proportions to reproduce bulk spectral properties. Although such components can be identified and accurately mapped at ~ 140 μ m spot sizes or smaller, the bulk spectrum represents a nonlinear spectral mixing system. Specifically, the aqueously altered phyllosilicate-rich matrix is overrepresented in the bulk spectra, and the distribution and abundance of primary anhydrous phyllosilicates is only accurately observed at finer spatial scales.

2.5.4 Implications for other meteorites and returned asteroid samples

The results of this work have important implications for the spectroscopic study of dark primitive asteroids like the near-Earth rubble pile asteroid 101955 Bennu and 162173 Ryugu. Researchers have hypothesized that asteroid Bennu exhibits at least two and as many as five distinct lithologies that are distinguishable based on albedo and morphological characteristics (Jawin et al., 2022, 2023). Aside from evidence of exogenous pyroxene-rich boulders (DellaGiustina et al., 2020) and carbonate veining occurring in some boulders (Kaplan et al., 2020), disk integrated and moderate spatial resolution visible and infrared

spectral maps of Bennu suggest the surface to be rather homogeneous (Hamilton et al., 2019; Barruci et al., 2020). Ryugu similarly exhibits a small population of potentially exogeneous boulders but otherwise appears spectrally homogeneous at the meters-scale (Tatsumi et al., 2021; Kitazato et al., 2019). In contrast, laboratory analyses on fragments returned from Ryugu have revealed brecciated textures with clasts exhibiting subtle but distinct spectral differences at 3 μm and MIR wavelengths (Storz et al., 2024). This raises the question of whether distinct lithologies can be resolved or accurately interpreted based on spectral datasets acquired at spatial scales greater than the size of individual boulders and cobbles.

Different lithologies of monomict (and likely polymict) breccias like the Aguas Zarcas meteorite can indeed exhibit reflectance spectra with distinct 3 μm and MIR spectral features. We suggest that within each lithology, the fundamental control on the strength, position, and shape of spectral features is the petrologic subtype. More specifically, the abundance of pyroxene and other mafic silicates relative to matrix phyllosilicates, which are aqueous alteration products of the former. However, the bulk spectral properties of samples with multiple lithologies can clearly be biased towards one lithology. In the case of the samples studied here, there is a bias towards the most altered (phyllosilicate rich) lithologies, and lithologies with more olivine/pyroxene have a weaker contribution to the bulk spectral signature. In the absence of spatially resolved elemental or spectral data, this bias could lead to an overestimation of the degree of aqueous alteration experienced by a meteorite (or asteroid) and an underappreciation of true compositional heterogeneity. On the positive side, and in the context of spectral observations of asteroids, our results suggest

that compositionally distinct lithologies should be resolvable when imaged at spatial scales on the order of the size of the lithologies themselves.

These results also have important implications for the study of carbonates on dark primitive asteroids and in chondritic samples. The presence of carbonate veins observed along the boundaries of different lithologies has important implications for the timing and number of episodes of aqueous alteration that occurred on the Aguas Zarcas parent body. Yet, the overall modal abundance of carbonate in these samples is less than 1 wt.%, as measured via EPMA mapping. Furthermore, though evidence of carbonate is readily observed by EPMA, we see scant evidence of this phase in the reflectance spectra. There are several mid-IR fundamental vibrational absorption features attributed to carbonate that occur at $\sim 6.9\ \mu\text{m}$ and $\sim 11.4\ \mu\text{m}$ (Bishop et al., 2021), along with absorptions at $\sim 3.3\text{--}3.4\ \mu\text{m}$ attributed to overtones and $\sim 3.8\text{--}4.0\ \mu\text{m}$ and $\sim 5.5\text{--}5.6\ \mu\text{m}$ attributed to combinations of fundamental vibrations (Bishop et al., 2021). The UM-1 section had the highest abundance of carbonates ($\sim 0.9\ \text{vol.}\%$), which are intimately embedded in the matrix as micron to tens of micron sized grained within the matrix. In its matrix phyllosilicate spectral endmember a weak $11.4\ \mu\text{m}$ feature is present, but this could be due to pyroxene. Spectral noise due to atmospheric absorptions complicates interpretations in the $6\ \mu\text{m}$ region, but there is no clear evidence for carbonate there either. We also observe multiple absorption features near $\sim 3.4\ \mu\text{m}$ in all spectra that could be due to carbonates. However, organics also have competing absorptions that overlap with these carbonate features in this region (Kaplan and Milliken, 2018, Kaplan et al., 2019), which renders interpretations based solely on this feature ambiguous. The $\sim 3.8\text{--}4\ \mu\text{m}$ absorption feature, which is more diagnostic of

carbonate, is absent in the spectra, as are any clear features that should be found at any of the longer wavelengths. In the absence of other carbonate features, the observed 3.4 μm features are better attributed to organic compounds that are known to occur in the Aguas Zarcas meteorite (Pizzarello, et al., 2020; Garvie, 2021; Kerraouch et al., 2022). In summary, some of the samples have clear carbonate, including as veins, but there is no clear evidence for carbonate in the spectral data at the spatial scale acquired here.

These observations provide important constraints on the detection limits of carbonate grains and veins at these spatial scales. Using OVIRS near-IR reflectance spectra, Kaplan et al. (2020) reported carbonate in dark boulders on asteroid Bennu that appeared to be associated with large veins that accounted for $<0.1\%$ area of the OVIRS footprint. Unlike the carbonate grains and veins that occur in our AZ samples, which are only observable in EPMA elemental oxide maps and not visually, the possible carbonate veins on Bennu are distinctly bright, linear features that are a few centimeters in width and meters long. Notably, Kaplan et al., (2020) also did not observe features near $\sim 4\ \mu\text{m}$ diagnostic of carbonate. The difference between the detection limits for these two observations may be explained in part by the difference in their spatial scale. The carbonate grains in the Aguas Zarcas samples are on the order a few to tens of microns in size and consequently are more intimately mixed with the dark fine-grained matrix of these meteorite sections. Multiple scattering effects at these smaller spatial scales can introduce nonlinear absorption effects in which opaque phases have a disproportionately strong effect on the absorption of photons. Consequently, photons interacting with these carbonate grains may be attenuated by subsequent interaction with fine-grained opaque particles. Regardless, the lack of obvious carbonate

features in the bulk reflectance spectra or lithology-averaged spectra of the AZ samples studied here highlights an important limitation on our spectral interpretations of dark, primitive meteoritic and asteroidal samples. The occurrence of these phases, even at minor abundances (<1 vol.%), has important implications for the history of fluid circulation and water-rock interactions on the parent bodies of these materials. Consequently, the lack of detection of carbonates in reflectance spectra of dark primitive chondritic materials or asteroids does not necessarily imply their absence, and they may even occur as vein material.

2.6 Conclusions

We have performed a coordinated petrographic and spectroscopic investigation of several sections of the Aguas Zarcas meteorite. These sections exhibit a wide range of petrographic features and host at least three separate lithologies that to some level appear to have a shared petrogenesis. Our findings include new observations of carbonate veining between the CM1/2 and CM lithologies (in sections UM-2 and UM-3), suggesting at least one episode of post-brecciation aqueous alteration, with a possible additional episode occurring prior. By comparing the relative abundance of olivine, pyroxene, and matrix phyllosilicates in these lithologies, we determined that pyroxene may be preferentially consumed at a rate of 2:1 compared to olivine during the progressive aqueous alteration that leads to the formation of matrix phyllosilicates. These insights contribute to a deeper understanding of the alteration processes that have shaped the Aguas Zarcas meteorite.

Our spectroscopic investigations of each section reveal that each lithology (Met-1, CM1/2, CM) exhibits a distinct spectral signature that appears to be influenced by the relative abundance of mafic silicates found in chondrules and lithic fragments (olivine and pyroxene) to matrix phyllosilicates. Specifically, pyroxene appears to be the principal component responsible for the transition in spectral features in the MIR while olivine is systematically underestimated. We also observed a rough negative correlation between the wavelength position and strength of the 3 μm absorption feature and the abundance of phyllosilicate matrix. This correlation may serve as a useful tool for estimating phyllosilicate abundance within the context of the Aguas Zarcas lithologies. In the broader context of CM chondrites as a group, our findings indicate that the AZ sections with the highest petrologic subtypes feature 3 μm absorption positions that are too low. Additionally, we found no correlation with the relative abundance of either the Mg-rich or Fe-rich phyllosilicate component of the matrix.

The efficacy of linear mixing models as a method to interpret composition were also explored here. Our findings indicate that linear unmixing at the component/pixel-level of our μFTIR -generated spectral maps produced the most accurate results, with errors typically on the order of 5–10 vol.%. Conversely, linear unmixing of the bulk spectrum using endmember spectra acquired from the lithologies themselves performed much poorer, with errors averaging on the tens of vol.%. Taken together, this supports the idea that dark and primitive planetary materials can be effectively analyzed for composition using μFTIR spectral mapping techniques when measurement spot sizes are at least on the order of some of the smallest components (a few tens of microns). Spectral unmixing methods that use

laboratory-derived spectra to model a laboratory-, spacecraft-, or telescope-derived bulk reflectance spectrum may however present additional challenges that should continue to be explored and mitigated. Refinement of these spectral unmixing methods, especially for bulk sample analysis, remains crucial for advancing our compositional analysis capabilities.

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2.8 Figures and Tables

Table 1: Number of pixels (spectra) and pixel size for the μ FTIR infrared spectral maps made for each of the four Aguas Zarcas sections. Here pixel size refers to the side length of the square spectral footprint for each measurement. The measurement area was quadrupled (side length doubled) for the Field-1 because of its much larger size compared to the other sections analyzed.

	Total Number of Map Pixels (Spectra)	Pixel Size (Spectral Footprint)
UM-1 (Met-1)	1951	70 μm
Field-1 (CM1/2)	1470	140 μm
UM-2 (CM1/2 CM)	829	70 μm
UM-3 (CM1/2 CM)	797	70 μm

Table 2: Estimates of major mineral phases present in each Aguas Zarcas section and lithology. These estimates are based on a Maximum Likelihood supervised classification algorithm performed on the nine-element EPMA maps acquired for each section.

Component	Percent abundance of section / lithology (%)					
	UM-1	Field-1	UM-2		UM-3	
	(Met-1)	(CM1/2)	(CM1/2)	(CM)	(CM1/2)	(CM)
Chondrule	26.31	11.19	5.55	24.46	15.00	38.70
Olivine	10.05	6.45	5.55	15.22	9.57	12.74
Pyroxene (low-Ca)	10.69	4.53	n.d.	9.24	0.99	7.32
Pyroxene (high-Ca)	4.03	0.22	n.d.	n.d.	1.94	18.64
Matrix	68.88	87.84	92.06	70.92	83.50	55.10
Mg-phylllosilicate	50.07	40.36	47.13	35.15	36.73	n.d.
Fe-phylllosilicate	18.81	44.38	44.93	35.77	46.77	55.10
CAI	1.57	n.d.	0.37	n.d.	n.d.	n.d.
Sulfide	0.43	0.25	1.31	3.85	0.78	5.96
Metal	1.94	n.d.	n.d.	n.d.	0.03	n.d.
Carbonate	0.88	0.72	0.70	0.46	0.68	0.24

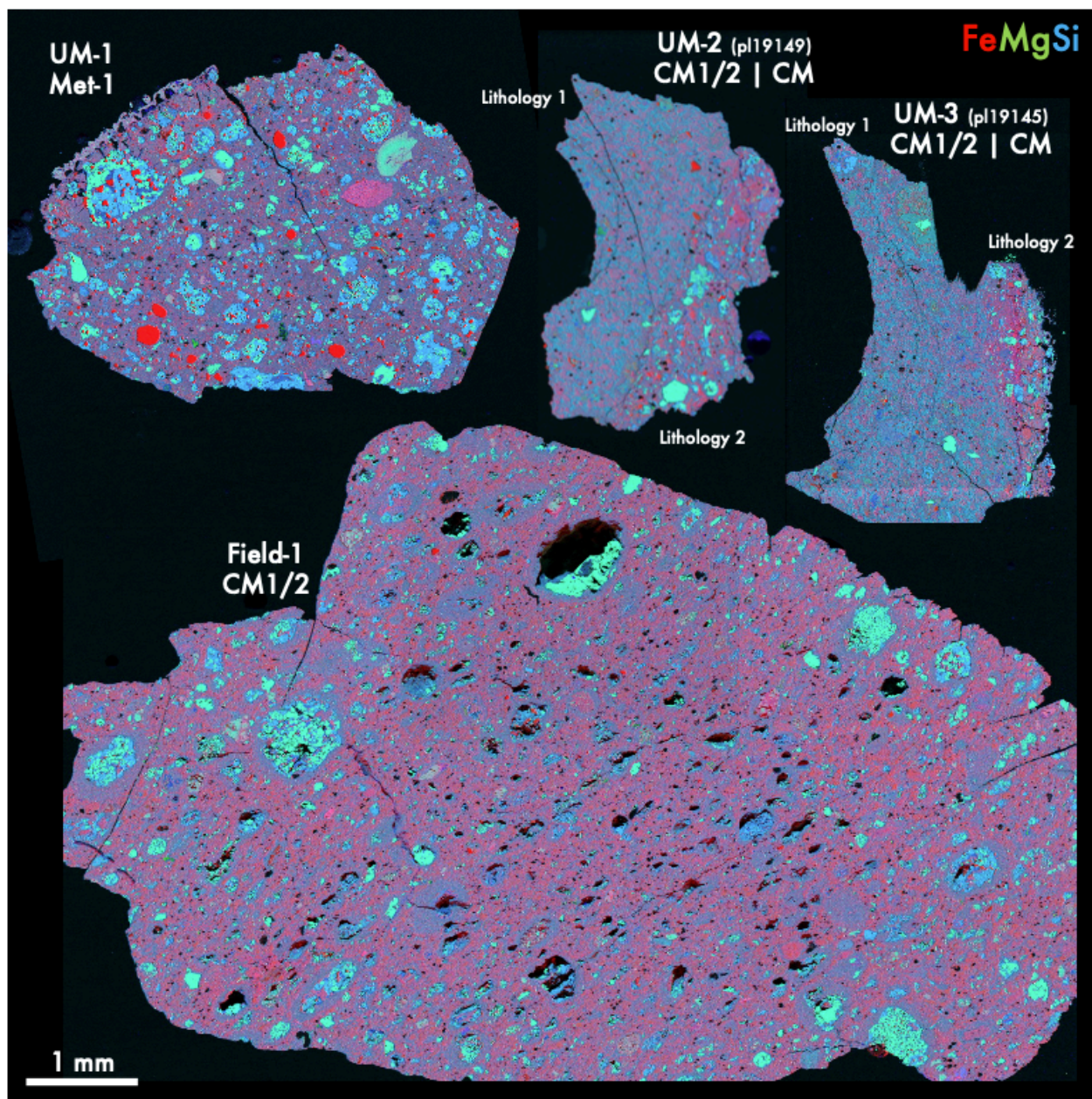


Figure 1: A false color FeO-MgO-SiO₂ (RGB) elemental oxide map of the four Aguas Zarcas sections studied. Metal appears as bright red, forsteritic olivine appears as seafoam green, Mg-rich low-Ca pyroxene appears as light blue, and fine-grained matrix phyllosilicates appear as varying shades of red and blue.

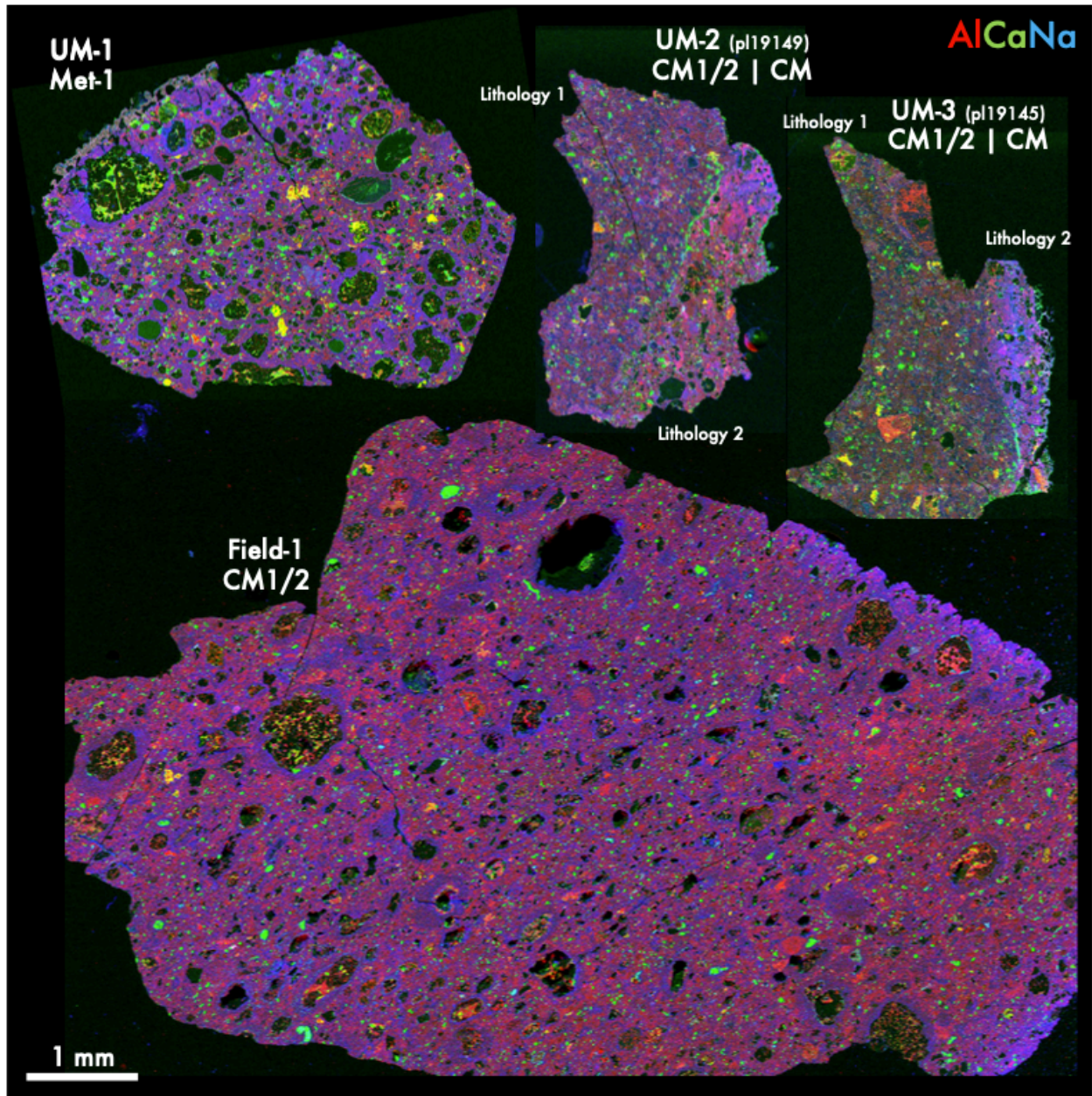


Figure 2: (a) As in Figure 1, a false color Al_2O_3 -CaO- Na_2O (RGB) elemental oxide map. (b) Enlarged Al-Ca-Na maps of the UM-2 and UM-3 sections to highlight the Ca-rich carbonate veins (bright green) present that lie along portions of the boundary separating the two lithologies present in each section.

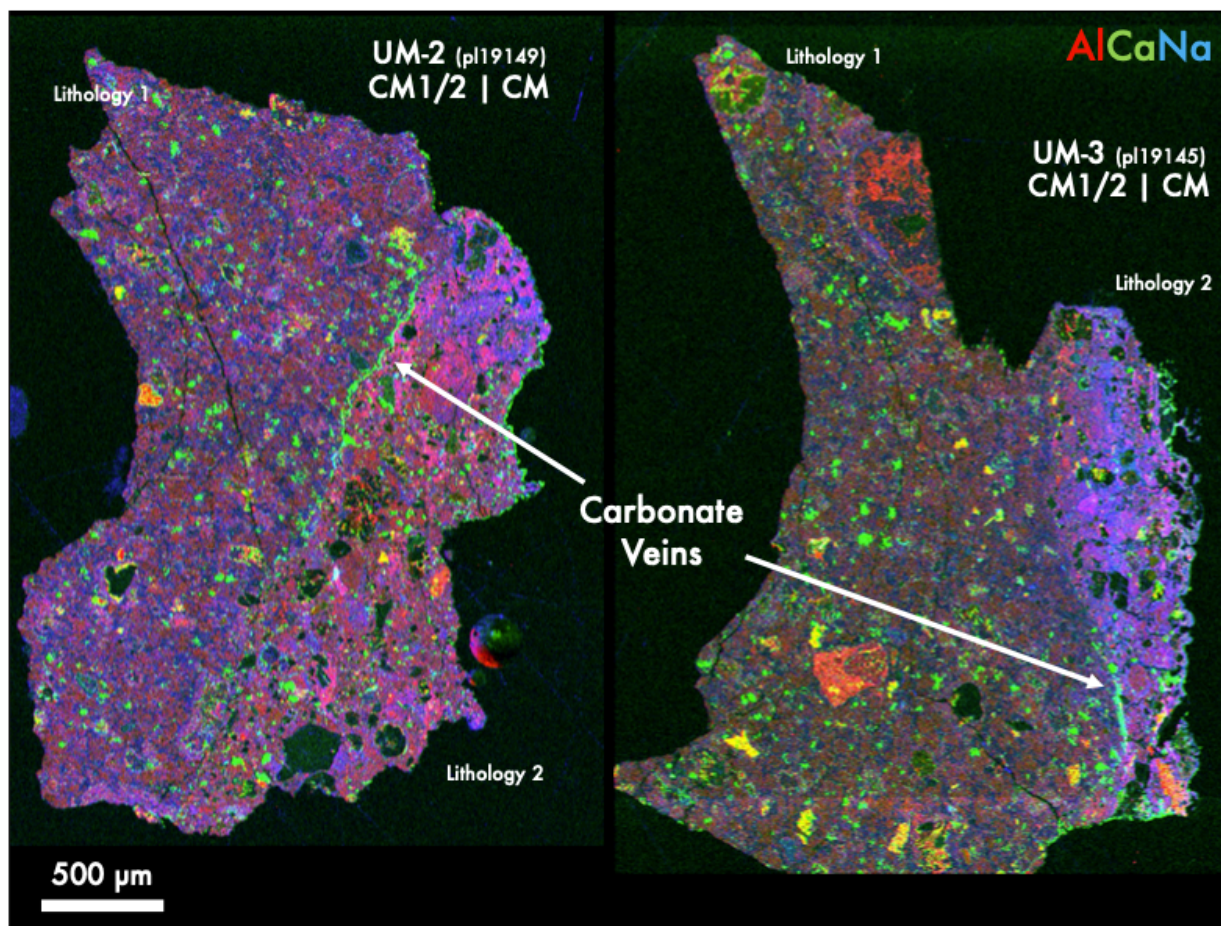


Figure 2: (a) As in Figure 1, a false color Al-Ca-Na (RGB) elemental map. (b) Enlarged Al-Ca-Na maps of the UM-2 and UM-3 sections to highlight the Ca-rich carbonate veins (bright green) present that lie along portions of the boundary separating the two lithologies present in each section.

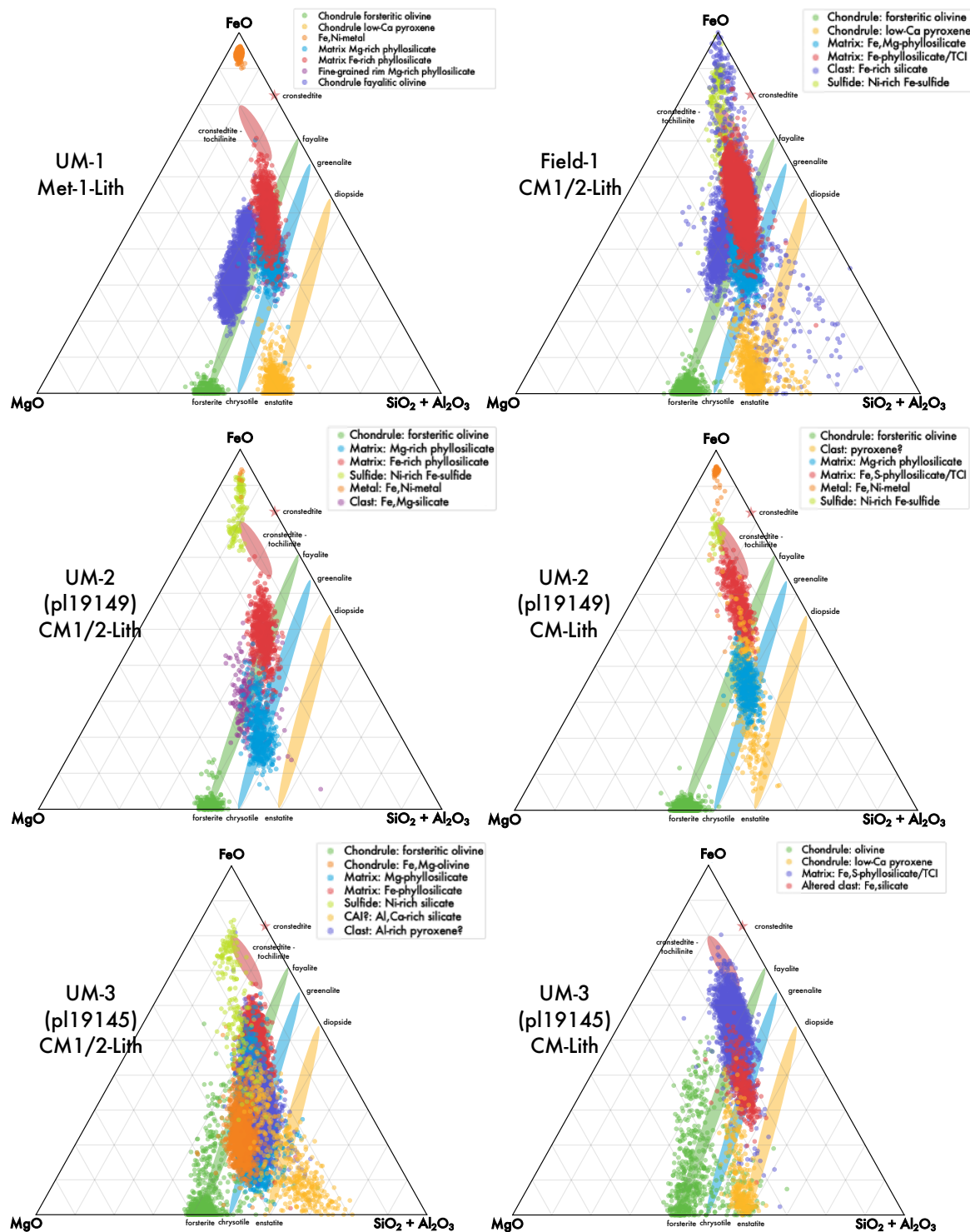


Figure 3: FeO-MgO-SiO₂+Al₂O₃ ternary diagrams showing the chemistries of some of the major components for each section and lithology. Color background fields represent the stoichiometric chemistries for some of the most common phases present in CM chondrites.

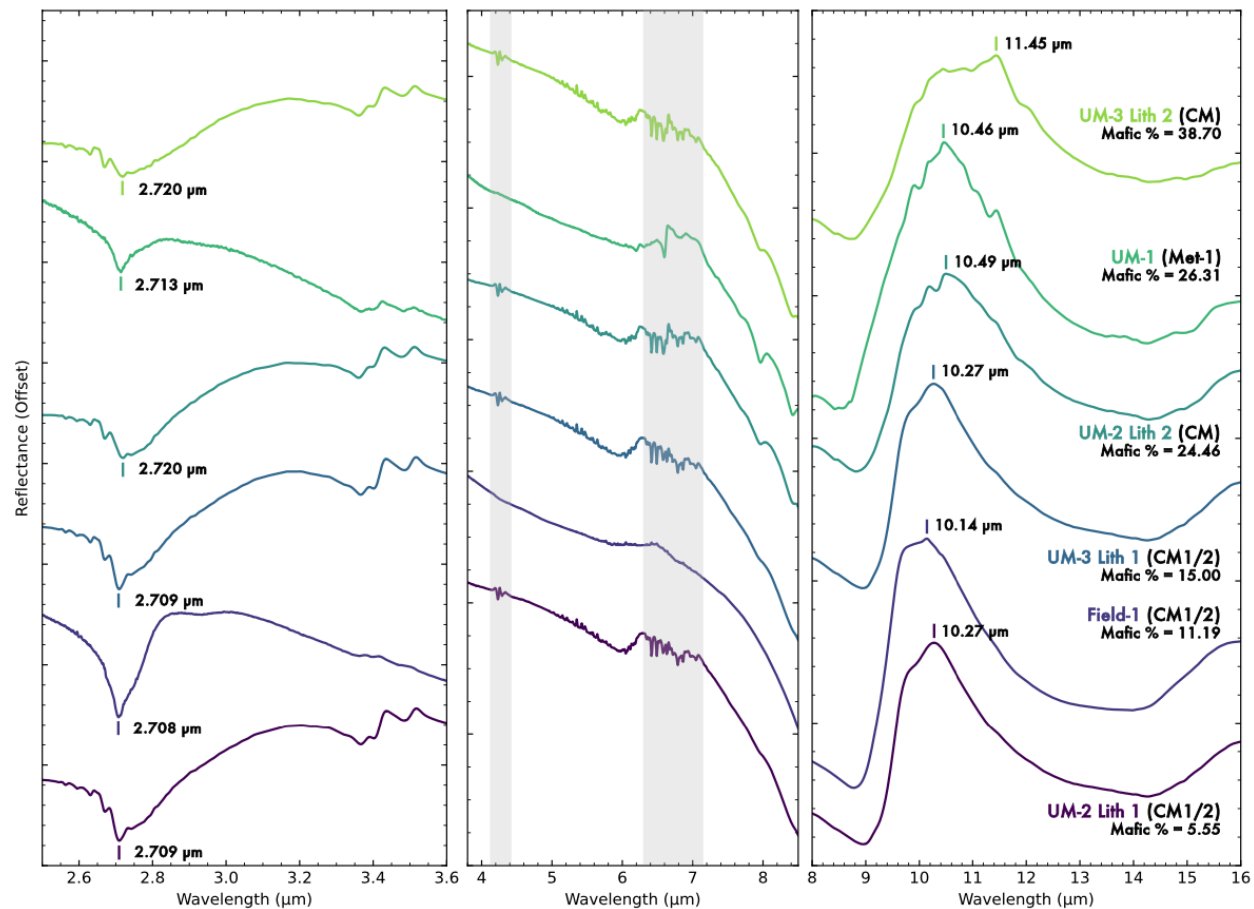


Figure 4: Bulk infrared reflectance spectra for each section and lithology studied. All spectra are offset and organized into three separate spectral regions to enhance spectral contrast for comparison.

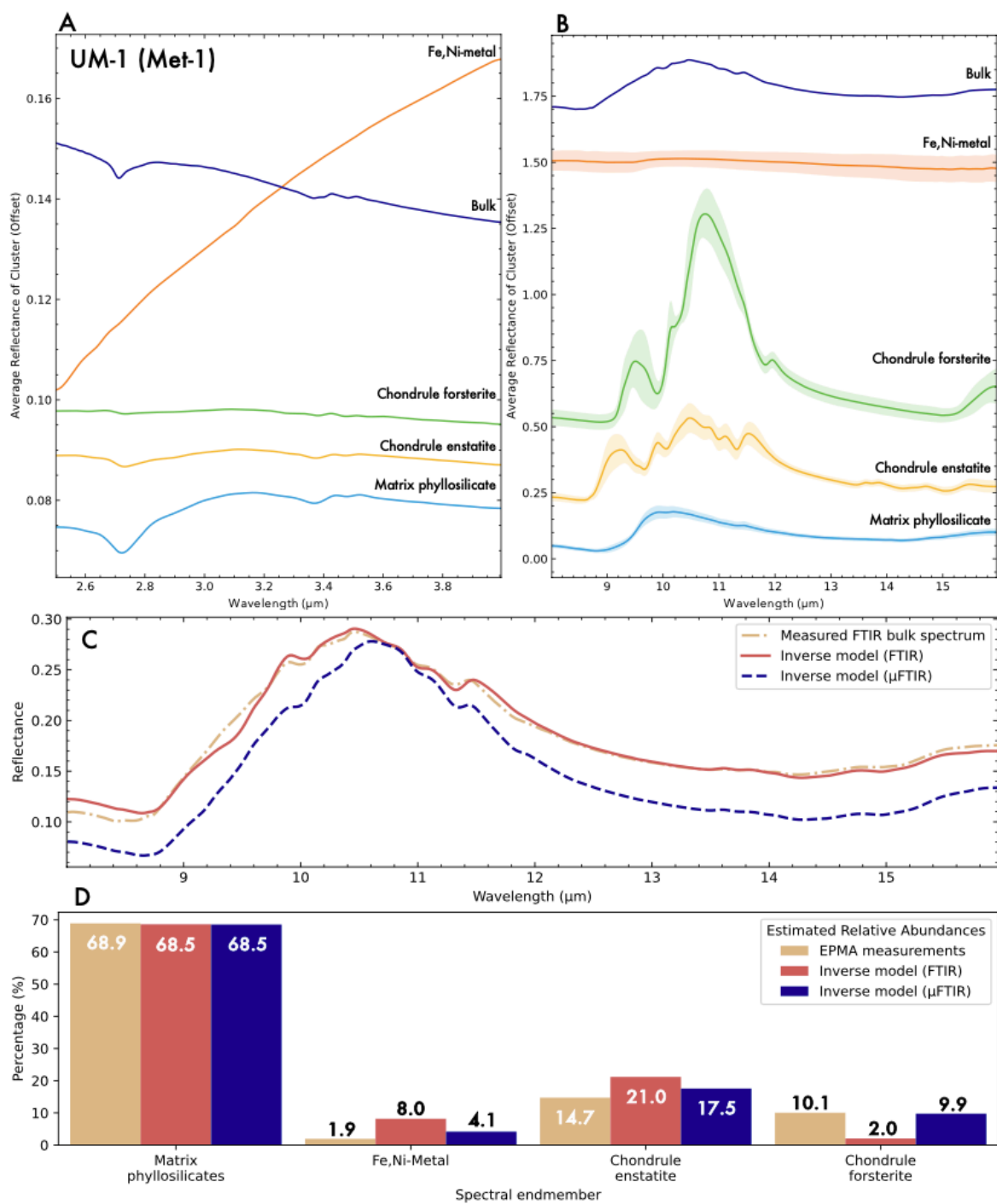


Figure 5: UM-1. The μFTIR map-derived spectral endmembers used for linear inverse modeling of the bulk spectrum for the 3 μm region (Panel A) and the MIR region (Panel B). Panel C shows the estimated spectral contribution of each endmember predicted from the bulk spectrum inverse modeling and μFTIR spectral inverse modeling compared to EPMA estimated abundances. Panel D shows the forward modeled spectra based on the estimated abundances in Panel C.

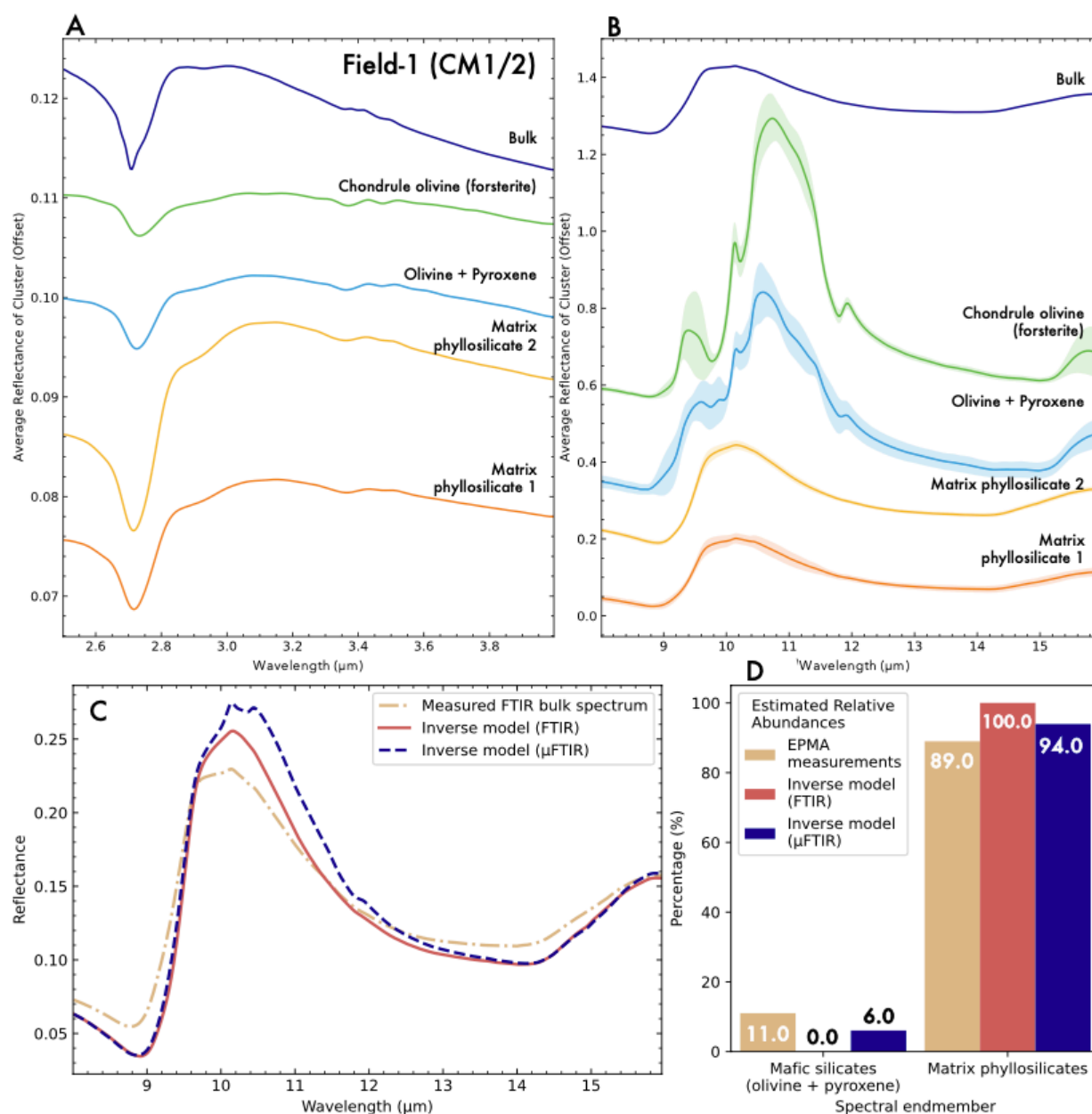


Figure 6: Field-1. The μFTIR map-derived spectral endmembers used for linear inverse modeling of the bulk spectrum for the 3 μm region (Panel A) and the MIR region (Panel B). Panel C shows the estimated spectral contribution of each endmember predicted from the bulk spectrum inverse modeling and μFTIR spectral inverse modeling compared to EPMA estimated abundances. Panel D shows the forward modeled spectra based on the estimated abundances in Panel C.

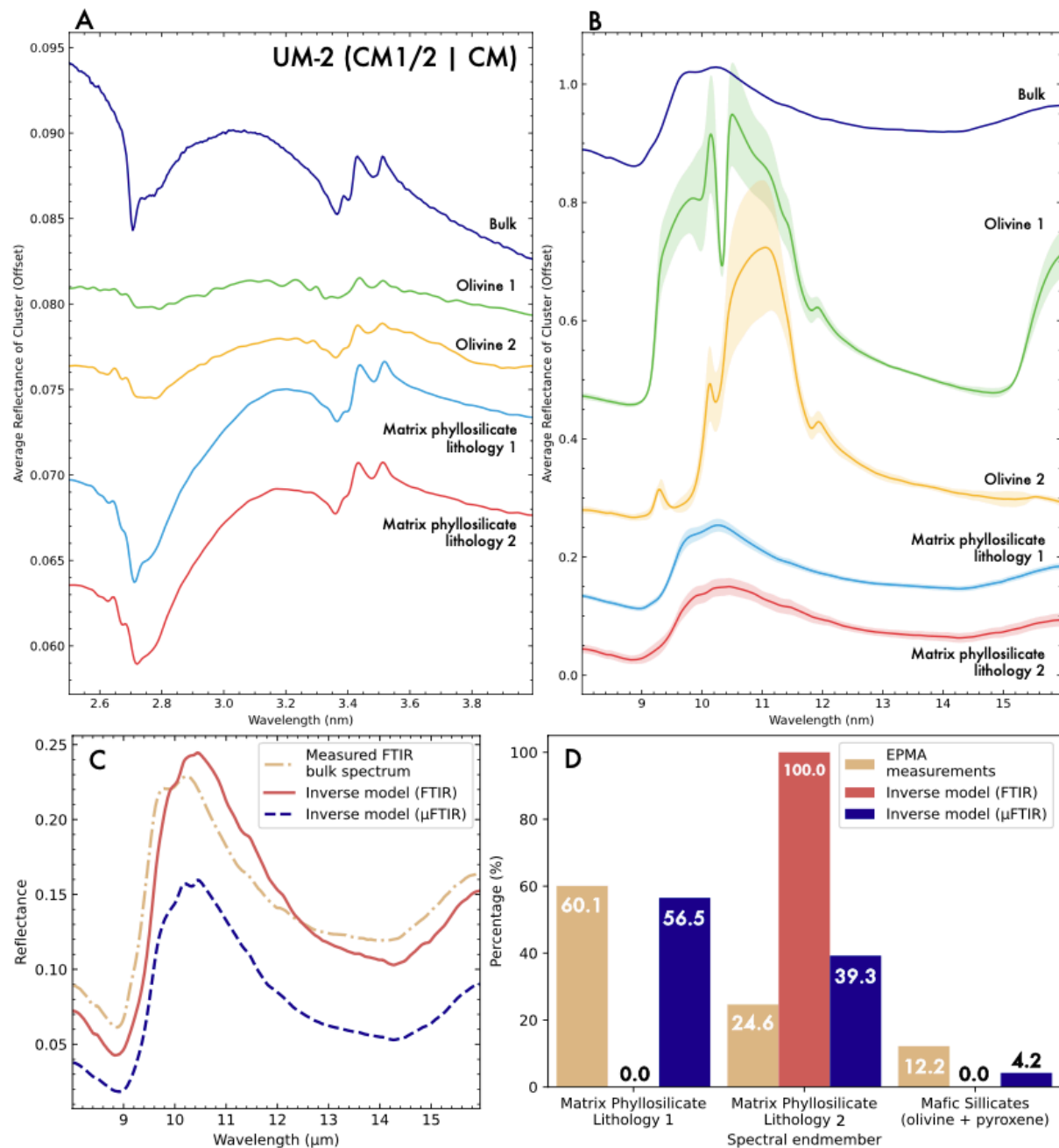


Figure 7: UM-2. The μ FTIR map-derived spectral endmembers used for linear inverse modeling of the bulk spectrum for the 3 μ m region (Panel A) and the MIR region (Panel B). Panel C shows the estimated spectral contribution of each endmember predicted from the bulk spectrum inverse modeling and μ FTIR spectral inverse modeling compared to EPMA estimated abundances. Panel D shows the forward modeled spectra based on the estimated abundances in Panel C.

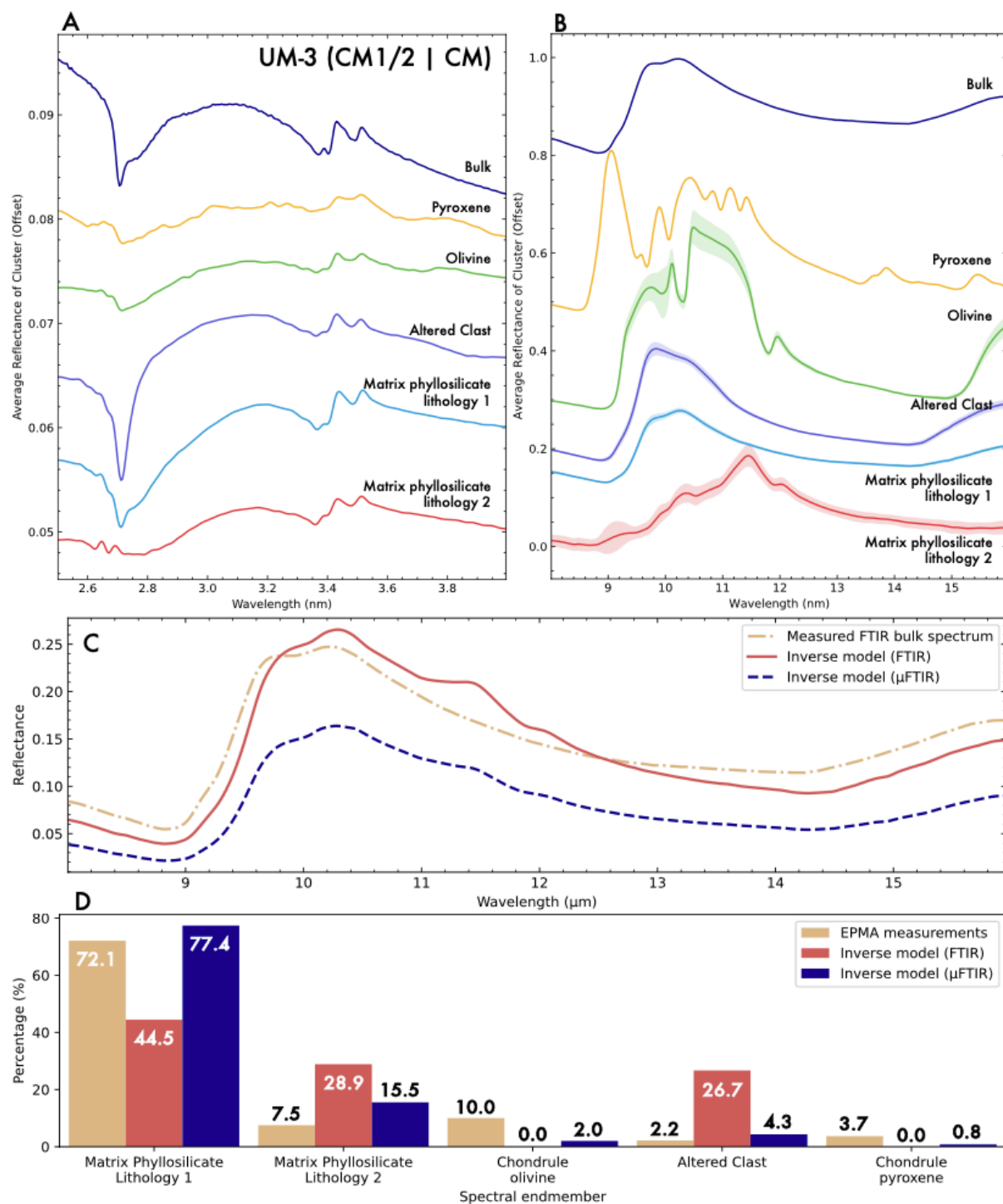


Figure 8: UM-3. The μFTIR map-derived spectral endmembers used for linear inverse modeling of the bulk spectrum for the 3 μm region (Panel A) and the MIR region (Panel B). Panel C shows the estimated spectral contribution of each endmember predicted from the bulk spectrum inverse modeling and μFTIR spectral inverse modeling compared to EPMA estimated abundances. Panel D shows the forward modeled spectra based on the estimated abundances in Panel C.

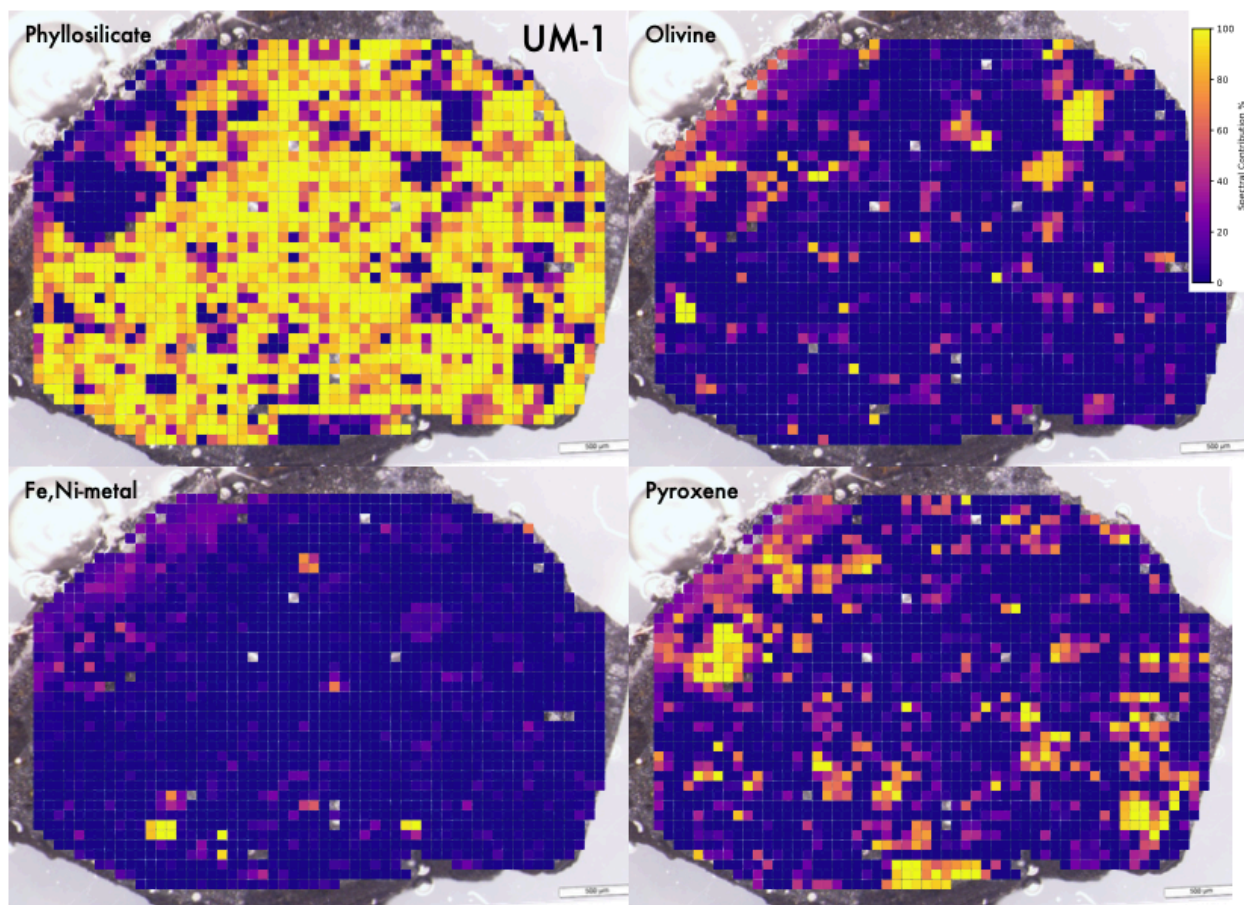


Figure 9: Spectral contribution maps from the μ FTIR spectral inverse modeling for UM-1.

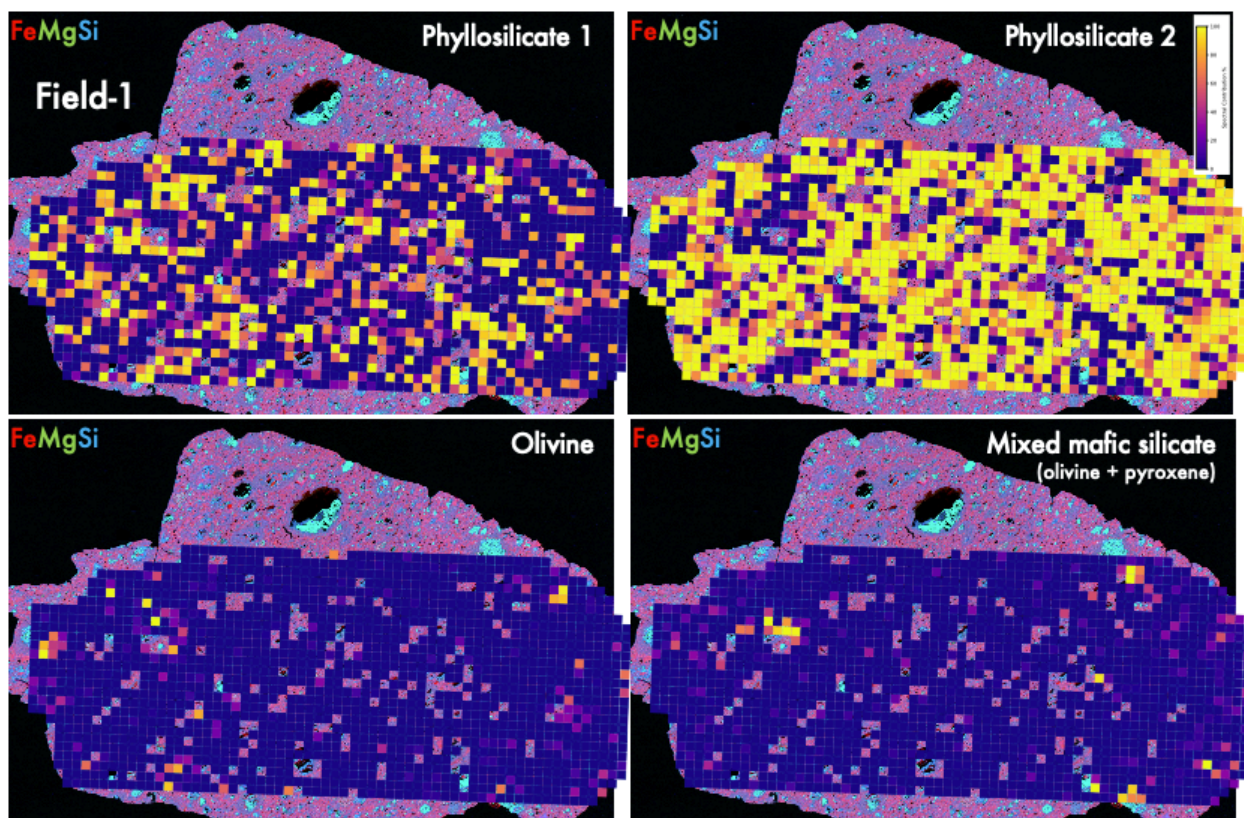


Figure 10: Spectral contribution maps from the μ FTIR spectral inverse modeling for Field-1.

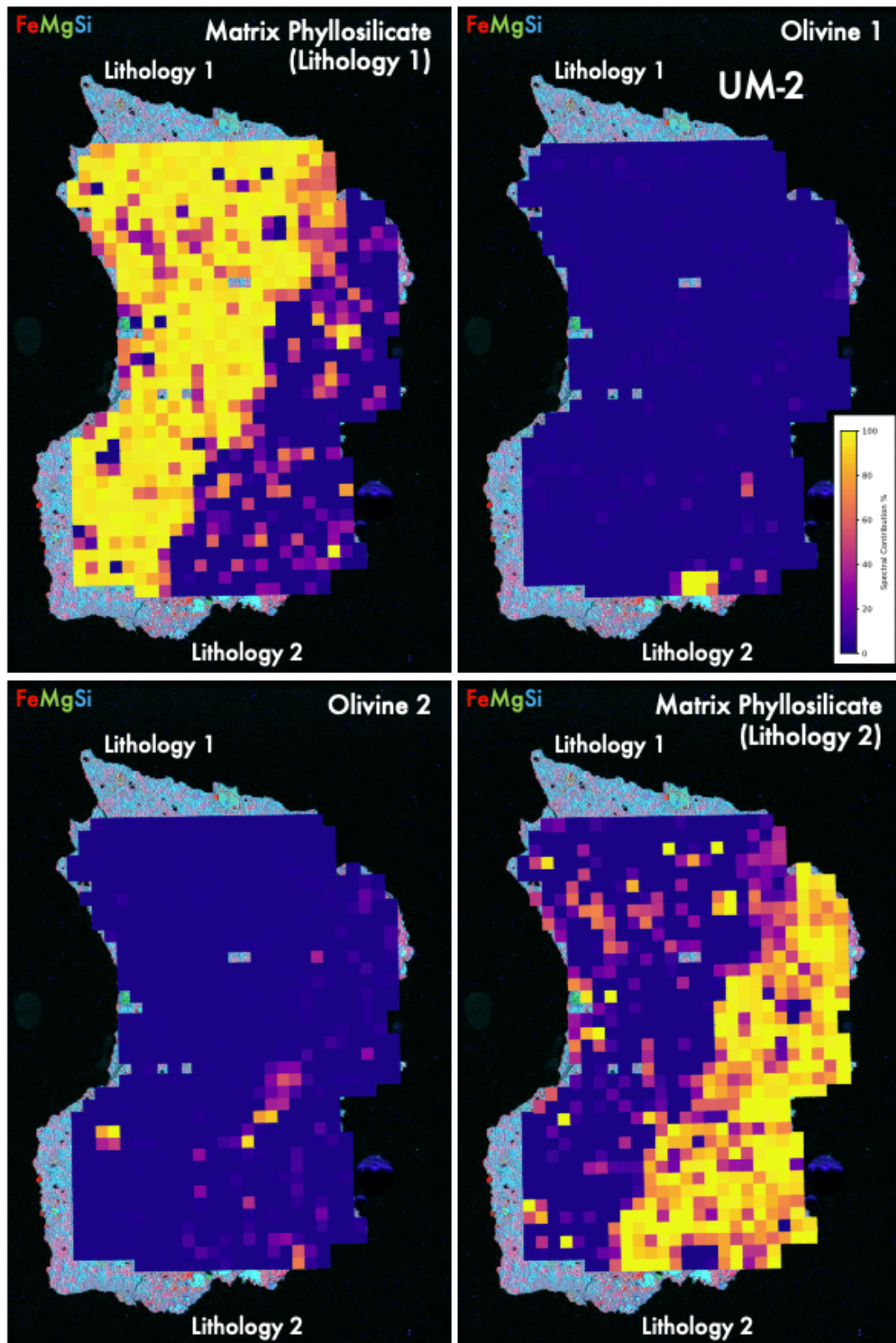


Figure 11: Spectral contribution maps from the μ FTIR spectral inverse modeling for UM-2.

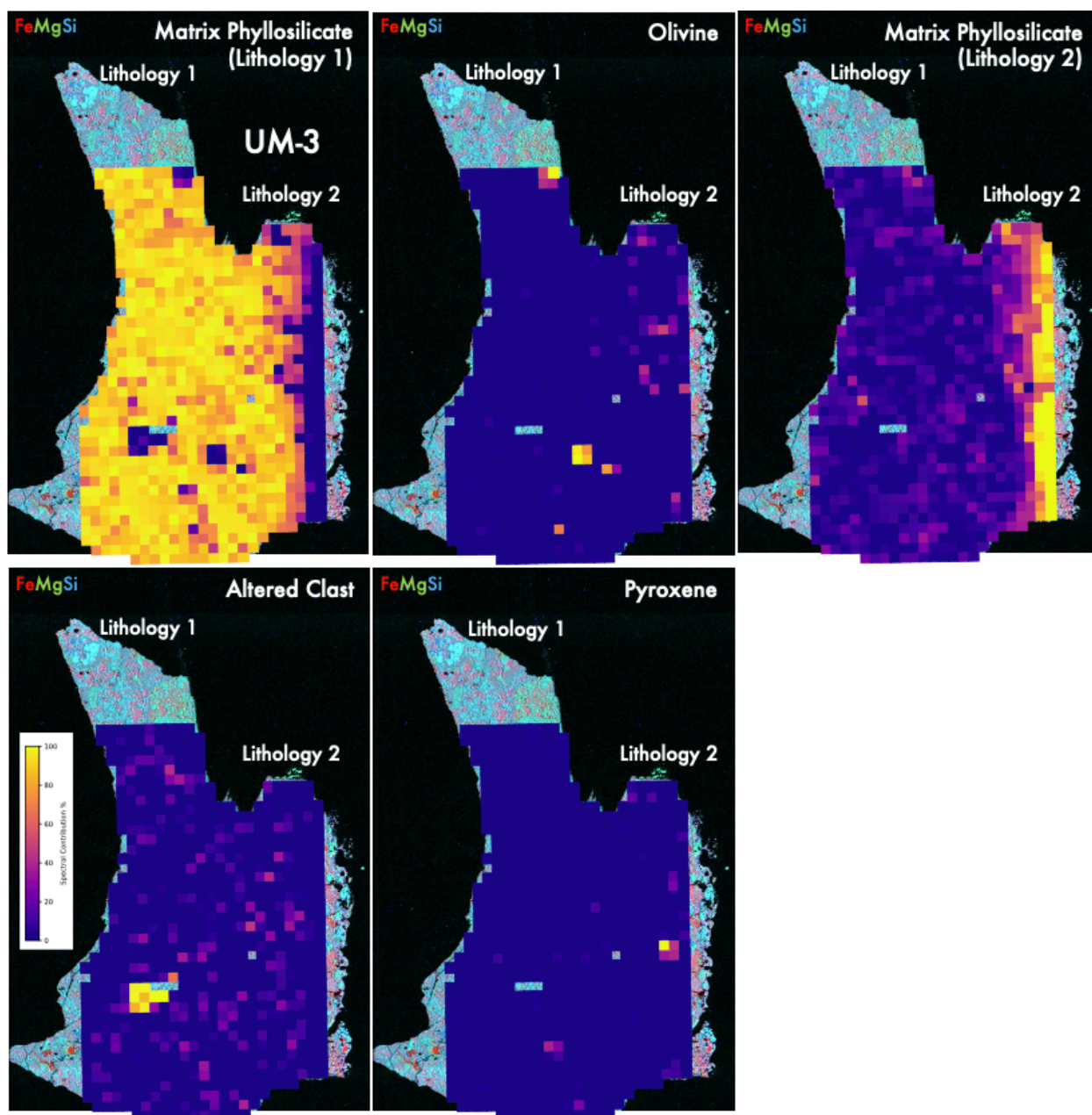


Figure 12: Spectral contribution maps from the μ FTIR spectral inverse modeling for UM-3.

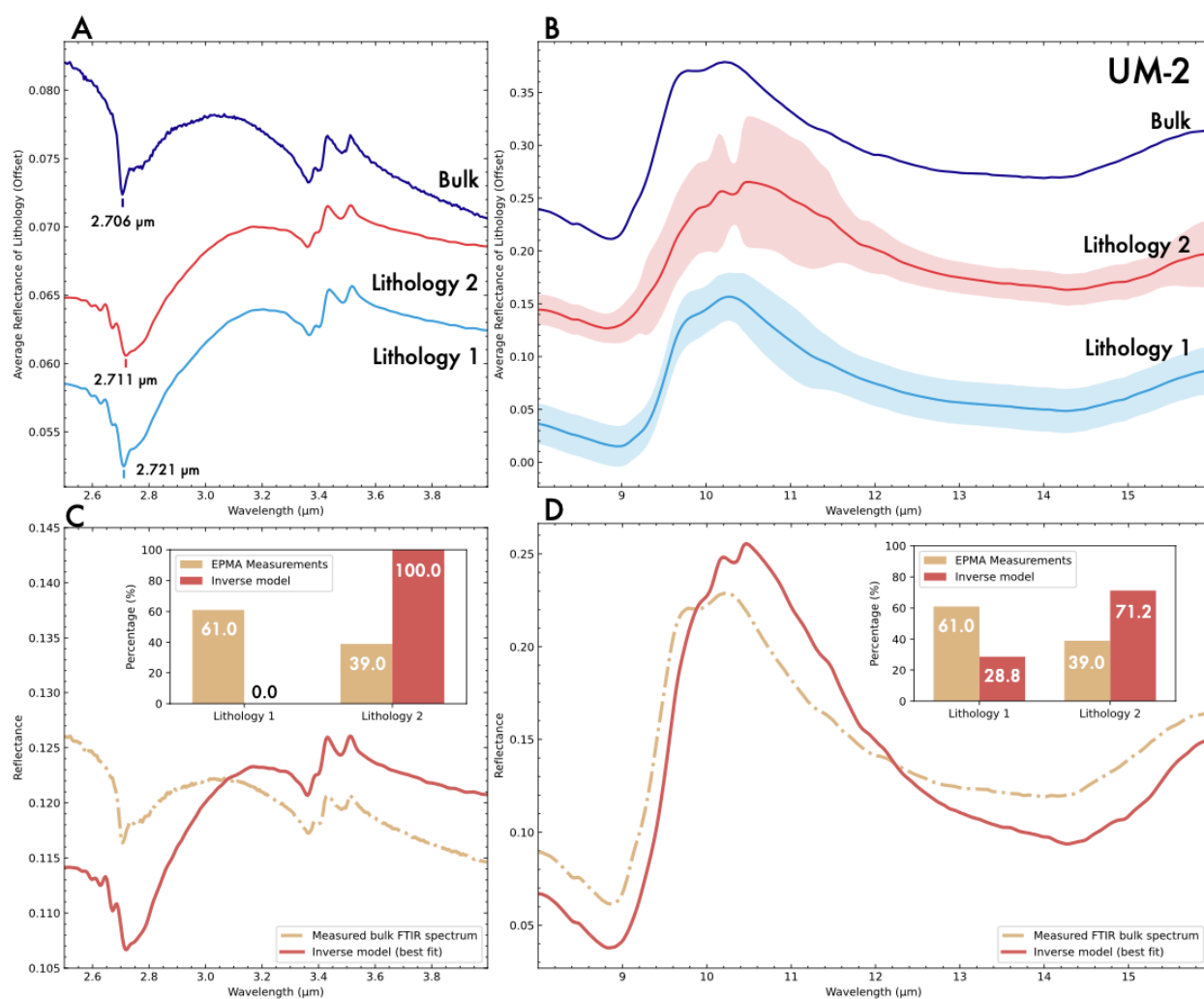


Figure 13: UM-2. Panels A and B show the average spectrum for the CM1/2 and CM lithologies alongside the bulk FTIR spectrum acquired over both lithologies in both the 3 μm region (A) and MIR region (B). Panels C and D shows the estimated spectral contribution of each lithology (inset) as well as the forward modeled bulk spectrum based on these estimates.

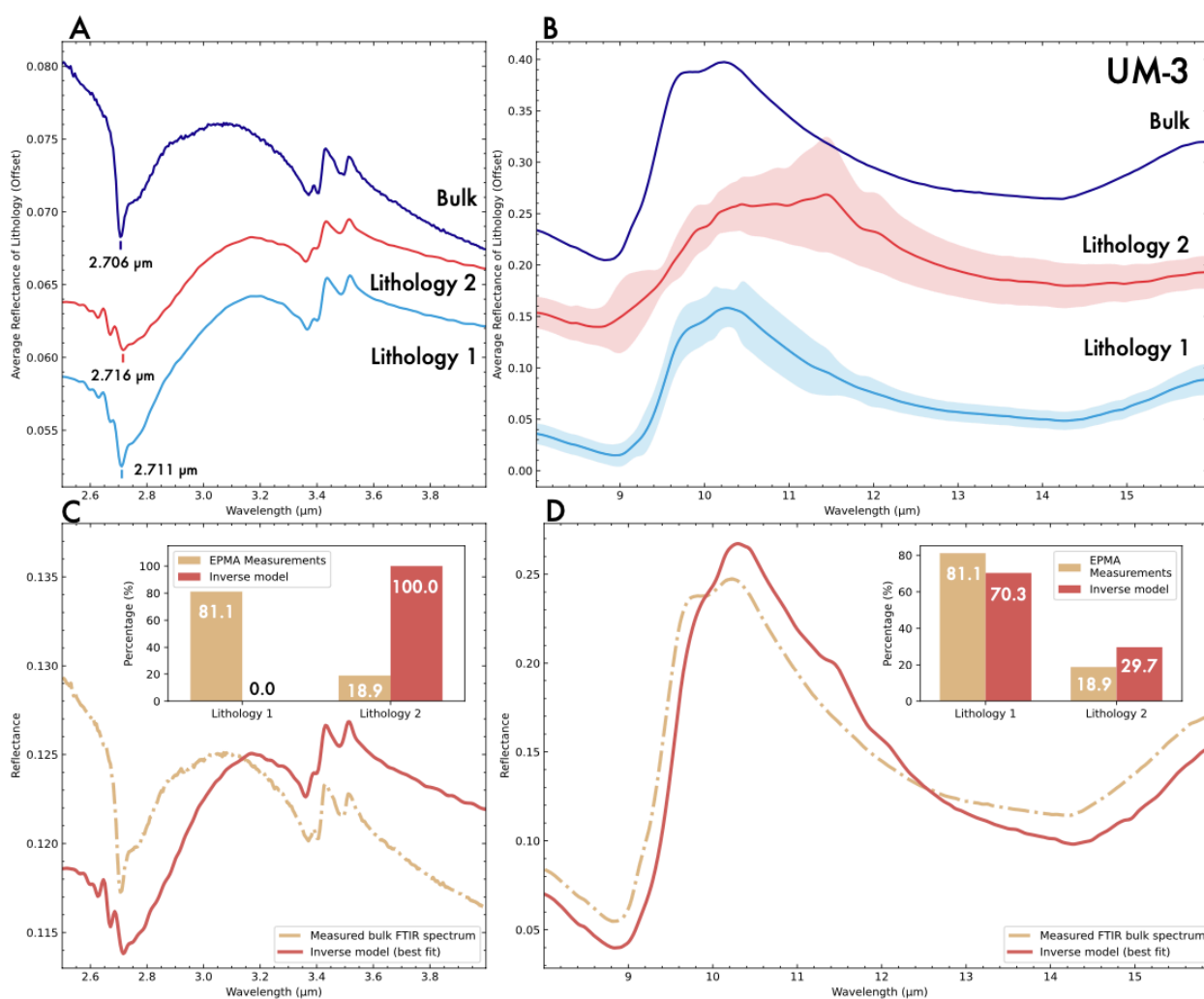


Figure 14: UM-3. Panels A and B show the average spectrum for the CM1/2 and CM lithologies alongside the bulk FTIR spectrum acquired over both lithologies in both the 3 μm region (A) and MIR region (B). Panels C and D shows the estimated spectral contribution of each lithology (inset) as well as the forward modeled bulk spectrum based on these estimates.

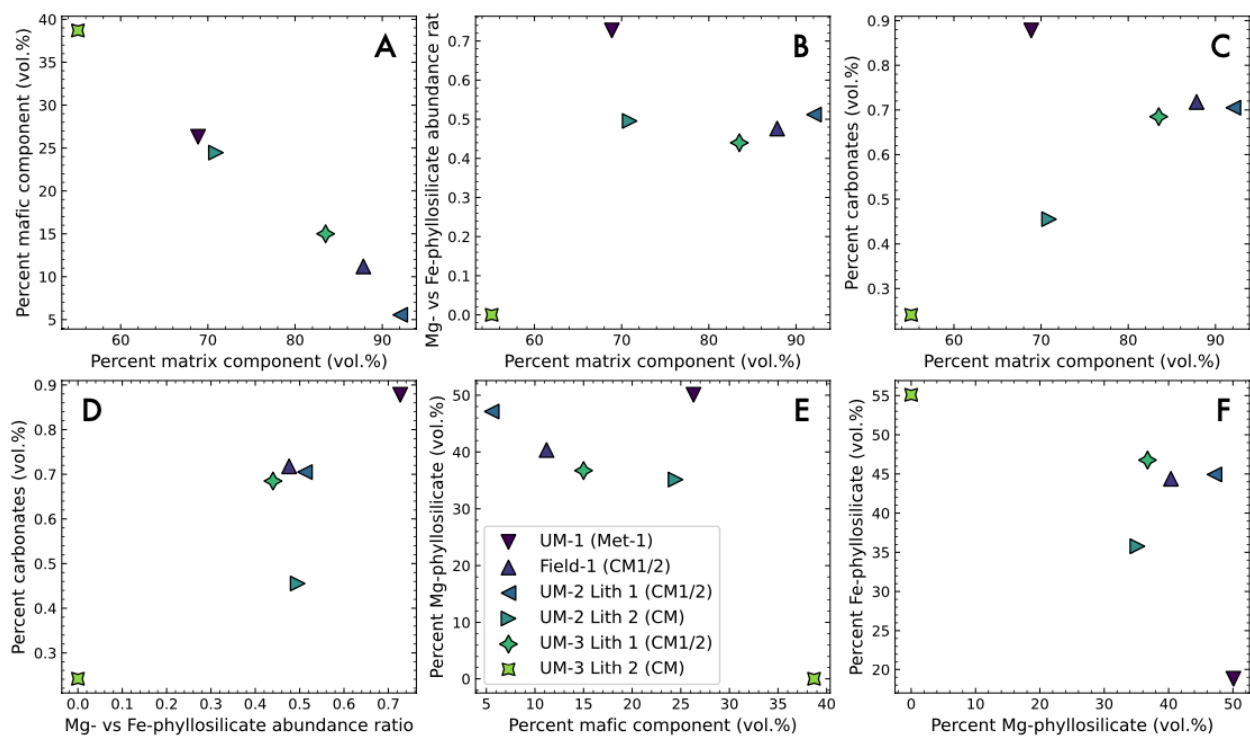


Figure 15: Volume percent estimates of the major petrographic features, including volume percent matrix component, mafic component, carbonate component, and Mg-/Fe-phyllsilicate component for all sections and lithologies. These quantities are derived from the Maximum Likelihood supervised classification algorithm performed on the nine-element EPMA maps.

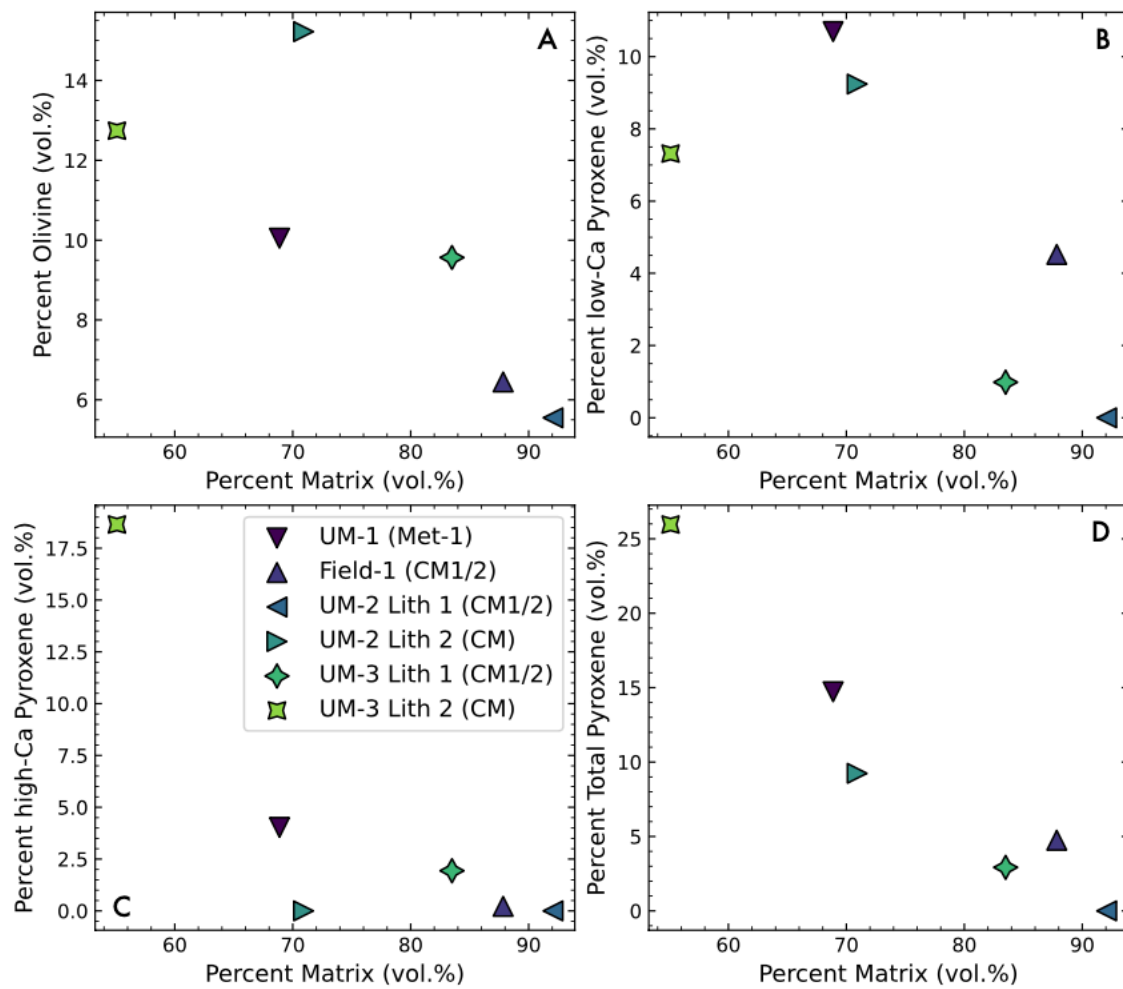


Figure 16: Like Figure 15, volume percent estimates of the major phases present for each section and lithology, including volume percent matrix, olivine, low-Ca pyroxene, high-calcium Pyroxene, and total pyroxene component.

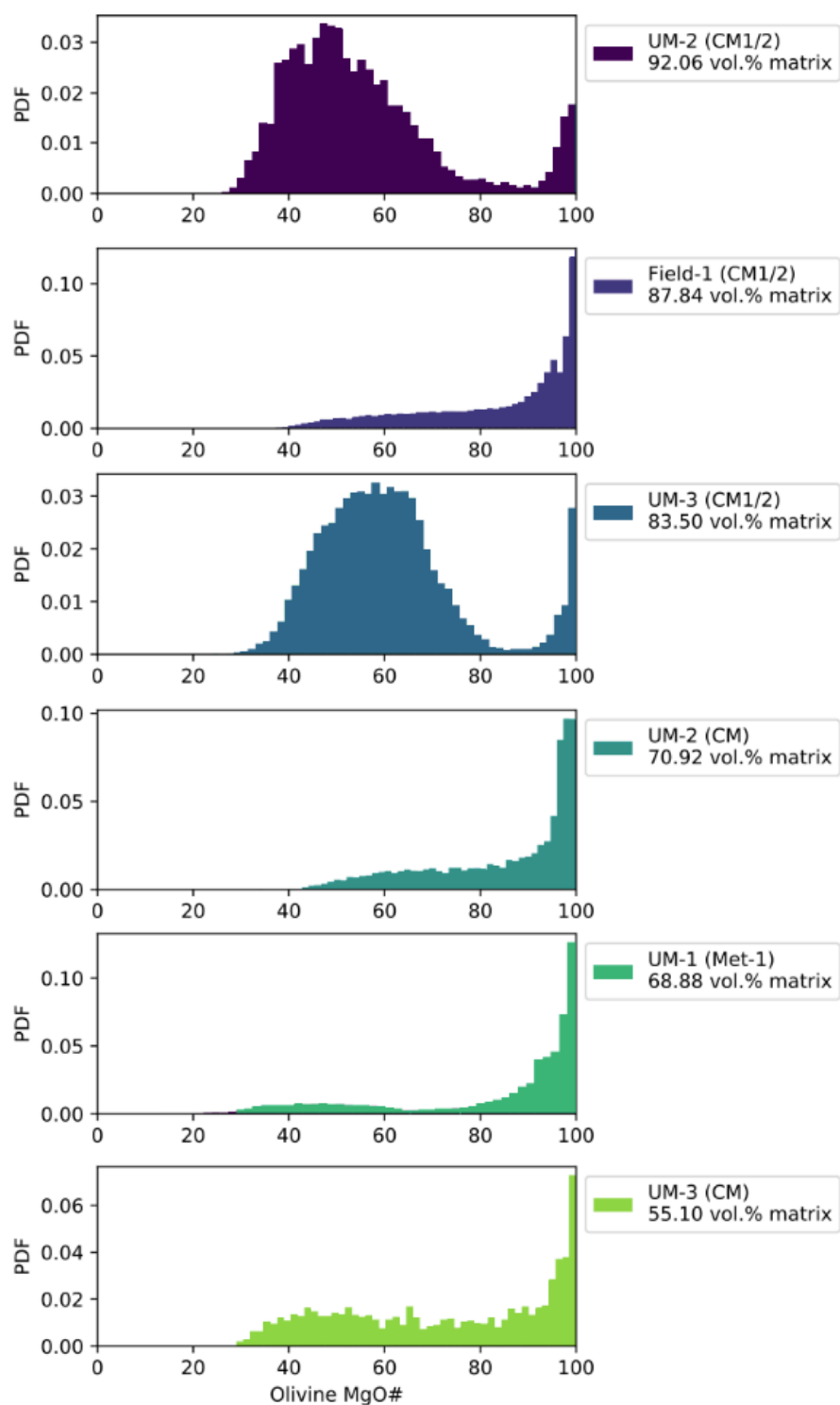


Figure 17: Probability Density Functions showing the MgO numbers ($\text{MgO}/(\text{MgO} + \text{FeO})$) for each olivine class pixel for each section and lithology. Plots are organized from bottom to top by increasing percent volume matrix component. Though the Field-1 section is classified as a CM1/2 lithology based on matrix abundance, its olivine chemistry appears more consistent with the CM lithologies found in the UM-2 and UM-3 sections.

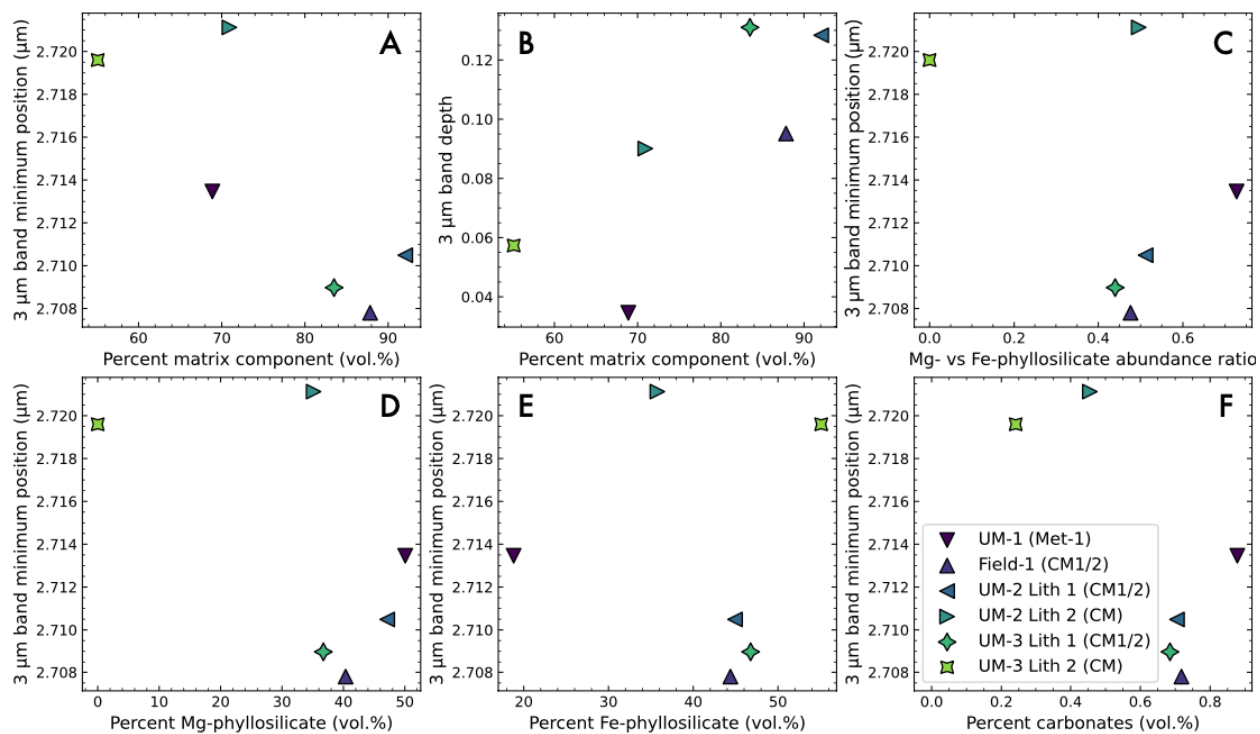


Figure 18: A comparison of key spectral parameters (3 μm band minimum position, 3 μm band depth) with key petrographic features (volume percent matrix, etc.) for each section and lithology.

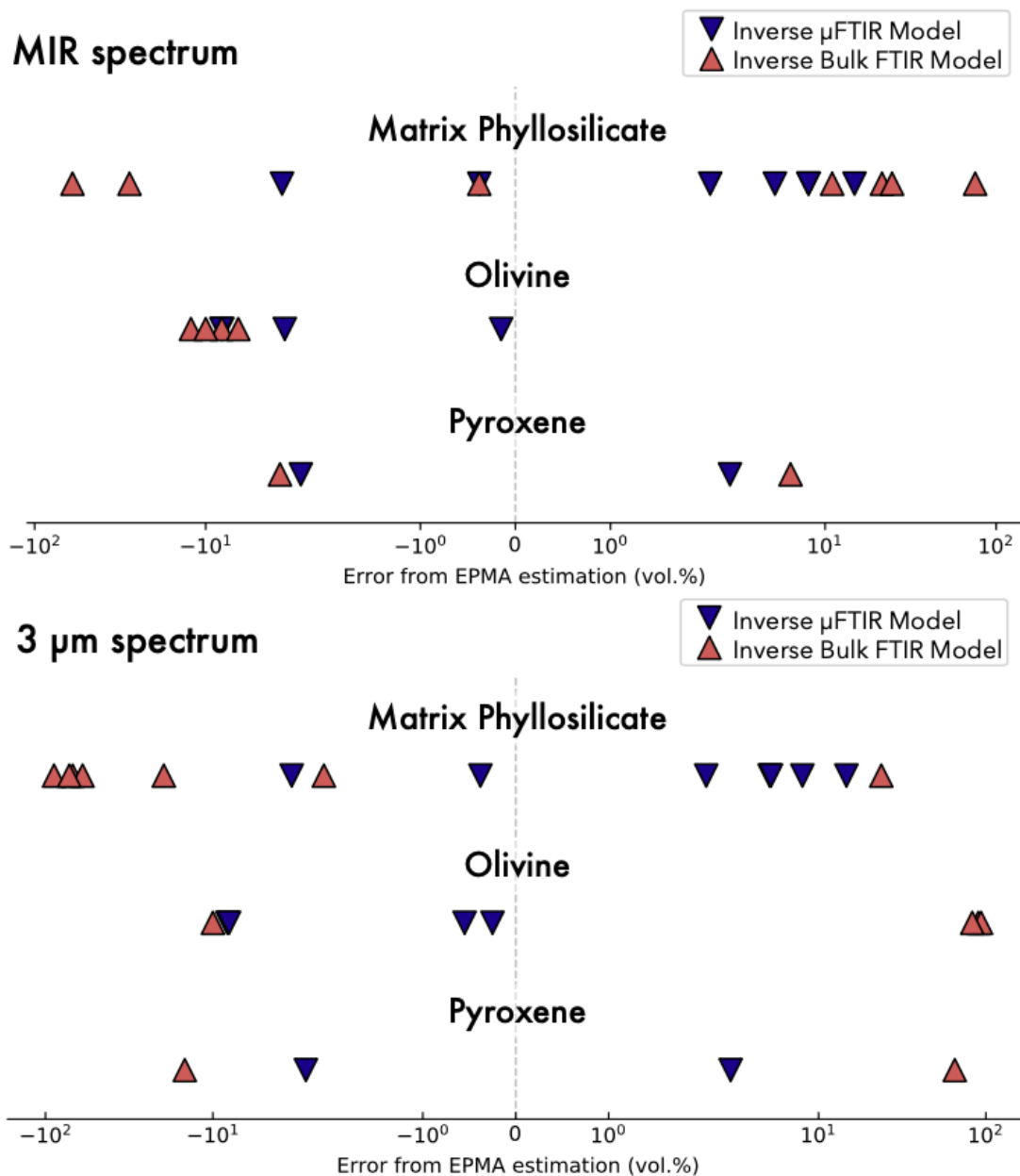
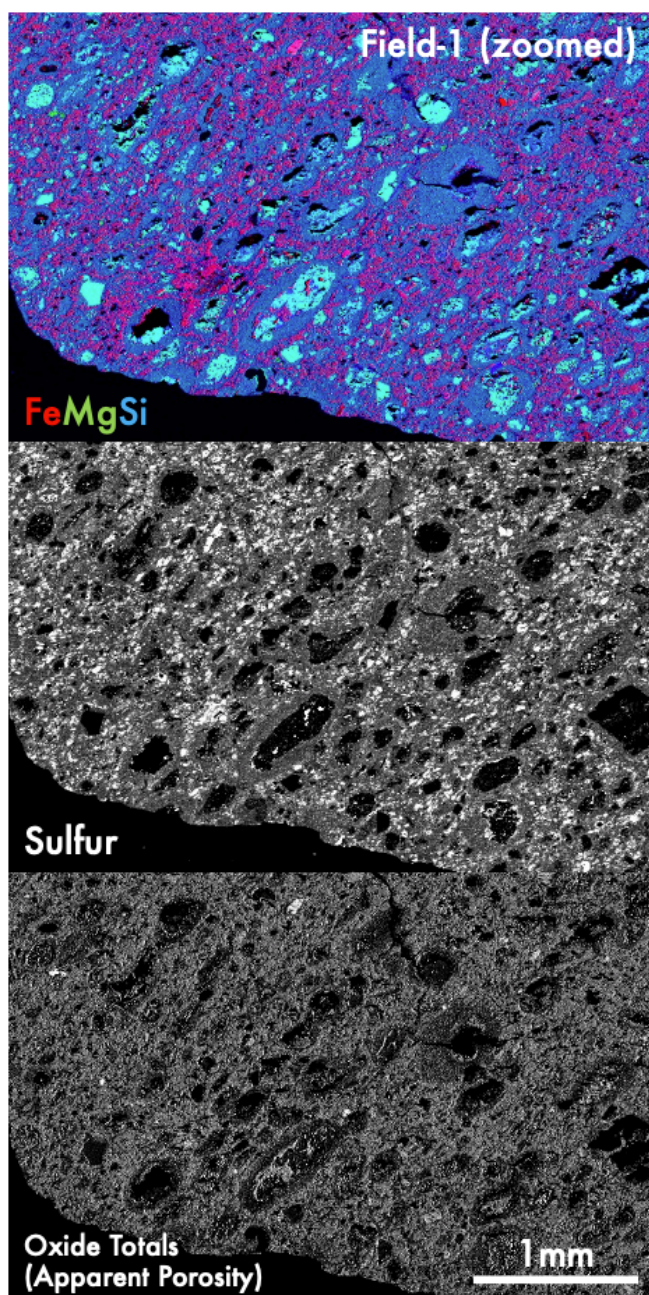
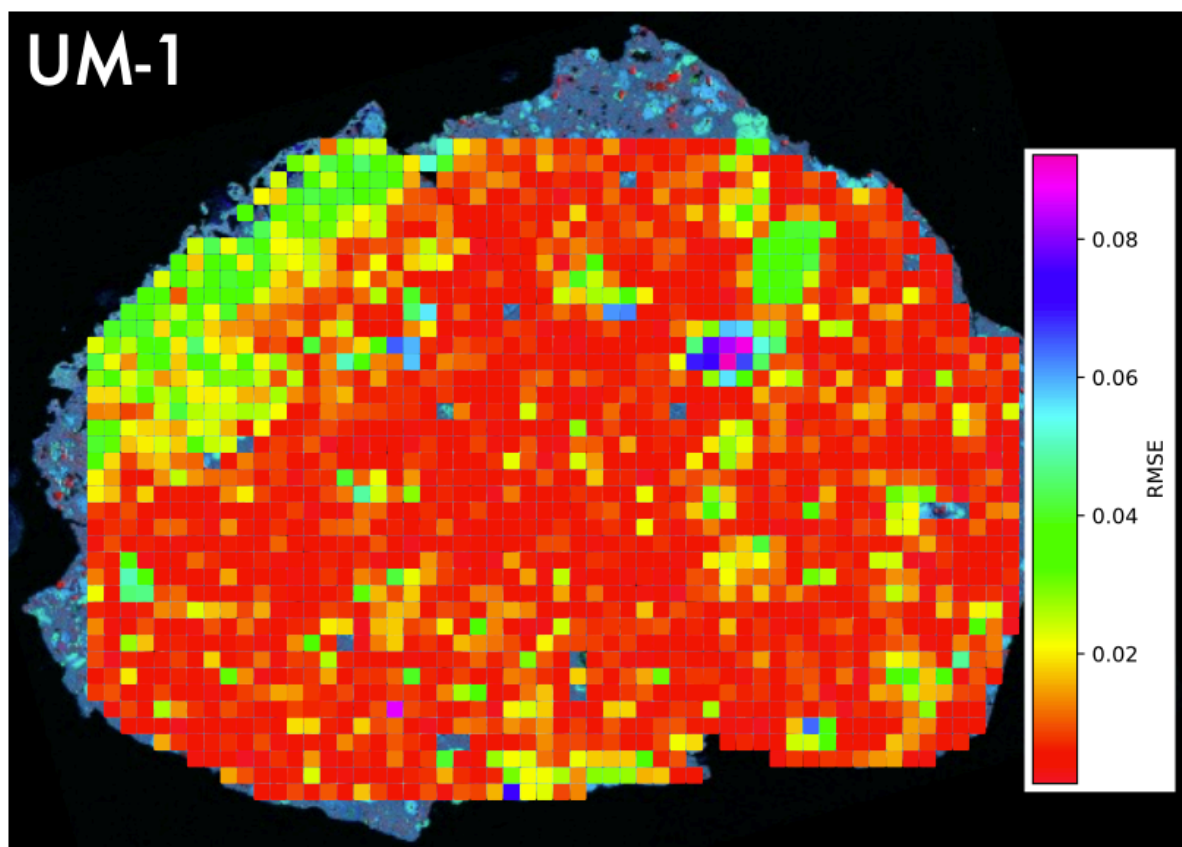


Figure 19: The differences in estimates for the μ FTIR spectral inverse modeling and bulk FTIR inverse modeling compared to the EPMA estimates (bar charts in Figure 7) for each relevant phase in all sections and lithologies for both the MIR and 3 μ m spectral regions. Positive values are overestimates whereas negative values are underestimates. Values are plotted on a log-scale because of the range in estimate errors (< 0.5 vol.% to > 90 vol.%). Most errors are < 10 vol.%.



Supplementary Figure 1: The EPMA elemental oxide maps of a region of the Field-1 section show the distribution of MgO, FeO, and SiO₂+Al₂O₃ (top), the distribution of SO₂ (middle), and the apparent porosity, which is proportional to the summed total of all elements measured with EPMA (bottom). Summed elemental oxide totals in these sections are typically less than 100 wt.%, which can be attributed to several factors, like the presence of OH/H₂O and other unmeasured phases. The biggest driver of these differences though likely results from differences in the porosity throughout the sample compared to the mineral standards that the EPMA was calibrated against. We include these maps to highlight important differences in both S abundance and apparent porosity that is not captured in simple three-element ternary projections but that were important in the automated classification of the pixels in these maps.



Supplementary Figure 2: A representative RMSE map for the UM-1 section. Areas in red to green color generally show good modeling agreement between the measured μ FTIR spectrum and the forward modeled spectrum using endmember estimates from the linear unmixing (inverse modeling) of each spectrum. Areas in blue to purple color show poorer agreement and are typically located in areas where unique and/or minor phases are present (e.g., an Fe-rich olivine chondrule just northeast of center).

Chapter 3 | The Curious Case of the Missing Mantle and How Carbonaceous Chondrites May Confound the Spectral Identification of Partially Differentiated Asteroids

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3.1 Abstract

Carbonaceous asteroids and meteorites are among the darkest naturally occurring planetary materials with albedos as low as 2–3%. Abundant evidence in the form of brecciated meteorites and spacecraft observations of asteroids indicates widespread mixing of carbonaceous material through the natural collisional evolution of small bodies. This work explores the significant and nonlinear spectral darkening and suppression of diagnostic absorption features that occurs when carbonaceous chondrite material is intimately mixed with silicate/metal mixtures analogous to the putative olivine- and pyroxene-rich mantles of partially melted chondritic bodies. Visible and near-infrared (VNIR) reflectance spectra were acquired for systematic mixtures of fine and coarse-grain CM or CV chondrite material and mantle analog material made from varying combinations of olivine, orthopyroxene, clinopyroxene, plagioclase, and iron metal meant to simulate the melt residues, i.e. mantles, of CM and CV parent bodies. When introducing artificial noise

that simulates the SNR (signal-to-noise) error common for telescopic observations of near-Earth and main-belt Asteroids, we find that upwards of 30–65 wt.% of mantle analog material can be effectively spectrally masked. This indicates that telescopically acquired VNIR reflectance spectra of rubble pile asteroids consisting of similar mixtures of differentiated and undifferentiated material may belie the true nature and composition of these bodies. Specifically, these bodies may harbor significant amounts of undetected or underestimated olivine- and/or pyroxene-rich mantle material, providing a possible explanation for the apparent scarcity of mantle material in the asteroid belt colloquially referred to as the ‘Missing Mantle Conundrum’.

3.2 Introduction

Asteroids and their meteoritic progeny are primordial materials left over from a bygone era of planetary formation. Written into their chemistry and mineralogy are pristine records of the conditions of the early solar system and the processes that governed the formation and evolution of planets. One of the most enduring mysteries in our study of the evolution of these bodies is the perceived shortage of olivine-rich mantle material, colloquially referred to as the Missing Mantle Conundrum (DeMeo et al., 2015). Despite the abundant evidence indicating that planetesimals reached temperatures that allowed for differentiation and melt segregation, the apparent scarcity of olivine- and pyroxene-rich mantle material in meteorite collections and remote sensing data of asteroids has been a long-standing mystery.

Current models of planetesimal evolution suggest that sufficient heating from ^{26}Al melted the interiors of planetesimals larger than ~ 20 km in radius, which would result in a metallic iron core overlain by a silicate mantle, which at the low pressures in planetesimals would later differentiate into olivine-rich cumulates and later-stage evolved silicate melts (Elkins-Tanton et al., 2013). Iron and other achondritic meteorites provide us with a crucial but imperfect record of these evolutionary processes and together imply the existence of more than 60 distinct parent bodies (Wasson, 1995; Burbine et al., 2002) that melted early in solar system history (Schersten et al., 2006; Gardner-Vandy et al. 2013). Yet, aside from the Howardite, Eucrite, and Diogenite (HED) meteorites linked to the asteroid (4) Vesta, there is a puzzling scarcity of igneous mantle and crustal material within these collections. Similarly, large-scale spectroscopic surveys of asteroids have shown differentiated material to be exceedingly rare in both the main belt and among near-Earth objects (Bus and Binzel, 2002a; Binzel et al., 2004; Lazzaro et al., 2004; Carvano et al., 2010; DeMeo and Carry, 2013). These surveys show that olivine-rich A-type asteroids account for less than 0.16% of all main-belt objects larger than 2 km (DeMeo et al., 2019).

Several hypotheses have been put forth in an attempt to explain this perceived shortage of mantle material, but none have garnered broad consensus within the scientific community. Suggestions include that either (1) the relative weakness of mantle and crustal materials resulted in the preferential loss of this material relative to iron core fragments (Burbine et al., 1996; Bottke et al., 2006; Scott et al., 2015), (2) impacts were not fully accretionary and lost silicate was re-accreted onto growing planets (Asphaug and Reufer, 2014), or (3) the classical view of planetesimals differentiating into a pyroxene-rich crust,

olivine-rich mantle, and iron core may be uncommon (Consolmagno et al., 2015), and these bodies may instead be capped by a primitive and undifferentiated chondritic lid that obscures evidence of internal differentiation (Elkins-Tanton et al., 2013). However, asteroid families resulting from the partial to complete disruption of differentiated planetesimals should provide glimpses into the modified interiors of such bodies, but detailed spectroscopic studies have found little evidence for differentiation in asteroid families (DeMeo et al., 2019).

In this work we address this long-standing issue by testing a hypothesis that posits that differentiated olivine- and pyroxene-rich asteroids interiors are present in the main asteroid belt but their diagnostic spectral signatures are effectively masked by dark, chondritic materials mixed and incorporated through the natural collisional evolution of these bodies. It is now recognized that there are likely far more rubble pile asteroids than previously thought, with virtually all bodies between 0.2–100 km likely being gravitational aggregates of loosely consolidated material (Jourdan et al., 2023; Walsh, 2018; Michel et al., 2015; Campo Bagatin et al., 2001; Asphaug et al., 2002; Richardson et al., 2002). If a subset of these were produced through the catastrophic disruption and re-accretion of a heterogeneous mix of differentiated and undifferentiated material, their spectral signatures may belie their true nature and composition.

We explore this hypothesis by examining mixtures of analog mantle material and primitive meteoritic material. The former are made from well-characterized mineral endmembers that reflect the composition of mantle materials expected to form from the partial melting of chondritic parent bodies (Collinet and Grove, 2020). We focus on

mixtures and likely mantle compositions derived from CM and CV chondrite starting material because of their purported link to partially differentiated parent bodies (Carpözen et al., 2011; Cournede et al., 2015; Mothé-Diniz and Carvano, 2005). They are also among the lowest albedo planetary materials in our meteorite collection and should provide the strongest example of how chondritic materials may confound spectral characterization of evolved bodies. The starting mantle analog materials were size separated and mixed in a series of systematic proportions with the corresponding carbonaceous chondrite material from which each composition was derived. Reflectance spectra of the mixtures were acquired and assessed to determine the relative abundance of mantle material that is necessary for it to be spectrally identifiable when mixed with primitive chondritic material. We then determined the same detection thresholds for synthetically degraded spectra that simulate the noise present in telescopic observations of near-Earth and main-belt asteroids, with the goal of ultimately applying this framework to spectroscopic observations and surveys of these small bodies.

3.3 Methods

3.3.1 Carbonaceous Chondrite Samples

The CM and CV carbonaceous chondrite groups were chosen for this study because of their potential link to partially differentiated parent bodies, their low albedo, and previous characterization of their experimental melt products given by Collinet and Grove (2020). For the CM chondrite we selected a 2.4 g stone of the Jbilet Winselwan CM2 chondrite,

purchased from The Meteorite Exchange, Inc. For the CV chondrite we selected a 3.1 g stone of the Allende CV3 meteorite, purchased from Aerolite Meteorites.

The Jbilet Winselwan sample had a fusion crust present on several sides of the stone that exhibited oxidized weathering veins, typical of other chondrite meteorites found in Northwest Africa. These surfaces were removed by gently breaking up the stone and polishing/removing the weathered surface. The Allende sample did not appear to exhibit any surface weathering that would significantly interfere with this study. Both meteorites were ground with an agate mortar and pestle and then dry-sieved to produce 25–45 μm and 75–125 μm size separates. Representative visible and infrared reflectance spectra of both meteorites are presented in Figure 1.

3.3.2 Analog Mantle Materials

The analog mantle materials created here were meant to represent likely compositions of mantles derived from CM and CV chondrite parent bodies that were partially melted at a variety of peak temperatures and oxygen fugacities. These compositions were based on the experimental products from a study by Collinet and Grove (2020), in which those workers melted a mixture of oxides and metals that together approximate the major element composition of CM and CV chondrites. The analog mantle materials produced here consist of silicate minerals and metal mixed in proportions designed to approximate the phase assemblages of the melt residues from the CM and CV experiments reported by Collinet and Grove (2020) (Table 1). These mineral mixtures are meant to

represent the likely mantle compositions of the CM/CV body when melted at a given temperature and oxygen fugacity.

The expected mantle phase assemblages are described in Collinet and Grove (2020) in terms of chemistry and wt.% abundance of olivine, clinopyroxene, orthopyroxene, plagioclase, and metal. We used these values to recreate the assemblages, but it was necessary to compromise on the precise chemistry of the silicates in order to use mineral endmembers that are readily available, well-characterized, and relatively free from impurities. These minor differences in chemistry (e.g., specific pyroxene composition) are not expected to influence the overall goal of the study – assessing spectral detectability of possible mantle material – because these differences primarily affect the position and not the presence of diagnostic absorption features.

Due to the limited amount of chondritic material available for study, we limited our investigation to exploring only two possible mantle analog compositions for each meteorite group: an olivine-rich and pyroxene-rich assemblage. The mineral endmembers used to create the analog mantle assemblages were previously characterized by Bramble et al., (2020a, 2020b), but we summarize key details below.

Our olivine endmember is sourced from near San Carlos, Arizona, USA and is a common standard and reference material for geological analyses (e.g., Jarosewich, 2002). This olivine exhibits a forsterite number of $\sim\text{Fo}_{90}$ (e.g., Fournelle, 2011), which differs from the Fo_{70-89} composition of the olivines experimentally found by Collinet and Grove (2020). The pyroxene compositions of the melt residues are described by Collinet and Grove (2020) as being either orthopyroxene, pigeonite, augite, or clinopyroxene, each with variable Mg,

Fe, and Ca chemistries. In our simplified approach we sourced only two types of pyroxenes, an enstatite-like orthopyroxene and a diopside-like clinopyroxene. The low-calcium orthopyroxene endmember was sourced from Bamble, Norway and is well-matched in chemistry to a sample with composition $(\text{Mg}_{0.907}\text{Fe}_{0.093})(\text{Mg}_{0.595}\text{Fe}_{0.405})\text{Si}_2\text{O}_6$. The high-calcium clinopyroxene endmember was sourced from Skardu, Pakistan and is matched to a sample with composition $(\text{Mg}_{0.88}\text{Fe}_{0.90}\text{Al}_{0.03})(\text{Ca}_{0.95}\text{Na}_{0.01}\text{Fe}_{0.04})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_6$. The relevant plagioclase phases found by Collinet and Grove (2020) ranged from andesine (An_{32}) to Bytownite (An_{81}). Again, for simplicity, we sourced a single plagioclase endmember in our study, which was found to have a composition intermediate between $\text{Ca}_{0.65}\text{Na}_{0.32}(\text{Al}_{1.62}\text{Si}_{2.38}\text{O}_8)$ and $\text{Ca}_{0.491}\text{Na}_{0.499}(\text{Al}_{1.488}\text{Si}_{2.506}\text{O}_8)$, which suggests a composition intermediate between Bytownite towards Labradorite. The metal endmember was pure Fe metal acquired from EPSI Metals. Visible and near-infrared (VNIR) reflectance spectra of each endmember are presented in Figure 1.

Mineral endmembers were first ground using an agate mortar and pestle and then wet-sieved to size separates of $< 25 \mu\text{m}$, $25\text{--}45 \mu\text{m}$, and $75\text{--}125 \mu\text{m}$. For each size separate, the endmember minerals were mixed in proportions described in Table 1 to achieve the target wt.% ratios for the different desired mantle compositions. Masses of the resulting analog mantle mixtures were within $< 1 \text{ wt.}\%$ from target masses (Table 1).

3.3.3 Analog Mantle-Chondrite Mixtures

The analog mantle materials were mixed with their corresponding chondrite to produce mantle/chondrite wt.% ratios of 100/0, 95/5, 90/10, 80/20, 50/50, 20/80, 10/90,

5/95, and 0/100. This suite of mixtures was produced for three different particle sizes: 25–45 μm , 75–125 μm , and a suite consisting of the 25–45 μm chondrite mixed with the 75–125 μm mantle analog. The last suite was used to explore the spectral effects of coarser mantle rocks having a finer layer of chondritic ‘dust’, a condition that may be produced due to the weaker strength and more friable nature of C chondrites compared to igneous rocks. The typical mass of each mixture was on the order of ~ 30 mg.

3.3.4 Spectral Reflectance Measurements

All mixtures described above were fully loaded into 4-5 mm diameter black-coated aluminum dishes for visible-near infrared (VNIR) spectral reflectance measurements. The zero-background black coatings and fully loaded dishes ensured that scattering effects from the dish itself were negligible. The VNIR reflectance spectrum of each sample was acquired in ambient lab conditions (relative humidity of $\sim 35\%$) using an ASD FieldSpec3 portable spectroradiometer with wavelength coverage from 0.35–2.5 μm . A fiber optic light source with a QTH bulb was used to illuminate the sample at an incidence angle (i) of 30° , while the receiving fiber optic bundle was positioned at an emergence angle (e) of 0° . A small Spectralon^(R) disk from Labsphere was used as a reflectance standard. All reflectance spectra were corrected for minor absorptions present within the Spectralon standard by multiplying the sample reflectance spectrum by the absolute reflectance spectrum of Spectralon.

3.3.5 Signal-to-Noise and Error Analysis

Reflectance spectra measured under controlled and ideal laboratory conditions with high signal-to-noise instruments (spectrometers) often have uncertainties or levels of noise that are negligible for identifying broad absorption features relevant to the materials and goals of this study. However, the proper characterization of signal error and uncertainty becomes much more important when describing reflectance spectra acquired from ground-based telescopes and/or spacecraft, where telluric absorptions, slit losses, instrument artifacts, and lower signal-to-noise can be more pronounced. In an effort to assess the implications of this study for telescopic reflectance spectra of small bodies, we systematically degraded the laboratory spectra by adding noise at a level that is typical of signal-to-noise conditions for observations of near-Earth and main-belt asteroids. The degraded reflectance spectrum, $R_n(\lambda)$, is calculated as:

$$R_n(\lambda) = R_t(\lambda) + N(\lambda) \quad (1)$$

where $R_t(\lambda)$ is the original spectrum and $N(\lambda)$ is the noise spectrum created by randomly sampling a Gaussian distribution with standard deviation $\sigma_N(\lambda)$. The standard deviation is set by the desired signal-to-noise, using the equation described by Swayze et al. (2003) as:

$$S/N_N(\lambda) = \frac{R_{50\%}(\lambda)}{\sigma_N(\lambda)} \quad (2)$$

where $R_{50\%}(\lambda)$ is a spectrum with uniform 50% reflectance. For analyses involving spectral ratios and absorption band depths, this uncertainty was propagated using the formulas:

$$\sigma_R = R \sqrt{\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2} \quad (3)$$

and

$$\sigma_S = S \sqrt{\left(\frac{\sigma_R}{R}\right)^2 + \left(\frac{\sigma_C}{C}\right)^2} \quad (4)$$

Here, A and B are the original spectra in a ratio, R is the ratioed spectrum, C is the spectral continuum (defined as part of the continuum-removal process, Clark and Roush, 1984?), and S is the continuum-removed spectrum. The corresponding standard deviations are represented by σ_A , σ_B , σ_R , σ_C , and σ_S . Because we explicitly define a linear spectral continuum, we assume σ_C is negligible and drop this term from the equation (4).

3.3.6 Band Depth Calculations

The absorption strength, or band depth, of the 1000 nm absorption feature that results from Fe^{2+} in octahedral coordination (e.g., olivine and pyroxene) was calculated by first performing a continuum-removal on the original spectrum. The spectral continuum was assumed to be linear and was defined using the convex hull method (e.g., Schultz et al., 2023), which uses an upper convex hull across a truncated portion of the original spectrum, typically ~500 nm to 2000 nm, to define a piecewise linear continuum. The truncated portion of the original spectrum was then divided by the spectral continuum to produce a continuum-removed reflectance spectrum. An example of this method is demonstrated in

Figure 2. The band depth was then calculated at the reflectance minimum of the continuum-removed spectrum using the equation:

$$B_{depth} = 1 - R_{min}$$

where R_{min} is the reflectance value of the continuum-removed spectrum at the reflectance minimum across the 1000 nm absorption feature.

3.4 Results

3.4.1 Reflectance Spectra

The VNIR reflectance spectra of the chondrite-mantle mixture suites, which include the endmembers, are shown in Figure 3 and Figure 4. At these wavelengths, spectra of the olivine-rich mantle analog samples (CM64, CV64, and CV39) are dominated by a broad absorption centered near ~1000 nm. This absorption consists of three distinct but partially overlapping absorptions that arise from crystal field transitions of Fe^{2+} ions situated in the M1 and M2 crystallographic sites within the olivine structure, with the exact position controlled by the relative abundance of Fe versus Mg (Burns, 1993; Sunshine and Pieters, 1998). The orthopyroxene-rich analog mantle suite (CM43) exhibits characteristic absorptions at ~1000 and ~2000 nm that are attributed to Fe^{2+} in the M2 site in the pyroxene-crystal structure, as well as a weaker feature near ~1250 nm due to Fe^{2+} in the M1

site (Adams 1974; Cloutis and Gaffey 1991a; Klima et al., 2007). These absorptions are modified by the substitution of Ca^{2+} , as occurs in clinopyroxenes like the diopside endmember present in sample CV39, which modifies the strength and wavelength position of these absorption features (Klima et al., 2011).

Unlike olivine and pyroxene, VNIR reflectance spectra of plagioclase and iron metal have much more subtle features, thus their spectral influence in the mixtures is less obvious. Spectra of plagioclase can exhibit a moderate to weak absorption between 1100-1300 nm due to electronic transitions of Fe^{2+} in the crystal structure (Adams and Goullaud, 1978), whereas metallic iron exhibits a relatively featureless spectrum but positive (red) slope across VNIR wavelengths. The most obvious contribution from either of these phases is a reduction in the overall brightness of each spectrum, especially for the CM43 mantle analog (Figure 3), which is attributed to the incorporation of the much darker metallic iron. Contributions from plagioclase appear negligible.

The CM2 chondrite Jbilet Winselwan exhibits an extremely dark spectrum (~3–4 % reflectance at ~550 nm) with a broad shallow feature centered near ~1000 nm and a strong drop in reflectance shortward of 600 nm (Figure 1). The spectrum of the coarser (75-125 μm) size fraction has a neutral to slightly “blue” slope across the VNIR range while the finer (25-45 μm) size fraction has a positive “red” slope. The CV3 chondrite Allende is brighter (~6–10 % reflectance) and also exhibits a broad but better resolved absorption near ~1 μm that is consistent with the presence of olivine (Figure 1). Similarly, the coarser size fraction has a negative blue slope across the VNIR region while the finer separate exhibits a positive

red slope, a relationship consistent with particle size effects seen in other studies of similar materials (e.g., Cloutis et al., 2018).

It is also evident in Figure 3 and Figure 4 that increasing the abundance of CM2 and CV3 material results in an intense darkening and suppression of diagnostic olivine and pyroxene-attributed absorption features within all mixture suites. At mantle abundances ≥ 50 wt.%, diagnostic olivine/pyroxene absorptions are reduced but still distinct and resolvable. At lower mantle abundances, particularly ≤ 20 wt.%, these absorptions are dramatically reduced, and spectra of the mixtures become indistinguishable from their corresponding chondrite spectrum.

To assess the linearity or nonlinearity of spectral mixing (e.g., absorption suppression) in these suites, we examined the strength of the 1 μm absorption feature as a function of increasing relative abundance of chondritic material (Figure 5). In these plots, the band depth was based on the reflectance minimum (absorption maximum), which for olivine-rich samples occurs near 1060 nm and for orthopyroxene-rich samples occurs near 920 nm. For both CM and CV compositions, the relationship between band depth and chondrite abundance is highly nonlinear for the finer fraction, with the curve appearing steepest between 0–20 wt.%. In contrast, relationships for the coarser size fractions are more linear. Importantly, for the same chondrite abundance, the finer size fraction darkens and suppresses the 1000 nm absorption feature to a much greater extent, often by twice as much, compared with the coarser size fraction. Interestingly, the mixed particle size series consisting of the 25–45 μm chondrite size separates and the 75–125 μm analog mantle separates, also exhibits strongly nonlinear behavior, appearing much more consistent with

the finer particle mixtures. Notably, band depths for the pyroxene-rich CM43 mixed particle size series is indistinguishable from the fines-only mixture series. These results suggest that finer particles of chondrite material have a much stronger control on the brightness of the mixtures and the strength of diagnostic silicate absorption features in a way that is nonlinear and disproportionate to the relative abundance of this material in mixture.

3.4.2 Spectral Ratios

As expected, the addition of carbonaceous chondrite material has a profound effect on the strength and shape of absorption features that would be associated with mantle material. However, it is important to assess the likely amount of chondrite material that would need to be present in order for the reflectance spectrum of mantle-bearing material to become indistinguishable from that of pure chondrite material. This can then be used to effectively address the key objective of determining how much mantle material can be spectrally concealed by dark chondritic material.

Spectral ratios provide an effective way to investigate and highlight subtle differences in the shape and strength of absorptions features between two spectra. For example, if two spectra are extremely similar, save for the presence of a particular absorption, the resulting ratio spectrum should appear as a relatively flat or gently sloped line with a dip (or peak) in the region where that unique absorption occurs in the original spectrum. Though both the overall reflectance level and spectral shape are modified by increasing amounts of chondrite in the mixture spectra, we chose to focus on differences in overall spectral shape rather than

reflectance level because of its greater utility in comparing spectra across different instruments, spatial scales, and acquired under different viewing geometry.

In Figure 6 and Figure 7 we show the spectral ratios for all analog mantle and mixture spectra relative to their corresponding chondrite spectrum for the 25–45 μm size separates. This size was chosen because spectra for these mixture suites exhibited the strongest suppression of absorption features. We choose to focus our analysis on the 1000 nm absorption feature because it is the most intense absorption and is present in both olivine and pyroxene.

The spectral ratios are relatively flat and featureless for mantle abundances less than 50 wt.%. This indicates these mixture spectra are highly similar or identical in shape to their respective pure chondrite materials, despite the significant abundance of olivine and pyroxene. For mixtures of 50 wt.% mantle and higher, a shallow feature appears near 1000 nm that increases in strength with increasing abundance of olivine and pyroxene. For spectra that have been degraded to simulate the SNR that is typical of telescopic spectra of near-Earth and main-belt asteroids, these subtle differences are reduced even more. With an SNR of 200, the spectrum of the 50/50 chondrite/mantle mixture is relatively flat for both the CM and CV mixtures. This suggests even more mantle-like material may be effectively masked in remote observations of small bodies.

3.5 Discussion

3.5.1 Spectral Masking and Mantle Detection Thresholds

The addition of carbonaceous chondrite material in mixtures with mantle analog material effectively darkens the overall reflectance spectrum and suppresses key absorption features important for the identification and compositional assessment of these mantle analog mixtures. Importantly, we demonstrate that this is a highly nonlinear process (Figures 5), where only small amounts of chondritic material are required to disproportionately darken and suppress these spectra. For example, only 10–20 wt.% chondrite material is required to more than halve the diagnostic 1000 nm absorption feature (Figure 5). To further illustrate this point, in Figure 8 we compare spectra of the 90/10, 50/50, and 10/90 ratio mixtures to their modeled spectra, calculated by linearly mixing the CM2 Jbilet Winselwan spectrum with the CM64 and CM43 mantle analog spectra at the same 90/10, 50/50, and 10/90 ratios. This disproportionate suppression of overall bright and absorption strength is most notable in the 25–45 μm and mixed particle size series of the olivine-rich CM64 mixtures. A linear combination of 90 wt.% mantle analog and 10 wt.% chondrite produces a spectrum with 60–70 % peak bright and a strong, well resolved 1000 nm olivine feature. The spectrum measured of the physical mixture is instead three times dark, with a peak brightness closer to 20 %, even darker than the modeled 50/50 mixture spectrum. This intense nonlinear behavior precludes the use of simple linear mixing methods to accurately assess endmember abundances, even for relatively simple binary mixtures. It also highlights the potential ambiguity of compositional and taxonomic interpretations based on spectra acquired for similar materials.

To first order, this confirms our hypothesis that chondritic material will effectively mask diagnostic spectral signatures of analog mantle material, which would lead to the

systematic underestimation of mantle material when relying solely on spectral interpretations. However, a 1000 nm feature that is subtle to moderate in strength is present until the relative abundance of mantle material reaches ~50 wt.% and lower, which implies that olivine and pyroxene-rich mantle material should be at least detectable for these fractional abundances.

A key goal of this work is to quantify the amount of mantle-like material that can be spectrally masked when mixed with dark chondrite material, therefore precluding its detection. To do this, we revisit the spectral ratios which were used to assess the differences in spectral shape of mixture spectra to their corresponding baseline chondrite spectrum. In our mixtures, this difference was observed as an absorption in the 1000 nm region for olivine and pyroxene-rich samples (and 2000 nm region for orthopyroxene-rich samples) that increased in strength with increasing mantle abundance (Figures 6 and 7).

To assess the point at which this feature becomes statistically unresolvable, we compare the band depth of this 1000 nm feature in the ratioed spectra to the propagated noise and measurement uncertainty present in each spectrum for SNRs of 1000, 200, and 50. These SNRs define a range of measurement noise that spans from near laboratory quality (SNR 1000) to the quality typically observed for large main-belt objects (SNR 200) to the quality observed for moderately sized near-Earth bodies (SNR 50).

We define an absorption as being statistically detectable if the band depth of the feature at its reflectance minimum (in this case, ~1000 nm) is equal to or greater than twice the standard deviation of the measurement error associated with each SNR. This threshold was chosen because it represents maximum depth of an apparent absorption whereby a

straight line can still be drawn through the curve and still be within 1σ error, thereby representing a zero absorption non-detection.

It should be noted that using band depth as a measure of detectability is a simple, one-dimensional way of assessing an absorption and should therefore be seen as a relatively conservative approach to quantifying detection thresholds. Nevertheless, it remains a robust and useful parameter for measuring and comparing the strength of key absorption features.

In Figure 9 and Figure 10, we show the band depth of the diagnostic 1000 nm absorption feature in the ratioed spectra along with the $2 \times 1\sigma$ standard deviation for all SNRs as a function of the wt.% abundance of mantle analog material in each mixture. Regions where the band depth curve is greater than and above the $2 \times 1\sigma$ standard deviation curve represent a positive detection of the mantle analog material in mixture. Conversely, regions where the $2 \times 1\sigma$ standard deviation is greater than the band depth represent false detections, or areas where the 1000 nm band was not sufficiently strong enough to be resolvable through the measurement noise set by the SNR.

Across all mixtures and compositions, we find that as SNR decreases and noise increases, an increasing amount of analog mantle material is required for their ratioed reflectance spectra to exhibit a resolvable 1000 nm. This indicates that significant amounts of mantle material can be effectively masked at SNRs typical for main-belt and near-Earth asteroid observations. Ratios of the SNR 1000 spectra often always exhibited a resolvable 1000 nm absorption feature, such that typically no more than a few, but up to ~25 wt.% analog mantle material could be masked. Degrading the reflectance spectra to a SNR of 200, typical for high-quality telescope spectra of main-belt asteroids, allowed anywhere

from ~30–60 wt.% mantle to be spectrally masked, with CM chondrites appearing especially effective at suppressing these features. For example, at the finest size fraction (25–45 μm) the CM chondrite masks up to ~10 wt.%, 66 wt.% and over 99 wt.% mantle material for the CM64 olivine-rich mantle analog composition at SNRs of 1000, 200, and 50. For a nearly identical olivine-rich mantle analog, the CV chondrite masks 0 wt.%, and up to 33 wt.% and 85 wt.% mantle analog material, again for the spectra with a SNR 1000, 200, and 50. At even lower SNR values of 50, CM chondrites were consistently successful at masking upwards of 94 wt.% sample, with the pyroxene-rich CM43 composition not registering any detections. At a similar SNR, the CV chondrites were only able to mask ~50–90 wt.% mantle analog material. Particle size had the most pronounced effect for spectra with a SNR of 200, where the finer size fraction was able to consistently obscure an additional ~30 wt.% mantle material over the coarser size fraction. This is also true for the mixed particle size mixtures, where detection thresholds were consistent with, and sometimes even exceeded those for the finest size fraction.

These data indicate that significant amounts of olivine- and pyroxene-rich mantle material can be effectively masked when intimately mixed with carbonaceous chondrite-like material. Importantly, particle size appears to play a fundamental role. Finer chondrite size fractions are shown to have a disproportionately stronger effect on suppressing the overall brightness and strength of diagnostic features, no matter the particle size of the mantle analog material. Precluding the ability to detect such significant amounts of igneous material would result in a dramatic underestimation of the amount of differentiated material potentially present in the main asteroid belt. This thereby opens the real possibility that

olivine- and pyroxene-rich mantle material may be much more ubiquitous than previously thought but is instead simply masked by carbonaceous chondrite-like material.

3.5.2 Sources of Dust and Carbonaceous Material

Assessing under which scenarios this work is relevant, we identify at least two potential pathways for how near-Earth and main-belt asteroids may end up with surfaces exhibiting mixed igneous and chondritic materials: exogenous delivery and disruption and re-accretion of partially differentiated bodies, both of which are expected natural outcomes of the collisional evolution of the solar system.

The ubiquity of impact cratering throughout the solar system provides irrefutable evidence for cross-contamination and mixing of bodies throughout the solar system. Polymict meteorites provide some of the most compelling evidence for the widespread transfer and preservation of material throughout the solar system, including mixing from bodies believed to have formed in different reservoirs throughout the solar system (Goodrich et al., 2015; Bischoff et al., 2006 and references therein). Work on pristine grains returned from asteroid (25143) Itokawa by the Hayabusa mission revealed an exogeneous origin for organic carbon and H₂O (Chan et al., 2021). Additional in situ evidence in the form of carbonaceous and volatile-rich material present on the surface of asteroid (4) Vesta (Reddy et al., 2012), bright ordinary-chondrite like boulders on the surface of asteroid (162173) Ryugu, and bright V-type asteroid-like boulders observed on the surface of asteroid (101955) Bennu (DellaGiustina et al., 2021; Le Corre et al., 2021) further demonstrates this mixing. And though this process has been robustly demonstrated in both meteorites and asteroids,

it is yet unclear if this process alone can be responsible for the modification of a globally integrated reflectance spectrum. Some evidence for this can be found on bodies like (16) Psyche, which appears to exhibit a 3 μm hydration feature (Takir et al., 2017) that may be due to the exogenous delivery of hydrated C chondrite-like material (e.g., Avdellidou et al., 2018), though an indigenous source cannot be ruled out.

While impact events have undoubtedly modified the surfaces of small bodies, experimental and modeling work has demonstrated that impactors can indeed survive hypervelocity collisions with porous targets (Schultz and Gault, 1990; Svetsov, 2011; Turrini and Svetsov, 2014; Daly and Schultz, 2015, 2016, 2018; Avdellidou et al., 2016, 2017). Surviving material would occur in the form of projectile relics, projectile-contaminated glasses, and projectile-bearing breccias (Daly and Schultz, 2016). Estimates of the delivery and retention of impactors based on impact experiments and dynamical modeling suggest that some of the largest bodies (e.g., Ceres, Vesta, Psyche, and the hypothetical (495) Eulalia parent body) may retain exogenous material equivalent to a global layer up to several meters thick (Daly and Schultz, 2015, 2016; Avdellidou et al., 2018; Le Corre et al., 2021). Indeed, single impacts from large bodies can be responsible for the delivery of debris equivalent to a tens to hundreds of meters thick global layer for bodies like Ceres (de Elia and Di Sisto, 2011; Daly and Schultz, 2015).

Many of these works have explored the effects of composition, porosity, and orbital characteristics on impactor flux and retention, but only for the largest main-belt bodies. Consequently, estimates for smaller main-belt asteroids ($\sim 1\text{--}100$ km) remain poorly constrained. As such, additional modeling work is required to fully assess impactor flux and

retention efficiency for a wider range of main-belt bodies. Nevertheless, these works suggest that exogeneous delivery is ubiquitous and all bodies in the asteroid belt likely host large amounts of meteoritic debris in vertically mixed regolith layers. As our experiments show, this should have a profound effect on the spectral properties of these potential bodies.

An alternative delivery mechanism we consider is asteroidal and cometary dust sourced from the zodiacal cloud. The zodiacal cloud consists of a population of submicrometer-sized dust grains to centimeter-sized meteoroids that pervades the inner solar system that is maintained by a steady state contribution of micrometeoroids derived from asteroids and comets (Nesvorny et al., 2011). Briani et al. (2011) modeled the probability of low-velocity collisions of these dust grains with a variety of main-belt asteroids to constrain the relative contribution of asteroidal and cometary material delivered to these bodies. We extend their results and methods to calculate the total mass contribution of asteroidal and cometary dust to these bodies.

Assuming spherical particles 200 μm in size with a density of 2 g cm^{-3} , Nesvorny et al. (2011) estimated the total mass of the zodiacal cloud between 2 and 4 AU (as is relevant for main-belt collisions) to consist of $1.08 \times 10^{19} \text{ g}$ of cometary micrometeoroids and $7.7 \times 10^{17} \text{ g}$ of asteroidal micrometeoroids. We then multiply these masses by the mean collisional probability for each reservoir (Table 2 of Briani et al., 2011), elapsed time ($4 \times 10^9 \text{ yr}$), and divide by 4π to obtain the total mass of dust per surface area for six main belt asteroids. Summing both cometary and asteroidal contributions and dividing by the average assumed particle density (2 g cm^{-3}) provides the estimated thickness of this exogenous dust source. We find that the mass deposited per km^2 ranges from $0.524\text{--}7.34 \times 10^7 \text{ g}$, which translates

to an equivalent global layer of dust ranging from ~3–26 μm in thickness for the different bodies studied here (Table 2). While a thin dust layer tens of microns in thickness is sufficient to spectrally obscure asteroidal surfaces, local surface processes like regolith gardening, local dust production due to thermal exfoliation and micrometeorite bombardment, and larger impacts and cratering events precludes the likelihood of a dust layer persisting over the age of the solar system. Though, the collection and ponding of this dust on the surface of the body in topographic and gravitational lows may contribute to the appearance of a heterogeneous surface.

A second and more likely scenario that would result in the heterogeneous distribution of chondritic and igneous materials is the partial to complete disruption and re-accretion of partially differentiated asteroid parent bodies. The existence of dozens of achondrite groups and ungrouped achondrites provides evidence that planetesimals experienced varying degrees of melting and differentiation (Scheinberg et al., 2015b). Driven by the radioactive decay of short-lived radioactive nuclides, large-scale melting should have initiated on bodies larger than 10 km accreting within just a few million years after the formation of calcium aluminum inclusions (Elkins-Tanton et al., 2011; Hevey and Sanders, 2006; Sahijpal et al., 2007; Sahijpal and Gupta, 2011). Interestingly, some modeling work suggests that a subset of these bodies may have formed metallic cores and partially or totally melted mantles but retained an unmelted chondritic lid (Carpenter et al., 2011; Elkins-Tanton et al., 2011; Sahijpal and Gupta, 2011; Weiss et al., 2010). Following formation, collisions and large-scale impacts would then continue to modify the interiors and structures of these bodies. Some of the largest bodies above 100 km in size should

retain most of their material but consist of significant volumes of scrambled mantle and core material (Scott et al., 2001; Davis et al., 1999; Love and Ahrens, 1996; Lucas et al., 2022). Petrologic studies of both chondrite and achondrite groups further indicates that many parent bodies experienced catastrophic impacts that mixed together materials from diverse depths (Keil et al., 1994). For smaller bodies, observational and numerical modeling work indicates that rubble piles are far more abundant than previously thought, with virtually all bodies between a few hundred meters to 100 km in size likely being gravitational aggregates of loosely consolidated material (Jourdan et al., 2023; Walsh, 2018; Michel et al., 2015; Campo Bagatin et al., 2001; Asphaug et al., 2002; Richardson et al., 2002). Additionally, processes that rework the surfaces of these bodies, like impact gardening (e.g., Costello et al., 2021; Ballouz et al., 2020; Sugita et al., 2019) and thermal exfoliation (Delbo et al., 2014; Molaro et al., 2019, 2017), may aid in the mixing of these materials and the production of regolith, as is observed on small asteroids (Veeverka et al., 2001; Yano et al., 2006; Dombard et al., 2010; Gundlach and Blum, 2013). And while the higher porosity of C-type materials may slow regolith production via micrometeoroid bombardment (Cambioni et al., 2021), thermal exfoliation is predicted to erode the same C-type materials more rapidly than S asteroid-like materials (Delbo et al., 2014).

All told, collisions and large impacts resulting in the partial to complete disruption of variably processed parent bodies likely led to the widespread formation of scrambled and rubble pile asteroids consisting of mixtures of both indigenous and exogenous differentiated and undifferentiated materials. Continuous exogeneous contamination and regolith gardening processing would continue to further modify and mix the surfaces of these bodies,

further obscuring the spectral signatures of phases key to properly interpreting the evolution of these bodies.

3.5.3 On The Missing Mantle Conundrum and the Ambiguity of Asteroid Taxonomy

The persistence of the missing mantle conundrum (or Great Dunitite Shortage) owes itself to the complexity of the problem and the challenge of obtaining convincing observational evidence. Indeed, large-scale spectroscopic surveys have found differentiated material to be exceedingly rare in both the main belt and among near-Earth asteroid (Bus and Binzel, 2002a; Binzel et al., 2004; Lazzaro et al., 2004; Carvano et al., 2010; DeMeo and Carry, 2013). While several processes have been identified that act to mute diagnostic absorption features (e.g., space weathering, shock darkening), we demonstrate here that the natural collisional evolution of variably differentiated bodies can result in mixtures that exhibit reflectance spectra that belie their true nature and composition. Specifically, bodies with reflectance spectra that present as having affinities to the C and X complexes, which are estimated to account for upwards of 70 % the mass of the main asteroid belt, could be extremely compositionally diverse and contain significant amounts of differentiated material. Asteroid (21) Lutetia may be among such bodies, as albedo measurements (Sierks et al., 2011) and near-IR reflectance spectra suggest a C-complex affinity, which is at odds with its inconsistently high-density measurements (Weiss et al., 2012).

While this work opens up the exciting possibility of the future discovery of igneous materials in the asteroid belt, it also highlights the challenges in relying solely on

spectroscopic surveys in the VNIR wavelength regime. The distribution of asteroid taxonomic types inferred from these surveys in both the main asteroid belt and near-Earth space provides one of the most important constraints on models of solar system evolution (Morbidelli et al., 2015). A reassessment of the relative distribution of asteroid compositional types in light of the ambiguity of our spectral taxonomic interpretations may require us to revisit these constraints in future iterations of these models. Additional spectroscopic measurements at mid-infrared wavelengths, which can also be highly diagnostic of silicate mineralogy, may hold the key to better constraining the compositions of these enigmatic small bodies, especially in the C and X complexes.

We also note that space weathering processes, which act to modify the chemistry and physical properties of the surfaces of airless bodies, should also confound the accurate interpretation of certain asteroid spectral types even further. Black chondrites and gas-rich chondrites provide some of the best examples of how shock-induced heating can reduce reflectance, redden spectral slope, and weaken absorption features (Briitt and Pieters, 1991, 1994). These effects are a result of the mobilization and dispersion of micron-scale FeNi metal and troilite. For lunar-style space weathering where optically active opaque particles are produced (e.g., nanophase metallic iron), the effects on spectra can similarly be seen as a reddening in the VNIR spectral slope and a reduction of absorption features diagnostic of silicate mineralogy (e.g., Pieters et al. 2000; Hapke 2001; Brunetto et al. 2006; Gaffey 2010). Similar processes acting to darken and redden reflectance spectra also operate on near-Earth and main-belt asteroids, though to varying degrees of intensity depending on heliocentric distance, composition, texture and mass (Pieters and Noble, 2016). Exploring the

intersection of mantle detection thresholds for these mixtures with the effects of space weathering will be an important advance in our understanding of asteroid spectral properties.

3.6 Conclusion

In this work we explored the spectral masking effects of primitive C chondrite material when mixed with silicate mineral assemblages analogous in composition to the hypothetical mantles of the CM and CV chondrite parent bodies. We found that the addition of increasing amounts of C chondrite material acts to significantly darken the overall reflectance spectrum of the mixture and strongly suppresses VNIR absorption features diagnostic of the silicate mantle mineralogy. Critically, this darkening and suppression was found to be highly nonlinear, thus demonstrating that the opaque C chondrite material has a disproportionately stronger control on the overall strength and shape of the VNIR reflectance spectrum, with these effects being the most intense for the CM chondrite mixtures and at finer particle sizes (25–45 μm). In an effort to extrapolate this work beyond the laboratory, we synthetically degraded the quality of our reflectance spectra to simulate the signal-to-noise typically observed in observations of near-Earth and main-belt asteroids. In doing so, we found that upwards of 30–65 wt.% mantle material was spectrally masked by the corresponding amount of C chondrite in mixture for the finest size fractions at an SNR of 200.

This work demonstrates that a significant amount of olivine- and/or pyroxene-rich mantle material may be present in the near-Earth and main-belt population of asteroids. Rubble pile asteroids, which likely make up the vast majority of bodies in the hundreds of meters to ~ 100 km size range, that are re-accreted from disrupted partially differentiated parent bodies should be most susceptible to mischaracterization due to the intimate mixing of differentiated and undifferentiated materials. Furthermore, this work demonstrates the ambiguity and degeneracy of our current taxonomic paradigm based on VNIR spectra of asteroids, whereby some taxonomic subtypes defined by their spectral properties could have multiple interpretations, including partial differentiation.

In the future we plan to test a broader range of potential compositions of mantle material for CM and CV chondrites in addition to mixtures of ordinary chondrites and their putative mantle assemblages. Crustal assemblages representing the melt products generated by these bodies will also be tested, as these may also be important components of disrupted and re-accreted asteroids. We will also perform a robust comparison to the current catalog of near-Earth and main belt asteroids and test the variability of spectra within asteroid families and within taxonomic groups of asteroids to see if the diversity of spectra can be explained by mixtures consisting of variable amounts of differentiated and undifferentiated material. We anticipate that this work will help us better characterize the composition of small bodies in our solar systems and the processes that governed their formation and evolution.

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3.8 Figures and Tables

Table 1: Ideal and actual wt.% fractions of mineral endmembers mixed to produce mantle analogs for each composition. Ideal wt.% fractions are derived from the experimental findings of Collinet and Grove (2021).

Sample ID	Mineral Endmember (wt.%) – Ideal				
	olivine	opx	cpx	plagioclase	Fe-metal
CM64	92.3	0	0	0	7.7
CM43	39.72	33.77	0	4.04	22.46
CV64	90.74	0	0	0	9.26
CV39	70.3	0	13.63	7.66	8.41

Sample ID	Mineral Endmember (wt.%) – Actual (25–45 μm)				
	olivine	opx	cpx	plagioclase	Fe-metal
CM64	92.53	0	0	0	7.47
CM43	39.74	33.82	0	4.04	22.39
CV64	90.63	0	0		9.37
CV39	70.53	0	13.52	7.84	8.11

Sample ID	Mineral Endmember (wt.%) – Actual (75–125 μm)				
	olivine	opx	cpx	plagioclase	Fe-metal
CM64	92.38	0	0	0	7.62
CM43	39.69	33.91	0	3.98	22.42
CV64	90.59	0	0	0	9.41
CV39	70.35	0	13.62	7.7	8.33

Table 2: Estimated deposition of chondritic dust on representative main belt asteroids calculated from mean collisional probabilities found by Briani et al. (2011).

Target	mass deposited per km ² (g) x 10 ⁷	deposited thickness per cm ² (μm)
4 Vesta	2.87	14.34
6 Hebe	7.34	3.67
8 Flora	2.033	10.17
15 Eunomia	5.67	2.84
158 Koronis	0.524	26.2
170 Maria	1.05	5.27

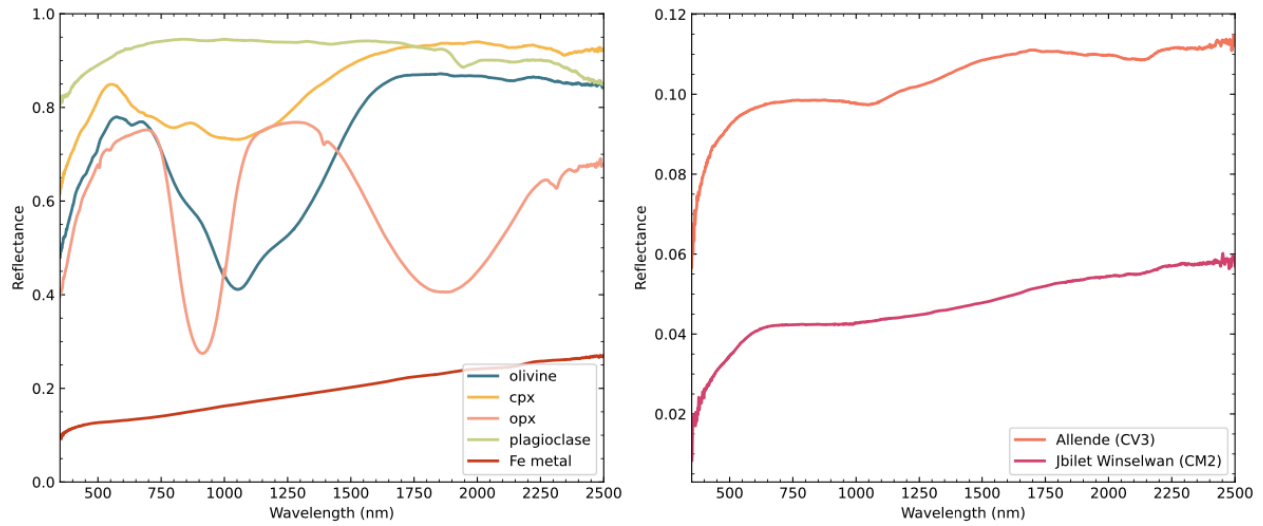


Figure 1: Visible and near-infrared reflectance spectra of mantle analog mineral endmembers (a) and carbonaceous chondrite endmembers (b) used in this study.

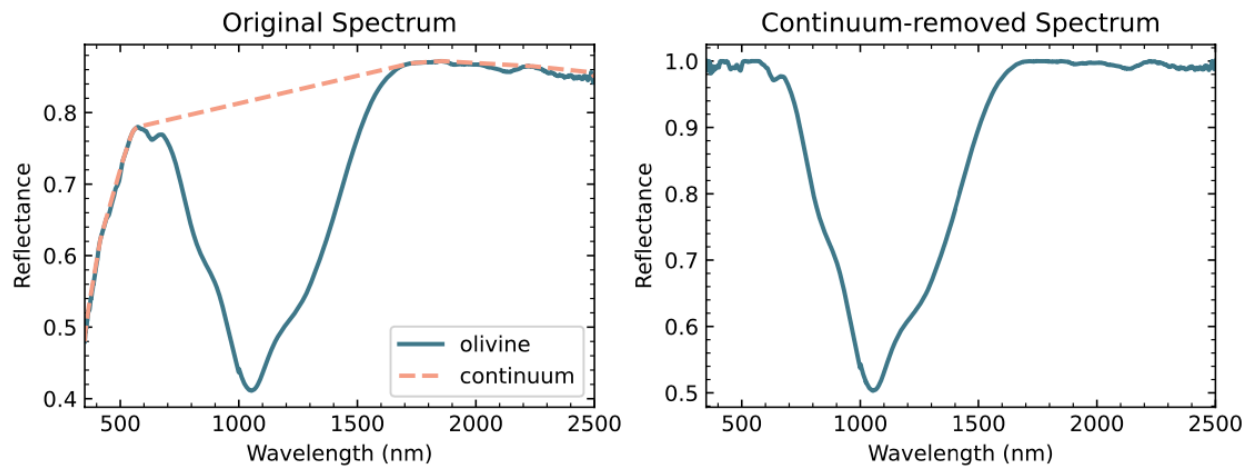


Figure 2: An example of the continuum removal process applied to the VNIR reflectance spectrum of olivine. Panel (a) shows the original unmodified olivine spectrum (blue solid line) along with its continuum (orange dashed line) calculated via the convex hull method. Panel (b) shows the continuum-removed spectrum calculated by dividing the original spectrum by its continuum.

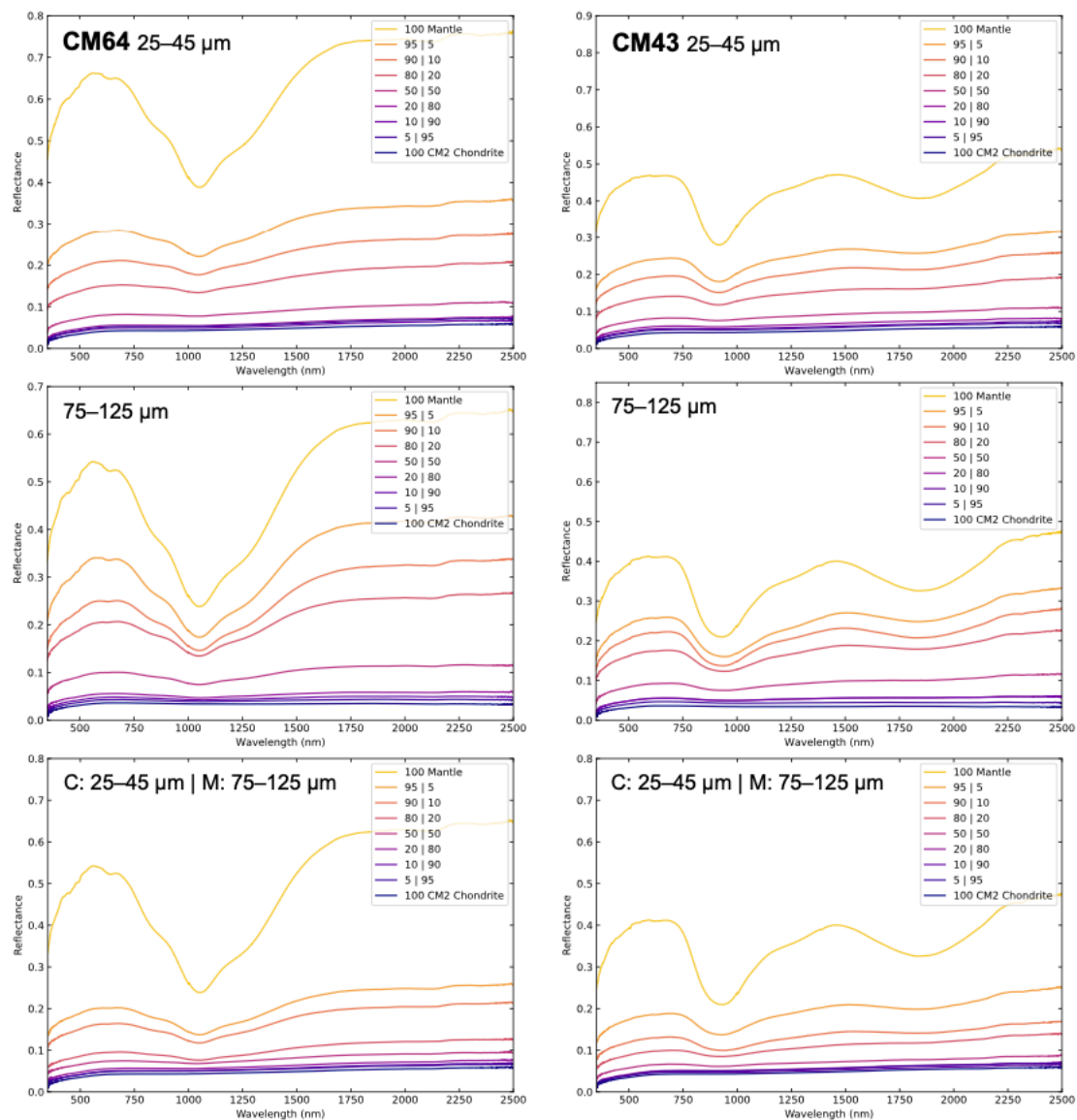


Figure 3: VNIR reflectance spectra of the CM2 chondrite and mantle analog mixtures for three particle size separates (rows) and for two mantle analog compositions (columns) labeled CM43 and CM64 (see Table 1 for mantle analog compositions). Figure legends show the relative wt.% fraction of each mantle analog and chondrite endmember for each sample measured.

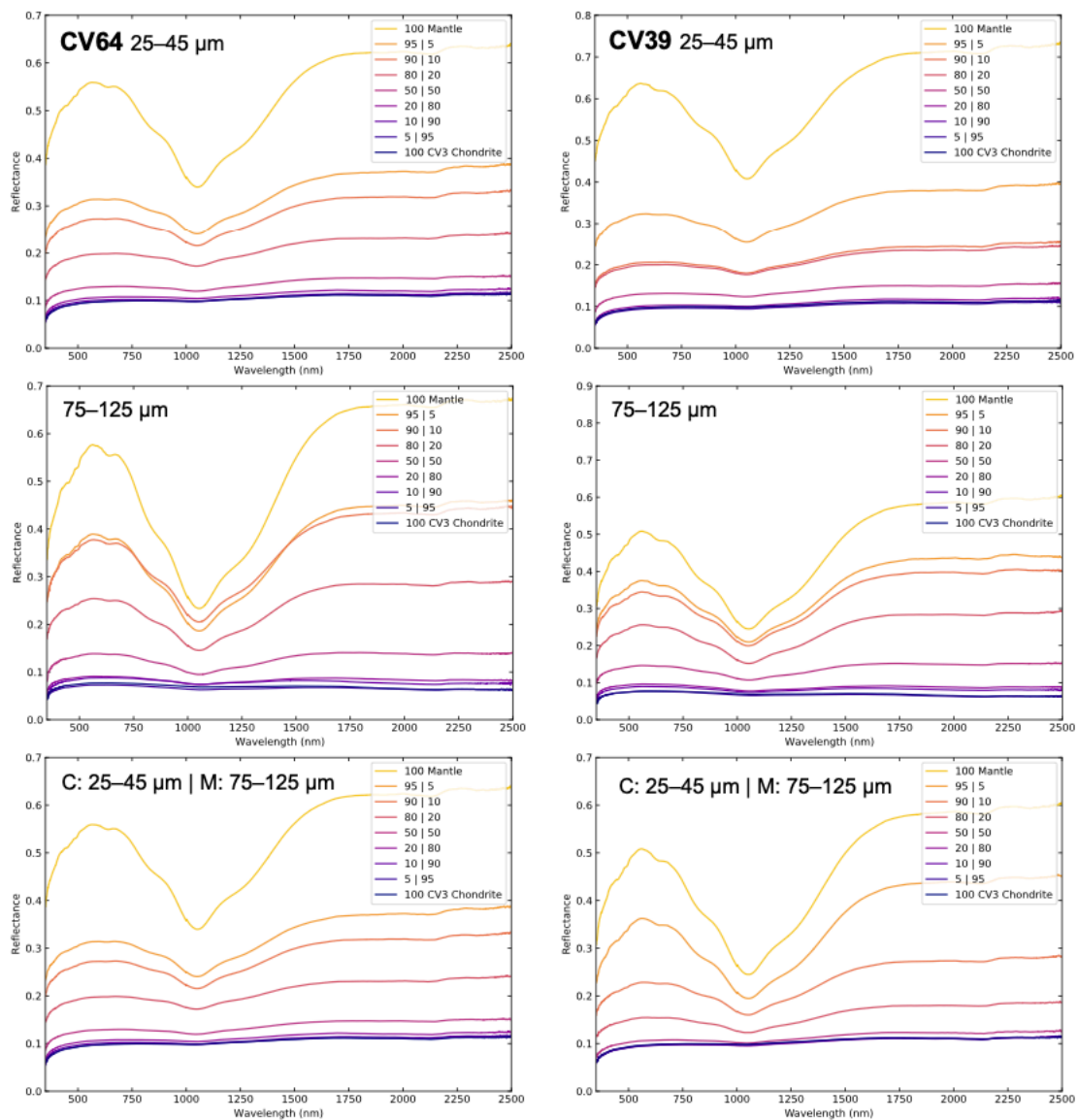


Figure 4: VNIR reflectance spectra of the CV3 chondrite and mantle analog mixtures for three particle size separates (rows) and for two mantle analog compositions (columns) labeled CV64 and CM39 (see Table 1 for mantle analog compositions). Colors and figure legends show the relative wt.% fraction of each mantle analog and chondrite endmember for each sample measured.

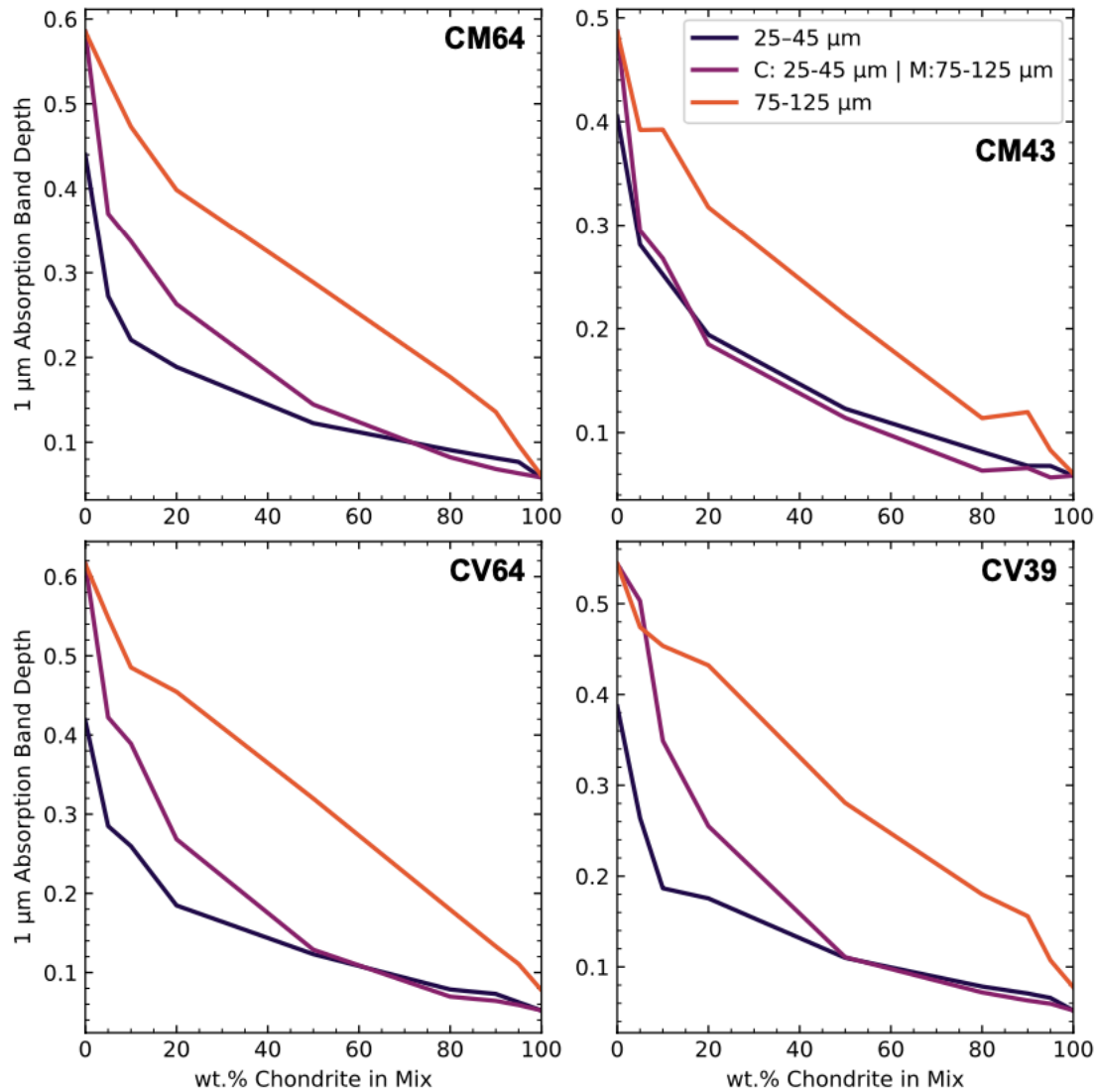


Figure 5: Strength of the $\sim 1 \mu\text{m}$ olivine/pyroxene absorption feature as a function of wt.% chondrite in mixtures with mantle analogs for all four mantle analog compositions. Red and dark blue lines represent trends for the 25–45 μm and 75–125 μm size separates, respectively. Purple lines represent trends for the mixed particle size separate (25–45 μm for the chondrite endmember and 75–125 μm for the mantle endmember).

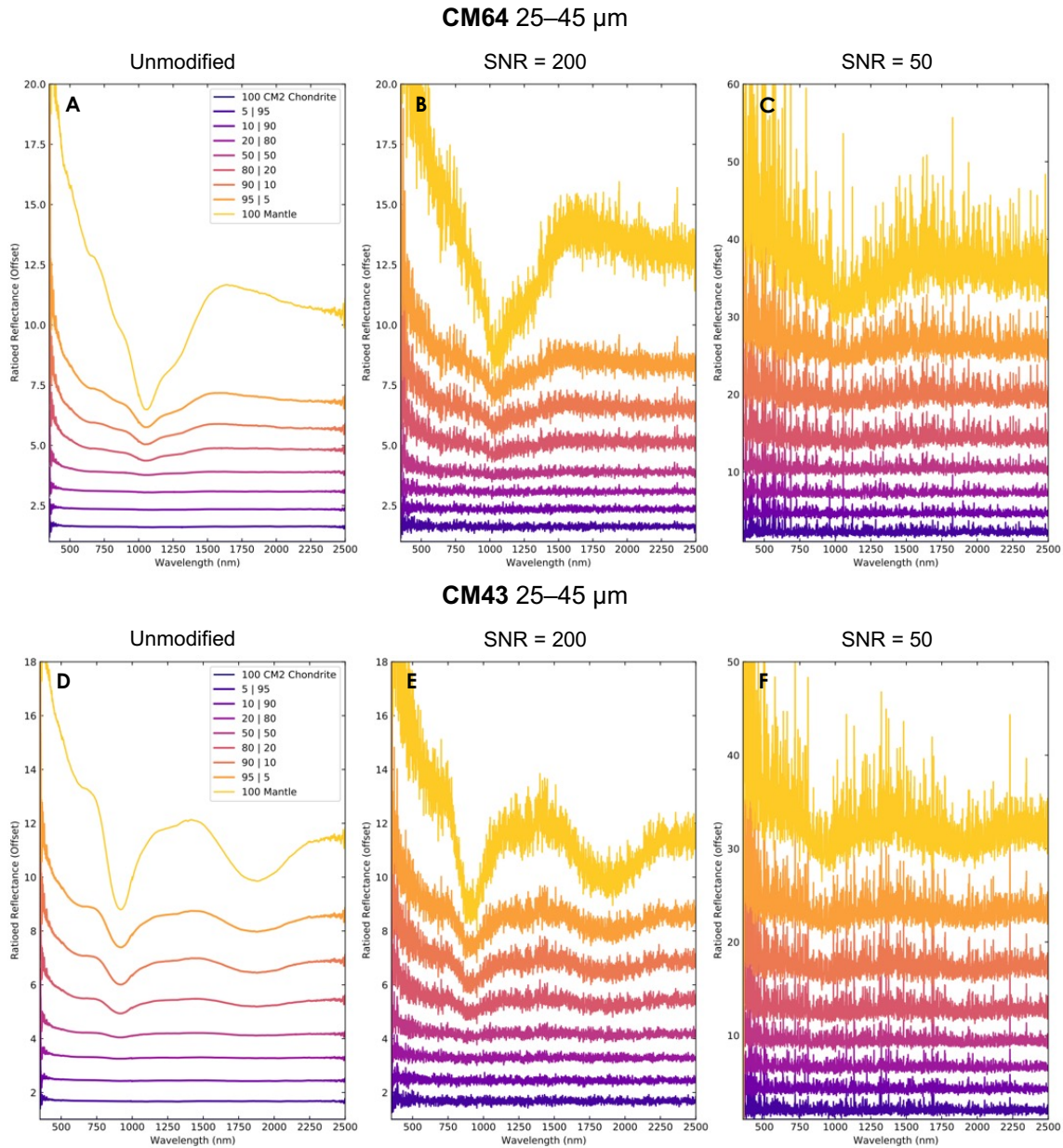


Figure 6: Reflectance spectra of CM2 mantle analog endmembers and mantle analog + CM2 chondrite mixtures ratioed to the reflectance spectrum of the CM2 chondrite endmember, Jbilet Winselwan. Columns are ratios of original unmodified spectra (a, d) and ratios of spectra that were synthetically degraded to simulate signal-to-noise values of 200 (b, e) and 50 (c, f). Colors and figure legends correspond to the relative wt.% fraction of each mantle analog and chondrite endmember for each sample measured.

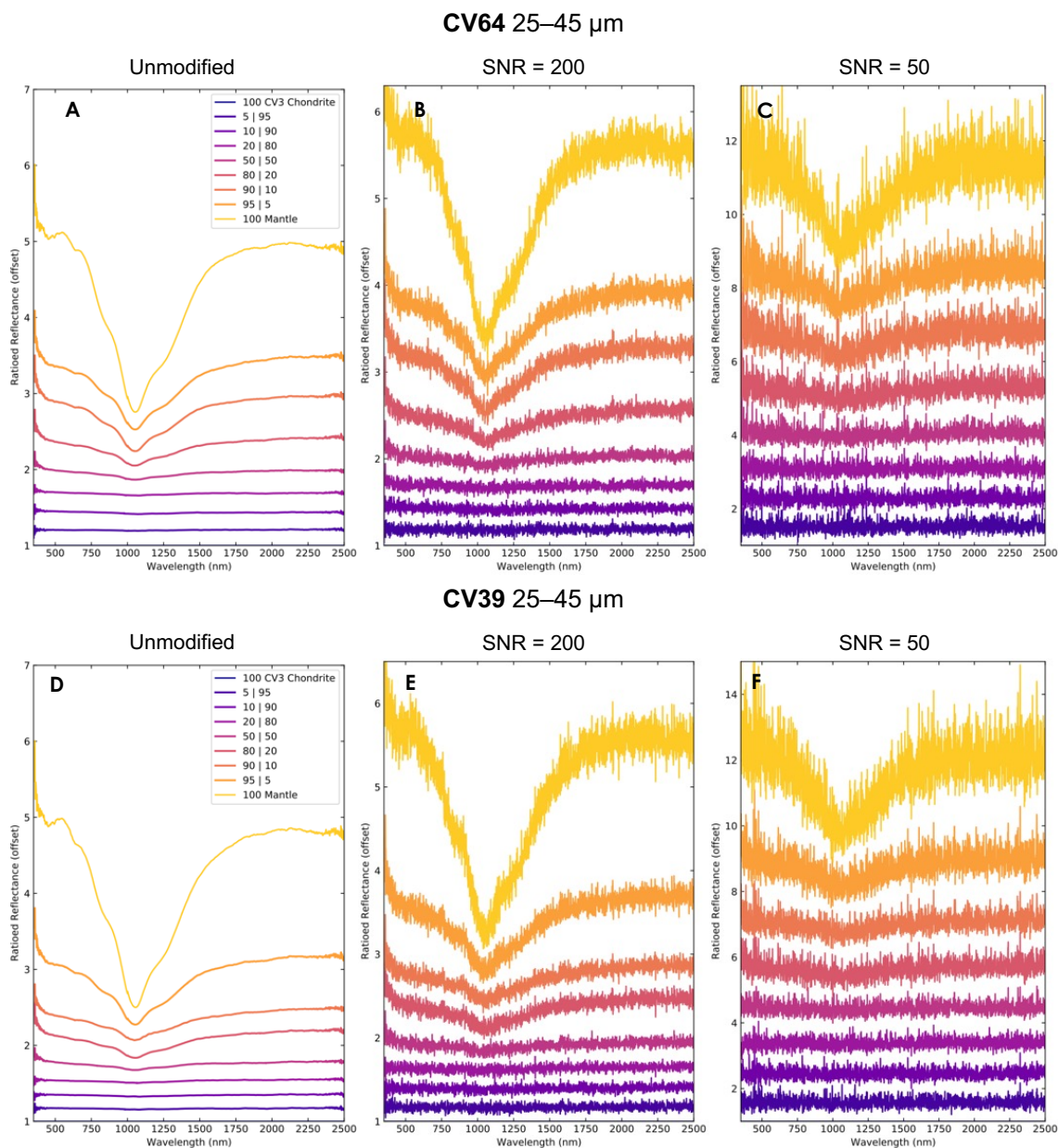


Figure 7: Reflectance spectra of CV3 mantle analog endmembers and mantle analog + CV3 chondrite mixtures ratioed to the reflectance spectrum of the CV3 chondrite endmember, Allende. Columns are ratios of original unmodified spectra (a, d) and ratios of spectra that were synthetically degraded to simulate signal-to-noise values of 200 (b, e) and 50 (c, f). Colors and figure legends correspond to the relative wt.% fraction of each mantle analog and chondrite endmember for each sample measured.

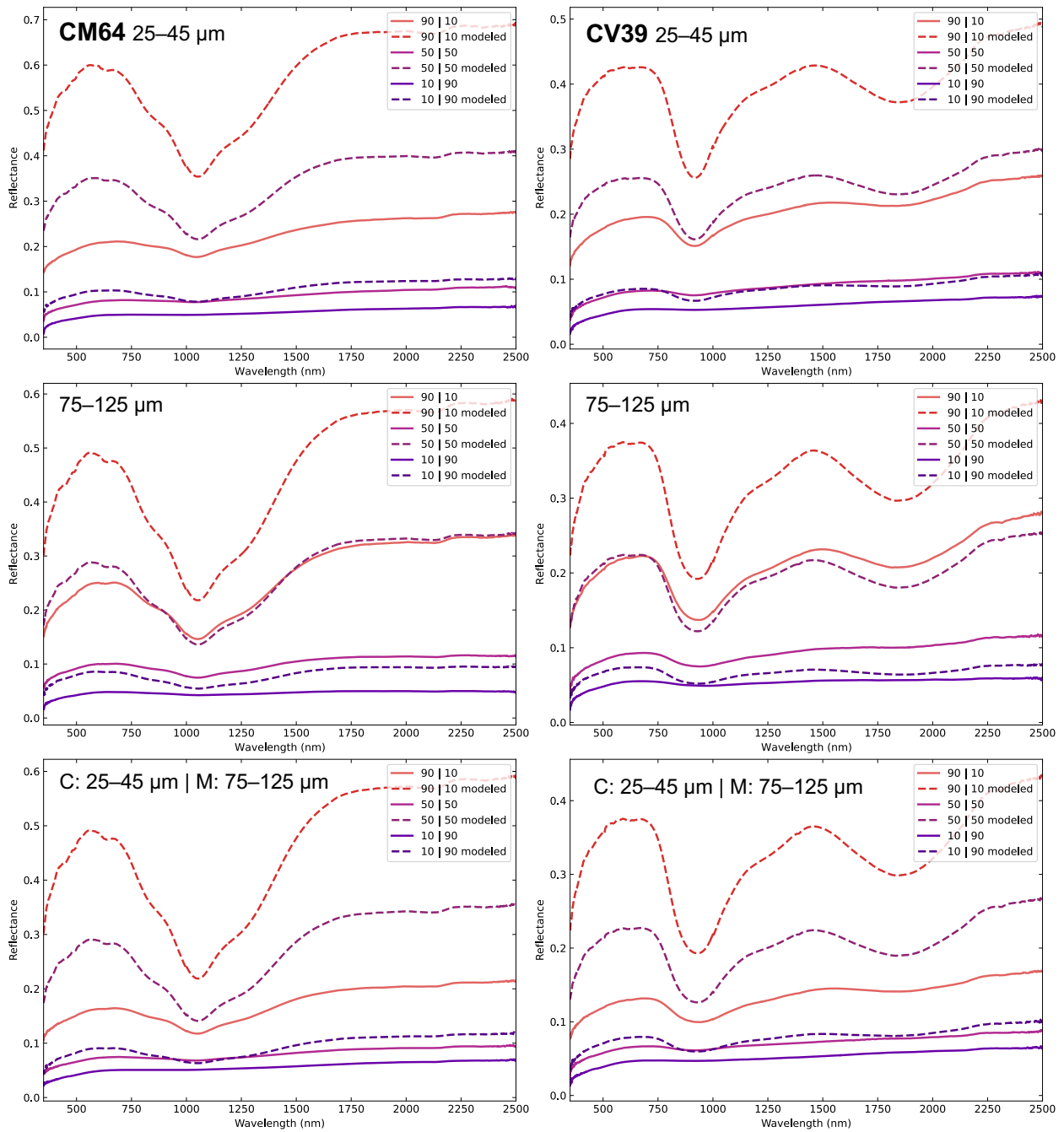


Figure 8: Reflectance spectra of the measured 90/10, 50/50, and 10/90 ratio mixtures (solid lines) compared to their modeled spectra (dashed lines) calculated as linear combinations of chondrite and mantle analog endmember spectra at the corresponding ratios.

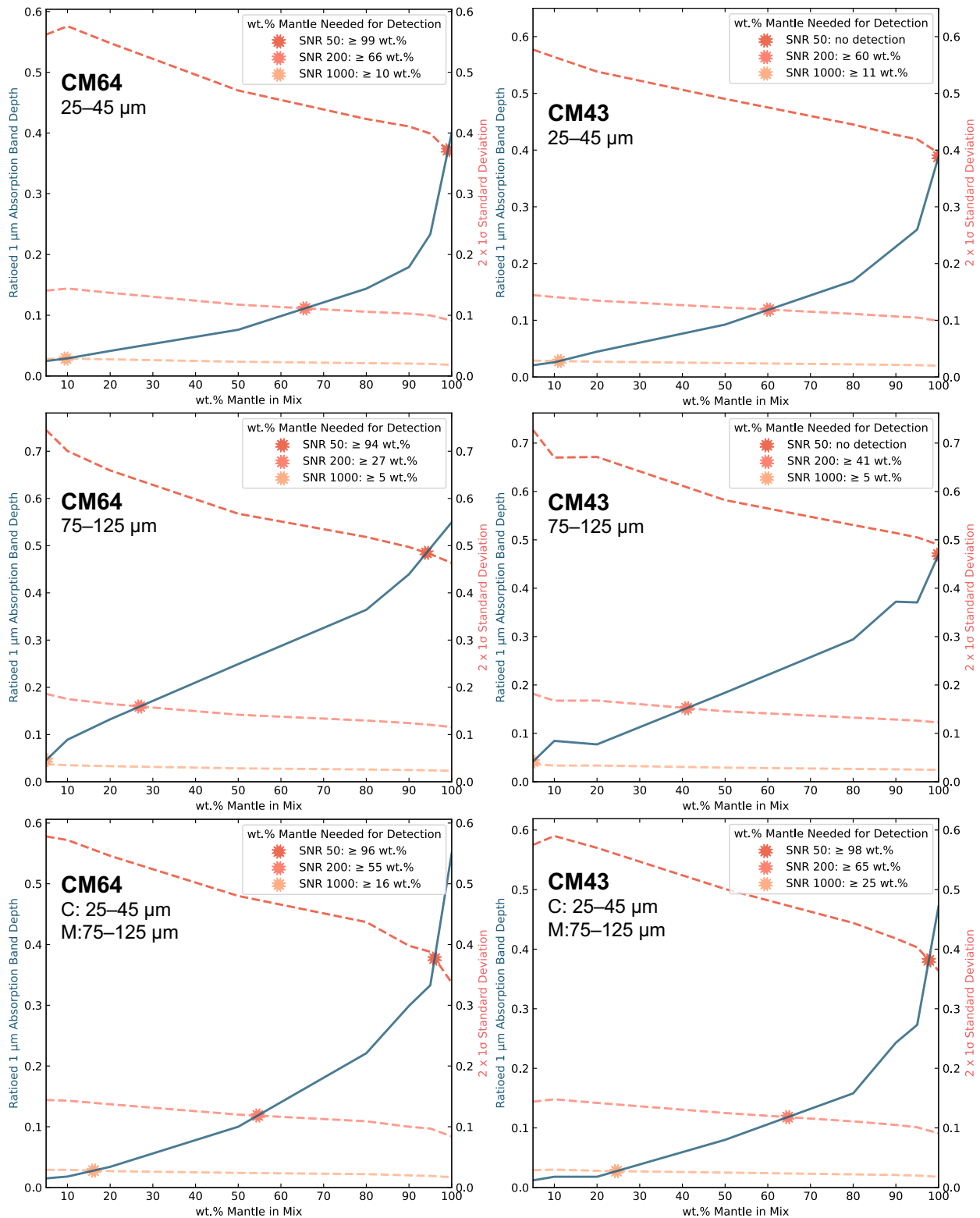


Figure 9: Thresholds for detecting a 1 μm absorption feature in ratioed spectra of CM2 chondrite and mantle analog mixtures. Solid blue lines show the 1 μm absorption band depth in ratioed spectra as a function of relative wt.% fraction of each mantle analog in mixture. Increasing mantle wt.% results in an increase in the strength of the 1 μm band

depth. Dashed lines indicate the $2 \times 1\text{-}\sigma$ standard deviation for synthetically degraded spectra simulating SNRs of 1000, 200, and 50. Points of intersection indicate how much mantle material is required in mixture to produce a ratioed $1\text{ }\mu\text{m}$ band depth equal to or greater than the $2 \times 1\text{-}\sigma$ standard deviation, i.e., the detection threshold.

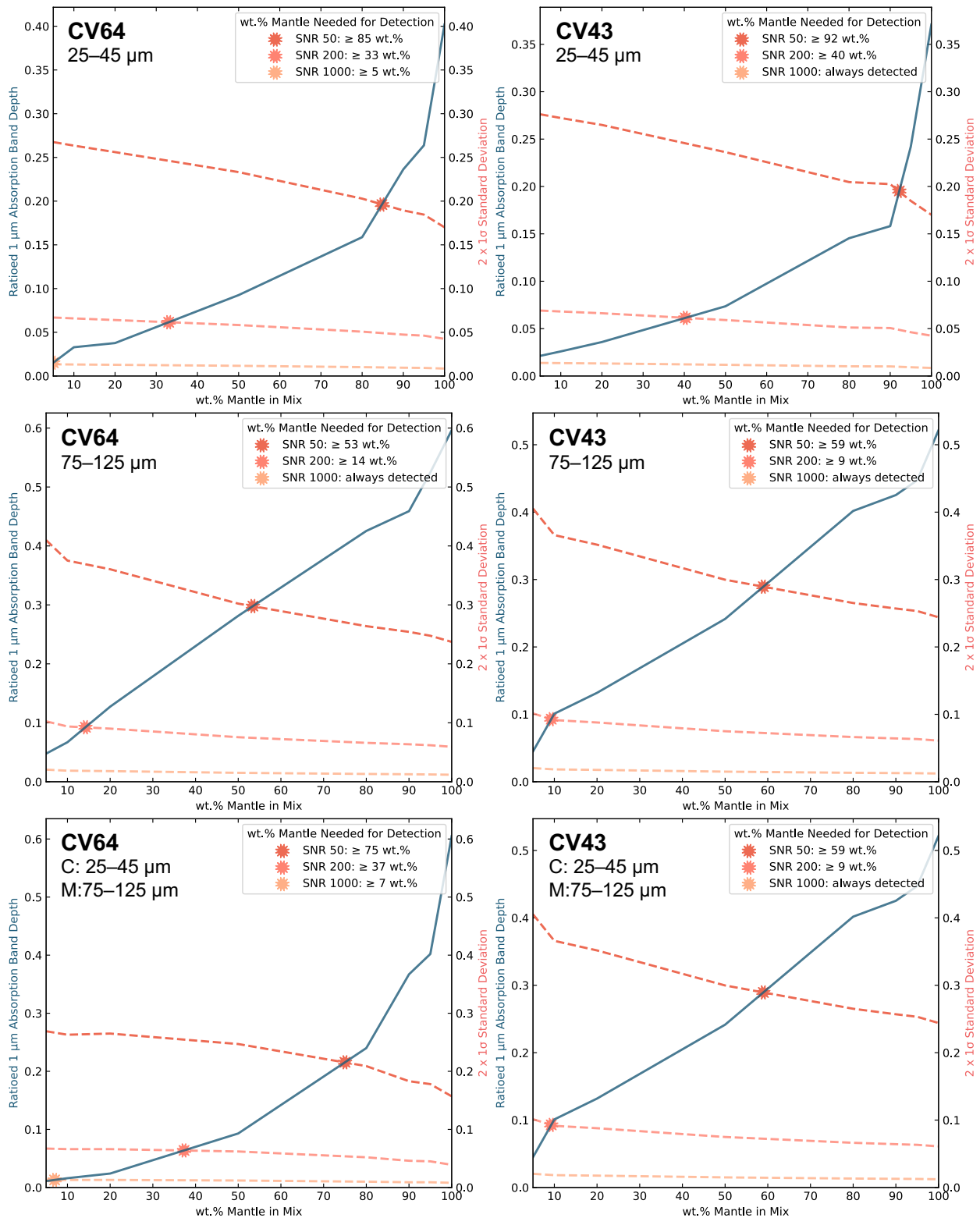


Figure 10: Thresholds for detecting a 1 μm absorption feature in ratioed spectra of CV3 chondrite and mantle analog mixtures. Solid blue lines show the 1 μm absorption band depth in ratioed spectra as a function of relative wt.% fraction of each mantle analog in mixture. Increasing mantle wt.% results in an increase in the strength of the 1 μm band

depth. Dashed lines indicate the $2 \times 1\text{-}\sigma$ standard deviation for synthetically degraded spectra simulating SNRs of 1000, 200, and 50. Points of intersection indicate how much mantle material is required in mixture to produce a ratioed $1\text{ }\mu\text{m}$ band depth equal to or greater than the $2 \times 1\text{-}\sigma$ standard deviation, i.e., the detection threshold.

Supplementary Table 1: Values of ratioed 1 μm absorption band depths and $2 \times 1\text{-}\sigma$ standard deviations calculated for SNRs of 1000, 200, and 50 for all compositions and mixture ratios. Red cells indicate where the 1 μm absorption band depth is less than the calculated error for that SNR. For these spectra, the 1 μm absorption feature is not intense enough to be statistically detectable given the noise and uncertainty for that SNR. Mantle analog material in these mixtures is consequently considered undetected. These data are used to construct the plots in Figures 9 and 10.

CM64 (25–45 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.400	0.018	0.091	0.365
95	5	0.233	0.020	0.100	0.399
90	10	0.179	0.021	0.103	0.411
80	20	0.144	0.021	0.106	0.423
50	50	0.076	0.024	0.118	0.470
20	80	0.041	0.027	0.137	0.548
10	90	0.029	0.029	0.144	0.576
5	95	0.025	0.028	0.141	0.562

CM43 (25–45 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.388	0.020	0.099	0.395
95	5	0.260	0.021	0.105	0.419
90	10	0.230	0.021	0.107	0.427
80	20	0.170	0.022	0.111	0.445
50	50	0.092	0.025	0.123	0.490
20	80	0.045	0.027	0.135	0.538
10	90	0.026	0.028	0.141	0.564
5	95	0.021	0.029	0.144	0.577

CM64 (75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.549	0.023	0.116	0.463
95	5	0.495	0.024	0.121	0.482
90	10	0.439	0.025	0.124	0.497
80	20	0.364	0.026	0.130	0.518
50	50	0.249	0.028	0.142	0.568
20	80	0.132	0.033	0.165	0.659
10	90	0.089	0.035	0.175	0.701
5	95	0.046	0.037	0.186	0.745

CM43 (75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.469	0.025	0.123	0.490
95	5	0.371	0.025	0.126	0.505
90	10	0.372	0.026	0.129	0.514
80	20	0.294	0.027	0.133	0.531
50	50	0.184	0.029	0.146	0.582
20	80	0.077	0.034	0.168	0.671
10	90	0.084	0.034	0.168	0.670
5	95	0.042	0.036	0.182	0.727

CM64 (C: 25–45 μm M: 75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.550	0.017	0.084	0.337
95	5	0.333	0.019	0.097	0.388
90	10	0.299	0.020	0.100	0.398
80	20	0.221	0.022	0.109	0.437
50	50	0.100	0.024	0.120	0.480
20	80	0.034	0.027	0.137	0.546
10	90	0.018	0.029	0.143	0.572
5	95	0.015	0.029	0.144	0.578

CM43 (C: 25–45 μm M: 75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 $\times$ 1- σ Standard Deviation		
Mantle	Chondrite		SNR = 1000	SNR = 200	SNR = 50
100	0	0.472	0.018	0.091	0.364
95	5	0.273	0.020	0.101	0.403
90	10	0.243	0.021	0.105	0.418
80	20	0.158	0.022	0.111	0.444
50	50	0.080	0.025	0.125	0.501
20	80	0.018	0.028	0.142	0.570
10	90	0.018	0.030	0.148	0.590
5	95	0.012	0.029	0.144	0.575

Supplementary Table 1: Values of ratioed 1 μm absorption band depths and $2 \times 1\text{-}\sigma$ standard deviations calculated for SNRs of 1000, 200, and 50 for all compositions and mixture ratios.

Red cells indicate where the 1 μm absorption band depth is less than the calculated error for that SNR. For these spectra, the 1 μm absorption feature is not intense enough to be statistically detectable given the noise and uncertainty for that SNR. Mantle analog material in these mixtures is consequently considered undetected. These data are used to construct the plots in Figures 9 and 10.

CV64 (25–45 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.402	0.009	0.043	0.170
95	5	0.264	0.009	0.046	0.185
90	10	0.236	0.009	0.047	0.189
80	20	0.159	0.010	0.051	0.203
50	50	0.093	0.012	0.058	0.233
20	80	0.038	0.013	0.064	0.256
10	90	0.033	0.013	0.066	0.263
5	95	0.015	0.013	0.067	0.268

CV39 (25–45 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.371	0.009	0.043	0.170
95	5	0.242	0.009	0.046	0.185
90	10	0.158	0.010	0.051	0.202
80	20	0.145	0.010	0.051	0.205
50	50	0.074	0.012	0.059	0.236
20	80	0.036	0.013	0.066	0.265
10	90	0.026	0.014	0.068	0.272
5	95	0.021	0.014	0.069	0.276

CV64 (75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.596	0.009	0.043	0.170
95	5	0.525	0.009	0.046	0.185
90	10	0.459	0.009	0.047	0.189
80	20	0.425	0.010	0.051	0.203
50	50	0.281	0.012	0.058	0.233
20	80	0.127	0.013	0.064	0.256
10	90	0.067	0.013	0.066	0.263
5	95	0.048	0.013	0.067	0.268

CV39 (75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.522	0.012	0.061	0.244
95	5	0.447	0.013	0.063	0.253
90	10	0.425	0.013	0.064	0.257
80	20	0.402	0.013	0.066	0.265
50	50	0.242	0.015	0.075	0.300
20	80	0.132	0.018	0.088	0.352
10	90	0.101	0.018	0.091	0.366
5	95	0.045	0.020	0.101	0.405

CV64 (C: 25–45 μm M: 75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.605	0.008	0.039	0.157
95	5	0.402	0.009	0.045	0.178
90	10	0.367	0.009	0.046	0.183
80	20	0.240	0.010	0.052	0.209
50	50	0.093	0.012	0.062	0.247
20	80	0.024	0.013	0.066	0.265
10	90	0.016	0.013	0.066	0.263
5	95	0.011	0.013	0.067	0.269

CV39 (C: 25–45 μm M: 75–125 μm)					
Relative Abundance (wt.%)		Ratioed 1 μm Band Depth	2 x 1- σ Standard Deviation		
			SNR = 1000	SNR = 200	SNR = 50
Mantle	Chondrite				
100	0	0.531	0.008	0.040	0.162
95	5	0.486	0.008	0.042	0.169
90	10	0.325	0.009	0.047	0.189
80	20	0.230	0.011	0.053	0.212
50	50	0.070	0.013	0.063	0.253
20	80	0.027	0.013	0.067	0.268
10	90	0.016	0.013	0.067	0.268
5	95	0.012	0.013	0.067	0.269

Chapter 4 | Bennu's History of Aqueous Alteration and Space Weathering

Inferred from Spectral Heterogeneity of Returned Samples

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4.1 Abstract

Primitive carbon-rich meteorites and their asteroidal progenitors are among the oldest solar system materials available for study and provide important clues to the processes that governed their formation and evolution. However, terrestrial alteration is a process that overprints these records by modifying original mineral assemblages and introducing new contamination phases. The surface materials of asteroid (101955) Bennu returned by the OSIRIS-REx spacecraft are pristine samples from a B-type asteroid that are free from terrestrial alteration and provide us with an unbiased record of the processes that formed and modified Bennu and its parent body. Here we report on the particle-to-particle variability of mineral phases observed in 79 particles from a pristine aggregate sample (803124-0) of material returned from Bennu. Carbonates, organic molecules, and hydrated phases are ubiquitous, confirming spacecraft observations, but exhibit significant variability in the shape, strength, and position of spectral features diagnostic of mineral chemistry. We also observe spectra of exotic hydrated and organic-rich phosphate grains as well as a single

silica-rich grain. These observations provide evidence for space weathering and extensive aqueous alteration by evolving fluids that together, provide a glimpse into both the ancient and contemporary processes that govern the evolution of small primitive bodies.

4.2 Introduction

The Origins-Spectral Interpretation, Resource Identification, and Security-Regolith Explorer (OSIRIS-REx) spacecraft arrived at near-Earth asteroid (101955) Bennu in December 2018, and after a nearly two-year observational phase, collected surface material from the Nightingale Site on 20 October 2020 (Lauretta et al., 2021, 2022). During this observational phase, the OSIRIS-REx Visible and Infrared Spectrometer (OVIRS) collected spectral data over the wavelength range from 0.4 to 4.3 μm (Reuter et al., 2018). Global and local characterization of the surface of Bennu by OVIRS revealed a globally present 2.74 μm absorption feature, indicative of widespread OH- and possibly H₂O-bearing minerals, likely in the form of Mg-rich phyllosilicates (Hamilton et al., 2019; Simon et al., 2020a). A similarly ubiquitous 3.4 μm absorption feature, sensitive to CO₃²⁻ and C-H stretching vibrations, suggests globally dispersed carbon-bearing materials, including a mix of organics and carbonates (Simon et al., 2020a,b; Kaplan et al., 2020, 2021). The presence of these phases, and in particular the observation of bright cm-thick and m-long carbonate veins in boulders, suggests both km-scale hydrothermal alteration on the Bennu parent body and a relatively young surface needed to preserve the spectral signatures of organics.

The Nightingale sampling site is located in Hokioi crater, a 20-m-diameter impact feature thought to be one of Bennu's most recent impact features based on its small size and redder sloped visible and near-infrared (VNIR) spectrum (DellaGiustina et al., 2020). Interestingly, the Nightingale site appears rich in organics (Kaplan et al., 2020; Ferrone et al., 2021) and features an OH/H₂O absorption positioned at ~2.71 μm , which is blueshifted compared to Bennu's global average (Deshapriya et al., 2021), indicating that space weathering processes may be actively modifying Bennu's optical surface. On 24 September 2023, nearly three years after the sampling event, the OSIRIS-REx spacecraft successfully returned ~120 g of pristine carbonaceous material from the Nightingale site on Bennu (Lauretta et al., 2024).

In this study, we investigated the infrared reflectance spectra (~2–16 μm) of 79 individual particles from an aggregate sample (Sample ID: 803124-0; Figure 1) collected from within the TAGSAM sample container, with particles ranging in size from ~100–950 μm . Our hypothesis driven approach to this study (Lauretta et al., 2023) was to investigate the mineralogy, chemistry, and spectral properties of returned sample to evaluate the efficacy of remote compositional analyses of Bennu and glean insights into the conditions of formation of Bennu and the processes that modified it throughout solar system history.

4.3 Methods

4.3.1 Sample Selection and Laboratory Spectroscopy

The collection of Bennu surface material studied here is a bulk aggregate of loose fine- and intermediate-sized particles weighing approximately 19.2 milligrams and is given the unique Bennu sample ID: OREX-803124-0. It is a subsample of the ~201 mg bulk aggregate sample OREX-800029-0, which was previously studied by Lauretta et al. (2024). Particles typically range in size from a few to tens of micrometers up to 1–1.5 millimeters. Prior to arriving in our lab, the sample was curated in cleanroom conditions at NASA's Johnson Space Center and held under a high-purity nitrogen gas. The sample was transported in a sealed stainless-steel container and re-opened in our lab also in a high-purity nitrogen filled glovebox. For spectral measurements the sample was gently poured into a standard 9-mm diameter black Teflon-coated aluminum dish.

Infrared reflectance spectra of individual particles were measured using a Bruker LUMOS microscope Fourier transform infrared spectrometer (μ FTIR) at Brown University in Providence, RI. The FTIR was operated in point mode and collected reflectance spectra with 4 cm^{-1} spectral resolution over the wavelength range of $\sim 1\text{--}16\text{ }\mu\text{m}$ using a LN_2 -cooled MCT detector. A knife-edge aperture produced square measurement spot sizes with side lengths that typically ranged from $100\text{--}140\text{ }\mu\text{m}$. A gold mirror was used as a standard spectral reference. All measurements were performed under purged dry-air conditions (dew point of -70°C). Approximately 200 scans were acquired and internally averaged to produce each reflectance spectrum. Particles were only briefly exposed to ambient laboratory conditions ($\sim 22^\circ\text{C}$ and $\sim 35\%$ relative humidity) for a few seconds as sample was transported between the purged dry-air chamber where measurements were made and the high purity nitrogen-filled glovebox where the sample was stored.

Additional “bulk” IR reflectance spectra (not presented here) were acquired using a Nicolet NEXUS 870 FTIR equipped with a DTGS in the NASA RELAB facility also at Brown university. A diffuse gold reflectance standard was used as a spectral reference. NIR spectra (0.8–5 μm) were collected at 4 cm^{-1} spectral resolution using a CaF_2 beam splitter and white light source. MIR spectra (1.5–25 μm) were also collected at 4 cm^{-1} but using a KBr beam splitter and IR (globar) source. These bulk (whole sample) spectra were acquired within days of sample acquisition prior to our μFTIR measurements and several weeks afterwards to inspect for any spectral changes that may have occurred due to atmospheric exposure during the transport and storage of our sample within our lab. We report that all spectra acquired of the sample appear identical before and after our μFTIR measurements, indicating that no observable effects from terrestrial contamination impacted our sample over this period.

4.3.2 Band Parameters Analysis

Due to the extremely dark nature of the particles studied here, high-frequency noise was often encountered in individual spectra. To minimize the effects of this noise on our spectral analysis and band position assignments, we implemented a low-pass filter. Specifically, we used a combination of SciPy’s Butterworth filter (`scipy.signal.butter`) and the ‘`filtfilt`’ function (`scipy.signal.filtfilt`) (Virtanen et al., 2020). The Butterworth filter is a type of signal processing filter designed to have a maximally flat frequency response in the passband, making it particularly effective at preserving the signal’s original shape while reducing noise. Here we used a 3rd order filter with a critical frequency of 0.10. The ‘`filtfilt`’

function applies the digital filter forward and backward to the signal, resulting in a zero-phase filter that preserves the original characteristics and avoids phase distortion. Together, this filter technique is exceptionally effective at reducing high-frequency noise while preserving the original signal characteristics. For completeness, we present both the original ‘raw’ spectra in red along with the filtered spectra in purple, unless indicated otherwise.

Absorption band depths and wavelength positions of the ~3 μm absorption band minima were calculated by first performing a continuum-removal across the ~2.6–3.3 μm region of the filtered spectrum. This range was chosen to avoid influence from organic and carbonate absorptions near ~3.4 μm . The spectral continuum over this region was assumed to be linear and was defined using the convex hull method (e.g., Schultz et al., 2023). This method uses an upper convex hull across the wavelength region of interest to define a piecewise linear continuum. The filtered spectrum was then divided by the spectral continuum to produce a continuum-removed reflectance spectrum. The 3 μm band minimum was then calculated as the overall reflectance minimum of the continuum-removed spectra, which for these particles was driven by the relative strength of OH- and H₂O-related absorptions occurring between ~2.71–3.10 μm . Band depths at this band minimum position as well as at 2.9 μm were then calculated using the equation:

$$B_{\lambda} = 1 - R_{min,\lambda}$$

Where B_{λ} is the calculated band at the wavelength λ and $R_{min,\lambda}$ is the reflectance value of the continuum-removed spectrum also at wavelength λ . Using the same approach, the

wavelength position of the ~ 6.4 μm asymmetric stretching carbonate feature was also calculated. The spectral continuum was bound from 6.05–7.175 μm . We also calculated the band area of this feature by applying Simpson's method to integrate over the continuum-removed ~ 6.4 μm carbonate absorption from 6.05 to 7.175 μm .

4.4 Results

4.4.1 Heterogeneity of the 3 μm OH/H₂O Hydration Band

OH- and H₂O-bearing phases provide details of the history of fluid flow and aqueous alteration on asteroids and meteorite parent bodies (Brearley et al., 2006). These phases give rise to diagnostic absorptions in the 2.7–3.0 μm wavelength region; specifically, the OH symmetric and asymmetric stretching modes occurring from 2.7–2.85 μm , the H₂O symmetric and asymmetric stretching modes occurring from 2.85–2.99 μm , and an overtone of the H₂O bending mode, which occurs at ~ 3.1 μm . Together these features are often convolved to produce a broad and complex absorption hereafter referred to as the ~ 3 μm (hydration) feature. In Figure 2 and Figure 3 we show the variation in the strength, shape, and position of the 3 μm hydration feature from particle to particle and note significant spectral heterogeneity. The strength of the absorption at the band minimum position (often near 2.7 μm) and at 2.9 μm is linked to the abundance of OH-bearing and H₂O-bearing phases. The ratio of these two band parameters is therefore a useful proxy not only for band shape but the relative abundances of these phases (Figure 2a). We therefore refer to and use this ratio as a proxy for band shape of the ~ 3 μm absorption feature. Normalizing this

ratio by the 2.9 μm band depth (Figure 2b) allows us to see significant particle-to-particle heterogeneity in the strength and shape of this feature. Shapes of the ~ 3 μm band range from sharp, weak, and narrow features, indicative of OH-rich and H_2O -poor serpentine-like phases to broader features with deeper H_2O absorptions, likely indicating the presence of H_2O -bearing smectite-like phases (Figure 2, spectrum 1 and spectrum 4, respectively). Several particles exhibit extremely deep and wide 3 μm features, which appear to be dominated by H_2O -related absorptions.

The wavelength position of the OH stretching mode, which is often the overall band minimum, is strongly influenced by the polarizing power of the octahedral metal cation the OH-group is bonded to (Bishop et al., 1994). This results in ~ 3 μm bands centered at shorter wavelength positions (~ 2.71 – 2.73 μm) for Mg-bearing phyllosilicates and longer wavelengths (~ 2.74 – 2.78 μm) for Fe-bearing phyllosilicates (Bishop et al., 2002, 2008; Takir et al., 2013). In Figure 3 we show band shape as a function of the wavelength position of the overall 3 μm band minimum. For most particles, the wavelength position of this features varies from ~ 2.706 – 2.725 μm (Figure 3, inset). This is roughly consistent with the wavelength position of the same feature measured at Hokioi by the OVIRS instrument (~ 2.72 μm ; Deshapriya et al., 2021) but shorter than the global average of 2.74 μm (Hamilton et al., 2019; Simon et al., 2020a). Interestingly, this range in position is nearly double of that observed for similarly altered CM2 chondrites (Schultz et al., 2023). Though, the meteorite groups that appear most consistent with these data include CM1 and C2-ungrouped (Tagish Lake, Tarda) as well as spectra from returned samples of asteroid Ryugu (Hiroi et al., 2023). Several particles here exhibit 3 μm band minima positioned at much longer wavelengths

(2.78–3.1 μm) and are highly correlated with having broader and deeper ~ 3 μm features dominated by H_2O -related absorptions. Visible light images show that these anomalous particles appear white and much brighter than the typical background material, and likely belong to the Na,Mg-phosphate-bearing mottled morphologies found in Laurretta et al. (2024).

4.4.2 NH_4^+ -bearing Phases

Seven particles exhibit distinct absorptions centered near 3.06 μm , consistent with the presence of NH_4^+ -bearing phases (Supplementary Figure 1). This location is also near the second bending overtone of H_2O (~ 3.1 μm). However, the lack of strong additional features attributed to H_2O stretching modes near ~ 2.9 μm suggests that H_2O is not the dominant species. A ~ 3.05 μm feature was not observed to be widespread on Bennu (Simon et al., 2020a) but is present on many C-complex main-belt asteroids (e.g., Ceres and Themis, Rivkin and Emery, 2010; Usui et al., 2019) and is observed in several carbonaceous chondrites (e.g., Cold Bokkeveld, Ehlmann et al., 2018) and is typically attributed to the presence of ammoniated clays.

The shape and position of this feature in our sample set, along with the presence of additional absorptions occurring near ~ 3.25 and ~ 5.57 μm , is consistent with the presence of ammoniated smectitic clays, where the NH_4^+ cation resides in the interlayer sites exchanging for other cations (Bishop et al., 2002; Ehlmann et al., 2018). However, at present, other NH_4^+ -bearing phases (e.g., ammonia-bearing organics, amine salts) cannot be ruled out as possible sources of this feature. Nevertheless, the occurrence of NH_4^+ -bearing

phases provides important constraints for the species of ices accreted by Bennu's parent body, which is directly tied to heliocentric distance at which it formed.

4.4.3 A Menagerie of Carbonates and Organics

Carbonates and organic molecules are common but minor components of C chondrites (Brearley et al., 2006), especially the CM and CI chondrites, and have also been detected at Ceres (De Sanctis et al., 2016) and at Bennu (Simon et al., 2020a; Kaplan et al., 2020). Their presence is readily detected due to the fundamental and combination/overtone of four vibrational modes of the CO_3^{2-} anion (Bishop et al., 2021); these include the symmetric stretching, out-of-plane bending, asymmetric stretching, and in-plane bending modes. At Bennu, carbonate species including dolomite, magnesite, and others were detected by the characteristic shape and position of the $\sim 3.4 \mu\text{m}$ doublet combination and overtone absorption. Organics, often in the form of insoluble organic matter (IOM), are an important component of C chondrites (Kaplan et al., 2019) and also exhibit absorptions in this region due to aliphatic and aromatic C-H bonds, often complicating interpretations. Indeed, only a fraction of spectra at Bennu could be attributed solely to carbonates (Simon et al., 2020a; Kaplan et al., 2020, 2021).

A broad and complex $\sim 3.4 \mu\text{m}$ feature is ubiquitous in the spectra of our samples, indicating a widespread mixture of carbonate and organic phases. To study carbonates phases in more detail, we measured the strength and wavelength position of the asymmetric stretching feature, which manifests as a prominent reflectance maximum (peak) positioned near $\sim 6.4 \mu\text{m}$ (Figure 4). Supplementary Figure 2 shows the strength of this feature, as

measured by the $\sim 6.4\ \mu\text{m}$ band area, plotted against other parameters of interest, including the wavelength position of this carbonate feature as well as the position and band depth of the $3\ \mu\text{m}$ absorption feature. Interestingly, the position of this feature varies from ~ 6.3 – $6.75\ \mu\text{m}$ and clusters in three regions near ~ 6.3 , ~ 6.55 , and $\sim 6.73\ \mu\text{m}$. The position of this feature is strongly linked to the size of the effective ionic radii of the cation the CO_3^{2-} group is bonded to. The cluster of spectra at the shorter wavelengths, i.e., ~ 6.3 and $\sim 6.55\ \mu\text{m}$, are most consistent with phases like Mg-calcite and magnesite, and aragonite and siderite, respectively (Bishop et al., 2021). Features positioned at longer wavelengths are not well matched by library spectra of carbonates but may be consistent with Na-carbonate (natrite) or nitrates (e.g., Bishop et al., 2021). Figure 4 shows representative spectra of particles that exhibit strong $\sim 6.4\ \mu\text{m}$ absorptions and their corresponding ~ 3.4 and $4\ \mu\text{m}$ regions. It is notable that the intensity of this feature does not appear to correlate with either the position or strength of the $3\ \mu\text{m}$ band.

Organic molecules, typically in the form of IOM make up $>70\ \text{wt.}\%$ of the meteoritic carbon budget (Cody and Alexander, 2005; Alexander et al., 2017). Meteoritic IOM, an acid-insoluble kerogen-like macromolecule, exhibits at least four absorptions in the $\sim 3.4\ \mu\text{m}$ region from the symmetric and asymmetric stretching modes of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$). These features are often difficult to observe due to the overlapping nature of CO_3^{2-} absorptions due to carbonates. To study these features due to organics in isolation, we select several spectra that lacked an apparent $\sim 6.4\ \mu\text{m}$ carbonate feature. This is typically the strongest feature in spectra of carbonates (Bishop et al., 2021) and we take its absence to mean these particles hosted negligible amounts of carbonate. In Figure 5 we show the

~3.4 μm region spectra for several of these particles, along with a representative meteoritic IOM from Kaplan et al. (2019).

We observe absorptions consistent with aliphatic $-\text{CH}_2$ and CH_3 bonds at 3.38, 3.42, and 3.48 μm in all spectra. The presence of these spectral features indicates that the minimum hydrogen to carbon ratio (H/C) ratio is greater than 0.3 (Kaplan et al., 2019). Comparing estimates of the band depths of the 3.42 μm absorption with C chondrite trends observed by Kaplan et al. (2019) suggests a bulk carbon abundance of 2–3 wt.% and an H/C ratio of ~0.7, consistent with values for CM and CI chondrites and predictions made from the OVIRS instrument at Bennu (Kaplan et al., 2021). The presence of these aliphatic features also suggests a surface exposure age of less than a few million years (Kaplan et al., 2021; Thompson et al., 2020), which are readily broken down by space weathering processes and converted to aromatic molecules (Clark et al., 2023). Interestingly, we also observe an apparent absorption near 3.28 μm in several particles (Figure 5), which is consistent with aromatic CH absorptions (Kaplan et al., 2019). The presence of this feature co-occurring with aliphatic absorptions in several particles may suggest incipient alteration of these aliphatic molecules to aromatic structure due to space weathering of a freshly exposed surface.

4.4.4 The Exotics

Among the most unexpected results in the initial analysis of returned samples from Bennu was the presence of Mg-, Na-, and Ca-phosphate grains dispersed throughout the sample as a common but minor constituent (Lauretta et al., 2024). They occur as isolated particles,

euohedral to anhedral grains, and veins and surface coatings and are readily detected by their optically apparent bright white nature. In Figure 6 we present reflectance spectra acquired for several of these particles that appeared to exhibit these bright white surface properties. Characteristic of all these particles are massive $\sim 3\ \mu\text{m}$ absorption features dominated by H_2O absorptions with minima positions ranging from $2.77\text{--}3.10\ \mu\text{m}$. One particle in particular exhibits exceptionally well-resolved absorptions in the $\sim 3.4\ \mu\text{m}$; specifically at $3.260, 3.360, 3.379, 3.481,$ and $3.505\ \mu\text{m}$, broadly consistent with carbonate- and organic-related absorptions. Additional features near ~ 4.0 and ~ 6.3 further support an interpretation for carbonate. Several other particles (p78, p31, p15) also exhibit evidence of $\sim 3.4\ \mu\text{m}$ region absorptions but are less well resolved.

Also presented in Figure 6 is reflectance spectra acquired from a particularly bright $\sim 325\ \mu\text{m}$ -sized particle with absorption features that are strikingly consistent with quartz (Michalski et al., 2003). There are a variety of silica (SiO_2) polymorphs that are relevant to planetary materials that form under a variety of fluid, pressure, and temperature conditions, including quartz, opal, tridymite, cristobalite, and coesite. These minerals and other amorphous silica phases have been found in virtually all major groups of meteorites, save for carbonaceous chondrites (Rubin and Ma, 2017). In most cases they are associated with impact melt and shock processes but in enstatite chondrites they occur in chondrules and chondrule rims (Rubin and Ma, 2017). The detection here would provide the first evidence for the occurrence of this phase in carbonaceous astromaterials and raises interesting questions regarding its origin. For many planetary and terrestrial systems, silica polymorphs occur as products of hydrothermal alteration, impact and shock processes, igneous

processes, and potentially as nebular condensates. Also in the spectra of this particle is a broad absorption centered at $\sim 2.95\ \mu\text{m}$, consistent with H_2O , and minor absorptions at $3.42\ \mu\text{m}$ and $3.51\ \mu\text{m}$, consistent with aliphatic CH absorptions. The presence of these phases suggests formation in a low temperature hydrothermal system. An alternative interpretation would be an exogenous origin (e.g., DellaGiustina et al., 2020), though further analyses are needed to fully explore this.

4.5 Discussion

To first order, the results on the particle-to-particle spectral variability confirm the remote sensing observations and characterization of Bennu (Hamilton et al., 2019, 2021; Simon et al., 2020a, 2020b; Kaplan et al., 2020, 2021a). Key observations presented here that must be accounted for in models of Bennu's formation and solar system history include: (1) particle-to-particle variability in the shape and position of the $3\ \mu\text{m}$ absorption feature, (2) the apparent shortward shift of this same feature ($\sim 2.71\text{--}2.72\ \mu\text{m}$) relative to Bennu's global average (~ 2.74 , Hamilton et al., 2019; Simon et al., 2020a; Deshipriya et al., 2021), (3) the presence and chemical diversity of carbonate species, (4) the prevalence of aliphatic absorptions that sometimes co-occur with aromatic absorptions, and (5) the presence of hydrated phosphate and quartz particles. We suggest here that these features are best explained by a combination of temporally protracted and/or spatially heterogeneous low-temperature fluid flow and space weathering processes.

4.5.1 Hydrothermal alteration of Bennu's parent body and evolving fluid compositions

Hydrated phases are present in every particle studied here. Mg-rich phyllosilicates (serpentine and saponite) appear to be the dominant phase, as indicated by diagnostic OH and H₂O absorptions with band minima positioned near ~2.71–2.72 μm (Bishop et al., 2002a, 2002b, 2008; Takir et al., 2013). These Mg-rich phyllosilicates form from the alteration of magnesian olivine and pyroxenes. In CM and CI chondrites, which have been suggested as potential analogs for Bennu (Hamilton et al., 2019, 2021), these phases are dominant in only the most extensively altered meteorites (Tomeoka and Buseck, 1985; Zolensky et al., 1989, 1993; Takir et al., 2013; Howard et al., 2009; Suttle et al., 2021). And indeed, the spectra presented here are consistent with highly altered CM1 and C2-ungrouped meteorites.

The variation in shape and position of the 3 μm absorption band observed here is consistent with the presence of serpentine and saponite that occur in varying relative amounts from particle to particle. Both minerals have overlapping temperature and pH stability fields (Zolensky et al., 1989), but the presence of organics suggest that temperatures remained relatively low (i.e., $\leq 0\text{--}100^\circ\text{C}$). Saponite, though, has been suggested to form at much higher water-to-rock ratios than serpentine (Zolensky et al., 1989; Bourcier and Zolensky, 1992). In meteorites like Bells, an unusual saponite-rich CM2 chondrite, increased silica activity ($a\text{SiO}_2$) from the extensive dissolution of low-Ca pyroxene has also been suggested as an important driver of saponite formation (Brearley, 1995), an intriguing possibility given the observation of a quartz particle in our sample. As such, the variable

occurrence of serpentine and saponite likely reflects extensive low-temperature aqueous alteration of fluids that changed in composition in space and/or time.

Carbonates, which are also products of aqueous alteration, are similarly abundant in C chondrites (Brearley et al., 2006), and are recorders of evolving fluid chemistries (Lee et al., 2014). In many studies of carbonate grains in C chondrites and Ryugu particles, evidence for disequilibria is often taken to suggest complex variations in fluid composition through time, likely as these fluids progressively equilibrated with host rock over millions of years (Riciputi et al., 1994; Brearley et al., 1999; Brearley and Hutcheon, 2000, 2002; Benedix et al., 2003; Lee et al., 2014; McCain et al., 2023). The complex assemblage of carbonates of different chemistries that occur here likely reflects a similar process, of extensive alteration by fluids with evolving compositions. Also notable in our data is the absence of correlation between the $\sim 6.4\ \mu\text{m}$ carbonate stretching feature and both the position and strength of the $3\ \mu\text{m}$ band. As the latter is taken as a proxy for extent of aqueous alteration (Tomeoka and Buseck, 1985; Zolensky et al., 1993; Takir et al., 2013; Howard et al., 2009), it then shows that the precipitation of these carbonate species does not preferentially occur at any point in this alteration process, but rather all throughout it.

The widespread occurrence of Mg-rich phyllosilicates, carbonates, organics, and the minor occurrence of NH_4^+ -bearing phases suggests the formation of Bennu's parent body in the outer solar system. In this environment, it was able to accrete significant amounts of ices that were later sufficiently heated to create a fluid, which extensively modified the body at the scale at which these samples were sourced.

4.5.2 Space weathering and a young Hokioi crater

An alternative, but not mutually exclusive, explanation for the difference in 3 μm band minima position of our samples compared to Bennu's global average is space weathering. Solar wind has been suggested to be the dominant space weathering process for young ($< 10^7$) inner solar system surfaces (e.g., Vernazza et al., 2009; Noguchi et al., 2014; Bonal et al., 2015). In laboratory experiments simulating solar wind irradiation on C chondrites and phyllosilicates using H^+ and He^+ , the ~ 2.7 μm OH stretching band was observed to shift by 10–20 nm towards longer wavelengths (Lantz et al., 2015; Rubino et al., 2020; Nakauchi et al., 2021). In this context, the particles in our sample, with band minima near ~ 2.71 – 2.72 μm , represent less space weathered material compared to Bennu's older surface (Walsh et al., 2019; Bierhaus et al., 2022; Barnouin et al., 2022), with an average band minimum near ~ 2.35 – 2.4 μm (Deshipriya et al., 2021; Hamilton et al., 2019; Simon et al., 2020a). This ~ 20 nm shift is perfectly consistent with previously mentioned laboratory results and supports the idea that Hokioi crater, the location of the Nightingale sampling site, is one of the youngest and least-weathered features on Bennu's surface (DellaGiustina et al., 2020; Barnouin et al., 2022). These observations also align well with Clark et al., (2023) who predict that the least weathered particles should have ~ 3 μm band minima occurring at shorter wavelengths and have sharper features, while more weathered particles should have 3 μm band minimum occurring at longer wavelengths.

Estimates of the age of Bennu's surface range from ~ 50 Myr to 1 Gyr (Walsh et al., 2019; Bierhaus et al., 2022), which is older than the predicted timescales for solar wind-based space weathering effects to occur (10^4 – 10^6 yr, Clark et al., 2023). Considering that

Bennu's surface has been exposed to relatively high temperatures since it was implanted in near-Earth space ~1–2.5 Myr ago (Ballouz et al., 2020), the detection of aliphatic CH groups further supports the notion that Hokioi crater is a relatively young feature on Bennu's surface. The presence of minor aromatic CH groups indicates that several of the particles in this aggregate sample have begun to experience incipient heating and/or space weathering (Kaplan et al., 2021). Incipient space weathering of these particles may also explain the variability in the shape and position of the 3 μm band observed in our data, including the strengthening of absorptions from 2.72–2.85 μm (Nakauchi et al., 2021). Shifts in 3 μm band minima positions were observed at Ryugu in both returned samples and in spectra of pre- and post-SCI experiments and are similarly explained by space weathering via solar wind irradiation (Kitazato et al., 2019; Hiroi et al., 2023; Le Pivert-Jolivet et al., 2023).

4.6 Conclusion

The value of the returned samples studied here is immeasurably strengthened by the context provided by spacecraft observations of Bennu and the Nightingale sampling site from which these samples originate. Our findings suggest that Bennu's primary mineralogy was almost completely modified by extensive low-temperature aqueous alteration from fluids with progressively evolving compositions. We also find evidence for a relatively young Hokioi crater incipiently modified by space weathering processes compared to Bennu's older terrains. These findings greatly enhance our understanding of small body processes and provide a clarified framework for spectral interpretations of primitive bodies.

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4.8 Supplementary Text

4.8.1 Reference Spectra

In **Figure 2** and **Figure 3** we compare the variability in position, shape, and strength of the 3 μm absorption feature with those calculated for Hokioi crater, the Ryugu particle C0002, and a variety of C chondrite meteorites. The spectrum of Hokioi crater is an average of 36 spectra collected over across the feature prior to the TAGSAM event. The observational configuration of the spacecraft and IDs for each individual spectra are provided in **Supplementary Table 1**. The spectrum of Ryugu particle C0002 is from Hiroi et al. (2023). The C chondrites referenced here are from Hiroi et al. (2021) and include: C2-ungrouped (Tagish Lake, Tarda), CI1 (Orgueil, Alais), CM2 (Nogoya, Murray, Murchison, Mighei, Dhofar 225, Crescent, Banten), CR2 (Al Rais), and CM1 (Moapa Valley). All spectra were collected from the RELAB database on NASA's PDS Geoscience Node Spectral Library. These spectra were also processed identically to the Bennu sample spectra as described in the preceding **Band parameters analysis** methods section.

Reflectance spectra for the carbonate minerals dolomite, natrite, magnesite, and siderite are presented in **Figure 4** as references for comparison to the carbonate features present in our samples. These spectra are from Bishop et al. (2021). In **Figure 5** we show a spectrum of IOM from the ALH 85013 acquired by Kaplan et al. (2019). These carbonate and IOM spectra were similarly downloaded from the PDS Spectral Library.

4.9 Figures and Tables

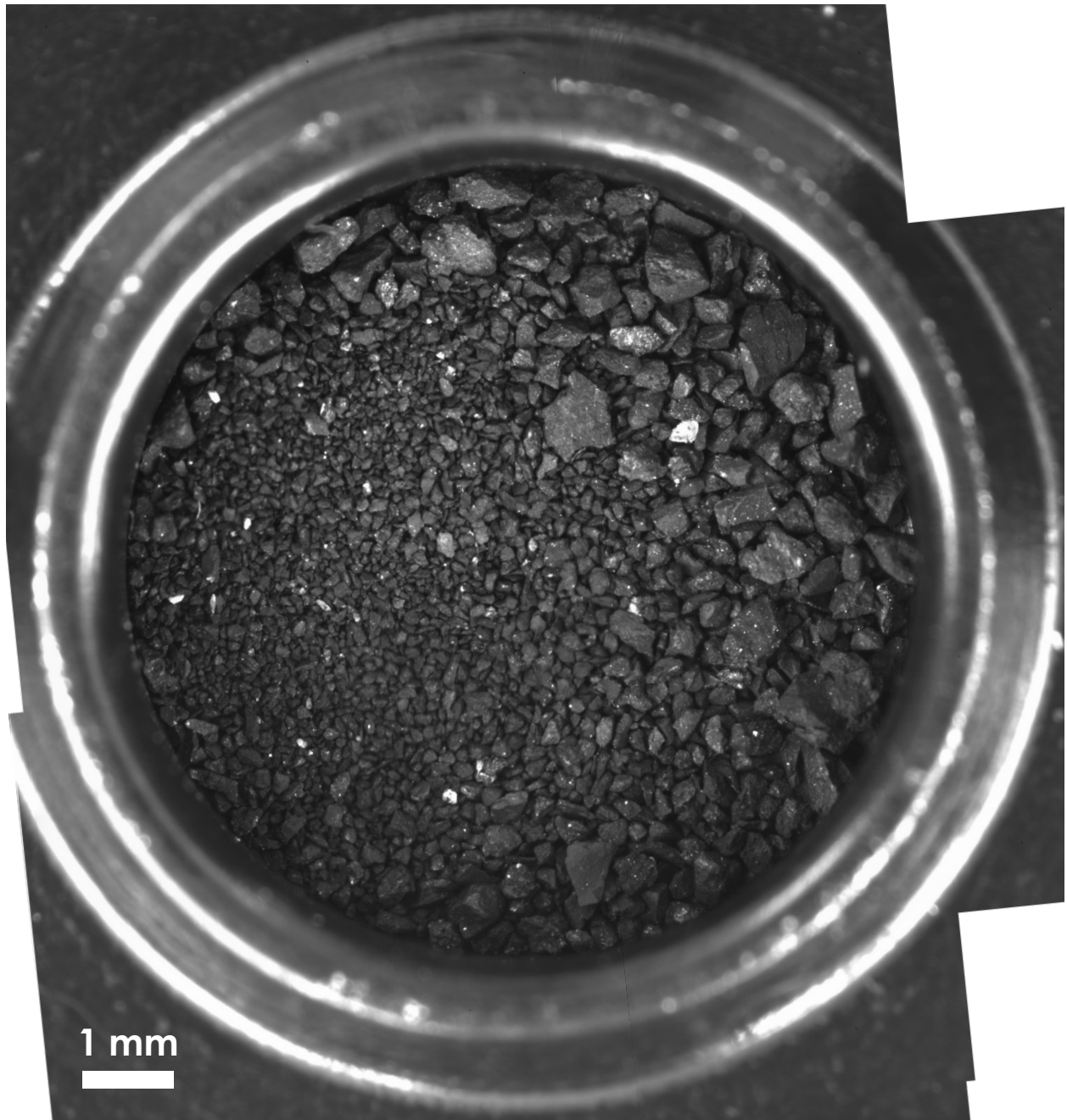


Figure 1: Multiband image of the bulk aggregate sample OREX-803124-0. This greyscale image was captured using a THORLABS Kuralux 8.9-megapixel monochrome CMOS camera with a Navitar 12x zoom lens. 20 individual images were collected and later mosaiced together to produce the full image.

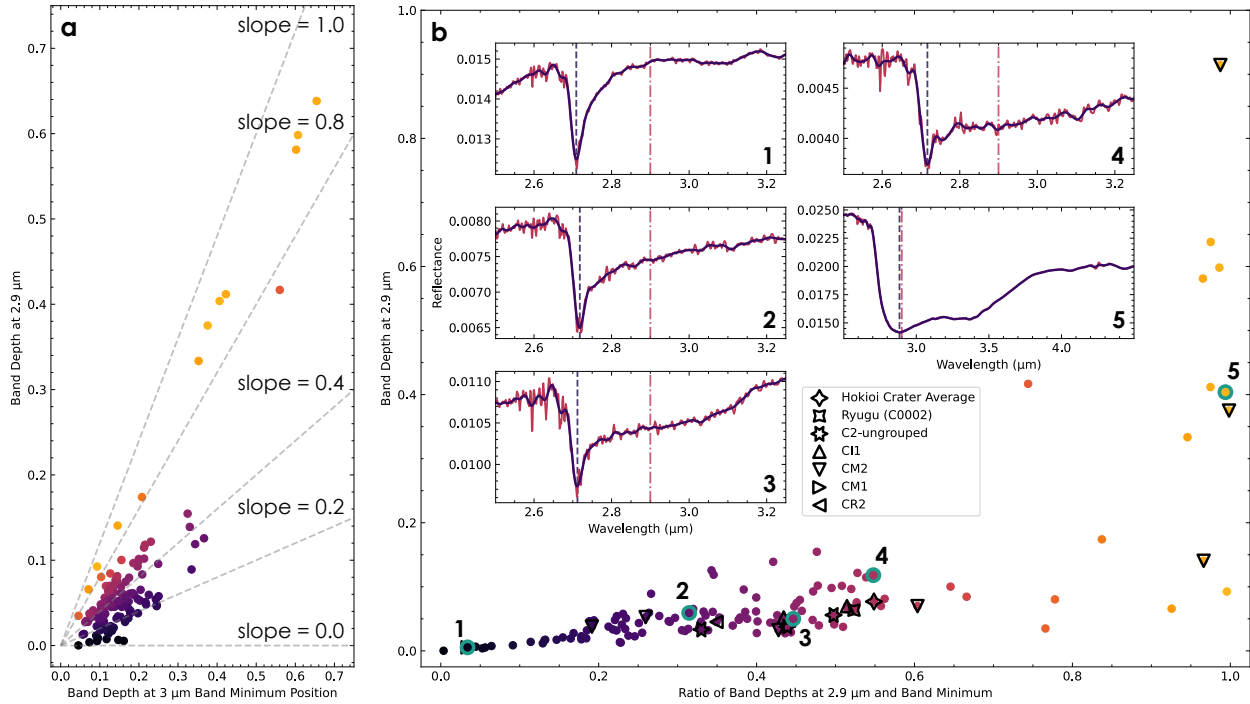


Figure 2: Diversity of the the shape and strength of the 3 μm hydration feature. a, band depths at 2.9 μm and the overall $\sim 3 \mu\text{m}$ band minimum. The color of the markers correspond to the ratio of these ratio parameters, or the slope of a line starting at the origin and posing through each data point. Color values vary from black/dark purple for 3 μm features with sharp absorptions and weak band depths at 2.9 μm to yellow for spectra with broader $\sim 3 \mu\text{m}$ features and a stronger 2.9 μm band. This ratio is a useful proxy for $\sim 3 \mu\text{m}$ band shape and is used, along with this color scheme, throughout the remainder of the paper. Normalizing these values by the strength of the 2.9 μm band depth (b) shows a strong trend in shape of the broad $\sim 3 \mu\text{m}$ feature as it evolves from a sharp and narrow OH feature (Spectrum 1) to a much broader feature marked by the increasing strength of H_2O -related absorptions (Spectrum 4). Several particles, here in yellow/orange, exhibit extremely large and wide 3 μm absorption features (Spectrum 5). The vertical dashed lines (b, inset spectra) correspond to the position of the overall band minimum (purple) and 2.9 μm (red) where band depths are calculated and ratioed. Black markers correspond to the same band parameters calculated from spectra of Hokioi crater, Ryugu particle C0002, and a variety of compositionally relevant carbonaceous chondrites.

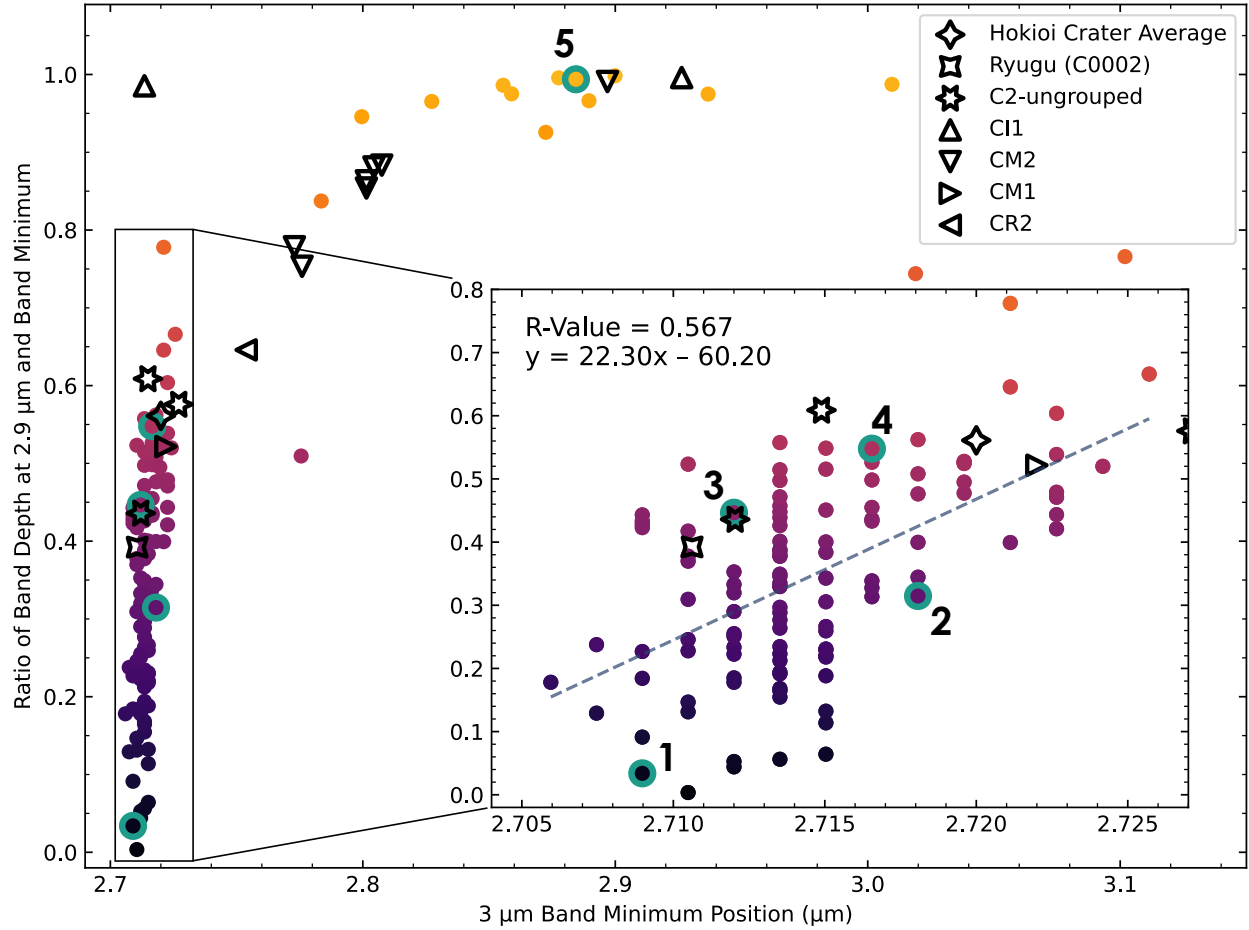


Figure 3: Diversity in position and shape of the 3 μm feature. The ~3 μm band shape (ratio of band depths at 2.9 μm and the band minimum) plotted against the 3 μm band minimum position. Several particles exhibit extremely broad ~3 μm band positioned at much farther wavelengths (~2.77–3.1, yellow markers). Most spectra exhibit features that range from ~2.705–2.275 μm (inset). For these spectra we observe a moderate position correlation (dashed line) with an R^2 value of 0.567. This indicates that features with band minima at shorter wavelengths tend to have narrower ~3 μm features whereas features positioned at longer wavelengths have broader features and strong 2.9 μm absorptions, likely attributed to increased H₂O abundance. Black markers correspond to the same band parameters calculated from spectra of Hokioi crater, Ryugu particle C0002, and a variety of compositionally relevant carbonaceous chondrites.

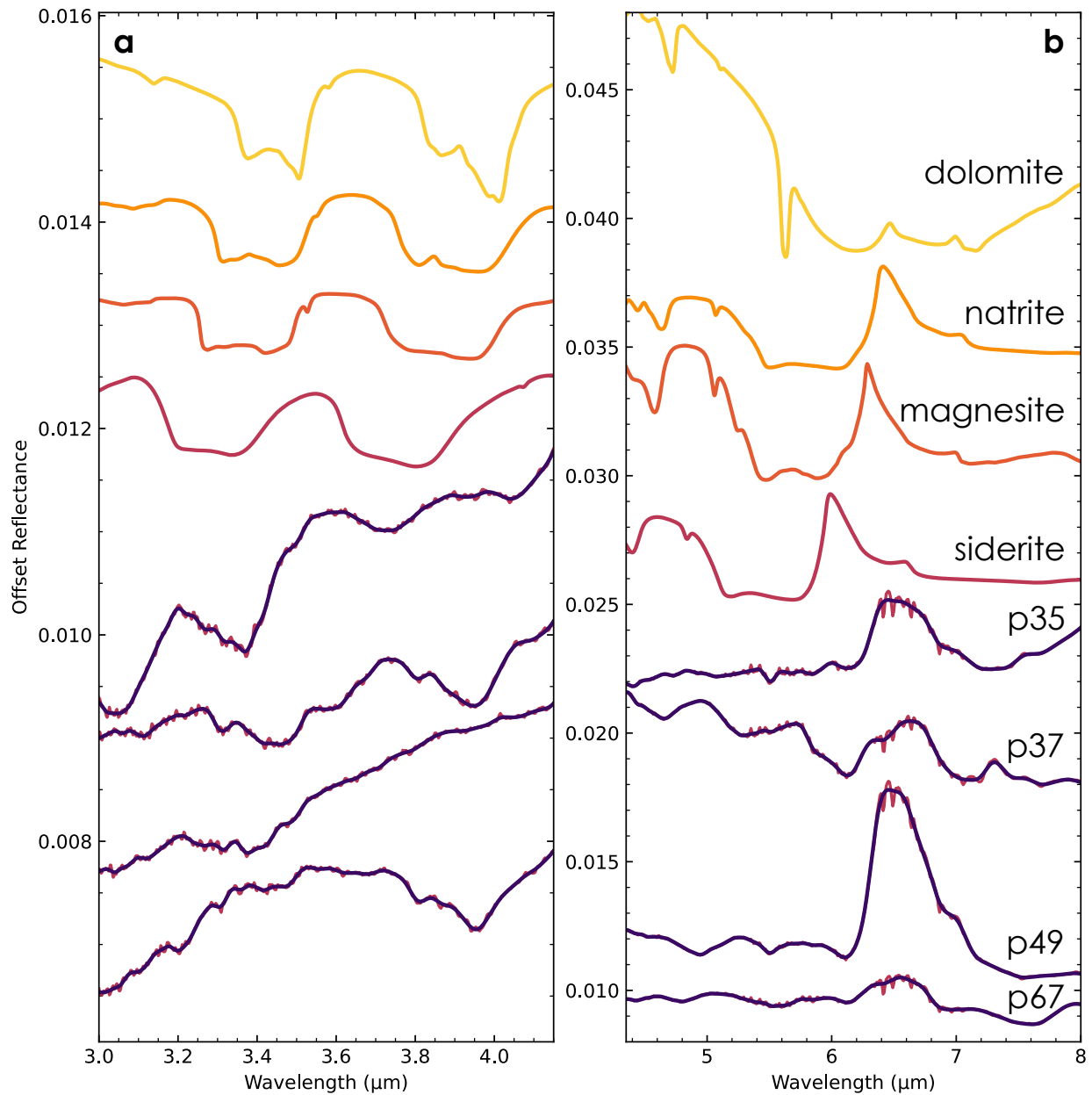


Figure 4: Select spectra exhibiting strong carbonate features compared with reference spectra of relevant carbonates. a, the $\sim 3.4 \mu\text{m}$ region reflectance spectra of particles that exhibit strong $\sim 6.4 \mu\text{m}$ carbonate peaks (b). Both the original (red) and low-pass filtered spectra (purple) are shown for the Benu particles. Also shown are spectra of relevant carbonate minerals from Bishop et al. (2021) that have absorptions consistent with those in the Benu particle spectra. All spectra are offset for clarity. Carbonate spectra are also scaled for clarity to exhibit similar spectral contrast to Benu particle spectra. Numbers indicate the co-registered particle number each spectrum corresponds to (Supplementary Figure 1).

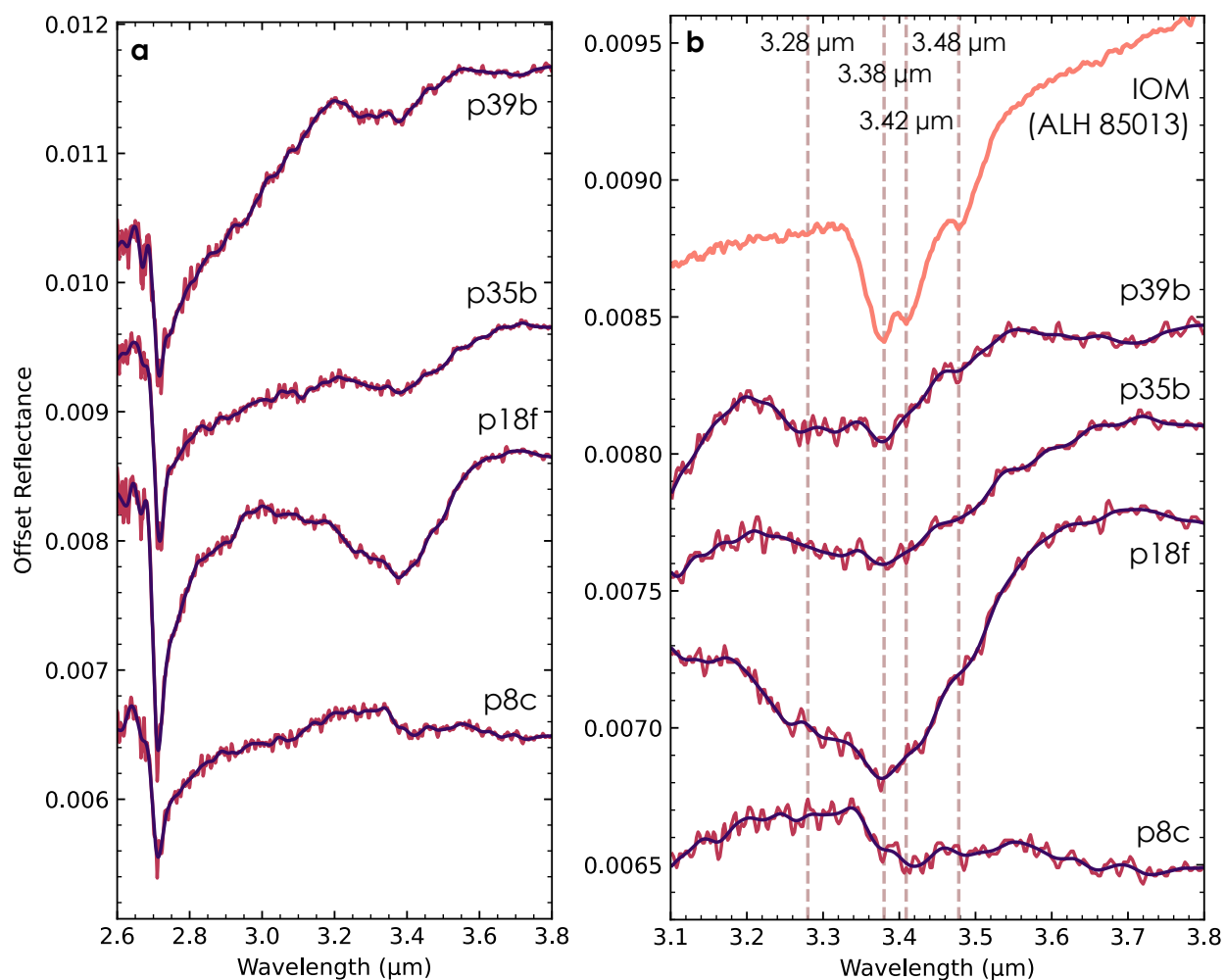


Figure 5: Select spectra exhibiting strong organic features compared with a reference spectrum of meteoritic IOM. The ~ 3.4 μm region reflectance spectra of particles that do not exhibit ~ 6.4 μm carbonate peaks, indicating the absence of carbonate. a, including the ~ 3 μm region provides broader context for the spectral contrast of these features. b, shows only the 3.4 μm region, where absorptions attributed to aliphatic and aromatic CH bonds occurs. Also presented is a spectrum of meteoritic IOM (b) from the CM2 chondrite ALH 85013 measured by Kaplan et al. (2019). Dashed vertical lines indicate the positions at which aliphatic (3.38, 3.42, and 3.48 μm) and aromatic (3.28 μm) CH absorptions are known to occur, as is observed in the IOM spectra. Numbers indicate the co-registered particle number each spectrum corresponds to (Supplementary Figure 1).

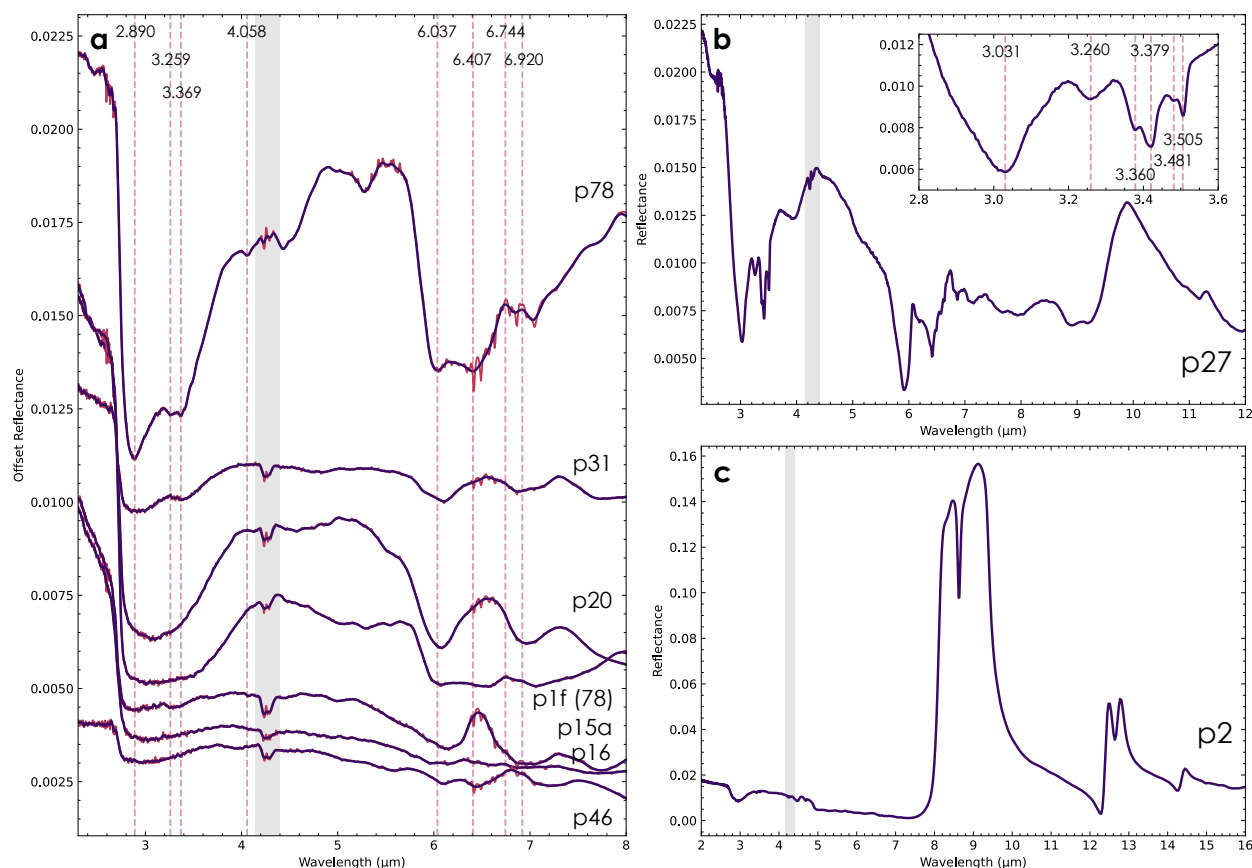
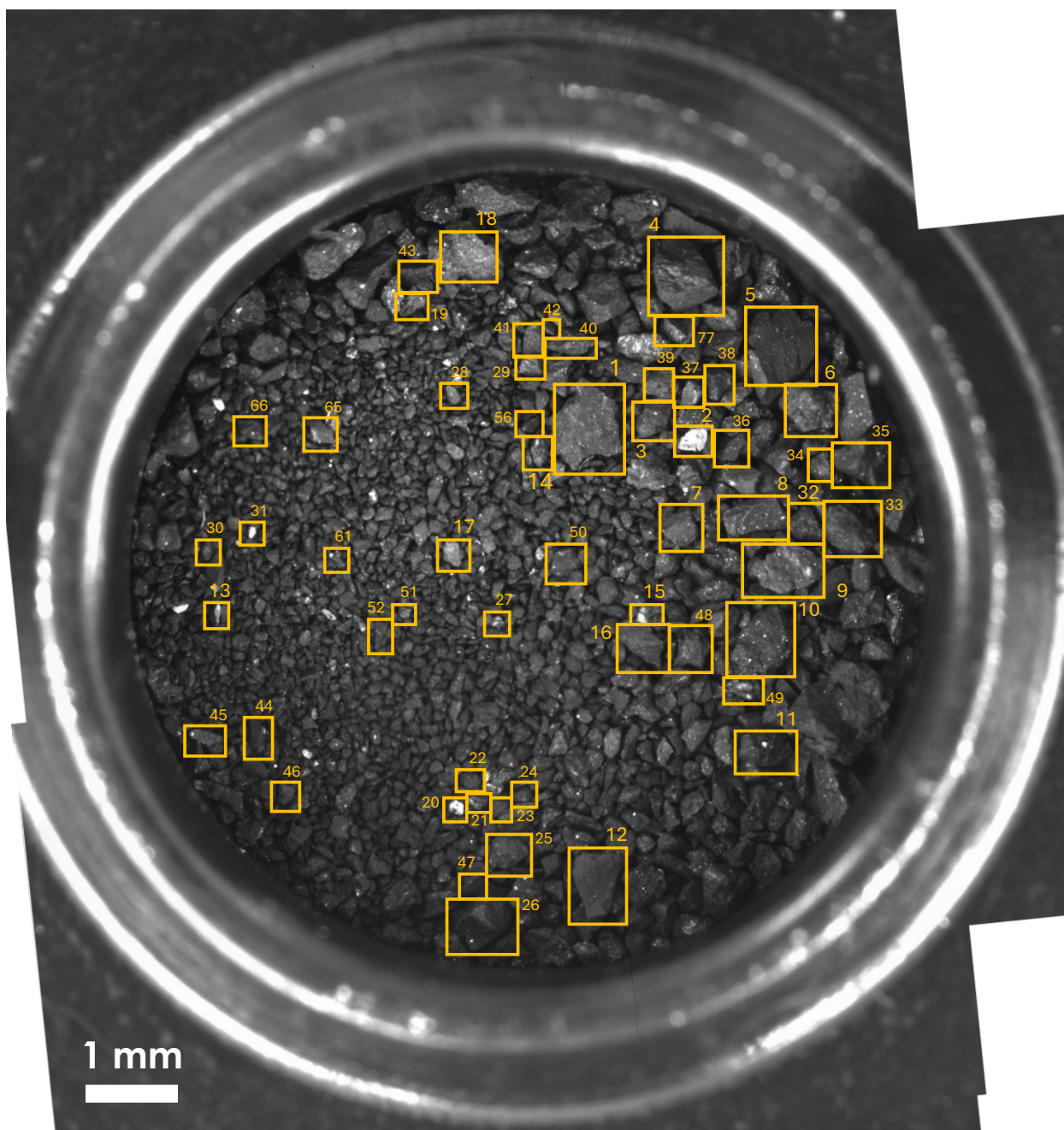
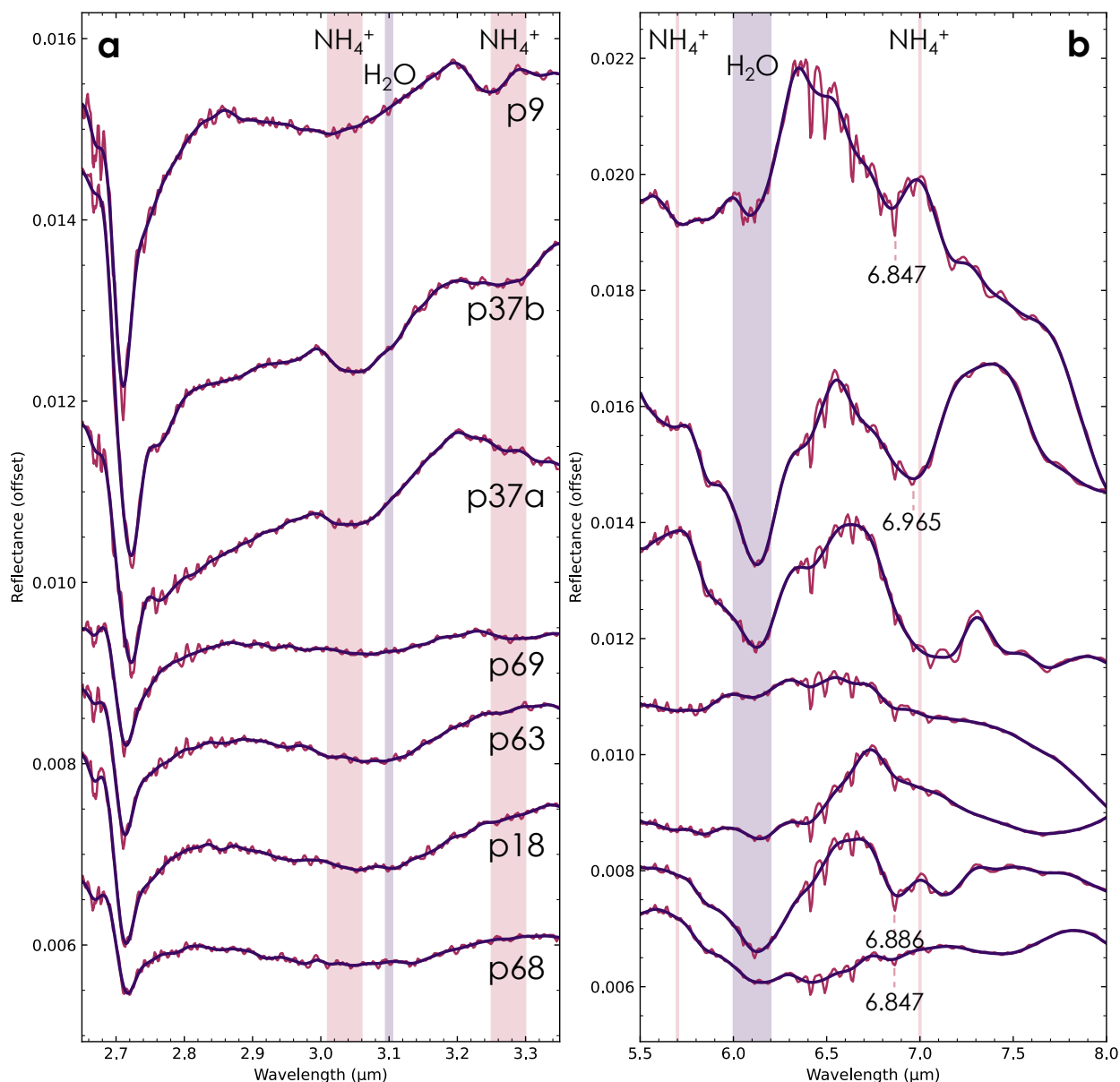


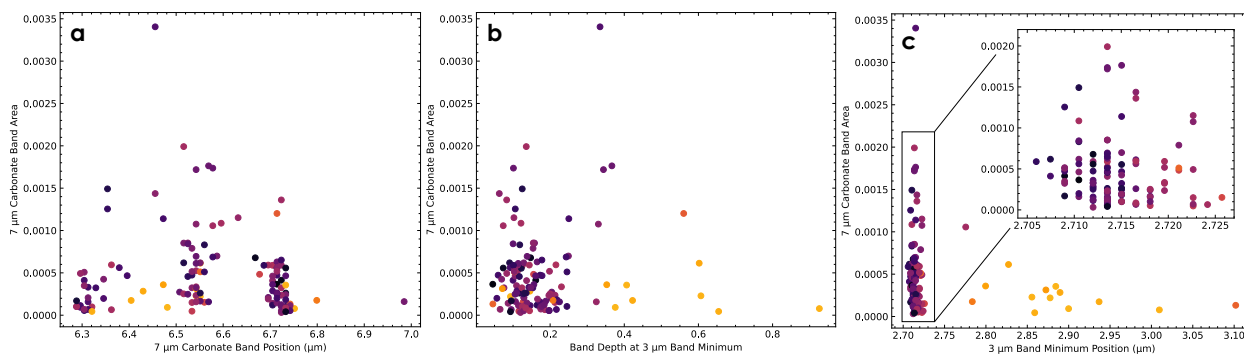
Figure 6: Select spectra of mottled particles, a quartz grain, and other anomalous particles. a, spectra of particles that visually appear to have affinities to the Na,Mg-phosphate-bearing mottled stones observed in Lauretta et al. (2024). Affinities are determined based on the bright white color of the particles themselves or surface coatings on darker particles. b, the spectrum of one of these stones with particular well resolved features in the ~ 3.4 region (b, inset), possibly indicative of carbonates and/or organics. c, a spectrum of a bright white particle with absorptions features consistent in shape and position with quartz. Numbers indicate the co-registered particle number each spectrum corresponds to (Supplementary Figure 1).



Supplementary Figure 1: Multiband image of OREX-803124-0 with measured stones selected. The same image as in Figure 1 but annotated with boxes and numbers to indicate each measured particle and its assigned number that corresponds to the spectra presented here.



Supplementary Figure 2: Select spectra with NH_4^+ -bearing absorptions. a, spectra of particles exhibiting strong and distinct features near $\sim 3.05 \mu\text{m}$ consistent with the presence of ammoniated NH_4^+ -bearing phases. b, the same spectra, but at longer wavelengths (5.5–8.0 μm) where additional features attributed to NH_4^+ are also known to occur. Vertical shaded lines indicate the approximate position of where NH_4^+ -related absorptions (red) and H_2O -related absorptions are known to occur. All spectra are vertically offset for clarity, but not scaled. Numbers indicate the co-registered particle number each spectrum corresponds to (Supplementary Figure 1).



Supplementary Figure 3: Comparative scatter plots of carbonate and phyllosilicate absorption features. The asymmetric stretching mode of the CO_3^{2-} group in carbonates manifests as a reflectance peak positioned near $\sim 6.4 \mu\text{m}$ and is the strongest carbonate feature present in our spectra. The band area of this feature is plotted against (a) the position of the same carbonate feature, (b) the band depth of the overall $\sim 3 \mu\text{m}$ band minimum, and (c) the wavelength position of the $\sim 3 \mu\text{m}$ band minimum. The inset in c zooms into the core group of non-anomalous particles.

Supplementary Table 1: Sample IDs and observational configurations for Hokioi crater spectra.

ID	sclk	latitude	longitude	incidence angle	phase angle	emission angle
402641	610695810	60.932716	2.6109734	60.969326	10.1659155	66.07622
402642	610695810	56.117237	2.8190098	59.312954	10.091364	62.879562
402643	610695810	51.193565	2.9747572	56.80912	10.024979	60.966427
402812	610695940	49.57016	359.42737	53.908855	9.960833	57.71577
402813	610696000	54.10088	359.2531	56.733418	10.02627	61.247185
402814	610696000	57.89796	359.06656	48.892117	10.092338	52.34788
402897	610696060	58.28611	357.30994	58.47193	10.074161	65.947655
402898	610696060	54.243084	357.45633	47.96281	10.007761	52.444595
402899	610696060	49.992287	357.57944	54.280293	9.935088	61.461666
404433	610697470	56.07864	324.9203	48.786762	9.629711	55.662918
404603	610697600	48.980568	321.5259	47.889435	9.468247	52.574745
404604	610697600	52.682743	321.40845	46.068283	9.528056	51.30399
404605	610697600	57.161606	321.26483	43.832527	9.588412	51.811687
404606	610697600	60.36975	321.1213	44.749157	9.64949	51.206463
404688	610697660	60.815353	319.3937	45.457375	9.633277	53.305103
404689	610697660	57.73275	319.4868	50.140533	9.572028	56.073124
404690	610697660	53.000916	319.58606	44.423958	9.511604	50.293827
404691	610697660	49.0228	319.64575	48.598328	9.445678	51.334774
404860	610697860	52.114357	316.02493	46.884827	9.45548	49.550774
404861	610697860	56.55229	315.89456	59.912052	9.514969	64.69782
404862	610697860	60.25264	315.74942	45.699276	9.575094	48.830788
404945	610697920	58.029778	314.05276	45.356873	9.52209	46.332207
404946	610697920	53.975956	314.138	60.465813	9.462321	65.83251
404947	610697920	50.281162	314.20023	36.96422	9.403438	38.26294
405095	610698050	55.074913	310.49866	53.00761	9.436097	58.89287
405118	610698110	58.771915	310.3687	57.39694	9.49527	61.323048
419650	610711420	58.632458	3.2280369	54.808033	7.8645597	51.190353
419651	610711420	54.86158	2.8811805	66.00871	7.8834276	61.806828
419652	610711420	51.06201	2.5832088	58.102993	7.9037285	55.79117
419825	610711550	49.025513	358.9619	52.09976	7.9272175	50.65744
419827	610711550	56.326492	359.41177	52.40658	7.886114	47.627686
419826	610711550	52.563618	359.15448	52.260048	7.9061284	51.698727
419828	610711550	59.723568	359.69867	68.49067	7.867121	64.16371
419916	610711620	57.974648	357.61288	58.132133	7.881143	57.807472
419917	610711620	54.709076	357.32318	58.45185	7.9012103	54.97762
419918	610711620	51.341526	357.06345	48.48924	7.9251356	47.84612

Chapter 5 | The Rainbow Connection: A synthesis for meteorite and asteroid exploration via laboratory and remote spectroscopy

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5.1 Introduction

Kermit the Frog once mused “What’s so amazing that keeps us stargazing, and what do we think we might see?” The rainbow connection, as an allusion to the visions and dreams that call us to explore, offers an apt ending to this dissertation and the beginning of a new one beyond the PhD. Visions of NASA missions and solar system origins recorded in stone were my rainbow connection. And the thrill of exploration, the hopes of discovery, and the curiosity-driven quest for knowing has been the fundamental motivation of this body of work. Though in the context of this body of work, the rainbow connection takes on a double and more literal meaning. Rainbows are the expression of light interacting with matter that only within the last few centuries we learned to harness as a tool for exploring once unconquerable frontiers. Spectroscopy is this tool and has been my instrument of choice for investigating what I consider to be some of the most enigmatic and revealing solar system bodies. As these chapters show, the throughline of this dissertation is the pursuit of connections: connections between primitive stones and spectral properties, between

spectral properties and composition, and between composition and the processes that governed the origins and evolution of small bodies. And through these connections, my hope is that we will arrive at a more complete understanding of the story of our part of the cosmic neighborhood and our place within it.

5.2 Synthesis

Asteroids and their meteoritic progeny remain among the most accessible yet mysterious solar system materials available for study. Their own story presents a complex mystery full of many characters and many settings, though not in isolation. The processes that modified the composition and orbits of these bodies carries consequences for the evolution of every other solar system body, most notably, Earth. Here, meteorites are thought to have delivered a significant fraction of Earth's oceans and seeded the planet with the prebiotic organic molecules that may have been incorporated into the first cells. Knowing the abundance, form, and distribution of water and organics as they occur in small bodies throughout the solar system has thus been key to piecing together these histories.

Significant advancements have been made, particularly in the study of meteoritics, to help address these questions. The carbonaceous- and non-carbonaceous (CC/NC) dichotomy has been among the most transformative, providing robust evidence that carbonaceous chondrites indeed formed in the outer solar system, beyond the orbit of Jupiter (Warren, 2011). Here in the outer solar system, beyond the frost line, water ice and other volatiles were efficiently incorporated into growing CC planetesimals. For many of

these bodies, internal heating largely due to the decay of short-lived radionuclides (e.g., ^{26}Al , ^{60}Fe) melted these ices. Hydrothermal reactions between these fluids and the host rock facilitated the modification of primitive textures and the production of secondary alteration minerals. Among the most important of these alteration products includes phyllosilicates, carbonates, magnetite, and sulfides, which together help reveal the conditions under which these processes took place.

Infrared spectroscopy has greatly advanced our understanding of how water occurs in C chondrites and primitive asteroids. Both OH and H₂O feature prominent fundamental vibrational modes along with overtones and combination bands that occur from ~1–12 μm . In C chondrites, the symmetric and asymmetric stretching mode of OH and the stretching and bending overtone of H₂O are the most important. Together, these overlapping absorptions give rise to a broad and complex absorption that occurs between 2.65–3.15 μm (hereafter referred to as “the 3 μm feature”). Within the last decade, workers have tried to link the shape and precise wavelength position of this feature to the hydration state, or, extent of aqueous alteration, of the meteorite sample (Takir et al., 2012, 2013, 2015). The challenge with these prior works is that they were performed on powdered samples, which by their nature are homogenized bulk averages that have lost all petrographic context. The central motivation of **Chapter 1** was to break the ambiguity by mapping the spectral properties of intact sections of C chondrites. This allowed us to understand the association of spectral signatures of hydration with the phases they occur in, e.g., matrix, chondrules, and other inclusions. We observed that within all these phases, and particularly the phyllosilicate-rich matrices, there can be a great deal of heterogeneity in the shape, strength,

and position of the $\sim 3\ \mu\text{m}$ hydration feature (Schultz et al., 2023). The analysis of these samples at multiple spatial scales allows us to properly contextualize “bulk” spectral measurements with the actual diversity of alteration phases, which itself provides clues to how water modified the chemistry and textures of these samples.

It should be no surprise in finding out that the mineralogy of C chondrites, which has been reworked by aqueous, thermal, and collisional processes, is complex (Brearley, 2006). But what can be appreciated from this work is a framework that provides better contextualization for the interpretation of spectral observations. Specifically, the most altered samples exhibit $3\ \mu\text{m}$ absorptions positioned at lower wavelengths that exhibit minimal heterogeneity. This is likely due to the chemical and mineralogical homogenization that comes with more extensive aqueous alteration. On the other hand, the least altered samples exhibit “bulk” $3\ \mu\text{m}$ absorptions centered at longer wavelengths, which exhibit much more heterogeneity in the position, shape, and strength of this feature. For these samples, the bulk measurements belie the true compositional diversity of these samples. The heterogeneity for these less-altered samples likely comes from the pronounced but incomplete alteration of precursory phases, which preserved, to some extent, the primitive chemical heterogeneity of the sample.

C chondrites are brecciated at all spatial scales (Bischoff et al., 2006). All are accretionary breccias assembled from diverse components with distinct geologic histories (e.g., chondrules, CAIs, matrix, presolar grains, etc.). Many C chondrites also host distinct clasts of other meteoritic materials either similar to or distinct from the host rock (Bischoff et al., 2006). Recent work by Lentfort et al. (2021) demonstrated how many brecciated

Mighei-like (CM) chondrites host a variety of clasts with diverse alteration histories. These analyses provide extra context and further demonstrate the challenge of inferring petrologic type from simple spectral proxies based on homogenized samples. This begged the question of whether these clasts exhibited reflectance spectra distinct from the host rock, and if so, how are those signals convolved to produce a bulk spectrum? Kerraouch et al. (2021, 2022) analyzed a particularly puzzling meteorite, the Aguas Zarcas meteorite, which was found to exhibit at least five petrographically and chemically distinct lithologies that all share the same association of being sourced from a single object in space. In **Chapter 2** I analyzed the spectral and mineralogic properties of several of these sections from the Aguas Zarcas meteorite, demonstrating they do indeed exhibit distinct spectral signatures. Importantly, we found that the mid-IR spectra appeared to be the most effective as distinguishing one lithology from another, as these features were largely influenced by the relative abundance of pyroxene versus phyllosilicates. The unique opportunity of having multiple petrologic subtypes of the same meteorite provided a way for us to understand how aqueous alteration modified the Aguas Zarcas parent body. Comparing results to terrestrial experiments on the dissolution of minerals allowed us to make estimates of the pH and temperature of the fluids that modified the Aguas Zarcas parent body.

Brecciation remains an underappreciated and underutilized feature of many C chondrites. Like we demonstrated here, systematic comparisons of the mineralogy and chemistry of distinct clasts within a single meteorite and/or meteorite group will allow others to potentially gain new insights into the alteration histories of the meteorite parent bodies.

New observational evidence continues to emerge showing how diverse types of rocks, boulders, and clasts can be found on a single body. *In situ* observations from both the Hayabusa2 and OSIRIS-REx mission have observed evidence for anomalously bright boulders with spectral properties distinct from the background population of boulders (Tatsumi et al., 2021; DellaGiustina et al., 2020). These observations were surprising in some sense because pre-encounter disk-resolved spectra of these bodies provided no evidence for the presence of these ordinary chondrite and HED-like boulders. A natural curiosity emerges—what else might we be missing in our interpretations of the spectra of asteroids?

Visible and near-infrared spectroscopy provides the foundation for the modern taxonomic classification of asteroids (Tholen, 1984; Bus and Binzel, 2002; DeMeo et al., 2009). Emerging views show us though that most, if not all, asteroids less than 100 km in size should be rubble piles. These rubble pile asteroids, like Bennu and Ryugu, are (at least) second generation bodies formed from the catastrophic disruption and gravitational reassembly of a progenitor parent body. It is still an open question today as to what part of the parent body any given rubble pile asteroid might sample. Both modeling and observational work suggests that these gravitational agglomerates likely sample parent bodies that were at least 100 km in diameter (e.g., Jourdan et al., 2023; Barnouin et al., 2019; Walsh, 2018; Michel et al., 2015; Campo Bagatin et al., 2001; Richardson et al., 2002). As such, they may provide a means to explore the interiors of these long-gone bodies and understand the processes that shaped their evolution.

From this, we can ask: if rubble pile asteroids do sample distinct lithologies and rock types, what are the detection thresholds for being able to interpret their presence in their spectra. In **Chapter 3** of this dissertation, we explored this question, specifically as it relates to the “Missing Mantle Conundrum”. This longstanding challenge in the study of asteroids and meteorites is born from the lack of evidence for widespread mantle material in the asteroid belt despite the evidence that suggests bodies were large enough and hot enough to melt and differentiate. In this work, we show that diagnostic VNIR spectral features attributed to olivine- and/or pyroxene-rich mantle materials can be strongly reduced and even completely masked when these materials are mixed with C chondrite-like material. The darkening and spectral suppression properties of some fine-grained C chondrite powders are so strong that upwards of 30–65 wt.% of mantle material could be effectively hidden in spectra typical for main-belt asteroid observations. From this work we suggest that perhaps mantle material is not missing at all. If rubble pile asteroids do sample the scrambled interiors of partially differentiated bodies, then unmelted chondrite-like material may simply be masking diagnostic spectral signatures of the differentiated component.

There is plenty more work yet to do to fully explore this problem and the extent of its implications. However, it is reasonable to suspect that our longstanding interpretations of the compositions of some asteroids and asteroid types based on visible and near-IR may not hold up to continued scrutiny. From this work alone, we know that many meteorites, the progeny of these primitive bodies, are complex breccias with bulk spectra that often belie their true nature and compositional diversity. Taken together, these results begin to provide important constraints for the range in composition that any given body may exhibit.

And while there is always more work to be done, we provide here a starting point for more comprehensive spectral analyses that can be used to create more accurate and effective frameworks for interpreting the spectra of asteroids.

Chapter 4 is very much a culmination of all the experience and insight gained through these prior projects applied to one of the most important sample sets of my time. In September 2023, NASA's OSIRIS-REx mission returned over 120 grams of pristine material from asteroid Bennu. This came after a multi-year observational campaign of the asteroid by the OSIRIS-REx spacecraft (Lauretta, 2023). Equipped with multiple high-resolution camera systems as well as a visible and infrared spectrometer and a thermal emission spectrometer, the spacecraft extensively characterized the spectral properties of Bennu. Initial results confirmed that Bennu was indeed a primitive volatile- and organic-rich body extensively modified by aqueous alteration and collisional processes (Hamilton et al., 2021; Kaplan et al., 2020; Simon et al., 2020; DellaGiustina et al., 2020; Hamilton et al., 2019). What was surprising though was just how boulder-rich and regolith-poor Bennu was, preventing a significant challenge to sample collection. Nevertheless, multiple candidate sites for sample collection were identified and eventually the Nightingale site, located inside Hokioi crater, was selected. This feature is thought to be one of the youngest on Bennu and was also notable as being one of the darkest, reddest, and most organic-rich.

Analyses of these samples followed a detail hypotheses-driven approach, that set out to validate key ideas generated during the observational phase of the mission. As part of the sample spectroscopy team, I had the privilege of being among the first to analyze the spectral properties of an aggregate selection of hundreds of particles. The results from

Chapters 1 and **2** provided much of the foundation for interpretations of the particle-to-particle spectral properties. The search for distinct lithologies and providing context for any observed heterogeneity within the Bennu sample set was a high priority. In a survey of 79 distinct particles tens to hundreds of microns in size, I observed significant heterogeneity in the shape, strength, and position of the 3 μm OH/H₂O feature (see **Chapter 4**). There is abundant evidence for the presence of aliphatic and possibly aromatic organic molecules as well as multiple species of carbonates. A strong ~ 3.05 μm absorption was also observed, which indicates that some particles are like ammonia-rich. Interestingly, I also observed the spectra for several anomalous particles including H₂O-rich phosphate grains and a single quartz particle. Synthesizing these results together, I invoke two processes that together explain many of these finds, extensive aqueous alteration by a fluid with evolving composition and space weathering. The spectral heterogeneity in the 3 μm region is best interpreted as the mixed presence of Mg-rich serpentines and saponite-like phyllosilicates. The formation of serpentine and saponite occurs under different conditions, including temperature, pressure, and water availability. In particular, the presence of H₂O-bearing saponite indicates that liquid water was readily available for water-rock interactions. The presence of ammonia-bearing species, either clays or organics, also points at a volatile-rich inventory likely inherited from formation in the outer solar system. Like the phyllosilicates, each carbonate species observed also indicated differences in conditions of formation, included which cations were available in the fluid to precipitate the carbonates. The strong spectral features associated with aliphatic organics indicates that these collections of particles are relatively fresh, as the breakdown of these molecules to aromatic carbon

structures readily occurs with solar wind-driven space weathering. For a few particles, I observed evidence for these aromatic features that suggests the Nightingale site is indeed a young feature on the surface of Bennu beginning to experience incipient space weathering. Space weathering has also been shown to modify the wavelength position of the 3 μm feature, shifting it to longer wavelengths with progressive space weathering. While space weathering was likely incipient, this provides an alternative explanation for the significant heterogeneity in the shape and position of the 3 μm hydration feature.

Far from over, these early results are providing us with only the first hints of the nature and history of this enigmatic and strange body. Still, significant questions remain about the history of Benn and its parent body. If Bennu did indeed come from a 100–200 km parent body, from what regions of that body do the re-accreted boulders of Bennu come from? Do the different boulder types and lithologies come from different stratigraphic layers or are these perhaps local heterogeneities? Are the bright pyroxene-rich boulders on Bennu actually exogeneous or could they instead represent vestiges of the precursory rock types that characterize the pre-aqueous alteration composition of Bennu's parent body? Important questions remain but will no doubt guide future investigations into this sample collection.

5.3 Future Directions

Much of the work in this dissertation demonstrates the ambiguity of spectral datasets when observations are not fully contextualized. Visible and near-infrared spectroscopy has no doubt dominated most telescope- and spacecraft-based observations of small bodies.

This is in part thanks to the development and availability of these spectrometers for scientific use, but also because reflected light is most intense at these wavelengths, leading to better signal to noise. But as we show here, multiwavelength observations of planetary materials, especially the dark carbon-rich asteroids and meteorites, are often required to fully characterize the nature of these materials. We demonstrate that at VNIR wavelengths, you can hide significant amounts of mantle analog material in mixtures with C chondrites. But does this also hold up at mid-IR wavelengths? Future laboratory work should continue to explore how these key diagnostic features of mantle-like material are modified by the presence of chondritic material at these mid-IR wavelengths. Additionally, there are numerous more compositions to explore with these mixing experiments and more questions to be addressed. Can primitive olivine and pyroxene commonly found in chondrites be distinguished from the same minerals formed from melt processes? And how effective may radiative transfer models be at accurately “unmixing” the compositions of C chondrites and other primitive bodies.

The parameterization of spectral features as proxies, which have been met with mixed success, still hold the promise for simple and rapid assessment of these bodies. With a renewed appreciation for the complex brecciated nature of C chondrites, future spectral surveys of meteoritic samples should focus on resolving distinct lithologies from the host material.

The Aguas Zarcas meteorite presented in **Chapter 2** leaves much work to be done, specifically on the carbonate minerals found as grains and veins within brecciated samples. How many episodes of aqueous alteration did the Aguas Zarcas parent body experience

and where might they fit within the relative timeline of events of other processes? Dating the carbonate grains as well as the veins should provide some answers to this question.

If the recently returned samples of asteroids Ryugu and Bennu have taught us anything, it's that studies of meteorites may have been deceiving us in some fundamental ways. Terrestrial contamination is known to take place almost immediately. Much of the "water" observed and studied in meteorites, especially C chondrites, is likely terrestrially derived. To mitigate the effects of this contamination on spectral studies of chondrites and other analog materials, measurements should be performed in asteroid simulated environments. Similarly, there is emerging evidence that asteroid types once thought to be nominally anhydrous may indeed host some amount of H₂O. Going back and studying the volatile budget in non-carbonaceous, being sure to distinguish terrestrially adsorbed water from endogenous water, will provide new insights into the abundance and distribution of water in these bodies. The James Webb Space Telescope perhaps holds the most promise for our study of water in small bodies throughout our solar system. Its ability to resolve key spectral features attributed to OH, H₂O, and common igneous minerals will provide new details on the nature of water and its geologic role in the evolution of small bodies.

So, if we ask ourselves again, what's so amazing that keeps us stargazing, and what do we think we might see? It's the thrill of exploration and discovery, and the promise of knowing the cosmos and our place within it, the rainbow connection.

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