

Spectral Characterization of Volcanic Materials on Earth and Venus

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Doctor of Philosophy
Degree
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DEDICATION

To my Dad, who has supported me in every adventure.

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Chapter 1 utilized archival data provided by the ASI Space Science Data Center (SSDC), as well as data from Hamilton et al. (2001) and Wyatt et al. (2001), obtained with the assistance of Dr. Vicky Hamilton, and data from Williams & Ramsey (2019), obtained with the assistance of Dr. Daniel Williams. The modeling codes used in Chapter 1 were written by Cai Ytsma. The Hapke model package developed by Dr. Eli Sklute served as the base code which was modified in Chapter 2 with her helpful discussions and support. Chapters 2 and 3 were supported by Europlanet under the European Union's Horizon 2020 research and innovation program under grant agreement No 871149 and by NASA grant 80NM0018D0004 to the VERITAS mission. Dr. Darby Dyar provided invaluable insights and guidance on all three chapters.

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ABSTRACT

Earth and Venus are dominated by volcanic landforms, making accurate characterization of the diversity of igneous compositions on the planets' surfaces key to understanding their geologic histories. Spectral observations in the visible-near-infrared (VNIR) and mid-infrared (MIR) provide rapid characterization of surface composition and mineralogy but are not without limitations. Spectra are sensitive to a number of factors, including observation geometry, collection method (emissivity or reflectance), grain size, phase assemblage, and composition. It is impossible to constrain the combined effects of all factors when interpreting orbital data, and simplifications are made, guided by laboratory investigations.

A common goal of remote spectral observations is to obtain surface composition or phase assemblage. Partial least squares (PLS) regression models provide quantitative predictions that are insensitive to compounding factors, minimizing the assumptions necessary to obtain surface composition. Chapter 1 investigates the utility of PLS models in characterizing the oxide composition and crystallinity of volcanic samples from VNIR and MIR data over multiple spectral resolutions. PLS efficacy is observed to be largely insensitive to variations to spectral resolution, making it a powerful tool for maximizing data analysis.

Changes in reflectance spectra due to observational geometry are commonly ignored when interpreting remote VNIR spectral data. Venusian surface spectra, however, are collected in the uncommon VNIR configurations of hemispherical reflectance or directional emissivity. Chapter 2 investigates the differences that collection in bi-directional or hemispherical reflectance geometries can have on VNIR spectra. Changes to spectral slope and spectral feature shape are observed between the two geometries, particularly for mafic materials. Chapter 2 also investigates how applicable radiative transfer modeling is to convert between the two geometries.

Chapter 3 investigates the detectability of sulfate alteration on Venus surface compositions using hemispherical VNIR reflectance analyses of basalt-hematite-sulfate mixtures. Multi-phase surfaces are more difficult to interpret spectrally than monomineralic surfaces as spectral signals from the phases interact. Hematite and two sulfate phases, anhydrite and thenardite, are used to simulate alteration mineralogy, resulting in different trends in spectral variability relative to sulfate content. In the spectra of samples with greater than 20% alteration phases, primary basalt spectral features are completely obscured.

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Attachment TableS1.xlsx contains supplementary information on the spectral data used in Chapter 1. All spectra utilized in this work are identified by spectrum name and sample name, from original source, given in the rightmost column. 'x' in middle columns indicate that the sample had the associated data. Modal abundance of glass is denoted as '% glass'. Bulk oxides refer to the sample's bulk composition wt. % SiO₂, FeO, and Na₂O+K₂O, and glass oxides to the glass phase composition wt. % SiO₂, FeO, and Na₂O+K₂O; if any oxide was missing, the sample was not used.

INTRODUCTION

This dissertation is composed of three chapters which collectively explore the applications and limitations of spectral data in characterizing volcanic material on Earth and Venus. Each chapter focuses on a different issue encountered when using spectral data. Chapter 1 focuses on the utility of machine learning in spectral analysis, specifically when a glass phase is present. Chapter 2 focuses on the influence of collection geometry on the resulting spectra. Chapter 3 focuses on the obscuring effects of spectrally bland sulfate minerals. Each of these chapters work towards maximizing the information gained from spectral data. Accurate interpretation of spectral data is key to fully characterizing remote surfaces where sampling is not possible, as spectral observations may be the only means of constraining surface composition.

1. Other Planets as Natural Laboratories

Earth is, in many ways, an unique planet. It is the only planet in our solar system with stable liquid water at its surface, and the only planet with a mobile-lid style of plate tectonics. As a consequence of subduction, and the subsequent re-introduction of volatiles into the mantle, Earth has extensive silicic volcanism not seen on other terrestrial bodies (Green, 2015). Mid-ocean ridges are similarly the result of plate tectonics, which allows for the globally-distributed zones of decompression melting (Hofmann, 1997; Tackley, 1995). However, the plate tectonic process has also erased much of Earth's geologic past, and to understand Earth's evolution, we must look to other planets. Venus provides a unique contrast to Earth, as it is nearly the same size, with a similarly young crust and bulk composition (Basilevsky & Head, 1998; Gilmore et al., 2017; McKinnon et al., 1997; Strom et al., 1994; Treiman, 2007). Venus is volcanically active in the present-day (Herrick & Hensley, 2023; Smrekar et al., 2010; Stofan et al., 2016; Sulcanese et al., 2024), but, in contrast to Earth, lacks evidence for mobile-lid plate tectonics (Basilevsky & Head, 1998; Gilmore et al., 1998; Sandwell & Schubert, 1992). Tesserae, stratigraphically-old and tectonically deformed regions of the crust, may represent continental-type crust (Romeo & Turcotte, 2008), potentially providing insight into early-stage plate tectonics (Elkins-Tanton, 2007).

Volcanic features dominate Venus' surface, and if we remove the terrestrial oceans, most of Earth's surface as well. Venus' surface appears to be dominantly basaltic, on the basis of morphology and the few geochemical analyses returned by the Venera and Vega landers (Head et al., 1992; Ivanov et al., 2015; Treiman, 2007); felsic compositions have been suggested for both the steep-sided, flat-topped pancake domes and the low-emissivity tessera (Fink et al., 1993; Gilmore et al., 2015; Hashimoto et al., 2008; Head et al., 1992). The full range of igneous compositions on Venus is unknown, but appears similar to Earth; geochemical modeling shows that felsic compositions are completely plausible on Venus (Shellnutt, 2018).

Volcanism provides a glimpse into the planet's interior composition, dynamics, and evolution (Anderson, 1973; Balta & McSween, 2013; Hauri, 1996; Hofmann, 1997; Saal et al., 2008). Alkaline basalts arise through a lower extent of source melting than tholeiitic basalts, making the distribution and timing of basalt compositions informative

of local and global mantle dynamics. As magmas evolve along relatively-well defined trends, composition can be used to suggest temporal relationships for deposits emanating from the same vent (Boudon et al., 2008; Eichelberger et al., 2006). Changes in crystallinity or surface texture of terrestrial lava flows can also be used to differentiate compositionally identical lava flows (Byrnes et al., 2004; Crisp et al., 1990; Ramsey & Fink, 1999). Shield volcanos may produce small volumes of felsic material, indicating the cessation of magma feeding into the volcano (Geist et al., 1995) or the mingling of an older fractionated lava with newer, hotter magma, as occurred in the 2018 eruption of Kilauea (Gansecki et al., 2019; Wieser et al., 2022). In either case, identifying felsic material on one of Venus' many shield volcanos would provide insight into local mantle convection and the timing of magmatic recharge to individual volcanic centers.

Remote observations are key in characterizing planetary volcanism. Many terrestrial volcanos are remote, making sampling and *in situ* monitoring challenging, if not impossible; remote observations may be the only data available of an otherwise inaccessible volcanic eruption. Terrestrial characterization of active eruptions via satellite data has mostly focused on detection via thermal anomalies, but these data are capable of characterizing the type of eruption, eruption rate, and volume erupted (Harris et al., 1997; Ramsey & Harris, 2013; Steffke & Harris, 2011; Wright et al., 2002). Methods for characterizing the temperature and crystallinity of active basaltic lava flows have recently been established (Naduvvari et al., 2020; Thompson & Ramsey, 2020). Once cooled, myriad methods of characterizing a volcanic deposit from remote observations exist, including its texture, crystallinity, and composition (e.g., Baird, 1984; Byrnes et al., 2004; Cannon et al., 2017; Mustard & Pieters, 1987; Rader et al., 2022; Ramsey & Christensen, 1998; Williams & Ramsey, 2022). Similar characterization of Venus' surface from orbital data is completely feasible, particularly when paired with terrestrial studies that use both remote characterization and ground-truthing for comparison.

2. Spectral Features of Igneous Rocks

This study focuses on the use of spectral data to obtain the composition of volcanic surfaces. Spectral observations measure how light interacts with a surface, be that reflection, emission, absorption, or transmission. This dissertation focuses on reflectance and emission spectra in the visible-near-infrared (VNIR; $\sim 0.3\text{-}2.5\ \mu\text{m}$) and mid-infrared (MIR; $\sim 4\text{-}35\ \mu\text{m}$) regions, both of which can be used to constrain a surface's mineralogy. Volcanic materials have a relatively constrained compositional range, and thus, spectral characterization of igneous mineralogies focuses on spectral features that arise from silicate lattice stretching and bending vibrations, water presence, and transition metal ions.

The reststrahlen bands – fundamental stretching vibrations of Si-O lattice structures – occur between 8 and 12 μm (Lyon, 1965; Salisbury & Walter, 1989; Walter & Salisbury, 1989). The exact location of the reststrahlen band is dependent on the silicate structures and abundance of Si, relative to other atoms, in the material (Lyon, 1965; Walter & Salisbury, 1989). The reststrahlen band emissivity minimum occurs near 10 μm for mafic material, near 9.5 μm for intermediate material, and near 9 μm for felsic material (Logan & Hunt, 1970; Lyon, 1965). The reststrahlen band width increases with increasing diversity of Si-O bonds (Simon & McMahon, 1953); silicate glasses, which lack long-

range crystal structures, can be differentiated from crystalline material of the same composition by the presence of broader and smoother features, and typically fewer features, than their crystalline counterparts (Fu et al., 2017; Minitti et al., 2002; Varatharajan et al., 2023).

Just short of the fundamental silicate feature, silicates' real index of refraction, n , rapidly changes and can approach the n of the surrounding medium, usually air or vacuum, resulting in a scattering minimum (Walter & Salisbury, 1989). This scattering minimum, or the Christiansen feature, appears as a reflectance minimum or emissivity maximum between 7.5 and 9 μm , following the same trend in position as the Si-O feature (Moroz et al., 2009; Salisbury & Wald, 1992; Varatharajan et al., 2023; Walter & Salisbury, 1989). When observed under an atmosphere, the Christiansen feature is insensitive to grain size, making it a potential indicator of a surface's bulk silica composition (Cooper et al., 2002; Mustard & Hays, 1997; Salisbury & Wald, 1992; Shirley & Glotch 2019).

Water, both bound with crystalline structures and adsorbed onto sample surfaces, can cause spectral features in igneous samples. Combinations and overtones of unbound H_2O vibrations produce features at ~ 0.9 , 1.14, 1.4, and 1.9 μm (Clark et al., 1990; Hunt, 1977). Below ~ 2 μm , electronic transition features become increasingly dominant. Crystal field effects – the distortion of the location and energy of a metal ion's outer orbitals due to the metal's site in the crystal structure – result in diagnostic spectral features for metal-bearing phases (Burns, 1993). Fe^{2+} in olivine, for example, produces a broad feature from ~ 0.7 -1.6 μm , the shape and exact position of which trends with Fe abundance (Sunshine & Pieters, 1998). Charge-transfer features, where outer electrons are transferred, either between nearby metal ions or between the metal ion and nearby oxygen ligands, are particularly important in the spectra of oxides (Burns, 1993; Gaffey et al., 1993; Rossman & Ehlmann, 2019). These features occur below ~ 1 μm .

3. Additional Factors Affecting Spectral Behavior

Recognizing features in a spectrum is enough for positive identification that a given phase is present on the surface, but insufficient for quantitative analysis. Multiple factors besides composition affect the spectral response of a surface, including environmental conditions, observing geometry, grain size, vesicularity, and porosity. The exact position of the Christiansen feature, for example, is directly dependent on the surrounding environment. Grain size affects the quantity of available scattering surfaces, so that reflectance increases and emission decreases with decreasing grain size (e.g., Adams & Filice, 1967; Mustard & Hays, 1997; Vincent & Hunt, 1968). Grains can also become optically thin when the grain size is close to the observed wavelength of light; this occurs in the MIR region for grains $\leq \sim 60$ μm (Salisbury & Wald, 1992).

These factors can inhibit direct correlation between the appearance, depth, and shape of a spectral feature and quantitative assessment of a surface's composition. Chapter 1 explores the utility of partial least squares regression (PLS) models to quantitatively predict the composition of igneous materials. The use of PLS enables assessment of individual oxide or phase abundance without needing to directly correct for compounding factors.

Particulate surfaces do not scatter light perfectly equally in all directions and thus observational geometry will affect the measured spectrum (Adams & Filice, 1967; Gradie & Veverka, 1986; Hapke & Wells, 1981; McGuire & Hapke, 1995). Reflectance spectra are typically collected as bi-directional reflectance, which measures one angle of incident light (i) and one angle of emergent light (e) (Martonchik et al., 2000; Schaepman-Strub et al., 2006). Reflectance can also be measured in directional-hemispherical geometry, with one angle of incident light and measuring all emergent light, as hemispherical-directional reflectance, or as bi-hemispherical reflectance (Martonchik et al., 2000; Schaepman-Strub et al., 2006). Emissivity spectra are generally measured as directional emissivity, collecting one angle of emergent light. Bi-directional reflectance spectra and directional emissivity spectra show minor changes in band depth, shape, and position with changes to either the angle of incident light (i) or angle of emergent measured light (e) due to the changes in path length of refracted light (Adams & Filice, 1967; Gradie & Veverka, 1986; Johnson et al., 1992; Pieters, 1983; Salisbury, 1993; Vincent & Hunt, 1968; Wald & Salisbury, 1995).

It has been robustly established in the MIR region that spectral feature shapes change between directional-hemispherical and bi-directional reflectance spectra, such that neither geometry can provide quantitative predictions of the other (Bartholomew et al., 1989; Mustard & Hays, 1997; Salisbury & D'Aria, 1989). This has not been established in the VNIR region; Chapter 2 addresses this by providing a comparison of VNIR directional-hemispherical and bi-directional reflectance spectra and investigates the changes observed between the two observational geometries.

Volume scattering occurs when grains are optically transparent. In the VNIR, geologic materials tend to have a small ($10^{-3} - 10^{-6}$) imaginary index of refraction, k , and light can interact with multiple particles before being absorbed or refracted out of the surface. The value of k tends to be large ($k \approx 0 - 10$) in the MIR, minimizing volume scattering for large particles. With significant volume scattering the spectral response of a surface can be dominated by a small volume of strongly-absorbing material, and the presence of optically transparent minerals may not be apparent. Chapter 3 investigates the ability of optically thin minerals to modify and obscure the spectral signature of basalt in the VNIR hemispherical reflectance spectra.

CHAPTER 1.
COMPOSITIONAL CHARACTERIZATION OF GLASSY
VOLCANIC MATERIAL FROM VSWIR AND MIR SPECTRA
USING PARTIAL LEAST SQUARES REGRESSION MODELS

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This paper was written by C. J. Leight, who was also in charge of data collection, processing, and handled revisions during the review process. C. Ytsma wrote the machine learning code used in this work, assisted in writing the methods section and addressing reviewer comments on the methodology. M.C. McCanta and M.D. Dyar assisted in developing the methodology and provided guiding edits during the writing process. T. D. Glotch provided guiding edits to the article prior to submission. The article was accepted May 2024 after one round of revisions.

Abstract

The glass phase in volcanic rocks presents a challenge to obtaining compositional data from visible and short-wave-infrared (VSWIR) and mid-infrared (MIR) spectral data of remote surfaces due to its amorphous structure and variable composition. Nonetheless, glass is a common phase in volcanic materials because it forms via the rapid quench of magma and can constitute up to the entirety of a volcanic deposit. Use of partial least squares regression (PLS) to predict glass contents creates models that are insensitive to viewing geometry and sample conditions such as grain size and spectrally inactive compositional variables, enhancing the ability to detect glasses with remote sensing. PLS models are used here to predict crystallinity and oxide composition of samples from VSWIR and MIR spectral data using training spectra from natural volcanic rocks and geologically relevant synthetic samples. Three spectral resolutions of VSWIR and MIR spectra (1, 10, and 100 nm/band, and 1.9, 19, and 190 cm^{-1} /band, respectively) were tested to assess the effects of collection configuration on different spectrometers. PLS models trained on 1 nm and 1.9 cm^{-1} datasets have the lowest uncertainties of glass modal abundance for VSWIR and MIR, respectively. MIR models predicting sample wt. % SiO_2 and FeO, and VSWIR models of wt. % FeO provide accurate estimates (e.g., RMSE-P of 3.4 wt. % FeO) at all spectral resolutions. Results are based on training datasets skewed to mafic compositions, which affects model accuracies.

1. Introduction

Glass is a common and important phase in volcanic rocks, both in effusive and explosive materials. Formed via the rapid quench of melt during eruption, volcanic glass provides physical and compositional information on the magma storage region, providing key insights into planetary interiors and eruption processes (Anderson, 1973; Hauri, 1996; Saal et al., 2008). In terrestrial mixed-source areas (e.g., sedimentary basins), the presence and abundance of a glass phase can be used to discriminate between volcanic deposits (Carter et al., 1995; Cassidy et al., 2014; Lowe, 2011; Shane, 2000). Glass

readily alters to palagonite and smectite clays (e.g., Jakobsson, 1978; Stroncik & Schmincke, 2002), so the preservation of volcanic glasses provides constraints on surface alteration history (Gonçalves et al., 1990; Jakobsson, 1978).

The composition of a glass is not constrained by steric considerations, unlike the composition of minerals. Glass composition can vary widely, by several weight percent, within a single volcanic center over its eruptive history (Eichelberger et al., 2006; Pallister et al., 1996) or within a single eruption. The bulk chemistry of erupted material provides information on petrogenesis of source magmas, as well as their transport, storage, and eruptive dynamics (Gansecki et al., 2019; Soderberg & Wolff, 2023; Stock et al., 2020; Stolper & Walker, 1980). Differences in crystallinity may be used to distinguish compositionally identical lava flows (Crisp et al., 1990) and can provide constraints on pre-eruptive magma storage conditions and eruptive behavior (Cashman & Sparks, 2013; Geist et al., 2021). Differences between glass and bulk composition also provide information on magma recharge and storage, informing hazard mitigation efforts during active eruptions (Gansecki et al., 2019). More broadly, the Fe content of glass in basalts is sensitive to source melt hydration and subsequent plagioclase crystallization (Grove & Brown, 2018). Therefore, it is desirable to develop methods to accurately measure SiO₂, Na₂O, K₂O, and FeO of glasses from spectral data.

Identifying and characterizing the distribution and composition of glassy materials on planetary surfaces is imperative to understanding the volcanic histories of those bodies. More evolved (felsic) magmas may contain significantly higher volatiles (H₂O, CO₂, SO₂, etc.) than mafic magmas, and are more likely to erupt explosively (Papale et al., 2006). Terrestrial basaltic centers often evolve to produce small volumes of more silicic magmas (Jónasson, 2007; Sigmarsson et al., 1991; Wanless et al., 2010; Wieser et al., 2022). In plume-fed volcanic centers such as the Galapagos and Hawaiian Islands, intermediate-composition material can erupt from isolated sills or dikes, such as in the 2018 eruption of Kilauea that produced andesitic lava nearly coeval with basaltic lavas (Gansecki et al., 2019; Wieser et al., 2022). Extensive fractional crystallization at Icelandic volcanoes has been suggested to originate from either partial melting of the hydrated basaltic crust (Lacasse et al., 2007; Sigmarsson et al., 1991) or fractional crystallization within large magma chambers (Geist et al., 2021). High-silica materials have also been identified on the Moon (e.g., Glotch et al., 2010; Wilson et al., 2015), Mars (Bandfield et al., 2004; Phillips et al., 2022; Sautter et al., 2015), and potentially on Venus (e.g., Basilevsky et al., 2012; Mueller et al., 2009).

Obtaining quantitative chemical and physical information using remote methods is difficult when glass is present. Magnetic susceptibility (MS), X-ray fluorescence (XRF), spectrophotometry, and visible- to short-wave-infrared (VSWIR; 0.4-2.5 μm or $\sim 4,000$ -25,000 cm^{-1}) spectroscopy have been used to identify tephra layers in sediment drill cores (Aymerich et al., 2016; Beget et al., 1994; Cassidy et al., 2014; Gehrels et al., 2008; McCanta et al., 2015; Schiff et al., 2010), but have not been fully utilized to extract chemical compositions. Spectral deconvolution methods and band parameters have been employed to identify the mineralogy of volcanic material using VSWIR and mid-infrared (MIR; 2.5-25 μm or 400-4000 cm^{-1}) spectra (Cannon et al., 2017; Farrand et al., 2018; Hamilton et al., 2001; Horgan et al., 2014; McCanta et al., 2015; Rogers & Christensen,

2007; Sinha & Horgan, 2022; Williams & Ramsey, 2022). Although these methods can detect glass or tephra using spectral data, each has constrained compositional applications, and limited ability to quantify glass composition.

Spectral measurements can differentiate glasses and crystalline material of the same composition, particularly in laboratory settings (e.g., Fu et al., 2017; Minitti et al., 2002). However glasses as a phase lack unique, diagnostic spectral features due to their amorphous nature (Dalby & King, 2006; Minitti et al., 2002). Accurate remote characterization of volcanic samples is further complicated by the variable phase assemblages of volcanic deposits. At low modal abundances, the variable composition of volcanic glass makes it difficult to identify spectrally (Adams & McCord, 1971; Cannon et al., 2017; Horgan et al., 2014; McCanta et al., 2015).

This study uses machine learning to explore the use of VSWIR and MIR spectra for identification and characterization of volcanic material remotely and in the laboratory. Partial least squares regression (PLS) models, which have been successfully used to obtain oxide abundances from geologic materials (e.g., Dyar, Carmosino, Tucker, et al., 2012; L. Li, 2006), are here applied to VSWIR and MIR spectra to predict the modal abundance of glass and sample composition at varying spectral resolutions. As part of its focus on methodology for recognizing glass in volcanic samples via remote sensing, this study compares three spectral resolutions to investigate how differences in spectral resolution affect quantification of compositional parameters from VSWIR and MIR spectral data

2. Background

Volcanic rocks are primarily classified using a total alkali versus silica diagram (Le Bas et al., 1986). Silica concentration of the melt phase exerts primary control on magma evolution, eruptive behavior, and mineral phase assemblage of the resultant rock (Bottinga & Weill, 1972; Giordano et al., 2004). Low-SiO₂ basaltic magmas have viscosities that are orders of magnitude lower than high-SiO₂ rhyolitic magmas (10² poise and 10⁸ poise, respectively; Bottinga & Weill, 1972) and contain significantly lower amounts of dissolved volatile species (e.g., H₂O, CO₂, SO₂, etc.).

In addition to SiO₂, other elements can be used to further discriminate among magmas and can affect physical properties. Alkalis are network modifiers that modulate silicate structures and resultant magma properties, as well as modulating mineral assemblages (Mysen et al., 1982; Neuville, 2006). Iron is abundant in silicate melts, affecting physical properties such as viscosity and volatile abundance. Fe³⁺ acts as a network-forming cation, while Fe²⁺ is a network-modifying cation (Mysen et al., 1980; Stabile et al., 2021; Stanley et al., 2011). More broadly, the Fe content of glass in basalts is sensitive to source melt hydration and subsequent plagioclase crystallization (Grove & Brown, 2018).

2.1. Glass Spectral Studies and Spectral Detection

The VSWIR region records electron transitions in transition metals and the overtones of vibrational bands (Gaffey et al., 1993; Hunt, 1979). Spectral features from inter-element electron transitions between nearby Fe ions occur below 1 μm (Hunt, 1977). Crystal field transitions of Fe²⁺ produces spectral features around 0.9 μm , with the exact shape and location depending on the surrounding crystal lattice. Overtones of

fundamental -OH and H₂O vibrations occur at 1.4, 1.9, and 2.2 μm in spectra from hydrous (and sometimes, anhydrous) minerals and glasses, and from surface adsorption (Clark et al., 1990; Hunt, 1979). The MIR region contains the reststrahlen bands produced by fundamental vibrations and stretching of silicate lattices (Dalby & King, 2006; Lyon, 1965; Ramsey & Christensen, 1998). The Christiansen feature (CF) appears at wavelengths slightly shorter than the fundamental silicate vibration band, where the index of refraction, n , of the surface and surrounding medium are approximately equal, and the extinction coefficient, k , of the surface approaches zero (Salisbury & Walter, 1989). The shapes and positions of the reststrahlen bands and CF are primarily controlled by variations in the Si-O bonds; the position of both spectral features shifts to longer wavenumbers (shorter wavelengths) with decreasing silicate polymerization (Lyon, 1965; Salisbury & Walter, 1989).

Glass is difficult to interpret spectrally because its chemical composition and atomic arrangement are quite variable and there is no long-range structure (Adams & McCord, 1971; Dalby & King, 2006; Minitti et al., 2002). The breadth of varying VSWIR and MIR spectral characteristics of low-silica glasses has been well-characterized (Cannon et al., 2017; Dalby & King, 2006; Dufresne et al., 2009; Dyar & Burns, 1981; Farrand et al., 2016; Minitti et al., 2002). Higher-silica glasses have also been studied (e.g., Carli et al., 2016; Fu et al., 2017; Minitti & Hamilton, 2010; Pisello et al., 2022; Williams & Ramsey, 2019). Glasses may contain multiple structural units that result in broadening and smoothing of spectral features (Crisp et al., 1990; Dalby & King, 2006; King et al., 2004; Moroz et al., 2009). In the VSWIR, glasses have shallower absorption features and lower albedo than crystalline material of the same composition (e.g., Minitti et al., 2002; Moroz et al., 2009). In the MIR, glasses display a shift in the position of the primary silicate stretching features to shorter wavelengths (longer wavenumbers) with increasing polymerization, similar to what is observed with minerals (e.g., Fu et al., 2017; King et al., 2004; Minitti et al., 2002; Pisello et al., 2019; Varatharajan et al., 2023). In spectra of intimate mixtures, low modal abundances of minerals ($\geq 20\%$ of the phase assemblage; Cannon et al., 2017; Horgan et al., 2014; Minitti et al., 2002) can obscure spectral features of a glass phase.

Linear deconvolutions provide estimates of mineral and glass abundances using variations on least-squares-fit regressions that fit library spectra to an unknown spectrum (Ramsey & Christensen, 1998; Rogers & Aharonson, 2008). While these techniques are powerful, successful application of linear deconvolution requires broad endmember spectral libraries (Hapke, 1981; Ramsey & Christensen, 1998; Rogers & Aharonson, 2008; Shkuratov et al., 1999). This can limit compositional characterization to endmember constituents and may not provide quantitative assessments of unknown compositions.

Linear spectral mixing is expected for large grain sizes relative to the wavelength of light in the MIR, and not at all at VSWIR wavelengths. Conversion of spectra into single-scattering albedo prior to application of the least squares regression may mitigate nonlinear mixing (e.g., Cannon et al., 2017; Y. Liu et al., 2016; Zastrow & Glotch, 2021), but does not provide a total solution. Models to calculate single-scattering albedos are sensitive to particle size as optically small particles - on the order of magnitude or smaller

than the wavelength of light being considered- are poorly modeled using spectra from larger grain sizes (Johnson et al., 1992). The inclusion of fine particle sizes as endmember spectra in linear deconvolutions can somewhat overcome this effect (e.g., Y. Liu et al., 2016; Ramsey & Christensen, 1998; Williams & Ramsey, 2022). Spectral mixing is also affected by sample porosity. Surface reflections occur in pore spaces, so increased porosity in fine particle samples can result in photons interacting with multiple particles before exiting the surface, resulting in nonlinear mixing (Mustard & Hays, 1997; Ramsey & Fink, 1999; Salisbury & Eastes, 1985).

Identification of glass based upon band parameters in the VSWIR has been previously studied. Horgan et al. (2014) used mineral mixture-based models to identify several band parameters indicative of the presence of basaltic glass in orbiter-based spectral observations. Rader et al. (2022) used the average reflectance between 0.5 and 1.0 μm to estimate the modal abundance of glass in basaltic lavas. McCanta et al. (2015) used a band parameter developed for andesitic compositions, in conjunction with other techniques (point counting, magnetic susceptibility), to identify cryptotephra units, or non-visible layers of tephra, in ocean drill cores. All of these studies provide suitable methods of glass or tephra detection within their constrained compositional applications.

Machine learning is a potentially powerful tool for quantifying sample phase abundances directly from their spectra, based on successes with other spectroscopic methods where it has been used to characterize sample compositions from spectral observations in reference libraries. One of the oldest regression techniques is partial least squares regression (PLS), which has been successfully used to quantify chemical composition and mineral abundances for geologic materials from LIBS, Raman, and MIR data (Breitenfeld et al., 2018, 2021, 2022; Clegg et al., 2009; Dyar, Carmosino, Breves, et al., 2012; Gasda et al., 2021; Hecker et al., 2012; Pan et al., 2015). PLS has also been used on VSWIR spectra of lunar soil replicates and Venus-analog spectra to successfully quantify Fe abundances (L. Li, 2006; Dyar et al., 2020). PLS has been of limited usefulness for quantifying phase assemblages using VSWIR spectra (L. Li, 2006; S. Li et al., 2012; B. Liu et al., 2014), but has been used more successfully for this purpose in the MIR (Breitenfeld et al., 2021; Hecker et al., 2012; Pan et al., 2015).

2.2. Spectral Band Number, Placement, and Resolution

Any method for recognizing the contribution of glass to remote-sensed spectra must be robust enough to be useful for data acquired using multiple types of instruments. Instruments may collect over the same spectral range, but have varying numbers of spectral bands, band placement, and spectral resolutions (wavelengths a band is sensitive to). Spectral bands vary in shape between instruments, and can be defined either using the center wavelength or FWHM spectral response function. Most laboratory VSWIR and MIR spectrometers are hyperspectral and collect thousands of spectral bands at a high spectral resolution. VSWIR laboratory spectrometers like the ASD FieldSpec and the Spectral Evolution OreXpress collect 2152 bands, at 1 nm/band resolution. The Reflectance Experiment Laboratory (RELAB) collects VSWIR spectra at 10 nm/band (Pieters, 1983). MIR laboratory spectrometers typically collect with spectral resolution of 1.9 cm^{-1} /band or 4 cm^{-1} /band. Onboard satellite or orbital spectrometers, multispectral imagers, or radiometers have coarser spectral resolution and sometimes unevenly

distributed bands compared laboratory spectrometers. The Landsat 8 and 9 Earth-observing satellites collect nine bands between 0.43–1.3 μm and two bands in the IR (Knight & Kvaran, 2014; Masek et al., 2020; Reuter et al., 2015). ASTER was designed with nine bands between 0.52–2.43 μm and five bands between 8.125–11.65 μm , with spectral resolutions varying between 10 nm/band and 700 nm/band (Yamaguchi et al., 1998), though the SWIR subsystem (1.6–2.4 μm) has been offline since 2008. Orbiting Mars, CRISM covers 0.362–3.920 μm with 543 or 72 channels depending on the observational mode (Murchie et al., 2007) and TES covers 6–50 μm with a spectral resolution of 5 or 10 cm^{-1} /channel depending on the observation mode (Philip R. Christensen et al., 1992). Mars rover-based spectrometers have variable spectral resolution depending on their design. MASTCAM-Z on the Perseverance rover has 11 channels covering 0.44–1.02 μm (Bell et al., 2021). Mini-TES, on the Curiosity rover, covers 5–29.5 μm at 9.99 cm^{-1} resolution (Silverman et al., 2006).

The placement and number of spectral bands control whether or not a spectral feature is sampled (e.g., the 2.2 μm feature is resolved at 1 nm resolution, but not in the 10 and 100 nm resolution spectra in Figure 1 d-e). Low spectral resolution may affect the ability of a spectrum to accurately represent spectral shapes, making spectral resolution a limiting factor in extracting compositional information from multispectral planetary data if it is coarser than the scale of the features (Crisp et al., 1990).

However, PLS is not necessarily restricted by reduced spectral resolution, or band scarcity. For example, Breitenfeld et al. (2021) used laboratory MIR spectra resampled from $\sim 1.93 \text{ cm}^{-1}$ /band to $\sim 8.66 \text{ cm}^{-1}$ /band, the spectral sampling of the OSIRIS-REx Thermal Emission Spectrometer (OTES), to model the surface mineralogy of asteroid Bennu. Dyar et al. (2020) showed that PLS models can be used to differentiate mafic and felsic compositions with only six spectral bands from 0.85–1.18 μm . The number and placement of spectral bands varies by necessity with resolution, so that the lower resolution spectra have few bands spaced further apart. Here, rather than replicating specific instruments, the distance between bands is the same as the spectral resolution.

3. Methods

3.1. Datasets

Machine learning methods such as PLS require a training data set composed of both the input variables (spectra) and predicted variables (known compositional parameters of standards, here wt. % SiO_2 , $\text{Na}_2\text{O}+\text{K}_2\text{O}$, FeO , and % glass), from which the models are built. Increasing the size of the training data set may improve model performance (Dyar & Ytsma, 2021) and accurate machine learning models are typically built from hundreds of unique spectra (e.g., Breitenfeld et al., 2021; Ytsma et al., 2020). Robust spectral and compositional data sets are time-consuming and costly to build, so this study combines new spectra with those from published works to amass sufficient training data (Table 1).

Natural volcanic samples are utilized to ensure the models were trained and tested on realistic phase assemblages and compositions. Igneous compositions broadly evolve along well-defined trends, though samples' complex phase assemblages may be difficult to reproduce with artificial mixtures. Altered volcanic material was excluded from the datasets, though some of the data sources include altered samples (e.g, Farrand et al.,

2018). Data from synthesized pure glasses provide compositionally diverse endmembers to expand upon natural high- and pure-glass samples, which tend to be high-silica. Utilized synthetic glasses were either made from scratch using synthetic chemical compounds (Cannon et al., 2017; Minitti et al., 2002; Minitti & Hamilton, 2010) or fused from natural materials (Carli et al., 2016; Pisello et al., 2022). Sample characterization methods varied between data sources but were all of high analytical accuracy.

VSWIR data (Figure 1.1) were measured as bidirectional reflectance from 0.35–2.5 μm at varied phase angles. MIR spectral data (Figure 1.2) were collected as emissivity measurements from 400–1600 cm^{-1} in purged or dry air at temperatures of around 80°C. While available in the wider literature, MIR data collected as hemispherical reflectance are not used in this work. Similarly, emissivity measurements collected under a vacuum or high temperature ($>150^\circ\text{C}$) are excluded due to the effects of vacuum and temperature on the position of the Christiansen feature (Donaldson Hanna et al., 2012; Henderson & Jakosky, 1997; Logan & Hunt, 1970).

3.2. Spectral Preprocessing

Spectral data were resampled using in-house software (Carey et al., 2017). VSWIR spectral resolutions tested included 1 nm/band (2146 bands), 10 nm (216 bands), and 100 nm (22 bands; Figure 1.1), and MIR spectral resolutions tested were 1.9 cm^{-1} (632 bands), 19 cm^{-1} (64 bands), and 190 cm^{-1} (7 bands; Figure 1.2). Spectral resolutions were not chosen to match specific spectral instruments, but rather to be even order-of-magnitude reductions in spectral resolution; the finest resolution was based off the data's initial spectral resolutions. Fe-features in the VSWIR appear from $\sim 0.5\text{--}1\text{ }\mu\text{m}$, with the width of the feature dependent on the minerals hosting Fe, while -OH absorbances are narrower, $\lesssim 100\text{ nm}$. In the MIR, the reststrahlen band can cover 800–1200 cm^{-1} , with the CF appearing at $\sim 1200\text{ cm}^{-1}$, and $\approx 100\text{ cm}^{-1}$ wide. The spectral resolutions therefore range from over-sampling spectral features (1 nm and 1.9 cm^{-1}) to <5 spectral bands defining any given feature. In the VSWIR, narrower features $<100\text{ nm}$ wide may not be visible in the 100 nm resolution spectra.

For each compositional parameter, the intensities of all spectra were normalized to either the maximum intensity or to the intensity at a specific spectral band (band normalization) using MATLAB. In the former method, intensity at each band was divided by its highest reflectance or emissivity value, while in the latter, the reflectance or emissivity value at all band intensities was normalized to be equal at a specific spectral band. The best spectral band for band normalization was identified by testing multiple band normalizations for models of glass abundance, bulk wt. % SiO_2 and wt. % FeO , and glass wt. % SiO_2 and wt. % FeO . VSWIR and MIR datasets from Leight et al. (2023) were used as the training dataset, with no withheld test dataset. RMSE-CV was used to evaluate model performance. VSWIR spectra were normalized to 2.17 μm (Figure 1.1b), except the 100 nm/band-VSWIR spectra, which did not have a band at 2.17 μm , and were normalized to the intensity at 2.15 μm . MIR spectra were normalized to the emissivity at 1100 cm^{-1} (Figure 1.2b).

3.3. Partial Least Squares Regression

PLS regression is a multivariate regression technique used to predict explanatory variables from observational data. A variant of least-squares regression, PLS explains covariance in both the predictor variables, p , and predicted elements (Stone & Brooks, 1990). For this study, p is the number of spectral bands in the collected spectra and the predicted elements are the known sample abundance of bulk wt. % SiO₂, Na₂O+K₂O, FeO, glass wt. % SiO₂, Na₂O+K₂O, FeO, or modal % glass; each predicted element is modeled independently. This gives an input matrix X with the dimensions of the number of spectra and the number of spectral bands (p).

A least squares regression model takes the form:

$$f(X) = \beta_0 + \sum_{j=1}^p X_j \beta_j \quad (1)$$

where X_j are the input variables taking the vector form $X^T = (X_1, X_2, \dots, X_p)$, and β_j are the coefficients taking the vector form $\beta = (\beta_0, \beta_1, \dots, \beta_p)^T$ used to predict $f(X)$, or the compositional parameter, with p being the length of the input vector X^T (Hastie et al., 2009). Here, each component of X_j is a spectral band. Spectra and the collected compositional data provide a training set used to estimate the coefficients, β . PLS models place the largest coefficient values on components (in this case, spectral bands) that have high variance and high correlation with the predicted values (Hastie et al., 2009; Stone & Brooks, 1990).

PLS is a shrunken regression technique, which means that the algorithm assumes the input variables (p) are correlated and can be reduced (Hastie et al., 2009). The PLS algorithm reduces p to an absolute number of terms by creating a series of new, orthogonal (uncorrelated), hybrid variables, also referred to as components that are linear combinations of the original bands (Hastie et al., 2009; Wold et al., 2001). The ideal number of components, n , for a data set or prediction model must be determined by testing and is characteristic of the data set or prediction model in question (Wold et al., 2001). Larger numbers of components ($n > 10$) expose the model to overfitting to training data (Dyar, et al., 2012), and small numbers of components correspond to the most generalizable models. This study limits $n \leq 10$.

PLS models were built and tested using a suite of Python programs built to train and test multivariate regressions on spectral datasets for each compositional variable (Ytsma, 2022). To ensure that the models were tested on unseen data, a random subset of approximately 20% of the total dataset was held out as a test dataset (Dyar & Ytsma, 2021). Which samples were used as the test set varied for each predicted compositional parameter. If a sample had multiple spectra, they were all assigned to the same dataset; this resulted in unevenly sized datasets but was necessary to ensure that the models were not essentially tested on the training data. Table 2 lists the number of samples and spectra in the training and test sets for each model.

The remaining samples, $\approx 80\%$ of the total dataset, were used as training data to calibrate the model (Table 2). The number of components, n , was optimized using five-fold cross-validation (CV) (Dyar & Ytsma, 2021). The five folds were built within the PLS algorithm by randomly selecting spectra from the training dataset, keeping spectra from the same standard in the same fold. To perform CV, a fold was iteratively held out

from the training data and a regression performed on the remaining training data. Spectra in the withheld fold were then predicted by that regression, and the root mean squared error (RMSE) between predicted and actual values of the withheld fold was calculated. Once every fold had been tested, the RMSE values of each fold were averaged, giving the RMSE-CV of the n -component model. The n -component model with the lowest RMSE-CV was chosen as the final model and the calibration RMSE (RMSE-C) was calculated using the entire training dataset. Both the RMSE-CV and RMSE-P test model performance on data included in model training. Model prediction accuracy (RMSE-P) was determined by testing that final model on the held-out test dataset. R^2 correlation assesses the variance in the test predictions to the ideal 1:1 line of prediction. Here we report the R^2 metric adjusted for the size of the dataset.

4. Results

To maximize the predictive capabilities of models and their applicability to different geologic environments, data used here encompass a large compositional range (Table 1.1 and attachment Table S1.xlsx). Not all available spectral data had all of the desired compositional information— glass abundance, bulk wt. % SiO_2 , $\text{Na}_2\text{O}+\text{K}_2\text{O}$, FeO, or glass wt. % SiO_2 , $\text{Na}_2\text{O}+\text{K}_2\text{O}$, FeO data (attachment Table S1.xlsx) – but spectral data were included in as many datasets as possible (Table 1.2), resulting in varyingly sized training and test sets. Insufficient MIR spectra of samples with known glass compositions were available so only bulk compositions and modal abundance of glass could be considered for those data. Several published VSWIR data sets were sampled at >1 nm/band, and so were only included in the 10 nm and 100 nm spectral resolution data sets. Figure 1.3 compares the compositions encompassed in the utilized data sets for the four modeled parameters.

PLS models predicted the compositional parameters from VSWIR and MIR spectra at each spectral resolution. Compositional variables were chosen to address first-order scientific questions in identifying volcanic deposits: the modal abundance of glass, the bulk wt. % SiO_2 , $\text{Na}_2\text{O}+\text{K}_2\text{O}$, FeO, and glass phase wt. % SiO_2 , $\text{Na}_2\text{O}+\text{K}_2\text{O}$, FeO. Model uncertainties given as RMSE-P were used to quantify accuracies and validate model performance (Table 1.3). R^2 correlations in Table 3 were used to assess the difference between predictions and true values from the ideal 1:1 line (Figure 1.4 and Figure 1.5) and are useful for validating model performance.

Both normalization to maximum intensity and a specific spectral band were applied to the spectral data before building PLS models. For most predicted parameters, normalization minimally affected model accuracy. The VSWIR models performed best with the band normalization, while the MIR models were best modeled with the max normalization, with two exceptions. The 10 nm and 100 nm VSWIR glass abundance models performed significantly better using the maximum normalization, rather than the band normalization (Table 1.4).

Model efficacy varied with changing spectral resolution. The VSWIR 1 nm models have the largest RMSE-P (worst accuracy) and smallest R^2 values for each parameter (Table 1.3); the one exception is the glass abundance models, where the 1 nm model has a lower RMSE-P and higher R^2 (RMSE-P = 12 %, $R^2 = 0.83$) than the 10 and 100 nm models (RMSE-P = 15 %, and 15, $R^2=0.79$ and 0.77 , respectively). RMSE-P does not

vary between the VSWIR 10 and 100 nm models of glass abundance (RMSE-P = 15 %) and bulk wt. % FeO (RMSE-P = 3.4 wt. %) with minimal (~ 0.02) change in R^2 . The MIR glass abundance and bulk wt. % Na₂O+K₂O models have the same RMSE-P for all resolutions (RMSE-P = 12 % and RMSE-P = 0.9 wt. %, respectively.) For all of the modeled parameters, MIR model R^2 values change only slightly (e.g., the glass abundance R^2 are 0.77, 0.77 and 0.75 for the 1.9, 19, and 190 cm⁻¹ models, respectively) between spectral resolutions, except for the bulk wt. % FeO models. There are also several parameters where the model with the lowest RMSE-P or highest R^2 is the 19 cm⁻¹ or 10 nm spectral resolution: the MIR bulk wt. % SiO₂, VSWIR glass wt. % FeO, bulk and glass wt. % Na₂O+K₂O models. The lack of a coherent pattern of model performance and spectral resolution indicates that spectral resolution is not strongly restricting PLS as a predictive method.

With RMSE-P of 12-15 %, PLS models can differentiate well between low and high glass abundance at all resolutions of both VSWIR and MIR data. The 10 and 100 nm VSWIR models predict a wide spread of values for the pure-glass samples (Figure 1.4); all the MIR models have a wider spread of predicted values at low glass abundances (Figure 1.5). Therefore, these models are capable of discriminating between a sample with 20% modal glass from one with 90% glass. The 1.9 and 19 cm⁻¹ MIR and 10 and 100 nm VSWIR bulk wt. % FeO models have different uncertainties (MIR RMSE-P of 2.4-2.5 wt. %, VSWIR RMSE-P of 3.4 wt. %), though all of the models have similar R^2 near 0.55, indicating that both regions provide the same predictive capability for bulk wt. % FeO, and are able to distinguish low-Fe samples from high-Fe samples. The MIR models are most accurate below ~ 10 wt. % FeO, underpredicting higher FeO samples (Figure 1.5). Both MIR and VSWIR wt. % Na₂O + K₂O models have poor R^2 ($R^2 = 0.02$ -0.43), indicating poor model accuracy. The MIR models generally over-predict wt. % Na₂O + K₂O, (Figure 1.5), and the VSWIR models have unsystematically bad predictions for this parameter (Figure 1.4). The MIR wt. % SiO₂ models have small enough RMSE-P (3.9-2.4 wt. %) to distinguish between low (40-50 wt. %) and high silica (>65 wt. %; Figure 1.5); the VSWIR models have poor R^2 (0.27-0.38), indicating they cannot separate mafic and felsic samples (Figure 1.4).

5. Discussion

The most accurate models are those with spectral features that are known to be directly affected by the predicted parameter, such as the VSWIR wt. % FeO models, and the MIR wt. % SiO₂ models. Because both the CF and reststrahlen bands are produced by the SiO₄ tetrahedra in minerals, their position is indicative of silicate polymerization. Network-modifying cations such as Fe, Na, and K affect the silicate structure, and therefore change the CF and reststrahlen bands. Conversely, none of the predicted compositional parameters in the VSWIR region has a specific feature except Fe. Spectral albedo in the VSWIR generally increases with increasing SiO₂ content, though this may not be apparent after normalization. The low R^2 of the MIR and VSWIR wt. % Na₂O + K₂O models show the importance of available spectral features in model performance. In the MIR, the models are more successful at predicting alkali contents because the steric configurations of SiO₄ tetrahedra are modified by Na⁺ and K⁺. Na⁺ and K⁺ do not directly influence any spectral features in the VSWIR region, and so the models perform poorly.

The VSWIR wt. % FeO models are successful because spectral features related to Fe are located in the VSWIR region.

The PLS models have uncertainties similar to previously published statistical methods of predicting bulk oxide content or mineral abundance from VSWIR or MIR data. For example, the spectral parameter predicting bulk wt. % SiO₂ from Hook et al. (2005) has a RMSE = 5.5 - 8.4 wt. % SiO₂ (as calculated from their tables 4 and 5). Predictions of bulk wt. % FeO via spectral parameters by Lucey et al. (1995) and Wilcox et al. (2005) have errors of 2.16 %, 1.5 wt. % FeO, respectively. The VSWIR glass abundance parameter from Rader et al. (2022) has an error of 8.4 %. These spectral parameters are intended for very limited compositional or phase ranges (i.e., basalts); the PLS models apply to a much larger compositional or phase range than any of these examples. All of these examples note that their predictions are sensitive to grain size. The training datasets for the PLS models include a wide range of grain sizes, and so the models are not strongly influenced by sample grain size (Figure 1.6).

Predictions of phase abundance via linear deconvolution of MIR data by Feely & Christensen (1999) and Wyatt et al. (2001) had errors of 3-11% and 2.5-12%, respectively. The MIR glass abundance PLS models have 12% uncertainty, and the VSWIR have 15% uncertainty, which are respectively equal to and larger than the error in Feely & Christensen (1999) and Wyatt et al. (2001). However, most works utilizing linear deconvolution methods do not assess the model prediction error, but assume an error of 5-10%. The PLS model methodology provides a more rigorous quantitative assessment of both model precision and accuracy by utilizing a large known test dataset. Linear deconvolution methods are limited by the size of the reference library and the encompassed compositional range (e.g., Ramsey & Christensen, 1998; Rogers & Aharonson, 2008). Crucially, predictions of glass abundance via linear deconvolution methods are influenced by the included glasses' compositions (e.g., Cannon et al., 2017; Wyatt et al., 2001), whereas PLS models decouple predictions of phase abundance and composition.

5.1. Relative Linearity of VSWIR and MIR Spectra and Potential Effects on Prediction Accuracies

In both the VSWIR and MIR regions, spectral features from individual phases overlap and combine to produce the observed spectra. How spectral features combine is controlled by k , the imaginary index of refraction, or extinction coefficient, which describes how light attenuates as it propagates through a material. In the MIR, where k is large, light does not propagate far into the material, and thus spectral features are produced predominantly by surface scattering from a single phase (Hapke, 1981; Salisbury & Wald, 1992). At fine particle sizes ($< 70 \mu\text{m}$), light may not fully attenuate within a single particle, resulting in transparency features and non-negligible volume scattering (Hunt, 1977; Moersch & Christensen, 1995; Mustard & Hays, 1997). In the VSWIR, k is orders of magnitude smaller than at MIR wavelengths. Light can propagate into the surface and may interact with more than one phase, resulting in nonlinear volume scattering of light (Mustard & Pieters, 1989; Mustard & Hays, 1997). Surface scattering causes linear spectral mixing, with phases contributing to the observed spectrum in proportion with their areal abundance, while volume scattering produces nonlinear

spectral mixing (Moersch & Christensen, 1995; Mustard & Hays, 1997). Thus, it might be expected that MIR predictions would be more straightforward.

Previous applications of PLS to VSWIR data largely focused on quantifying the phase assemblage of lunar soils, producing models with limited predictive capabilities (L. Li, 2006; S. Li et al., 2012; B. Liu et al., 2014). These results, when contrasted to successful PLS models for MIR data, have led to speculation that spectral mixing may influence the success of PLS modeling, limiting the method to spectral regions with linear mixing (S. Li et al., 2012; Pan et al., 2015). In contrast, other studies (Breitenfeld et al., 2021; Pan et al., 2015) show that use of a range of particle sizes in training data, including some fine enough to have nonlinear mixing in the MIR, produces MIR models that are insensitive to particle size, suggesting that PLS can overcome effects of nonlinear mixing. Results from this study further this conclusion. MIR datasets contain fine-grained samples that display features arising from volume scattering (Leight et al., 2022), but the models nonetheless perform well, and do not display a sensitivity to particle size (Figure 1.6). The VSWIR models predicting wt. % FeO and glass abundance, which solely use data in a nonlinear mixing wavelength regime, are only slightly less accurate than those of the respective MIR models. These VSWIR results indicate that nonlinear spectral mixing does not wholly inhibit the predictive capabilities of PLS models, though further work is needed to fully investigate this conclusion.

5.2. Influence of Size and Distribution of Data Sets

Large, compositionally diverse data sets are particularly important when predicting parameters without obviously correlative spectral features. Previous work by Dyar & Ytsma (2021) established that increased training data set size improves PLS model performance for laser-induced breakdown spectra. The current study provides a comparable test for VSWIR spectra. Here, the increase in data set size between the 1 nm and 10 nm resolution VSWIR bulk datasets (due the availability of more data in the literature), and accompanying compositional breadth, results in improved model accuracy for the 10 nm-resolution bulk and glass wt. % FeO models (Table 1.3, Figure 1.4). The VSWIR bulk wt. % SiO₂ and Na₂O + K₂O models exhibit marginal improvement with additional training data but low accuracy overall due to lack of spectral features at this wavelength, as discussed above.

Previous successful applications of PLS to quantify phase assemblages used MIR data of mineral mixtures (e.g., Breitenfeld et al., 2021; Hecker et al., 2012; Pan et al., 2015). In the VSWIR, minerals have spectral features arising from their crystal structures to which the PLS models can be tuned to determine abundance. Spectral features in glasses are less consistent and can vary with composition and quench rate (Minitti & Hamilton, 2010; Pisello et al., 2022). Published VSWIR PLS models for glass abundance use small data sets (number of samples < 80) and result in limited predictive accuracy over a narrow compositional range (L. Li, 2006; S. Li et al., 2012; B. Liu et al., 2014). In this study, the accuracy of models that predict glass abundance likely reflects the large sample size and compositional diversity of the training sets, which encompass the entire range of potential glass abundances - from near-zero to 100%- with no trend between glass composition and abundance (Figure 1.3).

The range of compositions encompassed in a training set, and the spread of data within that compositional range, affect model accuracy. It is difficult, however, to achieve even coverage of oxide compositions using natural samples; intermediate compositions of ~57–67 wt. % SiO₂ are surprisingly uncommon in natural volcanic rocks (Bennefoi et al., 1995; Charlier et al., 2011; Geist et al., 1995). Minor gaps like the ones in our training sets may be compensated for either by inclusion of samples on either side of the compositional gap or by strategic use of synthetic samples. The bias towards mafic compositions in the data used here results from the emphases of previous studies that focused on predominantly mafic samples analogous to the Moon and Mars. High-alkaline compositions are similarly underrepresented in all data sets, especially in the MIR.

The distribution of the training data inherently limits the calibration to unknowns within that same range, and model accuracy will most likely get worse for unknown compositions outside that range. Many of the compositional data sets include sparse data at compositional extremes (Figure 1.3) that may limit model accuracy toward endmember compositions (e.g., the MIR wt. % FeO model predictions for samples with >10% FeO; Figure 1.5). The narrower range of the MIR data oxide compositions relative to the VSWIR data sets may contribute to the better accuracy of MIR models relative to those in the VSWIR.

5.3. Effects of Spectral Preprocessing

Spectral preprocessing is an important step when utilizing machine learning. It is particularly important for building the data sets utilized in this work because spectral data collection protocols are variable among data sources. Normalizing spectral data can minimize differences in instrumentation or experimental configuration because these variations change the magnitude of measured reflectance or emission (e.g., Sklute et al., 2015). Normalization may also reduce spectral differences between different size fractions of a single sample, thus influencing model predictions (i.e., L. Li, 2006; Pan et al., 2015). As shown in Table 4, model accuracy is indeed sensitive to the normalization method used. Most VSWIR models performed better when spectra were normalized to 2.17 μm , except for the 10 and 100 nm glass abundance models, which performed best when the spectra were normalized to maximum intensity (Table 1.4). The MIR models all performed best when the spectra were max normalized, though the difference between normalizations is significantly less than the VSWIR models. Because only two normalization methods were tested in each spectral region, it is quite possible that different normalizations (i.e., a band normalization at 0.50 μm) would work better when predicting other variables.

5.4. Spectral Resolution

Spectral resolutions tested here were chosen to reflect differences in spectral resolution between laboratory spectrometers and multispectral instruments such as ASTER, which has 9 VSWIR bands and five bands in the MIR. The 1.9 cm^{-1} , 1 nm, and 10 nm resolutions used in this study are directly comparable to the resolutions of available data. The relative accuracies of the band-sparse models indicate that hyperspectral data with the high resolution of laboratory spectral are not needed for PLS models to accurately quantify sample composition. The difference in model efficacy

between the 19 cm^{-1} and 190 cm^{-1} models, and between the 10 nm and 100 nm models, is minimal despite the order of magnitude reduction in spectral bands (Figure 1.4 and Figure 1.5, Table 1.3). The MIR models are less affected by differences in spectral resolution than the VSWIR models. This is probably due to the sensitivity of the available spectral bands to the predicted parameters, but is likely also influenced by the relative width of the spectral bands compared to the coarse spectral resolutions of 190 cm^{-1} and 100nm.

Band-sparse spectra may sample narrow spectral features at only one or two points. Narrow spectral features, such as -OH absorptions at 1.4, 1.9, and 2.2 μm , are over sampled at the 1 nm and 1.9 cm^{-1} resolutions, but at only 10s of nm wide, may only affect one or two spectral bands at a 10 nm or 19 cm^{-1} resolution, and would not be visible at the 100 nm or 190 cm^{-1} resolution, though the features will still affect the observed spectrum (Figure 1.1 and Figure 1.2). Conversely, Fe absorptions in the VSWIR can affect reflectance values between 0.5 and 1.0 μm , depending on the crystal lattice; at 100 nm resolution, 5 bands sample this feature. The reststrahlen band in the MIR is similarly wide, and affects three bands at 190 cm^{-1} resolution. The position of spectral bands will also influence the ability of PLS to make accurate predictions, as the location of spectral bands affects how spectral band shapes are reproduced in band-sparse spectra. The emissivity maximum caused by the Christiansen feature (CF), for example, falls between the centers of two bands in the 190 cm^{-1} dataset, affecting the emissivity values of both. Unlike the 190 cm^{-1} and 100 nm datasets, most multispectral instruments do not have evenly spaced spectral bands. Earth-orbiting instruments frequently lack bands near 1.4 and 1.9 μm due to atmospheric water absorptions (e.g., Knight & Kvaran, 2014; Yamaguchi et al., 1998). Both the spacing and resolution will affect the observed spectrum and how well PLS can use the data for predictions.

Resampling of the 1.9 cm^{-1} MIR datasets and 10 nm VSWIR datasets through ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer; Yamaguchi et al., 1998) spectral bands provides a test of the importance of band placement on PLS model efficacy. The nine VSWIR bands range in width from ~8 to 100 nm and the five MIR bands have widths of 350 and 700 nm; spectral bands are placed unevenly over the sampled wavelength range (points in Figure 1.7; Yamaguchi et al., 1998). Resampled spectra (Figure 1.7) have varying resolution and reduced spectral range compared to the other datasets used here (0.56-2.4 μm in the VSWIR, and 8.26-11.24 μm , or 890-1208 cm^{-1} in the MIR). PLS models were made following the methods in section 3, and the results are reported in Table 1.5. VSWIR ASTER-band PLS models generally have greater error than the 1, 10, and 100 nm resolution VSWIR models. However, several of the 1 nm models perform equally to or worse than the ASTER-band models (e.g., for bulk wt. % FeO, the 1 nm model RMSE-P = 2.2, and $R^2=0.02$, while the ASTER-band VSWIR model RMSE-P=3.4, $R^2=0.55$). This difference in performance is attributed to the larger size of the ASTER resolution dataset. The ASTER-band MIR models have worse RMSE-P and R^2 than the 1.9, 19, and 190 cm^{-1} models (e.g., RMSE-P of 4.2 wt. % SiO_2 for the 190 cm^{-1} and 5.4 wt. % SiO_2 for the ASTER-band model; Table 1.4 and Table 1.5) except for the bulk $\text{Na}_2\text{O}+\text{K}_2\text{O}$ models. However, this difference is negligible, as the RMSE-P of the 1.9 cm and ASTER-band models are 0.9 and 0.8 wt. %

Na₂O+K₂O, respectively. The reduction in spectral bands and spectral range likely factors into the larger model uncertainties for the ASTER-band models compared to the 100 nm and 190 cm⁻¹ spectra and models; ASTER-band MIR spectra do not sample the minima caused by the Si-O bend at 500-700 cm⁻¹ (King et al., 2004) nor fully sample of the reststrahlen band past 1200 cm⁻¹ while in the VSWIR, only three bands sample the Fe-absorption region. However, the similar RMSE-P and R² of the VSWIR and MIR ASTER-bands models to the 100 nm and 190 cm⁻¹ models indicates that spectral band spacing and spectral resolution are less influential on model efficacy than the relevance of spectral features present to the modeled variable.

5.5. Prediction Accuracies for Glass Composition

Because glass composition is used to distinguish between volcanic deposits (Brown et al., 1992; Carter et al., 1995; Lowe, 2011; Westgate & Gorton, 1981), it is important for evaluating eruption dynamics and correlating tephra units across large regions. Quantifying the composition of an individual phase within a sample has previously been intractable with MIR or VSWIR data, though multivariate techniques show promise. Hecker et al. (2012) modeled plagioclase composition in granitic rocks using PLS, but the large uncertainties in the feldspar composition training data affected their model accuracies. Utilizing sample characterization methods with high analytical accuracy is key to training accurate PLS models, as the models cannot be more accurate than the training dataset.

The absence of spectral features dependent on Si⁴⁺, Na²⁺, or K²⁺ in the VSWIR inhibits accurate prediction of glass wt. % SiO₂ or wt. % Na₂O+K₂O (Figure 4; Table 3). Models predicting wt. % FeO in glass, however, are slightly more accurate than models predicting bulk wt. % FeO (Table 1.3). Model uncertainties do not permit discrimination of minor differences between bulk and glass composition, as is observed in natural samples (e.g., Leight et al., 2022) and of interest for volcanological study. However, larger datasets are seen to increase prediction accuracy, suggesting this degree of accuracy may be possible with a larger training set.

Unfortunately, only 28 samples in the MIR dataset have known glass compositions, most from a single data source. These data are insufficient for training PLS models. However, the accuracy of the 190 cm⁻¹ MIR models suggest that glass composition could be quantified with 190 cm⁻¹ spectral resolution should sufficient training data be amassed.

6. Conclusions

Identification of volcanic deposits relies on identification of a glass phase. Both the MIR and VSWIR spectral regions can be used to identify the presence of glass in all three of the tested spectral resolutions using PLS models. These PLS models provide a method of quantifying glass abundance, independent from other parameters, generalizable to a wide range of bulk composition, and largely independent of particle size. Identifying and quantifying glass abundance in multiphase samples using other methods, such as band parameters or least-squares regressions, is difficult and sensitive to composition, particle size, and glass abundance (e.g., Cannon et al., 2017; Horgan et al., 2014; Williams & Ramsey, 2022). The glass abundance models here do have a higher uncertainty than the 5-10% modal error typically assumed for linear deconvolutions based off work by

Ramsey & Christensen (1998) and Feely & Christensen (1999). However, the uncertainty of our PLS models provides a significantly more quantitative assessment of both model precision and accuracy by virtue of using a known test dataset than this assumed error. PLS models presented here predict composition and glass abundance of volcanic samples from VSWIR and MIR spectral data with quantified accuracies over a wide range of composition, grain size, and spectral resolution. MIR models have better prediction accuracies than VSWIR models when predicting the same compositional parameters due to the presence of relevant spectral features in each region that are indicative of the predicted variable. The efficacy of the VSWIR glass wt. % FeO abundance models indicates that parameters directly related to available spectral features such as specific mineral compositions, can be modeled using PLS provided a sufficiently large training data set is available.

The spectral resolution of the data does affect model efficacy but sparse resolution does not preclude accurate PLS model predictions. Models using 100 nm and 190 cm^{-1} resolution provide useful predictions of glass abundance and bulk wt. % FeO with accuracies of 15 and 12 % modal glass abundance and 3.4 and 3.1 wt. % FeO, respectively. The quantity and compositional range of training data are equally influential on the PLS model accuracy as the number of spectral bands. VSWIR and MIR PLS models are always influenced by the available training data when data sets are small or compositionally restricted, as is the case here. Additional spectral libraries of natural rock samples with quantified phase assemblages, phase compositions, and bulk compositions will undoubtedly improve model performance and likely produce quantitative predictions.

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Appendix A

Table 1.1 Data sources.

VSWIR					
Source	Resolution	Wavelength range, μm	Grain size range, μm	# Samples	# Spectra
Minitti et al. (2002)♡	10 nm	0.32-2.55	75-500, <75, <45	8	10
Carli et al. (2016)♡	1 nm	0.35-2.5	224-250, 200-224, 180-200, 150-180, 125- 150, 100-125, 75- 100, 50-75, 25-50	4	36
Cannon et al. (2017)♡	10 nm	0.32-2.55	<53	16	28
Farrand et al. (2018)♡	5 nm	0.3-25.0	<400	9*	9
Scudder et al. (2021)♡	1 nm	0.35-2.5	<125	40*	40
Pisello et al. (2022)♡	1 nm	0.35-2.495	<36	13	13
(Leight et al. 2023)§	1 nm	0.35-2.5	250-500, 125-250, 63- 125, <63	22	82
MIR					
Source	Resolution	Wavelength range, cm^{-1}	Grain size range, μm	# Samples	# Spectra
Hamilton et al. (2001)◇	1.9 cm^{-1}	382-1599	hand sample	31*	31
Minitti & Hamilton (2010)♡	1.9 cm^{-1}	200-2000	>500	5	5
Farrand et al. (2018)♡	1.9 cm^{-1}	222-2000	hand sample	9*	9
Williams & Ramsey (2019)◇	1.9 cm^{-1}	400-2000	>150, 63-150, 45-63	5	15
Scudder et al. (2021)♡	1.9 cm^{-1}	220-2000	125-250	40*	40
(Leight et al. 2023)§	1.9 cm^{-1}	399-2500	250-500, 125-250, 63- 125, <63	19	76

*Limited compositional information.

§Dataset produced by authors. ◇Dataset obtained via direct request. ♡Dataset obtained via repository download.

Note. Attachment TableS1.xlsx gives each spectrum by name, and specifies available compositional information for each sample.

Table 1.2 PLS Model datasets used in this study.

Spectral Resolution	Variable	Samples		Spectra	
		# Training	# Test	# Training	# Test
VSWIR	1 nm				
	Bulk wt. % FeO	62	15	121	23
	Bulk wt. % Na ₂ O+K ₂ O	40	10	111	33
	Bulk wt. % SiO ₂	40	10	118	26
	Glass wt. % FeO	40	10	104	33
	Glass wt. % Na ₂ O+K ₂ O	34	9	108	29
	Glass wt. % SiO ₂	34	9	107	30
	% Glass	34	9	136	35
	10 and 100 nm				
	Bulk wt. % FeO	65	16	153	36
	Bulk wt. % Na ₂ O+K ₂ O	65	16	160	29
	Bulk wt. % SiO ₂	65	16	167	22
	Glass wt. % FeO	54	13	141	34
	Glass wt. % Na ₂ O+K ₂ O	54	13	148	27
MIR					
	1.9, 19, and 190 cm ⁻¹				
	Bulk wt. % FeO	62	16	114	31
	Bulk wt. % Na ₂ O+K ₂ O	62	16	114	31
	Bulk wt. % SiO ₂	62	16	107	38
	% Glass	62	15	117	27

Note. The total number of spectra and samples included in each dataset are given.

Table 1.3 Model summary statistics

Spectral Resolution	Model	RMSE-CV	RMSE-C	RMSE-P	R ²
MIR Models					
1.9 cm ⁻¹	% Glass	16	15	12	0.77
	Bulk wt. % FeO	1.7	1.2	2.4	0.58
	Bulk wt. % Na ₂ O+K ₂ O	1.5	1.5	0.9	0.43
	Bulk wt. % SiO ₂	4.0	3.2	4.2	0.71
19 cm ⁻¹	% Glass	17	15	12	0.77
	Bulk wt. % FeO	2.0	1.5	2.5	0.53
	Bulk wt. % Na ₂ O+K ₂ O	1.5	1.5	0.9	0.43
	Bulk wt. % SiO ₂	4.1	3.3	3.9	0.75
190 cm ⁻¹	% Glass	16	14	12	0.75
	Bulk wt. % FeO	2.6	2.4	3.1	0.28
	Bulk wt. % Na ₂ O+K ₂ O	1.6	1.5	0.9	0.46
	Bulk wt. % SiO ₂	5.2	4.8	4.2	0.71
VSWIR Models					
1nm	% Glass	16	13	12	0.83
	Bulk wt. % FeO	2.1	1.8	2.2	0.03
	Bulk wt. % Na ₂ O+K ₂ O	2.2	1.9	1.7	0.02
	Bulk wt. % SiO ₂	8.4	7.3	6.9	0.38
	Glass wt. % FeO	2.6	2.1	2.9	0.16
	Glass wt. % Na ₂ O+K ₂ O	2.5	2.6	2.5	0.28
	Glass wt. % SiO ₂	7.8	7.4	10.6	-0.11
10nm	% Glass	18	16	15	0.79
	Bulk wt. % FeO	4.8	3.8	3.4	0.56
	Bulk wt. % Na ₂ O+K ₂ O	2.1	2.0	1.7	0.47
	Bulk wt. % SiO ₂	6.9	6.1	4.6	0.27
	Glass wt. % FeO	4.7	4.3	2.8	0.71
	Glass wt. % Na ₂ O+K ₂ O	2.6	2.6	1.5	0.43
	Glass wt. % SiO ₂	8.3	8.0	7.3	0.06
100nm	% Glass	19	16	15	0.77
	Bulk wt. % FeO	4.9	4.0	3.4	0.56
	Bulk wt. % Na ₂ O+K ₂ O	2.1	2.0	1.7	0.41
	Bulk wt. % SiO ₂	6.8	6.0	4.9	0.29
	Glass wt. % FeO	4.8	4.4	3.0	0.67
	Glass wt. % Na ₂ O+K ₂ O	2.6	2.6	1.7	0.33
	Glass wt. % SiO ₂	8.3	8.0	7.5	0.03

Note. Models are grouped by spectral resolution. RMSE-CV, RMSE-C, and RMSE-P are given in the unit of the predicted variable, e.g., wt. %. R² is unitless.

Table 1.4 Effect of normalization method on VSWIR and MIR glass abundance and bulk wt. % FeO model summary statistics

VSWIR	Spectral Resolution	Normalization	RMSE-CV	RMSE-C	RMSE-P	R ²
% Glass	1nm	2.17 μm	16	13	12	0.83
		max	17	16	16	0.70
	10 nm	2.17 μm	20	16	16	0.75
		max	18	16	15	0.79
	100 nm	2.15 μm	25	21	22	0.50
		max	19	16	15	0.77
Bulk wt. % FeO	1nm	2.17 μm	2.1	1.8	2.2	0.03
		max	2.1	1.8	2.2	0.02
	10 nm	2.17 μm	4.8	3.8	3.4	0.56
		max	4.8	3.5	5.5	0.19
	100 nm	2.15 μm	4.9	4.0	3.4	0.56
		max	5.8	4.6	4.8	0.13
MIR						
% Glass	1.9 cm^{-1}	1100 cm^{-1}	17	15	12	0.74
		max	16	15	12	0.77
	19 cm^{-1}	1100 cm^{-1}	17	15	13	0.73
		max	17	15	12	0.77
	190 cm^{-1}	1100 cm^{-1}	16	15	13	0.73
		max	16	14	12	0.75
Bulk wt. % FeO	1.9 cm^{-1}	1100 cm^{-1}	1.8	1.4	2.4	0.57
		max	1.7	1.2	2.4	0.58
	19 cm^{-1}	1100 cm^{-1}	1.9	1.4	2.5	0.53
		max	2.0	1.5	2.5	0.53
	190 cm^{-1}	1100 cm^{-1}	2.7	2.5	3.2	0.24
		max	2.6	2.4	3.1	0.28

Table 1.5 ASTER-resolution VSWIR and MIR model summary statistics.

MIR				
Model	RMSE-CV	RMSE-C	RMSE-P	R ²
% Glass	20	19	16	0.58
Bulk wt. % FeO	3	3	3	0.16
Bulk wt. % Na ₂ O+K ₂ O	2	2	1	0.57
Bulk wt. % SiO ₂	6	6	5	0.53
VSWIR				
Model	RMSE-CV	RMSE-C	RMSE-P	R ²
% Glass	25	23	25	0.35
Bulk wt. % FeO	4.6	3.9	3.4	0.55
Bulk wt. % Na ₂ O+K ₂ O	2.2	2.1	1.7	0.28
Bulk wt. % SiO ₂	6.6	6.3	4.9	0.39
Glass wt. % FeO	4.7	4.3	3.1	0.64
Glass wt. % Na ₂ O+K ₂ O	4.3	4.1	4.1	0.43
Glass wt. % SiO ₂	8.1	7.9	7.3	0.07

Note. RMSE-CV, RMSE-C, and RMSE-P are given in the unit of the predicted variable, e.g., wt. %. R² is unitless.

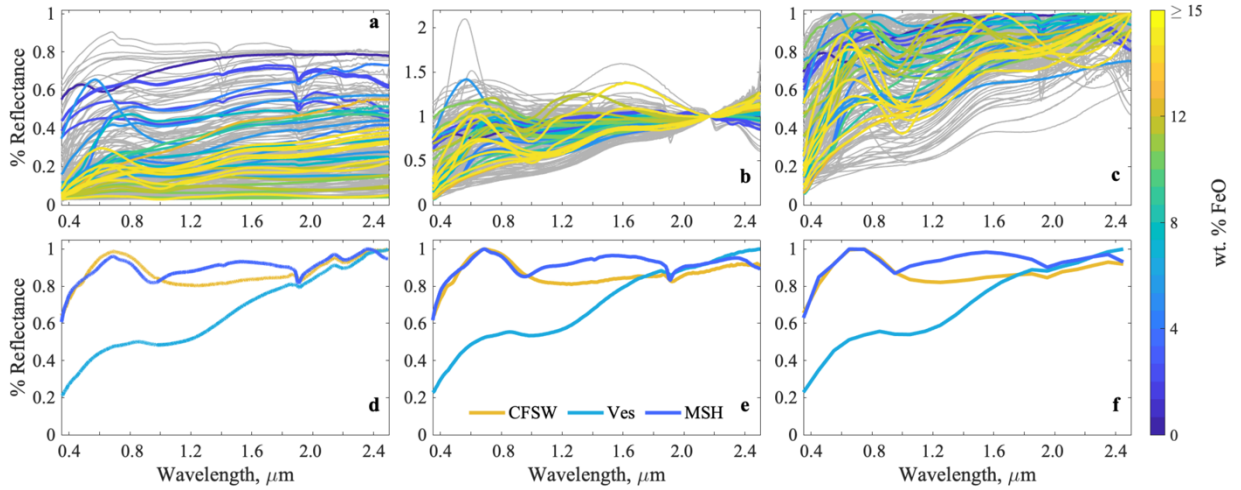


Figure 1.1 VSWIR spectral data.

The 10 nm resolution spectra are shown in (a) with no normalization, (b) with normalization to % reflectance at 2170 nm, and (c) with normalization to the maximum % reflectance. Bulk wt. % FeO Test dataset spectra shown colored by bulk wt. % FeO, all other data shown in grey. The spectral resolutions of (d) 1 nm/band, (e) 10 nm/band, and (f) 100 nm/band are shown using max-normalized spectra of samples CFSW (yellow line), Ves (light blue line) and MSH (dark blue line) from (Leight et al., 2023).

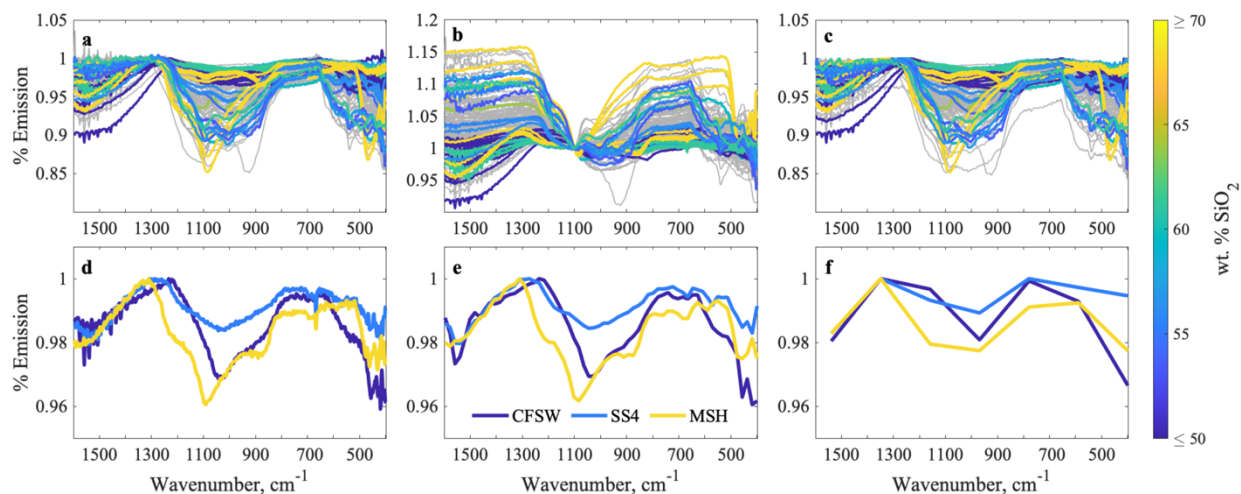


Figure 1.2 MIR spectral data.

The 1.9 cm^{-1} resolution spectra are shown in (a) with no normalization, (b) with normalization to % emission at 1100 cm^{-1} , and (c) with normalization to the maximum % emission. Bulk wt. % SiO_2 test dataset spectra shown colored by bulk wt. % SiO_2 , all other data shown in grey. The different spectral resolutions of (d) 1.9 cm^{-1} /band, (e) 19 cm^{-1} /band, and (f) 190 cm^{-1} /band are shown using spectra of samples CFSW (purple line), SS4 (blue line) and MSH (yellow line) from (Leight et al., 2023).

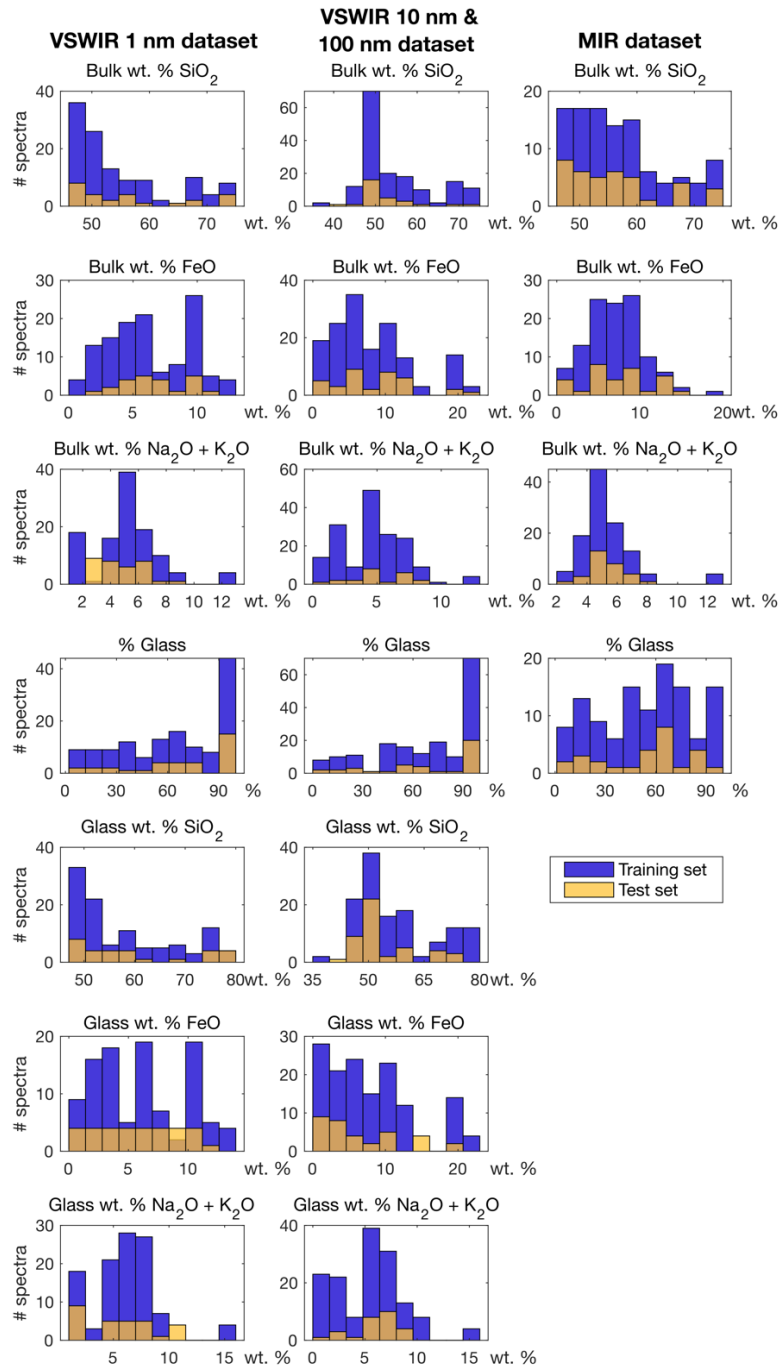


Figure 1.3 Distributions of training and test datasets by the number of spectra in each dataset.

The 10-nm sampled and 100-nm sampled VSWIR data sets are the same. Training set is shown in purple and the test set is shown in yellow.

VSWIR model predictions

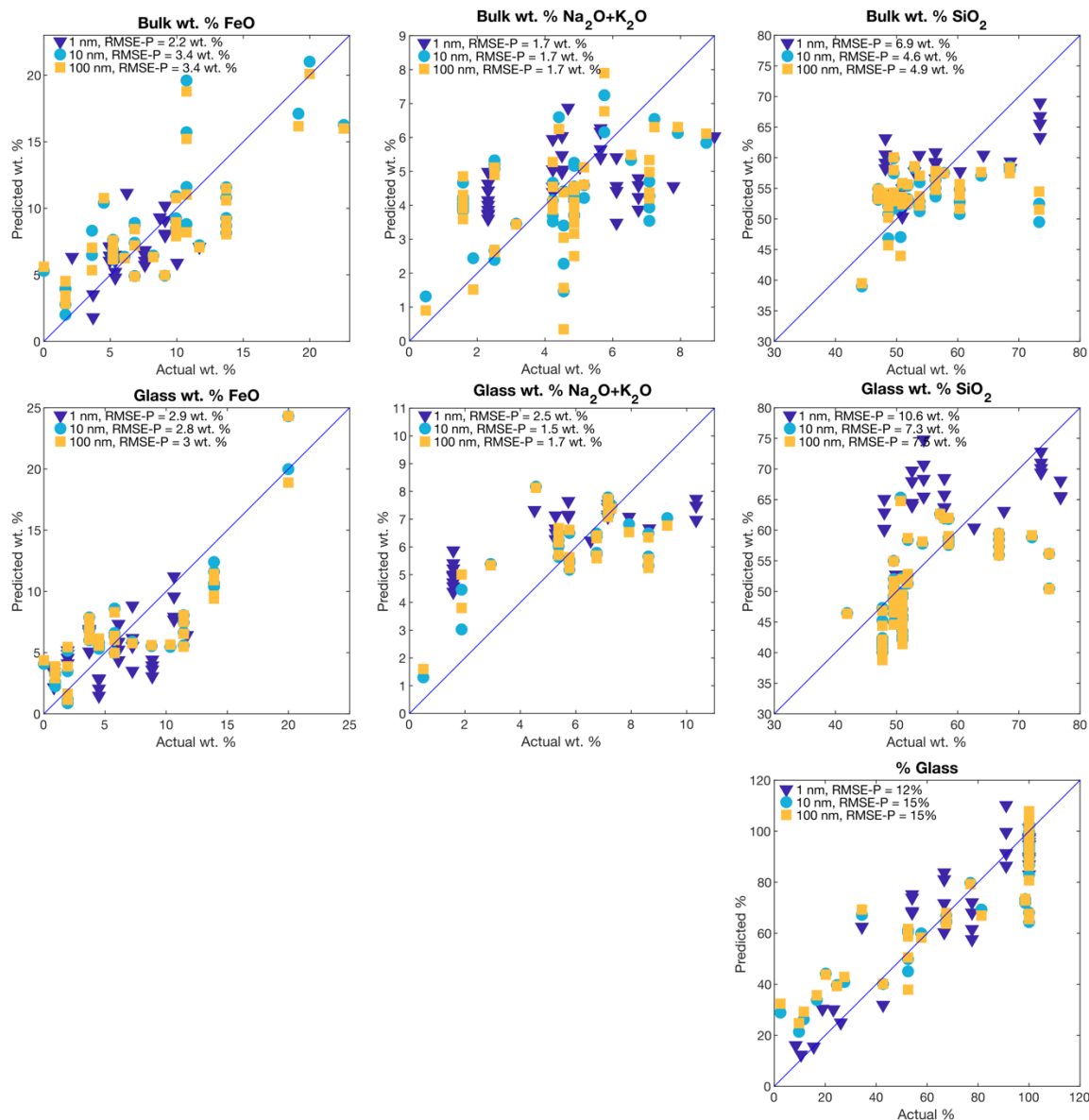


Figure 1.4 VSWIR model predictions.

Triangles are the 1 nm resolution model predictions, circles are the 10 nm resolution model predictions, and squares are the 100 nm resolution model predictions. The blue reference line shows a 1:1 relationship.

MIR model predictions

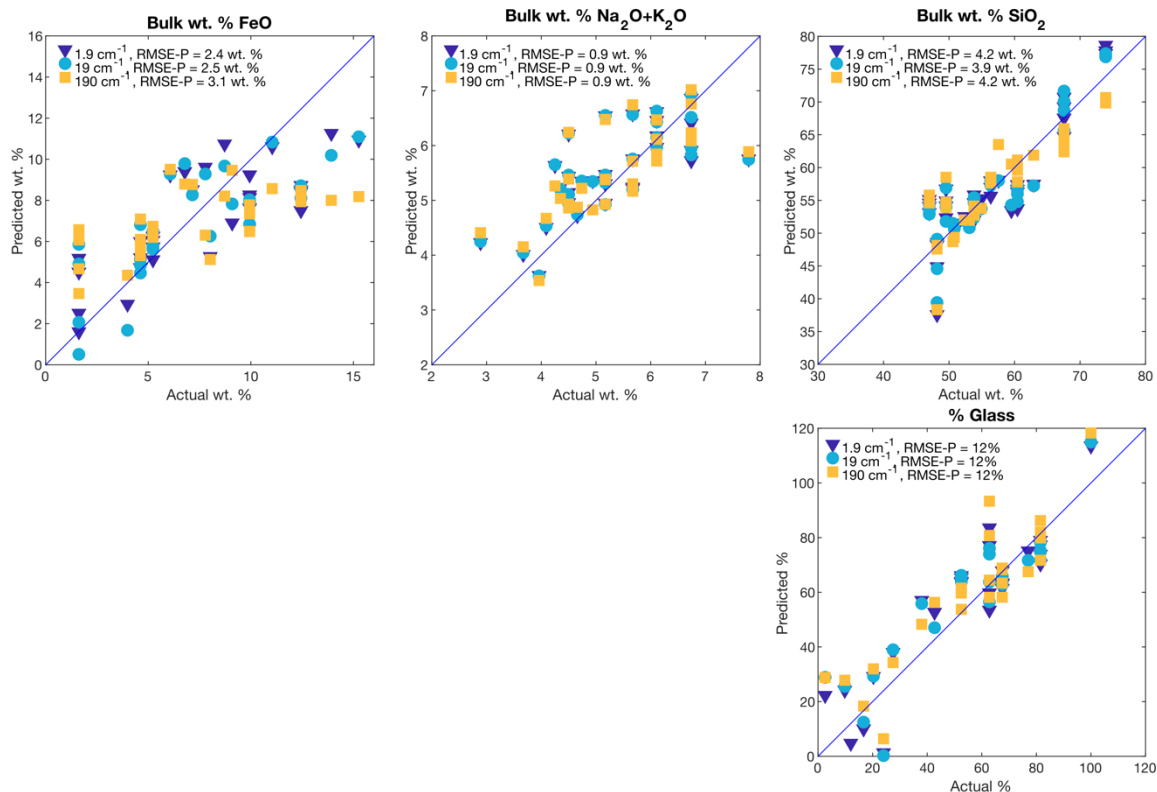


Figure 1.5 MIR model predictions.

Triangles are the 1.9 cm⁻¹ resolution model predictions, circles are the 19 cm⁻¹ resolution model predictions, and squares are the 190 cm⁻¹ resolution model predictions. The blue reference line shows a 1:1 relationship.

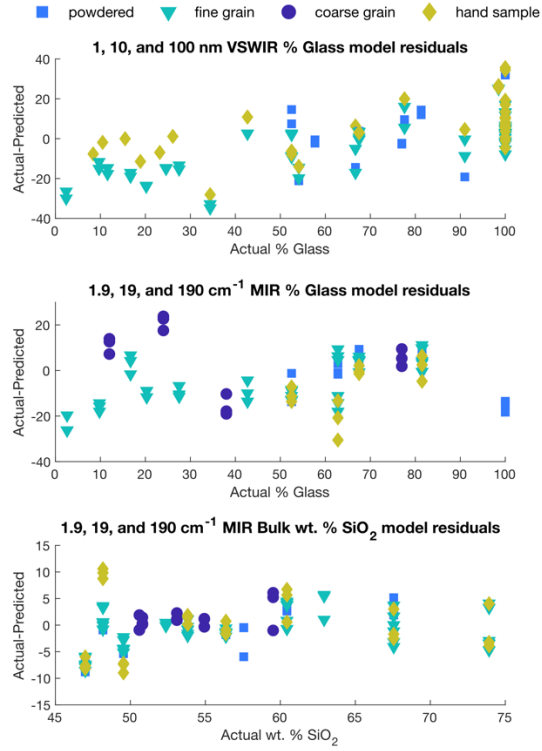


Figure 1.6 Grain size effect on prediction residuals.

Residuals for all VSWIR % glass models (top), all MIR % glass models (middle), and all MIR bulk wt. % SiO₂ models (bottom) colored by grain size. Published grain sizes are grouped into powdered ($\leq \sim 75 \mu\text{m}$), fine grained ($\sim 75 - \sim 500 \mu\text{m}$), coarse grained ($\sim 500 \mu\text{m} - 2 \text{ mm}$), and hand samples.

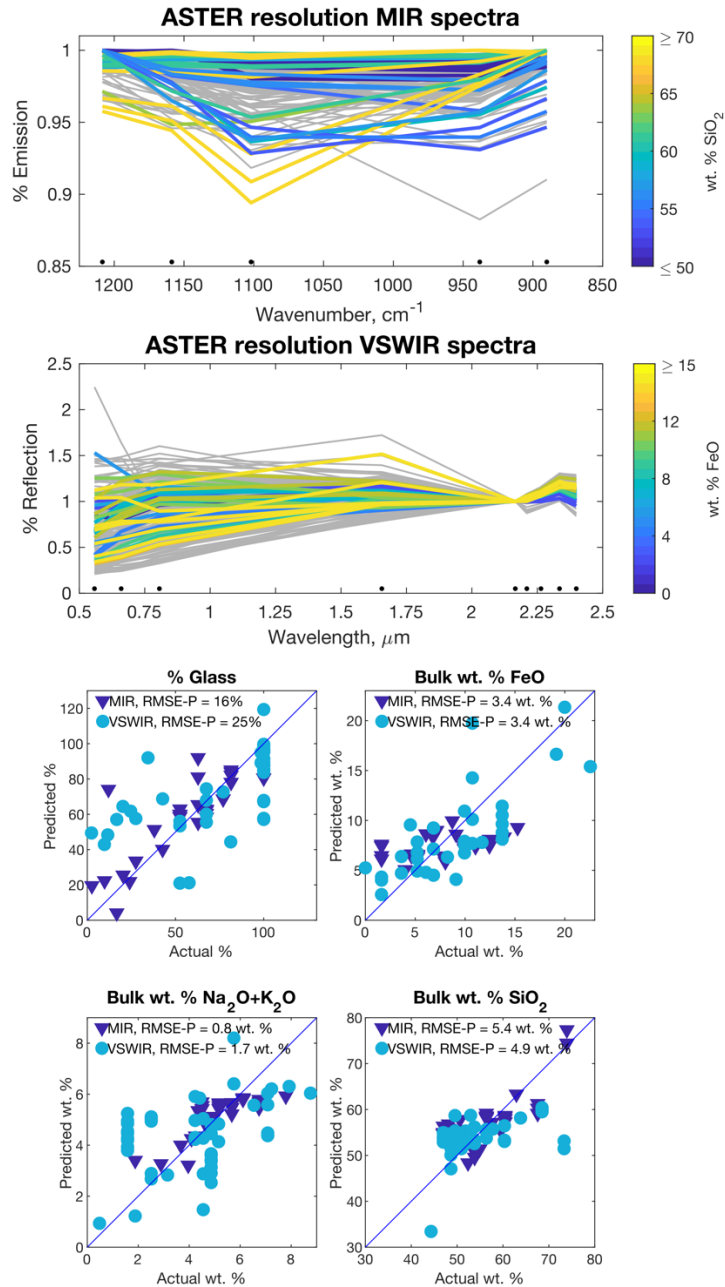


Figure 1.7 MIR and VSWIR spectral data resampled through ASTER bandpasses, and PLS model results.

MIR spectra are max normalized, and the test dataset colored by bulk wt. % SiO_2 . VSWIR spectra are normalized to $2.17 \mu\text{m}$, and the test dataset is show colored by bulk wt. % FeO. The black dots in the MIR and VSWIR spectral plots show the center of the ASTER bandpasses. MIR model results are shown as purple triangles, VSWIR model predictions shown as blue circles.

CHAPTER 2.
Comparison of Bi-Directional and Hemispherical Reflectance
Geometries in the Visible-Near-Infrared

Abstract

Venus' atmosphere limits the upcoming missions to Venus to collecting spectral data of the surface in visible-near-infrared (VNIR) region as either hemispherical reflectance or directional emissivity (Garvin et al., 2022; Helbert et al., 2018). The vast majority of laboratory VNIR spectral data relevant to interpreting venusian surface spectra are bi-directional reflectance measurements. A bi-directional reflectance geometry is typical for orbital VNIR reflectance measurements, but cannot be used for venusian surface observations due to Rayleigh scattering from the cloud layers. While hemispherical reflectance and emissivity are reciprocal, the relationship between bi-directional and hemispherical reflectance in the VNIR region has not been well established, hindering interpretation of scientific data to be returned by the upcoming missions. This study compares the bi-directional and hemispherical reflectance spectra of Venus-relevant samples. Changes in measured reflectance, continuum slope, and spectral feature shape are observed between the two observational geometries, create challenges in using bi-directional spectra to interpret hemispherical reflectance or emissivity data in the VNIR region. Current understandings of radiative transfer modeling suggests that spectral data can be converted between geometries using the single-scattering albedo; this assumption is tested using published Hapke models of bi-directional and hemispherical reflectance. This study finds that the extant model of bi-directional reflectance is unable to independently produce a single-scattering albedo that can be used to model hemispherical reflectance.

1. Introduction

Modeling by Nicodemus (1965) established that bi-directional reflectance and directional emissivity measurements are not quantitatively equivalent. Studies of bi-directional and hemispherical reflectance or directional emissivity in the mid-infrared (MIR) established that spectral trends are qualitatively similar between observational geometries, reflectance, and emission, though band intensities are different (e.g., Bartholomew et al., 1989; Hecker et al., 2010; Hunt & Vincent, 1968; Mustard & Hays, 1997). Importantly, band position and relative depth were proven to be equivalent between both hemispherical reflectance and emissivity MIR spectra.

These studies validated the use of Kirchhoff's Law to convert between reflectance, r , and emissivity, ε , measurements as $\varepsilon = 1 - r$ (Nicodemus, 1965; Salisbury, 1993). This conversion works because the wavelengths of light which are absorbed, rather than reflected, by an opaque surface are the same wavelengths which are emitted by the surface. Notably, this conversion ignores transmission and assumes thermal equilibrium. Kirchhoff's Law does not convert between observational geometries, and so is strictly true only for directional emissivity and directional-hemispherical reflectance data at the same temperature (Salisbury, 1993).

Directional-hemispherical reflectance is the scattering of an incident parallel beam of light from a single direction by a surface into the hemisphere above the surface (Figure 2.1a; Martonchik et al., 2000; Schaepman-Strub et al., 2006). This quantity cannot be directly measured, as the incident beam of light is infinitesimally small (Martonchik et al., 2000; Schaepman-Strub et al., 2006). Conical-hemispherical reflectance is the closest directly measurable quantity, and is frequently referred to as directional-hemispherical, or

simply hemispherical, reflectance (Figure 2.1b). This is the reciprocal scattering behavior for directional emissivity, which measures light emitted from a surface in a single direction.

Bi-directional reflectance is the scattering of an incident parallel beam of light from one direction to another by a surface (Figure 2.1c; Martonchik et al., 2000; Schaepman-Strub et al., 2006). Biconical reflectance, which can be directly measured, utilizes solid angles, or cones, of incident and collected beams of light (Figure 2.1d), and is frequently referred to as bi-directional reflectance (Schaepman-Strub et al., 2006). For simplicity the more common terms of bi-directional and hemispherical reflectance are used for their directly measured counterparts. Bi-directional spectra have a single incidence angle (i) and emergence angle (e), giving phase angle (g). Hemispherical spectra have a hemisphere of emergence angles, $e = 0 - 180^\circ$, and utilize a single i . Both i and e are measured from the surface normal.

Bi-directional and hemispherical MIR spectra show different trends in overall reflectance and in band depth with grain size (Hunt & Vincent, 1968; Mustard & Hays, 1997). Hunt & Vincent (1968) noted differences in band minima position and shape between bi-directional reflectance and directional emissivity. They attributed this to the different role of volume scattering in bi-directional reflectance as compared to directional emissivity.

The differences observed in these studies (Hunt & Vincent, 1968; Mustard & Hays, 1997) suggest that bi-directional and hemispherical spectra are not likely to be identical in the visible-near-infrared (VNIR) region. The direct application of these results in the VNIR region is limited, however, due to the differences in scattering regimes in the two wavelength regions. Reflection is dominated in the MIR by surface scattering when particle sizes are larger ($\sim > 63 \mu\text{m}$) due to the large imaginary index of refraction, k , which minimizes volume scattering. The value of k is small in the VNIR, and as a result light can penetrate the surface and interact with multiple particles before being refracted outward, resulting in nonlinear volume scattering and minimal surface scattering. This difference in scattering behavior means that trends in MIR band depth, for example, cannot be directly applied to the VNIR.

The utility of bi-directional geometry to provide quantitative predictions of hemispherical reflectance and emissivity spectra has not been investigated in the VNIR region. This is largely because a bi-directional geometry is assumed for orbital VNIR reflectance data, and VNIR laboratory data are commonly collected in this geometry, negating the need for hemispherical data. Though the phase angle, g , may vary between orbital and laboratory measurements, the locations of fundamental bands do not meaningfully change for monomineralic surfaces with variations in phase angle (Gradie & Veverka, 1986; Pieters, 1983). The effect of observational geometry is thus frequently assumed to be negligible when interpreting orbital observations in the VNIR (e.g., Hapke, 1981; Mustard & Glotch, 2020; Mustard & Pieters, 1989; Shkuratov et al., 1999). The spectral variation due to non-geometric factors such as temperature, pressure, or grain size additionally reduce the importance of phase angle variations in modulating the observed reflectance from a surface (e.g., Burns, 1993; Dyar & Burns, 1981; Hapke & Wells, 1981; Hinrichs & Lucey, 2002).

Forthcoming missions to Venus and the data to be returned necessitate investigation into the VNIR emissivity of geologic materials. Most geologic materials do not significantly emit in the VNIR range at normal temperatures ($\sim 25^\circ\text{C}$). At venusian surface temperatures of $\sim 460^\circ\text{C}$, however, significant emission is expected from the surface, and indeed, has been measured (e.g., Baines et al., 2000; Hashimoto et al., 2008; Helbert et al., 2008; Lecacheux et al., 1993; Mueller et al., 2009). At present, the vast majority of available VNIR spectral data relevant to Venus are bi-directional reflectance measurements (e.g., Gilmore et al., 2015; Kokaly et al., 2017). Conversion of bi-directional reflectance data to hemispherical reflectance could greatly increase the spectral data available to interpret the venusian surface spectra collected during upcoming missions. A long-standing assumption is that via radiative transfer modeling, a surface's single scattering albedo, w , can be used to convert between bi-directional and hemispherical reflectance geometries (e.g., Hapke, 2012; Johnson et al., 1992). However, experimental proof of this conversion has not been established.

Three upcoming missions to Venus – DAVINCI (Deep Atmosphere Venus Investigation of Noble Gases, Chemistry, and Imaging), VERITAS (Venus Emissivity, Radio Science, InSAR, Topography And Spectroscopy), and EnVision – will all collect VNIR spectral data as either hemispherical reflectance or directional emissivity (Garvin et al., 2022; Helbert et al., 2018). Therefore, the relationship between VNIR laboratory measurements, collected in bi-directional geometries, and returned hemispherical reflectance measurements needs to be established to maximize the scientific data to be returned. Current understandings of radiative transfer modeling suggest these models can be used to convert data between observational geometries. This study presents a comparison of bi-directional and hemispherical VNIR reflectance data of Venus-relevant geologic materials to constrain the importance of observational geometry. The ability of currently published radiative transfer models (Hapke, 2012) to convert between the two geometries is also tested.

2. Background

Spectral measurements are sensitive to the optical path length of measured light, and thus variations in viewing geometry, as changing the measured optical path results in minor changes in observed spectra (Adams & Filice, 1967; Gradie & Veverka, 1986). Spectral albedo is generally brightest at small ($<10^\circ$) phase angles and decreases with increasing phase angle, modulated by the abundance of internal scattering surfaces (McGuire & Hapke, 1995; Pieters, 1983; Shepard & Helfenstein, 2007). Changes to phase angle can also result in minor changes to spectral feature shape, mostly at large angles ($>30^\circ$) (e.g., Gradie & Veverka, 1986; Mustard & Pieters, 1989; Pieters, 1983). This does not inhibit recognition of surface composition but can complicate data interpretation of multi-phase surfaces.

The effects of variable phase angle on spectral observations can be removed by calculating the single scattering albedo, w , of the surface (e.g., Clark & Roush, 1984; Johnson et al., 1992; Mustard & Pieters, 1989). The single scattering albedo, describes the interaction of light with a particle independent of observational geometry and is defined as the ratio of scattering to extinction as light travels through a medium (Hapke, 2012). The single scattering albedo can be calculated as a function of the optical

constants n and k , internal scattering coefficient s , and optical path length (or effective grain size) $\langle D \rangle$, making w theoretically dependent only on the composition and size of the particles which constitute the observed surface. Hypothetically, the single-scattering albedo of a surface can be used to convert spectral data between bi-directional and hemispherical geometries (Johnson et al., 1992), but this has not been formally tested.

The single-scattering albedo of a surface can be found using radiative transfer models. There are two primary radiative transfer models: the Hapke model (Hapke, 2012) and the Shkuratov model (Shkuratov et al., 1999). The Shkuratov model does not consider illumination and viewing geometry, rendering the model irrelevant to this scenario. The Hapke model accounts for the effect of observational geometry on spectra but does make three additional assumptions: (1) particle size is larger than the wavelength of light, (2) particles are closely packed as to be touching and continuous, and (3) particles are randomly oriented so that multiply scattered light can be assumed to be isotropic (Hapke, 2012).

For samples referenced against a Lambertian scatter, the measured bi-directional and hemispherical reflectance at a given wavelength can be modeled respectively as:

$$r_d(i, e, g) = \frac{w}{4} \frac{1}{\mu_0 + \mu} \{ [1 - B(g)] p(g) + H(\mu_0) H(\mu) - 1 \} \quad (1)$$

$$r_h(i) = 1 - \gamma H(\mu_0) + b \left\{ \mu_0 - \frac{1}{2} [H(\mu_0) - 1] \right\} \\ \times \left\{ \frac{w}{2} \left[\frac{1}{2} - \mu_0 + \mu_0^2 \ln \left(\frac{1+\mu_0}{\mu_0} \right) \right] + \frac{1}{2} \left[\frac{1}{H(\mu_0) - \gamma} \right] - \frac{w}{4} \left[1 - \mu_0 \ln \left(\frac{1+\mu_0}{\mu_0} \right) \right] \right\} \quad (2)$$

where i and e are the incidence and emergence angles, measured from normal to the surface, g is the phase angle, w is the single-scattering albedo, μ_0 and μ are the cosine of i and e , respectively, $B(g)$ is the backscatter coefficient, $p(g)$ is the phase function, which describes initial diffractive scattering, $H(x)$ are the Ambartsumian–Chandrasekhar H-functions, or multiple-scattering functions (Chandrasekhar, 1960), and r_0 is the hemispherical reflection of a Lambertian scatterer (Hapke, 2012). Hemispherical reflectance quantities are denoted with subscript ‘h’, and bi-directional reflectance quantities with subscript ‘d’. Subscript ‘d’ is used rather over the more-obvious choice of ‘b’ to avoid accidental confusion with other parameters designated with a ‘b’. $B(g)$ is generally assumed to be 0 at $g \geq 15^\circ$ and contribute negligibly to r_h ; this is the assumption used to calculate Equation 2 (Hapke, 2002) and carried through the rest of this work. The phase function can be approximated as a one- or two-term Legendre polynomial:

$$p(g) = 1 + b \cos(g) \quad (3a)$$

$$p(g) = 1 + b \cos(g) + c [1.5 \cos^2(g) - 0.5] \quad (3b)$$

with coefficient b describing the degree of forward and backscattering, and coefficient c describing the degree of side scattering (Mustard & Pieters, 1989a). The phase function is frequently shortened to one term; Equation 2 utilizes the one-term solution. When a surface scatters isotropically, $p(g) = 1$.

The H-functions can be taken from a lookup table of $H(x)$, μ , and w from Chandrasekhar, (1960), or when w is not near 1, approximated. Several approximations exist; this work used:

$$H(x) = \left\{ 1 - wx \left[r_0 + \frac{1-2r_0x}{2} \ln \left(\frac{1+x}{x} \right) \right] \right\}^{-1} \quad (4)$$

where $\gamma = \sqrt{1 - w}$, and $r_0 = (1 - \gamma)/(1 + \gamma)$ (Hapke 2012).

While the above models are approximate, they provide the best method of parametrizing reflectance and potentially converting between observational geometries.

3. Materials and Methods

3.1. Sample Preparation

Natural volcanic rocks were used as a starting material for sample mixes to achieve realistic phase assemblages. The surface of Venus is expected to be primarily mafic in composition though felsic compositions have been suggested (e.g., Gilmore et al., 2017; Hashimoto et al., 2008). Samples analyzed were a tholeiitic basalt from Husavik, Iceland, a dacitic tephra from Mount Pinatubo, Philippines, and a rhyolite from the Bishop Tuff, California (Table 2.1).

Pure hematite (Fe_2O_3) and thenardite (Na_2SO_4) were used to simulate potential alteration phases present on the Venus surface based on previous alteration experiments (Reid et al., 2021; Renggli & King, 2018; Teffeteller et al., 2022). Experimental alteration of basalt in Venus-analog atmospheric conditions indicates rapid alteration of a basaltic surface via oxidation and sulfurization to an anhydrous phase assemblage containing some mixture of these minerals (Cutler et al., 2020; Esvan et al., 2022; Reid et al., 2021; Teffeteller et al., 2022). Hematite was sourced from Wards Scientific and was crushed and wet sieved to remove clinging fines. Thenardite was synthesized via dehydration of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) at 100°C for >24 hrs. Thenardite, along with all other volcanic samples (basalt, dacite, rhyolite), was dry sieved to a grain size of 250-500 μm . In addition to single phase samples, five two-phase mixtures of basalt and hematite were made in varied volumetric proportion of 90% basalt-10% hematite to 80% hematite-20% basalt (Table 2.1) to replicate weathering from a fresh basalt to maturely altered surface. These samples are named in reference to their endmember proportions, e.g., sample 6B:4H is 60% basalt and 40% hematite by volume.

3.2. Bi-directional and Hemispherical Spectral Collection

Bi-directional and hemispherical spectra from 0.72-2.5 μm were collected using a Bruker Vertex 80V spectrometer at the Planetary Spectroscopy Laboratory at DLR Berlin (Figure 2.2). Bi-directional data were collected with a phase angle of 30° and spectral resolution of 0.96 cm^{-1} . Hemispherical data utilized a gold-coated integrating sphere, with an incidence angle of $i = 13^\circ$, and a spectral resolution of 0.96 cm^{-1} . All data were collected at room temperature ($\sim 25^\circ\text{C}$).

Data were preprocessed using MATLAB and resampled at 1 nm. A narrow Savitzky-Golay smoothing filter was applied to the data to reduce noise below 1 μm . This filter applies a moving best-fit polynomial to the data, resulting in lower noise and some loss of fine-scale structure in the spectra, as well as potentially broadening spectral features (Workman & Springsteen, 1998). This smoothing method was used over a moving-average (or boxcar) method because it is less sensitive to rapid changes in the data caused by poor signal-to-noise, while still preserving narrow spectral features (Workman & Springsteen, 1998).

Additional bi-directional data of basalt, hematite, and thenardite were collected at the University of Tennessee (UTK) using an OreXpress spectrometer at phase angles of 15°, 20°, 25°, 30°, 40°, 45°, and 55°. The data were collected with a spectral resolution of 1 nm and were normalized against a PTFE (polytetrafluoroethylene) standard, retaken at all phase angles and between samples. Incidence and emergence angles were varied, as reported in Table 2.2. Data were cropped to 0.72-1.8 μm to remove data from the last detector of the OreXpress, which had significant noise (Figure 2.3). Data were smoothed with a Savitzky-Golay filter. The UTK data were roughly scaled to the data from DLR, which had a consistently lower measured reflectance due to the different instruments. For each sample, the UTK spectra were divided by the percent difference between the UTK $g = 30^\circ$ and DLR spectra.

Additional incidence angles could not be taken for the hemispherical spectra.

3.3. Spectral analyses

Spectral band position and full width at half max (FWHM) were compared between bi-directional and hemispherical spectra of each sample. For each band, a local linear continuum was removed, and either an 8- 9-order polynomial fit to the spectral band, depending on which fit best. The bounds of the fit continuum and polynomial were manually iterated to find the best fit.

In order to compare the spectral slopes, a linear continuum was fit to all spectra as $C = c_1 + c_2\lambda$ using a least squares regression. The continuum was fit to the entire spectrum.

3.4. Single-Scattering Albedo Modeling

All data were down sampled to 5 nm spectral sampling. This step was taken to reduce computational expense, ensure all spectra had the same spectral channels, and provide additional noise reduction. None of the preprocessing meaningfully impacted the modeling results (Sklute et al., 2015).

Modified MATLAB code from Sklute et al. (2021) was used to find single-scattering albedos, w_d and w_h . In all cases $B(g)$ was assumed to be zero; this was done following the assumptions that backscatter is negligible at $g > 15^\circ$ in bi-directional geometry (Mustard & Pieters, 1989) and backscatter is expected to contribute negligibly to r_h (Hapke, 2012). Several cases were investigated to address common assumptions made when using radiative transfer models. Isotropic behavior is frequently assumed when deconvolving reflectance data collected from orbit with $10^\circ < i < 40^\circ$ and $e = 0^\circ$, as the surface particles are likely randomly oriented and irregular, increasing the scattering angles, and these observation angles avoid strongly forward- or backscatter (Mustard & Glotch, 2020; Mustard & Pieters, 1989). In this case, $p(g) = 1$, and Equations 1 and 2 reduce to:

$$r_d(i, e, g) = \frac{w}{4} \frac{1}{\mu_0 + \mu} \{H(\mu_0)H(\mu)\} \quad (6)$$

$$r_h(i) = 1 - \gamma H(\mu_0). \quad (7)$$

Utilizing a static phase function may be slightly more accurate, while still computationally quick and requiring minimal knowledge of surface composition. The value of coefficient b , static phase function single-scattering albedos, were calculated using estimates from Mustard & Pieters (1989) and Ye et al. (2021).

Obtaining the wavelength-variable phase function of a surface requires data at multiple, well-constrained angles. The phase function and single scattering albedo are mathematically separable provided sufficient spectral data over several $p(g)$.

Modified code from Sklute et al. (2021) was used to solve for b_d and w_d using bi-directional spectra collected at variable $p(g)$. To find the wavelength-variable w_d and phase function, an initial guess of w_d was found using a static phase-function and single-phase angle. The variable-phase function data collected at UTK (Table 2.2) were then used to solve for the wavelength-variable b_d and w_d using a least-squares minimization of Equation 1. There are multiple issues with the data in Table 2.2, namely the rough scaling and noise, which reduce the utility of the calculated b_d , w_d , and w_h . The calculated w and b_d are inapplicable to any use other than the rough estimation of model accuracy for conversion between geometries.

The linear regression of Equation 1 forced w_d to be constant across phase angle, with all observed variation in r_d due to the phase angle and compensated for by the phase function. A 1-term $p(g)$ (Equation 3a) was used as this phase function is more directly applicable to Equation 2. The value of b_d was allowed to vary between $-5 < b_d < 10$ provided the value of the phase function was positive; given the unrealistic nature of a 1-term phase function, limiting the values of b_d to $-1.7 < b_d < 1.7$, as done by Mustard & Pieters (1989), served no purpose (E. Sklute & J. Piatek, personal communication, January 2024). The approximate H-function (Equation 4) was used when modeling basalt and hematite; a look-up table of H-function values was used for thenardite and dacite. The calculated value of b_d was then used to solve for w_h via a least-squares minimization.

As the single scattering albedo and phase function should be the same in both bi-directional and hemispherical geometries, w and b can be found from r_d and r_h utilizing a least squares minimization where the values of $w_d = w_h$ and $b_d = b_h$ are forced to be equal. Equations 1 and 2, with the phase function represented by Equation 3a, were used to solve for w_o and b_o , with subscript ‘o’ for ‘one’. The approximate H-function (Equation 4) was used when modeling basalt and hematite; a look-up table of H-function values was used for thenardite and dacite. For this test the requirement that the phase function be positive was removed, and the value of b was allowed to vary however was necessary to successfully solve the regression.

4. Results

In all spectra, noise increased below $0.9 \mu\text{m}$, but was mostly removed by the smoothing filter. However, the hemispherical spectra are noisier than the bi-directional spectra in this region. All spectra are shown in Figure 2.2. The coefficients of the fit linear continua are listed in Table 2.3. The FWHM, band minima, and band depth from the polynomial fits to spectral features are given in Table 2.4 and Table 2.5.

4.1. Bi-directional Spectra

4.1.1. Pure Mineral Samples

The bi-directional spectrum of thenardite has reflectance values from 37-53 % and decreasing spectral continuum (Figure 2.2, Table 2.3). Water bands are present at 1.4,

1.9, and ~ 2.5 μm , indicating the sample was not fully dehydrated. Partial hydration is likely a two-fold result of ambient humidity resulting in adsorption and incomplete initial dehydration during synthesis.

The bi-directional hematite spectrum has reflectance values from 10-14 %, and a flat spectral continuum (Figure 2.2). The spectrum has the characteristic Fe^{3+} crystal field absorption band at 0.9 μm , which has a FWHM of 84 nm, and a depth of 26 % reflectance (Table 2.4). There is small feature at 1.9 μm from adsorbed water.

4.1.2. Rock Endmember Samples

The basalt has a very low reflectance of 2-3 %, and a flat continuum (Figure 2.2). The bi-directional basalt spectrum has a broad Fe^{2+} band at 1 μm , with a FWHM of 96 nm and a depth of 11 % reflectance (Table 2.4). The bi-directional spectrum of dacite has reflectance values of 21-25 %, and a flat continuum. The dacite spectrum has a shallow, broad Fe feature from ~ 0.8 -1.4 μm arising from the presence of Fe-bearing pyroxenes. Hydration absorption bands are present in the dacite spectrum at 1.4 and 1.9 μm , and below 2 μm . The rhyolite bi-directional spectrum has reflectance values of 19-43 %, and a decreasing continuum. The rhyolite spectrum has deep absorption features at 1.4, 1.9, 2.2, and ~ 2.5 μm . The hydration features observed in the basalt, rhyolite, and dacite spectra at 1.4 and 1.9 μm are likely due to a combination of adsorbed water and glass hydration. Volatile by difference calculations from electron microprobe analysis of the dacite and rhyolite suggest $\sim 1\%$ volatile content held in the glass phase (Leight et al., 2022).

4.1.3. Mixture Samples

The basalt-hematite mixtures have increasing reflectance with increasing hematite proportion (Figure 2.2); the reflectance of sample 9B:1H is 3-4%, 8B:2H is 5-6%, 6B:4H is 6-8%, 4B:6H is 7-10%, and 2B:8H is 9-13%. The mixtures' bi-directional spectra have flat continua (Table 2.3). The Fe^{3+} band at 0.9 μm is observed in all basalt-hematite mixtures with band depth decreasing and band width increasing, with increasing basalt proportion (Figure 2.4; Table 2.4). In the bi-directional spectrum of 2B:8H, the 0.9 μm band has a FWHM of 85 nm, and a depth of 30 % reflectance, whereas the 0.9 μm band in the spectrum of 9B:1H has a FWHM of 94 nm and a depth of 11 % (Table 2.4). In the spectrum of 9B:1H, very shallow absorption features are observed at 1.9 μm . A shallow band from adsorbed water is present in all mixture spectra at 1.9 μm .

4.2. Hemispherical Spectra

4.2.1. Pure Mineral Samples

The hemispherical reflectance of thenardite ranges from 59-80 %. In contrast to the bi-directional spectrum, there is a negative spectral continuum at wavelengths below ~ 1 μm . Water bands are present at 1.4, 1.9, and ~ 2.5 μm , indicating the sample was not fully dehydrated during sample preparation. The hemispherical reflectance of hematite is 14-21%, with a decreasing and concave continuum. The Fe^{3+} absorption feature at 0.9 μm has a band depth of 12 % reflectance, and a FWHM of 83 nm (Table 2.4)

4.2.2. Rock Endmember Samples

Basalt exhibits low hemispherical reflectance (8-12%), with a negative continuum. The curvature of the basalt spectrum obscures absorption features; removing a linear continuum across the entire spectrum results in a 'u' shaped spectrum with very shallow ($>0.01\%$ change in reflectance) features at 1.4 and 1.9 μm . Removing a continuum modeled as a 2-term polynomial from the hemispherical basalt spectrum reveals a similarly shallow feature at $\sim 1 \mu\text{m}$, likely due to Fe^{2+} . The best-fit gaussian models the 1 μm feature with a band minimum at 0.95 μm , a FWHM of 138 nm, and a depth of 2 % (Table 2.4).

The hemispherical spectrum of dacite has reflectance values of 29-37 %, and a decreasing continuum. A shallow Fe feature arising from the presence of Fe-bearing pyroxenes is observed from ~ 0.8 -1.4 μm . Absorption bands are also present in the dacite spectrum at 1.4 and 1.9 μm , and below 2 μm . The hemispherical rhyolite spectrum has reflectance values of 34-70 %, a decreasing continuum, and deep absorption features at 1.4, 1.9, 2.2, and $\sim 2.5 \mu\text{m}$. Hydration features observed in the basalt, rhyolite, and dacite spectra at 1.4 and 1.9 μm are likely due to a combination of adsorbed water and glass hydration, as discussed with the samples' bi-directional spectra.

4.2.3. Mixture Samples

Increasing hematite proportion in the basalt-hematite mixtures resulted in increasing reflectance (Figure 2.2). Reflectance of 9B:1H is 9-16%, 8B:2H is 9-16%, 6B:4H is 11-18%, 4B:6H is 15-21%, and 2B:8H is 17-24%. The mixtures' hemispherical spectra exhibit decreasing continua. The Fe^{3+} band at 0.9 μm is observed in all basalt-hematite mixtures, with the band depth decreasing with increasing basalt proportion, from a depth of 148 nm (2B:8H) to 37 nm (9B:1H). The 0.9 μm band narrows with increasing basalt proportion, from a FWHM of 83 nm (2B:8H) to a FWHM of 71 nm (9B:1H) (Figure 2.4; Table 2.4). In 9B:1H, there are very shallow absorption features at 1.4 and 1.9 μm , while a shallow band attributed to adsorbed water is present in all mixture spectra at 1.9 μm .

4.3. Radiative Transfer Modeling

Single-scattering albedos were calculated from the bi-directional and hemispherical spectra of thenardite, hematite, dacite, and basalt under three different assumptions: (1) isotropic behavior, (2) a static phase function, and (3) a wavelength-variable phase function (Figure 2.5). The three sets of assumptions produce different single scattering albedos, though in each geometry the isotropic and static phase function w have a similar shape. The variable phase function w have different shapes than the other w . All of the single scattering albedos calculated from the bi-directional and hemispherical models are not equivalent; for each sample, w_d and w_h have different values and different shapes (Figure 2.5).

Figure 2.6 shows the results of using w_d to model r_h , and vice versa, as Johnson et al. (1992) suggested should be possible. Given how dissimilar the isotropic and static- $p(g)$ single scattering albedos calculated from bi-directional and hemispherical spectra are, it is not surprising that the modeled spectra do not match the actual data, and do not produce the correct spectral shapes. The isotropic models produce a larger deviation from the original spectrum in modeling the other geometry than the static $p(g)$ models, but

these results are not any more correct than the spectra modeled with a static phase function (Figure 2.6).

The models with a 1-term variable phase function do the best at approximating the reciprocal geometry. The wavelength-variable w_h was only calculated using the phase function calculated from phase variable bi-directional spectra, due to the lack of hemispherical data at variable incident angles. Forcing the phase function to be the same in both geometries did not result in similar calculated single-scattering albedos (Figure 2.5), but these models did produce the most change from the source spectrum. The results are still not particularly accurate; none of the spectra modeled using a single-scattering albedo from the opposite geometry have the correct continuum slope or spectral shape (Figure 2.6).

Utilizing a wavelength-variable phase function does, however, produce a significant change in reflectance; the modeled bi-directional basalt spectrum has overlapping reflectance with the bi-directional spectrum (Figure 2.6). The modeled variable phase function spectra of thenardite and dacite spectra have lower reflectance than the actual bi-directional spectra, as well as flatter continuum slopes, though the modeled spectrum's slope is incorrect. However, the success of this model is limited, as can be seen in the modeled hemispherical spectra, which do not approach the correct reflectance for any sample (Figure 2.6). Ignoring calculated reflectance values, the variable phase function models did not accurately reproduce the changes observed to spectral shape or spectral features.

The geometry-independent w_o and phase function are capable of conversion between bi-directional and hemispherical geometries (Figure 2.6). Modeled spectra from w_o have the correct continuum slope and spectral shape in each geometry. The modeled spectra are not completely perfect, but the error is significantly below measurement uncertainty ($RMSE \approx 10^{-16}$). The calculated w_o for hematite is able to produce the shift in band width in modeled spectra. All samples utilize a negative phase function (Figure 2.7).

5. Discussion

5.1. Changes with observation geometry

Bi-directional and hemispherical spectra should not be expected to be identical. Hemispherical spectra collect reflected light over more emergent angles than bi-directional spectra and therefore should have larger reflectance values, as observed (Figure 2.2a). Overall, the change in measured reflectance trends with sample albedo, so that the samples with the highest albedo have the greatest change in measured reflectance between geometries. For example, thenardite has the largest increase in reflectance between geometries, and basalt has the least increase in reflectance. Additionally, the hemispherical spectra have a larger range in reflectance values compared to their respective bi-directional spectra.

Unexpected differences can also be seen between the collection geometries. For example, the continuum slopes are different between geometries (Figure 2.2b-c; Table 2.3). Hemispherical spectra of all samples have a negative continuum, while in the bi-directional geometry only the thenardite and rhyolite spectra have appreciable negative

slopes (Table 2.3). The bi-directional spectra of the hematite, basalt, dacite, and mixture samples all have relatively flat continua (Table 2.3).

In addition, the hemispherical basalt spectrum exhibits a strong concave-up curvature, obscuring the spectral features in the bi-directional spectrum (Figure 2.2). Past the 0.9 μm Fe^{3+} feature, the hemispherical spectra of the basalt-hematite mixtures also exhibit this concave spectral shape. The origin of this spectral shape is unclear. Potentially, the concavity results from the collection of low-angle (e.g., $\theta > 70^\circ$) and non-principle-plane scattered light in the hemispherical geometry. Bi-directional laboratory spectra are rarely collected at these angles. Measurement of low-angle scattering results in anomalous reflection peaks in the MIR (Salisbury & D'Aria, 1989) and irregular particles, such as those in the samples used here, preferentially scatter low-angle incident light relative to light incident at higher angles in the visible region (McGuire & Hapke, 1995). More spectral data are needed to fully address the cause of the observed concave-up spectral shape.

5.1.1. Changes in Spectral Features

Spectral features are generally deeper and wider in the bi-directional spectra than in the hemispherical spectra (Table 2.4, Table 2.5). This agrees with previous investigations into the effect of phase angle variations on bi-directional spectra, which found that the depth, width, and overall shape of spectral features can vary with phase angle in bi-directional spectra (Adams & Filice, 1967; Gradie & Veverka, 1986; Pieters, 1983). These observed changes are driven by variations in the optical path length (Adams & Filice, 1967), and so it is not surprising that spectral features are not identical in the bi-directional and hemispherical spectra.

The significant noise below 1 μm , combined with the strongly sloped continua, makes direct comparison of the 0.9 μm Fe^{3+} feature somewhat difficult. This work uses high-order polynomial fits to all spectral features to minimize the effect of spectral noise and spectral slopes when comparing spectral features between geometries. Changes in band width or minimum on the order of 1-10 nm are within the noise of the data, and though mentioned should not be over-interpreted.

The Fe^{3+} features in the hematite and hematite-basalt mixtures are both deeper (~10 %) and wider (~2-27 nm) in the bi-directional spectra relative to the hemispherical spectra (Figure 4 Table 2.4). The 0.9 μm feature is a part of a larger crystal-field absorption feature, which in bi-directional spectra continues at shorter wavelengths through 0.5 μm (Morris et al., 1985; Yamanoi et al., 2009). The left ~0.75 μm edge is a local maximum, rather than the left edge of the absorption feature (Morris et al., 1985; Yamanoi et al., 2009). This can faintly be seen in the bi-directional hematite spectrum, which decreases in reflectance below 0.75 μm (Figure 2.2). There is a clear change in the relative values of the 0.75 and 1 μm band edges: in the bi-directional geometry, the 0.75 μm maximum is lower than the 1 μm edge, while the edges are equal in the hemispherical spectrum. A similar pattern is seen in the spectra of 2B:8H, 4B:6H, and 6B:4H (Figure 2.2). The increased noise of the hemispherical spectra, even post-smoothing, complicate further analysis of this region below 1 μm .

In the spectra of the basalt-hematite mixtures, the Fe^{3+} band shows trends in both depth and width relative to hematite proportion. In both observational geometries, band

depth increases with increasing hematite proportion (Figure 2.4, Table 2.4). Band width, however, shows different trends in the two geometries. In the bi-directional spectra, the width of the Fe^{3+} band decreases with increasing hematite proportion, while the hemispherical spectra have an increasing band width with increasing hematite proportion. The strongly sloped continua in the hemispherical spectra of 9B:1H, 8B:2H, and 6B:4H likely affects the gaussian fits used to determine band width by obscuring the exact position of the feature's left edge.

The changes to the hydration bands at 1.4 and 1.9 μm in the dacite, rhyolite, and thenardite spectra between bi-directional and hemispherical spectra are less regular than is observed in the Fe^{3+} feature (Table 2.5, Figure 2.8). The features at 1.4 and 1.9 μm in the dacite and rhyolite only have a <3% change in depth (Table 2.5), while the thenardite features are deeper in the hemispherical spectrum. Both the 1.4 μm and 1.9 μm features have slightly (1-7 nm) different width and position between geometries, but these changes are more minor than is observed in the Fe^{3+} band.

The mechanistic reason for narrower, shallower bands in the hemispherical spectra relative to the bi-directional spectra is unclear. This may arise from collecting reflected light over a significantly wider range of angles in the hemispherical geometry. Light at wavelengths towards the edge of the absorption feature – wavelengths less preferentially absorbed across all observation angles – are preferentially reflected, resulting in higher reflectance at the band edges in the hemispherical geometry.

5.1.2. Agreement with MIR Geometry Comparisons

Slightly different behavior is observed when comparing data collected in the MIR versus VNIR regions. In previous studies, the bi-directional MIR reflectance data exhibit a higher reflectance than corresponding hemispherical reflectance data (Mustard & Hays, 1997); however, the VNIR data presented here have the opposite behavior (Table 2.3). The dissimilar behavior between geometries may be the result of Mustard & Hays (1997) using two different instruments to collect bi-directional and hemispherical reflectance measurements. The dissimilarity may also result from the different optical behavior between the MIR and VNIR regions. Additional data, preferably collected on additional instruments and over a range of compositions, are needed to fully explore this.

Shifts in exact band position between bi-directional reflectance and emissivity spectra have been noted in the MIR (Bartholomew et al., 1989; Hecker et al., 2010; Vincent & Hunt, 1968). A change is observed in the exact position of the Fe^{3+} band minima between the bi-directional and hemispherical data. In the MIR, the reststrahlen bands occur at longer wavelengths in the emissivity spectra relative to bi-directional reflectance spectra (Hecker et al., 2010; Hunt & Vincent, 1968). Here, the Fe^{3+} band falls at longer wavelengths in the bi-directional reflectance spectra relative to the hemispherical spectra. The reason for this behavior is unclear, but not wholly unexpected. The two spectral regions have differing optical behavior, which suggests minor differences in spectral feature behavior. Additionally, the MIR features and the Fe^{3+} band arise from different mechanisms – fundamental vibration features vs. crystal field distortions – and this could influence the feature's behavior.

5.2. Conversion between Geometries

Section 5.1 showed that bi-directional and hemispherical reflectance data are not equivalent in the VNIR region. Unfortunately, there is a paucity of spectral data relevant to interpreting hemispherical reflectance data. Modeling of a surface's single scattering albedo has long been assumed to remove any effect of geometry on the data, thereby providing a method to use bi-directional data in interpreting hemispherical data (e.g., Hapke, 2012; Johnson et al., 1992).

A geometry-independent single scattering albedo can be found by utilizing r_d and r_h and forcing w_d to equal w_h . As only two spectra are used to calculate w_o and b_o the parameter values are not unique. Calculating w_o and b_o with additional bi-directional and hemispherical geometries will produce different results. Extrapolating off the calculations of different bi-directional phase functions of jarosite from 2, 3, and 7 variable phase angle spectra by Sklute et al. (2015) suggests the overall pattern of w_o and b_o might be correct. Thus, the steep downward slope of the basalt, hematite, and dacite w_o with increasing wavelength might be retained if additional data are included, though the actual values of w_o and b_o would change.

Previously published single scattering albedos, calculated from bi-directional spectra, generally resemble the spectra from which they were calculated (e.g., Cord et al., 2003; Mustard & Pieters, 1989). This is true of the w_d and w_h calculated from with the isotropic and static phase function models in this study, e.g., the shape of hematite's bi-directional single-scattering albedo generally resembles the bi-directional reflectance spectrum, with different y-values. The geometry-independent w_o for basalt and hematite, are noticeably not equivalent to either bi-directional or hemispherical w both in shape and values. Dacite's w_o has a similar shape to its isotropic and static $p(g)$ single scattering albedos for both geometries, which are all different than its variable $p(g)$ w_d and w_h (Figure 2.9). The single-scattering albedo of thenardite shows little change in shape between geometries or in w_o , particularly when compared to the single-scattering albedos of basalt, hematite, and dacite. The values of all samples w_o are significantly different than the values of their w_b or w_h , regardless of visual similarity (Figure 2.9).

The discrepancy between w_d , w_h , and w_o could be taken to suggest that neither w_d or w_h approximate the true single-scattering albedo of the surface - if the calculated w approximated the true w of the surface, there would likely be closer agreement in at least general shape between the various single scattering albedos. However, the large caveats with the spectra used in calculating the variable phase functions undeniably reduce the accuracy of the modeling results. The values of the calculated variable phase function w_d and w_h are likely inaccurate compared to the sample's true single scattering albedo. The shape of the w_d and w_h is more likely to be correct, as the main issues in the UTK data are with the increased measured reflectance and noise relative to that collected at DLR.

5.2.1. Isotropic vs Anisotropic Scattering Behavior

This work tested both isotropic and anisotropic scattering models. The isotropic models (Equations 6 and 7) have been used to convert the hemispherical spectrum of a spectralon standard to bi-directional reflectance, and for geologic surfaces, represents the minimal set assumptions (Piatek, 2003). The isotropic w_d and w_h for the samples here,

however, fail to convert between geometries. As a result, the isotropic modeled reflectance spectra are closer to the correct reflectance but lack the correct continuum slope (Figure 2.6). The isotropic equations produce a w_o that more closely resembles the isotropic w_h , though spectra modeled from the isotropic w_o do not resemble the actual bi-directional or hemispherical spectra (Figure 2.10). The isotropic models do not accurately model the samples' reflectance, particularly in calculating w_o , and these results suggest that accounting for multiple-scattering and backscattering via the phase function is likely crucial.

The anisotropic spectral behavior observed here agrees with previous work utilizing bi-directional and hemispherical models (Johnson et al., 1992; Mustard & Pieters, 1989; Piatek et al., 2004). The anisotropic models used in this work (Equations 1 and 2) assume that the aggregate scattering behavior of the surface is sufficient to minimize any strongly anisotropic scattering of individual particles, resulting in only mild deviations from isotropic behavior. Within each geometry, this assumption appears valid, as the samples are better modeled by the anisotropic models than the isotropic. Moreover, for basalt, thenardite, and dacite, the variable phase function w_h can somewhat model r_d , producing a spectrum with lower reflectance than the hemispherical spectrum, and for thenardite and dacite, a change in slope (Figure 2.6).

However, the results of modeling w_o suggest that the independent bi-directional and hemispherical anisotropic models utilized in this work, and their derived parameters w and b , may not independently describe the fundamental scattering behavior of a surface. This suggestion agrees with the results of recent works explicitly investigating the ability of similar bi-directional models to extract fundamental properties of particulate surfaces, namely Piatek et al. (2004) and Shepard & Helfenstein (2007). Importantly, there is no basis from which to conclude that w_o is any more accurate than w_d or w_h , particularly given that the solutions for w_o ubiquitously require an unrealistic negative phase function.

5.2.2. Phase Function and Scattering

The phase-variable data used to calculate the wavelength variable w_d and b_d were all collected in the same plane, with the light source and detector set in a line. This is how most laboratory reflectance spectrometers are arranged. Orbital data might assume a similar geometry, with the sun can be treated as a point source and all incoming light is collimated (Clark & Roush, 1984). However, the incident and emergent light need not be in the same plane. Varying the azimuthal angle, in addition to the phase angle, of bi-directional spectra used to calculate the wavelength-variable single scattering albedo and phase function may produce better agreement between w_b , w_h and w_o .

As calculated, the bounds of phase coefficient b_o are significantly more negative than theory indicates should be physically reasonable: $-4.3 < b_o < -0.2$ as opposed to $-1.7 < b < 1.7$ (Mustard & Pieters, 1989). Taken as fundamental properties of the surface, these values for b suggest negative scattering (Figure 2.7; McGuire & Hapke, 1995; Mustard & Pieters, 1989). However, there are several reasons to ignore this implication. First, only a one-term function was solved; a two-term function would better parameterize scattering outside the measured bi-directional plane and change the value of b . As Equations 1 and

2 are written, the b_o parameter is functionally forced to correct for side-scattering. A negative b_o value therefore could be interpreted as indicating significant side-scattering.

Second, it is a completely theoretical constraint that the parameters in these models describe the actual fundamental scattering behavior of the surface; if ignored this negates the requirement that $p(g) \geq 0$. Recent works have called the derivation of fundamental scattering behavior via similar models into question (Piatek et al., 2004; Shepard & Helfenstein, 2007). The negative values of b_o found in this study fall in line with those studies.

Third, and in the same vein, there is minimal indication that the bi-directional and hemispherical models were ever meant to be combined to find w_o . This application was suggested in Johnson et al. (1992), on the basis that the same radiative transfer equation was used to derive both the bi-directional and the hemispherical models (Hapke, 2012). Significantly less effort has gone into refining the hemispherical model compared to the effort extended to the bi-directional model.

Coherent backscattering was ignored for all calculations in this work; this might be a critical over-simplification. Piatek et al. (2004) found that hematite strongly backscatters at phase angles $g \geq 40^\circ$. The other samples used in this study are composed of irregular multiphase or polycrystalline grains, which form internal scattering planes and increase backscatter (McGuire & Hapke, 1995). There is currently no published model hemispherical reflectance which considers backscatter.

A more complex phase function may also help reconcile the bi-directional and hemispherical models. The hemispherical model investigated here uses a 1-term Legendre polynomial as the phase function, which poorly parameterizes side-scattering. A two-term Legendre polynomial is more appropriate, as the first term parameterizes forward and backscattering and the second term side-scattering.

A two-parameter double Henyey-Greenstein phase function has also been used in the bi-directional Hapke model (e.g., Cord et al., 2003; McGuire & Hapke, 1995; Shepard & Helfenstein, 2007). Some works have found this phase function performs better than a Legendre polynomial over various limited wavelengths (Cord et al., 2003; McGuire & Hapke, 1995). However, Sklute et al. (2015) and Ye et al. (2021) both found a two-term Legendre polynomial performed better when considering several thousand wavelengths across the VNIR region (0.35-2.5 μm). Utilizing a Henyey-Greenstein equation is unlikely to reconcile w_d and w_h . Both Henyey-Greenstein and Legendre equations have been empirically fit to bi-directional data and lack a theoretical backing. Neither has been tested for hemispherical data.

5.2.3. Minor Additional Factors

Porosity, which is affected by grain size and reduced when multiple grain sizes are included, affects scattering behavior. Porosity can be corrected for by multiplying Equations 1 and 2 by a correction factor K , such that Equation 1 becomes:

$$r_d(i, e, g) = K \frac{w}{4} \frac{1}{\mu_o + \mu} \{ [1 - B(g)]p(g) + H(\mu_o/K)H(\mu/K) - 1 \} \quad (8)$$

(Hapke, 2012). As the porosity of the sample does not change between observational geometries, including this factor would change the calculated values but is unlikely to

reconcile w_d and w_h . This is unlikely to be a source of error (Hapke, 2012); mathematically, the porosity is included as a scalar correction.

Hapke modeling also assumes that all particles are significantly larger than the scale of wavelength used. The samples utilized here are composed of a range of grain sizes between 250 and 500 μm , which meets this assumption. Except for hematite, however, the samples were dry-sieved, which may leave some clinging fines. There are several indications that any presence of fines is likely not a source of error or unusual spectral behavior. First, the hematite sample was wet sieved to remove clinging fines and behaves identically to all other samples. Second, Piatek et al. (2004) found that Hapke models can be applied to grain sizes on the order of the wavelength considered in the VNIR region ($<63 \mu\text{m}$). Furthermore, while any fines would affect the reflectance of the surface and calculated single scattering albedo, their presence would not change any of the equations used.

5.3. Implications for Remote Sensing

A main goal of remote spectral observations is the determination of planetary surface composition. Band parameters and linear deconvolution are commonly employed to this end (e.g., Liu et al., 2016; Rogers & Aharonson, 2008; Sinha & Horgan, 2022; Viviano-Beck et al., 2014; Zastrow & Glotch, 2021), though machine learning methods such as random forest trees or partial least squares regression are increasingly common (e.g., L. Li, 2006; S. Li et al., 2012). These methods all assume that factors such as observational geometry can be ignored or corrected for via pre-processing or conversion to single-scattering albedo.

Normalization methods can address the higher reflectance values of hemispherical spectra relative to bi-directional spectra (Figure 2.11a,b). Removing a linear continuum reconciles the different slopes in the bi-directional and hemispherical spectra, though it does not address the concave behavior observed in the hemispherical basalt spectrum (Figure 2.11c). Neither pre-processing method fully removes the effects of the different observation geometries, particularly on the depth and width of the Fe band. Mineral detection methods utilizing the region near 1 μm are likely significantly affected by the change in observational geometry, as the width and depth of the Fe band changes between geometries in these samples. Mineral detection based off the hydration bands at 1.4 and 1.9 μm are likely least affected by the change in observational geometry once pre-processing methods have been applied to both reference and target spectra, as the continuum-removed depth of these features is the same.

In the VNIR region, conversion to single scattering albedo is frequently employed to remove the effects of volume scatter and geometry dependence as a larger part of linear deconvolution methods (e.g., Liu et al., 2016; Mustard & Pieters, 1989; Zastrow & Glotch, 2021). Tests performed in this study show that converting to single scattering albedo via currently published models does not result in accurate conversion between bi-directional and hemispherical geometries.

5.3.1. Venus

Venusian surface compositional characterization will rely on accurate characterization of the region between 0.8-1.2 μm to determine surface composition (Dyar et al., 2021;

Helbert et al., 2018). Venus' thick CO₂-rich atmosphere imposes limitations on spectral observations of the planet's surface. Daytime reflectance data are dominated by Rayleigh scattering from the cloud layers, inhibiting any view of the surface. Nighttime emissivity measurements of the surface can be taken, however, through five atmospheric windows in the visible-near-infrared (VNIR) range (0.85, 0.9, 1.1, 1.12, and 1.18 μm). The Venus Emissivity Mapper/VenSpec-M (VEM) onboard the VERITAS and EnVision missions will collect 6-band emissivity spectra from orbit through these windows (Helbert et al., 2018). The observed changes in the Fe³⁺ band and continuum presented in this study indicate that bi-directional reflectance data cannot be directly applied when interpreting emissivity data; hemispherical reflectance must be utilized.

DAVINCI's Venus Descent Imager (VenDI) will collect two band reflectance data of the surface during the mission's descent (Garvin et al., 2022). The reflectance data collected by VenDI will have a hemispherical-directional observational geometry; the intense Rayleigh scattering in the atmosphere will produce isotropic illumination of the surface. Hemispherical-directional reflectance has the same sensitivity to measured emergence angle as directional-hemispherical reflectance has to incidence angle (Hapke, 2012), meaning that surfaces viewed under these opposite conditions should have the same spectral response. Analysis of VenDI data need not involve conversion to or from emissivity, however, it is still clear that interpretation using bi-directional data will lead to inaccurate conclusions. The bi-directional and hemispherical spectra not only have different reflectance values when averaged through VenDI's broad and narrow bands, but also yield different band ratios (Figure 2.12).

6. Conclusions

Bi-directional and hemispherical VNIR reflectance spectra have been demonstrated to not be equivalent in both monomineralic and polymineralic materials. Differences between bi-directional and hemispherical geometries are most apparent for Fe-rich polymineralic materials like basalt, and least apparent in the Fe-poor rhyolite and dacite and Fe-free thenardite. In all samples, the hemispherical spectrum has a negative continuum not observed in the bi-directional spectrum, higher overall reflectance, and changes in the width and depth of spectral features. In the basalt spectra, these changes are enough that the samples bi-directional and hemispherical spectra appear unrelated.

To more completely constrain the differences observed, additional investigations utilizing geologic materials are needed. Spectral features besides the iron and hydration features investigated here may also change with observational geometry, even in monomineralic samples. Furthermore, the underlying mechanisms producing the observed differences between bi-directional and hemispherical spectra are not well described and cannot be addressed by this limited sample set. The effects of grain size, surface roughness, and porosity on hemispherical spectra are still poorly constrained, and can only be extrapolated from bi-directional VNIR reflectance and MIR studies.

A better understanding of any of these factors may improve modeling attempts to convert between geometries. Currently published radiative transfer models of bi-directional reflectance cannot independently provide accurate predictions of hemispherical reflectance, and vice versa. The anisotropic variable phase function models show marginally better success in modeling the opposite geometry than the isotropic

models. This strongly suggests that anisotropic assumptions should be used in future efforts to convert between observational geometries.

The anisotropic models of bi-directional and hemispherical reflectance tested in this study can successfully be combined to calculate a single scattering albedo, w_o , capable of converting between bi-directional and hemispherical reflectance. The combined model has not been rigorously tested and its physical relevance is minimal. In particular, the results here suggest negative scattering if treated as describing the fundamental scattering behavior of the surface. A more complex hemispherical model is needed; the use of a one-term phase function appears to be too simplistic. Further evolution of the hemispherical model to include a two-term phase function and backscatter will likely improve the modeling results.

7. Future Work

This study tested the radiative transfer models published in Hapke (2012) and found that modelled single-scattering albedos did not result in accurate conversions between observational geometries. There are, however, clear steps that could be taken to improve the tests run in this study.

The sample set used here is non-ideal for several reasons. The basalt has very low reflectance, even for basalts. In the spectra collected at DLR, this results in very shallow absorption features, making it impossible to confidently identify features in the hemispherical spectrum. For spectra collected at UTK, the basalt's low reflectance made collecting additional data difficult, and decreased the signal-to-noise relative to the other samples. Additionally, the thenardite sample was not fully anhydrous, and given how easily the mineral rehydrates, could have changed in hydration between bi-directional and hemispherical measurements. Changes observed between thenardite's bi-directional and hemispherical spectra below 1 μm may result from a change in sample hydration during analysis. Lastly, hematite can have significant backscatter, which was completely excluded from the hemispherical models. Repeating the modeling tests on a different sample set would, at minimum, increase the author's confidence in the results.

To further test these models, spectra used in calculating the variable phase function should be collected on the same instrument to reduce uncertainty. Different spectrometers have different response functions and thus report different reflectance values at the same bi-directional phase angle. The two labs – DLR and UTK – also normalize to different standards.

A two-term phase function, as well as the inclusion of a backscatter term, in the hemispherical model would likely improve the results. Future efforts should include the derivation of this complex model.

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Appendix B

Table 2.1 Sample Composition and Phase assemblages

Phase Assemblage										
	Rocks & Minerals					Mixtures*				
	Basalt	Dacite	Rhyolite	Hematite	Thenardite	9B:1H	8B:2H	6B:4H	4B:6H	2B:8H
Glass	57.20	70.18	79.64	-	-	51.5	45.8	34.3	22.9	11.4
Pyx	11.00	17.35	0.40	-	-	9.9	8.8	6.6	4.4	2.2
Feld	24.20	8.58	14.17	-	-	21.8	19.4	14.5	9.7	4.8
Apatite	0.00	1.36	0.00	-	-	0.0	0.0	0.0	0.0	0.0
Quartz	0.00	1.17	4.99	-	-	0.0	0.0	0.0	0.0	0.0
Oxides	4.40	1.36	0.80	-	-	14.0	23.5	42.6	61.8	80.9
Olivine	3.20	0.00	0.00	-	-	2.9	2.6	1.9	1.3	0.6
Total	100.00	100.00	100.00	-	-	100.0	100.0	100.0	100.0	100.0
Bulk Composition										
	Basalt	Dacite	Rhyolite	Hematite†	Thenardite†	9B:1H	8B:2H	6B:4H	4B:6H	2B:8H
SiO ₂	47.43	67.56	73.46	-	-	42.69	37.95	28.46	18.97	9.49
Fe ₂ O ₃ **	15.32	3.41	1.04	100	-	22.41	31.03	48.27	65.51	82.76
SO ₃	-	-	-	-	56.4	-	-	-	-	-
Na ₂ O	2.88	3.98	2.79	-	43.6	2.60	2.31	1.73	1.15	0.58
Glass Composition										
	Basalt	Dacite	Rhyolite	* Calculated inc. hematite						
SiO ₂	48.14	76.82	75.09	† Ideal						
Fe ₂ O ₃ **	17.34	0.92	0.73	** Measured as FeO by EMPA						

Table 2.2 Phase angles of UTK data

Phase angle		15	20	25	30	40	45	55
Incidence Angle		5	5	5	0	5	5	5
Emergence angle		-10	-15	-20	-30	-35	40	50
Location Taken		UTK	UTK	UTK	UTK	UTK	UTK	UTK
1-term P(g)	Hematite	X	X	X	X	X	X	X
	Basalt	X	X	X	X	X	X	X
	Thenardite	X	X	X	X	X	X	X
	Dacite	X	X	X	X	X	X	X

Table 2.3 Continuum fit coefficients and reflectance parameters

	Hemispherical				Bi-directional			
	% reflectance		Continuum Coefficient s		% reflectance		Continuum Coefficient s	
	Mini mum	Maxi mum	c1	c2	Mini mum	Maxi mum	c1	c2
Thn	59	80	89.0	-8.8	37	52	55.9	-6.3
Hem	14	21	23.7	-3.9	10	14	12.6	-0.2
2B:8H	17	24	26.2	-4.0	9	13	11.3	0.3
4B:6H	15	21	23.2	-3.7	7	10	9.1	0.0
6B:4H	11	18	20.2	-4.1	6	8	7.4	-0.3
8B:2H	9	16	18.7	-4.1	5	6	5.2	0.0
9B:1H	9	16	17.7	-3.7	3	4	3.8	-0.2
Basalt	8	12	12.4	-1.8	2	3	2.4	0.0
Dacite	29	37	37.6	-2.6	21	25	23.2	0.1
Rhyolite	34	70	84.2	15.0	19	43	50.0	-8.9

Note. Continuum fit to entire spectrum.

Table 2.4 Fe^{2+/3+} band width, center, and depth from polynomial fits

	FWHM, μm		Band center, μm		Band Depth, % r	
	Bi-directional	Hemispherical	Bi-directional	Hemispherical	Bi-directional	Hemispherical
Hem	0.177	0.174	0.887	0.883	22	12
2B:8H	0.181	0.174	0.889	0.884	25	13
4B:6H	0.182	0.175	0.889	0.887	22	12
6B:4H	0.177	0.172	0.889	0.883	18	8
8B:2H	0.188	0.177	0.898	0.880	16	5
9B:1H	0.196	0.169	0.903	0.883	10	3
Basalt	0.285	0.361	1.006	1.012	10	1
Dacite	0.376	0.393	1.008	1.010	7	3

Table 2.5 1.4 and 1.9 μm band width, center, and depth from polynomial fits

1.4 μm band	FWHM, μm		Band center, μm		Band Depth, % r	
	Bi-directional	Hemispherical	Bi-directional	Hemispherical	Bi-directional	Hemispherical
Dacite	0.043	0.045	1.407	1.406	2	2
Rhyolite	0.048	0.052	1.414	1.414	15	14
Thenardite	0.099	0.107	1.453	1.453	3	5
1.9 μm band	FWHM, μm		Band center, μm		Band Depth, % r	
	Bi-directional	Hemispherical	Bi-directional	Hemispherical	Bi-directional	Hemispherical
Dacite	0.044	0.044	1.908	1.908	8	6
Rhyolite	0.056	0.058	1.909	1.909	39	35
Thenardite	0.129	0.135	1.945	1.942	14	18

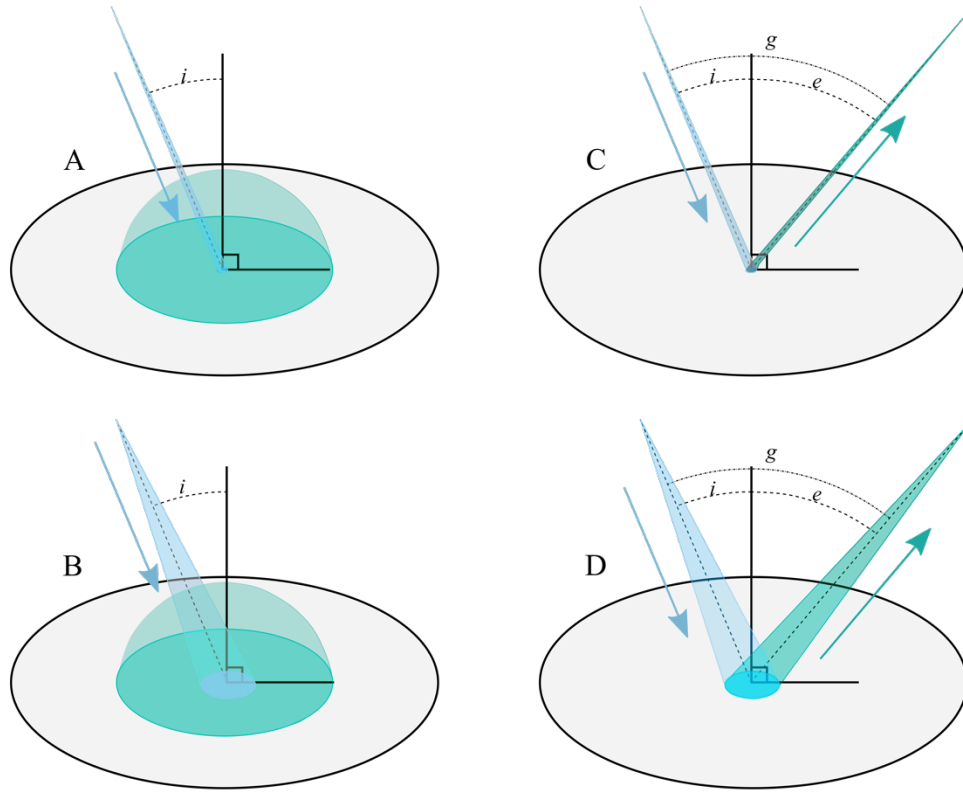


Figure 2.1 Cartoons of Observational Geometries

Incident light shown in blue, measured reflected light shown in green. True hemispherical reflectance (A) and the measurable quantity conical-hemispherical reflectance (B). True bi-directional reflectance (C) and measurable quantity biconical reflectance (D).

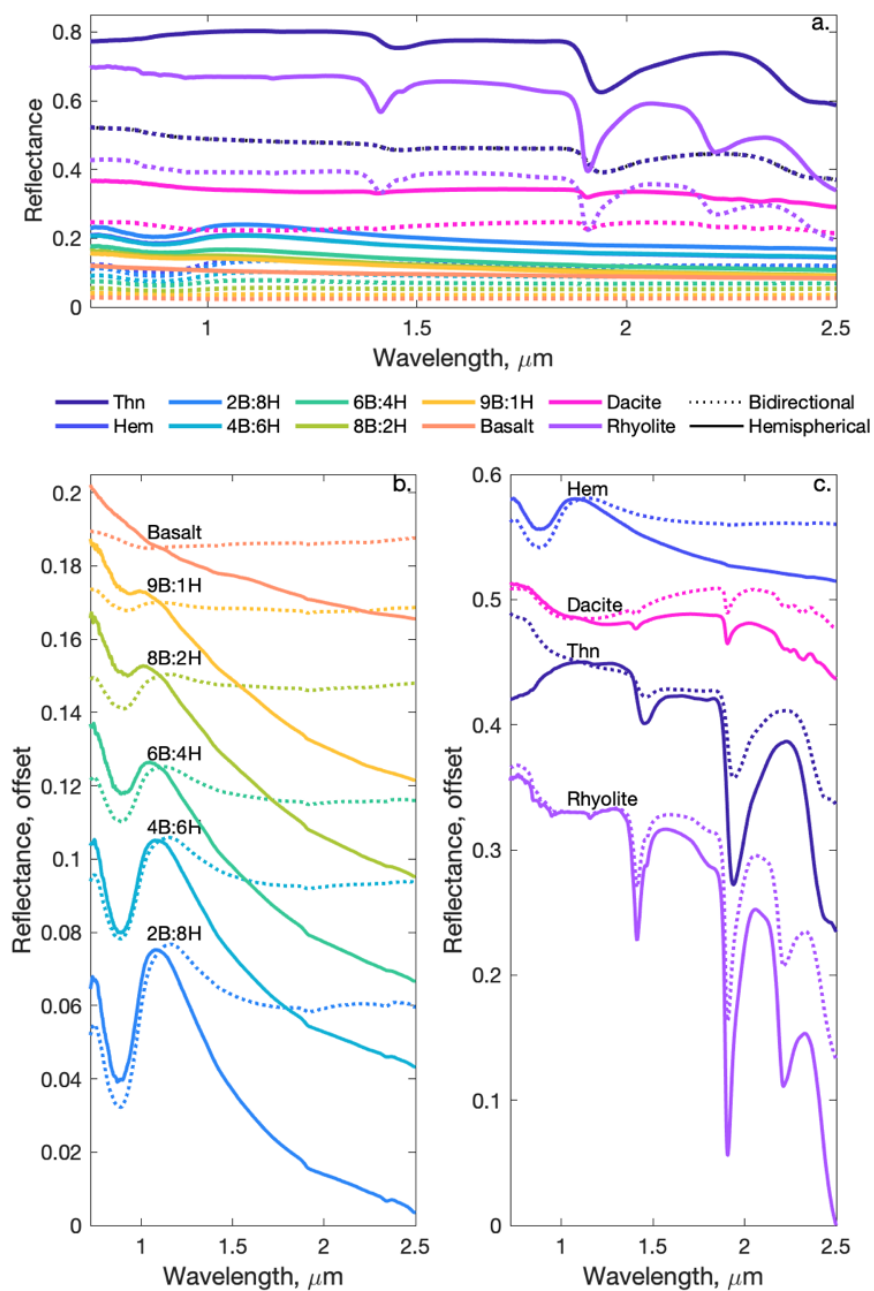


Figure 2.2 Bi-directional and hemispherical spectra of all samples

a. Bi-directional and hemispherical spectra of all samples. Bi-directional spectra are shown in dashed lines, hemispherical in solid lines. b and c plot the bi-directional and hemispherical spectra of each sample, with reflectance at 1.1 μm equal between geometries for ease of comparison. Spectra are otherwise not normalized so that relative reflectance values are preserved between samples, which are offset for clarity. Note the change in y-axis between a, b, and c. Colors are consistent between a, b, and c.

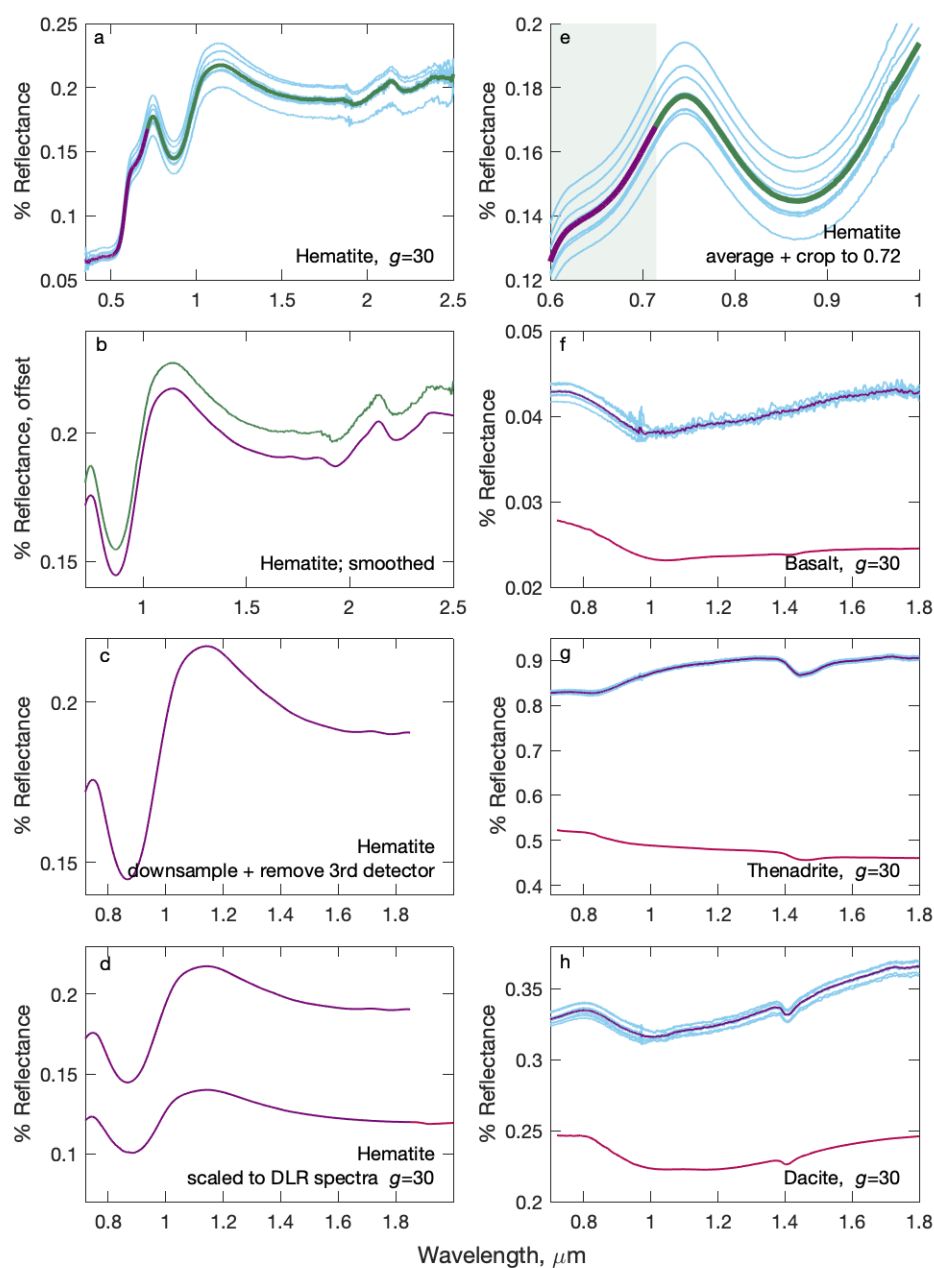


Figure 2.3 UTK spectral data processing steps

Preprocessing steps for UTK data for use in calculating the variable phase function. a. Hematite spectra at $g=30$. Multiple spectra were averaged and (e.) data below 0.72 μm cropped. b. Savitzky-Golay filter applied to smooth spectra. c. Spectra downsampled from 1 to 5 nm/channel. d. Spectra scaled to reflectance of DLR spectra at $g=30$; the same rough scaling factor was applied to all UTK spectra of a given sample. f. Basalt data at $g=30$. g. Thenardite data at $g=30$. h. Dacite data at $g=30$. In f, g, and h red line is final spectrum used in calculations.

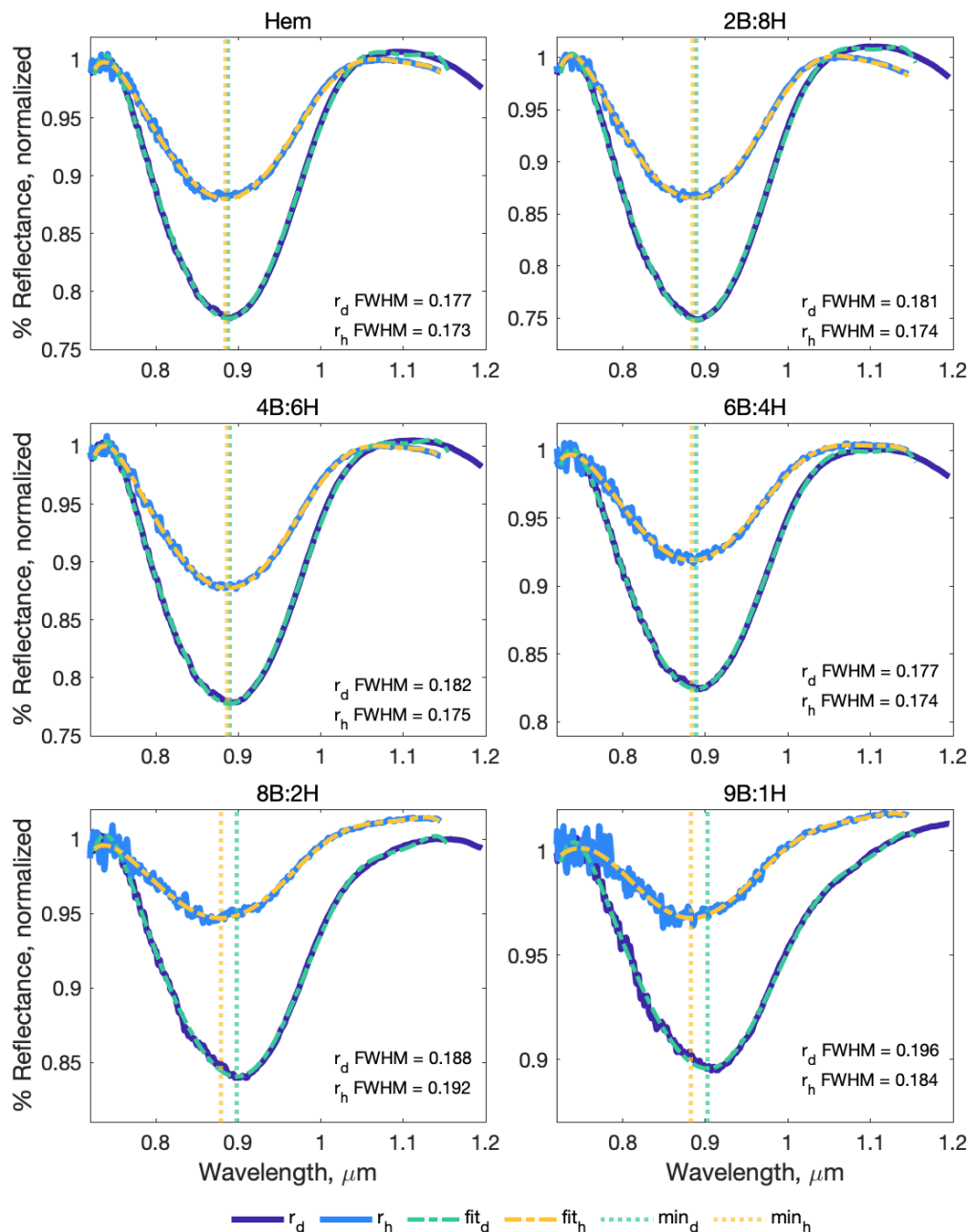


Figure 2.4 Polynomial fits to Fe bands

Polynomial fits to Fe^{3+} absorption band in the bi-directional and hemispherical spectra of hematite and the basalt-hematite mixes. Vertical lines show position of band minima.

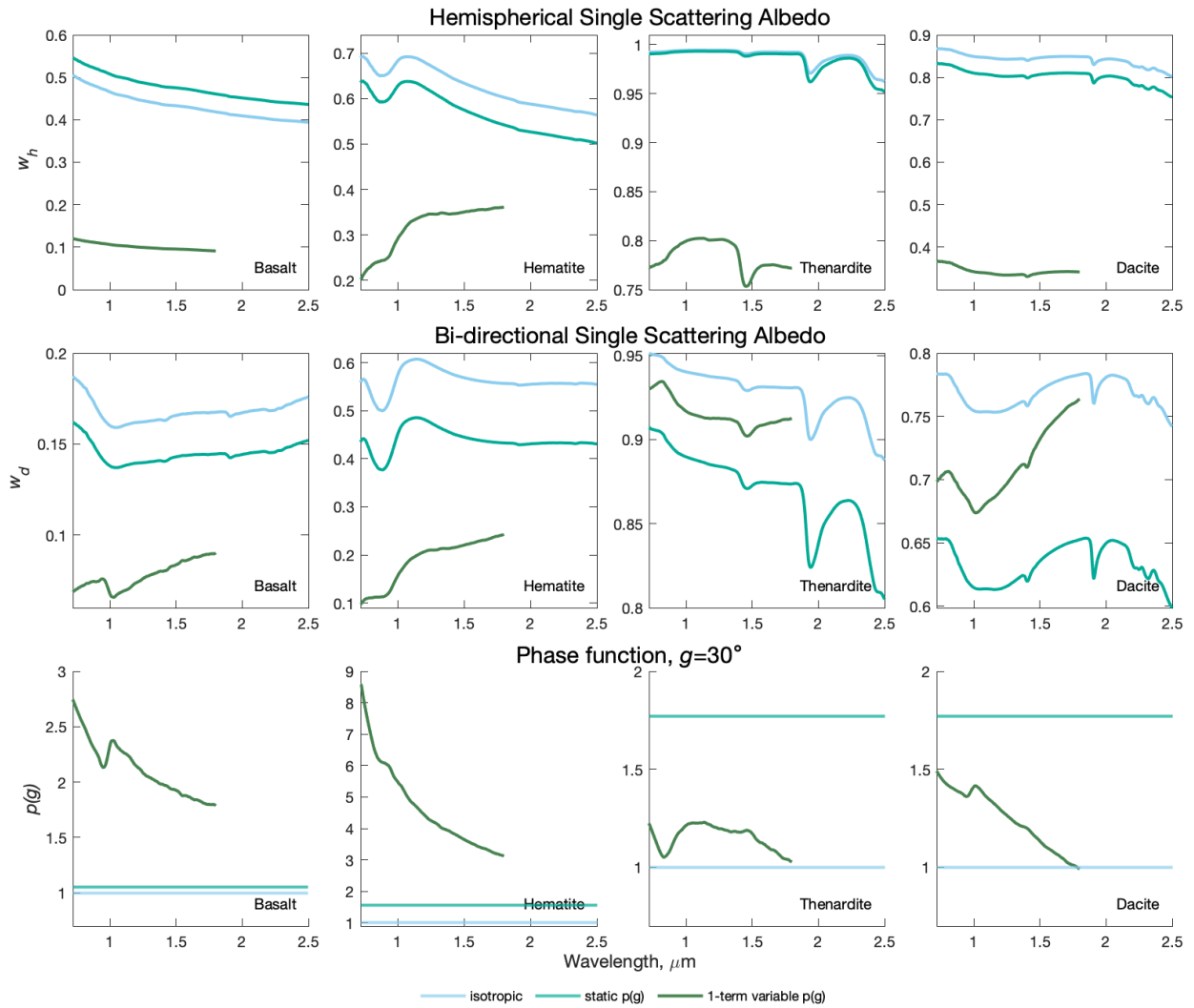


Figure 2.5 Single-scattering albedos and phase functions calculated from isotropic equations, with a static phase function, and with the 1-term variable phase function.

w_h (top row), w_d (middle), and phase function for $g = 30^\circ$ for basalt, hematite, thenardite, and dacite from the isotropic, static phase function, and 1-term variable phase function models.

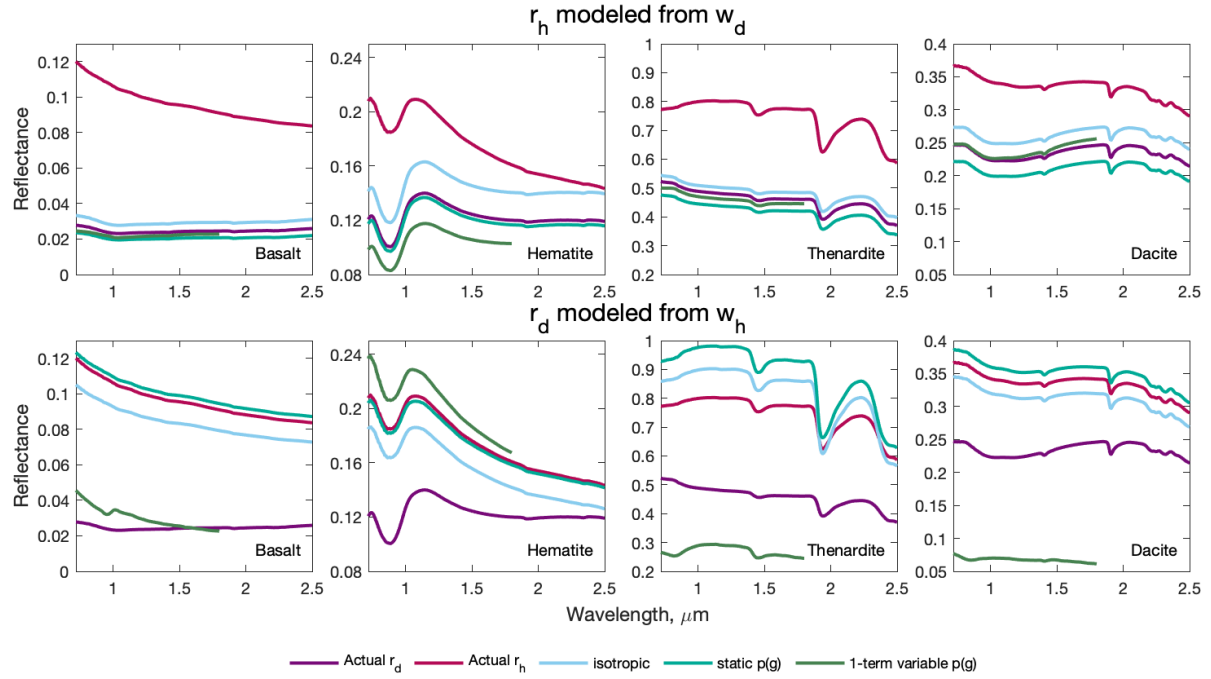


Figure 2.6 Actual and modeled spectra of basalt, hematite, thenardite, and dacite.

Top row shows r_h modeled from w_d , bottom row is r_d modeled from w_h . Red and purple lines show actual bi-directional and hemispherical spectra, respectively. Other colors match **Figure 5**.

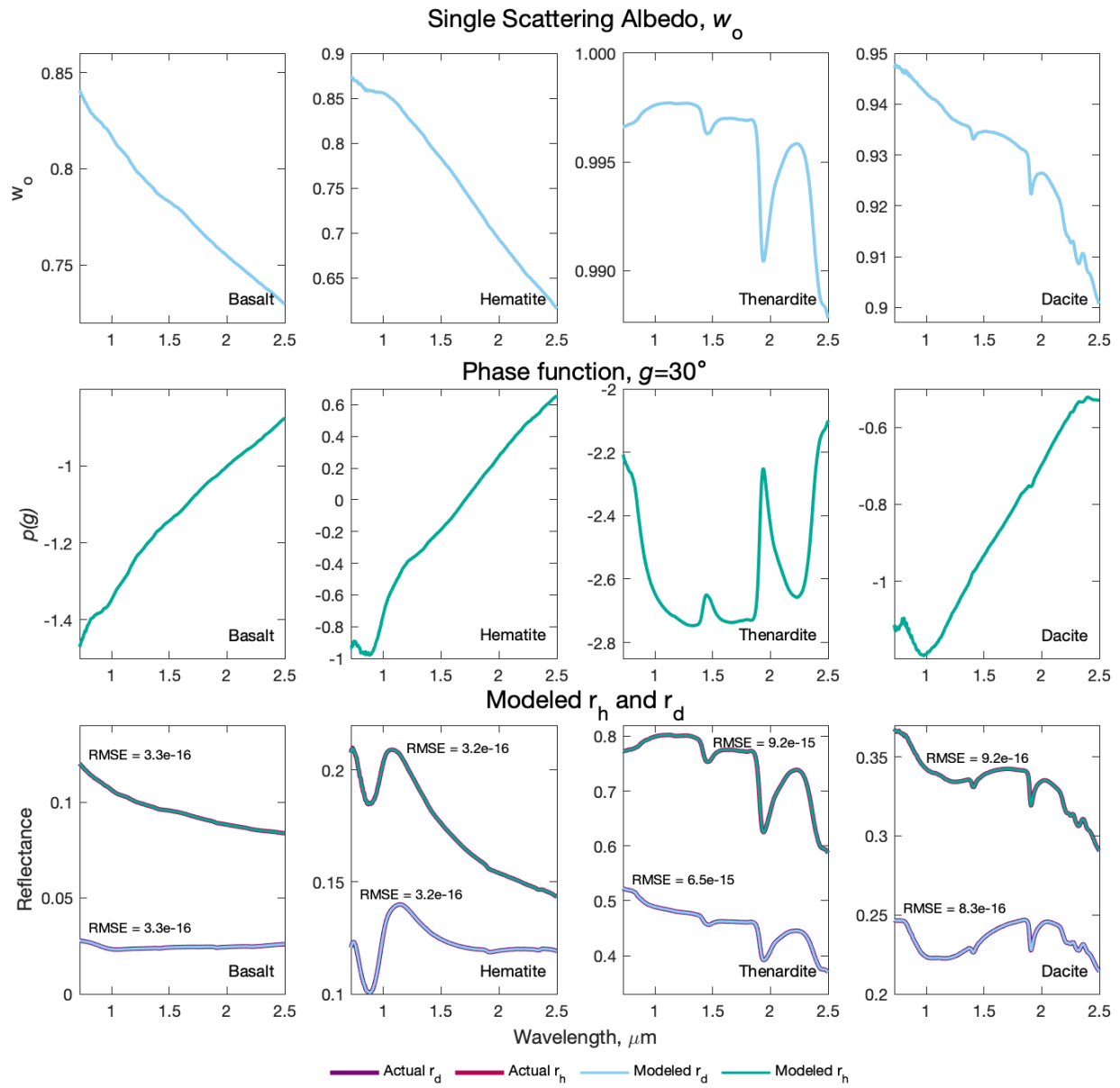


Figure 2.7 w_o , $p(30^\circ)$, and modeled spectra of basalt, hematite, thenardite, and dacite.

Top row shows the calculated w_o for each sample. Middle row shows calculated $p(g)$ at $g = 30^\circ$ for each sample; note that the value of each phase function is negative. Bottom row shows modeled and actual spectra, which overlap; the root mean squared error (RMSE) of modeled spectra is given.

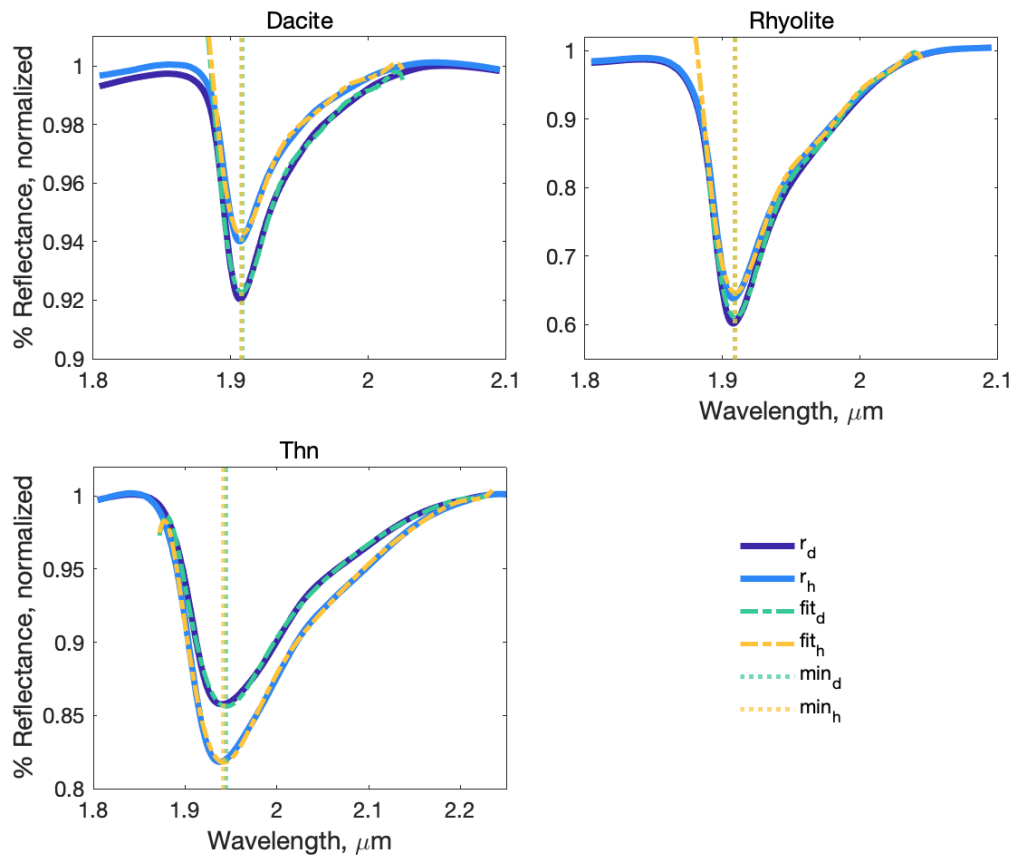


Figure 2.8 Polynomial fits to the 1.9 μm band in dacite, rhyolite, and thenardite

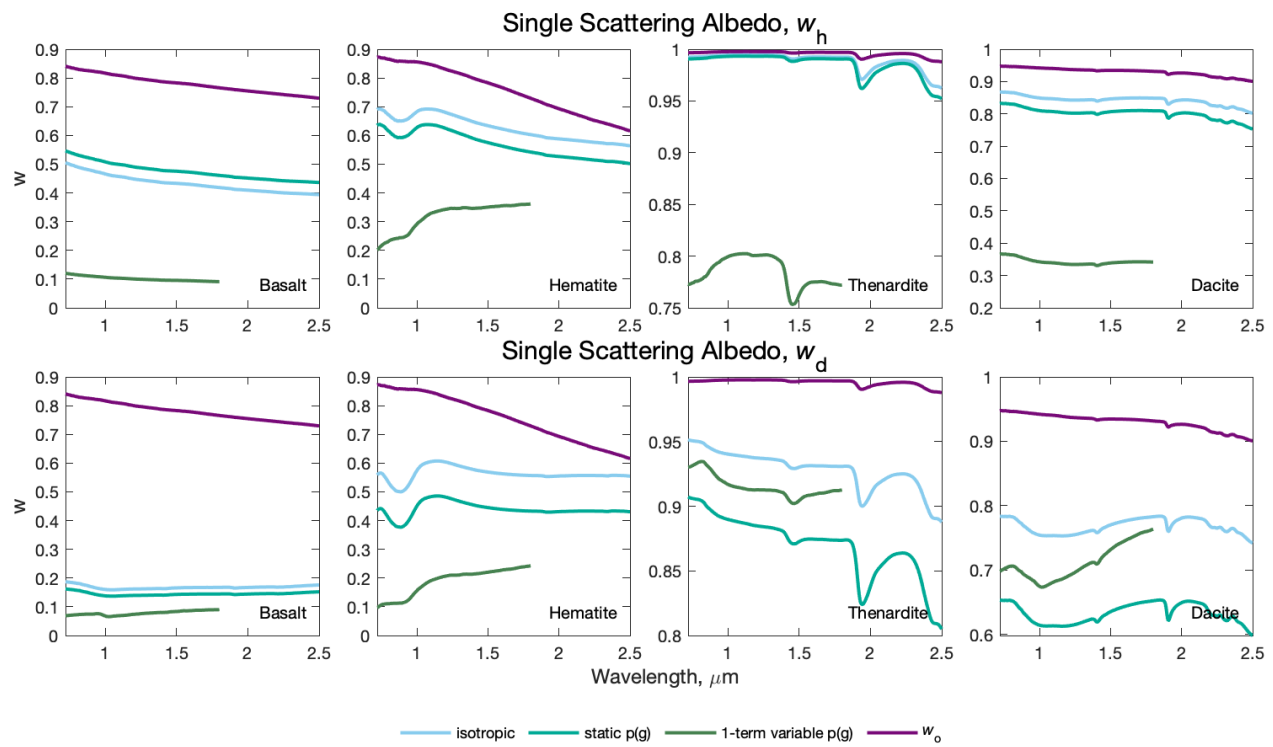


Figure 2.9 Single scattering albedos of basalt, hematite, thenardite and dacite.

Top row compares hemispherical w , bottom row bi-directional w . Purple line is w_o , and the same in both rows.

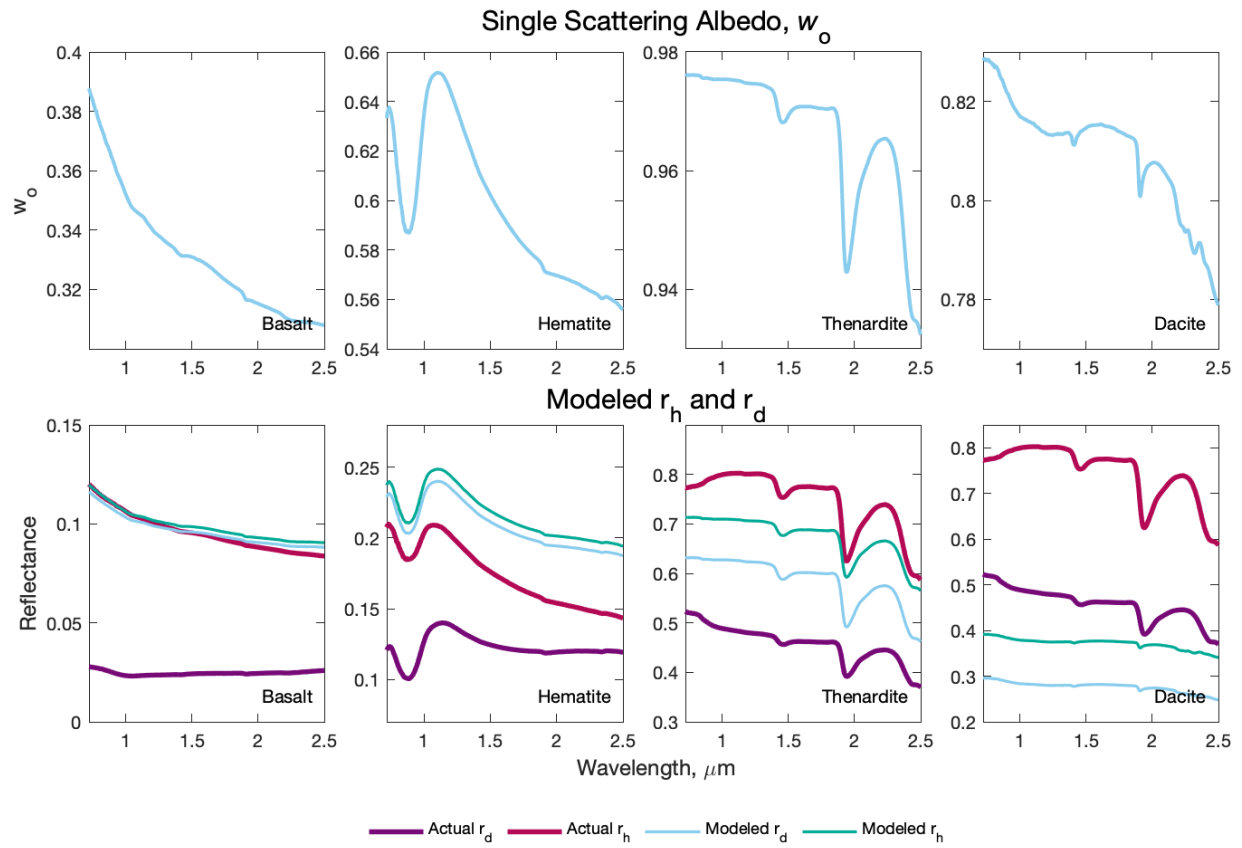


Figure 2.10 Isotropic w_o and modeled spectra.

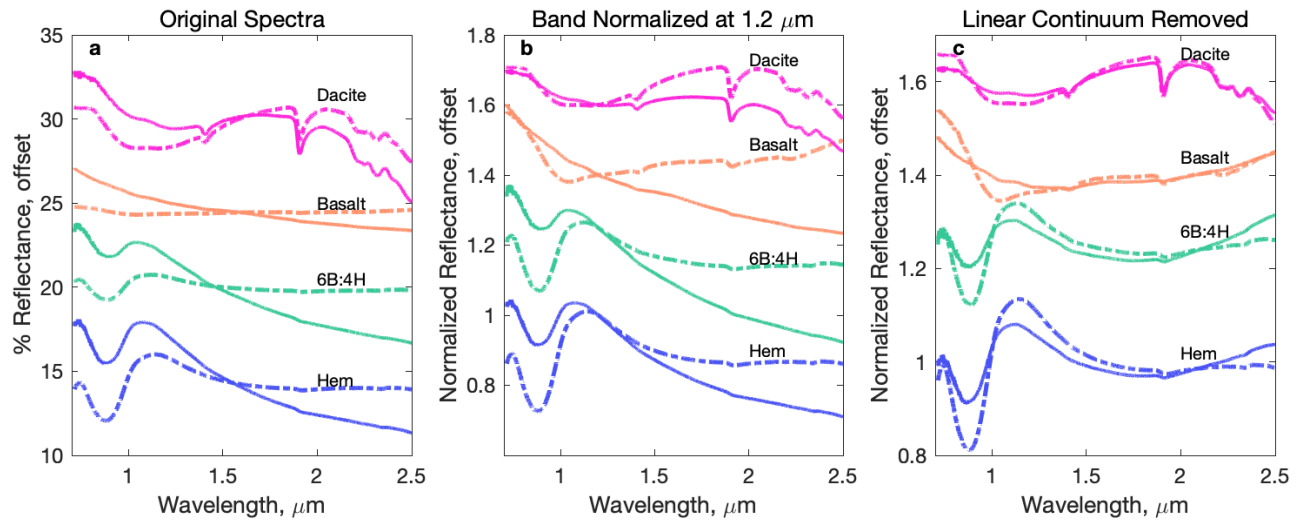


Figure 2.11 Comparison of preprocessing methods.

Bi-directional spectra plotted with dashed lines, hemispherical spectra plotted with solid lines. Colors match to Figure 1.

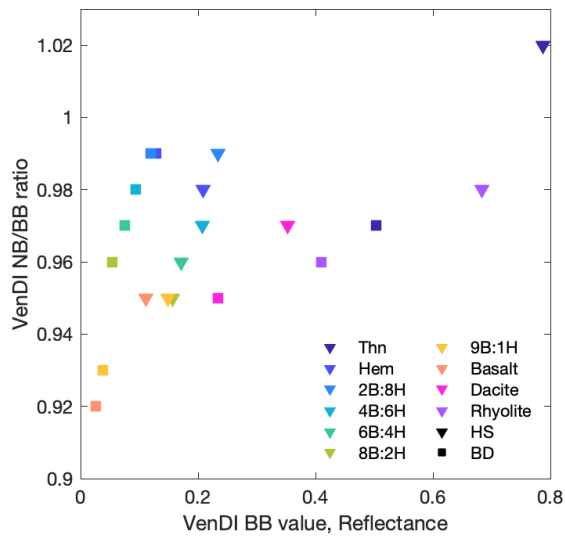


Figure 2.12 Effect of different geometries on VenDI band ratios.

VenDI has two bands, a broad band (BB) which collects from 0.74-1.03 μm and a narrow band (NB) from 0.98-1.03 μm (Garvin et al., 2022).

CHAPTER 3.
**Identification Despite Alteration: Spectral Discrimination of Fresh
Igneous Surfaces and Venus-Analog Basalt-Sulfate Mixtures.**

Abstract

Accurate interpretation of venusian surface spectra is key to constraining the composition of Venus' surface and its implications for the planet's evolution. Understood to be primarily basaltic in composition, the venusian surface is expected to rapidly react with atmospheric CO₂ and SO₂, undergoing oxidation and sulfurization. Venus' thick atmosphere, however, limits spectral data to a narrow region near 1.0 μm , where sulfates have no spectral features, making identification sulfate-bearing secondary mineralogies via spectral observations uncertain. This study investigates the influence of increasing proportions of sulfate and oxide alteration minerals on the hemispherical visible-near-infrared (VNIR) reflectance spectrum of basalt using 37 three-phase mixtures of basalt, hematite, and either anhydrite or thenardite. The data show that the presence of any alteration phase – anhydrite, hematite, or thenardite – increases the sample reflectance relative to fresh basalt. The spectra of samples with 10-20% alteration phases are distinct from the felsic endmembers, meaning that basaltic surfaces can still be identified after the onset of alteration. However, anhydrite has a more pronounced effect relative to thenardite, resulting in significant changes to spectra at lower abundance. At high abundance, anhydrite can partially obscure the characteristic Fe-feature of hematite.

1. Introduction

The surface of Venus is expected to readily react with the planet's atmosphere, undergoing primarily chemical weathering with minimal physical erosion (Gilmore et al., 2023; Zolotov, 2018). Unfortunately, direct compositional data are limited. Atmospheric CO₂ limits orbital observations of the surface to either radar wavelengths or a set of six narrow windows (0.77, 0.85, 0.90, 1.0, 1.10, and 1.18 μm ; Figure 3.1; Baines et al., 2000; Meadows & Crisp, 1996; Wood et al., 2022). Venus' surface pressure and temperature are approximately 92 bars and 470 °C, respectively (Zolotov, 2018), which limits the lifetime of any lander, making direct surface analyses difficult.

Accurate determination of surface composition is key to understanding the interior composition and evolution of Venus. The surface of Venus is geologically young – crater counting estimates suggest an average surface age of ~300-1600 Myr (Basilevsky & Head, 1998; McKinnon et al., 1997; Strom et al., 1994). The surface is dominated by volcanic terrains, with flow morphologies indicating low eruptive viscosities similar to basalt (Basilevsky & Head, 1998; Head et al., 1992). There are no obvious geomorphological markers of subduction and terrestrial-type plate tectonics, though the stratigraphically old tessera terrains appear tectonically deformed (Basilevsky & Head, 1998; Gilmore et al., 1998; Romeo & Turcotte, 2008). Due to their similar appearance to Earth's continental crust, it has been suggested the tessera may have a felsic composition (e.g., Romeo & Turcotte, 2008).

The five Venera and two Vega landers provide the only measured major-element geochemistry and visible images of Venus' surface, exclusively of lowland terrains, and only three of the landers measured major element abundances (Treiman, 2007). Although the uncertainties on the chemical analyses are high, the Venera 14 and Vega 2 measurements are consistent with tholeiitic basalt similar to those found at terrestrial mid-ocean ridges, and Venera 13 data are consistent with an alkali basalt (e.g., Treiman, 2007; Filiberto, 2014). These compositions suggest different petrologic origins; tholeiites

originate from a shallow source region, while the Venera 13 alkali basalt suggests deeper melting, potentially more similar to a plume source (Filiberto, 2014).

Despite the interpretation of Venera and Vega data as primary compositions, the measured surfaces may have been chemically altered. Geochemical data from Venera 13 and 14 and Vega 2 have high SO₃ concentrations relative to terrestrial mid-ocean ridge basalts (Gilmore et al., 2023). In addition, reflectance data from the photometers on Venera 9 and 10 suggest the presence of the alteration phase hematite (Pieters et al., 1986). Overall, the low unconfined compressive strength of rocks at the Vega 2 site, combined with high sulfate content, suggests a weathered and cemented clastic rock (Gilmore et al., 2023).

Alteration experiments of basalt under Venus-analog atmosphere suggest the surface will readily react to form secondary mineralogies, possibly on a timescale as short as 10,000 yrs -100 Myr (Cutler et al., 2020; Smrekar et al., 2010; Treiman et al., 2021). Common alteration reactions under CO₂ and CO₂+SO₂ atmospheric conditions are oxidation and sulfurization, resulting in the formation of Fe-oxides and sulfate-bearing phases (Berger et al., 2019; Esvan et al., 2022; Reid et al., 2021; Teffeteller et al., 2022). Despite limited surface spectral data, orbital spectral data has potentially observed chemical alteration at young volcanic centers (Mueller et al., 2009; Smrekar et al., 2010). A primary goal of upcoming NASA and ESA missions to Venus will be to determine surface composition and specifically to differentiate between mafic and felsic endmembers such as dacite and rhyolite. Therefore, it is important to constrain how spectral characteristics of altered surfaces change relative to fresh basalt, and to understand if secondary mineralogies can be differentiated from potential felsic surface materials.

This study builds off results of basalt alteration experiments under Venus-analog atmosphere conditions to investigate the spectral behavior of the secondary mineralogies. The goals of this work are twofold: first, to determine the threshold alteration mineral abundances at which basalt can no longer be recognized, and second, to explore if sulfate species can be differentiated spectrally at Venus-relevant wavelengths. Discriminating between minerals could provide constraints on the underlying basalt composition, as the composition and mineralogy of the sulfate species formed in alteration experiments depended on composition of the starting sample.

2. Background

2.1. Chemical Weathering Experiments

Venus alteration experiments have largely focused on basaltic starting compositions, as the majority of Venus' surface is thought to be basaltic. Experiments have determined that secondary mineral assemblages depend on atmospheric composition, oxygen fugacity (fO_2), temperature, and the starting composition of the reacting sample.

Oxides are the most frequent reaction product, and both magnetite (Fe₃O₄) and hematite (Fe₂O₃) have been observed in experiments, depending on the oxygen fugacity (e.g., Berger et al., 2019; Cutler et al., 2020; Esvan et al., 2022; Filiberto et al., 2020; Reid et al., 2021; Teffeteller et al., 2022). The oxygen fugacity of the near-surface venusian atmosphere is close to the magnetite-hematite buffer ($fO_2 = 10^{-20} - 10^{-21.7}$), which

suggests that if magnetite forms on the surface of Venus, it will quickly oxidize to hematite (Zolotov, 2018).

Experiments under a pure CO₂ atmosphere produced limited alteration compared to more reactive, and realistic, Venus-analog conditions (e.g., Berger et al., 2019). Some basalts reacting under a pure CO₂ atmosphere produced siderite (FeCO₃), calcite (CaCO₃), and magnetite (Teffetteller et al., 2022). Under CO₂+SO₂ atmospheric conditions, basalts reacted to form sulfate phases (Berger et al., 2019; Esvan et al., 2022; Reid et al., 2021). Notably, alkaline and tholeiitic basalts produced different alteration phases: siderite or anhydrite (CaSO₄) formed on tholeiitic basalts, while alkaline basalts produced calcite or thenardite (Na₂SO₄) (Reid et al., 2021; Teffetteller et al., 2022). Berger et al. (2019) also observed the formation of anhydrite, thenardite, and glauberite (Na₂Ca(SO₄)₂) on scoria in a CO₂+SO₂ atmosphere.

2.2. Orbital Spectral Data of the Venusian Surface

Spectral observations provide crucial data constraining the composition of Venus' surface. Daytime reflectance data of the surface cannot be taken from orbit due to the intense Rayleigh scattering in the Venus atmosphere (Baines et al., 2000; Meadows & Crisp, 1996). Nighttime emissivity from the surface can be collected through narrow windows in the CO₂-rich atmosphere, as geologic materials measurably emit at the high surface temperatures. To date, only single-band orbital emissivity data have been taken of Venus' surface. These one-band emissivity measurements are largely consistent with basalt, but consistently show variation in relative emissivity that correlate with topography and geologic regions (Hashimoto et al., 2008; Helbert et al., 2008; Mueller et al., 2009).

The measured variation in emissivity appears consistent with chemically weathered and oxidized basalt or felsic material (Smrekar et al. 2010; Gilmore et al. 2015). Data at 1.18 μm from the Galileo spacecraft Near Infrared Imaging Spectrometer (NIMS) showed that the highlands have lower average emissivity than the lowlands, which has been attributed to a more felsic composition (Hashimoto et al., 2008). Analyses of emissivity at 1.02 μm from the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) instrument on Venus Express has been interpreted as either the presence of distinct bulk rock compositions or optically thick layers of secondary minerals (Gilmore et al., 2015; Helbert et al., 2008). VIRTIS data also revealed anomalously high emissivity at some volcanic centers (Mueller et al., 2009) and changes to relative emissivity that were attributed to the absence of alteration phases (Smrekar et al., 2010). Recently, observations of the surface from the Wide-Field Imager for Parker Solar Probe (WISPR) instrument established a new atmospheric window at ~0.7 μm (Wood et al., 2022). The WISPR data also show regions of distinct emissivity that correlate with topography (Lustig-Yaeger et al., 2023).

Multiple bands are needed to differentiate between lower emissivity resulting from felsic surfaces and that due to the presence of secondary mineral phases. The upcoming missions to Venus – DAVINCI (Deep Atmosphere Venus Investigation of Noble Gases, Chemistry, and Imaging), VERITAS (Venus Emissivity, Radio Science, InSAR, Topography And Spectroscopy), and EnVision – will all carry multi-band spectrometers.

The Venus Emissivity Mapper/VenSpec-M (VEM) onboard the VERITAS and EnVision missions will collect nighttime 6-band emissivity spectra from orbit through five specific atmospheric windows (0.85, 0.9, 1.0, 1.12, and 1.18 μm ; Helbert et al., 2021; Dyar et al., 2020; Alemanno et al., 2023). The Venus Descent Imager (VenDI) onboard the DAVINCI mission will collect two-band reflectance data of Alpha Regio from below the cloud deck (Garvin et al., 2022).

2.3. VNIR Spectra

The Venus atmospheric windows near 1 μm fall in the visible-near-infrared (VNIR) wavelength region, where most laboratory reference spectra and planetary surface spectra are collected as bi-directional reflectance. Venus' thick clouds inhibit the collection of surface reflectance data from orbit, requiring collection of nighttime emissivity data through narrow windows of atmospheric transparency. Below the cloud deck, hemispherical-directional reflectance data may be collected within the 1 μm windows. As emissivity (ε) can be related to hemispherical reflectance (r) via Krichhoff's Law ($\varepsilon = 1 - r$; Nicodemus, 1965), trends derived from hemispherical reflectance data can be reciprocally applied to emissivity data.

Spectral signals near 1 μm arise from electronic transitions in metal ions; generally iron, which is in common geologic materials. The exact position and shape of the observed spectral features is sensitive to the crystal lattice surrounding the metal ion, such that major rock-forming minerals (e.g., olivine, pyroxene, hematite) and rock types can be distinguished (Adams & Filice, 1967; Clark et al., 1990; Hunt, 1977). In general, Fe-rich materials have lower reflectance and higher emissivity than Fe-poor materials, making VNIR spectra useful for identifying different classes of igneous rocks (e.g., Fe-rich basalts, Fe-poor rhyolites) that may be present on the surface of Venus.

Hematite has a Fe^{3+} crystal-field absorption feature centered at $\sim 0.86 \mu\text{m}$, bounded on the short wavelength side by a local reflectance maximum at $\sim 0.75 \mu\text{m}$, and on the long wavelength side by a bend at $\sim 1.03 \mu\text{m}$, reaching a maximum by $1.2 \mu\text{m}$ (Burns, 1993; Morris et al., 1985; Yamanoi et al., 2009). In bi-directional reflectance, the maximum at $0.75 \mu\text{m}$ is lower reflectance than the $1 \mu\text{m}$ edge (Morris et al., 1985; Yamanoi et al., 2009). At wavelengths longer than $1 \mu\text{m}$, hematite lacks spectral features in the VNIR. Fundamental vibrations of the Fe-O lattice occur well into the MIR, at ~ 19 , 22.2 , and $30.8 \mu\text{m}$ (325 , 450 and 525 cm^{-1} ; Christensen et al., 2000; Glotch et al., 2004).

Anhydrous Fe-free sulfates such as anhydrite or thenardite have high reflectance and lack diagnostic or unique spectral features in the VNIR except for those arising due to hydration (De Angelis et al., 2021; Bishop et al., 2004, 2014; Cloutis et al., 2006). The fundamental SO_4 vibrations occur in the MIR at ~ 9 , 10.2 , 16 , and $22 \mu\text{m}$ (451 , 613 , 981 , and 1104 cm^{-1} ; Bishop et al., 2004). In the near-infrared, features resulting from SO_4 combinations and overtones can occur near 3.2 , 3.7 , 3.9 , and $4\text{--}5 \mu\text{m}$ (De Angelis et al., 2021; Bishop et al., 2014; Cloutis et al., 2006). Cloutis et al. (2006) attribute bands at 2.2 , 2.27 , and $2.28 \mu\text{m}$ observed in gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) to S-O bending overtones, while other workers attribute these features to H_2O . Harrison (2012) attributed the $2.1 \mu\text{m}$ feature in their bassanite samples to both water and SO_4 . The exact position and shape of these features, as well as their general presence, is dependent on the mineral.

3. Methods

3.1. Sample Preparation

To simulate weathering of a fresh basalt to a mature altered surface, a total of 37 two- and three- component mixtures were made from basalt, hematite (Fe_2O_3), and either anhydrite (CaSO_4) or thenardite (Na_2SO_4), following the mixing scheme in Figure 3.2 (Table 3.1). For clarity, samples are named to give the volume proportion of each endmember in the sample, e.g., sample 8B:1H:1A is 80% basalt, 10% hematite, and 10% anhydrite, and sample 4B:0H:6T is 40% basalt, 0% hematite, and 60% thenardite. No samples have both anhydrite and thenardite.

Tholeiitic basalt from Husavik, Iceland, was used for all mixtures for consistency (Table 3.2). The hematite sample was sourced from Wards, and wet sieved to remove clinging fines. Anhydrite and thenardite were synthesized via dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) at 100°C for >24 hrs. All samples were ground and sieved to $250\text{--}500\text{ }\mu\text{m}$ prior to mixing. Compositional proportions in volume % for all mixed samples are summarized in Table 3.1.

Two felsic endmember samples were included for comparison: a dacite from Mount Pinatubo, Philippines, and a rhyolite from Bishop Tuff, California. Sample phase assemblages are given in Table 3.2. Felsic samples were also sieved to $250\text{--}500\text{ }\mu\text{m}$.

3.2. Spectral Methods

Spectra were collected in a hemispherical observation geometry utilizing a gold-coated integrating sphere, with an incidence angle of $i = 13^\circ$. Reflectance spectra were collected at room temperature ($\sim 25^\circ\text{C}$) from $0.72\text{--}2.5\text{ }\mu\text{m}$ with a spectral resolution of 0.96 cm^{-1} using a Bruker Vertex 80V spectrometer at the Planetary Spectroscopy Laboratory at the German Aerospace Center (DLR) in Berlin, Germany. Spectral data were preprocessed using MATLAB. Data were converted to wavelength and resampled at 0.67 nm/channel . A narrow Savitzky-Golay smoothing filter was applied to the data to reduce noise below $1\text{ }\mu\text{m}$.

MATLAB was used to fit both a line and two-term polynomial to each spectrum to parameterize the spectral slope and shape. Spectra were normalized to their maximum value prior to fitting so that variation in the fit coefficient values reflected changes to slope and shape, rather than the large changes in reflectance between samples. Regions with large absorption bands were ignored when fitting (Figure 3.3). MATLAB was also used to downsample the spectra through the Venus atmospheric windows (Table 3.3; Figure 3.1). When resampling spectra through the atmospheric windows, the width of each window as given in Table 3.3 was treated as the spectral resolution.

4. Results

Only wavelengths between $\sim 0.7\text{--}1.2\text{ }\mu\text{m}$ are directly relevant to this work, as the narrow Venus atmospheric windows fall within that range. However, the entirety of each measured spectrum is evaluated. The spectral behavior past $1.2\text{ }\mu\text{m}$ may be informative to the broader goal of evaluating how the presence of alteration mineralogies affect measured reflectance, specifically on other planets where wavelengths past $1.2\text{ }\mu\text{m}$ can be measured.

All spectra were observed to have a negatively sloped continuum. This is a noted feature of hemispherical geometry, as are minor (≤ 20 nm) shifts in band position relative to spectra collected in a bi-directional geometry (CHAPTER 2 above).

4.1. Rock and Mineral Endmembers

The pure anhydrite (0B:0H:10A) and thenardite (0B:0H:10T) samples have higher reflectance values of 33-87% and 58-80%, respectively (Figure 3.4). Anhydrite has a steeper slope than thenardite. Both samples have a slight concave-down curvature across the continuum, which is more apparent in the anhydrite spectrum.

Incomplete dehydration of anhydrite and thenardite is observed. In the spectrum of thenardite, both hydration features are caused by adsorbed (non-bound) water molecules. The 1.4 μm band minima is at 1.45 μm , indicative of H_2O rather than OH^- (Cloutis et al., 2006). In the spectrum of anhydrite, hydration features are observed near 0.95, 1.15, 1.4, 1.8, 1.9, and 2.5 μm . These features likely arise from a combination of adsorbed water and bound OH^- ; overtones and combination features from H_2O can occur near 0.94, 1.13, 1.38, 1.45, 1.88, and 2.55 μm , while OH^- has two overtones near 0.95 and 1.4 μm (Cloutis et al., 2006). The narrow width of the ~ 0.9 feature in anhydrite indicates this feature is not caused by $\text{Fe}^{2+/3+}$ contamination in the sample; if it were, the feature would be much broader (Cloutis et al., 2006). The hydration features do not affect thenardite data in the region of Venus atmospheric transparencies; the thenardite spectrum is featureless until wavelengths longer than 1.4 μm . The anhydrite spectrum has OH^- absorptions in the Venus region at 0.97 and 1.2 μm .

The reflectance of hematite (0B:10H:0A) is 14-21%. The characteristic 0.9 μm Fe^{3+} absorption feature is present, though distinct from that observed in bi-directional spectra (Morris, 1986), here the left and right edges of this feature are relatively equal reflectance (Figure 3.4). The spectrum is featureless at longer wavelengths, with a strong concave-up curvature.

Pure basalt has reflectance values between 8-12% (Figure 3.5). The spectrum of basalt has a strong concave curvature, which effectively overprints any spectral features which may be present in the spectrum. Minor ($<1\%$ change in reflectance) features are visible near 1.0, 1.4, and 1.9 μm when a two-term polynomial continuum is removed.

The dacite and rhyolite exhibit reflectance of 29-37% and 33-70%, respectively, and lack the concavity evident in the basalt spectrum (Figure 3.5). A broad Fe-absorption feature is present in the dacite spectrum, likely from the presence of abundant Fe-bearing pyroxenes. Hydration features are observed in the dacite and rhyolite spectra at 1.4, 1.9 and 2.2 μm . The hydration features observed in the basalt, rhyolite, and dacite spectra at 1.4 and 1.9 μm arise from a combination of adsorbed water and glass hydration. Volatile-by-difference calculations from electron microprobe analysis of the dacite and rhyolite suggest ~ 1 -2% volatile concentration in the glass phase (Leight et al., 2022).

4.2. Binary Mixtures

The presence of any alteration endmember affected the measured spectrum. The binary mixture spectra all exhibit increased reflectance relative to the basalt-only spectrum (Figure 3.4). Reflectance values range from 12-83% for the basalt-anhydrite

mixtures, 9-38% for basalt-thenardite mixtures, and 9-24% for the basalt-hematite mixtures.

4.2.1. Basalt-Thenardite Mixtures

Sample 9B:0H:1T, with 10% thenardite, has ~1% higher reflectance than the basalt and exhibits no meaningful change to the spectral shape or spectral features from pure basalt (Figure 3.4); the OH absorption at 1.9 μm is slightly more obvious in max-normalized spectra of 9B:0H:1T than the basalt, but the linear slopes are the same. Sample 8B:0H:2T has a ~3% higher reflectance than the basalt, a steeper slope, and decreased curvature. With increased thenardite (6B:0H:4T, 4B:0H:6T, 2B:0H:8T), reflectance increases, spectral slope steepens, and the curvature decreases (Table 3.4 and Table 3.5). All three of these samples have the ~2.5 μm absorption feature seen in the thenardite-only spectrum. In samples 4B:0H:6T and 2B:0H:8T the 1.9 μm feature is a doublet; this doublet shape is more pronounced than in the spectrum of thenardite.

4.2.2. Basalt-Anhydrite Mixtures

The addition of 10% anhydrite (9B:0H:1A, Figure 3.4) produced significant change to the spectral slope from that of basalt (Table 3.4). Sample 9B:0H:1A has ~15% higher reflectance relative to the basalt-only sample, as well as a steeper slope and decreased curvature. Sample 8B:0H:2A has lower reflectance than sample 9B:0H:1A (13-26% and 19-30%, respectively). The linear slope of sample 8B:0H:2A is steeper than that of sample 9B:0H:1A. All other basalt-anhydrite mixtures have increased reflectance and increasingly steep negative slopes with increased anhydrite abundance (Table 3.4). The hydration feature at 1.4 μm in samples 6B:0H:4A, 4B:0H:6A, and 2B:0H:8A has multiple minima, increasing in depth with increasing anhydrite abundance. Multiple other hydration features are present in these spectra.

4.2.3. Basalt-Hematite Mixtures

Sample 9B:1H:0A/T has ~8% higher reflectance than the basalt spectrum, and all basalt-hematite samples increase in reflectance with hematite proportion (Figure 3.4, Table 3.4). Sample 2B:8H:0A/T has higher reflectance than the hematite spectrum (17-24% and 14-21% reflectance, respectively). The basalt-hematite mixtures all have the hematite Fe^{3+} feature at 0.9 μm , increasing in depth with increasing hematite proportion (Figure 3.4). The basalt-hematite mixtures have a strong curvature past the 0.9 μm feature, though in samples 9B:1H:0A/T, 8B:2H:0A/T, and 6B:4H:0A/T, this curvature is observed at wavelengths short of this feature (Figure 3.4).

4.2.4. Hematite-Sulfate Mixtures

The hematite-anhydrite and hematite-thenardite mixtures all have higher reflectance than the hematite-only sample. The hematite-anhydrite mixtures have a larger spread of reflectance values than the basalt-anhydrite mixtures, while the hematite-thenardite mixtures have essentially the same range in reflectance as the basalt-thenardite mixtures (Figure 3.6, Table 3.4). The hematite-thenardite mixture samples show a nonlinear increase in reflectance and slight decrease of the spectral slope with increasing thenardite proportion. A curved spectral shape is observed in all of the hematite-thenardite mixture

samples (Figure 3.6). The hematite-anhydrite samples, in contrast, have different behavior depending on which endmember constitutes a larger portion of the sample (Figure 3.6). For example, the reflectance of samples 0B:8H:2A and 0B:6H:4A is 24-36% and 23-41%, respectively, while the reflectance of samples 0B:4H:6A and 0B:2H:8A is 23-76% and 25-69%, respectively. The spectra of samples 0B:2H:8A and 0B:4H:6A have similar slopes and concavity to the spectrum of anhydrite, and the slope and concavity of samples 0B:8H:2A and 0B:6H:4A are more similar to the spectrum of pure hematite (Figure 3.6; Table 3.4 and Table 3.5). Sample 0B:2H:8A has a lower reflectance than sample 0B:4H:6A.

The hematite-sulfate mixture spectra are all observed to have a hydration feature at 1.9 μm , with the depth of the feature generally increasing with increasing sulfate abundance. The 1.9 μm feature in the spectrum of 0B:8H:2T is more pronounced and narrower than the feature appears in the rest of the hematite-thenardite mixture spectra. All the hematite-sulfate mixture spectra show the characteristic hematite Fe absorption at 0.9 μm . The depth of this band generally decreases with increasing sulfate content, though this is more regular in the hematite-thenardite mixture spectra. The Fe band is modified by hydration features in the spectra of samples 0B:4H:6A and 0B:2H:8A, as evidenced by the shallow narrow dips at ~ 0.85 and ~ 0.95 μm within the larger Fe feature.

4.3. Ternary Mixtures

4.3.1. Basalt-Hematite-Thenardite Mixtures

The thenardite-bearing ternary mixture spectra have reflectance values ranging from 10-30%, overlapping in reflectance with hematite, and lower relative to thenardite (Figure 3.7). The spectra are observed to have increasing reflectance with decreasing basalt proportion, and for a set basalt proportion the sample reflectance increases as thenardite proportion increases. The spectra slope flattens with decreasing basalt proportion. The slope and overall shape is modulated by the relative proportions of hematite and thenardite; samples with a larger proportion of hematite have a more curved shape.

The 0.9 μm Fe^{3+} feature is seen in all the thenardite-bearing ternary mixture spectra. The depth of this feature increases with relative hematite proportion for a given basalt proportion (Figure 3.7). All spectra of basalt-hematite-thenardite mixtures with 20% or more thenardite have a hydration feature at 1.9 μm . Some samples also have a hydration feature at 1.4 μm , but its depth does not trend with thenardite abundance.

4.3.2. Basalt-Hematite-Anhydrite Mixtures

The reflectance of the anhydrite-bearing ternary mixtures ranges from 13-83%, generally falling between the spectra of hematite and anhydrite (Figure 3.7). The spectrum of sample 8B:1H:1A has lower reflectance than the hematite near hydration feature minima. Samples 2B:2H:6A and 4B:2H:4A have much higher reflectance (22-83% and 23-73%, respectively) than the other basalt-hematite-anhydrite samples; sample 2B:4H:4A has the next highest reflectance of the samples at 21-40% (Figure 3.7). None of the basalt-hematite-anhydrite mixture spectra have the curvature seen in the spectra of

basalt or hematite. For a given proportion of basalt, the linear slope steepens with increasing anhydrite abundance.

The 0.9 μm Fe^{3+} feature is seen in most of the anhydrite-bearing ternary mixture spectra; sample 8B:1H:1A may have an Fe^{3+} feature, but it is obscured by the strong spectral slope. The depth of the Fe^{3+} feature is affected by the anhydrite and basalt proportion (Figure 3.7). Narrow hydration features at ~ 0.85 and ~ 0.95 μm affect the Fe^{3+} feature, particularly for samples with 40% or more anhydrite.

5. Discussion

5.1. Hydration State of the Samples

Hydration features were observed in all sulfate-bearing mixtures. These features affect the spectra's minimum and average reflectance values, as well as the resultant slope fits. This highlights the difficulty of removing adsorbed water when working in humid environments such as Tennessee, where the samples were prepared. Within the thenardite series, the depth of the hydration features does not consistently vary with thenardite abundance – some low-thenardite samples have deeper hydration absorption features than near samples with greater sulfate proportion (e.g., 0B:8H:2T and 0B:6H:4T). This indicates that the thenardite was rehydrating either during sample preparation or transport.

Similarly, the anhydrite rehydrated between leaving the oven and before spectral measurement. The “anhydrite” is likely a mixture of bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and anhydrite, as was observed in the gypsum dehydration experiments of Harrison (2012). Harrison (2012) observed rehydration of their 63-125 μm grain size anhydrite to bassanite within a day at ambient conditions, though the rehydration reaction never reached gypsum. Other workers have observed similar hydration of ideally anhydrous sulfates and noted difficulty in keeping anhydrite and thenardite fully anhydrous (e.g., Cloutis et al., 2006; Bishop et al., 2004; De Angelis et al., 2021; Crowley, 1991).

Hydrated sulfate phases are not stable at Venus surface temperatures of $\sim 460^\circ\text{C}$. However, the wavelength region relevant to Venus surface observations (0.7-1.2 μm) is minimally affected by these hydration features (Figure 3.8) suggesting this data remains applicable to Venus studies.

Several of the anhydrite-bearing samples have higher reflectance than a sample with a larger anhydrite proportion (e.g., samples 0B:4H:6A and 0B:2H:8A; Figure 3.4). It is unclear why this occurred, but differences in grain shape between the anhydrite, thenardite, basalt, and hematite endmembers may have played a role. Anhydrite grains are more rectangular than grains of thenardite, basalt, and hematite, which are more spherical (Figure 3.9). The difference in grain shape may have led to inconsistent mixing of anhydrite through the sample container, affecting the distribution of anhydrite when the sample was poured into the sample cup for sample collection. Thus, while the sample by volume was, for example, 20% anhydrite, the top few cubic microns that were measured might have contained less than 20% anhydrite.

5.2. Venus Atmospheric Windows

The concentration of CO₂ in the Venus atmosphere restricts the collection of surface spectra to a narrow region near 1 μm . The well-established atmospheric windows are at 0.85, 0.9, 1.0, 1.12, and 1.18 μm (Figure 3.1). Using these windows as spectral bands understandably affects the measured spectra; the placement, number, and resolution of spectral bands determines whether a spectral feature is sampled, and how clearly the feature is resolved.

The Venus atmosphere windows limit observation the 0.9 μm Fe³⁺ absorption in hematite or the broad Fe-band in the dacite (Figure 3.8). The faint 1.0 μm Fe²⁺ absorption in the basalt is retained, though as a <0.01% change in reflectance in the continuum-removed spectrum. In contrast to the full spectrum, the reflectance of the downsampled basalt-hematite mixtures generally increases at longer wavelengths with the right edge of the Fe-band (Figure 3.8). Other trends observed for the full spectra generally hold when spectra are downsampled through the atmospheric windows to five bands (Figure 3.8). The mixture samples' reflectance increases with increasing sulfate or hematite proportion. The negative slope is retained in the basalt-anhydrite and basalt-thenardite mixtures' spectra, though the slopes change (Table 3.4).

5.3. Detection of Chemically Weathered Surfaces on Venus

5.3.1. Identifying Basalt

A primary aim of the upcoming missions to Venus is to characterize surface composition, specifically differentiating mafic and felsic surfaces, which is key to unraveling the planets' geologic history. The presence of secondary mineralogies, such as those investigated here, have the potential to obscure the underlying surface from spectral observation. Sulfate phases, in particular, increase the measured reflectance of basaltic surfaces, and can obscure diagnostic spectral features such as the Fe²⁺ absorption at ~1.0 μm .

Experiments have demonstrated that alteration phases will form as discontinuous coatings on the surface; the mixtures used in this study model the discontinuous aspect of alteration mineralogies. When taken as percent of the surface obscured by alteration material, the results here show that even low amounts (<20%) of secondary phases will affect the measured spectra. Furthermore, low amounts of alteration phases may result in detectable changes to reflectance spectra of basalt (Figure 3.10).

Previous studies of venusian surface spectra have utilized differences of 2% to 16% emissivity to identify compositional changes from VIRTIS 1.02 μm one-band emissivity data (Gilmore et al., 2015; Mueller et al., 2009; Smrekar et al., 2010; Stofan et al., 2016). At the lower end of this range (2%), only sample 9B:0H:1T cannot be differentiated from unaltered basalt (Figure 3.10). At the upper end of this range (16%), none of the basalt-hematite mixtures can be differentiated from the basalt-only spectrum. Sulfate presence is required in order to produce a 16% change in reflectance from basalt. The anhydrite-bearing samples require a lower sulfate proportion compared to the thenardite samples in order to have a 16% difference in reflectance relative to the basalt (Figure 3.10).

With a single spectral band it is impossible to fully differentiate basalt, basalt+alteration phases, and other igneous compositions, though reflectance regions of

relative likelihood can be made (Figure 3.11). Figure 3.11 shows regions of ‘basalt’ and ‘felsic’ reflectance as defined from emissivity data in Helbert et al. (2021); samples with alteration phases plot both in and between these regions. This study has one basalt endmember, however, work by Helbert et al. (2021) shows that mafic and felsic samples have discrete and relatively narrow emissivity ranges at Venus-relevant wavelengths, ~84-95 % and 62-70% emissivity (5-16% and 30-38% reflectance), respectively. If only the 1.01 μm band is considered, samples 9B:0H:1T, 9B:1H:0A/T, 8B:2H:0A/T, 8B:1H:1T, and 8B:0H:2T would all be classified as ‘mafic’, and none of the anhydrite series samples would be recognized as containing basalt. It can be seen from Figure 3.11 that fresh basalt can be differentiated from totally weathered basalt (the hematite-anhydrite and hematite-thenardite mixtures) with one-band data. None of the thenardite-hematite or anhydrite-hematite mixtures plot within the ‘mafic’ region in Figure 3.11, though these samples do overlap with the ‘felsic’ region.

Only the dacite sample falls in the ‘felsic’ region as defined using data from Helbert et al. (2021). This could be due to the limited number of samples (four) included in that study, or that those samples were cut slab surfaces rather than granular, or currently unquantified differences between hemispherical reflectance and high-temperature emissivity. More work exploring the spectral variability of felsic samples, particularly variability driven by grain size, is needed to further explore this discrepancy. Nonetheless, Figure 3.11 suggests that re-evaluation of previously collected one band data can be used to separate regions of fresh and minimally altered basalt from altered or felsic surfaces, but not to discriminate altered and felsic surfaces from each other.

The anhydrite and thenardite series spectra overlap in reflectance with the dacite and rhyolite (Figure 3.12). Significantly more of the anhydrite samples overlap in reflectance with the dacite and rhyolite, some samples have as little as 20% anhydrite. Mixtures with 60% thenardite approach the reflectance of dacite, but only the samples with 80% thenardite and the thenardite endmember have reflectance higher than the dacite (Figure 3.12).

Multiple spectral bands allow for the use of spectral features and continuum slope, expanding the variety of spectral analyses possible and reducing uncertainty. Over five spectral windows, only samples 9B:0H:1T and 2B:2H:6T have the same slope as the basalt (Table 3.4). All the anhydrite series samples and most samples with hematite have appreciably different slopes compared to the basalt, even with only 10% alteration mineral. The continuum slopes fit to just the Venus windows differ than those fit to the entire spectrum and have a much greater overlap in values (Figure 3.13). When considering the whole spectral range between 0.72-2.5 μm , the linear slope coefficient provides decent discrimination between basalt, basalt + alteration minerals, and the felsic samples (Figure 3.13a). This does not hold when downsampled through the Venus atmospheric windows (Figure 3.13d).

The first and second coefficients of two-term polynomials fit to the downsampled spectra can be used to separate basalt from the felsic samples and all mixtures except 9B:0H:1T (Figure 3.13e,f). Of course only one basalt and two felsic samples are shown in Figure 3.13, and other samples will have different slopes, however these samples suggest that unaltered surfaces should have different spectral shapes than the altered

samples. Regions of ‘basalt’ and ‘felsic’ values can be drawn for the coefficients, similar to what the one-band reflectance (Figure 3.13). The addition of more rock endmembers might develop a ‘fresh igneous’ region.

Caution should be taken if applying the polynomial or band fits to identify the presences of sulfate phases from noisier spectra. The data presented in this study have very low measurement uncertainty, meaning the nearly identical (<2% difference) reflectance of sample 2B:0H:8T and the dacite can be separated. The samples have different concavities, and so are distinguishable at the uncertainty of these laboratory spectra. With greater measurement uncertainty, as little as 1%, these spectra will be indistinguishable via any method.

The identification of altered surfaces, while not primary mineralogy, can be used for relative age dating. This has already been employed in concert with geomorphic analysis to identify young lava flows on Venus (Smrekar et al., 2010; Stofan et al., 2016). Changes to emissivity attributed to alteration have also been used to establish a relative emplacement order for geographically close lava flows (Brossier et al., 2021; D’Incecco et al., 2017; Klose et al., 1992). Alteration to anhydrite may be more readily detectable than alteration to thenardite in VNIR spectral data, due to the larger increase in reflectance at low anhydrite abundance. The larger range of reflectance values of the anhydrite-bearing samples, relative to the thenardite samples, also suggests that relative age dating via varying extents of alteration may be easier for anhydrite-bearing surfaces.

5.3.2. VenDI Reflectance Spectra

VenDI onboard the DAVINCI spacecraft will collect two bands of reflectance data – a narrow band at 0.98-1.03 μm , and a broad band at 0.74-1.04 μm – as it descends over Alpha Regio (Garvin et al., 2022). Differences in the band values, band ratio, and other manipulations will be used to identify compositional regions (Garvin et al., 2022). The results from this study suggest that these bands will be enough to separate fresh basalt from significantly altered basalt or felsic material, as fresh basalt has low reflectance (e.g., Figure 3.14).

In addition, fresh rocks and altered samples may also be differentiated via manipulation of these same bands. This is unexpected: the ability of VenDI data to differentiate felsic and altered material has until now been unclear (J. Filiberto, personal communication, February 2024). Figure 3.14 for example, shows the VenDI narrow band value vs. the broad band/narrow band ratio. The rock endmembers form a lower trend, and the mixtures plot above this line. Within this distribution, the thenardite and anhydrite mixtures have different trends, and at high sulfate abundance it is possible to use these trends to determine which sulfate is present in the sample (Figure 3.14).

There is some overlap between where the thenardite and anhydrite series plot, and with where the rock endmembers fall. To better constrain the uncertainties in these interpretations more fresh rock samples need to be analyzed. Nonetheless Figure 3.14 shows that the VenDI data may be used to differentiate fresh rock surfaces from those bearing alteration phases, provided a sufficiently robust reference spectral library.

5.4. Differentiating Alteration Phase Assemblages

5.4.1. Anhydrite and Thenardite

Both anhydrite and thenardite have high reflectance, and as a result, any proportion of either sulfate is enough to increase the measured reflectance from that of basalt or hematite. However, for a given sulfate abundance the anhydrite-bearing sample has a higher reflectance than the thenardite sample. This is not particularly surprising, as the pure anhydrite has a higher reflectance than the pure thenardite (Figure 3.4; Cloutis et al., 2006; De Angelis et al., 2021).

The increase in reflectance is nonlinear with increasing sulfate abundance in both the anhydrite and thenardite sample series, although the specific trends are different (Figure 3.15). This increase in reflectance is much clearer in thenardite series than the anhydrite series, as is the influence of hematite on sample reflectance. Thenardite series spectra increase in reflectance with hematite proportion for a given thenardite proportion, though this change is small (Figure 3.15). Hematite has a less clear-cut effect on the spectra of the anhydrite mixtures, though the spectra of the basalt-hematite-anhydrite and hematite-anhydrite mixtures all have higher reflectance than the basalt-anhydrite mixtures for a given anhydrite proportion. Only considering reflectance through the Venus atmospheric windows does not reduce the scatter. Given these spectra heavily sample the Fe^{3+} absorption from hematite, this indicates that the sulfates have a larger influence than hematite on overall sample reflectance (Figure 3.15).

The linear and polynomial fits to the spectra provide two parameterizations of spectral slope (Table 3.4 and Table 3.5; Figure 3.13). Visually, the spectral slopes of anhydrite and thenardite mixtures are similar (Figure 3.4), and this is also borne out in the fit coefficients (Table 3.4 and Table 3.5). When considering the entire wavelength range from 0.72-2.5 μm , the thenardite series spectra retain some of the concave shape of the basalt spectrum with as little as 20% basalt, while the anhydrite series spectra do not (Figure 3.4). This trend cannot differentiate anhydrite and thenardite mixtures, particularly at low sulfate abundance as there is complete overlap of the coefficient values (Figure 3.13a,b,c). The mild concave shape is also not seen when only considering Venus-relevant wavelengths (0.8-1.2 μm).

The slopes of the anhydrite and thenardite mixtures overlap, though the linear slope differs for the same proportion of anhydrite and thenardite (Table 3.4; Figure 3.13). The difference in the linear slope increases as sulfate proportion increases; the thenardite series spectra get flatter with increasing thenardite proportion, while the anhydrite series spectra retain a relatively negative slope (Figure 3.13a,d). However, there is significant overlap between the linear slopes of the anhydrite series, thenardite series, and basalt-hematite mixtures, reducing the utility of the linear slope for differentiating the sulfates (Figure 3.13a,d).

In practicality, determining the difference between anhydrite and thenardite in low abundance or when hematite is present will be difficult. The Fe^{3+} feature depth trends well with anhydrite proportion, and while depth decreases with increasing thenardite, this trend is not as clear as the anhydrite series (Figure 3.16). The Fe feature is generally greater in mixtures with thenardite relative to those with anhydrite, but this is not enough to distinguish the two sulfate series.

5.4.2. Hematite

Hematite has a lesser influence on the linear slope fit either to the entire spectrum (0.72-2.5 μm) or the Venus regions (0.8-1.2 μm) than either thenardite or anhydrite. The basalt-hematite mixtures have a consistent negative linear slope; thenardite presence flattens the spectral slope, while anhydrite steepens the slope (Table 3.4; Figure 3.13a,d).

All of the hematite-bearing samples have an Fe^{3+} absorption feature at 0.9 μm , making this feature incredibly useful for identifying hematite presence. The depth of this absorption is modulated by the relative proportion hematite and sulfates in a mixture; samples with more sulfate than hematite have a shallower feature. When downsampled through the Venus windows, the 0.9 μm feature is much harder to recognize, but is still present in the spectra of hematite-bearing samples, if only as a kink or knee at 0.9 μm . Hematite can be identified using a two-term polynomial fit to the linear-continuum-removed spectral channels that sample the Fe^{3+} feature (0.85, 0.9, and 1.0 μm ; Figure 3.17). The minima of this fit for hematite-bearing samples falls between 0.8-0.92 μm , and the minima for samples without hematite falls to longer wavelengths (Figure 3.17). The only samples for which this is not true contain more anhydrite than hematite (Samples 0B:4H:6A, 2B:2H:6A, and 4B:2H:4A), and the wavelength of the fit polynomial minimum does not otherwise trend with sample composition. The anhydrite series have a spread of fit minima locations, due to the stronger effect of anhydrite presence on the Fe band depth.

5.5. The Utility of Additional Spectral Channels

The atmosphere of Venus inherently limits the wavelengths that can be used to study surface composition. CO_2 is a strong absorber, and when compounded over the length of the atmosphere, leaves few transparencies (Knicely & Herrick, 2020). From the top of the atmosphere, well-established windows for surface spectra are at 0.85, 0.9, 1.0, 1.12, and 1.18 μm (Figure 3.1). These windows are closely grouped, and collectively are sensitive to primarily Fe-bearing compositions, though other less common crystal-field features also appear in this region (Burns, 1993).

As a result of the limited number of atmospheric transparencies, venusian surface spectra are band-limited. The limited number of spectral bands compounds difficulties in spectral classification and identification, and additional bands could reduce uncertainty. Many statistical methods of spectral analysis – such as maximum likelihood, spectral angle mapper, or partial least squares regressions – increase in accuracy with additional spectral bands.

Increasing the number of spectral bands can be done two ways: measuring additional windows at new wavelengths or measuring multiple bands within a window. The atmospheric windows are each several tens of nanometers wide and vary in width (Figure 3.1; Table 3.3). The 1.0 window, for example, is ~ 70 nm wide, from 0.96-1.03 μm (Knicely & Herrick, 2020); VEM, onboard VERITAS and EnVision, has two bands in this window centered at 0.99 and 1.02 μm (Helbert et al., 2020).

Recent results using data from WISPR utilized a previously unrecognized atmospheric transparency at ~ 0.77 μm (Lustig-Yaeger et al., 2023; Wood et al., 2022; shown in Figure 3.1 and Figure 3.18). Knicely and Herrick (2020) predict additional atmospheric transparencies for surface emissivity at ~ 0.94 and ~ 1.14 μm . Lowering the spectrometer

relative to the ground, particularly below Venus' cloud deck, increases the number of useable wavelengths; a narrow window at 1.27 μm is possibly usable if the detector is less than 12 km above the surface (Knically & Herrick, 2020). Unfortunately, CO_2 increases in opacity at wavelengths longward of 2 μm through radar wavelengths (cm – m scale), and so identifying transparencies in the MIR is unlikely (Knically & Herrick, 2020).

Figure 3.18 shows spectra at several spectral samplings to illustrate the utility of additional spectral bands. With VEM's 0.99 and 1.02 μm bands, for example, the ~ 0.95 μm OH^- feature in the anhydrite is resolved, and distinguishable from the Fe^{3+} features (though anhydrite would not have the ~ 0.95 μm OH^- feature on the surface of Venus). Similarly, adding a spectral band at 0.77 μm greatly increases the visibility of shallow 0.9 μm Fe^{3+} absorptions in samples like 6B:2H:2A and 4B:2H:4T. The broad Fe^{2+} feature in the dacite is also easier to identify with a spectral band at 0.77 μm , which provides a left edge to the feature, differentiating it from a spectral continuum. Although this study did not look at the utility of statistical methods of identifying sulfate presence, these methods would undoubtedly benefit from additional spectral bands.

5.6. Effect of High Temperature

The data in this study are most directly applicable in the interpretation of VenDI reflectance data. These data are less useful for understanding VEM/VenSpec-M data, both of which will collect high-temperature emissivity data. While hemispherical reflectance data can be converted via Kirchhoff's law to emissivity, this conversion does not address transmission nor the effects of temperature on the spectra (Nicodemus, 1965). Conversion between reflectance and emissivity has not been validated for high-temperature spectra in the VNIR, and there is currently a poor understanding how elevated temperatures will affect the spectral behavior of non-iron-bearing compositions, such as the sulfate phases.

The MIR emissivity of thenardite and anhydrite changes with variations in temperature between 100 and 1000 $^{\circ}\text{C}$. The fundamental SO_4 features near 8.8 and 16 μm (1130 and 600 cm^{-1}) widen and a shift to longer wavelengths with increasing temperature (Comodi et al., 2021; Vassallo & Finnie, 1992). The thenardite MIR spectra in Vassallo & Finnie (1992) also show a feature near 10 μm (990 cm^{-1}) that appears only in spectra taken between 300 and 800 $^{\circ}\text{C}$. The effect of low temperatures on thenardite VNIR spectra has also been studied (De Angelis et al., 2021; Comodi et al., 2021). Decreasing temperature produced an increase in reflectance, as well as minor changes in band depth and width, and position in the 3.6, 3.8, and 4-5 μm SO_4 features (De Angelis et al., 2021; Comodi et al., 2021).

There are currently no studies that address high-temperature VNIR spectra of thenardite. Preliminary results from Alemanno et al. (2024) comparing room temperature hemispherical reflectance and high temperature emissivity data of basalt and gypsum/anhydrite (Figure 3.19) suggest that temperature may have minimal effect on the spectral behavior of the samples in this study. However, Alemanno et al. (2024) did observe changes with temperature in the spectra of calcite-bearing samples, with new features apparent between 0.8-1.2 μm in the emissivity spectra.

Anhydrous iron-free sulfate phases, similar to calcite, lack spectral features at wavelengths below 1.2 μm , but may have overtones of fundamental bands in the VNIR region that only become apparent at elevated temperatures. While Alemanno et al. (2024) did not observe additional features in the high-temperature spectrum of gypsum, a transient temperature-dependent feature has been observed in the MIR spectra of thenardite (Vassallo & Finnie, 1992). This MIR feature suggests that thenardite could have similarly temperature-dependent features in the VNIR region at elevated temperatures. If such features appeared at useful wavelengths for Venus, they could allow for the discrimination of anhydrite and thenardite.

6. Conclusions

Determining surface composition is a key goal of the upcoming NASA and ESA missions to Venus, and a critical step in unraveling the planet's evolution, but is complicated by the thick atmosphere. The limited atmospheric windows for surface observation tightly constrain the wavelengths and spectral features that can be used in spectral analyses. Mafic and felsic surfaces have discrete emissivity ranges when viewed through the five atmospheric windows. However, low volumes (10-20%) of spectrally bland and optically transparent geologically-relevant alteration phases such as anhydrite and thenardite will affect measured spectra. The presence of anhydrite and thenardite increases surface reflectance of altered surfaces such that they overlap with the range of felsic surface reflectance. With one-band spectral data, mafic surfaces may be differentiated from altered and felsic surfaces, but felsic material and altered basalts cannot be distinguished.

Multi-band spectral data can differentiate between altered basalts and felsic surfaces. The spectral shapes of basalt, dacite, and rhyolite are distinct compared to the mixtures containing hematite, anhydrite, or thenardite. While the reflectance of sulfate-bearing samples overlaps with the felsic samples, parameterizations such as slope and two-term polynomial fits to the continuum provide methods to differentiate the felsic samples and basalts with alteration phases.

The results of this study suggest that it may be possible for upcoming missions to distinguish the composition and abundance of alteration phases. Constraining the extent of surface alteration would provide a method of determining local relative exposure ages. Low volumes of discontinuous anhydrite, thenardite, or hematite produce measurable changes to the spectra, and the presence of hematite+sulfate only increases the surface reflectance relative to a single phase. Increases in reflectance can therefore be interpreted as an increase in the extent of alteration that would correspond to an increased time of alteration.

The anhydrite and thenardite mixes have overlapping reflectance ranges, but the sulfates produce moderately distinct slopes and spectral shapes, particularly in combination with hematite. Identifying alteration mineralogies could help constrain the composition of the altering basalt, as experiments have indicated the sulfate species is dependent on the basalt's alkaline content. Additionally, anhydrite has a larger effect on sample reflectance than thenardite, and to a certain extent can obscure the hematite Fe^{3+} absorption feature, suggesting that anhydrite-bearing surfaces may be more readily detected in future mission datasets than those altering to thenardite.

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Appendix C

Table 3.1 Sample names and endmember proportions

Name	Basalt	Volume %	
		Hematite	Thenardite
0B:0H:10T	0	0	100
2B:0H:8T	20	0	80
4B:0H:6T	40	0	60
6B:0H:4T	60	0	40
8B:0H:2T	80	0	20
9B:0H:1T	90	0	10
8B:1H:1T	80	10	10
6B:2H:2T	60	20	20
4B:4H:2T	40	40	20
4B:2H:4T	40	20	40
2B:6H:2T	20	60	20
2B:4H:4T	20	40	40
2B:2H:4T	20	20	60
0B:8H:2T	0	80	20
0B:6H:4T	0	60	40
0B:4H:6T	0	40	60
0B:2H:8T	0	20	80

Name	Basalt	% Volume	
		Hematite	Anhydrite
0B:0H:10A	0	0	100
2B:0H:8A	20	0	80
4B:0H:6A	40	0	60
6B:0H:4A	60	0	40
8B:0H:2A	80	0	20
10B:0H:1A	90	0	10
8B:1H:1A	80	10	10
6B:2H:2A	60	20	20
4B:4H:2A	40	40	20
4B:2H:4A	40	20	40
2B:6H:2A	20	60	20
2B:4H:4A	20	40	40
2B:2H:4A	20	20	60
0B:8H:2A	0	80	20
0B:6H:4A	0	60	40
0B:4H:6A	0	40	60
0B:2H:8A	0	20	80

Name	Basalt	% Volume	
		Hematite	Anhydrite/ Thenardite
0B:10H:0A/T	0	100	0
2B:8H:0A/T	20	80	0
4B:6H:0A/T	40	60	0
6B:4H:0A/T	60	40	0
8B:2H:0A/T	80	20	0
9B:1H:0A/T	90	10	0
Basalt	100	0	0

Table 3.2 Rock endmember bulk compositions and phase assemblages

Bulk Composition			
	Basalt	Dacite	Rhyolite
SiO ₂	47.43 (0.57)	67.56 (0.97)	73.46 (1.83)
TiO ₂	3.70 (0.24)	0.40 (0.06)	0.10 (0.03)
Al ₂ O ₃	13.29 (0.38)	15.31 (0.43)	15.18 (1.28)
MgO	5.53 (0.27)	2.20 (0.10)	0.39 (0.12)
CaO	9.84 (0.20)	4.37 (0.21)	1.11 (0.19)
MnO	0.22 (0.01)	0.09 (0.01)	0.05 (0.01)
FeO	13.79 (0.46)	3.06 0.26	0.93 0.18
Na ₂ O	2.88 (0.19)	3.98 (0.22)	2.79 (0.20)
K ₂ O	0.76 (0.05)	2.04 (0.09)	4.33 (0.26)
Total	98.28 (0.44)	99.45 (0.60)	98.51 (1.41)

Phase Assemblage			
	Basalt	Dacite	Rhyolite
Glass	57	70	80
Pyx	11	17	0
Feld	24	9	14
Apatite	0	1	0
Quartz	0	1	5
Oxides	4	1	1
Olivine	3	0	0
Total	100	100	100

Note. Bulk compositions measured via EMPA; Phase assemblages from point counting via SEM. Methods in Leight et al. (2022).

Table 3.3 Established Venus Atmospheric Windows

Wavelength, μm	0.85	0.9	1.0	1.095	1.18
Width, approx., μm	0.04	0.04	0.035	0.012	0.012

Note. From Baines et al. (2000) and Knicely & Herrick (2020).

Table 3.4 Sample average reflectance and linear slope fit**Whole Spectrum**

Sample	Slope	Avg % R	Sample	Slope	Avg % R	Sample	Slope	Avg % R
0B:0H:10T	-4	78	0B:0H:10A	-19	78	0B:10H:0T/A	-21	17
2B:0H:8T	-15	33	2B:0H:8A	-18	52	2B:8H:0T/A	-20	20
4B:0H:6T	-19	24	4B:0H:6A	-19	44	4B:6H:0T/A	-20	17
6B:0H:4T	-24	17	6B:0H:4A	-24	24	6B:4H:0T/A	-23	14
8B:0H:2T	-28	13	8B:0H:2A	-27	17	8B:2H:0T/A	-23	12
9B:0H:1T	-15	11	9B:0H:1A	-17	25	9B:1H:0T/A	-22	12
8B:1H:1T	-23	13	8B:1H:1A	-23	21	0B:8H:2T	-22	23
6B:2H:2T	-22	17	6B:2H:2A	-23	25	0B:6H:4T	-18	26
4B:4H:2T	-23	19	4B:4H:2A	-21	33	0B:4H:6T	-16	29
4B:2H:4T	-19	20	4B:2H:4A	-23	64	0B:2H:8T	-13	39
2B:6H:2T	-21	22	2B:6H:2A	-23	27	0B:8H:2A	-21	32
2B:4H:4T	-20	24	2B:4H:4A	-22	34	0B:6H:4A	-22	36
2B:2H:6T	-16	27	2B:2H:6A	-26	73	0B:4H:6A	-24	68
Basalt	-15	10	Rhyolite	-21	60	0B:2H:8A	-23	32
			Dacite	-7	33			

Venus Windows

Sample	Slope	Avg % R	Sample	Slope	Avg % R	Sample	Slope	Avg % R
0B:0H:10T	7	79	0B:0H:10A	-5	86	0B:10H:0T/A	33	20
2B:0H:8T	-15	35	2B:0H:8A	-11	57	2B:8H:0T/A	45	22
4B:0H:6T	-23	26	4B:0H:6A	-16	48	4B:6H:0T/A	35	20
6B:0H:4T	-33	19	6B:0H:4A	-29	27	6B:4H:0T/A	5	16
8B:0H:2T	-41	16	8B:0H:2A	-35	19	8B:2H:0T/A	-13	15
9B:0H:1T	-29	11	9B:0H:1A	-22	27	9B:1H:0T/A	-19	14
8B:1H:1T	-19	15	8B:1H:1A	-20	24	0B:8H:2T	50	25
6B:2H:2T	1	19	6B:2H:2A	-7	28	0B:6H:4T	48	28
4B:4H:2T	24	21	4B:4H:2A	4	36	0B:4H:6T	41	31
4B:2H:4T	-1	22	4B:2H:4A	-5	70	0B:2H:8T	25	40
2B:6H:2T	48	23	2B:6H:2A	33	29	0B:8H:2A	32	34
2B:4H:4T	32	26	2B:4H:4A	8	38	0B:6H:4A	24	40
2B:2H:6T	12	29	2B:2H:6A	-4	80	0B:4H:6A	1	74
Basalt	-31	11	Rhyolite	-5	67	0B:2H:8A	2	66
			Dacite	-20	35			

Note. Whole-spectrum slopes fit to regions in **Figure 2** of maximum-normalized spectra. Average % reflectance is of non-normalized spectra.

Table 3.5 Two-term polynomial fit coefficients fit to whole spectrum

Sample	c ₁ term	c ₂ term	b	Sample	c ₁ term	c ₂ term	b	Sample	c ₁ term	c ₂ term	b
0B:0H:10 T	-8	19	87	0B:0H:10 A	-18	36	81	0B:10H:0T/ A	17	-81	169
2B:0H:8T	3	-22	115	2B:0H:8A	-5	-2	104	2B:8H:0T/A	18	-85	172
4B:0H:6T	5	-35	122	4B:0H:6A	-2	-13	110	4B:6H:0T/A	17	-80	168
6B:0H:4T	8	-49	130	6B:0H:4A	4	-37	124	6B:4H:0T/A	15	-75	158
8B:0H:2T	11	-60	137	8B:0H:2A	8	-50	131	8B:2H:0T/A	13	-70	150
9B:0H:1T	8	-40	122	9B:0H:1A	4	-28	118	9B:1H:0T/A	12	-65	145
8B:1H:1T	12	-64	144	8B:1H:1A	5	-40	127	0B:8H:2T	21	-93	178
6B:2H:2T	13	-67	151	6B:2H:2A	6	-42	132	0B:6H:4T	18	-82	169
4B:4H:2T	17	-81	167	4B:4H:2A	6	-41	134	0B:4H:6T	16	-72	161
4B:2H:4T	12	-59	144	4B:2H:4A	-12	19	89	0B:2H:8T	12	-53	145
2B:6H:2T	20	-89	175	2B:6H:2A	14	-71	162	0B:8H:2A	15	-73	162
2B:4H:4T	17	-77	165	2B:4H:4A	8	-48	140	0B:6H:4A	9	-54	148
2B:2H:6T	11	-55	145	2B:2H:6A	-19	39	76	0B:4H:6A	-13	20	90
Basalt	8	-40	121	Rhyolite	-17	34	81	0B:2H:8A	-7	0	104
				Dacite	-3	3	95				

Note. Fits of $r = c_1\lambda^2 + c_2\lambda + b$ to regions in **Figure 2** of maximum-normalized spectra.

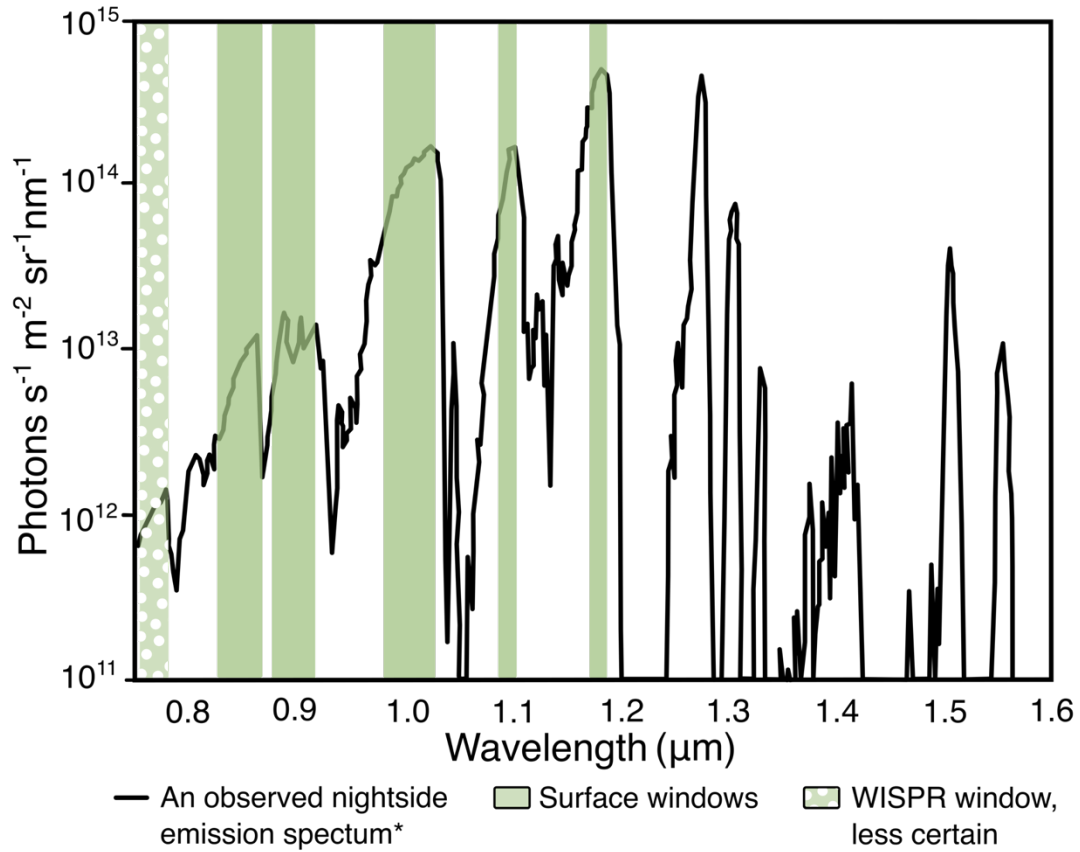


Figure 3.1 Venus Atmospheric Windows.

Nighttime emissivity spectrum from the top of the Venus atmosphere, adapted from Helbert et al. (2020), Baines et al. (2000) and Knicely & Herrick (2020). Solid green regions show well-established surface observation windows.

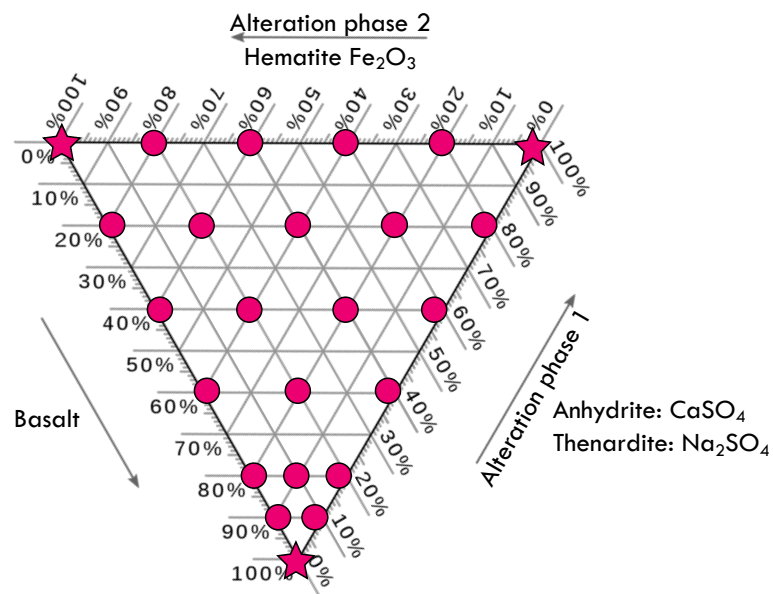


Figure 3.2 Sample Mixing Scheme

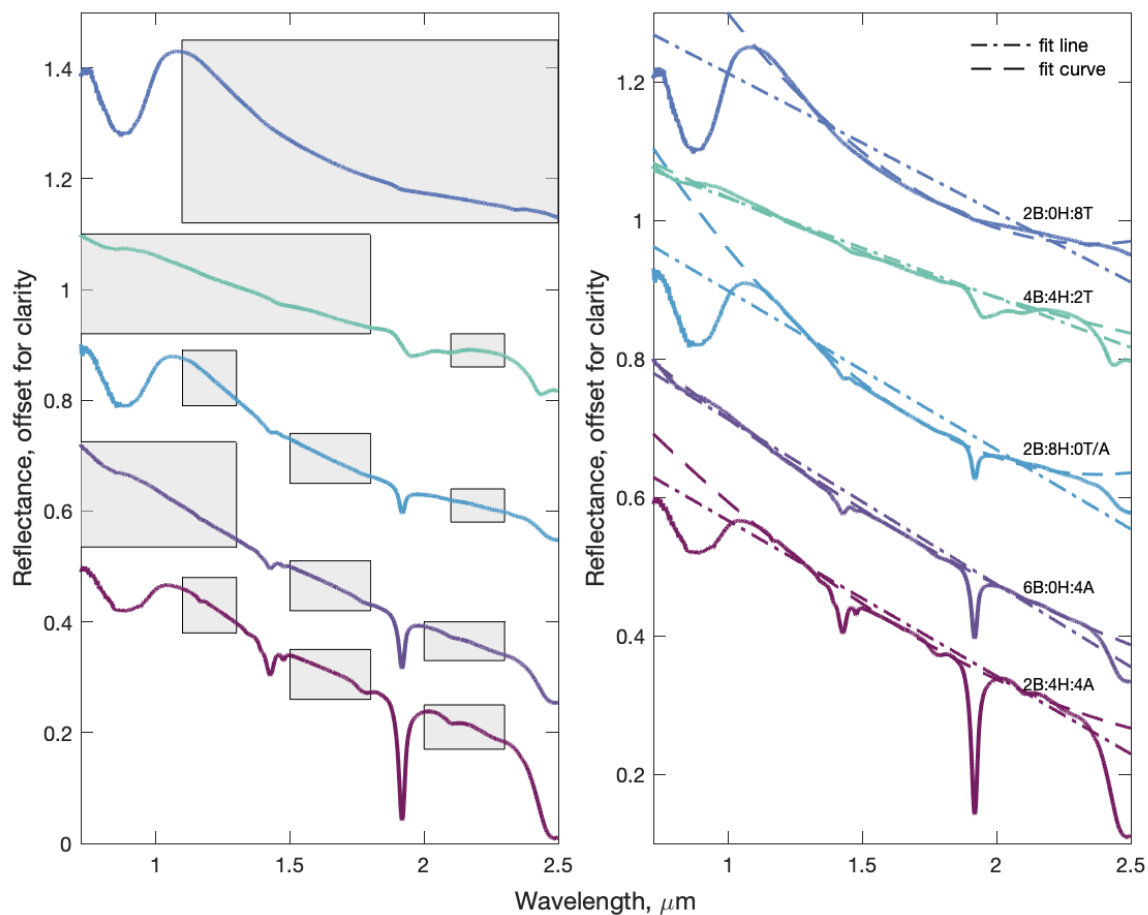


Figure 3.3 Regions used for fitting linear slopes and whole-spectra two-term polynomials

Grey boxes show regions of spectra used for linear and polynomial fits. Regions were chosen to exclude large absorption features. The same spectra are shown in the left and right panels.

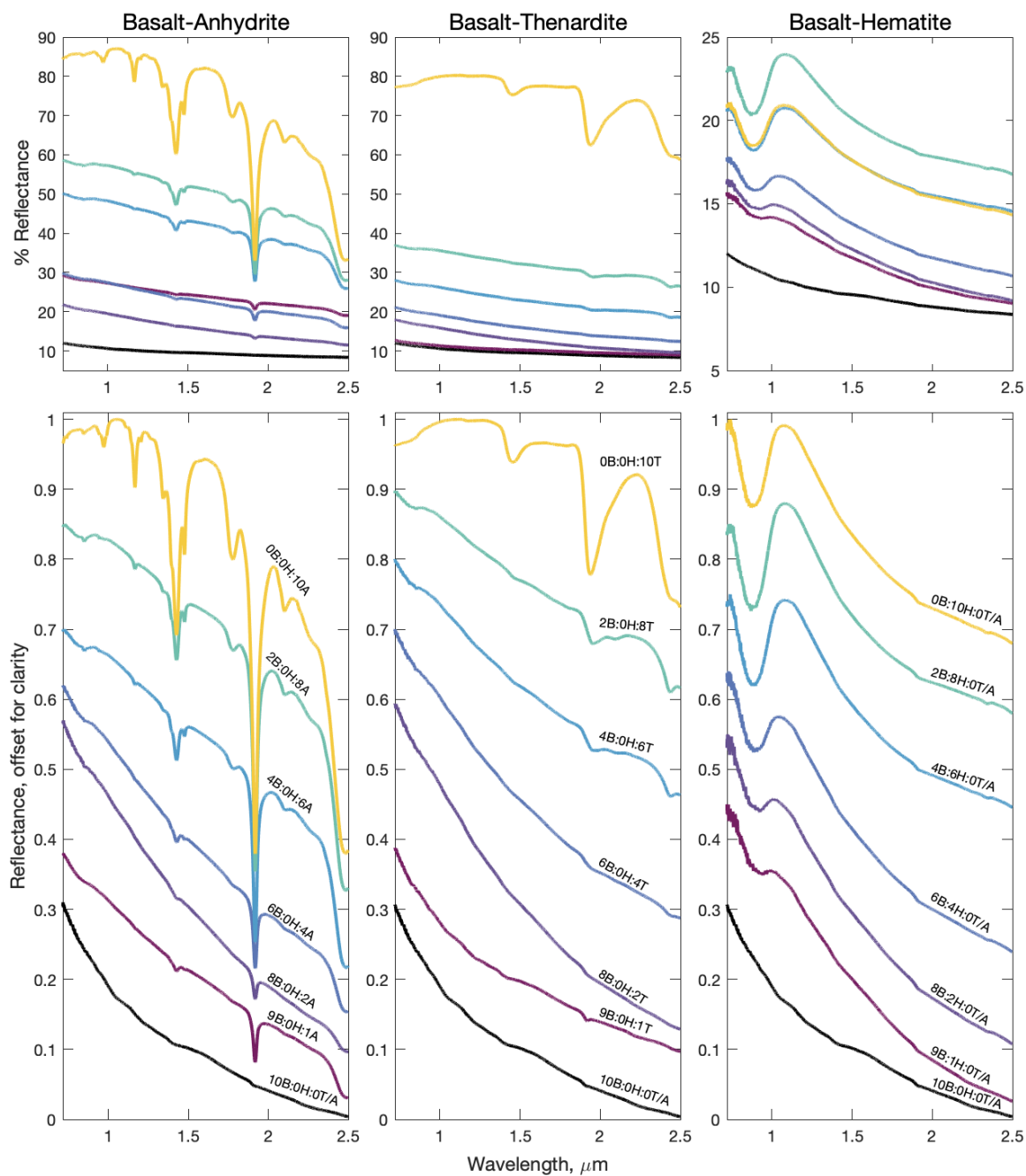


Figure 3.4 Binary Mixture Spectra

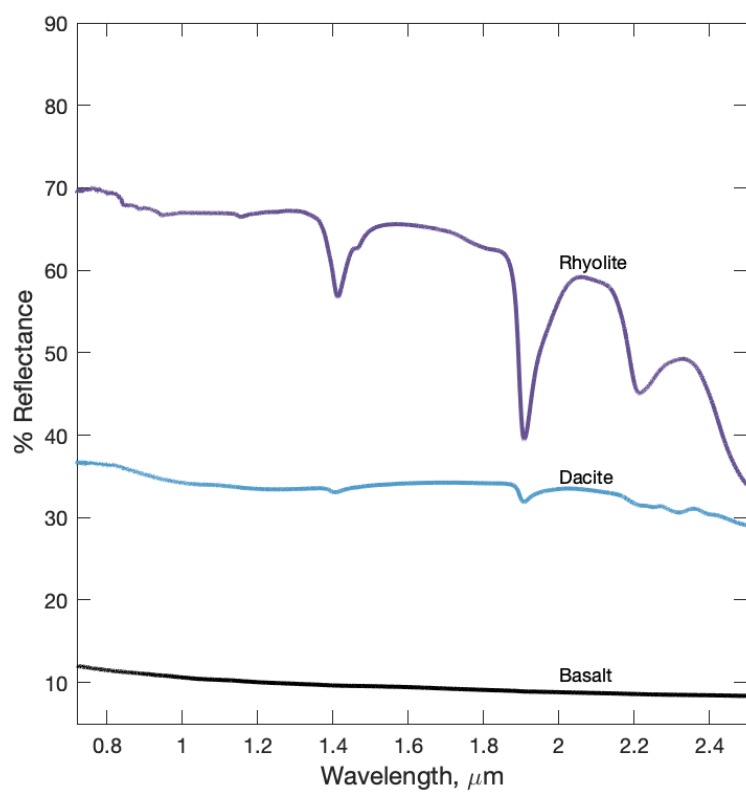


Figure 3.5 Rock Endmember Spectra

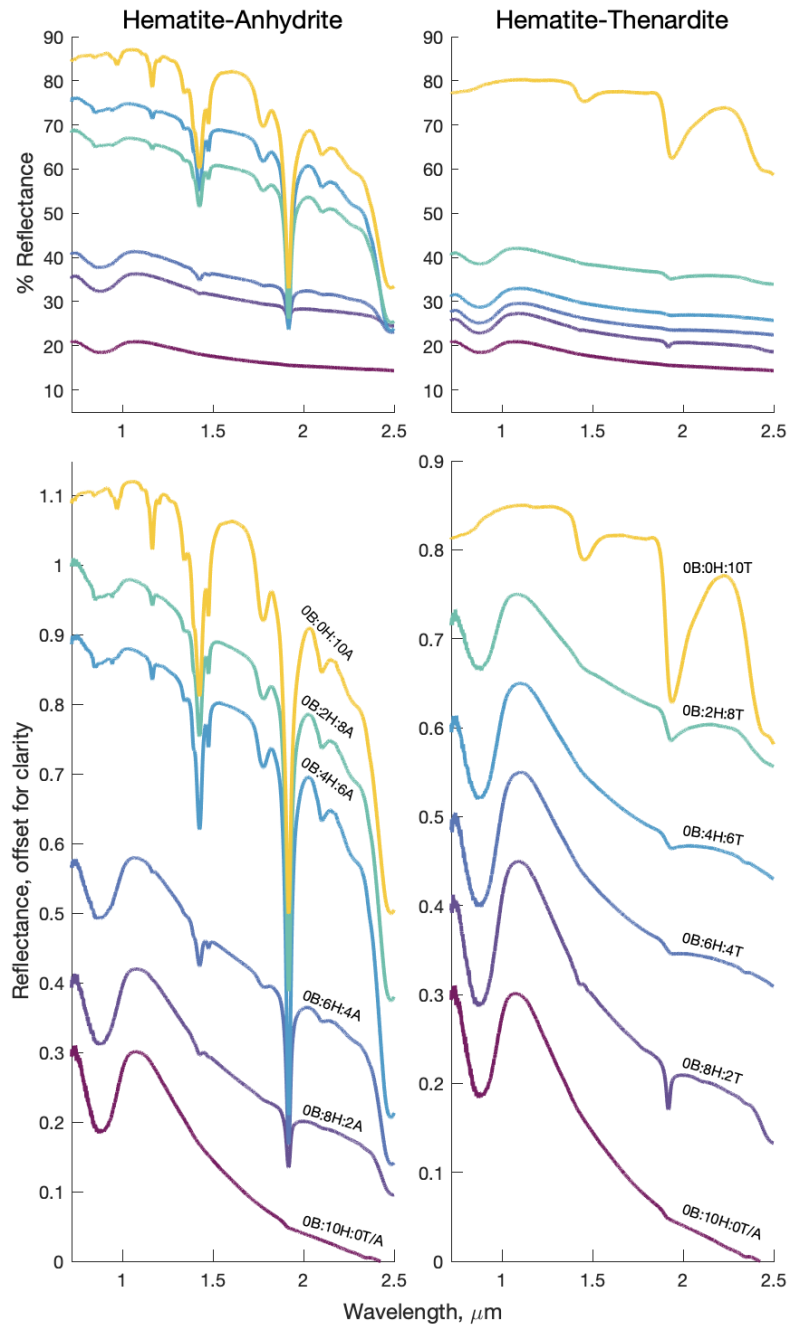


Figure 3.6 Hematite-Sulfate Mixture Spectra

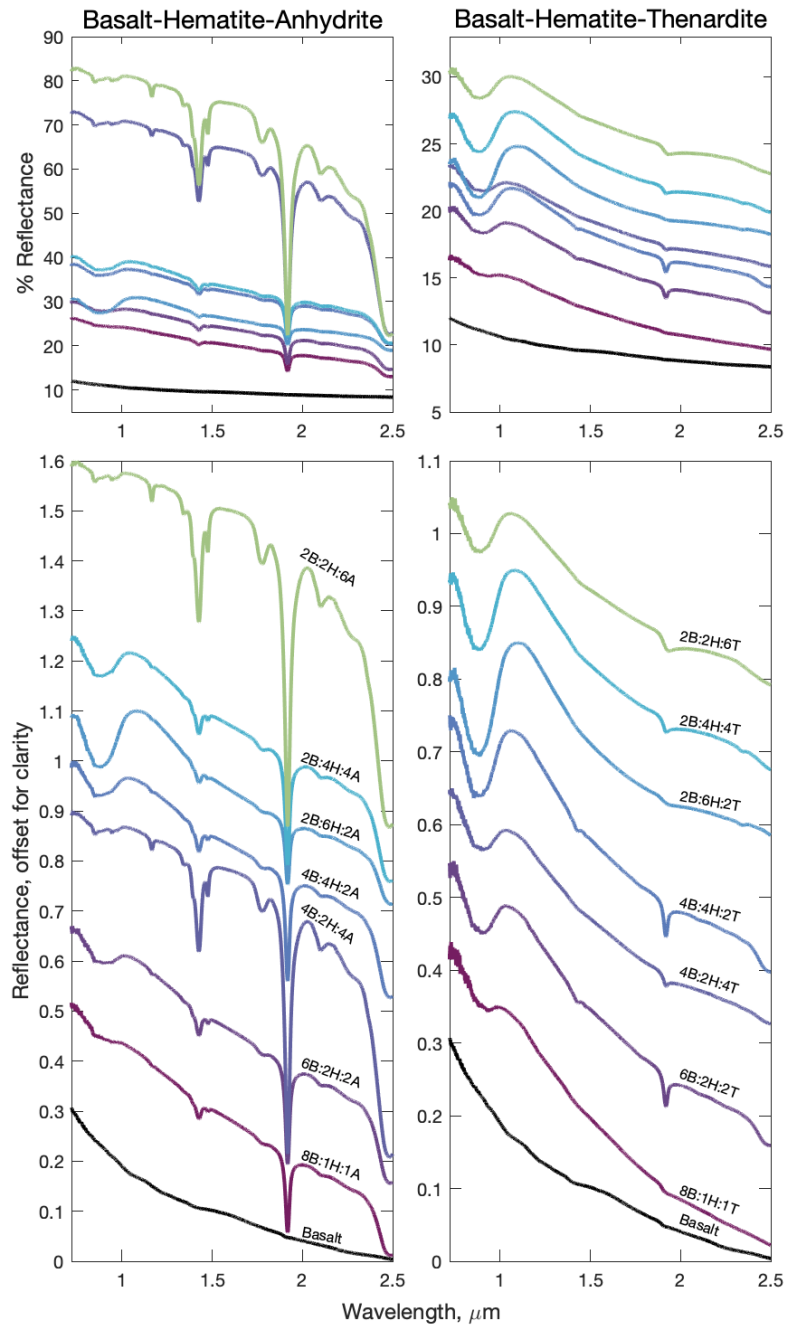


Figure 3.7 Ternary Mixture Spectra

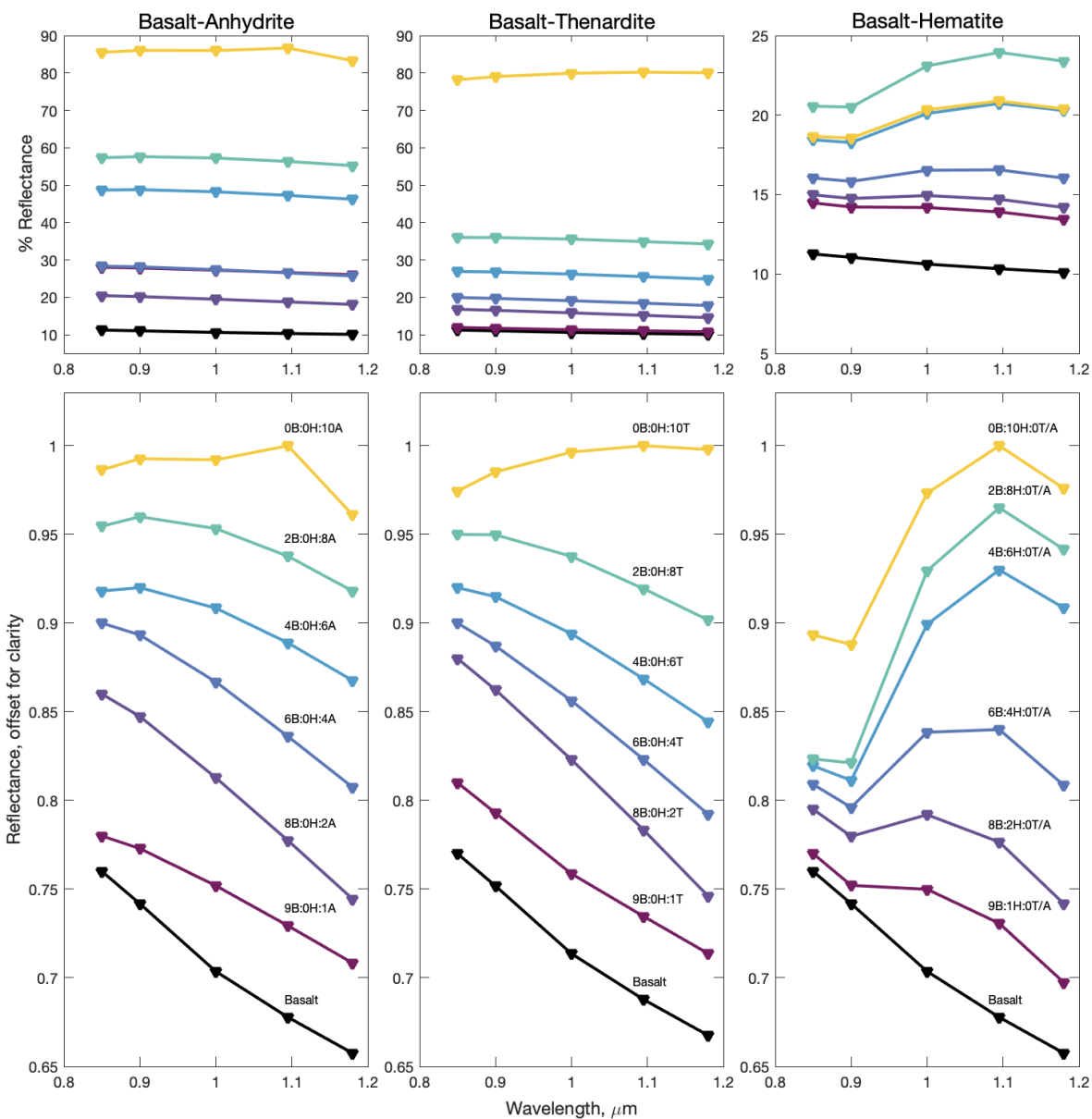


Figure 3.8 Binary Mixture Spectra, Venus Atmospheric Windows



6B:2H:2T



6B:2H:2A



Basalt



Hematite



Thenardite



Anhydrite

Figure 3.9 Sample Pictures showing grain shape.

Pictures of samples 6B:2H:2T and 6B:2H:2A, and outlines of grains of basalt, hematite, thenardite, and anhydrite from the images. Grain outlines were produced in inkscape.

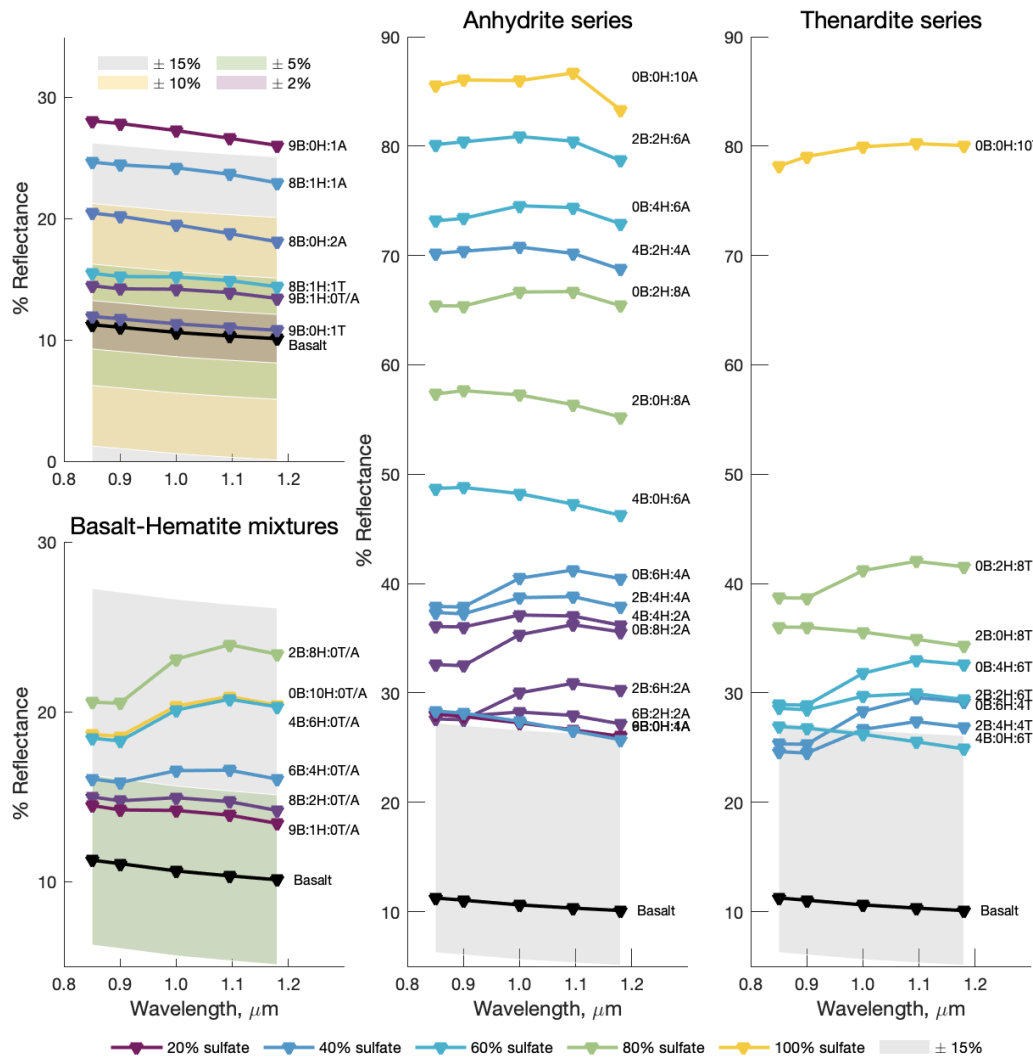


Figure 3.10 Basalt spectrum with 2, 5, 10, and 15% ‘uncertainty’

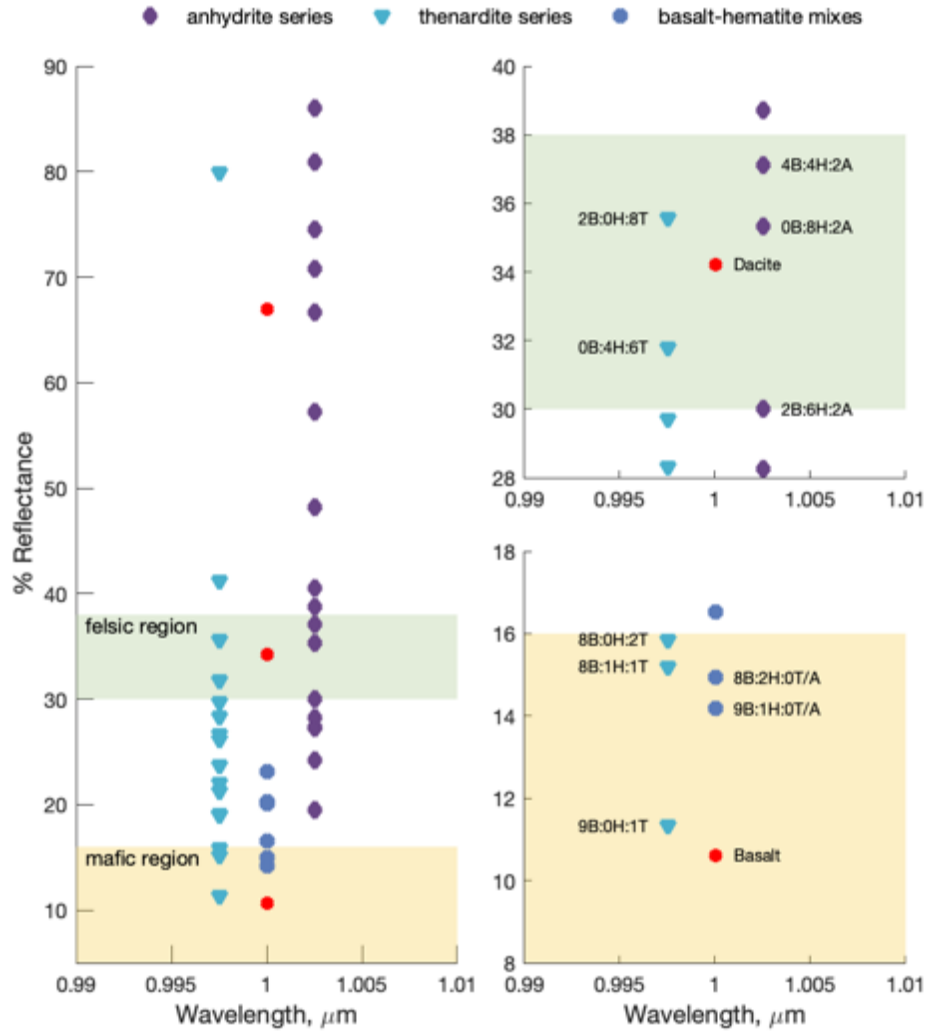


Figure 3.11 Plausible 1.0 μm band composition reflectance regions

Plausible reflectance regions suggestive of mafic and felsic compositions calculated from Helbert et. al., (2020).

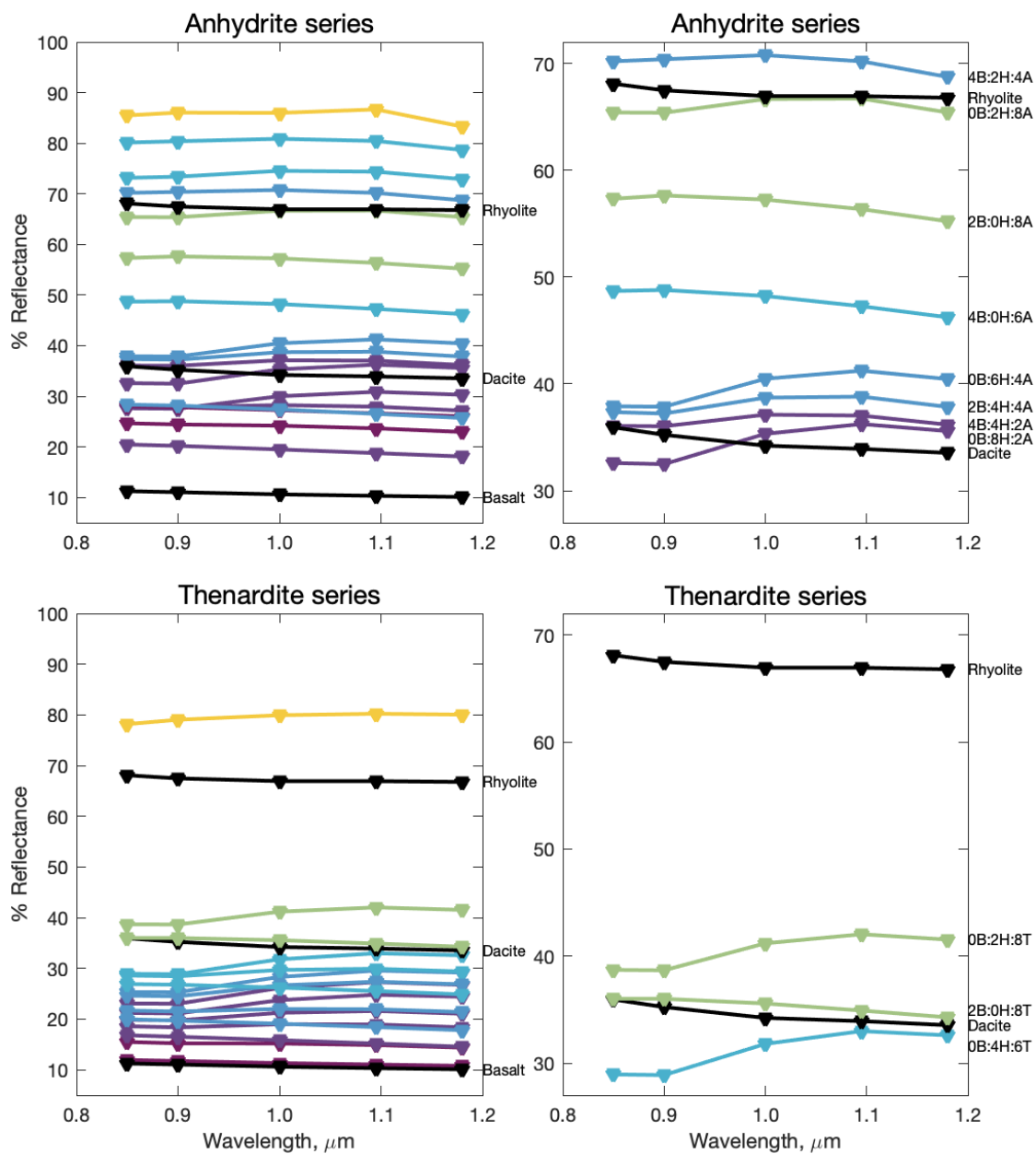


Figure 3.12 Felsic vs Mixture Venus-Window Spectra

Color indicates amount of sulfate present.

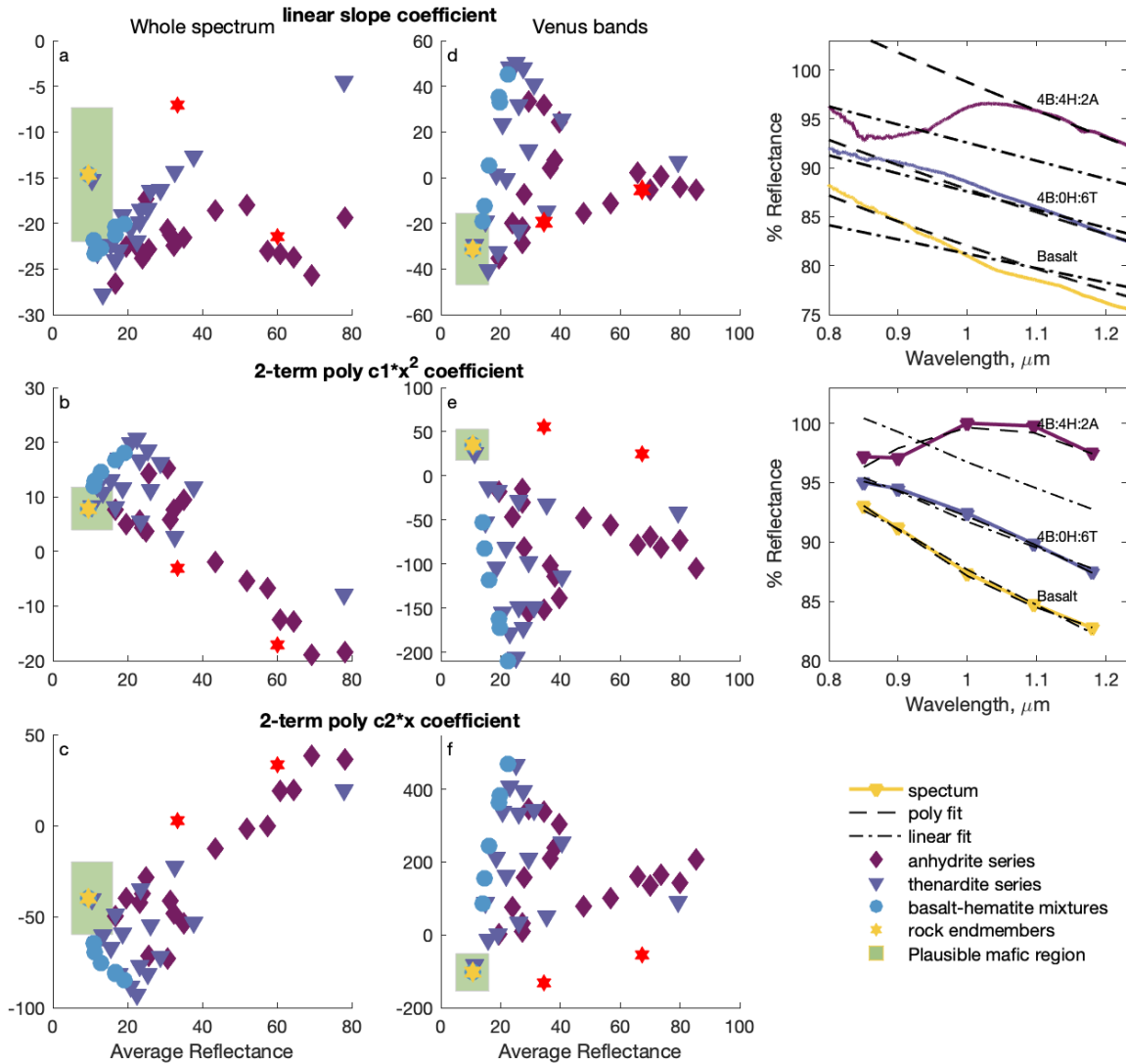


Figure 3.13 Continuum slope values

Plausible regions suggestive of mafic compositions calculated from basalt emissivity reported in Helbert et. al., (2020); vertical length of the regions was set to the plus or minus half of the basalt's coefficient value.

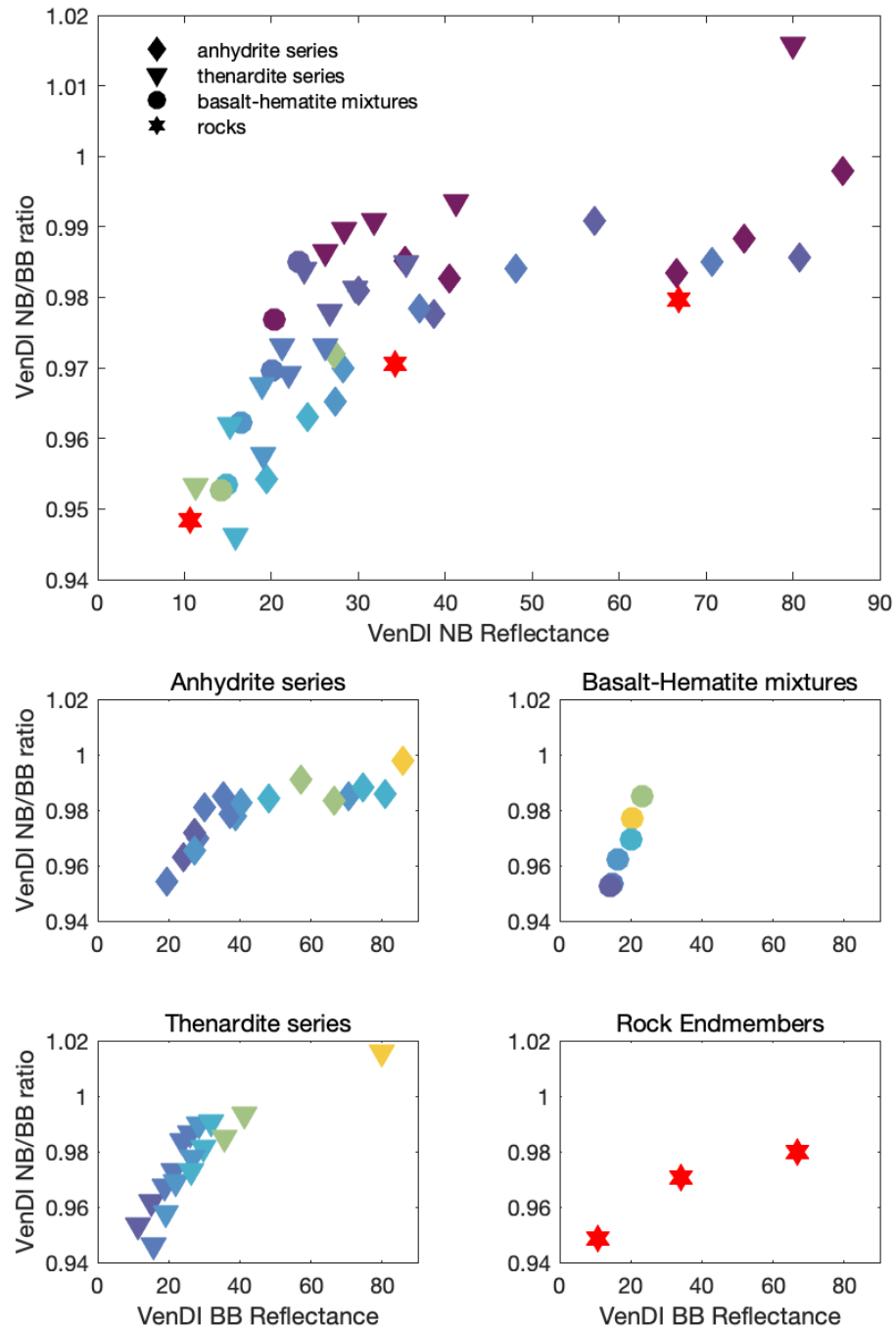


Figure 3.14 Manipulation of Modeled VenDI spectra for alteration detection

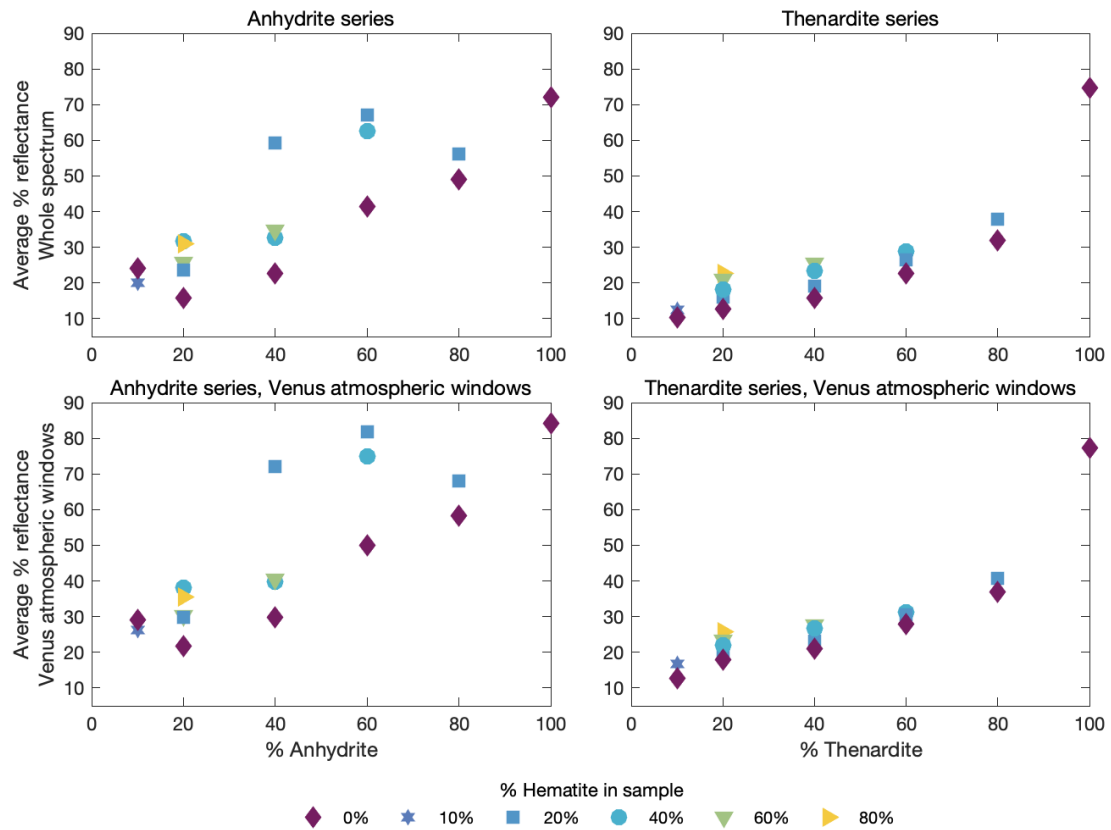


Figure 3.15 Average % Reflectance of Sulfate Series Spectra

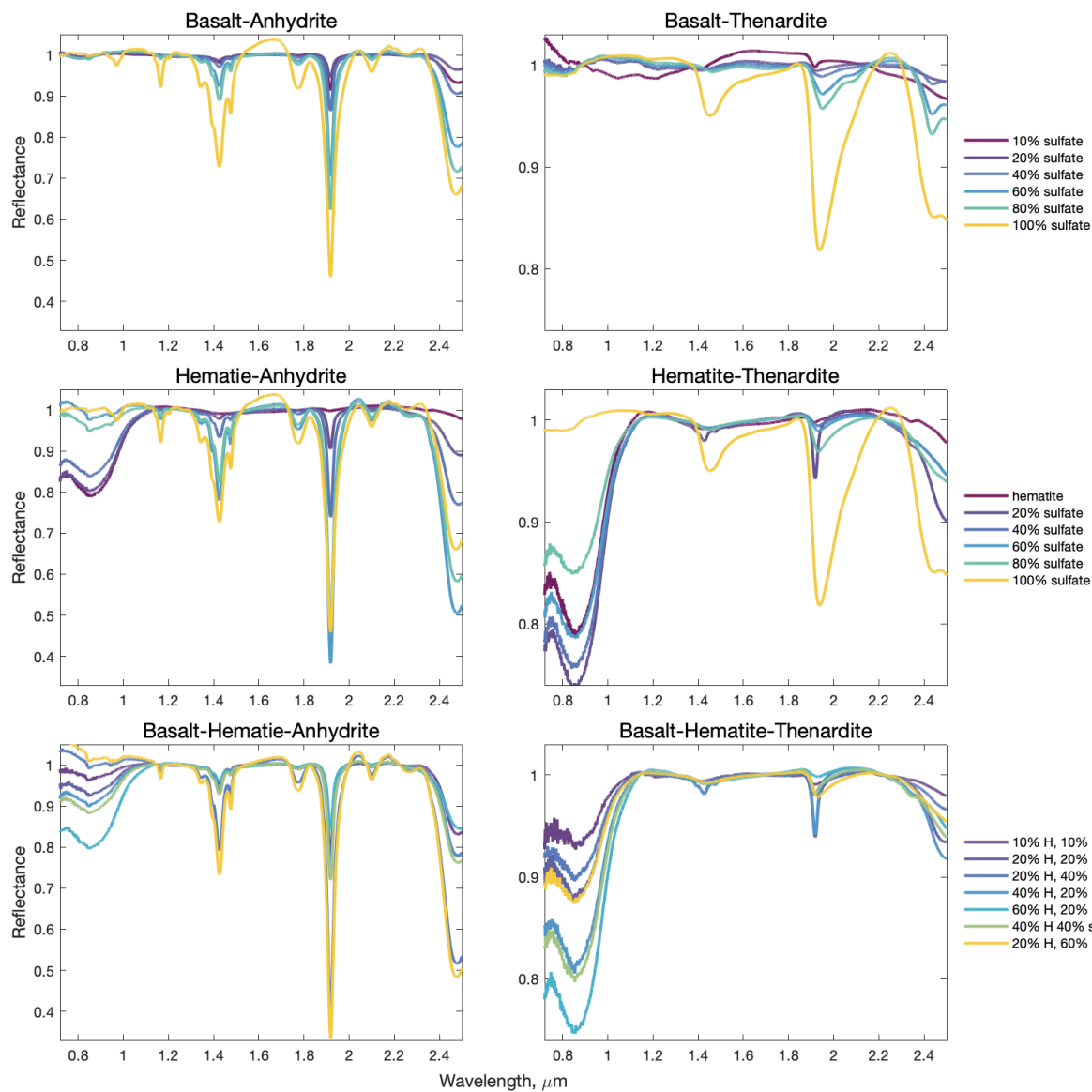


Figure 3.16 Polynomial-continuum removed basalt-sulfate mixtures

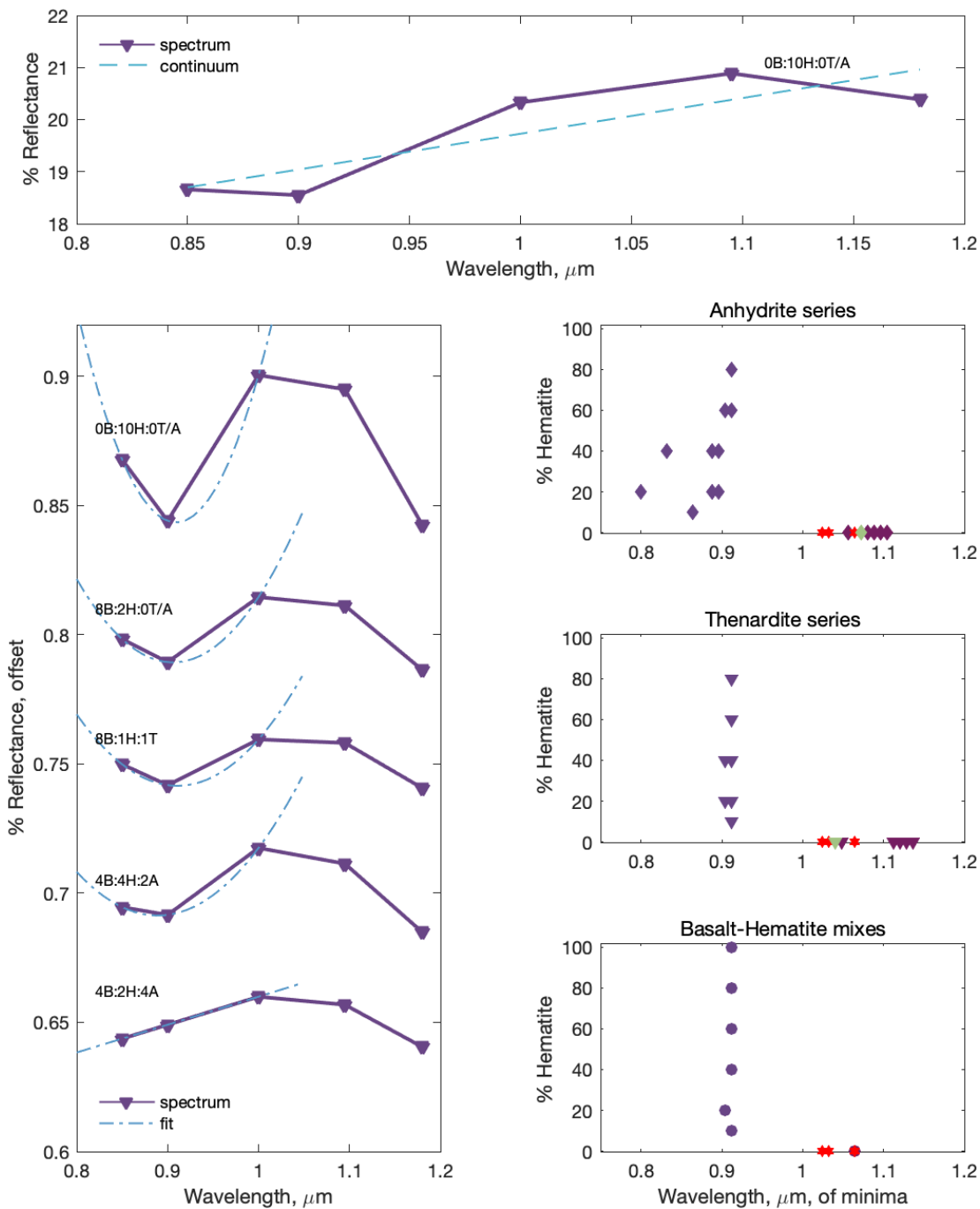


Figure 3.17 Polynomial fit to Fe Feature

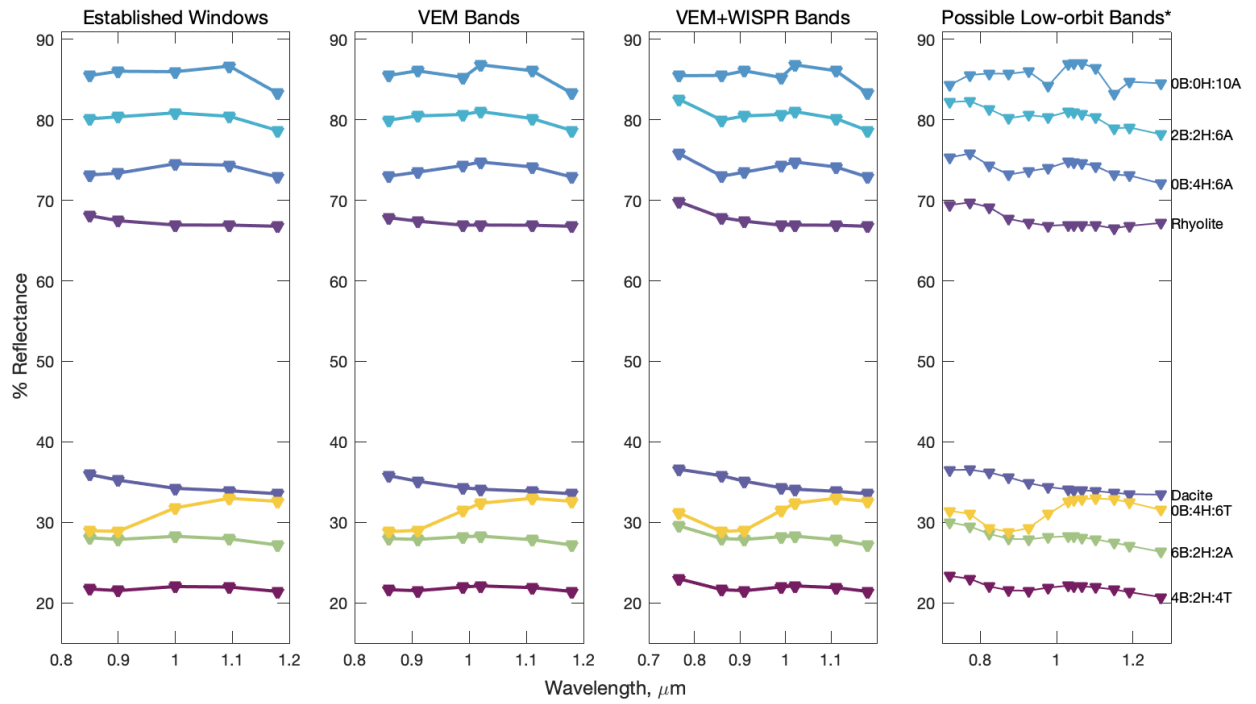


Figure 3.18 Alternative bands in Venus Windows

*spectral bands were chosen to evenly sample potential sub-cloud atmospheric transparencies suggested in Knicely and Herrik (2020).

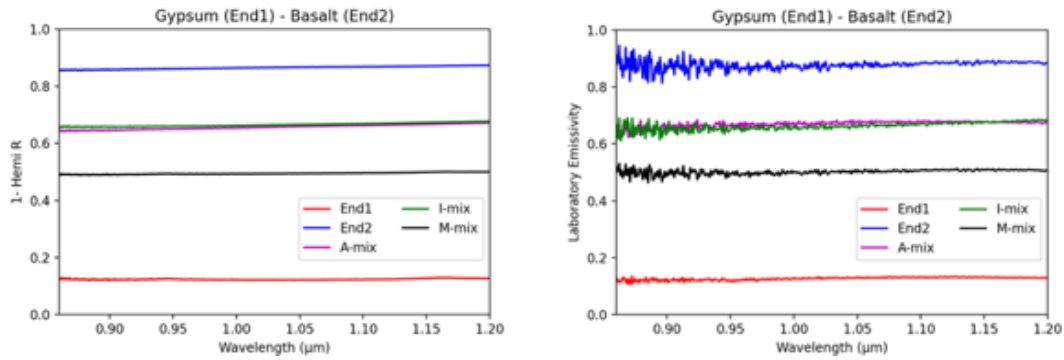


Figure 3.19 Hemispherical reflectance vs high-temperature emissivity of basalt and gypsum

From Alemanno et al. (2024): Left: laboratory emissivity spectra vs modelled spectrum obtained for the mixture gypsum (End1) + basalt (End2) 50:50; A-mix and I-mix are the laboratory spectra of the areal and intimate mixtures, respectively; while M is the modelled mixed spectra starting from the laboratory endmembers spectra. Right: same but in 1-hemispherical reflectance (1-hemi R). The similarity of the two plots suggests that Kirchhoff's law may be valid for room temperature hemispherical reflectance and high-temperature emissivity of some samples.

CONCLUSION

Characterizing the diversity of igneous compositions on the surface of Earth and Venus is crucial to understanding their diverging geologic histories. Volcanos provide insights into the planet's interiors, as the composition of erupted lavas, style of eruption, and longevity of the volcanic centers are determined by mantle dynamics. It is impossible to sample the entirety of Earth's surface, and sample return from Venus is currently unfeasible, making remote observations key to characterizing the planets' surfaces. Spectral observations in the VNIR and MIR region provide mineralogy, and may be only means of constraining surface composition of remote surfaces or transient features such as plinian plumes.

Laboratory analyses provide crucial insights and understandings as to how the interplay of compounding factors affect the spectral response of remote surfaces. The spectral response of a surface is affected by both intrinsic factors, such as phase assemblage and grain size, and extrinsic factors, such as observational geometry and environmental conditions. The three chapters of this dissertation use laboratory data to explore three issues in interpreting orbital spectral data of Earth and Venus.

A frequent aim of remote spectral observations is to obtain surface composition or phase assemblage. For volcanic surfaces, accurate remote characterization is complicated by variable phase assemblages, the presence of glass, and the range of potential bulk compositions. Chapter 1 investigated the utility of partial least squares regression (PLS) models to obtain quantitative estimates of surface oxide abundances and crystallinity from VNIR and MIR spectra at three spectral resolutions. PLS model performance was primarily influenced by the available spectral features in a region – the PLS models of wt. % $\text{Na}_2\text{O} + \text{K}_2\text{O}$ were limited in either spectral region because neither the VNIR or MIR contains spectral features directly resultant from either alkaline element. PLS models can differentiate low and high glass abundance at all resolutions of both VNIR and MIR data with uncertainty of 12-15 %. This uncertainty is greater than the modal error typically assumed for linear deconvolutions but is a more quantitative assessment of both model precision and accuracy. Both regions provide the same predictive capability for bulk wt. % FeO and are able to distinguish low-Fe samples from high-Fe samples. The MIR models predicting wt. % SiO_2 have low enough uncertainty to differentiate mafic, intermediate, and felsic compositions. The models can be applied to a wide range of bulk compositions, and the resulting predictions are independent from parameters besides the one predicted. The spectral resolution of the data does affect model performance, but sparse resolution does not preclude accurate PLS model predictions; the quantity and compositional range of training data are more influential. Additional spectral libraries of natural rock samples with quantified phase assemblages, phase compositions, and bulk compositions are likely to improve model performance. The results of Chapter 1 show that PLS can be used to obtain quantitative compositional estimates of remote volcanic surfaces to aid in their geologic interpretation.

VNIR reflectance data are typically collected in a bi-directional geometry, and this geometry is assumed for remote observations. As a result, observational geometry is frequently ignored when analyzing VNIR reflectance data. However, because of Venus's

thick atmosphere, venusian surface spectra are collected in either a hemispherical reflectance geometry or as directional emissivity. The direct comparison of bi-directional and hemispherical VNIR reflectance spectra in Chapter 2 showed that these spectra collected in these different geometries are not equivalent. For all samples, the hemispherical spectrum had a higher measured reflectance than the bi-directional spectrum, and a negative continuum slope that was not observed in the bi-directional spectra. Additionally, the depth and width of spectral features changed between the two geometries. The observed changes were significant enough to indicate that bi-directional reflectance spectra cannot be directly used to quantitatively interpret hemispherical reflectance spectra.

Isotropic and anisotropic radiative transfer models of bi-directional and hemispherical reflectance were tested to see if either was capable of independently producing a single scattering albedo that could be used to model the reciprocal geometry. This application for the reflectance models has been suggested in prior literature, but the tests performed in Chapter 2 found that the single scattering albedo produced from one geometry could not be used to model the other geometry. These results suggest the independent bi-directional and hemispherical models used in Chapter 2 are not accurately describing the full scattering behavior of the surface, though the anisotropic equations provide better approximations than the isotropic models. The anisotropic models of bi-directional and hemispherical reflectance tested in Chapter 2 can successfully be combined to calculate a single scattering albedo, w_o , capable of converting between the bi-directional and hemispherical reflectance spectra, though the isotropic equations cannot be combined in this way. A more complex anisotropic hemispherical model is needed; further evolution of the hemispherical model to include a two-term phase function and backscatter will likely improve the modeling results.

An aim of the upcoming missions to Venus is to determine the range of surface compositions, and a critical step in unraveling the planet's evolution. This is complicated by the atmosphere, which limits spectral data to a narrow region near 1.0 μm , and is expected to react with the basaltic surface to form sulfate and oxide alteration mineralogies. Chapter 3 investigated the ability of alteration minerals anhydrite, thenardite, and hematite to modify and obscure the spectral signature of basalt in VNIR hemispherical reflectance spectra. The results show that the presence of minor volumes anhydrite, thenardite, and hematite change the spectral shape and increase the sample reflectance relative to unaltered basalt. With one-band spectral data, mafic surfaces may be differentiated from altered and felsic surfaces, but felsic material and altered basalts cannot be distinguished. Multi-band spectral data can differentiate felsic, mafic, and altered basalt surfaces, even when viewed through the venusian atmospheric windows. The results of Chapter 3 also suggest that it may be possible for upcoming missions to distinguish the composition and abundance of alteration phases, potentially providing a method of determining local exposure ages and the composition of the underlying basalt.

VITA

CJ Leight was born and raised in Austin, Texas, where their interest in geology began as a fascination with the sinkholes and caves encountered near their home. CJ attended Mount Holyoke College, graduating in May 2018 with a Bachelors of Arts in Astronomy and a minor in Geology. While at Mount Holyoke, CJ played for the Lacrosse team, and assisted in Dr. Darby Dyar's Mineral Spectroscopy Laboratory with the Mossbauer and Raman spectrometers. CJ held three summer internships, working with Dr. Caleb Fassett on crater degradation rate on the Moon and Mercury in 2015, working with Dr. Edgard Rivera-Valentin at the Arecibo Observatory studying impact simulations of Rhea's surface in 2016, and working with Dr. Lillian Ostrach at the USGS Astrogeology Division conducting analysis of melt features in Mercurian craters in 2017. CJ presented their internship work at the Division of Planetary Sciences Conference and Lunar and Planetary Science Conference, and their work with Dr. Fassett led to two publications.

CJ began graduate school at the University of Tennessee in the fall of 2018, working under the guidance of Dr. Molly McCanta to build a spectral library of tephra. CJ received their Masters of Science in August 2020, and has continued to explore their interest in planetary geology at the University of Tennessee as a doctoral student. In the Volunteer spirit, CJ served as the Graduate Student Representative on the EEPS Diversity Council, participated as a student docent at the McClung Museum, and most recently, has joined the Organizing Committee of the Organization for Venus Early Career Networking. CJ has taught several of the introductory laboratory courses as well as the Planetary Science laboratory course, for which they earned the Excellence in Teaching by GTAs Upper Division Course Award. CJ has also received the University of Tennessee Diversity Enhancement Fellowship and the EEPS Diversity, Equity, and Inclusion Award. While at UTK, CJ published two first-author publications, a USGS data release, and presented at multiple conferences. CJ anticipates receiving their Doctor of Philosophy in August 2024.