

Characterizing Volcaniclastic Deposits Using Remote Sensing Observations

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Degree

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Abstract

Explosive volcanic products, i.e. tephra, are found on nearly every terrestrial planet in the solar system (e.g., Wilhelms, 1987; Hartmann et al., 1999; Byrne et al., 2018) and contain a heterogeneous mix of minerals, debris, and glass (quenched melt). Remote characterization of the terrestrial planets utilizes spectroscopic methods to constrain surface compositions, which in turn rely on robust laboratory calibration of spectral libraries. The presence of the glass component complicates spectral identification of tephra due to the amorphous nature of glass, which results in poorly-constrained spectral characteristics in both the visible-near-infrared (VNIR) and mid-infrared (MIR) spectral regions (Minitti et al., 2002; Dalby and King 2006; Horgan et al., 2014). Here we generate and characterize a spectral library of 21 natural tephra samples and use it to generate Partial Least Squares (PLS) regression models to predict the glass SiO₂ wt%, bulk SiO₂ wt%, phase percentage of glass, sample vesicularity, and size fraction of the spectra from the spectra. Samples were ground and sieved into five size fractions, and VNIR and MIR spectra were collected for each. Phase assemblages of samples were obtained via particle counting on a scanning electron microscope (SEM). Resin molds were made for point counting and electron microprobe analysis to obtain the glass, bulk, and mineral compositions, and glass beads were made for bulk compositional analysis. We find that PLS models built from either the VNIR or MIR spectra can predict the modal abundance of glass present, as well as the glass and bulk SiO₂ weight percent, sample size fraction, and sample vesicularity.

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Section 1: Introduction

At Earth's surface pressure and temperature conditions, less than a weight percent of magmatic volatiles entrained in a magma can result in explosive eruptions (e.g., Parfitt et al., 1995). With lower surface pressures, such as on the Moon, smaller amounts of volatiles are needed to produce an explosive event (Wilson and Head, 1994, 2007). Given that all terrestrial planets likely accreted with some volatile inventory (H₂O, CO₂, S, etc.; Drake, 2005), explosive volcanic deposits may be present on most terrestrial bodies.

Potential evidence of explosive eruptions on other planetary bodies has been observed, including on Mars (e.g., Hynek et al., 2003), the Moon (e.g., Wilson and Head, 1981, Gaddis et al., 1985), and Mercury (e.g., Kerber et al., 2011). Dark mantling deposits (DMD) on the Moon have been interpreted as pyroclastic deposits on the basis of morphological characteristics (e.g., Schmitt et al., 1967), and regolith returned by the Apollo missions contained glass beads interpreted to have formed in regional pyroclastic eruptions (e.g., Heiken et al., 1974; Pieters et al., 1974; Fogel and Rutherford, 1995). Due to its lower gravity, basaltic Plinian eruptions have been postulated on Mars (Wilson and Head, 1994), and the layered deposits of the Medusae Fossae Formation have been suggested to be tephra deposits on the basis of morphology (e.g., Hynek et al., 2003; Mandt et al., 2008). Additionally, spectral studies suggest that felsic volcanic material could be present on Mars (Bandfield et al., 2000; Carter and Poulet, 2013; Wray et al., 2013;), allowing for the potential of silicic explosive eruptions. Finally, on Mercury, multiple possible tephra deposits were identified using geomorphological and spectral characteristics (Head et al., 2008; Kerber et al., 2011; Goudge et al., 2012).

Remote sensing currently provides the most widely available means to study extraterrestrial bodies. Geomorphic analysis of geologic units can provide some insight into their origin;

however, spectral identification remains the primary method to remotely characterize the surface compositions of terrestrial bodies. Infrared spectroscopic methods in particular can provide positive identification of a material without requiring physical contact with a sample, and spectroscopic methods are regularly used to evaluate the compositions of planetary surfaces (e.g., Hunt 1974; Clark et al., 2003; Hook et al., 2005). Nonetheless, accurate remote identification of rocks and minerals is predicated on robust lab-characterized sample libraries to compare field spectra against.

A common product of extrusive volcanism is glass, which represents the rapid cooling of magma before crystallization. Glass is a particularly important component of explosive volcanic deposits, such as tephra. Tephra deposits contain a heterogeneous mix of mineral fragments, glass (quenched melt), and debris from previous eruptions. Tephra is associated with all types of terrestrial eruptive environments (e.g., fire-fountaining or Plinian eruptions such as Mount St. Helens) and igneous compositions from basaltic to rhyolitic (e.g., Jakobsson et al., 1973; Bernard et al., 1996; Anderson et al., 2000). These deposits are rapidly emplaced over potentially large areas (e.g., Brown et al., 1992; Trepte and Hitchman, 1992; Shane, 2000), but the phase assemblage and thickness of a tephra deposit can change over relatively short distances due to atmospheric or aqueous sorting (Shane, 2000; Cassidy et al., 2014). In order to properly interpret spectral data of tephra deposits, the effects of glass on spectral features must be constrained.

The structure of glass is amorphous, meaning that it does not have a defined crystalline structure like minerals. Due to this glass does not have well-defined spectral features, making identification difficult. Previous studies attempted to constrain the effect of glass on infrared spectral features, largely using synthetic glasses in order to control the sample compositions and phase assemblages (e.g., Minitti et al., 2002; Horgan et al., 2014; Dufresene et al., 2009). Natural

tephra samples present unique challenges in that they contain an amalgamation of glass, minerals, and debris, however, the glass-mineral mixtures in natural samples are more geologically relevant than glass alone. The study of natural samples also allows for the parameterization of other properties such as vesicularity and crystallinity; these properties can vary across a single continuous deposit and can affect spectra, which implies the importance for natural sample characterization.

This study addresses gaps in previous works by creating and characterizing a Visible and Near-Infrared (VNIR) and Mid-Infrared (MIR) spectral library of 21 natural tephra samples spanning a wide range of compositions and phase assemblages. Tephra samples were sorted into five size fractions to address particle size effects in the spectra, which are most prominent in the MIR, but do exist in the VNIR (Pieters and Englert, 1993; Mustard and Hays, 1997). Relationships between glass abundance, glass composition, and spectral features in the VNIR and MIR were constrained, allowing for the detection and characterization of glass present in the samples. These relationships were tested in a field study to determine the robustness of the method.

Section 2: Background

2.1 Tephra

Tephra are explosive volcanic deposits that contain a heterogeneous mix of mineral fragments, glass (quenched melt), and debris from previous eruptions. Tephra deposits are emplaced rapidly and can cover massive areas, frequently reaching thousands of kilometers away from the source vent (e.g., Brown et al., 1992; Shane, 2000). In particularly massive explosions, tephra may be transported into the stratosphere and deposited across the planet (Pyle, 1998; Lowe, 2011). The geologically-instantaneous method of deposition means that tephra layers act

as an isochronous geologic horizon (e.g., van den Bogaard et al., 1994; Lowe, 2010). However, tephra deposits from a single eruption frequently display a change in phase assemblage across the deposit as a result of mass-based aeolian or aqueous sorting (e.g., Shane, 2000; Cassidy et al., 2014). The bulk and glass compositions of a tephra deposit can change over the course of an eruption as well, reflecting the composition of the erupting magma chamber (e.g., Jakobsson 1973; Stoppa 2017).

Explosive volcanic eruptions are driven by the decompression of entrained volatile phases (commonly H₂O and CO₂; e.g., Wallace and Anderson, 2000; Stock et al., 2016) in a magma, and the speed of magma ascent (Wilson and Head, 1984; Parfitt et al., 1995). The most abundant volatiles involved in these types of eruptions are H₂O, CO₂, and S (Wallace and Anderson, 2000). Terrestrial explosive eruptions are most commonly associated with silicic magmas (e.g., rhyolitic magmas), which have a high viscosity and can effectively trap exsolving gases until eruption. Although more common with highly silicic magmas, basaltic magmas can ascend faster than gas can escape, resulting in explosive basaltic eruptions as well. Explosive eruptions typically result in the loss of nearly all of the original magmatic volatiles (Wallace and Anderson, 2000), thus it can be hard to constrain the original volatile concentration in the magma. However, on Earth, basaltic fire fountains have been observed in magmas with just 0.3–0.6 wt% H₂O, while silicic eruptions require 3–6 wt% H₂O (Wallace and Anderson, 2000).

2.2 Extraterrestrial Tephra

The other terrestrial planets, and the Moon, show signs of extensive volcanism (e.g., Wilhelms, 1987; Hartmann et al., 1999; Byrne et al., 2018). Explosive volcanic deposits are expected and have been identified on the Moon, Mars, and Mercury (e.g., Wilson and Head, 1981; Wilson and Head, 1994; Kerber et al., 2011). On Venus, the planet's thick atmosphere

results in surface pressures that prevent the exsolution of volatiles from magmas at rates which would result in explosive eruptions (Head et al., 1992).

2.2.1 Mercury

Mercury has had a long history of volcanism as evidenced by the large igneous provinces covering its surface (e.g., Byrne et al. 2018). A portion of Mercury's volcanic history is believed to be effusive; however, tephra deposits have been identified on the basis of spectral character, morphology, and association with possible source vents (e.g., Kerber et al., 2011). Tephritic deposits on Mercury were first identified after a flyby from Mariner 10 from which Rava and Hapke (1987) identified characteristics of pyroclastic deposits on the floor of Lermontov crater. The MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) mission allowed for the identification of over 150 locations which display diagnostic characteristics of explosive deposits: a red spectral slope, diffuse boundaries, spatial association with vent-like depressions, and a higher albedo than the surrounding terrain (e.g., Head et al., 2008, 2009; Kerber et al 2011; Goudge, et al., 2012; Thomas et al., 2014). Mercurian lavas have unusually high concentrations of sulfur (~3 wt%) (Namur et al. 2016). The explosive eruptions responsible for the tephra are suggested to require volatile contents of 0.36–1.35 wt% and a minimum eruption speed of 300 m/s, comparable to some terrestrial eruptions (Kerber et al., 2009). Pit-craters, rimless steep-sided depressions frequently found inside impact craters and not associated with extrusive volcanic flows, are interpreted to have possibly formed via the explosive degassing of dikes (Gillis-Davis et al., 2009; Kerber et al., 2011; Goudge et al., 2012).

2.2.2 The Moon

Lunar soil samples from the Apollo missions contained glassy beads which are interpreted to have formed in regional pyroclastic eruptions (e.g., Heiken et al., 1974; Pieters et al., 1974; Fogel and Rutherford, 1995). The eruption of the glassy beads were suggested to be the result of primary CO degassing from lunar magmas as they approached the surface, however, the relatively recent discovery of water in the lunar glass beads (Saal et al., 2008) suggests that H₂O degassing significantly contributed to the eruption (Rutherford et al., 2017). Dark mantling deposits (DMD) on the Moon were first recognized using Earth-based telescopes, with a suggested pyroclastic origin and global distribution (Gaddis et al., 1985). Regional DMD are large deposits found along the edges of the maria and are thought to have formed via fire-fountaining eruptions (Wilson and Head, 1981). Local DMD are smaller features frequently found in floor-fractured craters and thought to form due to the explosive release of gases (Head and Wilson, 1979).

2.2.3 Mars

Mars had active volcanism until the very recent past (potentially as recently as the last 10 Myr), largely of basaltic nature (Hartmann et al., 2000; Hynek et al., 2003; Horgan 2012). The thinner atmosphere on Mars means that significantly less volatiles in a magma are needed to produce an explosive eruption and the tephra deposits would spread over larger areas than analogous deposits on Earth (Wilson and Head, 1994). There is evidence that martian magmas could have water and CO₂ concentrations similar to Earth's basalts (Weis et al., 2017). Additionally, the extensive friable layered deposits surrounding the Tharsis region, such as the Medusae Fossae Formation, have been suggested to be ash deposits from the Tharsis volcanos on the basis of morphology and material properties (e.g., Hynek et al., 2003).

Recent work using spectra from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and Thermal Emission Imaging System (THEMIS) aboard Mars Odyssey suggest that there could be some felsic material present on Mars (Bandfield et al., 2000; Carter and Poulet, 2013; Wray et al, 2013; Horgan, 2013). Glass-bearing deposits have been speculated to exist in the low-albedo northern lowlands on Mars, based off deconvolutions of TES (Thermal Emission Spectrometer) data (Bandfield et al., 2000) and using the concavity of OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité) spectra (Horgan and Bell, 2013).

2.3 Spectra

Spectra are formed from interactions (absorption, reflection, transmission, or emission) between electromagnetic radiation (i.e., light) and matter (Hapke and Van Horn, 1963; Hunt, 1979; Christensen et al., 2000; Gupta, 2017), and can be recorded in terms of reflection, emissions, or transmission. Spectra contain features - bands or slope changes - which are controlled by the chemical composition, atomic geometry and bonds, grain size, and phase of the material under consideration (Hunt, 1979; Ramsey and Christensen 1998; Christensen et al., 2000; Clark et al., 2003). The physical condition of the material affects the spectra, for example, whether the surface under consideration is a polished slab or is composed of particulates (Hapke and Van Horn, 1963; Adams and Filice, 1967; Crown and Pieters, 1987). Environmental parameters at the time of spectral collection, such as atmospheric temperature and pressure, can also affect a spectrum.

2.3.1 Visible-Near Infrared Spectral Region (VNIR)

The VNIR region records spectral features associated with electron transitions between energy states (Pieters and Englert, 1993). This region records electronic transitions in metals, crystal field effects, and atomic bond vibrations. Electronic transitions occur in transition metals (Pieters and Englert, 1993; Minitti et al., 2009). Crystal field effects record unshielded electron transfer between energy levels as a result of a change in the external crystal field, and are largely controlled by the valence state of atoms in a crystal lattice (Gupta, 2017). Atomic bonds of all types (silicates, hydroxyls, carbonates, etc.) vibrate at specific, diagnostic frequencies (Burns 1993). The overtones of these vibrations are recorded between 1-3 μm (Burns 1993; Dufresne et al., 2009; Gupta 2017).

The VNIR region features a few prominent bands. H_2O and $-\text{OH}$ bands are possible near 1.4, 1.9, and 2.2 μm (Hunt, 1979; Crown and Pieters, 1987; Clark et al., 1990). The 1.9 μm feature, however, can be attributed to other atomic bonds such as Fe^{3+} substitution into tetrahedral coordination sites (Adams and Filice, 1967; Crown and Pieters, 1987). Ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron have bands at 0.7 and 1.0 μm (Adams and Filice, 1967; Pieters and Englert, 1993). Glass can give a broad band at 1.1 μm (Adams and Filice, 1967) and can decrease the albedo of spectra in the VNIR region (Adams and McCord, 1971; Crown and Pieters, 1987).

2.3.2 Mid-Infrared Spectral Region (MIR)

The mid-infrared (MIR) region records the primary tones of the anionic atomic bond vibrations as well as several different gas absorptions (Salisbury and Walter, 1989; Pieters and Englert, 1993; Christensen et al., 2000). Gas features in the MIR are typically sharp, narrow features, while the silicate features are broader. MIR spectra can be written as in both wavelength (μm) and wavenumber (cm^{-1}), which are related as:

$$x \text{ (cm}^{-1}\text{)} = \frac{10,000}{y \text{ (}\mu\text{m)}}$$

where x and y indicate the wavenumber and wavelength, respectively. The reststrahlen band at 7–12 μm is a silicate absorption feature, and its exact position depends on the fundamental molecular vibrations of the silicate structure, e.g., framework silicates or chain silicates (e.g., Salisbury et al., 1989; Ramsey and Christensen, 1998; Dably and King, 2006). The reststrahlen band changes with particle size (Pieters and Englert, 1993; Ramsey and Christensen, 1998). The Christiansen feature at 8.5–12 μm also results from the strongest molecular vibration band, and its exact position migrates depending on the amount of silica present in the material and the degree of polymerization (Conel, 1969; Fu et al., 2017). Unlike the reststrahlen band, however, the Christiansen feature is an emission feature, not absorption, and does not change with particle size (Salisbury et al., 1989; Ramsey and Christensen 1998).

2.3.3 Spectral Deconvolution

Spectral deconvolution is a method of data reduction derived from the principle that the emitted or reflected energy from a multipart surface is a combination of the energy radiated from each component in proportion with the components areal percentage (Ramsey and Christensen 1998). In theory, if pure endmembers are known, a spectrum can be deconvolved through a least squares linear fit (Ramsey and Christensen, 1998). The MIR spectral region behaves in a linear manner down to grain sizes of approximately 60 μm (Ramsey and Christensen, 1998). The VNIR region has been shown to mix non-linearly due to the high absorption properties of the particles with respect to wavelength (Hapke 1981; Ramsey and Christensen 1998). This can be slightly overcome for constrained scenarios (e.g., synthetically mixed two-phase mixtures) with linear radiative transfer equations (e.g., Hapke, 1981), but cannot be overcome in more complex

(e.g., four-phase mixtures or natural samples) scenarios. Non-linear unmixing methods have been derived (e.g., Shkuratov et al., 1999), for similarly constrained scenarios.

2.4 Glass in Spectra

There are few laboratory studies of glass spectra, with a small subset considering the MIR. Glass is amorphous; the inherent compositional and structural inconsistencies present in glass result in chemical variations that can affect the shape and position of spectral features (e.g., Dalby and King, 2006). Most previous studies (e.g., Horgan et al., 2014) have used synthetic glass samples, as natural glass presents unique challenges; masses of glass are discontinuous and frequently contain microlites (<10 μm diameter crystals), making single-phase point analyses difficult to collect or relate to bulk spectral features.

Given that glass is an amorphous solid, the locations of bands in the MIR are a function of the contributions of various Si bonds present in the glass to the overall structure (Dably and King, 2006; Dufresne et al., 2009). The shape and position of the reststrahlen band is therefore dependent on the polymerization in the glass, as well as the alkali content and possibly the amount of Fe^{3+} substituted into the tetrahedral site of TO_4 -tetrahedra (Minitti et al., 2002; Dably and King, 2006; Dufresne et al., 2009; Fu et al., 2017). With glasses, the placement of the reststrahlen band moves to higher wavelengths with increasing wt % SiO_2 (Dufresene et al., 2009), or with less polymerization (Dably and King, 2006; Fu et al., 2017), and becomes sharper with increasing crystallization (Minitti et al., 2002). Alkali concentration likely affects the reststrahlen band due to its effect on polymerization (e.g., Dufresene et al., 2009), however, the literature does not agree on the effect of varying alkali concentrations on reststrahlen band width, though it is commonly agreed that alkalis affect the width, not depth (e.g., Sweet and White, 1969).

The presence of glass in a sample affects the VNIR region as well; Minitti et al. (2002) found that with increasing crystallinity the VNIR band at 2.2 μm deepened, and that pure basaltic glass has weak absorptions at 1.1 and 1.9 μm . Horgan and Bell (2012) found that glass could be affecting the concavity of VNIR spectra on Mars. Horgan et al. (2014) used two-phase laboratory mixtures of glass and basaltic minerals to identify a 1 μm band parameter for the VNIR, which correlates with the presence of glass in these two-phase mixtures.

2.5 Partial Least Squares Regression

Partial least squares regression (PLS) is a variant of least square regression that can be used to predict explanatory variables from an observation (Stone and Brooks, 1990). For this study, the observations are the collected spectra, and the explanatory variables are the compositional parameters such as the sample's wt % SiO_2 or the vesicularity of the sample. This gives an input matrix $\mathbf{X}$ with the dimensions of the number of spectra (n) and the number of spectral channels (p). PLS has been previously used to model geologic compositional parameters off of spectral inputs with success (e.g., Clegg et al., 2009; Dyar et al., 2012a).

A least squares regression model takes the form:

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

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. 2017).

Here, each component of X_j is a spectral channel; the VNIR spectra have 2152 spectral channels and the MIR have 1090 spectral channels. The spectra and the collected compositional data serve

as a training set used to estimate the coefficients β . For the least squares regression, the coefficients $\beta = (\beta_1, \beta_2, \dots, \beta_p)^T$ that minimize the residual sum of squares (RSS) are chosen.

PLS is a shrunken regression technique, which means that PLS assumes the spectral channels, p , input into the algorithm are correlated and can be reduced (Hastie et al. 2017). Within the PLS algorithm the number of input variables, p , are reduced to an absolute number of terms by creating a series of new, orthogonal (uncorrelated), hybrid variables, c , that are linear combinations of the original channels (Dyar et al., 2012a; Hastie et al. 2017). PLS models seek to place the largest coefficient values on the components that have high variance and high correlation with the predicted values (Stone and Brooks, 1990; Hastie et al. 2017).

The number of hybrid variables, c , that a PLS algorithm produces can also be referred to as components and are an important output. The ideal number of components for a data set or prediction model must be determined by testing, and is characteristic of the data set or prediction model in question (Dyar et al., 2012b). Larger numbers of components ($c > 10$) increase the chance that a PLS model is applicable only to the sample set it is built from (Dyar et al., 2012b). This study uses K-fold cross-validation (K-fold CV) to determine the ideal number of components for a given PLS model. With K-fold CV, the data are split into K equal-sized groups, with $K - 1$ groups used as the training data, and the remaining group used to validate the model. The error in the model's predictions of the validation group is used to determine the error in the model. In this study, $K = 9$, which is approximately the square root of the number of spectra input into the PLS model. The error in the model is calculated using root mean square error (RMSE; Ytsma and Dyar, 2019), in which the errors between the actual and predicted values in each K-fold model are averaged and used to generate the RMSE-CV (Hastie et al.,

2009). This process of K-fold CV is repeated for PLS models with $2 \leq c \leq 10$, and the first local minimum RMSE-CV value was used to determine c .

The final outputs of the PLS models are the predictions in the form of the coefficient matrix β , the number of components, k , and the RMSE-CV error of the PLS model. The coefficient matrix can then be applied to new spectra with the same number of spectral channels to generate predictions with the RMSE-CV error accuracy.

2.6 Hypotheses

The goal of this work is to create a predictive model of the amount of glass present in a tephra sample and the glass' composition. However, other parameters, such as bulk composition, vesicularity, and size fraction, have been proven to affect the spectra of geologic samples (e.g., Adams and Filice, 1967; Pieters and Englert, 1993), are also investigated. To address the effects of bulk composition and phase assemblage, the samples chosen for this work range in bulk composition from basalt to rhyolite, with high-alkali endmembers, and have a range of phase assemblages (**Figs. 3.1.1, 4.1, Table 2**. All figures are in Appendix A, all tables are in Appendix B). To address the possible effect of weathering on the sample spectra, the samples chosen for this work come from multiple localities with different weathering rates (**Table 1**). PLS models predicting size fraction, bulk wt% SiO₂, and sample vesicularity are also built.

Section 3: Methods

3.1 Samples

Twenty-one tephra samples from ten different terrestrial locations spanning a wide range of compositions (bulk, glass, and mineral composition) were initially selected for study (**Table 1, Table 2, Table 3, Table 4**). Tephra samples were ground under ethanol, dried, and sieved into a variety of size fractions (>2 mm, 2 mm–250 μ m, >500 μ m, 500–250 μ m, 250–125 μ m, 125–63

μm , and $<63 \mu\text{m}$, noted in **Table 1**). The glass composition of the samples ranges from 46–80 wt.% SiO_2 , and 5–15 wt.% total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$). Bulk compositions of the samples range from 46–74 wt.% SiO_2 , and 4.2–12 wt.% total alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) (**Fig 3.1.1, Table 3**). This covers the range of possible extraterrestrial tephra compositions, which are largely thought to be basaltic (e.g., Wilson and Head, 1994; Hartmann et al., 1999), but could range up to dacitic (e.g., Christensen et al., 2005) or felsic (e.g., Wray et al., 2013). The tephtras also display a range of weathering grades; seven samples come from the arid Mojave Desert, four come from arctic environments, nine come from temperate to tropical environments, and one was collected immediately after eruption before weathering could occur.

3.2 SEM Analysis

A portion of the 250–125 μm size fraction was cast into epoxy plugs to provide a random sampling of the minerals and glass present in the deposit. Sample plugs were polished for Scanning Electron Microscope (SEM) imaging using the University of Tennessee Phenom Pro XL microscope. SEM backscatter (BSE) images were collected for particle counts to measure the crystallinity of each sample. BSE images were taken at 310–350x magnification, under low vacuum, and a voltage of 15 kV. BSE images were systematically scanned and ~500 particles per sample were characterized as glass or mineral type following the methods of McCanta et al. (2015) and Cassidy et al. (2014).

Vesicularity was also quantified using SEM BSE images collected during the particle counts. In five random images, the number of vesicles in each glass particle was counted, then averaged. The samples were assigned a vesicularity from zero to five: zero = no vesicles present, one = 1–5 vesicles, 2 = 6–20 vesicles, 3 = 20–30 vesicles, 4 = 30–50 vesicles, and five = too many to count and/or was more vesicle than glass.

3.3 Electron Microprobe analysis

Sample plugs were carbon coated for electron probe microanalysis (EPMA) on the University of Tennessee Cameca SX-100 electron probe. Compositional data were obtained using natural mineral standards for calibration and a 15 kV acceleration voltage. Spot size varied depending on the size of the target; for glass analyses, a larger size (10 μm) was preferred in order to reduce the electron beam-induced removal of sodium and other volatiles and not destroy the sample, but was not always obtainable due to the texture of the glass (e.g., pumice-like, such as the Pinatubo S2 sample) or high microlite (<10 μm diameter crystals) abundance (e.g., Cima 2). In these cases, a 3 μm spot size was used, a setting that did result in minor, localized destruction of the sample. A sodium loss routine was run for all glass analysis (Neilsen and Sigurdsson, 1981). A minimum of 15 points, or as many as are needed to have standard deviations an order of magnitude below most values, were averaged together in order to account for natural heterogeneities of the glass to define the glass composition.

3.4 Bulk synthesis and analysis

Glass beads of each sample were synthesized for bulk analyses. In a plastic chamber, a strip of molybdenum was clamped between electrodes to complete a circuit (**Fig. 3.4.1**). Approximately 0.1g of each sample (<63 μm size fraction) was placed on the molybdenum strip. The chamber was closed with a vented plastic lid, and the chamber flushed continuously with N_2 gas to prevent changes in oxidation state. After ten minutes of flushing, electricity was run through the circuit at increasing voltage to slowly heat the sample. The sample was held at its melting point until completely molten, then the electricity was shut off, and the bead quenched. The bulk beads were cast into resin plugs and carbon coated for EPMA. EPMA spot size was 15

μm , and a sodium loss routine was run during analysis. A minimum of 15 points were averaged together to define the glass composition.

3.5 VNIR analysis

An ASD Fieldspec4 spectrometer equipped with a contact probe was used to gather VNIR (Visible and Shortwave infrared, 350–2500 nm) reflectance spectra of each sample size fraction at the University of Tennessee. The contact probe was held vertically, via a clamp, 1.3 cm above the sample surface. The contact probe has an internal light source that was used for all spectra. All of the fluorescent room lights were turned off and screens angled away from the contact probe. Loose sample was poured onto weigh paper, and gently pressed with a second piece of weigh paper so that the grains formed as flat of a surface as possible and covered the entire field of view of the contact probe. Each sample was placed over the Spectralon calibration target, which stayed beneath the contact probe. Each sample's respective size fractions were collected in a single calibration of the spectrometer, in quick succession. White references were taken and the spectrometer re-calibrated and optimized before each sample, to minimize the amount of post processing. Discontinuities in the spectra that resulted from mis-calibration between the detectors of the spectrometer were removed in MATLAB.

3.6 MIR analysis

Bulk MIR (Mid Infrared, 400–2500 cm^{-1} , or 4–25 μm) emissivity data were obtained for the four smallest size fractions (2 mm–250 μm or 500–250 μm , 250–125 μm , 125–63 μm , and <63 μm) using a Nicolet 6700 FTIR spectrometer at Stony Brook University. The largest size fraction was excluded because there was insufficient sample to adequately cover the field of view. Samples were poured into sample cups, heated at 80°C for at least 2 hours to remove adsorbed water, then placed in the sample chamber. The chamber was purged using N_2 gas to minimize the

absorption features of H₂O and CO₂, which appear at wavelengths below 8 μ m and longer than 12 μ m (Ramsey and Christensen, 1998). 128 scans per sample were averaged into a single resistivity, which was processed into the resultant emissivity spectrum following the methods in Ruff et al. (1997) and the program Davinci at Stony Brook Univ.

3.7 Multivariate Analysis of Spectra

MIR spectra are known to deconvolve linearly (Ramsey and Christensen, 1998), however there is moderate disagreement as to how glasses affect the spectra (e.g., Dufresene et al., 2009). VNIR spectra, however, do not add linearly (Adams and Filice, 1967; Crown and Pieters, 1987), and thus bands cannot be directly attributed to a compositional parameter, particularly because the spectra do not represent a single phase, or even a three-phase mixture. Thus, rather than trying to characterize glass using single parameters, which has been done elsewhere (e.g., Horgan and Bell, 2012), the entire spectral region will be considered in building models to predict compositional parameters, though the VNIR and MIR will be considered separately.

VNIR and MIR spectra and compositional data were loaded into the Data Exploration and Visualization Analysis of Spectra (DEVAS) website (Carey et al., 2017), which is the Mount Holyoke College in-house laboratory website for spectral processing. The spectra were baseline corrected (continuum removed) and normalized using several methods to optimize the root mean square error with K-fold cross validation (RMSE-CV) of each regression model. The preprocessing steps were applied unilaterally to all spectra. The combination of baseline removal and normalization routine was chosen by cycling through all possible combinations to see which yielded the lowest RMSE-CV for each predictive model. PLS components were limited to a maximum of 10. Baseline correction and normalization routines utilized are listed in **Table 17**.

PLS analysis builds off of multiple linear regression but explains covariance in both the predictor variables and predicted element. PLS analysis uses all the predictor variables (spectral channels) to predict a compositional element. PLS models were built for both the VNIR and MIR spectra to predict the modal abundance of glass present in each sample, as well as the SiO₂ wt% of the glass and bulk sample, and vesicularity of the sample. A PLS model predicting the size fraction was also built.

Section 4: Samples Studied

Tephra compositional data is presented in Tables 2 and 3. Samples are grouped and described by locality.

4.1 Cima

Cima samples were collected by Dr. Lang of Mercyhurst University from a basaltic cinder cone in the Cima Volcanic field, Mojave Desert, California. The bulk compositions of Cima_1 and Cima_3 are basaltic and nearly identical in composition, while Cima_2 is more alkaline and plots in the basanite field (**Fig. 3.1.1, Table 3**). The glass composition of Cima_2 is within the uncertainty of the bulk (**Fig 4.1.1, Table 3, Table 4**). Cima_1 and Cima_3 glass compositions are more evolved, trachyandesite and tephriphonolite, respectively (**Fig 4.1.1**). Cima_1 contains labradorite, augite, pigeonite, olivine, and oxides (**Table 5**). Cima_2 contains orthoclase, labradorite, augite, olivine, and oxides (**Table 5**). Cima_3 contains labradorite, augite, olivine, and oxides (**Table 5**).

4.2 Crater Flats

Samples were collected from four sites in the Crater Flats volcanic field, Nevada (Nicholis and Rutherford, 2004). The bulk composition of Crater Flats U4 (CFU_4) is basaltic (**Fig. 3.1.1, Table 3**). Crater Flats U1 (CFU_1), U2 (CFU_2), and Southwest Little Cone (CFSWLC) all

have bulk trachy-basalt compositions, with CFU_1 falling between basalt and trachy-basalt (**Fig. 3.1.1, Table 3**). All four samples have a glass composition within the basaltic trachy-andesite field (**Fig 4.1.1, Table 4**). CFU_1 contains bytownite, olivine, and oxides (**Table 6**). CFSWLC contains bytownite, augite, and iron-oxides (**Table 6**). CFU_2 contains bytownite, olivine, augite, and oxides (**Table 6**). CFU_4 contains bytownite, olivine, and oxides (**Table 6**).

4.3 Heimaey

The sample from Heimaey (Hei) was collected from the 1973 eruption cinder cone on Heimaey Island, Iceland by Dr. McCanta. Heimaey's bulk composition is trachy-basaltic (**Fig. 3.1.1, Table 3**); the glass composition is within uncertainty of the bulk (**Fig 4.1.1, Table 4**). The mineral assemblage of Heimaey contains andesine, magnetite, and olivine (**Table 7**).

4.4 Vesuvius

The Vesuvius (Ves) ash came from the 1631 eruption, and was collected in 2004 from a quarry on the east side of the mountain by Dr. McCanta. Vesuvius has the highest alkaline concentrations of any studied sample, with a tephriphonolite bulk composition (**Fig. 3.1.1, Table 3**), and phonolite glass composition (**Fig 4.1.1, Table 4**). The mineral assemblage of Vesuvius contains leucite, augite, biotite, and anorthite (**Table 8**).

4.5 Summerland

Samples SS_1, SS_2, SS_3, SS_4, and r8d1 came from the Summerland site on Mt. Rainier, Washington (Venezky and Rutherford 1997). SS_1, SS_2, SS_3 have basaltic-andesite bulk compositions, increasing in SiO₂ and total alkali concentration from SS_1 to SS_2 to SS_3 (**Fig. 3.1.1, Table 3**). R8D1 bulk composition is andesitic, and Summerland S4 has a trachyandesitic bulk composition (**Fig. 3.1.1, Table 3**), with the highest SiO₂ and total alkali concentration of the sample group. The glass compositions of SS_3 and SS_4 are within error of each other; SS_1,

SS_3, SS_4, and R8D1 have andesitic glass compositions (**Fig 4.1.1, Table 4**). SS_2 has a dacitic-rhyolitic glass composition (**Fig 4.1.1, Table 4**). The Summerland samples all contain andesine and pigeonite (**Table 9**). SS_3, r8d1, and SS_2 also contain oxides, and SS_1, SS_2, and r8d1 contain augite (**Table 9**).

4.6 Okmok

These tephra samples are from the Okmok volcano, Aleutian Islands, Alaska, collected by Scott Applegate. Okmok AD (OAD) was collected from the rim of the largest volcanic crater and Okmok Ashishik Point (OAP) was collected from Ashishik point. OAD and OAP bulk compositions are andesite and dacite, respectively (**Fig. 3.1.1, Table 3**). OAP bulk composition is higher in SiO₂ and Na₂O+K₂O content than OAD. The OAP glass composition is trachytic (**Fig 4.1.1, Table 4**). OAD has two glass compositions, one a basaltic-andesite and the other rhyolitic (**Fig 4.1.1, Table 4**). The mineral assemblage of OAP contains labradorite, andesine, clinopyroxene, olivine, and oxides (**Table 10**). OAD contains olivine, labradorite, plagioclase, clinopyroxene, and oxides (**Table 10**).

4.7 Pinatubo

The Pinatubo tephtras are from the June 15, 1991 eruption, and were collected in July of 1991 from sites 10-15 km from the volcanic center (Rutherford and Devine, 1996). Pinatubo S2 (PS_2) and Pinatubo S3 (PS_3) bulk compositions are dacitic and rhyolitic, respectively (**Fig. 3.1.1, Table 3**). The PS_2 and PS_3 glass compositions are both rhyolitic (**Fig 4.1.1, Table 4**). PS_2 contains andesine, clinopyroxene, pigeonite, amphibole and oxides (**Table 11**). PS_3 contains labradorite and apatite, in addition to andesine, labradorite, pigeonite, amphibole, and oxides (**Table 11**).

4.8 Hotlum

The sample of Hotlum ash (HLA) was collected on the slopes north of Mt. Shasta, California by Drs. McCanta Dr. Rutherford. The bulk composition of HLA is andesitic (**Fig. 3.1.1, Table 3**), and the glass composition is rhyolitic (**Fig 4.1.1, Table 4**). The HLA mineral assemblage contains labradorite, pigeonite, and quartz (**Table 12**).

4.9 Mt St Helens

The Mt. St. Helens, Washington (MSH) ash was collected from deposits from the May 18, 1980 eruption by Dr. Rutherford Both the bulk and glass compositions of MSH are rhyolitic (**Fig. 3.1.1, Fig 4.1.1, Table 3, Table 4**). MSH contains labradorite, pigeonite, apatite, and oxides (**Table 13**).

4.10 Bishop Tuff

The Bishop Tuff (BT) sample was collected from an outcrop in California by Dr. Rutherford. Both the bulk and glass compositions of BT are rhyolitic (**Fig. 3.1.1, Fig 4.1.1, Table 3, Table 4**); the glass composition has more silica and alkalis than the bulk composition. BTs contains sanidine, albite, quartz, and magnetite (**Table 14**).

Section 5: Results

Spectral results are listed by locality

5.1 Cima

Cima_1 VNIR spectra (**Fig. 5.1.1**) and Cima_3 VNIR spectra (**Fig. 5.1.2**) have a positive spectral slope from 0.35 μm to 1.3 μm , and then a fairly flat continuum toward longer wavelengths. The Cima_2 VNIR spectra (**Fig. 5.1.3**) have a positive spectral slope. The >500 μm , 500–250 μm , 250–125 μm , and 125–63 μm size fraction spectra for all three samples plot close together. The <63 μm size fraction spectrum has a consistently higher reflectance. The

Cima_1 and Cima_3 spectra have reflectance values that range from 0.09 reflectance to 0.39 reflectance. The Cima_2 spectra have a positive spectral slope, with reflectance values at shorter wavelengths from 0.09–0.15 reflectance and increasing to 0.40–0.80 reflectance. All of the Cima spectra have absorbance features at 0.9 μm , 1.9 μm , and 2.2 μm (**Figs 5.1.1-5.1.3**). The 0.9 μm absorbance band is broad and asymmetrical. The 1.4 μm band is faint and barely distinguishable above the continuum, a drop of less than 0.5 reflectance. The 1.9 μm feature is sharp but shallow, and skewed towards the longer wavelengths. The 2.2 μm feature is shallow and roughly symmetrical.

The Cima_1 MIR spectra (**Fig. 5.1.4**), Cima_2 MIR spectra (**Fig. 5.1.5**), and Cima_3 MIR spectra (**Fig. 5.1.6**) have a flat spectral slope from near 350 to 650 cm^{-1} , a jump in emissivity with a flat slope from ~ 650 –1220 cm^{-1} , then a downslope from ~ 1220 –2500 cm^{-1} . The spectra have emission values from 0.60–1.00. The reststrahlen band is present from ~ 770 –1200 cm^{-1} , with two minima in the Cima_1 and Cima_2 spectra (**Table 15**). In the Cima_3 spectra there are 3 minima and the <63 μm size fraction reststrahlen band has a relatively flat bottom from 870–1056 cm^{-1} , with minima at 941 and 1050 cm^{-1} . The Christiansen feature is present in the Cima_1 and Cima_3 spectra at 1590 cm^{-1} and in the Cima_2 spectra at 1630 cm^{-1} (**Table 16**). A CO_2 absorption is observed at 667 cm^{-1} , as well as atmospheric water absorptions.

5.2 Crater Flats

The CFU_1 (**Fig. 5.2.1**), CFU_2 (**Fig. 5.2.2**), and CFSWLC (**Fig. 5.2.3**) VNIR spectra are very similar; all have a positive slope from 0.35 μm to 0.75 μm , a shallow-u-shaped continuum past 0.75 μm , and reflectance values that range from 0.05–0.26. The CFU_4 VNIR spectra (**Fig. 5.2.4**) have a slight positive slope that is most pronounced in the <63 μm size fraction, but present in all size fractions and reflectance values range from 0.05–0.34. For all the samples, the

<63 μm size fraction spectra have distinctly higher reflectance values than the other three size fractions. The spectra have absorption bands at 0.9 μm , 1.9 μm , and 2.2 μm . The 0.9 μm absorption is very broad with a minimum near 1 μm , and in CFU_1, CFU_2 and CFSWLC the right edge is difficult to distinguish from the u-shaped continuum. The 2.2 μm absorption band is shallow and skewed toward shorter wavelengths, and its band depth increases at smaller size fractions.

The CFU_1 (**Fig. 5.2.5**), CFU_2 (**Fig. 5.2.6**), CFU_4 (**Fig. 5.2.7**), and CFSWLC (**Fig. 5.2.8**) MIR spectra have a flat spectral slope from 400 to $\sim 1250\text{ cm}^{-1}$, then a downslope from 1230–2500 cm^{-1} . The spectra have emissivity values ranging from 0.81–1.00. The reststrahlen band is present from ~ 772 –1240 cm^{-1} . The CFU_1, CFU_2, and CFSWLC <63 μm size fraction spectra have two minima, while all other spectra for the sample have a single minimum (**Table 15**). All spectra of CFU_4 have a single minimum in the reststrahlen band, though the position varies between size fractions (**Table 15**). The Christiansen feature is present in the spectra near 1631 cm^{-1} (**Table 16**). The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

5.3 Heimaey

The Hei VNIR spectra (**Fig. 5.3.1**) have reflectance values from 0.04–0.17. The 125–63 μm and <63 μm size fractions have a positive spectral slope, while the other size fractions are fairly flat. The spectra have absorbance bands at 1.4 μm , and 2.2 μm . The absorption bands are very faint, with band depths less than 0.03 reflectance, and are most apparent in the <63 μm size fraction. All but the <63 μm size fraction spectra have a minimum at 0.47–0.5 μm .

The HEI MIR spectra (**Fig. 5.3.2**) have a flat spectral slope from 350–1250 cm^{-1} , then a downslope from 1250–2500 cm^{-1} . The spectra have emissivity values ranging from 0.82–1.00.

The reststrahlen band is present from 752–1230 cm^{-1} in all spectra. The 2 mm–250 μm , 250–125 μm , and 125–63 μm size fraction spectra have a minimum at 1037 cm^{-1} (**Table 15**). The <63 μm size fraction spectrum has minima at 871 and 1037 cm^{-1} . The Christiansen feature is present in the spectra at 1633 cm^{-1} (**Table 16**). The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

5.4 Vesuvius

The Ves VNIR spectra (**Fig. 5.4.1**) have a positive spectral slope across the entire spectrum. The slope is steepest in the <63 μm size fraction, and decreases as size fraction increases. The spectra have reflectance values ranging from 0.09–0.20 at shorter wavelengths and 0.34–0.69 at longer wavelengths. The spectra have absorbance features at 0.9 μm , 1.9 μm , and 2.2 μm . The 2.2 μm band is the most distinct in all size fractions. The 0.9 μm absorption feature is broad, and is a drop in ~ 0.02 reflectance. The 1.4 μm feature is sharp but faint in all size fractions.

The Ves MIR spectra (**Fig. 5.4.2**) have a flat spectral slope from 400–1250 cm^{-1} , then a downslope from 1250–2500 cm^{-1} . The spectra have emissivity values from 0.73–1.00. The reststrahlen band is present from 779–1247 cm^{-1} , with a minimum at 1035 cm^{-1} in all but the <63 μm size fraction, where there are two minima at 830 and 1035 cm^{-1} (**Table 15**). The Christiansen feature is present in the spectra at 1630 cm^{-1} (**Table 16**). The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

5.5 Summerland

The SS_1 (**Fig. 5.5.1**), SS_2 (**Fig. 5.5.1**), SS_3 (**Fig. 5.5.2**), SS_4 (**Fig. 5.5.3**), and R8D1 (**Fig. 5.5.4**) VNIR spectra have a positive slope from 0.35 to about 0.75 μm , and then a fairly flat to shallow positive continuum across the rest of the spectrum. In all Summerland samples, the <63 μm size fraction spectra have a noticeably higher and wider range of

reflectance values, ranging from 0.06–0.64, but the same overall spectral shape and bands as the other size fraction spectra. The other size fraction spectra have reflectance values from 6–50%. The spectra have absorbance bands at 0.9 μm , 1.9 μm , and 2.2 μm . The 0.9 μm band is broad and faint, with a band depth of less than 0.05 reflectance in all spectra. The 1.9 μm and 2.2 μm bands are likewise faint, but both are sharper. The SS_3 and SS_4 spectra have an additional absorption at 1.4 μm , which is very shallow and faint. The absorbance bands are most distinct in the <63 μm size fraction spectra.

The SS_1 (**Fig. 5.5.6**), SS_2 (**Fig. 5.5.7**), SS_3 (**Fig. 5.5.8**), SS_4 (**Fig. 5.5.9**), and R8D1 (**Fig. 5.5.10**) MIR spectra have a flat spectral slope from 350–1300 cm^{-1} , then a downslope from ~1300–2500 cm^{-1} . The spectra have emissivity values ranging from 0.74–1.00. The reststrahlen band is present from 776–1259 cm^{-1} in all SS_1 spectra, from 785–1270 cm^{-1} in all SS_2 spectra, from 782–1256 cm^{-1} in all SS_3 spectra, from 777–1256 cm^{-1} in all SS_4 spectra, and from 793–1286 cm^{-1} in all R8D1 spectra. For the SS_1, SS_2, SS_3, and R8D1 spectra, in all but the smallest size fraction (<63 μm), there is a minimum near 1050 cm^{-1} ; the SS_1 and SS_3 <63 μm size fraction spectra reststrahlen band has a minimum near 850 cm^{-1} (**Table 15**). The SS_2 and R8D1 <63 μm size fraction spectra have two minima, and the SS_4 <63 μm size fraction spectrum has three minima. The Christiansen feature is present in the Summerland spectra near 1600 cm^{-1} (**Table 16**). The spectra have an absorption from CO₂ at 667 cm^{-1} , and atmospheric water absorptions.

5.6 Okmok

OAP VNIR spectra (**Fig. 5.6.1**) have a slight positive slope across the entire spectrum, with a sharp positive slope from 0.35 μm –0.75 μm . The spectra have reflectance values ranging from 0.12–0.63. The 2 mm–250 μm and 250–125 μm size fractions are within 0.10 reflectance of each

other, and have maximum reflectance values of 0.31 and 0.35, respectively. The 125–63 μm and <63 μm size fractions have reflectance values within 0.05 reflectance of each other, with maximum reflectance values of 0.60 and 0.62, respectively. The OAP spectra have absorption features at 0.9 μm , 1.4 μm , 1.9 μm , and 2.2 μm , with a possible absorption at 2.5 μm cut off by the end of the spectra. The 0.9 μm absorption band is broad, with a minimum near 1.0 μm . The 1.4 μm feature is faint in all size fractions, but most clear in the smaller sizes. The 1.9 μm feature is a sharp, small band, with increasing band depth at smaller size fractions. The 2.2 μm feature is skewed towards the shorter wavelengths, and the absorption band deepens as size fraction decreases.

The OAP MIR spectra (**Fig. 5.6.2**) have a flat spectral slope from 400–1300 cm^{-1} , then a downslope from 1300–2500 cm^{-1} . The spectra have emissivity values from 0.72–1.00. The reststrahlen band is present from 790–1295 cm^{-1} . The largest size fraction (500 μm –250 μm) has a minimum at 1072 cm^{-1} . The other size fractions' spectra have minima at 850 and 1070 cm^{-1} (**Table 16**). The Christiansen feature is present in the spectra at 1630 cm^{-1} . The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

The OAD VNIR spectra (**Fig. 5.6.3**) have a positive slope across the entire spectrum in the smallest size fraction (<63 μm), while the other size fractions (2mm–250 μm , 250–125 μm , and 125–63 μm) have a flat continuum. The 2 mm–250 μm and 250–125 μm size fractions have reflectance values ranging from 0.065–0.09. The 125–63 μm size fraction has reflectance values ranging from 0.11–0.20, and the <63 μm size fraction has reflectance values ranging from 0.13–0.31. The OAD spectra have sharp but shallow absorbance bands at 1.9 μm and 2.2 μm . There is a broad downturn near 0.9–1.0 μm , with minima at 1.0 μm and 1.2 μm . None of the bands are very deep, with a change in reflectance of less than 0.05.

The OAD MIR spectra (**Fig. 5.6.4**) have a flat spectral slope from 400–1300 cm^{-1} , then a downslope from 1300–2500 cm^{-1} . The spectra have emissivity values ranging from 0.76–1.00. The reststrahlen band is present from 805–1290 cm^{-1} . The 2 mm–250 μm and 250–125 μm size fraction spectra have a minimum at 1065 cm^{-1} . The 125–63 μm and <63 μm size fractions have minima at 850, 1065, and 1204 cm^{-1} (**Table 15**). The Christiansen feature is present in the spectra at 1630 cm^{-1} (**Table 16**). The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

5.7 Pinatubo

PS_2 VNIR spectra (**Fig. 5.7.1**) range from 0.29–0.75 reflectance, with a positive spectral slope from 0.35–0.5 μm , and relatively flat continuum after. PS_3 VNIR spectra (**Fig. 5.7.2**) have a relatively flat continuum with reflectance values ranging from 0.47–0.87. For both Pinatubo samples, the two smallest size fractions are within 0.05 reflectance of each other. The PS_2 and PS_3 spectra have absorbance bands at 1.4 μm , 1.9 μm , and 2.2 μm . The 2.2 μm absorption band resolves into a doublet with minima at 2.2 μm and 2.3 μm . In the PS_3 2 mm–250 μm size fraction the 2.2- μm band has minima at 2.2 μm , 2.3 μm , and 2.4 μm . The PS_2 spectra have an 0.9 μm absorption band, which is also present in the PS_3 126–63 μm , and <63 μm size fraction spectra. The 1.4 μm feature is faint in all size fraction spectra.

PS_2 (**Fig 5.7.3**) and PS_3 (**Fig. 5.7.4**) have emissivity values from 0.57–1.00. The reststrahlen band is present in the spectra from 800–1300 cm^{-1} . The PS_2 and PS_3 2 mm–250 μm size fraction spectra have a single minimum in the reststrahlen band, as does the PS_3 250–125 μm size fraction spectrum. The PS_2 <63 μm , 125–63 μm , and 250–125 μm size fraction spectra have three minima, and the PS_3 <63 μm and 125–63 μm size fraction spectra have two

minima (**Table 15**). The Christiansen feature is present at 1630 cm^{-1} (**Table 16**). The spectra have a sharp absorption from CO_2 at 667 cm^{-1} and H_2O absorptions.

5.8 Hotlum

In the VNIR, the HLA samples have a strong positive slope from $0.35\text{--}0.8\text{ }\mu\text{m}$, with reflectance values ranging from $0.09\text{--}0.47$ (**Fig. 5.8.1**). The $250\text{--}125\text{ }\mu\text{m}$ and $2\text{ mm--}250\text{ }\mu\text{m}$ size fractions have reflectance values ranging from $0.09\text{--}0.27$, and a negative continuum slope from $0.8\text{--}2.5\text{ }\mu\text{m}$. The HLA spectra have absorption bands at $0.9\text{ }\mu\text{m}$, $1.9\text{ }\mu\text{m}$, and $2.2\text{ }\mu\text{m}$. The smallest size fraction ($<63\text{ }\mu\text{m}$) has a $1.2\text{ }\mu\text{m}$ absorption band that is not visible in the larger sizes. The $0.9\text{ }\mu\text{m}$ absorption band is most obvious in the $125\text{--}63\text{ }\mu\text{m}$ size fraction. The $1.9\text{ }\mu\text{m}$ and $2.2\text{ }\mu\text{m}$ absorbance features are skewed towards the shorter wavelengths.

The HLA MIR spectra (**Fig. 5.8.2**) have emissivity values ranging from $0.87\text{--}1.00$, with a slope up from 0.87 towards 1.00 from $2500\text{--}1300\text{ cm}^{-1}$. The spectra have a sharp absorption from CO_2 at 667 cm^{-1} . The reststrahlen band is present from $800\text{--}1300\text{ cm}^{-1}$, with a minimum near 1090 cm^{-1} (**Table 15**). The Christiansen feature is present at 1630 cm^{-1} (**Table 16**). The drop in emission, as well as the peak, are strongest in the smallest size fraction ($<63\text{ }\mu\text{m}$). There is considerable noise in the data below 500 cm^{-1} as well as above 2000 cm^{-1} , and noise is most evident in the smallest size fraction.

5.9 Mt St Helens

The MSH VNIR spectra (**Fig. 5.9.1**) have relatively flat continua, with reflectance values ranging from $0.37\text{--}0.77$ reflectance, with the two smallest size fractions ($125\text{--}63\text{ }\mu\text{m}$, $<63\text{ }\mu\text{m}$) having the highest reflectance values and the three other size fractions within 0.10 reflectance of each other. MSH has spectral absorption bands at $0.9\text{ }\mu\text{m}$, $1.4\text{ }\mu\text{m}$, $1.9\text{ }\mu\text{m}$, and $2.2\text{ }\mu\text{m}$, with a possible absorption band at $2.5\text{ }\mu\text{m}$, cut off by the end of the collected spectra. The $0.9\text{ }\mu\text{m}$

absorption band is the deepest, followed by the 1.9 μm absorption band; in the smallest size fraction ($<63 \mu\text{m}$), however, the 1.9 μm , absorption is deeper than the 0.9 μm . The 0.9 μm and 2.2 μm absorption bands are broad. The 1.9 μm band is narrow and not skewed.

The MHS MIR spectra (**Fig. 5.9.2**) have emissivity values from 0.70–1.00, with a slope up from 0.70 towards 01.00 from 2500–1300 cm^{-1} . The spectra have a sharp absorption from CO_2 at 667 cm^{-1} . The reststrahlen band is present from 800–1300 cm^{-1} , with two minima near 870 cm^{-1} and 1090 cm^{-1} (**Table 15**). The Christiansen feature is present near 1630 cm^{-1} (**Table 15**). The reststrahlen band and Christiansen feature are strongest in the smallest size fraction ($<63 \mu\text{m}$). There is considerable noise in the data below 500 cm^{-1} as well as after 2000 cm^{-1} .

5.10 Bishop Tuff

The BT VNIR spectra (**Fig. 5.10.1**) have a fairly flat continuum with reflectance values ranging from 0.41–0.92. The end of the spectra, $\sim 2 \mu\text{m}$ to 2.5 μm , have a negative slope, or a possible absorption band at 2.5 μm cut off by the end of the spectra. The size fraction spectra plot within 0.10 reflectance of each other. BT has sharp, distinct absorptions at 1.4 μm , 1.9 μm and 2.2 μm , and a broad absorption at 0.9 μm . The 1.4 μm absorbance band has a shoulder at 1.45 μm . The 1.9 μm absorption feature is deep, with a shoulder value of 0.79 reflectance and minimum reflectance value of 0.45 reflectance in the 250–125 μm size fraction, and similar band depths in the other size fractions. The broad 0.9 μm feature has two minima within the feature, one at 0.95 μm and one at 1.15 μm , and ends at the beginning of the of the 1.4 μm absorption band.

The BT MIR spectra (**Fig. 5.10.2**) have a flat spectral slope from 400–1250 cm^{-1} , then a downslope from 1250–2500 cm^{-1} . The spectra have emissivity values ranging from 0.69–1.00. The reststrahlen band is present from 818–1310 cm^{-1} , with minima at 866 and 1075 cm^{-1} , with an

additional minimum at 1203 cm^{-1} in the $<63\text{ }\mu\text{m}$ size fraction spectrum (**Table 15**). The Christiansen feature is present in the spectra near 1630 cm^{-1} (**Table 15**). The spectra have an absorption from CO_2 at 667 cm^{-1} , and atmospheric water absorptions.

Section 6: Discussion

6.1 Modeling Results

All PLS models called for some amount of preprocessing in the form of baseline removal or normalization, and frequently both. The application of baseline removal and normalization routines served to modify the spectra to draw out features and differences. The normalization routines scale the intensity (% reflectance or emission) of each spectrum under consideration based off of statistical parameters for each; the routines utilized in this study are given in **Table 17**. In a broader sense, the normalization routines worked to minimize peak intensity differences between spectra while preserving the relative intensity values of the individual spectra. The baseline removal techniques are different methods to remove a spectrum's continuum, listed in **Table 17**. A PLS model can be built without any preprocessing, however, preprocessing greatly improves the fit of the models, as is shown in **Fig. 6.1.1**. The combination of baseline removal and normalization routine for each predictive model varied, as did the number of components input into the model (**Table 18**). The number of components considered is relatively low, thereby reducing the chance of overfitting the model to the data (Hastie et al., 2017).

The PLS model parameters for each predictive model are listed in **Table 17**. The VNIR PLS models are best at predicting the bulk weight percent (wt%) SiO_2 , followed by vesicularity, glass wt% SiO_2 , glass phase %, and size fraction. The MIR PLS model with the best R^2 are the bulk wt% SiO_2 and vesicularity, followed by the size fraction, glass wt% SiO_2 , and glass phase %. The results of the PLS models for the MIR and VNIR, while different, agree with each other;

samples with low glass wt % SiO₂ are predicted to have low glass wt % SiO₂ by both the VNIR and MIR models.

The MIR PLS models have consistently better R² values than the VNIR models when predicting a variable, likely due to the inherent differences the spectral regions. Spectral features in the VNIR region do not deconvolve linearly, meaning that the depth of a spectral band cannot be linearly correlated with quantitative interpretations, for example, the amount of water present in a sample (Pieters and Englert, 1993). In the MIR region, spectra can be deconvolved linearly if all phases are known, for particles >63 µm in diameter (Ramsey and Christensen, 1998). PLS modeling is based off of least square regressions (Stone and Brooks, 1990) and the assumption that certain spectral channels can be more influenced by the parameters (Hastie et al. 2017). This influence can be measured by a set of regression coefficients (Dyar et al., 2012). The non-linearity of the VNIR spectral region works against PLS regressions' base assumption, and so reduces the effectiveness of the models. However, by relying on all spectral channels for predictions rather than limiting various regions of predictive reliance, the PLS models can accurately predict the compositional parameters using VNIR spectra.

6.2 Trends with Bulk Composition

As bulk SiO₂ wt% increases, the average VNIR reflectance values increase (**Fig 6.2.1**). The greatest exceptions to this trend are Cima sample Cima_2 and Okmok sample OAD; Cima_2 has 47 wt% bulk SiO₂ and up to 80% reflectance, and OAD has 60.9 wt% bulk SiO₂ and a maximum of 30% reflectance. The more felsic samples also tend to have a larger range of reflectance values (e.g., MSH ranges from 37–80%, while CFU_1 ranges from 5–20% reflectance). The increase in average reflectance correlates with the prominence of spectral bands in the VNIR, particularly bands at 1.4, 1.9, and 2.2 µm. The bulk FeO wt% does not correlate with the 0.9 µm

band depth (**Fig. 6.2.2**), largely attributed Fe^{2+} and Fe^{3+} , though the location of the right edge of the 0.9 μm band exhibits variations above 6 wt% FeO in the bulk (**Fig. 6.2.3**).

In the MIR spectra, bulk SiO_2 wt% correlates with the position of the right edge of the reststrahlen band (**Fig. 6.2.4**). The more silica-rich samples have the right band edge at larger wavenumbers (i.e., shorter wavelengths) compared to the more mafic samples. The Christiansen feature position does not correlate with bulk SiO_2 wt% (**Fig. 6.2.5**), which goes against the literature's conclusion (e.g., Conel, 1969; Fu et al., 2017) that the position of the Christiansen feature should correlate with the bulk wt% SiO_2 .

The MIR bulk wt% SiO_2 PLS model utilizes a cumulative normalization and the asymmetric least squares (ASL) baseline correction; the result of the preprocessing is that the spectra have intensity values from -0.056 to 1.0, and the spectral features have been emphasized, so that the reststrahlen band and Christensen features cover most of the intensity (y-axis) space. When the spectra are plotted and colored by bulk SiO_2 wt% (**Fig. 6.2.6**), the correlation between the change in the right edge of the reststrahlen band and bulk SiO_2 wt % is clearly visible. The PLS coefficients (**Fig. 6.2.7**) appear to emphasize (e.g., have larger PLS coefficient values compared to the mode) this region of the spectra, as well as the Christensen feature onward. The fit of the PLS model prediction varies non-uniformly with size fraction, but all predicted values are within uncertainty of the actual bulk SiO_2 wt%.

For the VNIR bulk wt% SiO_2 PLS model the spectra have a maximum normalization and ASL baseline removal. The result of these are spectral intensity values between -1 and 1, and when colored by bulk wt% SiO_2 , shows visible differences between samples with silica poor and silica rich bulk composition in numerous areas along the spectra (**Fig. 6.2.8**). The model predictions are off by, at most, 5.5 wt% SiO_2 , and do not systematically under or over predict the

wt% SiO₂ (**Fig. 6.2.9**). The PLS model coefficients emphasize the same areas as the glass wt% SiO₂ model coefficients, though the coefficient values are different. 96% of the PLS predictions are within uncertainty of the actual values.

6.3 Trends with Glass Composition

There is a moderate positive correlation between glass wt% SiO₂ and the average VNIR reflectance (**Fig. 6.3.1**). This likely occurs because the more basaltic bulk composition samples have more mafic glasses, which in turn have lower albedos. In the VNIR, the 0.9 μm band begins uniformly near 0.75 μm , however, the width of the band is not uniform. The position of the right edge of the 0.9 μm band exhibits variations above 4 wt% FeO in the glass, whereas in samples with <4 wt% FeO the 0.9 μm band ends at 1.1 μm (**Fig. 6.3.2**).

Electron microprobe analyses (EMPA) may be used to estimate silica-rich glass volatile concentrations (Devine et al., 1995). The Bishop tuff sample BT, which has the lowest compositional total (97.24 wt% $\pm$ 1.18 wt%, **Table 4**) for the glass composition, also has the deepest VNIR band depths at 1.2 μm , 1.4 μm , and 2.2 μm . Pinatubo sample PS_2, which has a doublet at 1.9 μm , also has a low total (97.24 wt% $\pm$ 1.81 wt%, **Table 4**) The other samples all have totals within 1 wt% of 100 wt%. The low totals from the EMPA suggests that BT and PS_2 may be hydrous glasses (Devine et al., 1995), with volatile concentrations of 2.76 wt% and 2.16 wt%, respectively, which may explain why they have such deep Al-OH bonds, rather than the subtle (<5% change in reflectance) absorption bands seen in the other spectra.

Glass SiO₂ wt% correlates with the reststrahlen band position of the MIR spectra (**Fig. 6.3.3**). In the samples with more felsic glasses, the right edge of the reststrahlen band occurs at larger wavenumbers than in basaltic glasses. The deepest minimum in the reststrahlen band loosely

correlates with glass wt% SiO₂ across all size fractions, with the strongest correlation seen in the <63 µm size fraction spectra.

The MIR glass wt% SiO₂ PLS model utilizes a cumulative normalization and the median filter baseline correction. The modified spectra have a flat baseline, but spectral features such as the reststrahlen band and H₂O absorptions are preserved (**Fig. 6.3.4**). The model predictions vary in each sample with size fraction, but the predicted values are within uncertainty of each other, and 91% of the samples' glass SiO₂ compositions are predicted within uncertainty (**Fig. 6.3.5**). The outliers with the largest error in the predicted values are the Okmok OAD glasses, discussed below. The amount of glass present does not affect the uncertainty of the PLS predictions.

The VNIR glass wt% SiO₂ PLS model utilizes an L₂ normalization and ASL baseline removal, which results in spectral intensities from -0.13 to 0.27 (**Fig. 6.3.6**). When the spectra are plotted and colored by glass wt% SiO₂, there are visible differences between samples with silica-poor and silica-rich glass. The model is least accurate in predicting the Okmok OAD glass compositions; the OAD sample has two distinct glasses, as discussed below. Overall, 86% of the samples glass SiO₂ compositions are predicted within uncertainty. The amount of glass present does not affect the uncertainty of the PLS predictions.

Both VNIR and MIR PLS models cannot compensate for the two glass compositions (56.8 and 73.8 wt% SiO₂) in the Okmok sample OAD, and as result OAD has the worst prediction for both models. The MIR PLS model predicts a glass wt% SiO₂ of 64.4–65.7, the smallest size fraction having the lowest predicted value and the 250–125 µm size fraction having the highest predicted value. The predicted values are above the bulk composition's wt% SiO₂ value of 60.86 wt%, which would incorrectly suggest the sample is dacitic, rather than andesitic. The VNIR

PLS model predicts a glass wt % of 64.1–65.9. It makes sense that the PLS model would predict a single composition for the OAD glass composition, despite it having two glasses, because the spectral signatures of both glasses are present in a single spectrum. Each unique spectrum will only have one prediction from the PLS model. By predicting a composition between the two glasses, the model does a good job of compensating for the presence of two distinct glasses.

6.4 Size Fraction and Phase Assemblage

Feldspar is present in all the samples used in this study. The presence of subtle 1.9 and 2.2 μm bands in the basaltic samples is due to the presence of plagioclase feldspars, which have absorption bands near 1.9 and 2.2 μm (Pieters and Englert, 1993; **Fig. 6.4.1**). The feldspar features are overprinted by strong Al-OH absorptions in the BT, PS_2, and PS_3 spectra. The amount of Fe-oxide present does correlate with the depth or location of the 0.9 μm band, which is at odds with previous findings (e.g., Pieters and Englert, 1993) because the 0.9 μm band is a result of $\text{Fe}^{2+,3+}$ bonds (**Fig. 6.4.2**). This suggests that $\text{Fe}^{2+,3+}$ present in other phases besides oxide are influencing the 0.9 μm band, which has been previously suggested; Horgan et al. (2014) used the region near 1 μm is to predict glass abundance in presence in three-phase mixtures.

The emission and reflectance of a sample's spectrum changes with size fraction, with the <63 μm reflecting the most and emitting the least (**Fig. 6.4.3**). This observed trend is consistent with previous research showing that size fraction will change the albedo, and thus reflectance, of a sample (e.g., Adams and Filice, 1967) or the emission (e.g., Lyon, 1965) while not changing the spectral features present. Different size fractions of a single material can have different spectral feature intensities in the VNIR (Gaffey, 1984), which explains the changes in band depth observed between the different size fraction spectra of a sample.

Select samples show evidence of changes in the phase assemblage with size fraction in their VNIR spectra. In the PS_2 VNIR spectra (**Fig. 6.4.4**), for example, the 2 mm–250 μm size fraction does not exhibit a doublet at 1.9 μm , while the other three size fractions do. It has been shown in the VNIR that absorption band presence in mineral mixtures can vary with particle size (e.g., Crown and Pieters, 1987), and this could be the driving factor behind the change of spectral features in the VNIR.

The reststrahlen band region ($\sim 7\text{--}12\ \mu\text{m}$, or $\sim 1,428\text{--}833\ \text{cm}^{-1}$) in the MIR records Si-O stretching vibrations. The presence of multiple minima in the reststrahlen band region is not unexpected; each minimum is the result of the different Si-O bond stretching vibrations within the sample. Glasses can contain several different Si tetrahedral units (King et al., 2004), and the Si-O bonds differ between the other main phase components (feldspar, olivine, and pyroxene). The variable numbers of reststrahlen band minima for different size fractions of the same sample (e.g., **Fig. 6.4.5**) could be due to slight changes in the phase assemblage between size fractions, particularly as there are changes in minima numbers between larger size fractions' spectra. The addition of an extra minimum in the smallest size fraction ($<63\ \mu\text{m}$) could also be the result of non-linear light-particle interactions as the particle size approaches the wavelength of light being observed (e.g., Lyon, 1965). The Christiansen feature is known to not change with size fraction in a uniform sample (Ramsey and Christensen, 1998). The fact that the shape of the Christiansen feature is observed to change as the spectra are varied by size fraction indicates that small changes in the phase assemblage could be occurring.

The MIR glass phase % PLS model uses cumulative normalization and tophat baseline correction. The cumulative normalization stretches the spectra to that the minimum value for each spectrum is 0, the maximum is 1, and spectrally bland regions remain that way. Combined

with the tophat baseline correction, the spectral noise has been maximized and any common spectral shape, including the reststrahlen band, has been minimized (**Fig. 6.4.6**). The MIR PLS models predict a different glass phase % for each size fraction of a sample; most of these are within error of each other (**Fig. 6.4.7**). 90% of the PLS predictions are within error of the actual values. The MIR PLS predictions are least accurate for CFSWLC and Hei, which are all off by over 14%. The model is not better at predicting any particular size fraction and gives a different value of each size fraction of a sample. The amount of glass present does not affect the uncertainty of the PLS predictions.

For the VNIR glass phase % PLS model the spectra have maximum normalization and a Kajfosz and Kwiatek baseline removal, resulting in the spectral intensities stretching from 0 to 1, with most of the spectral features suppressed, except for the edges and a peak near 1.8 μm that is not present in the non-preprocessed spectra (**Fig. 6.4.8**). The model predicts a different glass phase % for each size fraction of a sample and is not better at predicting any particular size fraction (**Fig. 6.4.9**). 81% of the PLS predictions are within error of the actual values. For the samples with the least amount of glass where the large amount of error could allow for an absence of glass, the model tends to underpredict the glass phase %, while for samples with more glass the model tends to overpredict the glass phase %.

The VNIR and MIR glass phase % models have the lowest and second lowest components of any PLS model, respectively, which minimizes the chance they only apply to the sample set the model is built from. However, both models have poor R^2 , which limits their accuracy and applicability. Unlike the VNIR PLS model coefficients, the MIR PLS coefficients are scattered across the spectra (**Fig. 6.4.7**). This suggests that the effect of glass in the MIR spectral region is not limited to a narrow wavelength range, but rather that it applies across the entire region.

The MIR size fraction PLS model preprocessing has both cumulative normalization and the MPLS baseline removal performed on it, which results in a stretch of intensities from -0.18-1, and a flat baseline (**Fig. 6.4.10**). The MIR PLS model has an R^2 of 0.982, and all of the PLS model predictions are within error of the correct size fraction (**Fig. 6.4.11**). The VNIR size fraction PLS model applies a minimum normalization, and has a poor fit with an R^2 of 0.546 (**Figs. 6.4.12, 6.4.13**); 69% of the predictions are within error of the correct size fraction.

6.5 Trends with Vesicularity

Within a chemically homogenous sample, vesicularity varies with size fraction, effecting both the grain shape and the sample spectra (e.g., Pieters and Englert, 1993; Valentine, 2001; Hooper and Necsoiu, 2014). In the VNIR spectral region, vesicularity affects the spectral brightness and band contrast, though it does not have a major influence on the position or presence of spectral features of silicates and oxides (Pieters and Englert, 1993). In the MIR spectral region, vesicles behave like spectrally neutral blackbody emitters (Ramsey and Fink, 1999). The level of vesicularity (coarsely vesicular or finely vesicular) within a chemically homogenous sample affects the depth of spectral features in emissivity spectra, with larger vesicles resulting in shallower spectral features (Ramsey and Fink, 1999; King et al., 2004). This effect of vesicularity is only apparent if all other parameters (e.g., composition, phase assemblage, grain size) remain constant (Ramsey and Fink, 1999).

Within this study, the vesicularity of the samples does not correlate with any spectral features; likely the effect of vesicularity on the spectral shape has been overprinted by more dominant factors such as composition and phase assemblage. Despite this, both the MIR and the VNIR PLS models produce moderately accurate predictions of a spectrum's size fraction; neither PLS model predicts whole numbers and the error is on the scale of the values predicted, however

the models can still differentiate between a completely degassed rock and a pumice. The MIR vesicularity PLS model applies cumulative normalization to the spectra (**Fig. 6.5.1**), and the PLS model parameters do not place an emphasis on a particular portion of the spectrum (**Fig. 6.5.2**). The VNIR vesicularity PLS model uses the cumulative normalization with ASL baseline correction (**Fig. 6.5.3**). The PLS model predicts different vesicularity values for each size fraction of a sample (**Fig. 6.5.4**).

Within the sample set presented in this work, vesicularity poorly correlates with any parameter, however, the MIR PLS model is able to predict sample vesicularity with accuracy. This suggests vesicularity influences the spectral shape, and with normalization and baseline removal, can be mathematically extracted over the entire spectrum. Both VSNIR and MIR PLS models rely on the entire spectrum, without major emphasis on any spectral region, supporting the theory that the effect of vesicularity on the spectra is subtle, agreeing with previous work discussed above.

6.6 Comparison with previous work

Several studies (discussed below) have used VNIR spectroscopy to identify glass or tephra using variations in band parameters. The approaches to calculating the band parameters differ, and the resulting applicability likewise vary. There are more studies than can reasonably be discussed, so here I will compare two.

McCanta et al. (2015) used VNIR spectroscopy in conjunction with other techniques (e.g., point counting, magnetic susceptibility), to identify cryptotephra, or non-visible layers of tephra, in ocean drill cores. This work used two-phase mixtures of tephra and oceanic sediment to build a band parameter, focusing on the 1.0 μm region, which is sensitive to the presence of tephra in the core. The band parameter derived in this work presents a method of non-destructive tephra-

presence identification for samples composed of tephra and oceanic sediment with more than 50% glass.

Horgan et al. (2014) used mineral mixture-based models to create several band parameters focusing on the 1.0- μm region to identify glass presence in orbiter-based spectral observations. This work observed that glass was most accurately detectable above 80 % using the parameters derived in the work. Horgan et al. (2014) performed preprocessing on the spectra, however, the baseline removal method used in Horgan et al. (2014) was different than any that were used in this study.

The VNIR glass phase % PLS model parameters were most dynamic near the edges of the spectra (**Fig. 6.4.9**), with no emphasis on the 1.0 μm region, counter to the focus of the band parameters in previous studies. The band parameters developed by Horgan et al. (2014) and McCanta et al. (2015) do not rely on the entire spectrum, instead focusing on the relatively narrow 1 μm region; this region contains absorption bands from Fe, and studies of basaltic glass spectra (e.g., Minitti et al. 2002) have shown that glass can have spectral features in this region . The use of band parameters allows for more direct application of their work to spectra with differing numbers of spectral channels. The PLS models presented here cover a wider array of compositions than the studies, which provides more flexibility in their application. The combination of the five PLS models tested in this study, however, allow for greater characterization of any glass present in a sample, and with greater accuracy than the band parameters.

6.7 Implications

The sample set presented here functions as a spectral library from which PLS models for glass detection and characterization have been built. This work demonstrates that PLS models can be used to quantify glass presence and compositional information from both VNIR and MIR spectra. Utilizing PLS models to predict compositional parameters for tephra rather than more traditional methods, such as band parameters, allows for a more robust characterization of samples.

The results of this study indicate that glass presence and composition can be predicted from PLS models built from the collected spectra. The tephra compositions included in the spectral library span a wide range of expected compositions for planetary volcanism (e.g., Jakobsson et al., 1973; Bernard et al., 1996; Anderson et al., 2000; Horgan and Bell, 2012). This study utilizes natural samples, which means that the library includes realistic, varying phase assemblages. The PLS models are able to accurately predict glass presence and composition across a wide array of phase assemblages. We also included a range of sample sizes, which allows for the PLS models to make predictions about a sample's composition and phase assemblage without assuming a particle size, while also providing a method to constrain the particle size.

The PLS models allow us to detect glass presence below what other studies have achieved using band parameters, and allow for the characterization of the glass present in a non-destructive or non-disruptive manner. This is important for studies where minimizing sample destruction is paramount, or samples might not be available. Cryptophera studies, for example, utilize cores of ice, peat, or sediments, and use extremely thin (mm-to nm thick) layers of tephra, relying on the detection of glass to both define and characterize the geochemistry of a tephra layer (Carter et al., 1995, Shane 2000; Lowe 2010; Brown et al., 1992). Cryptotephra studies

frequently identify previously unknown eruptions, increasing our knowledge of volcano's eruptive frequency and style, which can directly inform hazard assessments (Payne et al., 2008; Shane et al., 2013). For tephra deposits on other planets, sample return may be impossible for the near future, but characterizing the volcanic history of planets via remote sensing spectroscopy can inform our understanding of their magmatic history, formation, and evolution.

The PLS models were calculated to have a coefficient value for each spectral channel, resulting in 2152 coefficients for the VNIR models and 1090 coefficients for the MIR models. These models can be directly applied to spectra with the same spectral channels. However, for spectra with different channels, the PLS models will need to be re-calculated. The process for this is relatively simple; the library's spectra can be re-sampled through different spectrometers' bandpass functions, and then the PLS models re-calculated following the methods used in this work. The baseline correction and normalization for each will be determined by the re-calculation of the PLS models, also affecting the number of components used.

The PLS models show that accurately capturing the full spectrum is more important for glass parameterization than the high density of spectral channels (2152 VNIR and 1090 MIR spectral channels). The PLS model parameters (**Figs. 6.2.7, 6.2.9, 6.3.5, 6.3.7, 6.4.11, 6.4.13, 6.5.2, 6.5.4**) do not emphasize (e.g., have notably larger PLS coefficient values compared to the mean) narrow regions of the spectra. The MIR PLS model coefficients repeatedly get more scattered towards shorter wavelengths (larger wavenumbers), which is where the majority of the noise resides. This suggests that that part of the spectrum (above 2000 cm^{-1} or below $5\text{ }\mu\text{m}$) can be removed from consideration and the models would retain their accuracy. This is useful for remotely-gathered spectra, as there is a high density of water absorption features in the 2.5 to $5\text{ }\mu\text{m}$ spectral region that can easily obfuscate other spectral signals. The PLS parameters did get

more scattered towards the ends of the spectra, suggesting that the increased signal-to-noise near the edges of spectra introduced some error to the models.

From the calculated R^2 values and error values for both the VNIR PLS models and the MIR PLS models, both their predictive capabilities vary, leading to the conclusion that both spectral regions are required for a precise yet robust characterization of a volcanic deposit. While PLS models are a very effective method for describing the tephra deposits, their efficacy can be limited in VNIR spectral region. This is likely a result of the fact that the MIR region deconvolves linearly while the VNIR does not, and so the PLS methodology, which assumes linearity, works better on the MIR spectra. This work highlights the importance of the MIR PLS models, suggesting that developing a better understanding of glassy tephra deposits remotely requires increased emphasis on high-spectral-resolution MIR instruments. However, the more-commonly available VNIR spectra remain useful in performing bulk characterization and establishing whether glass is present in any great quantity.

6.8 Future Work

In order to assess the efficacy of the PLS models, they must be tested on sample spectra not included in the library. These models are designed to be used on both terrestrial and planetary remotely sensed spectral data, so the most comprehensive test would be to apply the models to various remote images that can be independently ground-truthed.

Continued work has begun by conducting field tests of the VNIR PLS models; MIR spectra are difficult to collect in the field due to instrument constraints. VNIR data at two resolutions (1cm and ~5cm per pixel) were collected of an outcrop of Bishop Tuff (BT) in the Pleistocene Tecopa lake beds in the Mojave Desert. The northwestern portion of the Tecopa lake beds, near

the town of Shoshone, CA, has outcrops of what is referred to as the “fresh glass facies,” which contains unaltered glass within the BT deposit despite aqueous deposition (Gilbert et al., 2011).

Two different spectrometers were used: the Spectral Evolution oreXpress (oreXpress) and Hyxpex Mjolnir VS-620 (Mjolnir). The oreXpress handheld spectrometer has a 1cm opening pistol grip and was used to collect point spectra along the outcrop. The oreXpress measures from 0.35–2.5 μ m with 2151 spectral channels, making it functionally analogous to the FieldSpec4 used in this work. Mjolnir is a pushbroom spectrometer measuring from 0.40–2.50 μ m with 490 spectral channels. It has a 20 degree vertical field of view, and captures 620 pixels per row. Mjolnir was mounted onto a tripod to capture an image cube of the target outcrop; pixels are a few centimeters per pixel. Point spectra of fresh surfaces were collected with the oreXpress, and samples were collected for every unit in the outcrop.

Other future work that could be explored would utilize PLS models to predict the other main phases present, e.g., feldspar, pyroxene, and olivine. This is difficult to do in the VNIR spectral region for multi-phase mixtures with traditional deconvolution methods. The addition of more samples to the library would be useful as well; the more samples included in building the PLS models the better both the internal error and R^2 are.

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Appendices

Appendix A: Figures

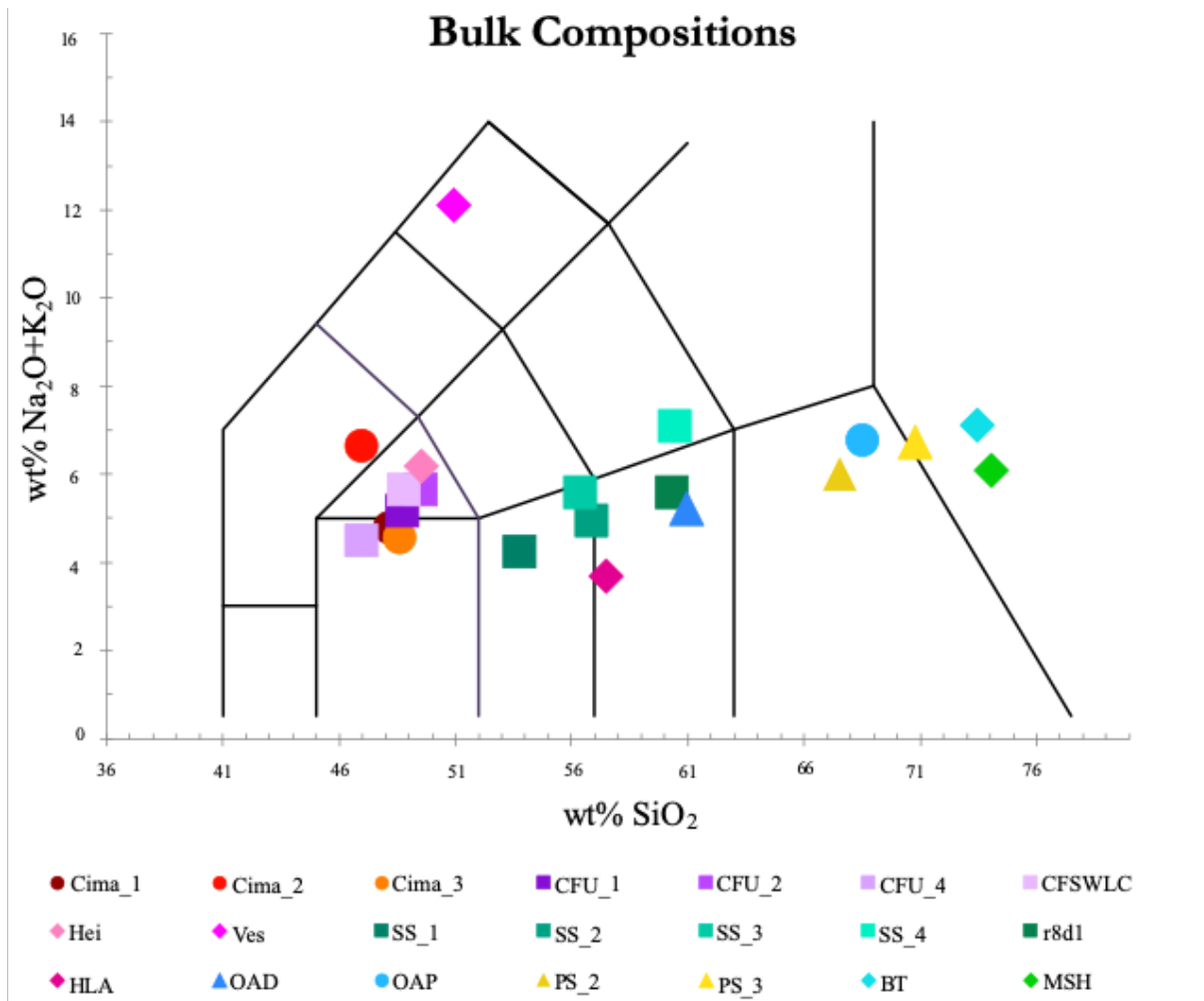


Figure 3.1. 1 Sample Bulk Compositions

Sample bulk compositions plotted by SiO₂ wt% and Na₂O+K₂O wt%, or total alkali vs. silica.



Figure 3.4 1 Instrument used to create glass beads for bulk analyses

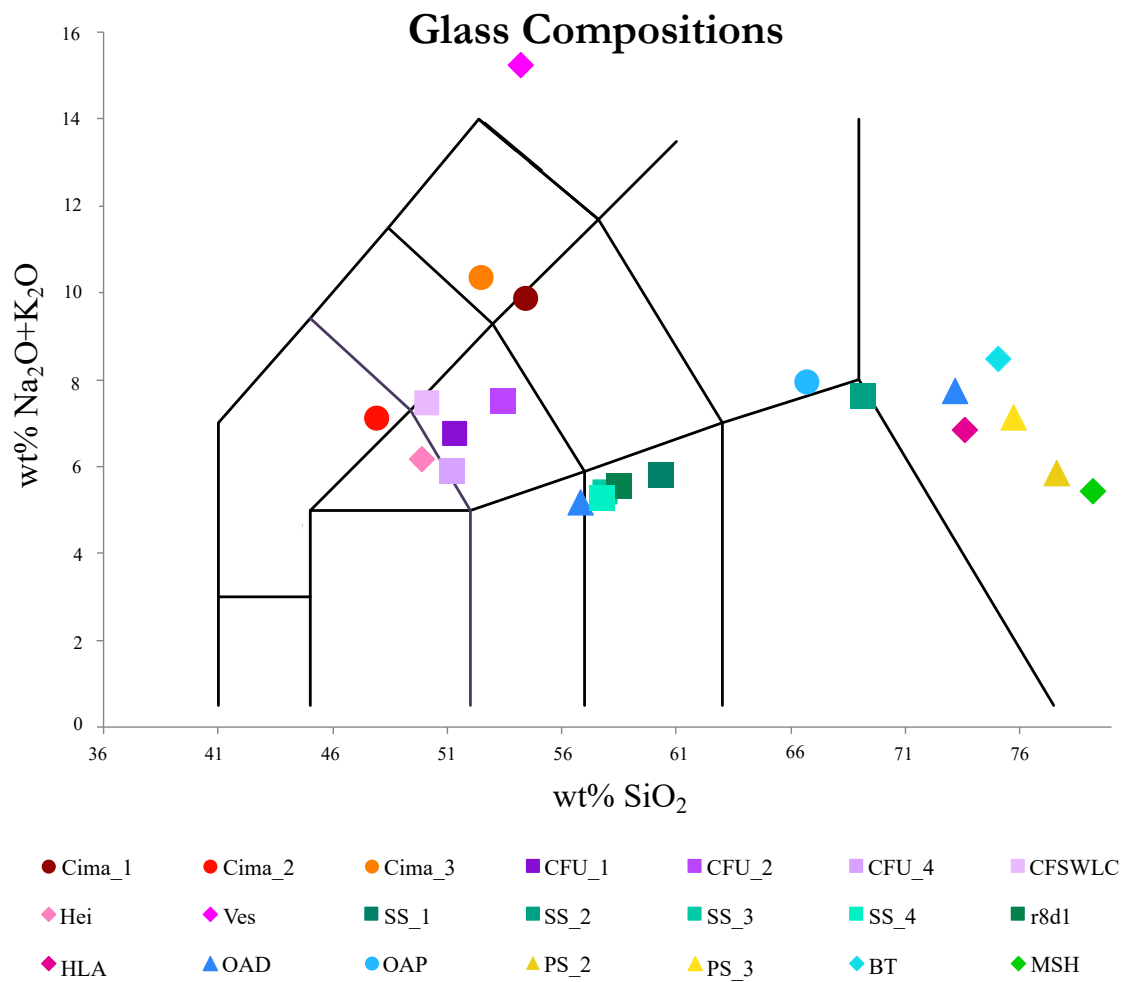


Figure 4.1. 1 Sample Glass Compositions

Sample glass compositions plotted by SiO₂ wt% and Na₂O+K₂O wt%, or total alkali vs. silica.

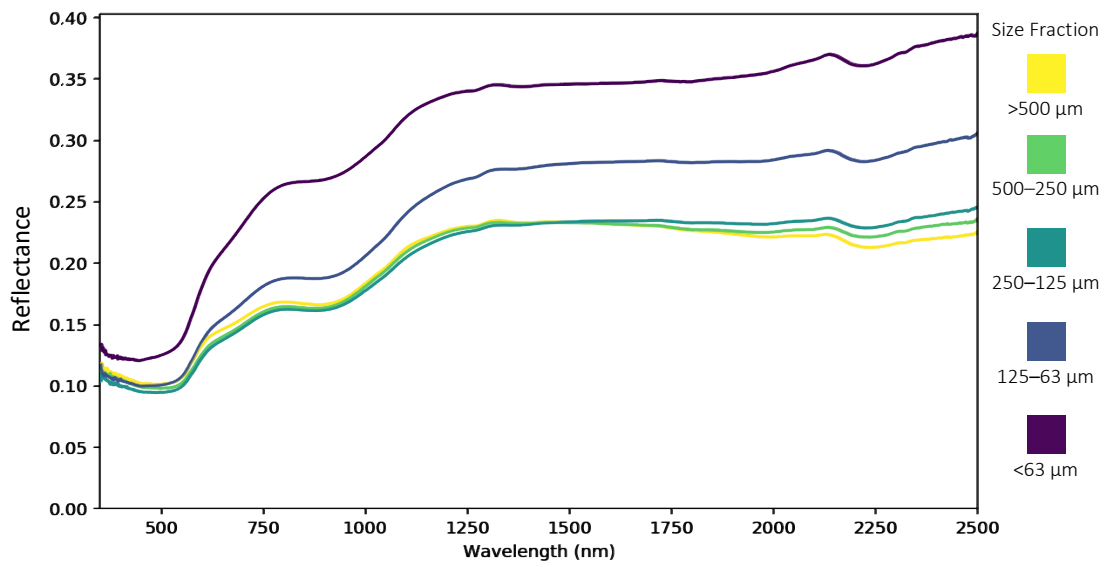


Figure 5.1. 1 Cima 1 VNIR Spectra

Cima_1 VNIR spectra, colored by size fraction.

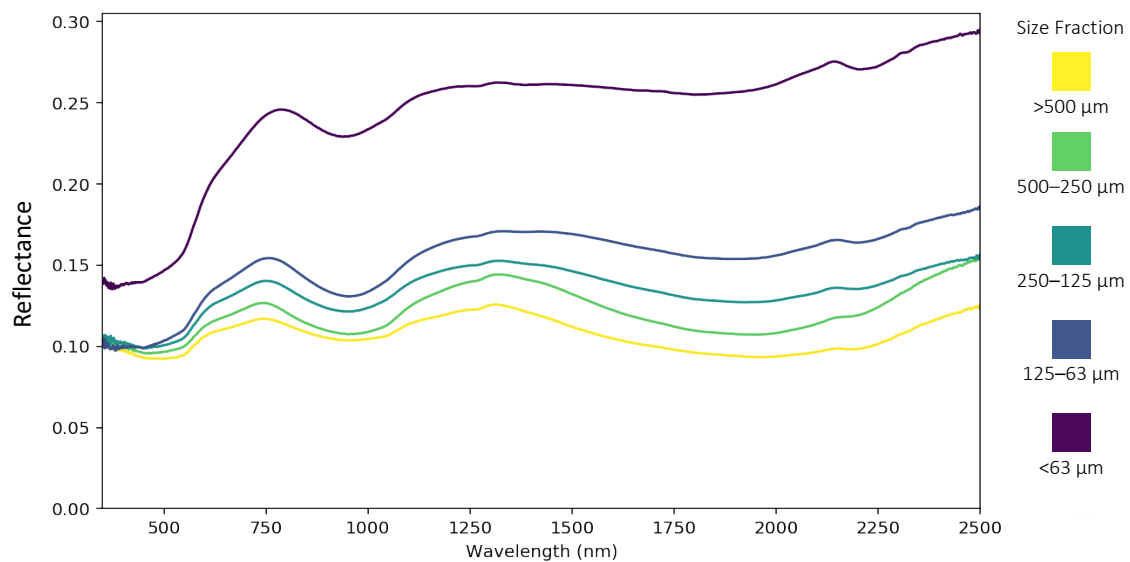


Figure 5.1. 2 Cima_3 VNIR spectra

Figure 5.1.3. Cima_3 VNIR spectra colored by size fraction.

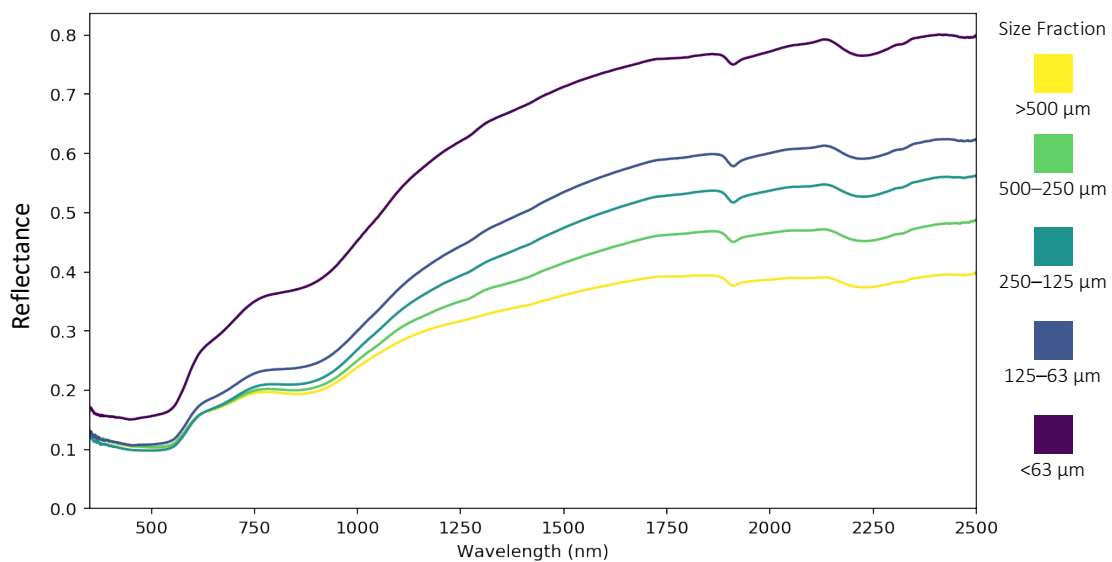


Figure 5.1. 3 Cima_2 VNIR spectra

Figure 5.1.2. Cima_2 VNIR spectra, colored by size fraction.

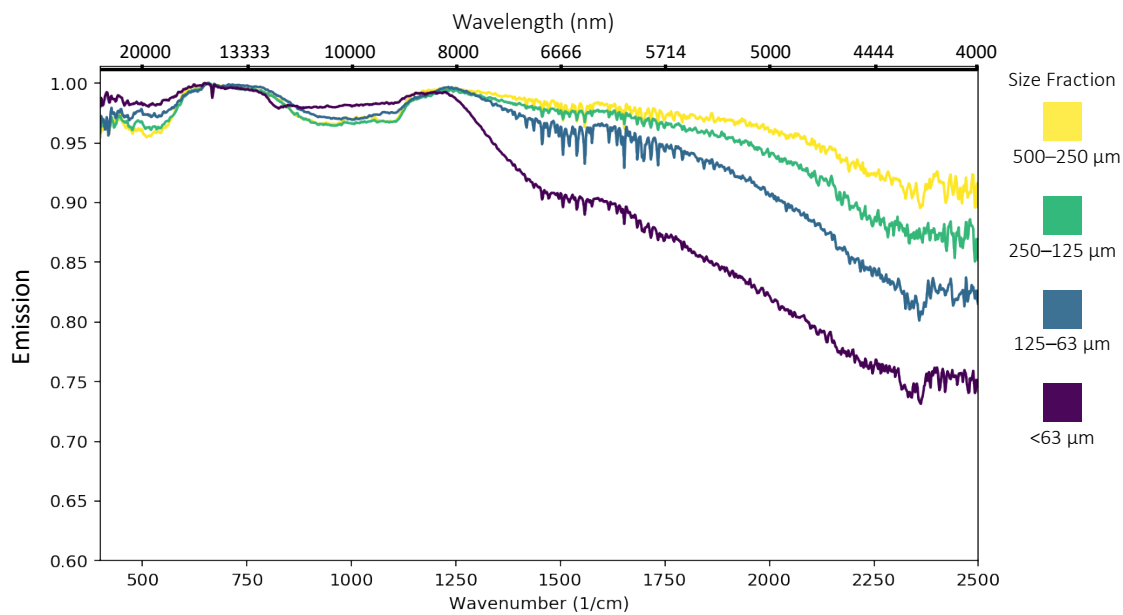


Figure 5.1. 4 Cima_1 MIR spectra

Figure 5.1.4 Cima_1 MIR spectra, colored by size fraction.

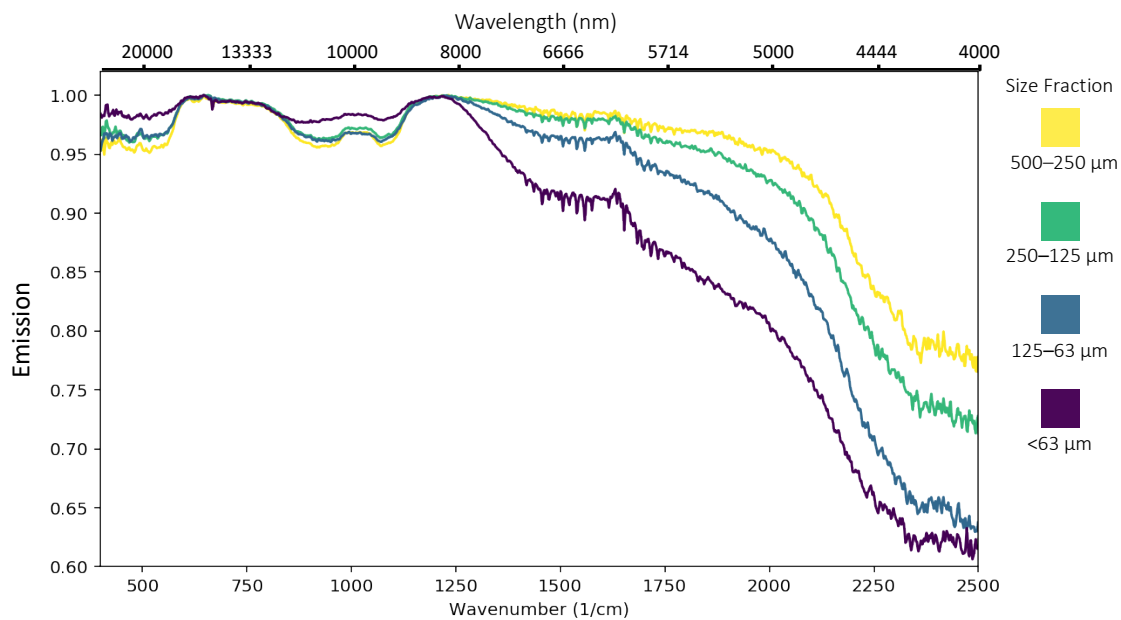


Figure 5.1. 5 Cima_2 MIR spectra

Figure 5.1.5. Cima_2 MIR spectra, colored by size fraction.

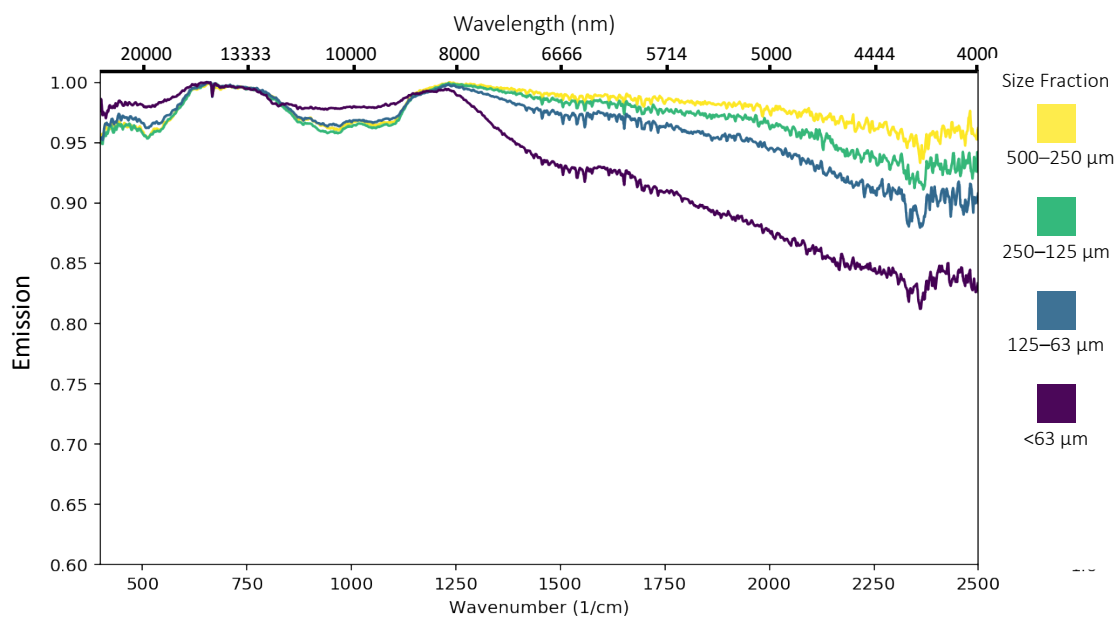


Figure 5.1. 6 Cima_3 MIR Spectra

Figure 5.1.6. Cima_3 MIR spectra, colored by size fraction.

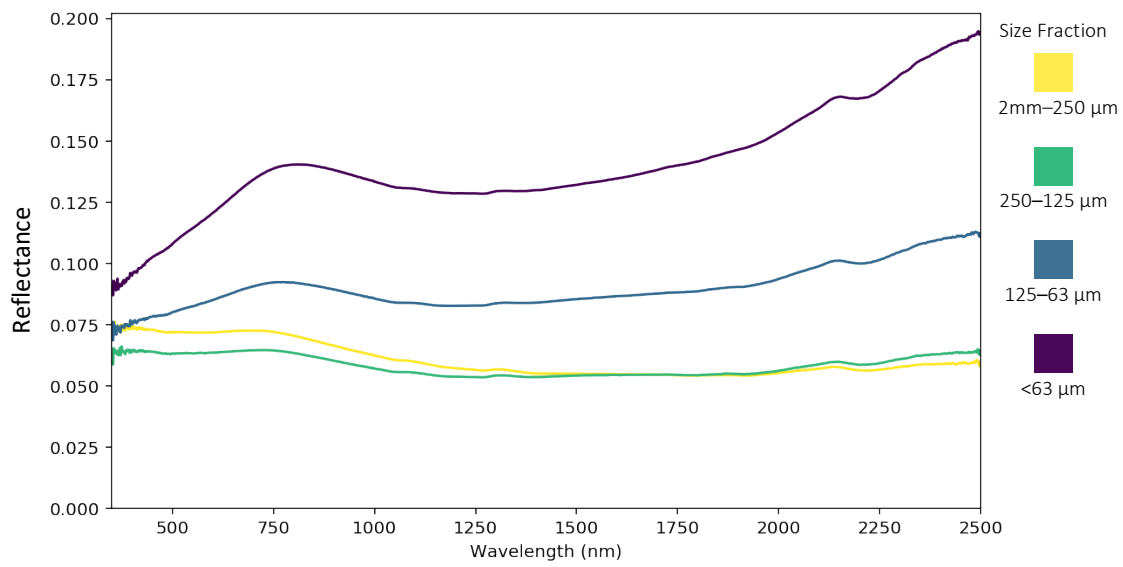


Figure 5.2. 1 CFU_1 VNIR Spectra

Figure 5.2.1, CFU_1 VNIR spectra, colored by size fraction.

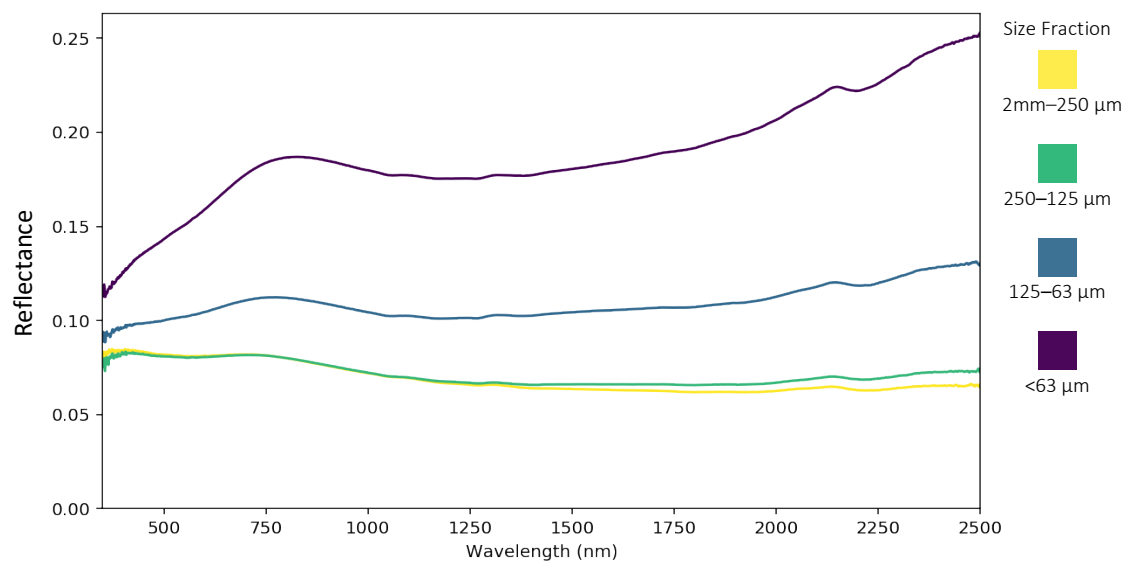


Figure 5.2. 2 CFU_2 VNIR spectra

Figure 5.2.2. CFU_2 VNIR spectra, colored by size fraction.

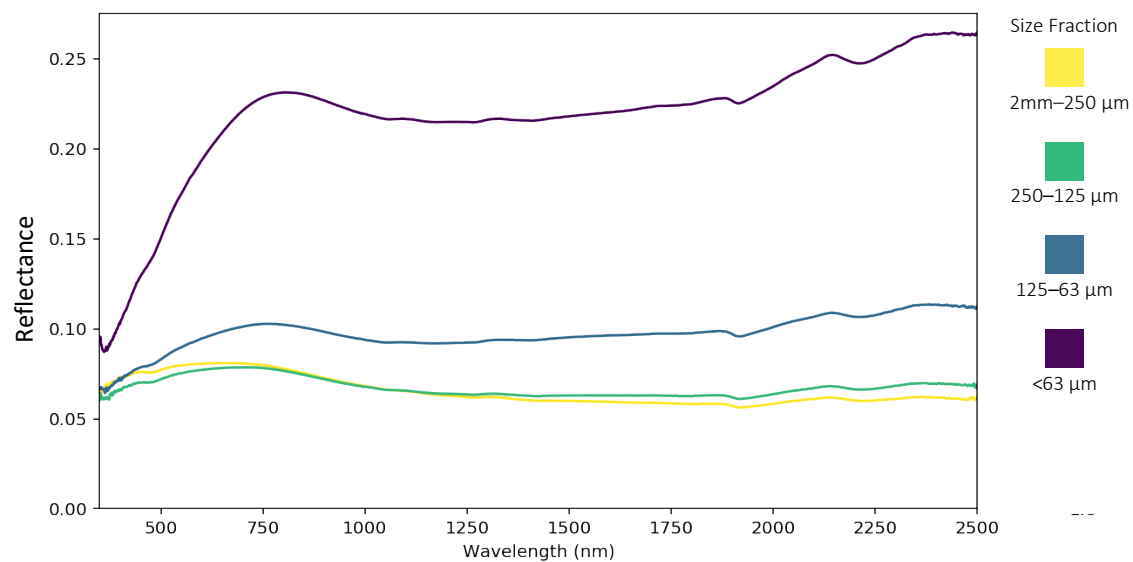


Figure 5.2. 3 CFSWLC VNIR spectra

Figure 5.2.3. CFSWLC VNIR spectra, colored by size fraction.

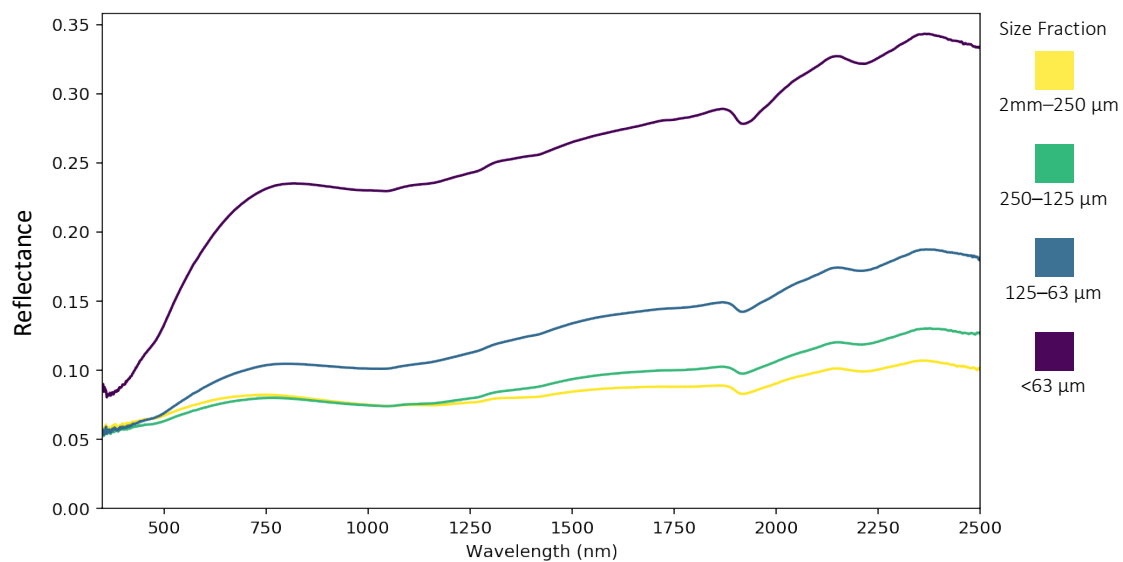


Figure 5.2. 4 CFU_4 VNIR Spectra

Figure 5.2.4. CFU_4 VNIR spectra, colored by size fraction.

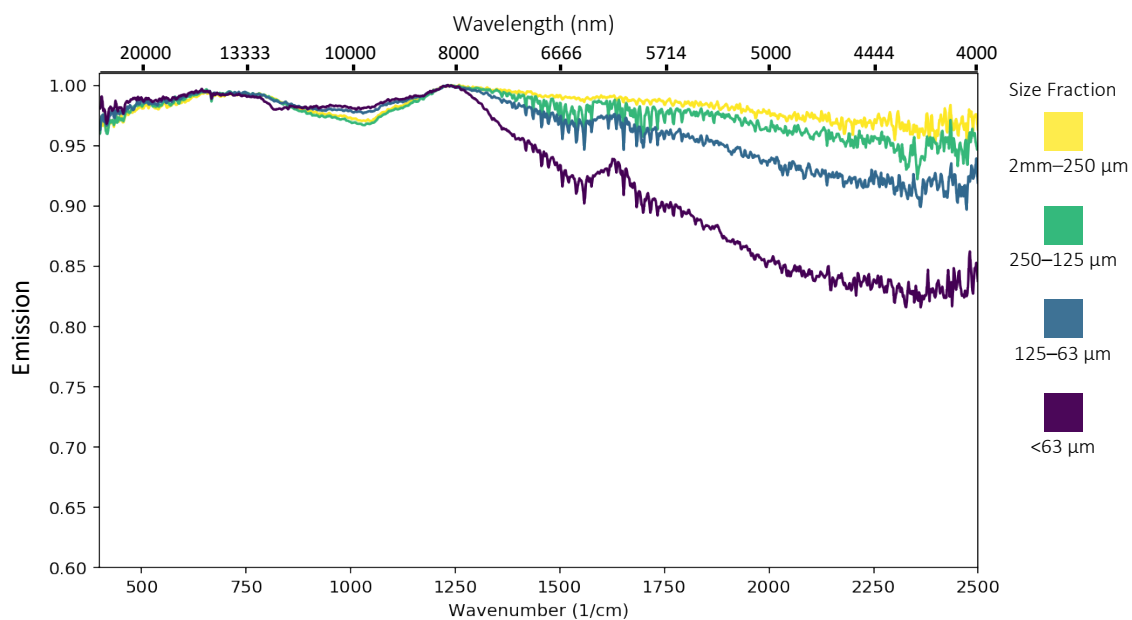


Figure 5.2. 5 CFU_1 MIR spectra

Figure 5.2.5. CFU_1 MIR spectra, colored by size fraction.

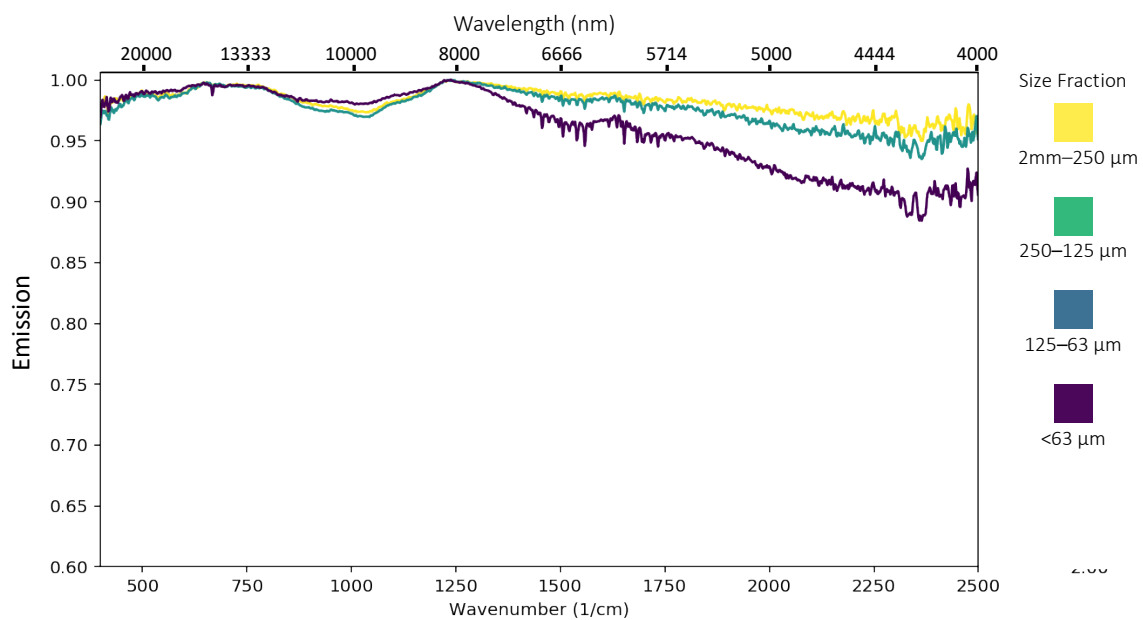


Figure 5.2. 6 CFU_2 MIR spectra

Figure 5.2.6. CFU_2 MIR spectra, colored by size fraction.

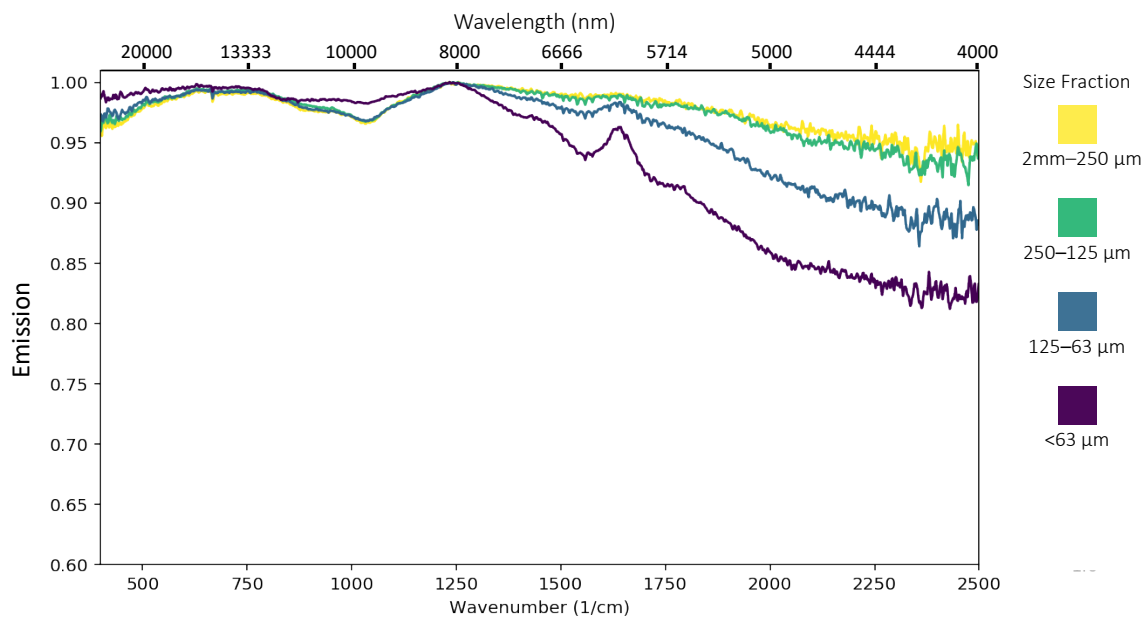


Figure 5.2. 7 CFU_4 MIR spectra

Figure 5.2.7. CFU_4 MIR spectra, colored by size fraction.

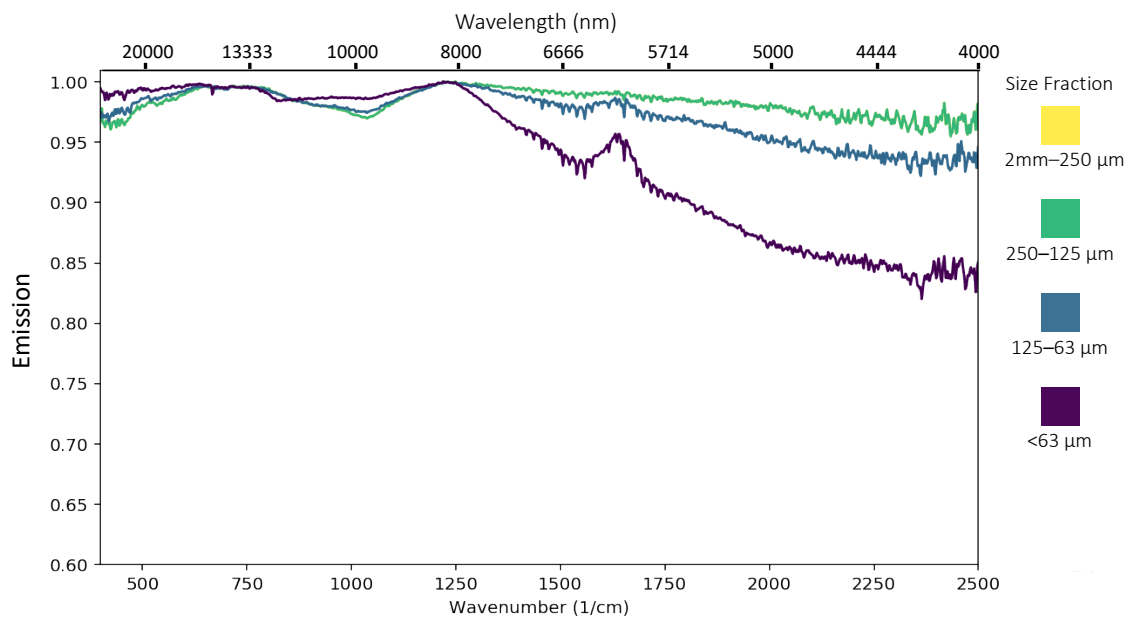


Figure 5.2. 8 CFSWLC MIR Spectra

Figure 5.2.8. CFSWLC MIR spectra, colored by size fraction. The 2mm-250 μm and 250-125 μm size fractions plot essentially on top of each other.

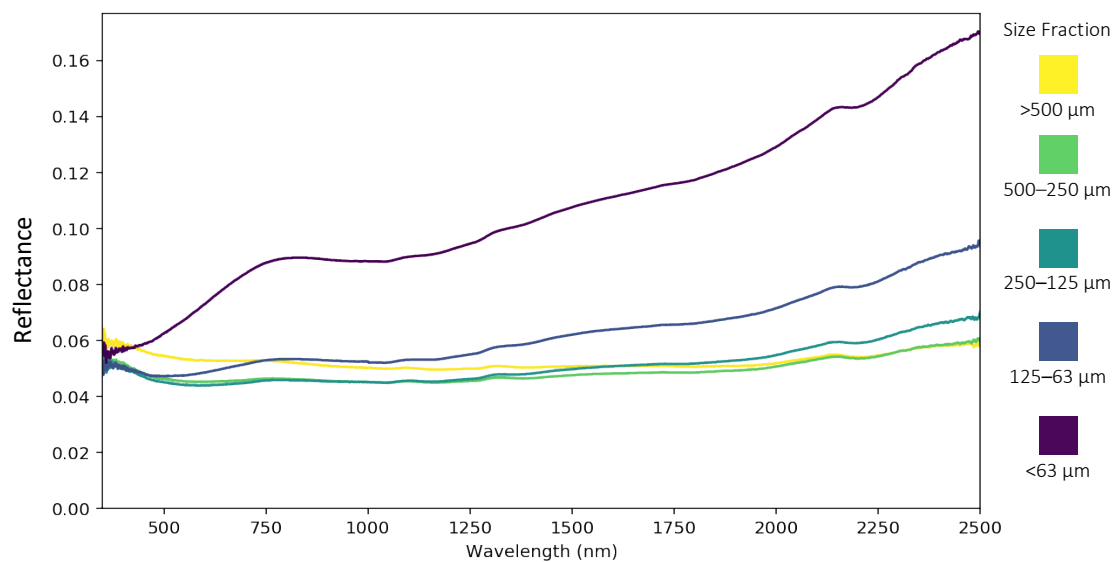


Figure 5.3. 1 Hei VNIR Spectra

Figure 5.3.1, Hei VNIR spectra, colored by size fraction.

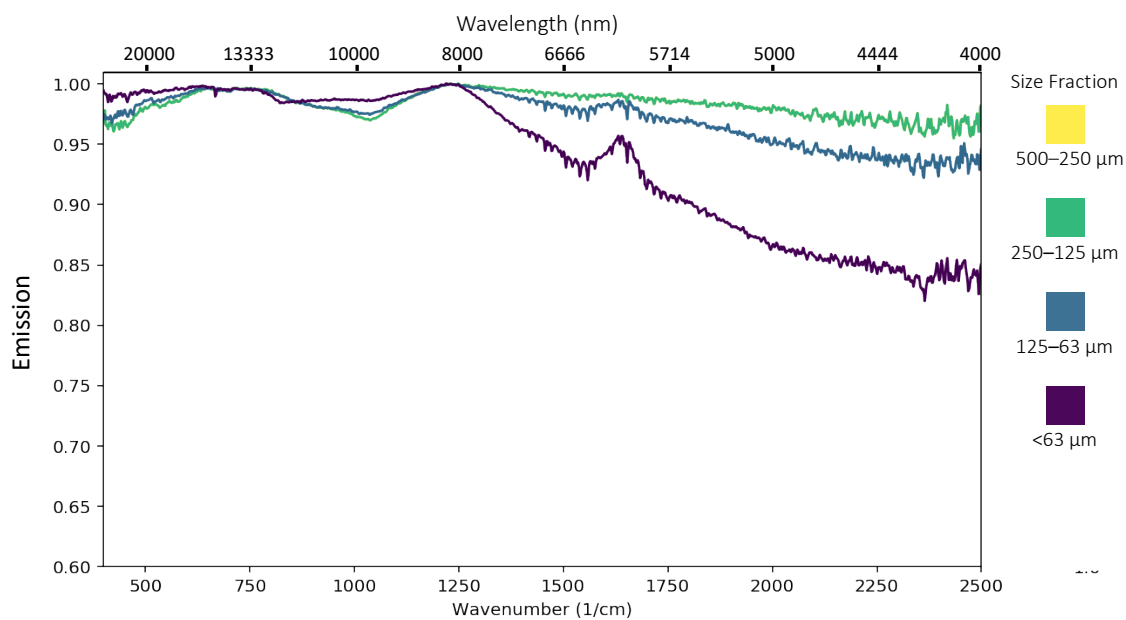


Figure 5.3. 2 Hei MIR spectra

Figure 5.3.2. Hei MIR spectra, colored by size fraction.

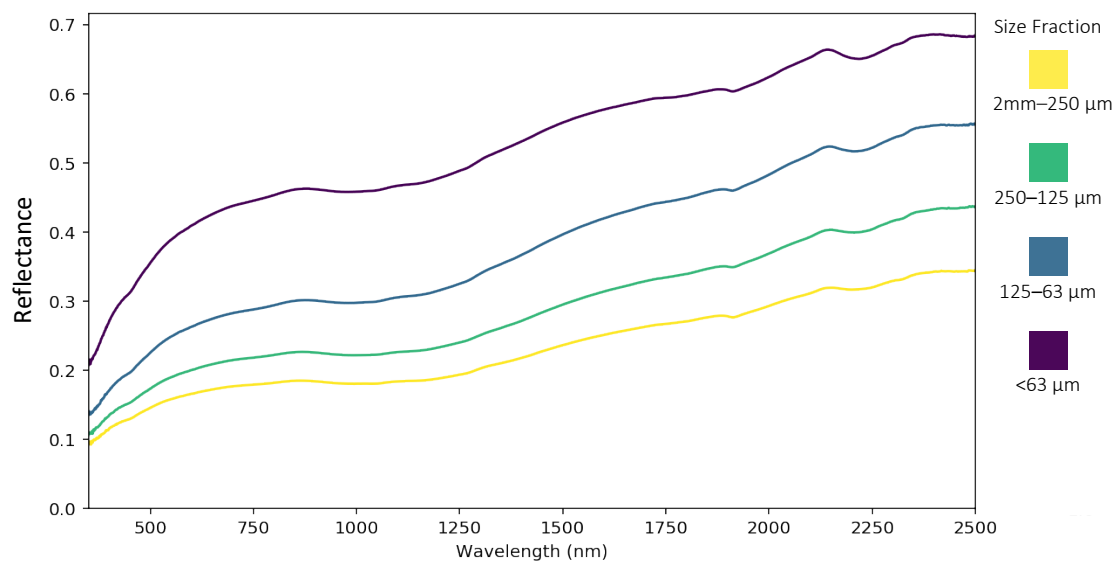


Figure 5.4. 1 Ves VNIR spectra

Figure 5.4.1. Ves VNIR spectra, colored by size fraction.

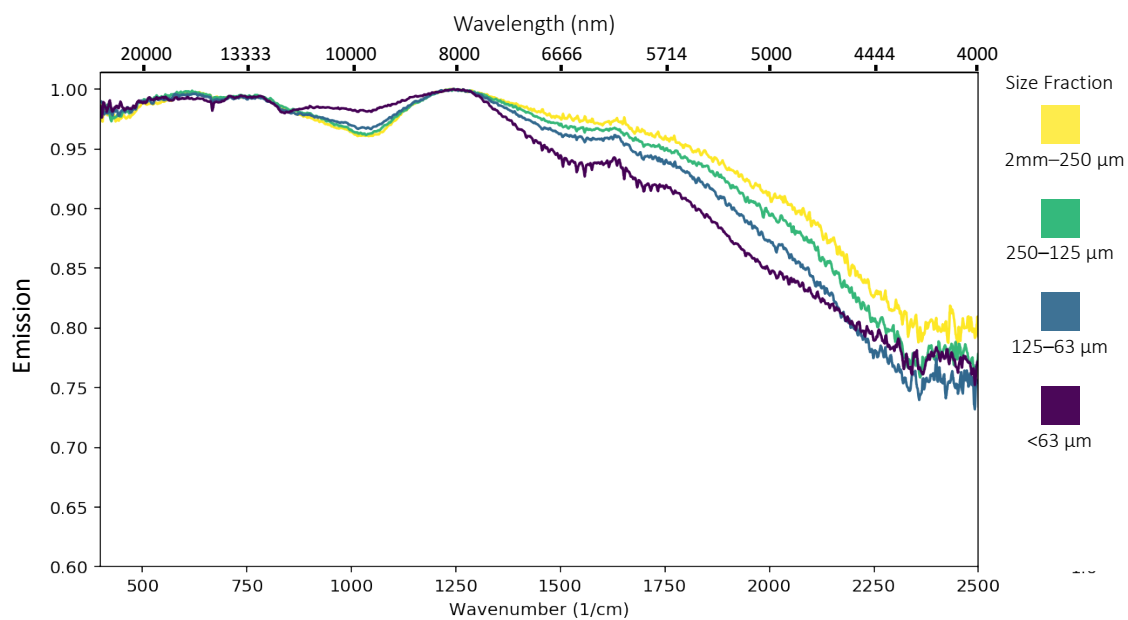


Figure 5.4. 2 Ves MIR Spectra

Figure 5.4.2. Ves MIR spectra, colored by size fraction.

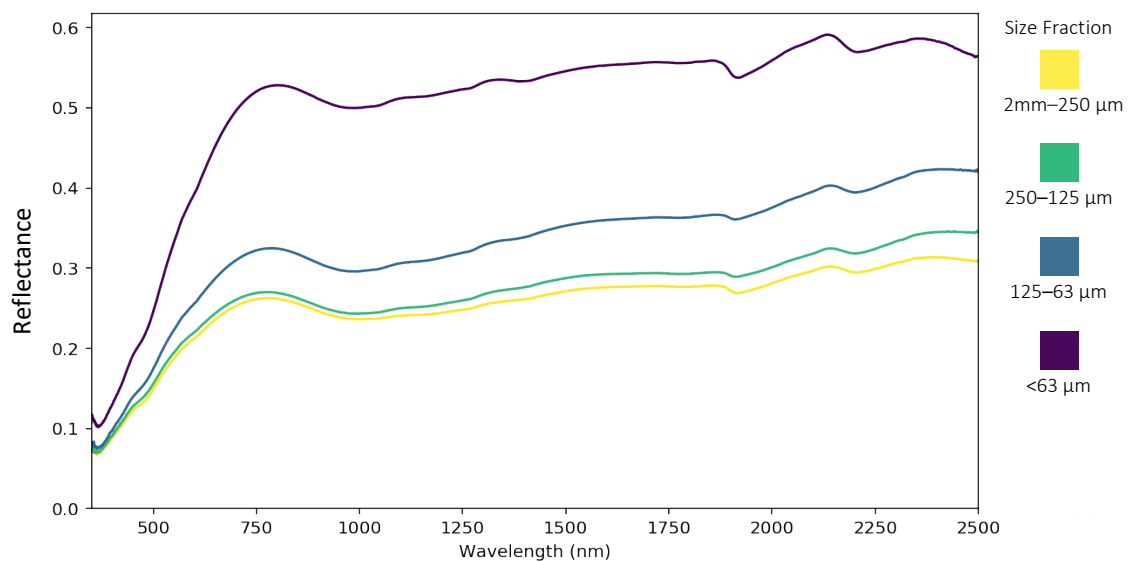


Figure 5.5. 1 SS_1 VNIR spectra

Figure 5.5.1. SS_1 VNIR spectra, colored by size fraction.

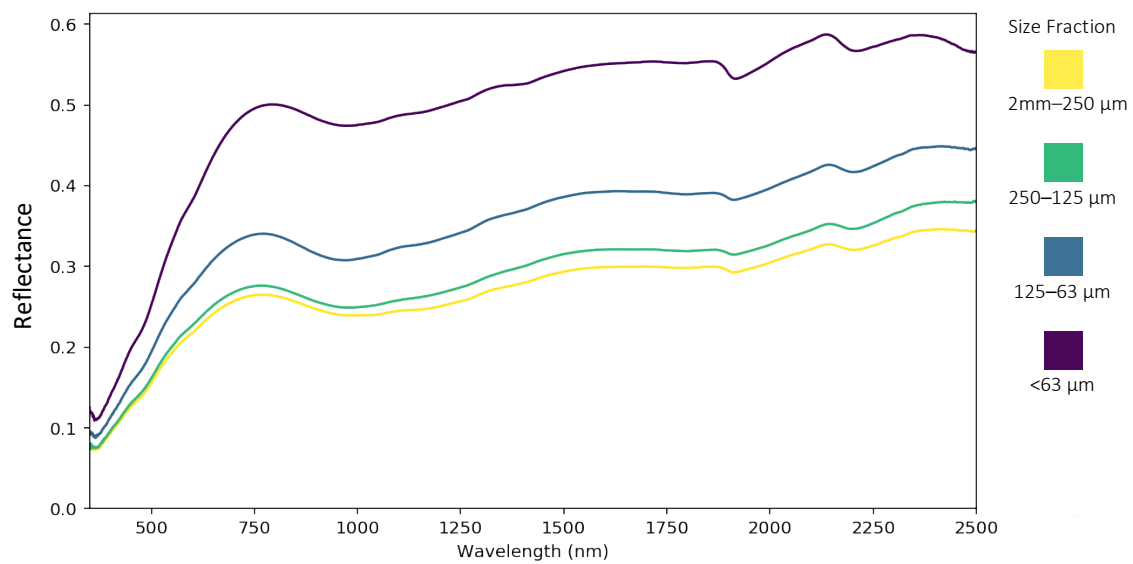


Figure 5.5. 2 SS_2 VNIR Spectra

Figure 5.5.2. SS_2 VNIR spectra, colored by size fraction.

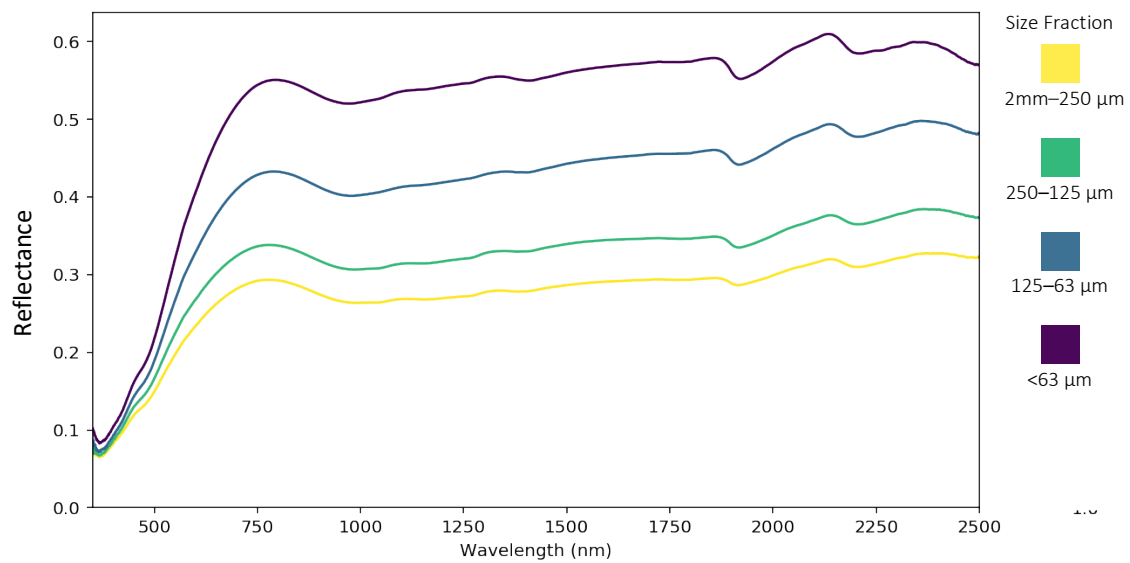


Figure 5.5. 3 SS_3 VNIR Spectra

Figure 5.5.3. SS_3 VNIR spectra, colored by size fraction.

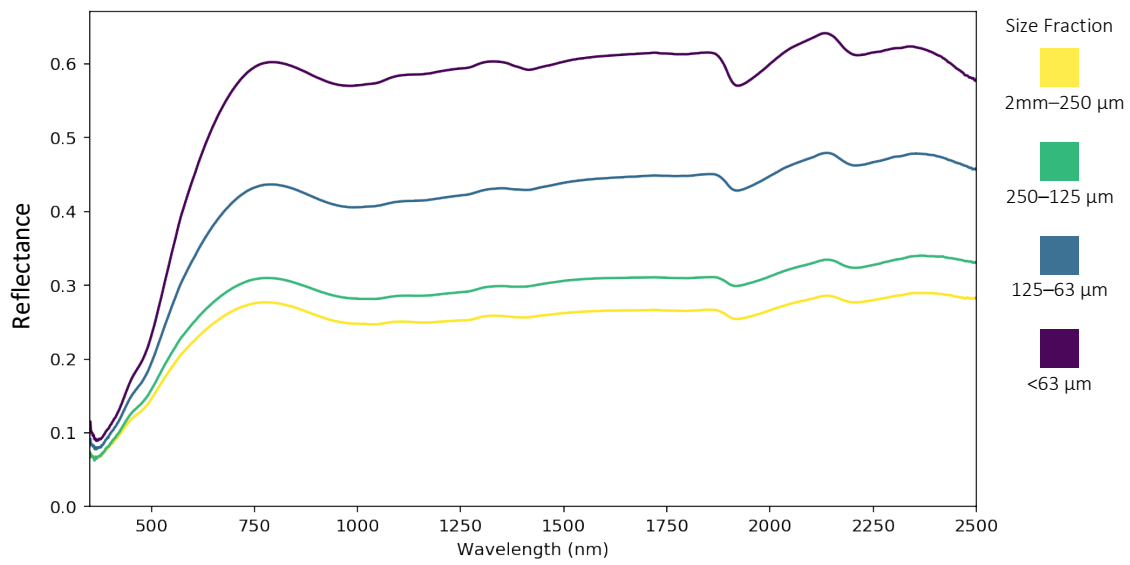


Figure 5.5. 4 SS_4 VNIR Spectra

Figure 5.5.4. SS_4 VNIR spectra, colored by size fraction.

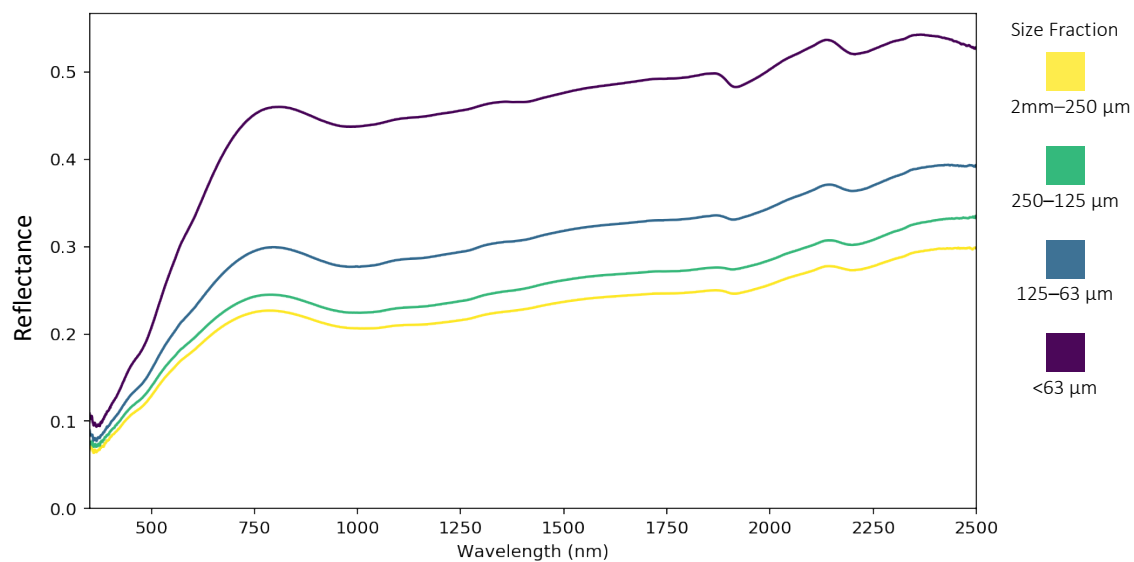


Figure 5.5. 5 R8D1 VNIR Spectra

Figure 5.5.5. R8D1 VNIR spectra, colored by size fraction.

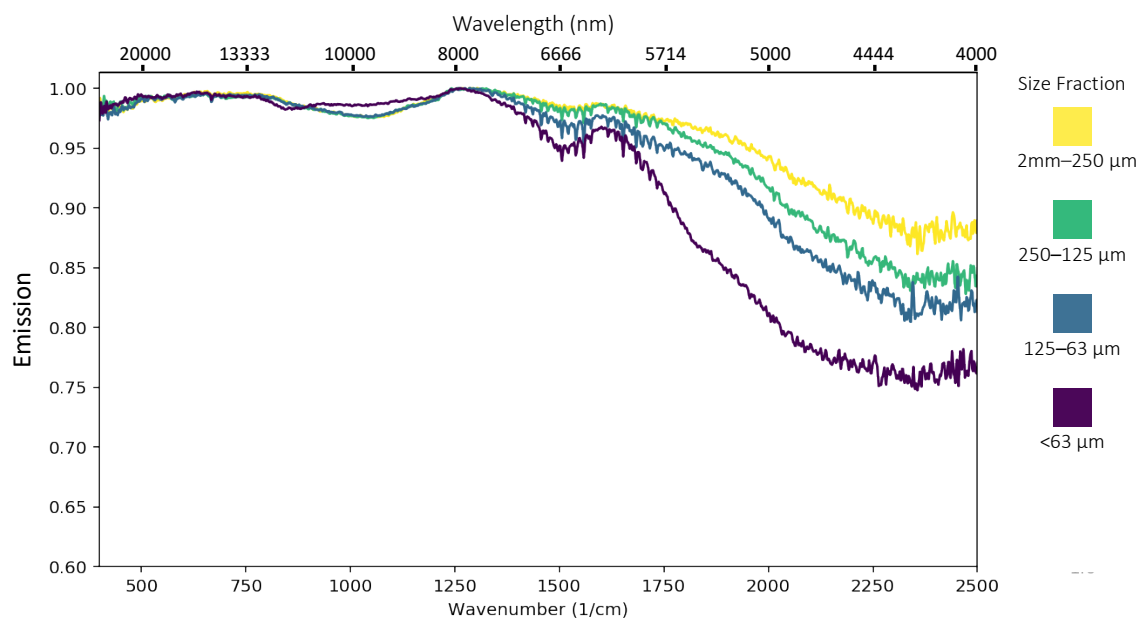


Figure 5.5. 6 SS_1 MIR Spectra

Figure 5.5.6. SS_1 MIR spectra, colored by size fraction.

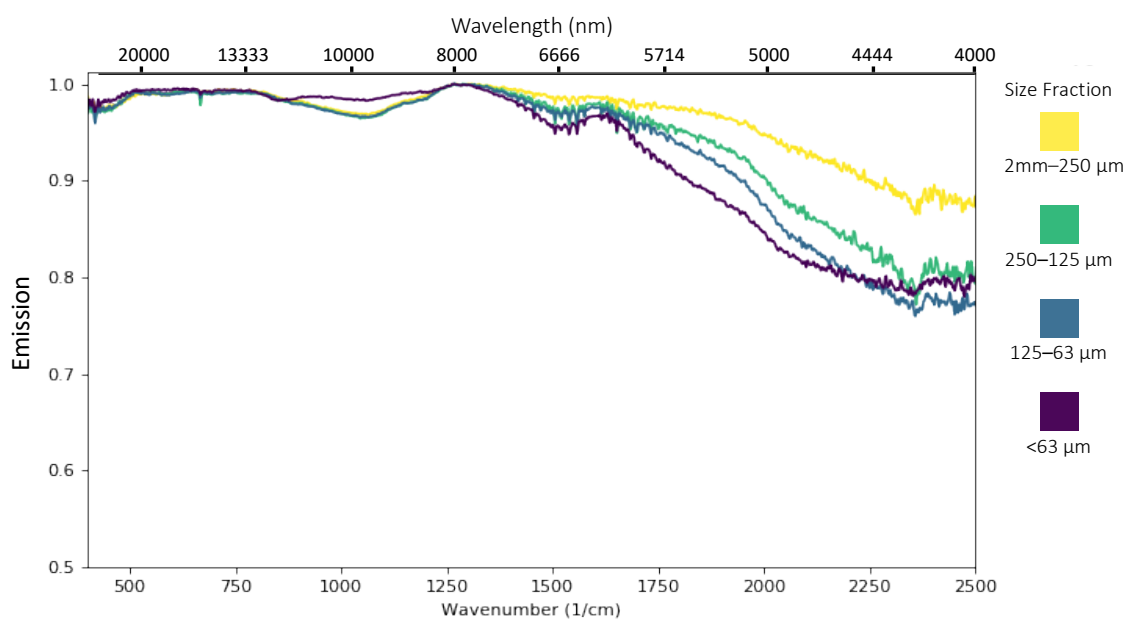


Figure 5.5. 7 SS_2 MIR Spectra

Figure 5.5.7. SS_2 MIR spectra, colored by size fraction.

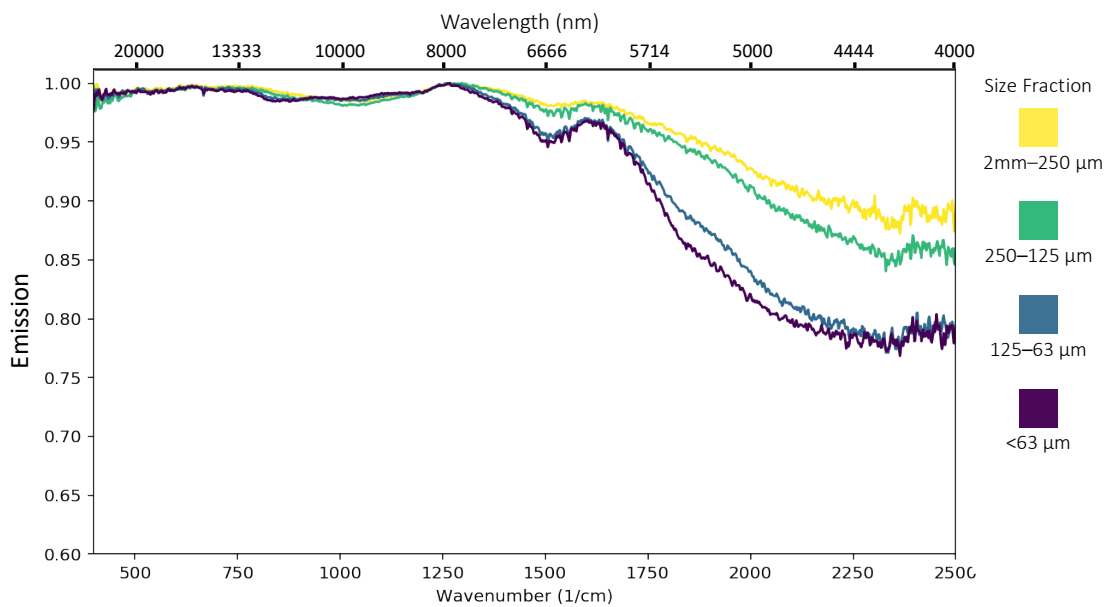


Figure 5.5. 8 SS_3 MIR Spectra

Figure 5.5.8. SS_3 MIR spectra, colored by size fraction.

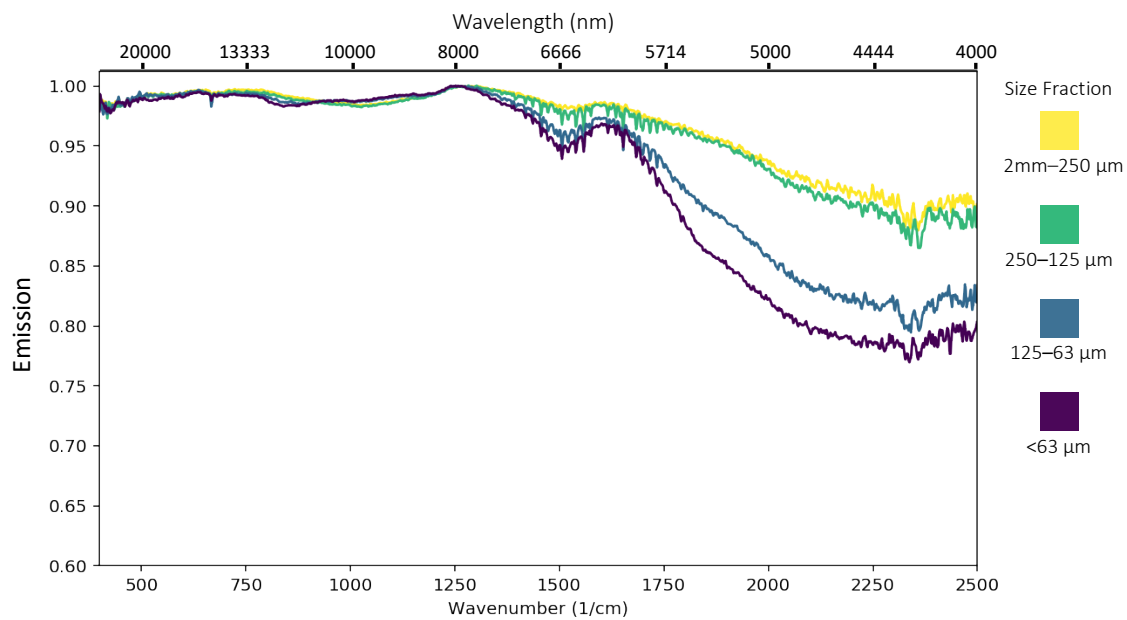


Figure 5.5. 9 SS_4 MIR Spectra

Figure 5.5.9. SS_4 MIR spectra, colored by size fraction.

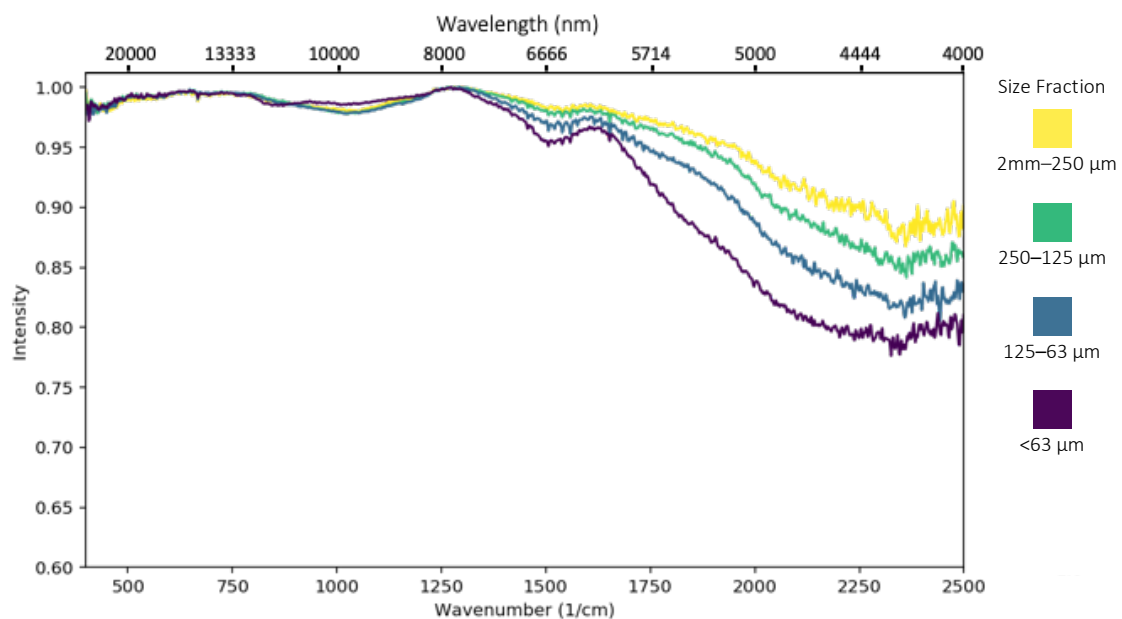


Figure 5.5. 10 R8D1 MIR Spectra

Figure 5.5.10. R8D1 MIR spectra, colored by size fraction.

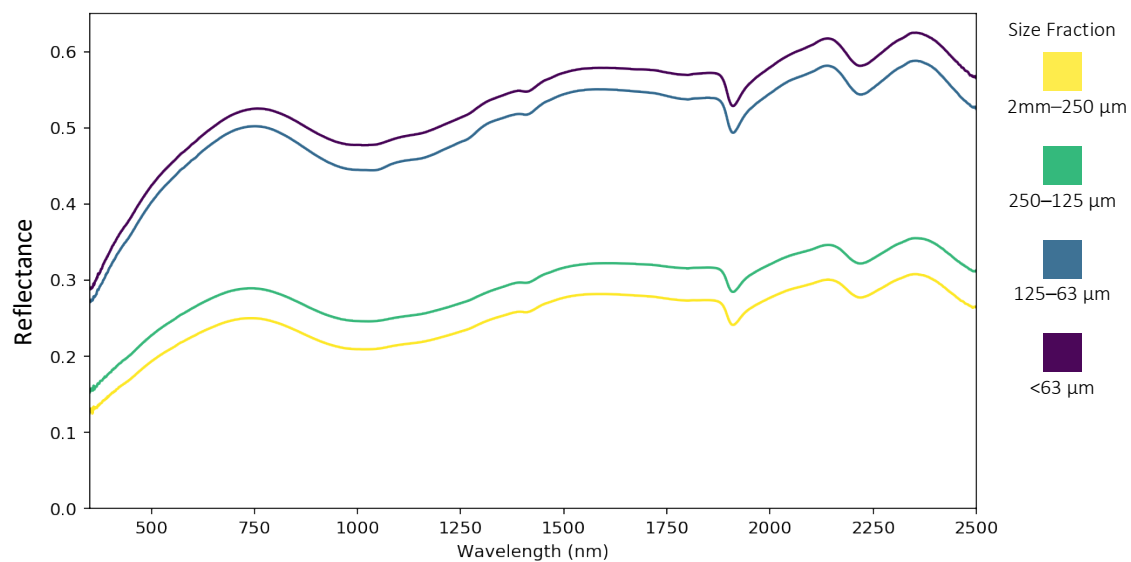


Figure 5.6. 1 OAP VNIR Spectra

Figure 5.6.1. OAP VNIR spectra, colored by size fraction.

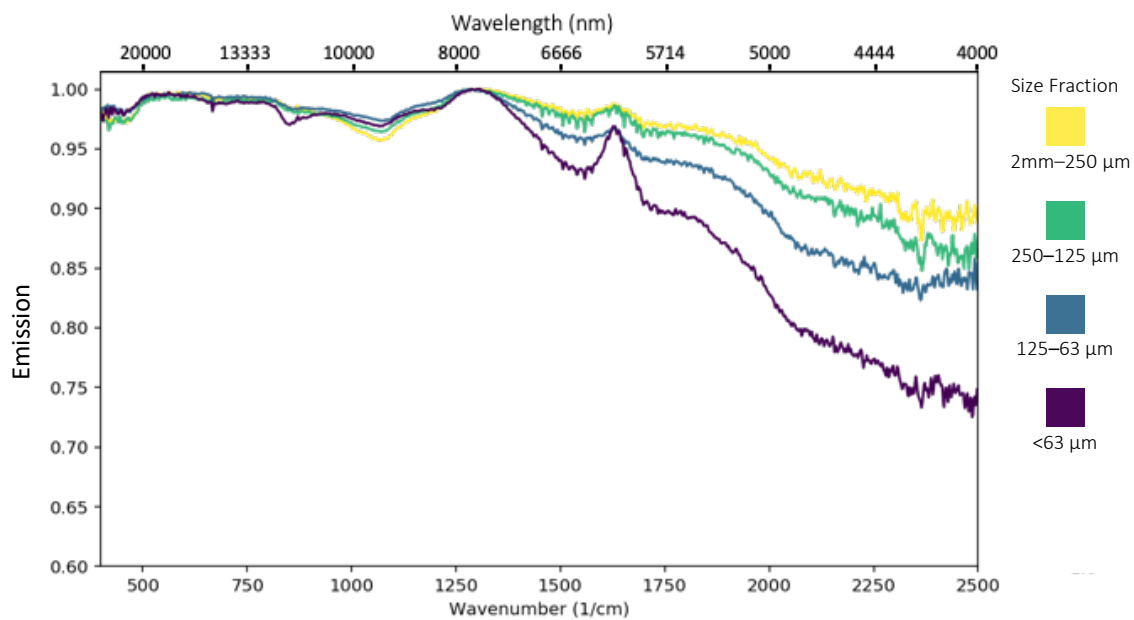


Figure 5.6. 2 OAP MIR Spectra

Figure 5.6.2. OAP MIR spectra, colored by size fraction.

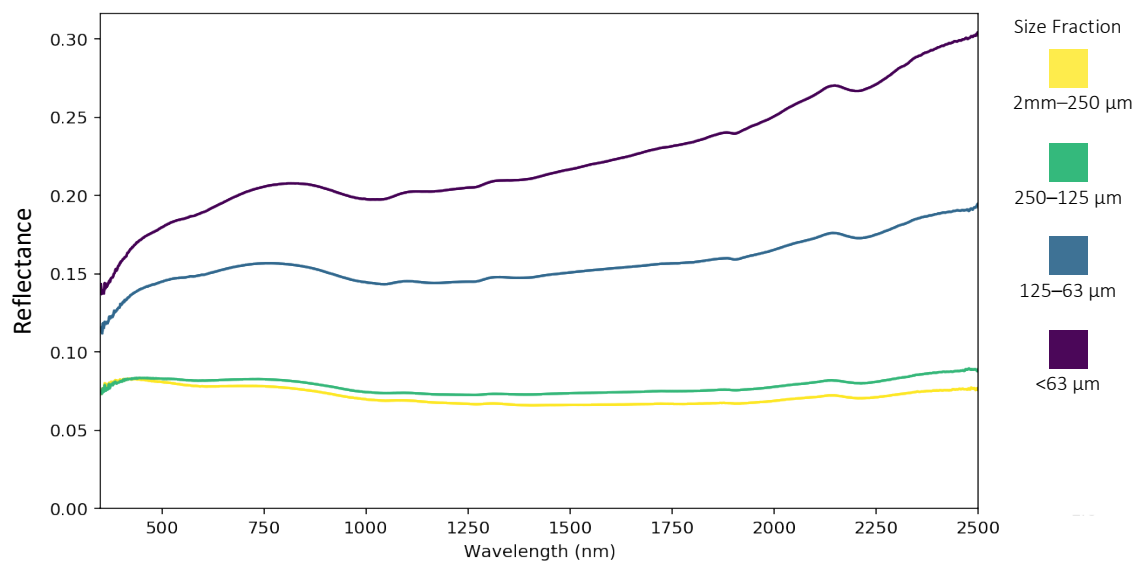


Figure 5.6. 3 OAD VNIR Spectra

Figure 5.6.3. OAD VNIR spectra, colored by size fraction.

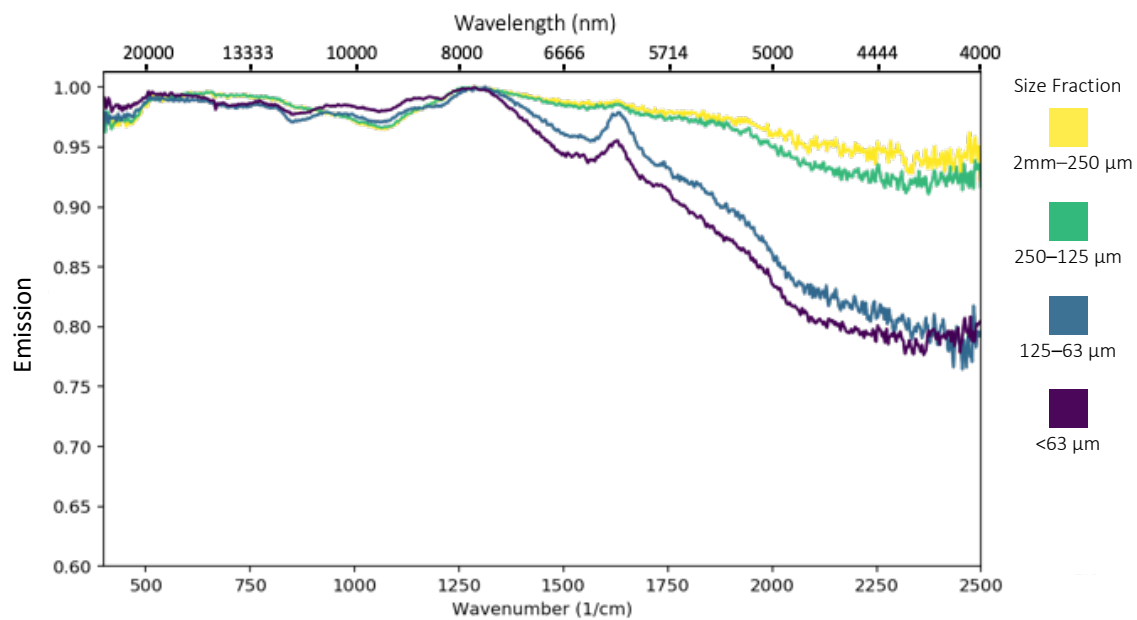


Figure 5.6. 4 OAD MIR Spectra

Figure 5.6.4. OAD MIR spectra, colored by size fraction.

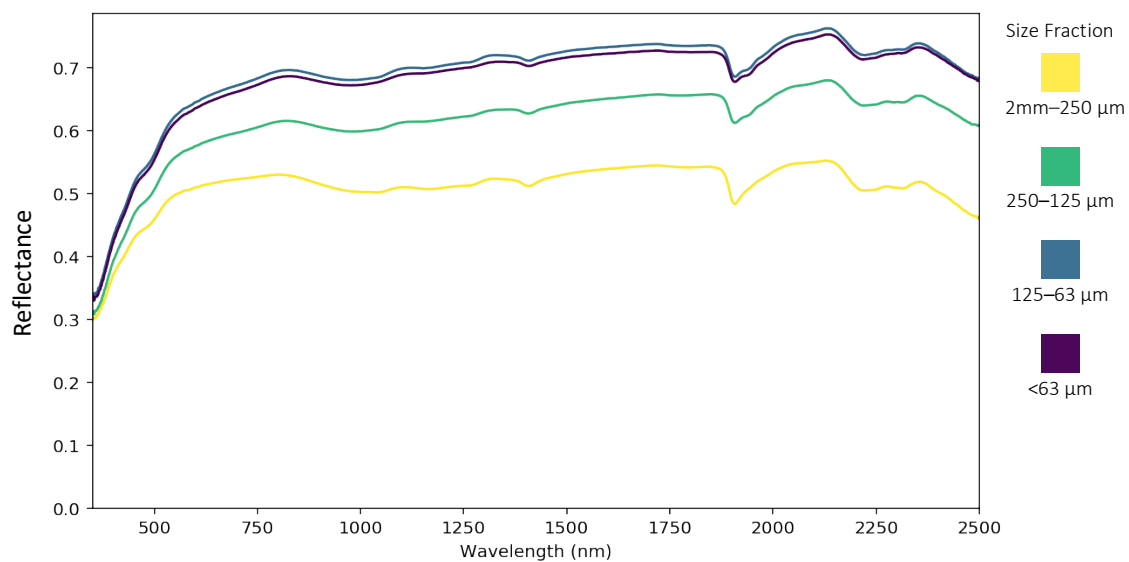


Figure 5.7. 1 PS_2 VNIR Spectra

Figure 5.7.1. PS_2 VNIR spectra, colored by size fraction.

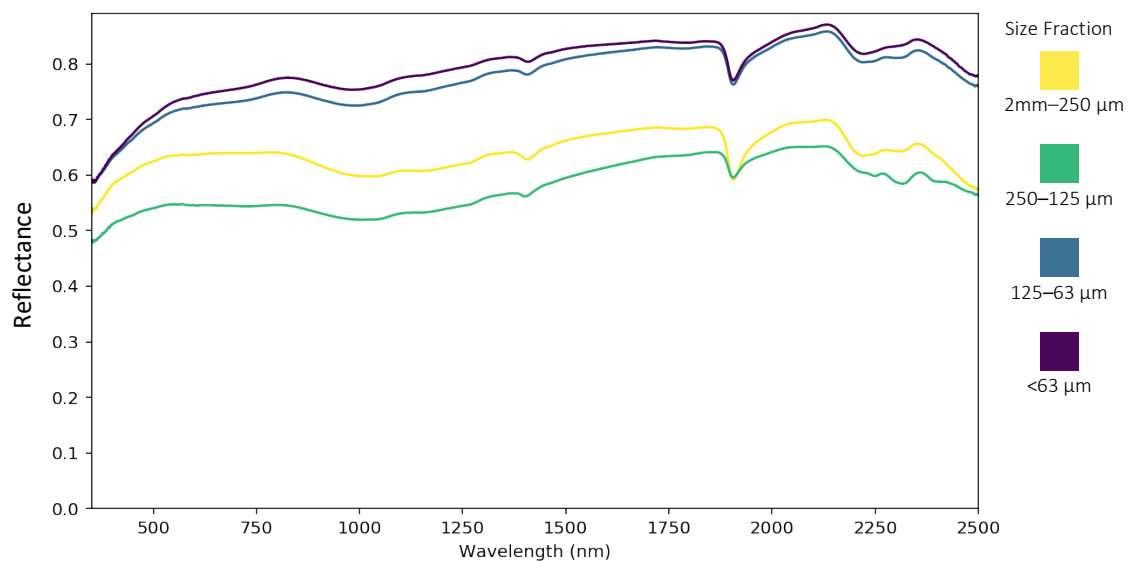


Figure 5.7. 2 PS_3 VNIR Spectra

Figure 5.7.2. PS_3 VNIR spectra, colored by size fraction.

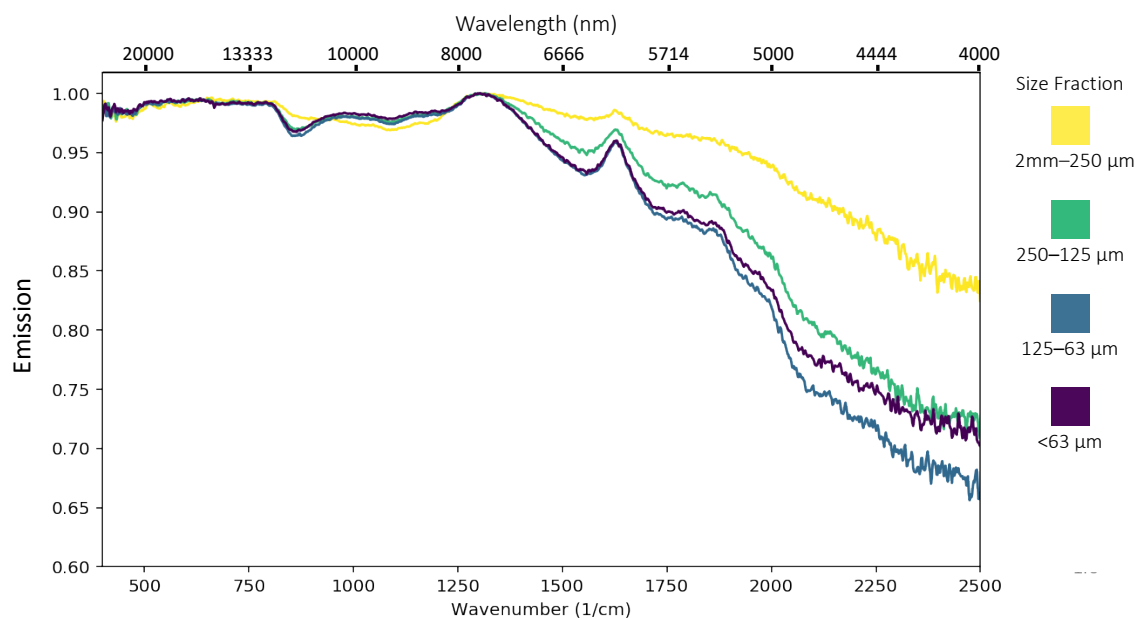


Figure 5.7. 3 PS_2 MIR Spectra

Figure 5.7.3. PS_2 MIR spectra, colored by size fraction.

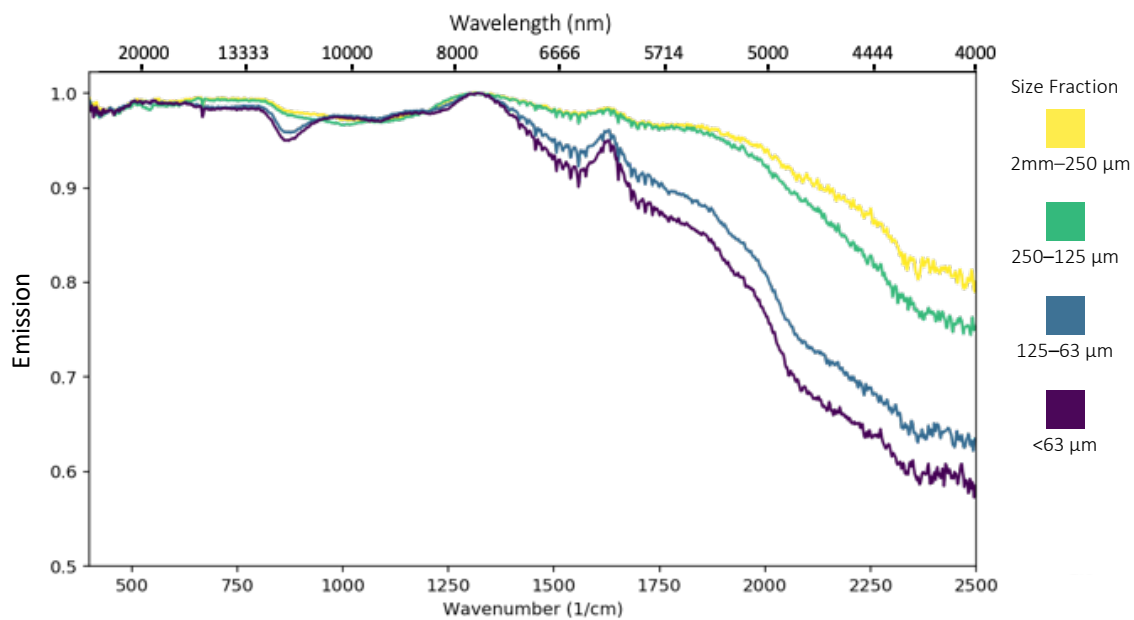


Figure 5.7. 4 PS_3 MIR Spectra

Figure 5.7.4. PS_3 MIR spectra, colored by size fraction.

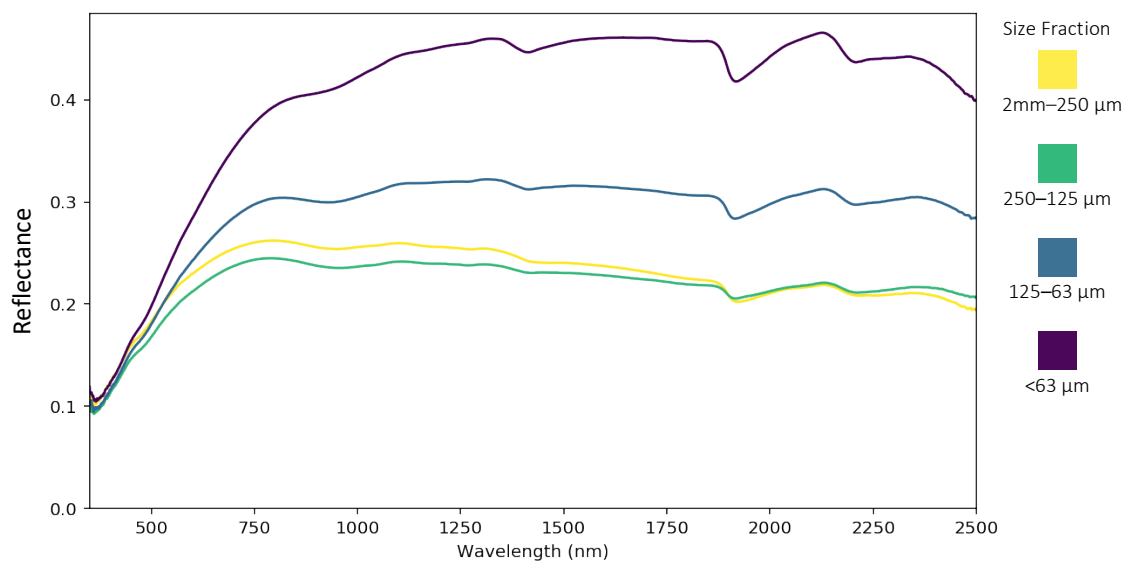


Figure 5.8. 1 HLA VNIR Spectra

Figure 5.8.1. HLA VNIR spectra, colored by size fraction.

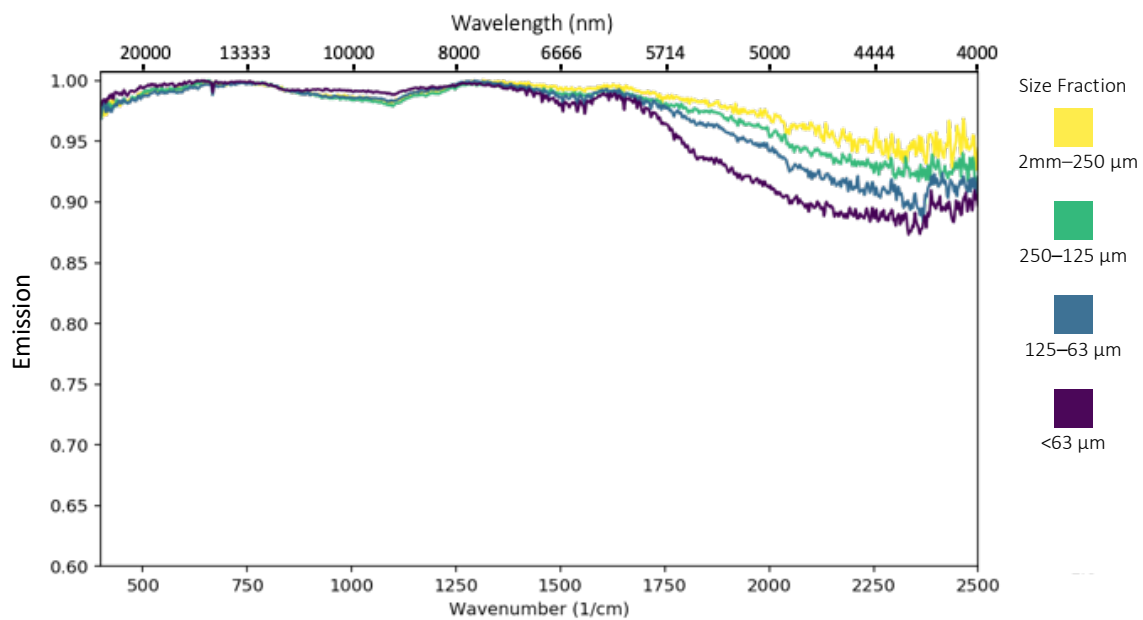


Figure 5.8. 2 HLA MIR Spectra

Figure 5.8.2. HLA MIR spectra, colored by size fraction.

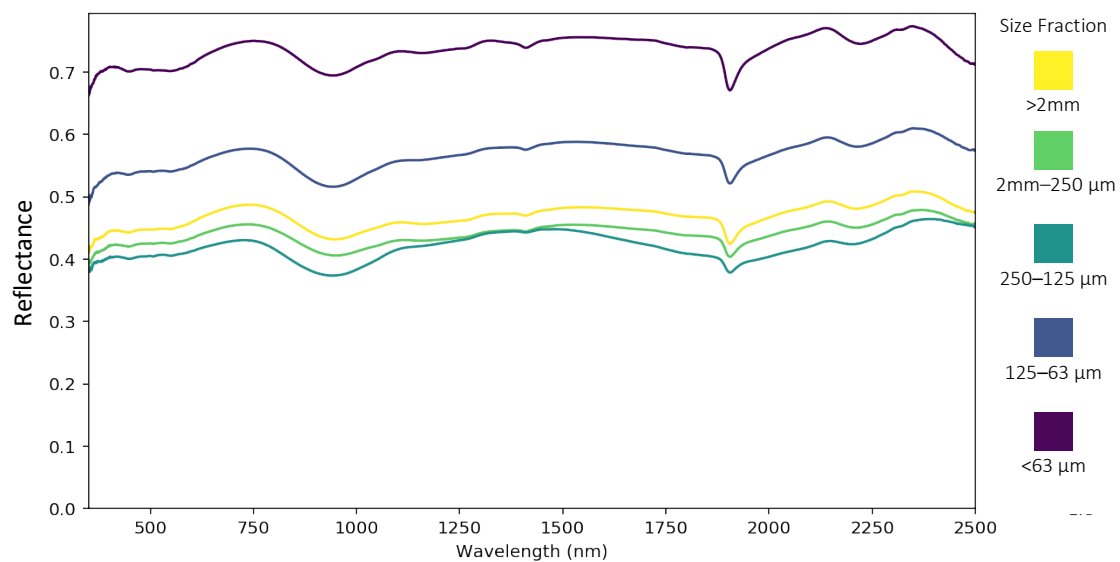


Figure 5.9. 1 MSH VNIR Spectra

Figure 5.9.1. MSH VNIR spectra, colored by size fraction.

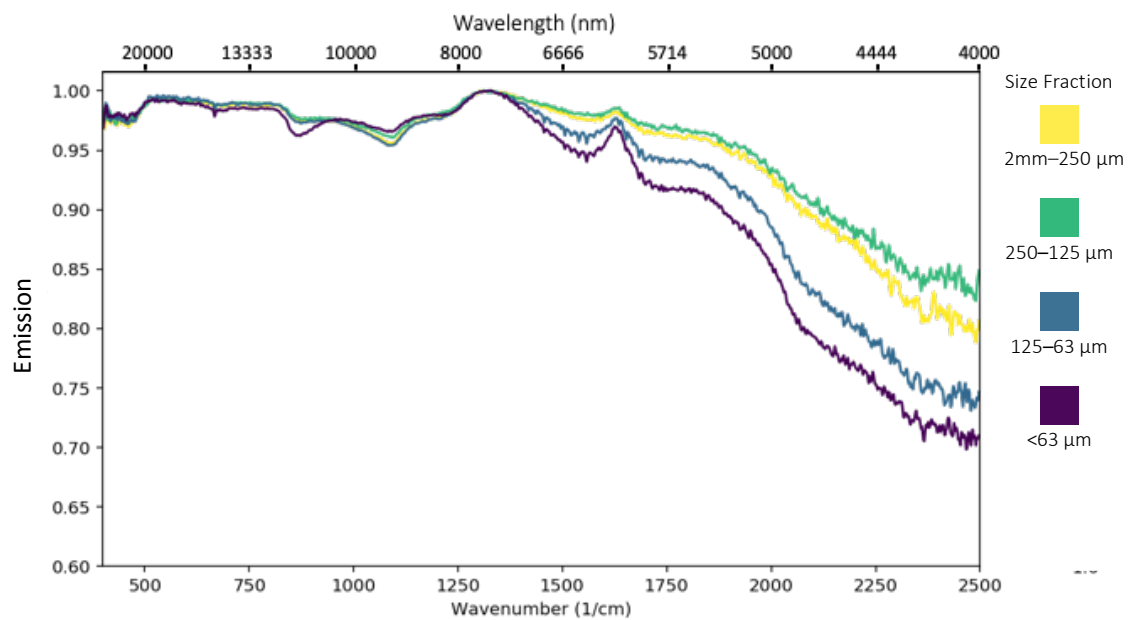


Figure 5.9. 2 MSH MIR Spectra

Figure 5.9.2. MSH MIR spectra, colored by size fraction.

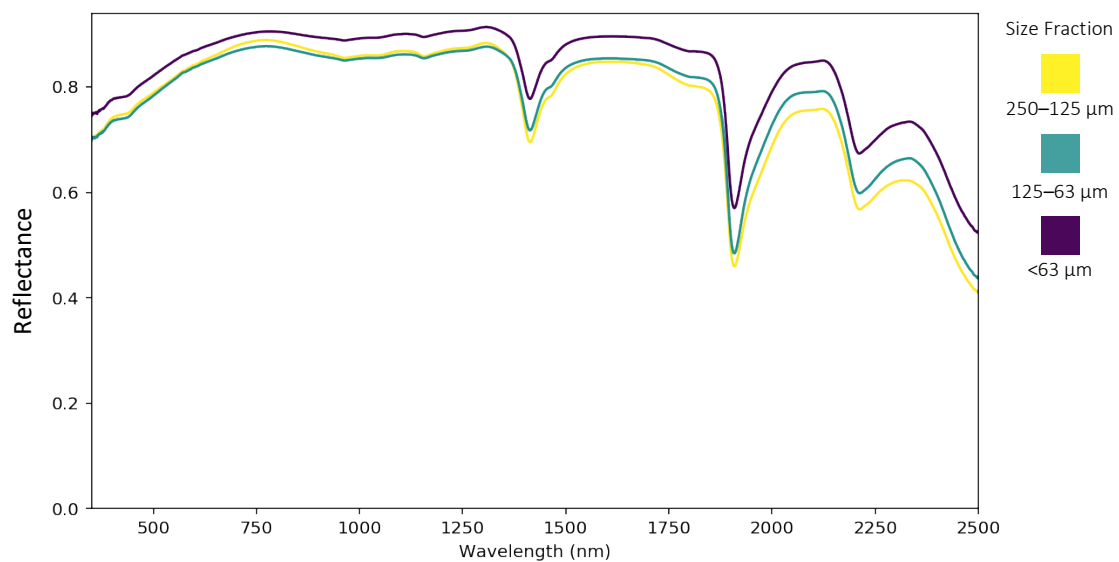


Figure 5.10. 1 BT VNIR Spectra

Figure 5.10.1. BT VNIR spectra, colored by size fraction.

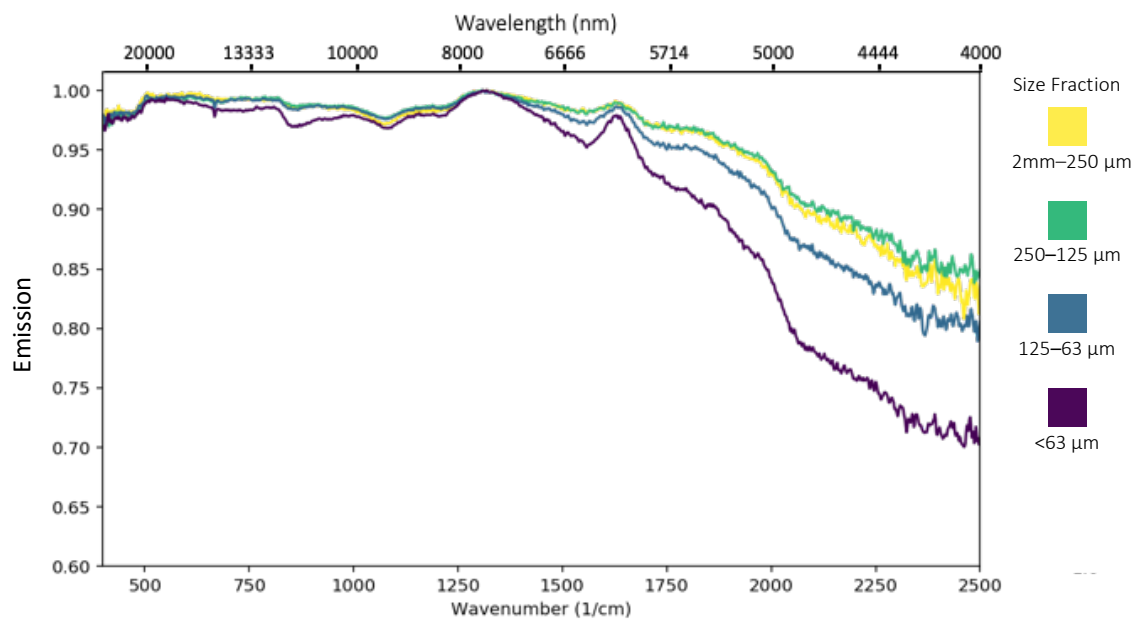


Figure 5.10. 2 BT MIR Spectra

Figure 5.10.2. BT MIR spectra, colored by size fraction.

VNIR PLS model predicting glass wt% SiO₂

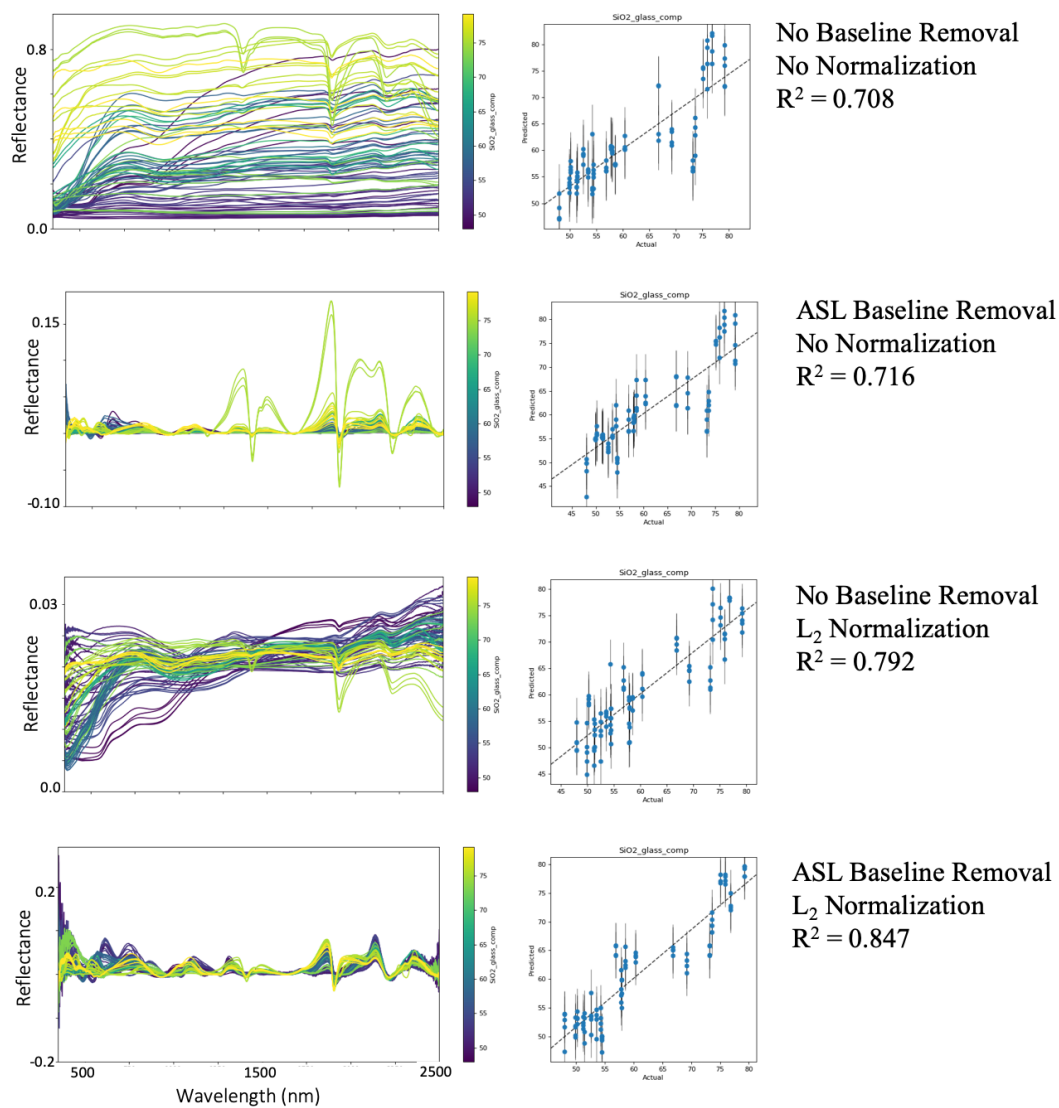


Figure 6.1. 1 VNIR PLS Models with varying preprocessing

Figure 6.1.1. VNIR PLS models predicting glass wt% SiO₂ with and without baseline correction and normalization.

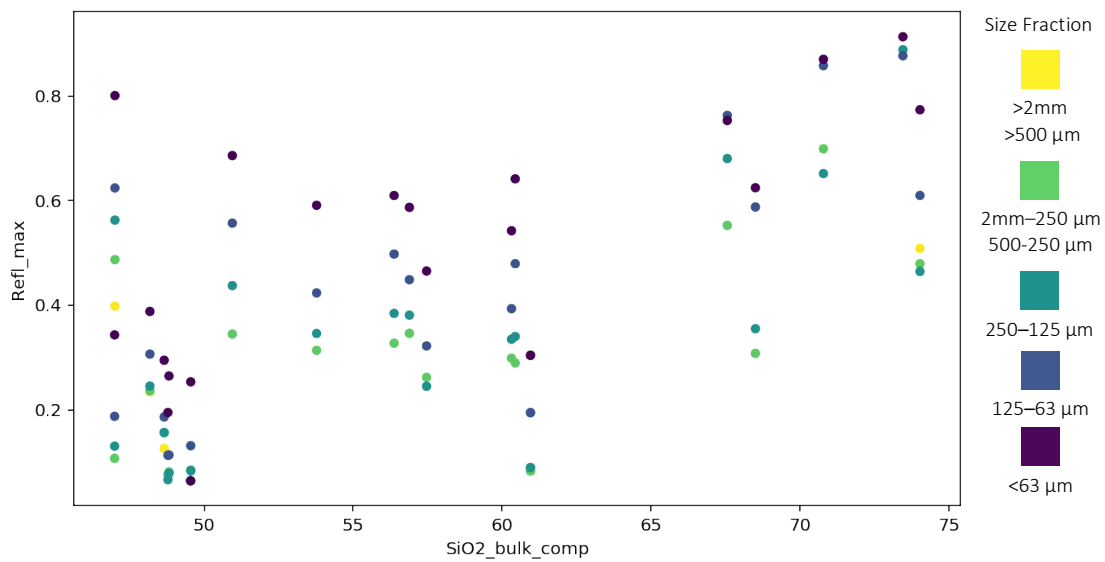


Figure 6.2. 1 VNIR max reflectance values vs. bulk wt% SiO₂

Figure 6.2.1. VNIR max reflectance values vs. bulk wt% SiO₂ for each spectra. Points colored by size fraction.

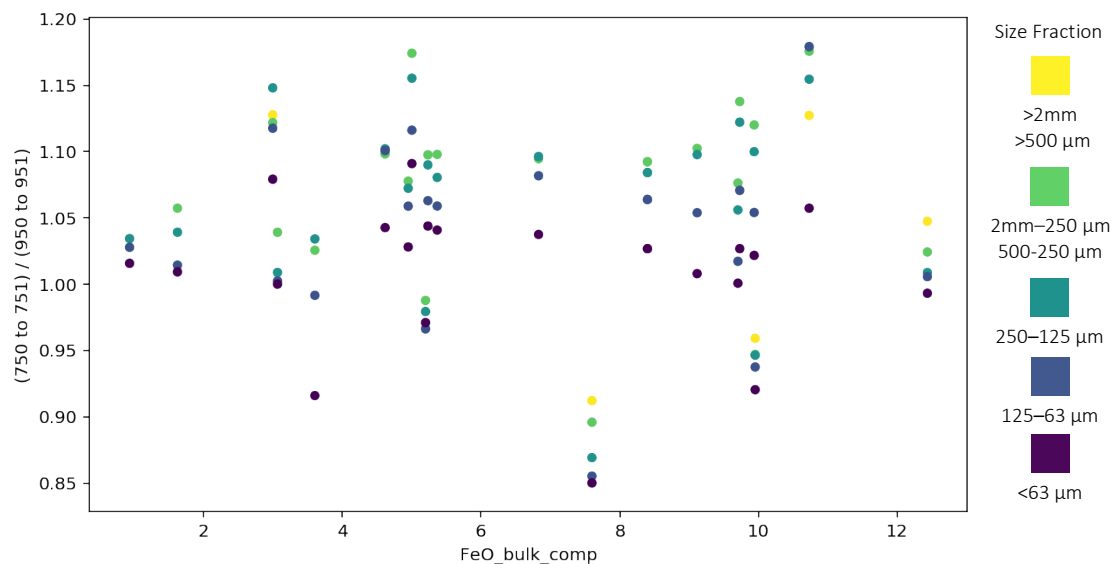


Figure 6.2. 2 0.9-μm band depth vs. bulk wt% FeO

Figure 6.2.2. 0.9 μm band depth vs. bulk wt% FeO. All size fractions are plotted and points are colored by size fraction. 0.9-μm band depth calculated by taking the ratio of reflectance values at 0.750:0.751 μm to the reflectance values from 0.950:0.951 μm.

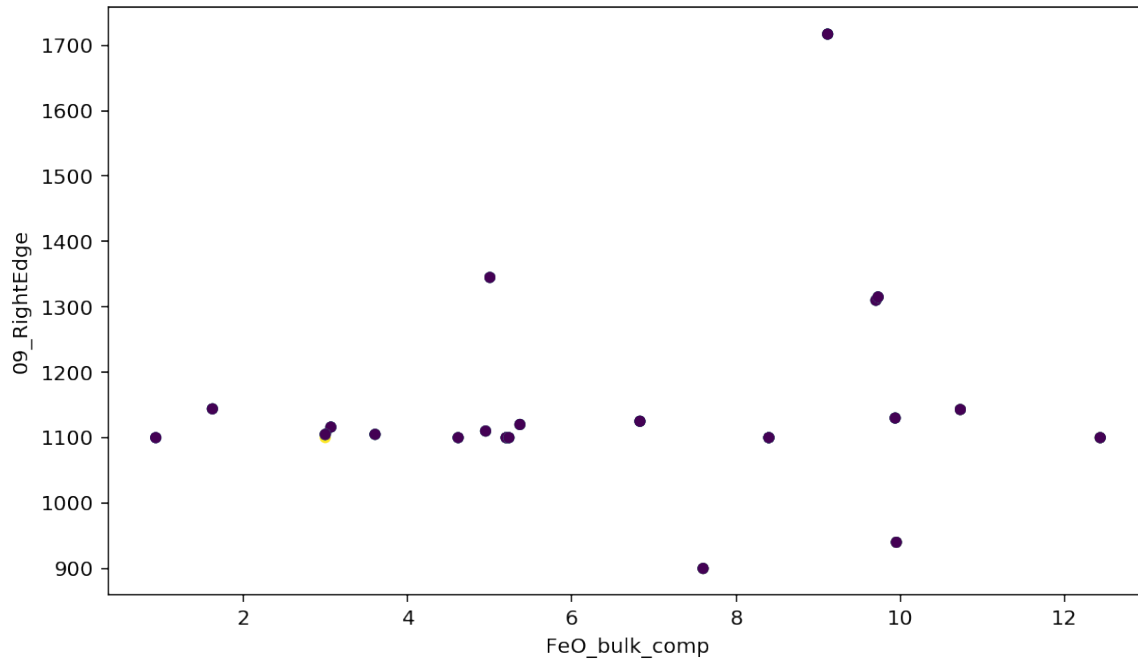


Figure 6.2. 3 Location of the right edge of the 0.9-μm band in nm vs. bulk wt% FeO.

Figure 6.2.3. Location of the right edge of the 0.9-μm band in nm vs. bulk wt% FeO.

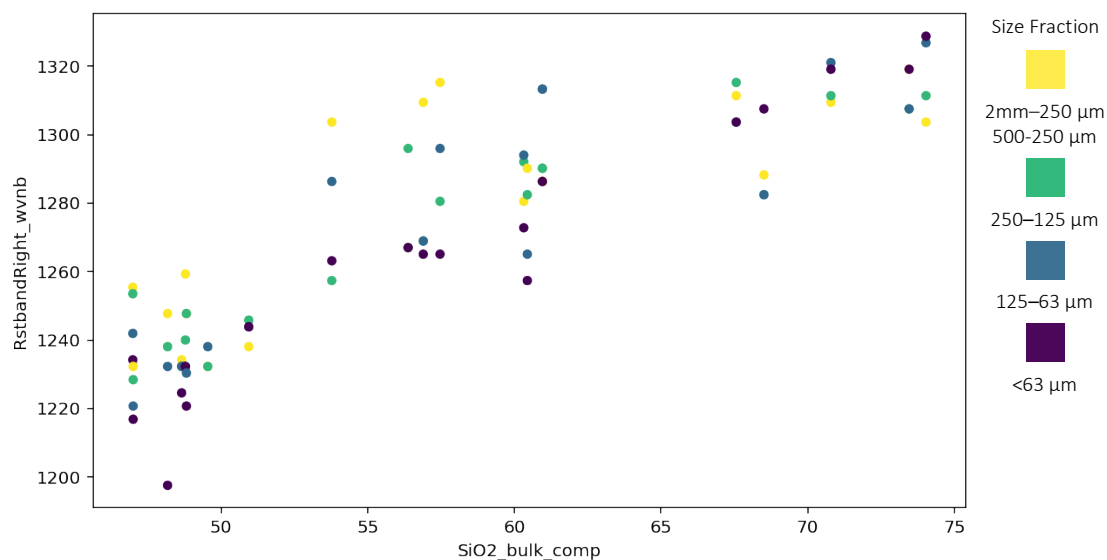


Figure 6.2. 4 Position of restrahlen band right edge vs. bulk wt% SiO_2

Figure 6.2.4. Position of the right edge of the restrahlen band (wavenumber) vs. bulk wt% SiO_2 . Colored by size fraction.

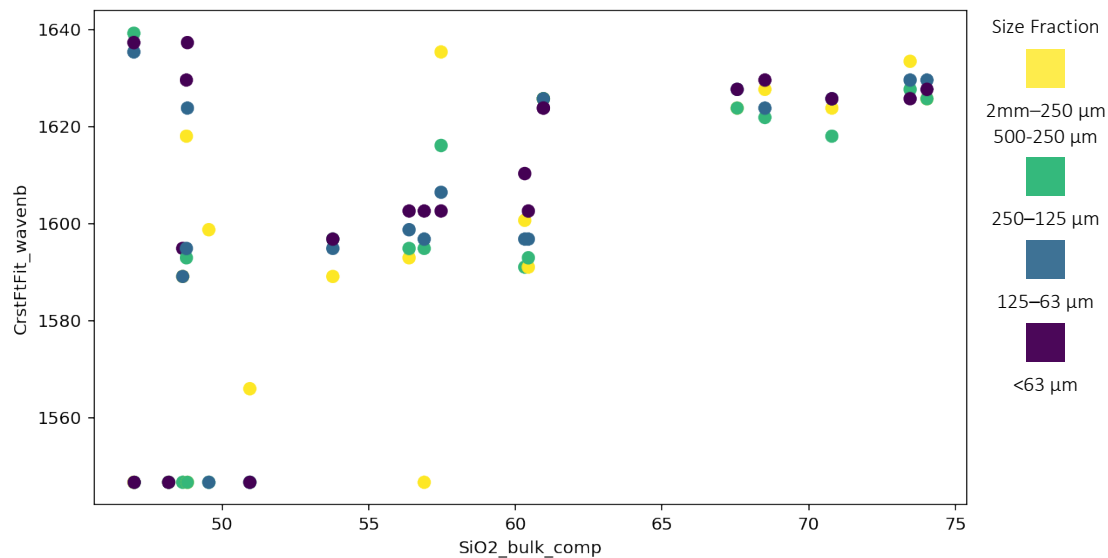


Figure 6.2. 5 Position of Christiansen feature vs. bulk wt% SiO₂

Figure 6.2.5. Position of the Christiansen feature (wavenumber) vs. bulk wt% SiO₂. Colored by size fraction.

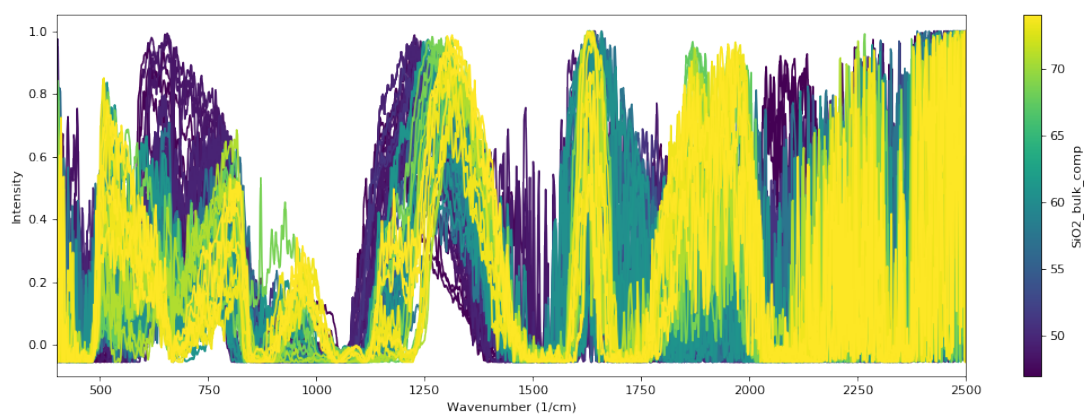


Figure 6.2. 6 MIR spectra with cumulative normalization and ASL baseline correction applied

Figure 6.2.6 All MIR spectra with cumulative normalization and ASL baseline correction applied. Spectra are colored by bulk wt% SiO₂ and all size fractions are plotted.

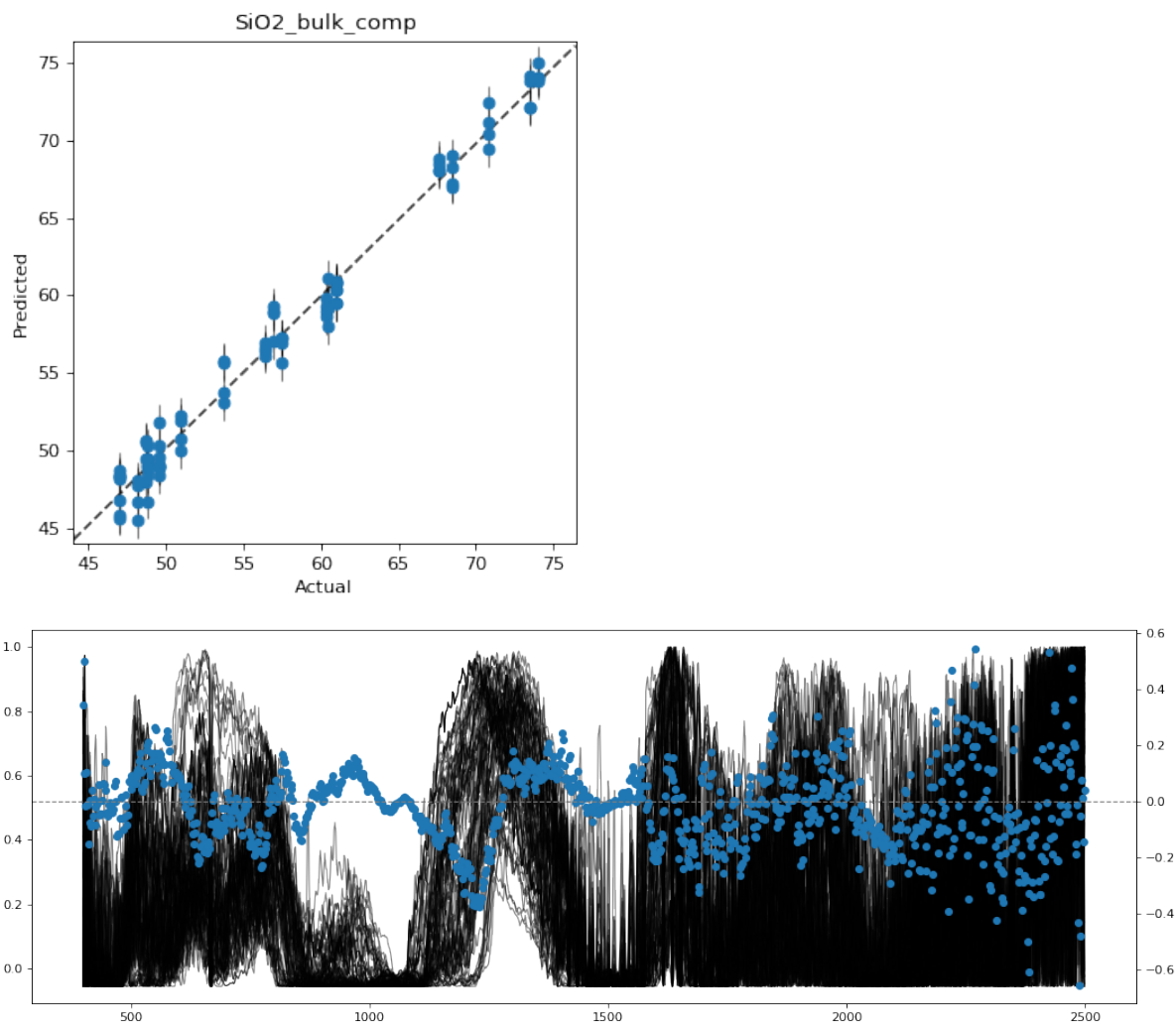


Figure 6.2. 7 MIR bulk wt% SiO₂ PLS model

Figure 6.2.7 Top, Plot of actual vs. predicted MIR bulk wt% SiO₂. Error in the prediction shown with black bars. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

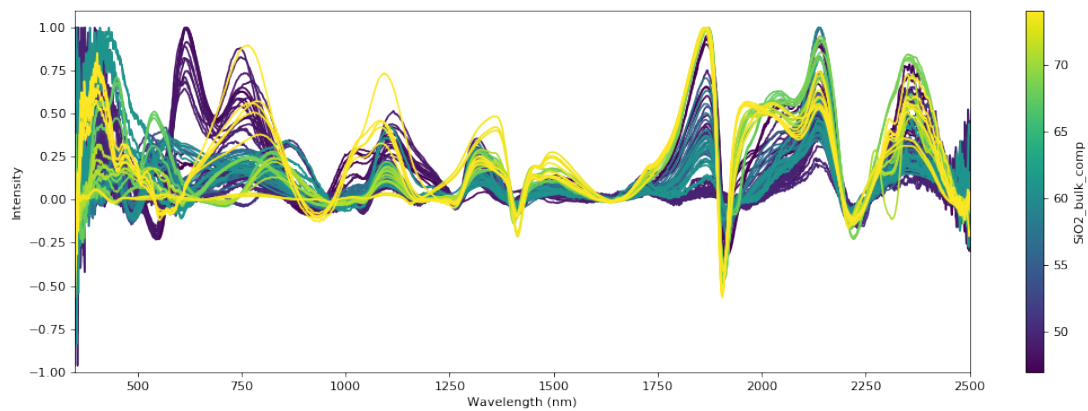


Figure 6.2. 8 VNIR spectra with maximum normalization and ASL baseline correction applied

Figure 6.2.8 VNIR spectra with maximum normalization and ASL baseline correction applied. Spectra are colored by bulk wt% SiO₂ and all size fractions are plotted.

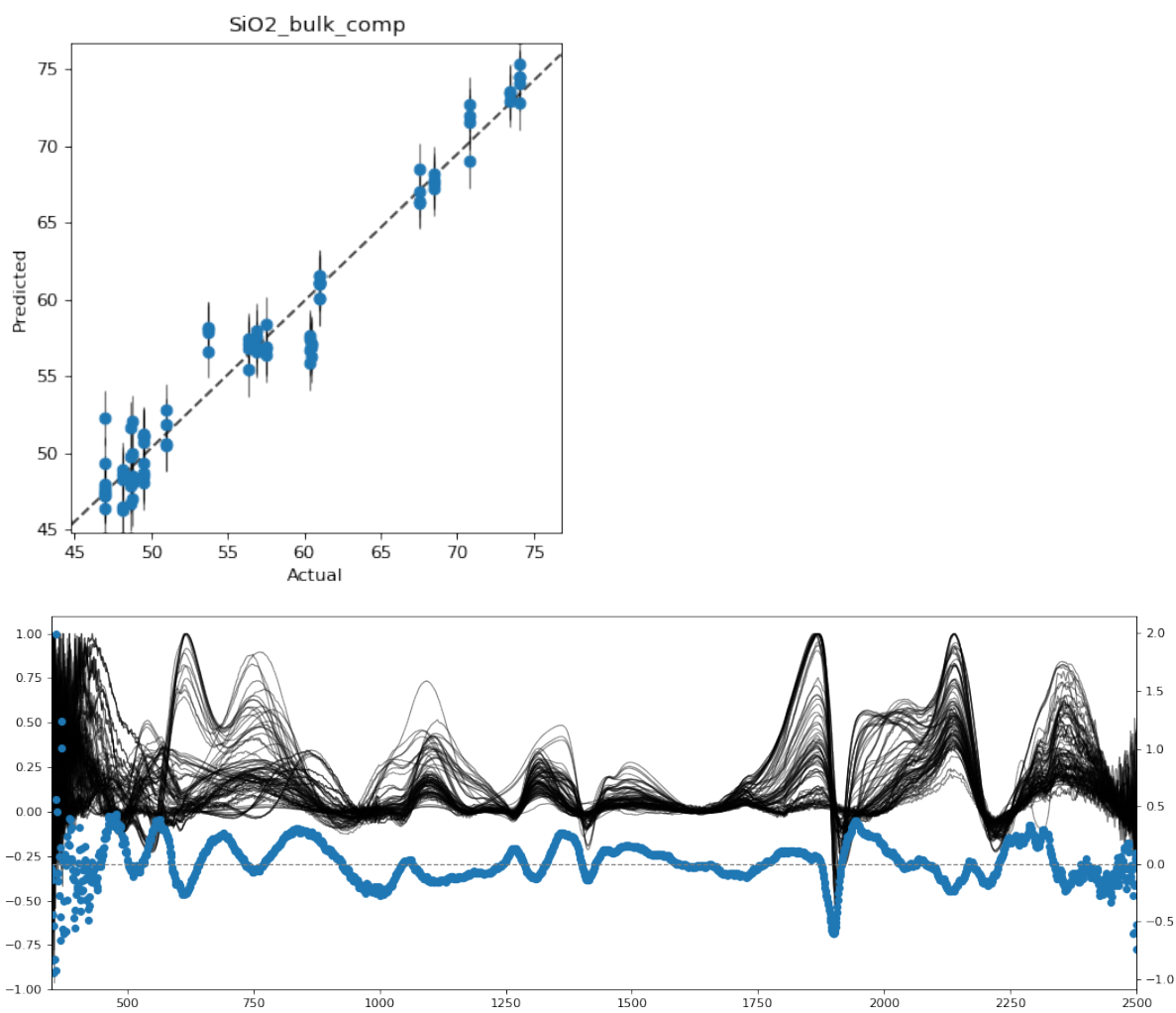


Figure 6.2. 9 VNIR Bulk wt% SiO₂ PLS Model

Figure 6.2.9 Top, Plot of actual vs. predicted VNIR bulk wt% SiO₂. Error in the prediction shown with black bars. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

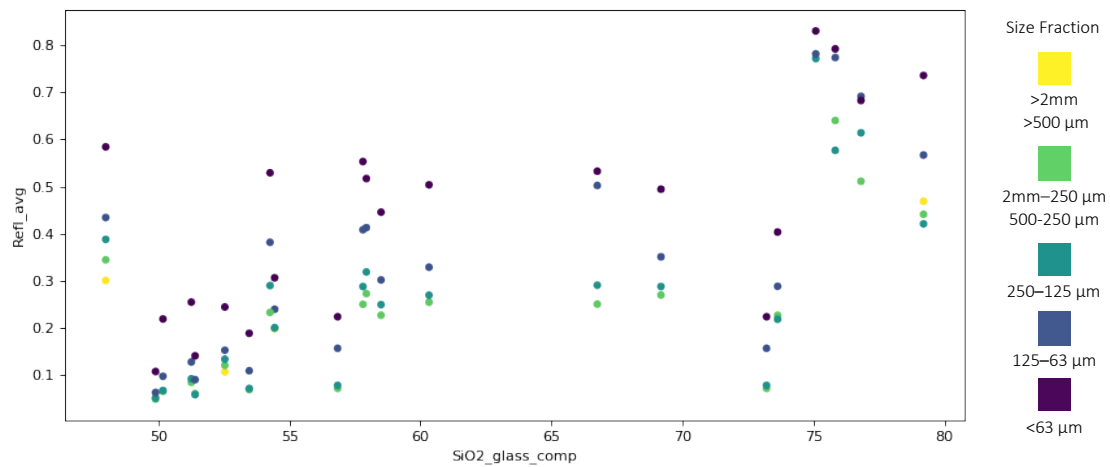


Figure 6.3. 1 Glass wt% SiO₂ vs. Average VNIR reflectance

Figure 6.3.1. Glass wt% SiO₂ vs. Average VNIR reflectance. Points colored by size fraction. All size fractions are plotted.

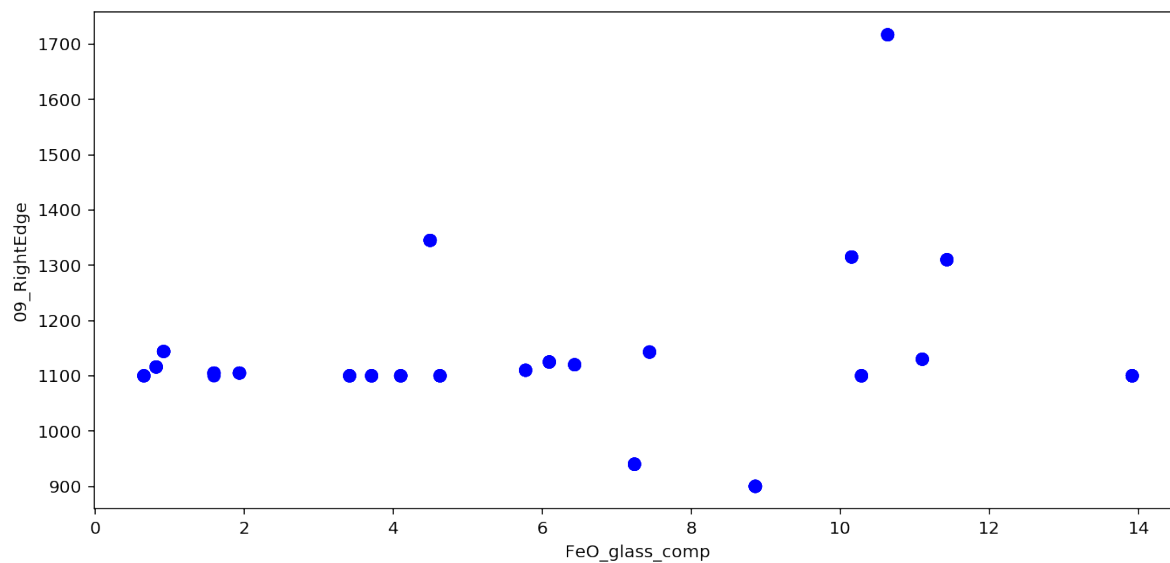


Figure 6.3. 2 Location of the right edge of the 0.9-μm band (nm) vs. glass wt % SiO₂

Figure 6.3.2. Location of the right edge of the 0.9-μm band (nm) vs. glass wt % SiO₂.

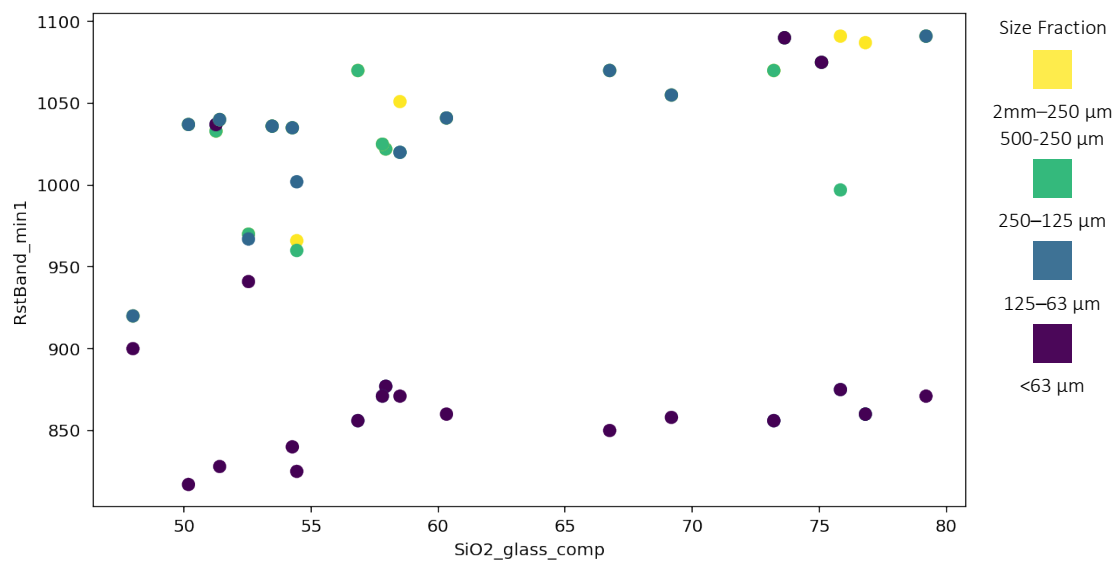


Figure 6.3. 3 Location of the deepest minimum in the restrahlen band vs. glass wt % SiO₂

Figure 6.3.3. Location of the deepest minimum in the restrahlen band (wavenumber) vs. glass wt % SiO₂. Points colored by size fraction.

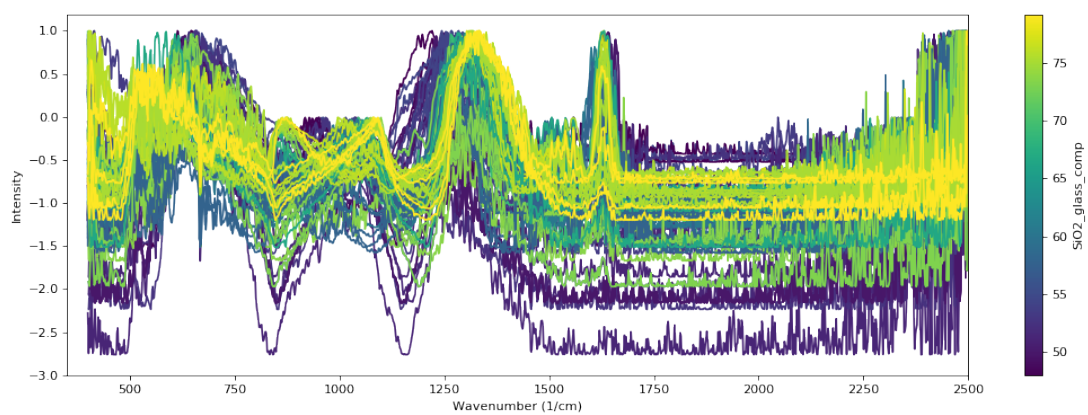


Figure 6.3. 4 MIR spectra with cumulative normalization and median filter baseline correction applied

Figure 6.3.4 MIR spectra with cumulative normalization and median filter baseline correction applied. Spectra are colored by glass wt% SiO₂ and all size fractions are plotted.

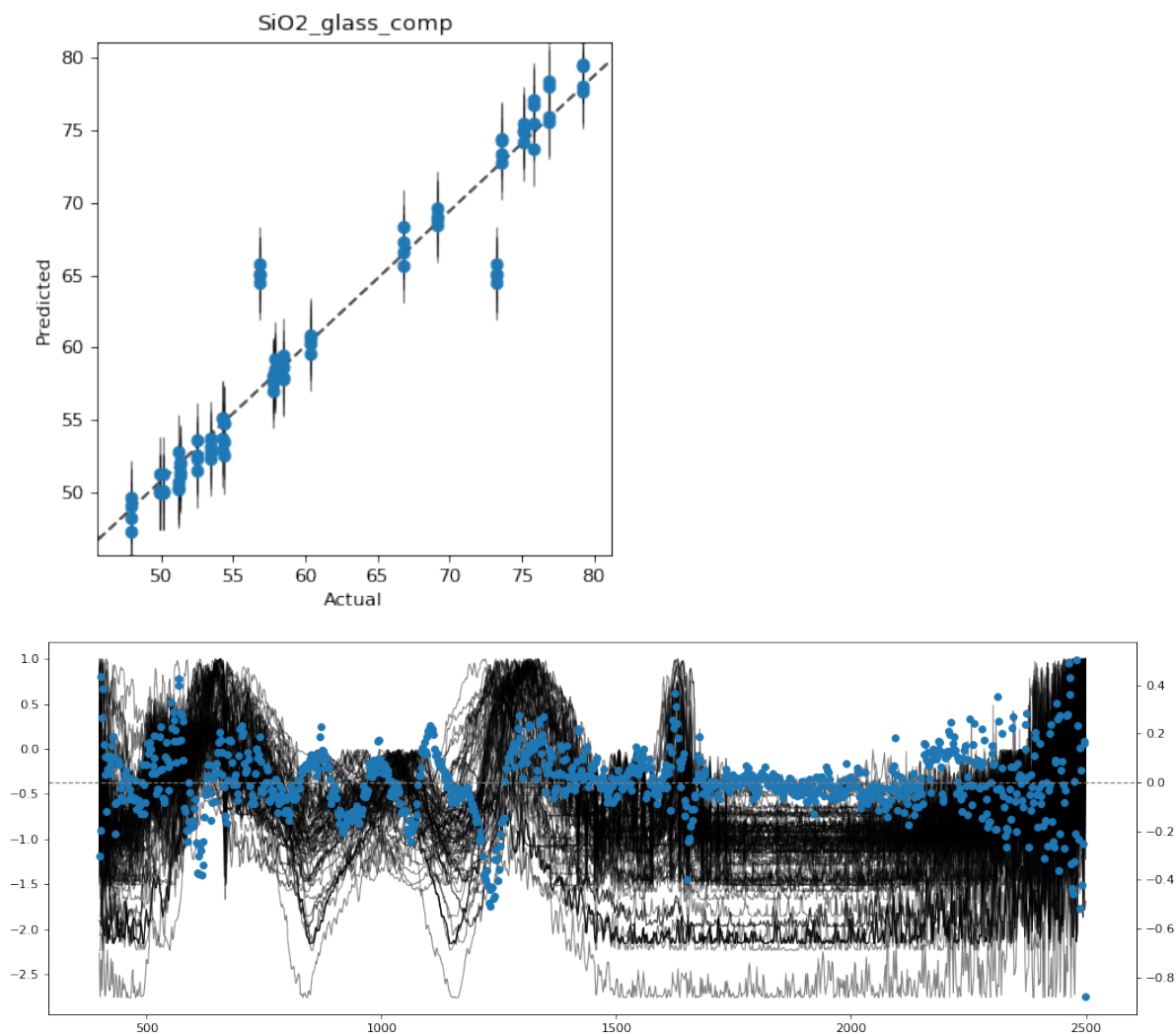


Figure 6.3. 5 MIR glass SiO₂ wt% PLS Model

Figure 6.3.5 Top, Plot of actual vs. predicted MIR glass wt% SiO₂. Error in the prediction shown with black bars. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

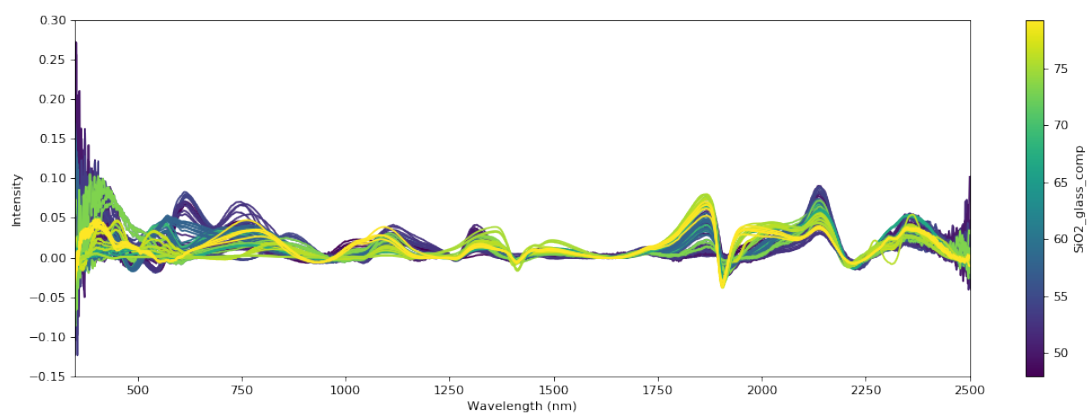


Figure 6.3. 6 VNIR Spectra with L_2 normalization and ASL baseline removal

Figure 6.3.6 VNIR spectra with L_2 normalization and ASL baseline removal applied. Spectra are colored by glass wt% SiO_2 and all size fractions are present.

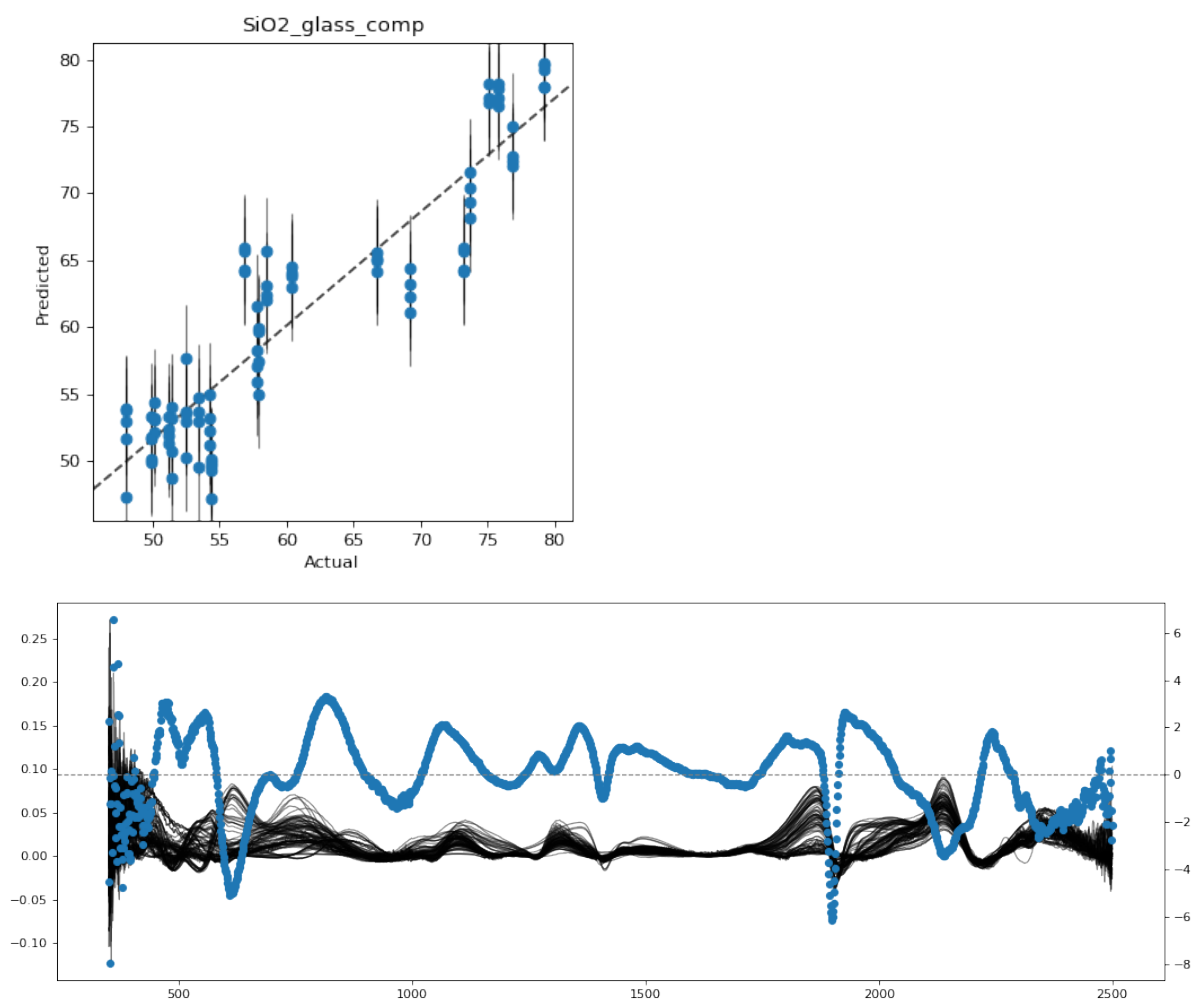


Figure 6.3. 7 VNIR glass SiO₂ wt% PLS models

Figure 6.3. 7 Top: Plot of actual vs. predicted VNIR glass wt% SiO₂. Error in the prediction shown with black bars. Bottom: PLS model parameters (blue dots) plotted over all spectra (black). PLS coefficients are unitless.

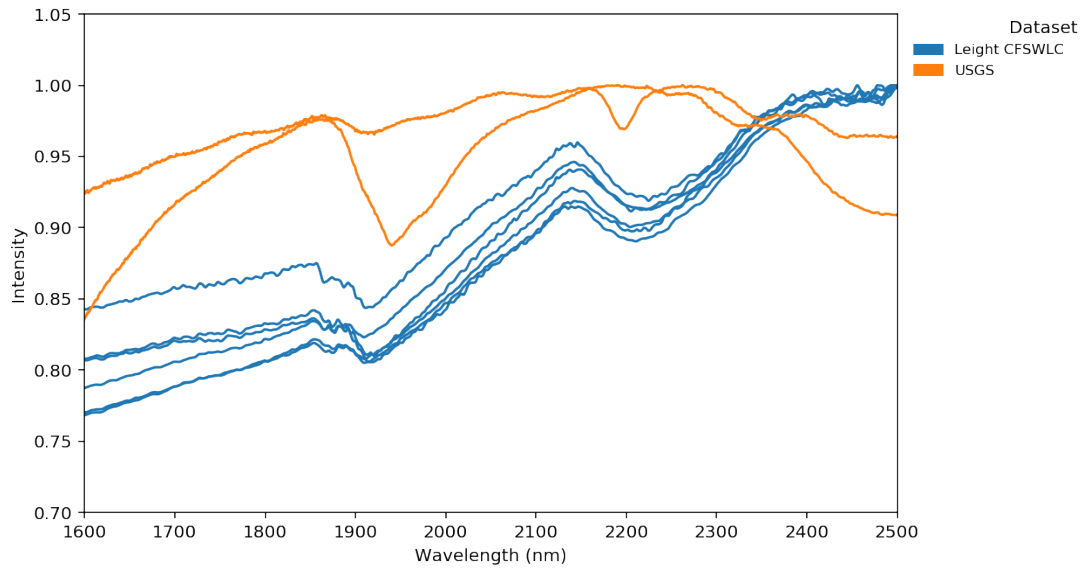


Figure 6.4. 1 Comparison between CFSWLC and USGS Feldspar VNIR spectra

Figure 6.4.1. Comparison between CFSWLC <63 μm and 125-63 μm size fraction VNIR spectra (blue) and USGS mineral library spectra (orange) of Albite (HS324.3B) and Bytownite (HS106.3B). Spectra have been max normalized to ease comparison. CFSWLC spectra were heated for 48 hrs at 100F to remove adsorbed water prior to spectra being collected.

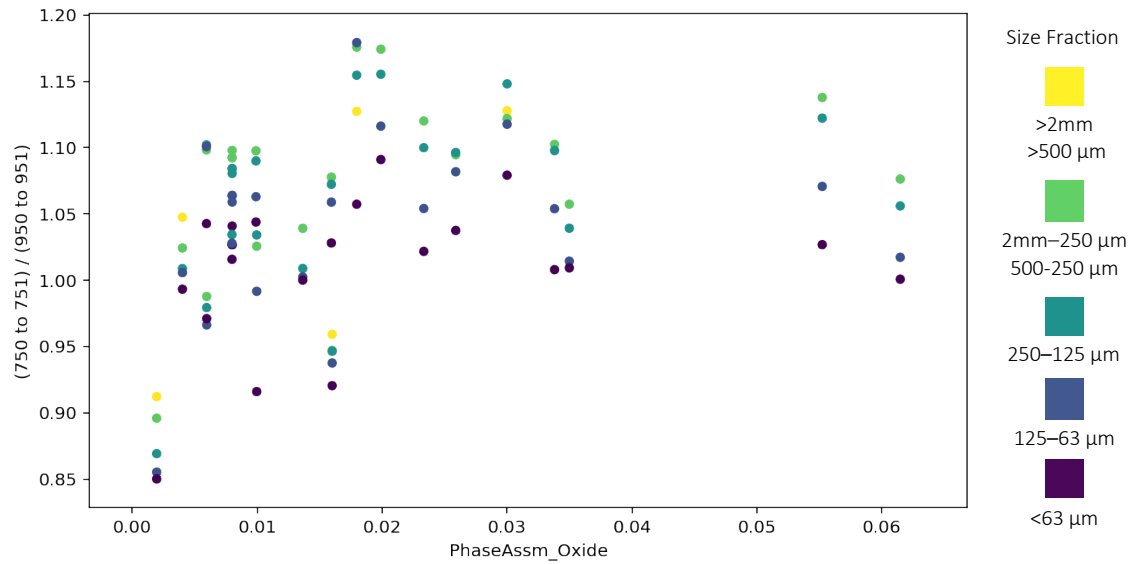


Figure 6.4. 2 Phase percentage oxide vs. 0.9-μm band depth

Figure 6.4.2. Phase percentage Oxide vs. 0.9-μm band depth. 0.9-μm band depth calculated by ratioing the reflectance values from 0.750:0.751 μm to the reflectance values from 0.950:0.951 μm. All size fractions are present, and dots are colored by size fraction.

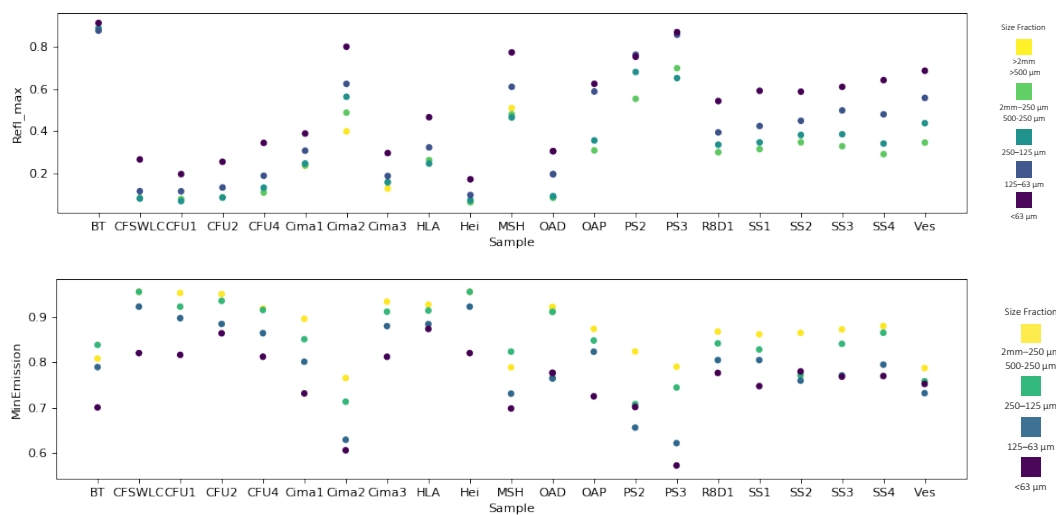


Figure 6.4. 3 Maximum reflectance and Emission values for each spectrum

Figure 6.4.3. Top, Maximum reflectance values of each VNIR spectrum, ordered by sample. Bottom, Minimum Emission values of each MIR spectrum. All size fractions are present, and dots are colored by size fraction.

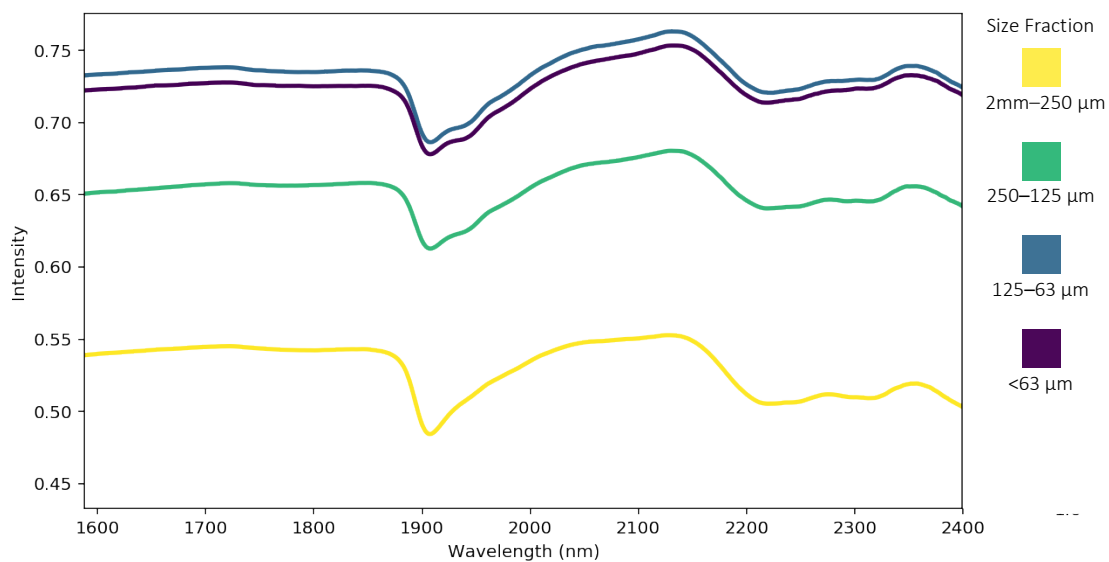


Figure 6.4. 4 PS_2 VNIR spectra from 1.6-2.4 μm

Figure 6.4.4. PS_2 VNIR spectra, colored by size fraction. Note how the largest size fraction (2mm-250 μm) does not have a doublet at 1.9 μm .

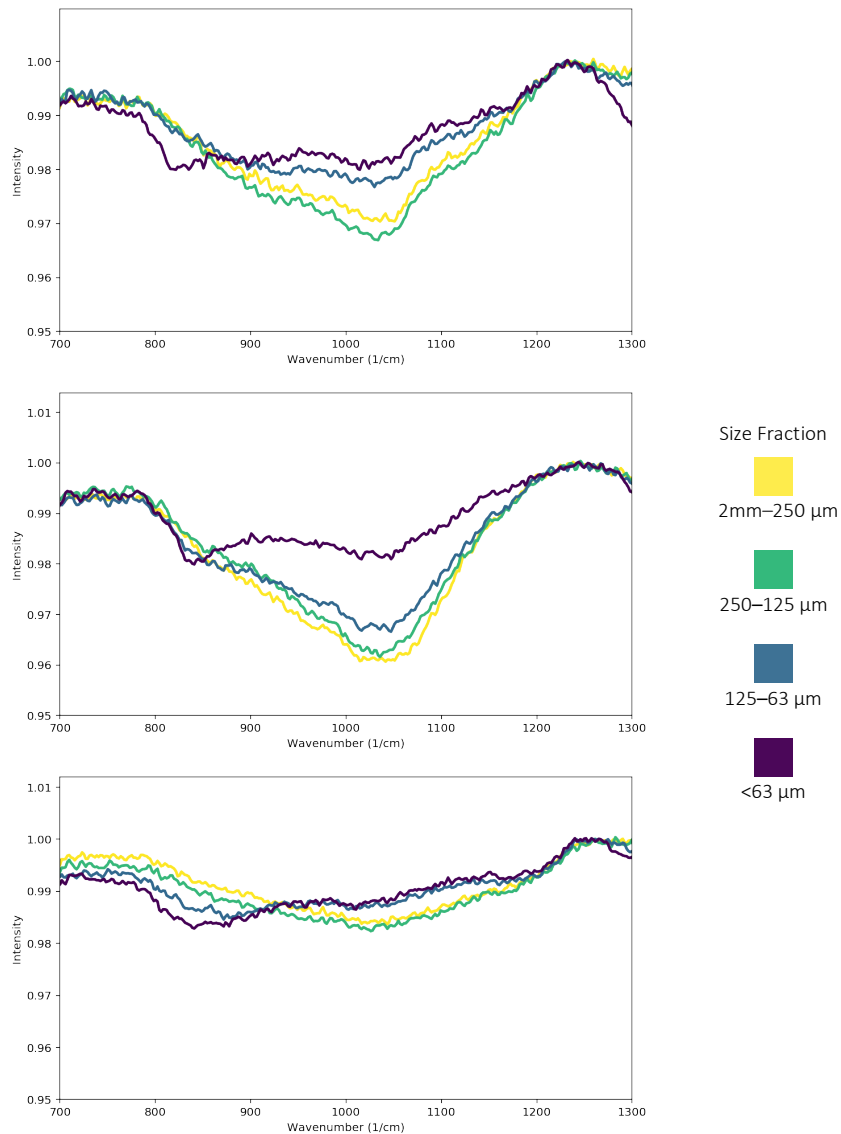


Figure 6.4. 5 Examples of changes in restrahlen band shape between size fractions

Figure 6.4.5. Examples of changes in the restrahlen band shape between size fraction spectra.
A. CFU_1 MIR spectra. B. Ves MIR spectra. C. SS_4 MIR spectra.

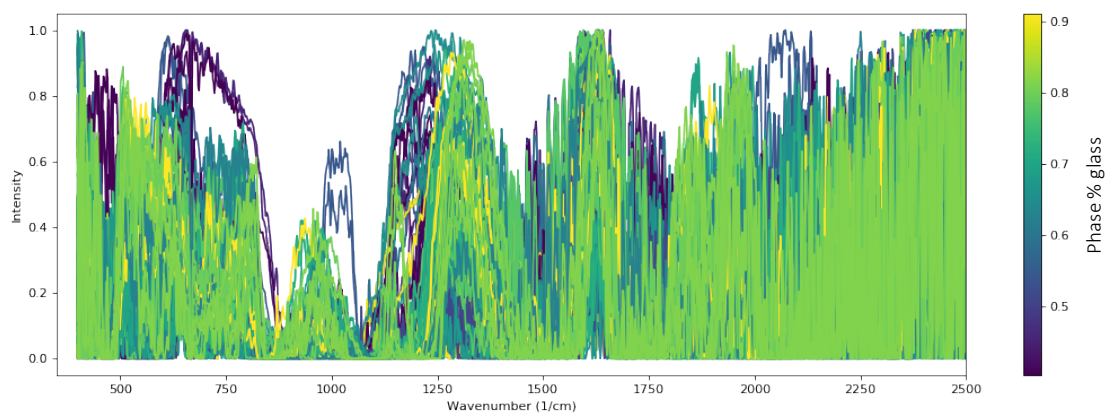


Figure 6.4. 6 MIR spectra with cumulative normalization and tophat baseline correction

Figure 6.4.6. MIR spectra with cumulative normalization and tophat baseline correction applied, colored by glass phase %. All size fractions are plotted.

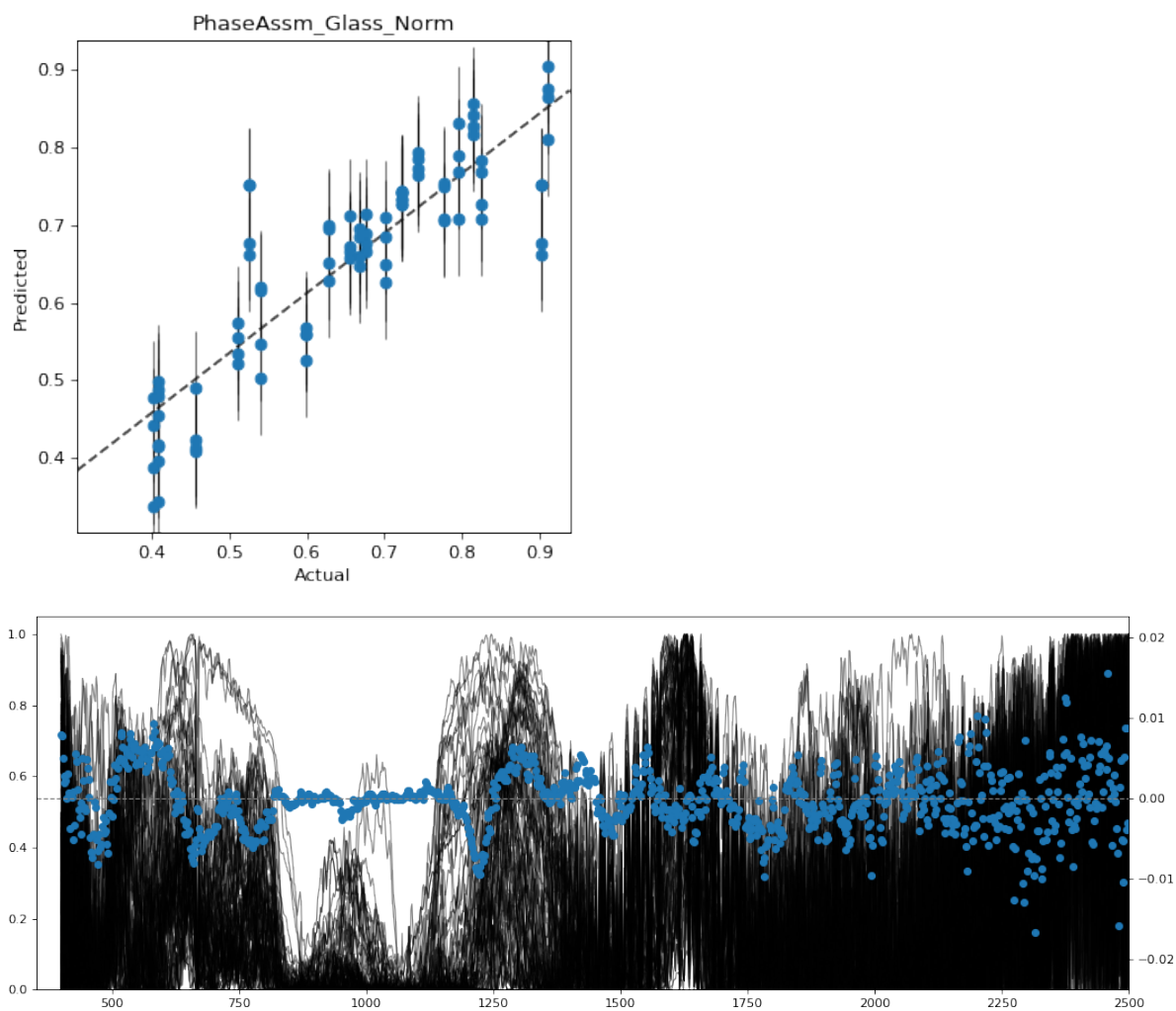


Figure 6.4. 7 MIR glass phase % PLS model

Figure 6.4.7. Top, MIR PLS model of glass phase %. Error in predictions shown by black lines. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

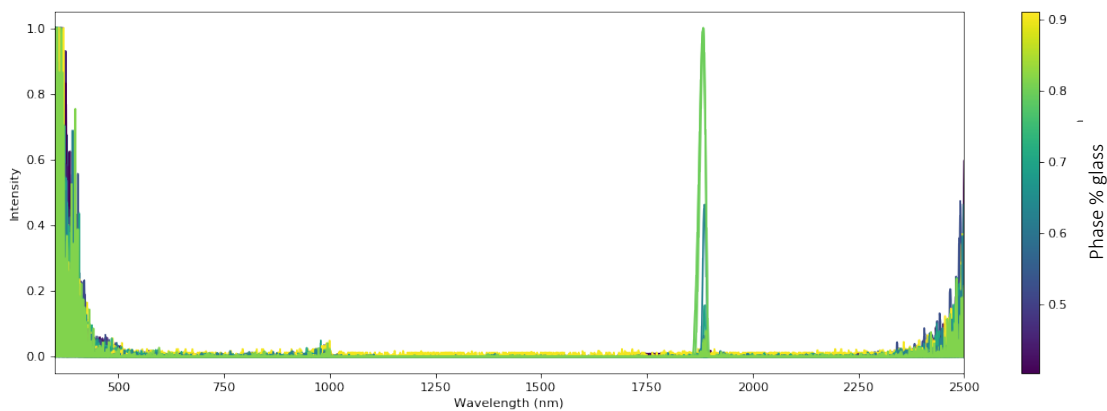


Figure 6.4. 8 VNIR spectra with maximum normalization and Kajfosh and Kwiatek baseline removal

Figure 6.4.8. VNIR spectra with maximum normalization and a Kajfosh and Kwiatek baseline removal applied, colored by glass phase %. All size fractions are plotted.

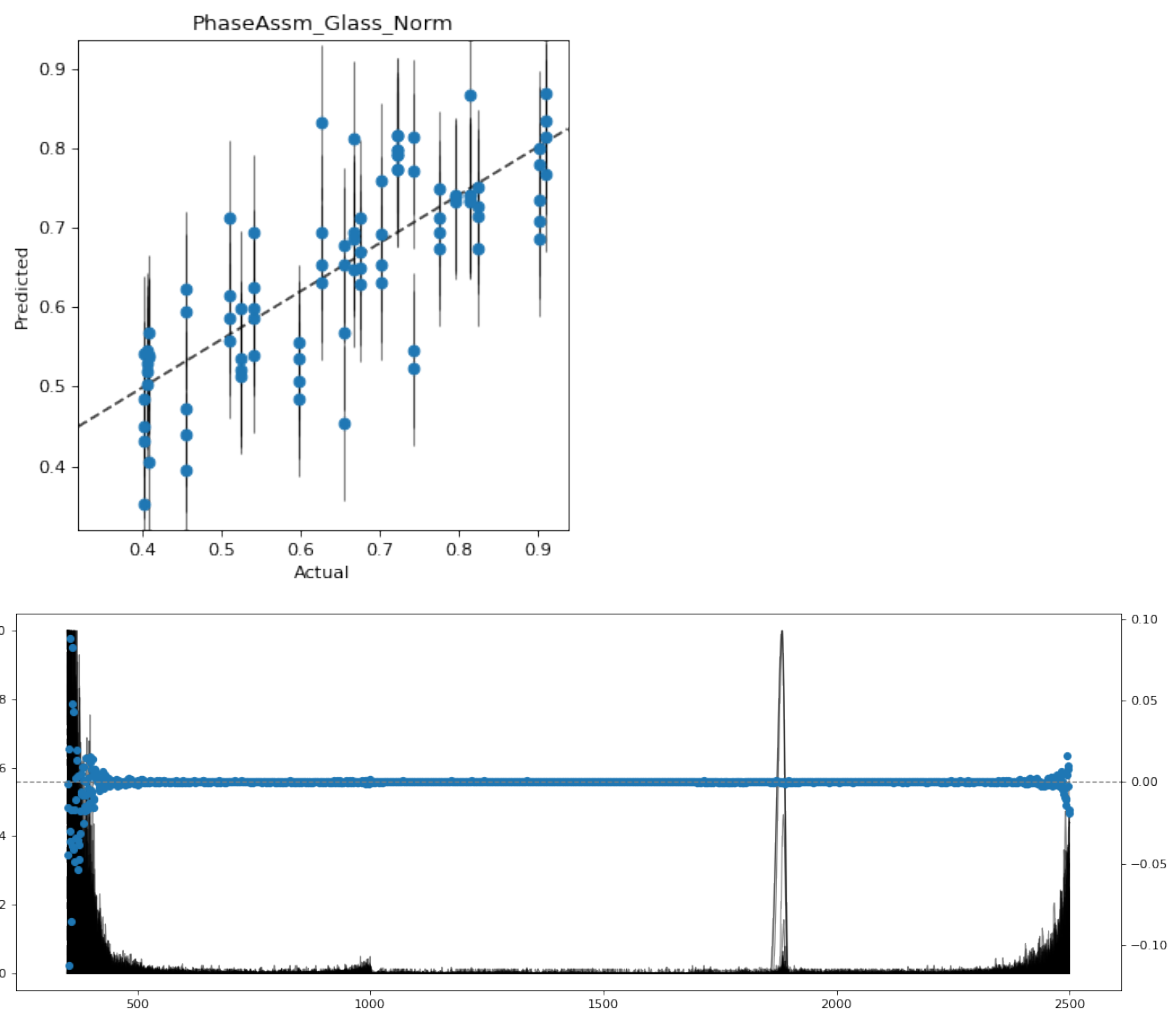


Figure 6.4. 9 VNIR glass phase % PLS model

Figure 6.4.9. Top, VNIR PLS model of glass phase %. Error in predictions shown by black lines. Bottom, PLS model parameters, plotted as blue dots. All spectra are present in black. PLS coefficients are unitless.

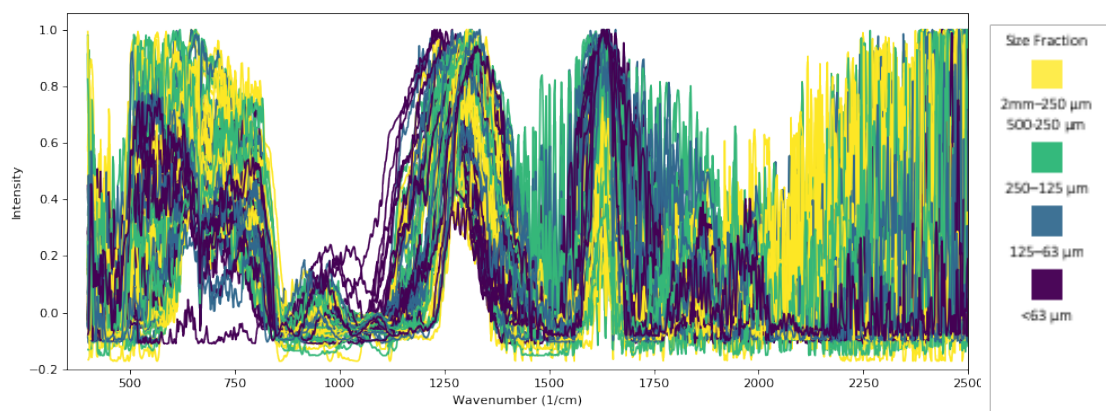


Figure 6.4. 10 MIR spectra with cumulative normalization and MPLS baseline removal

Figure 6.4.10. MIR spectra with cumulative normalization and MPLS baseline removal applied, colored by size fraction. All size fractions are plotted.

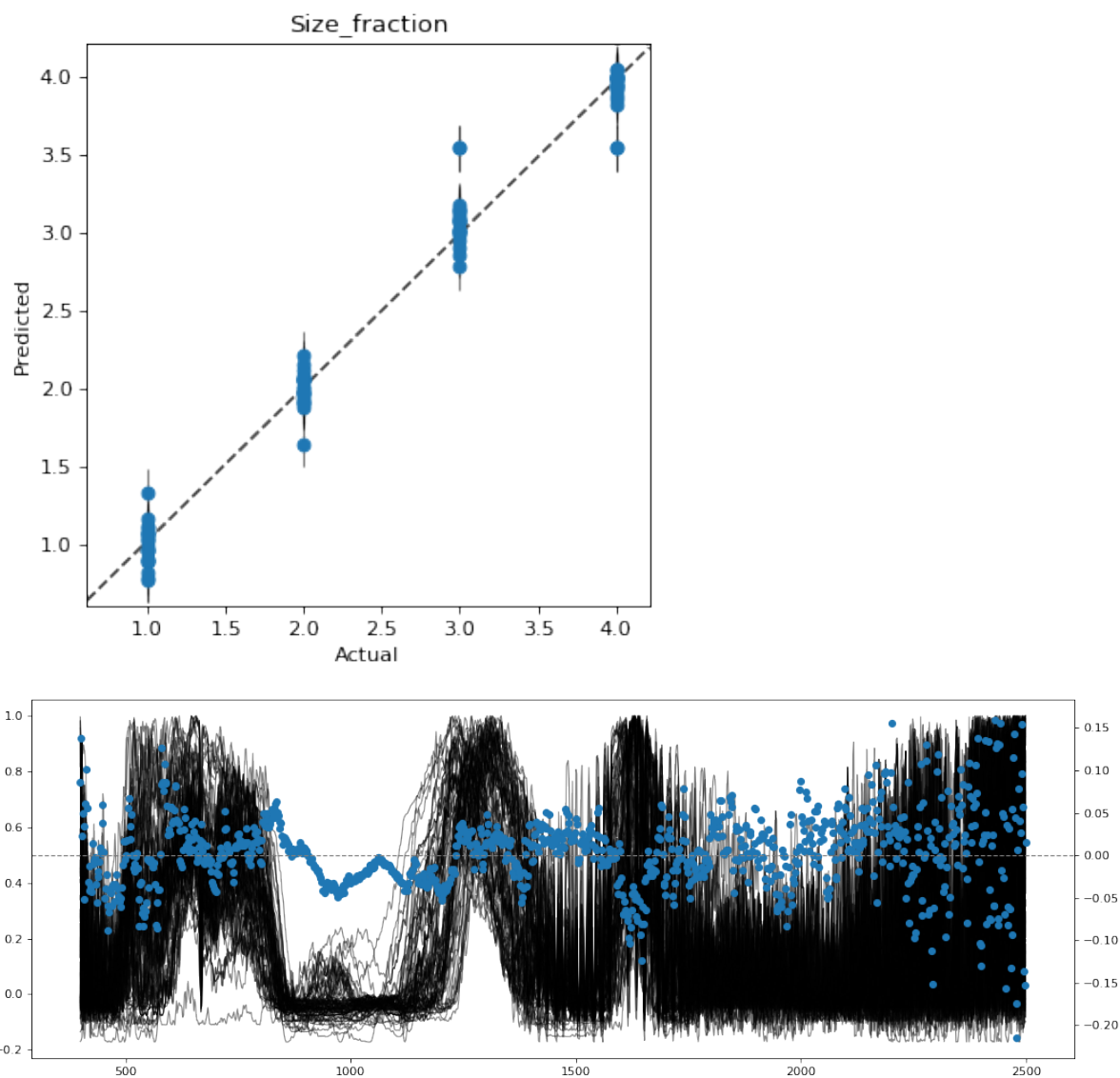


Figure 6.4. 11 MIR size fraction PLS model

Figure 6.4.11. Top, MIR PLS model of size fraction Error in predictions shown by black lines. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

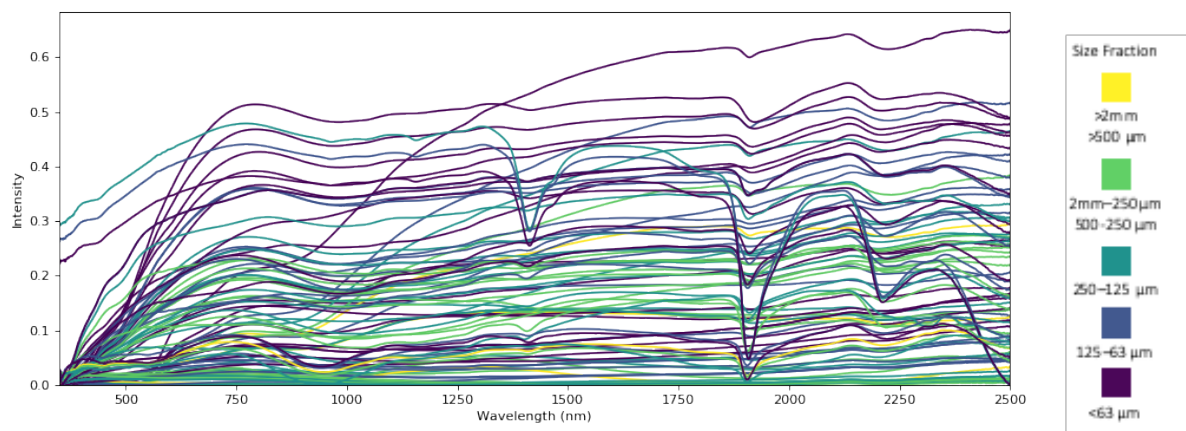


Figure 6.4. 12 VNIR spectra with minimum normalization

Figure 6.4.12. VNIR spectra with minimum normalization applied, colored by size fraction. All size fractions are plotted.

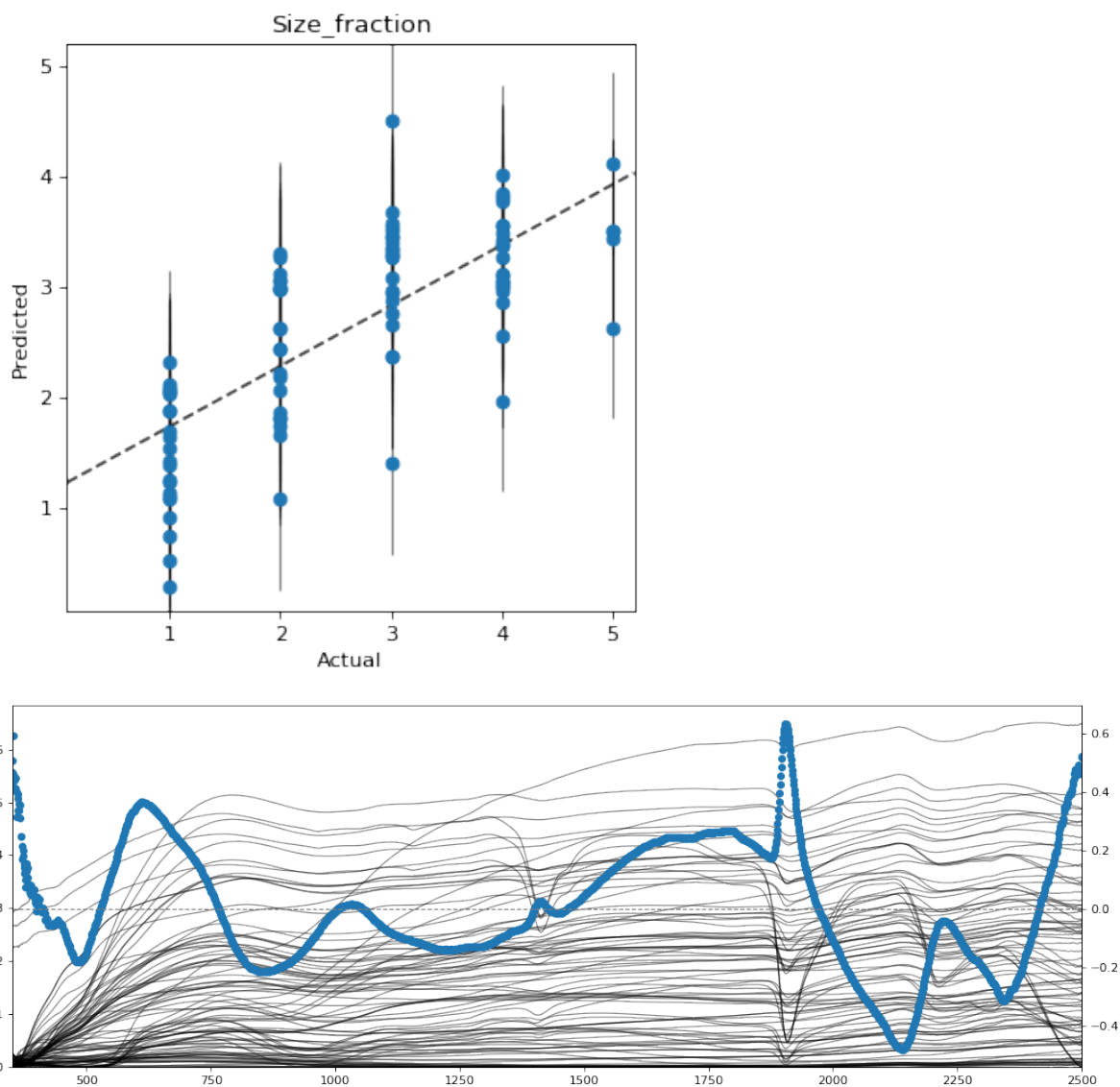


Figure 6.4. 13 VNIR size fraction PLS model

Figure 6.4.13. Top, VNIR PLS model of size fraction. Error in predictions shown by black lines. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

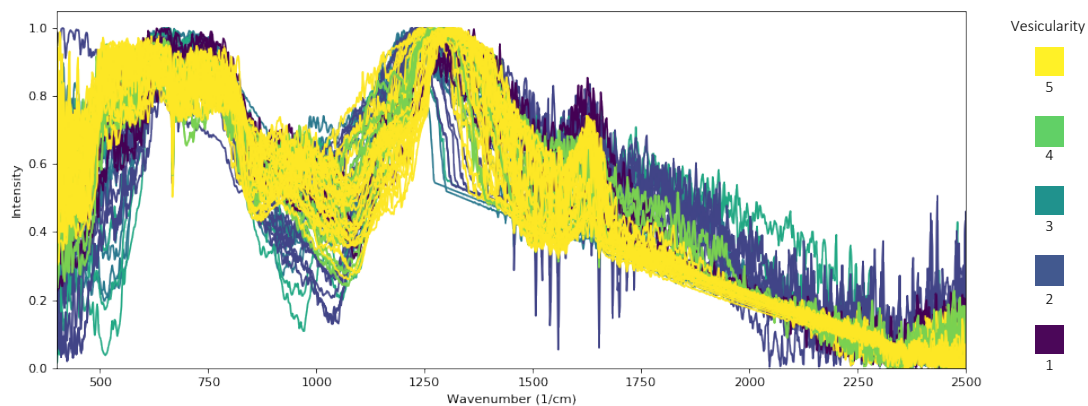


Figure 6.5. 1 MIR spectra with cumulative normalization

Figure 6.5.1 MIR spectra with cumulative normalization applied, colored by vesicularity. All size fractions are plotted.

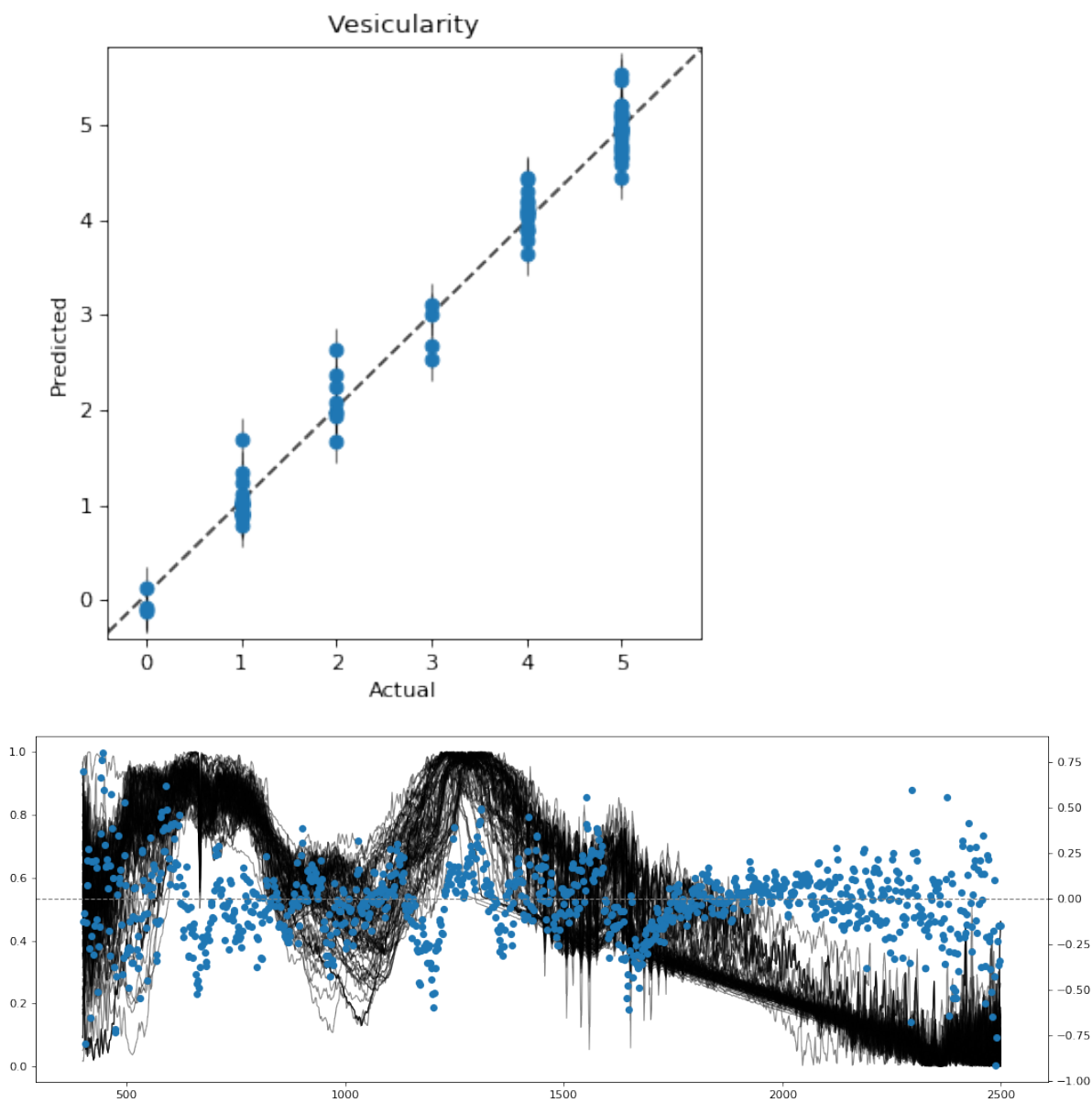


Figure 6.5. 2 MIR vesicularity PLS model

Figure 6.5.2. Top, MIR PLS model of vesicularity. Error in predictions shown by black lines. Bottom, PLS model parameters (blue dots) plotted over MIR spectra. PLS coefficients are unitless.

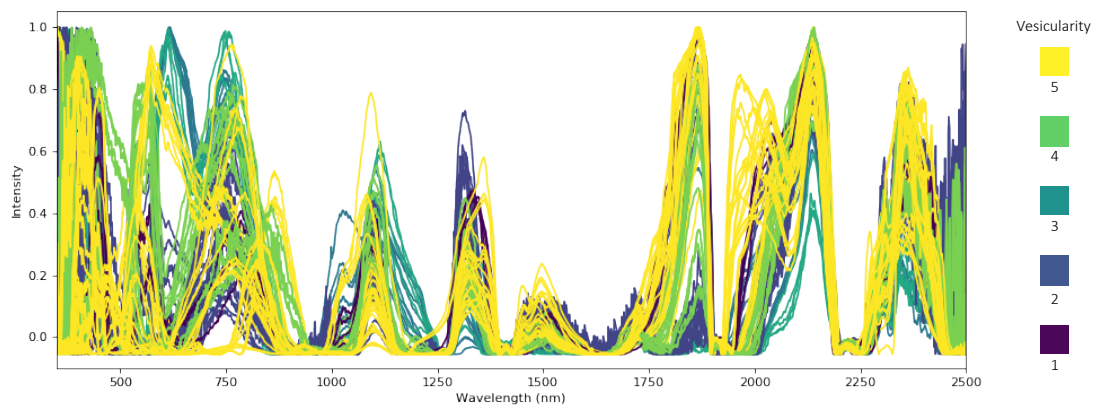


Figure 6.5. 3 VNIR spectra with cumulative normalization and ASL baseline removal

Figure 6.5.3 VNIR spectra with cumulative normalization and ASL baseline removal applied, colored by vesicularity. All size fractions are plotted.

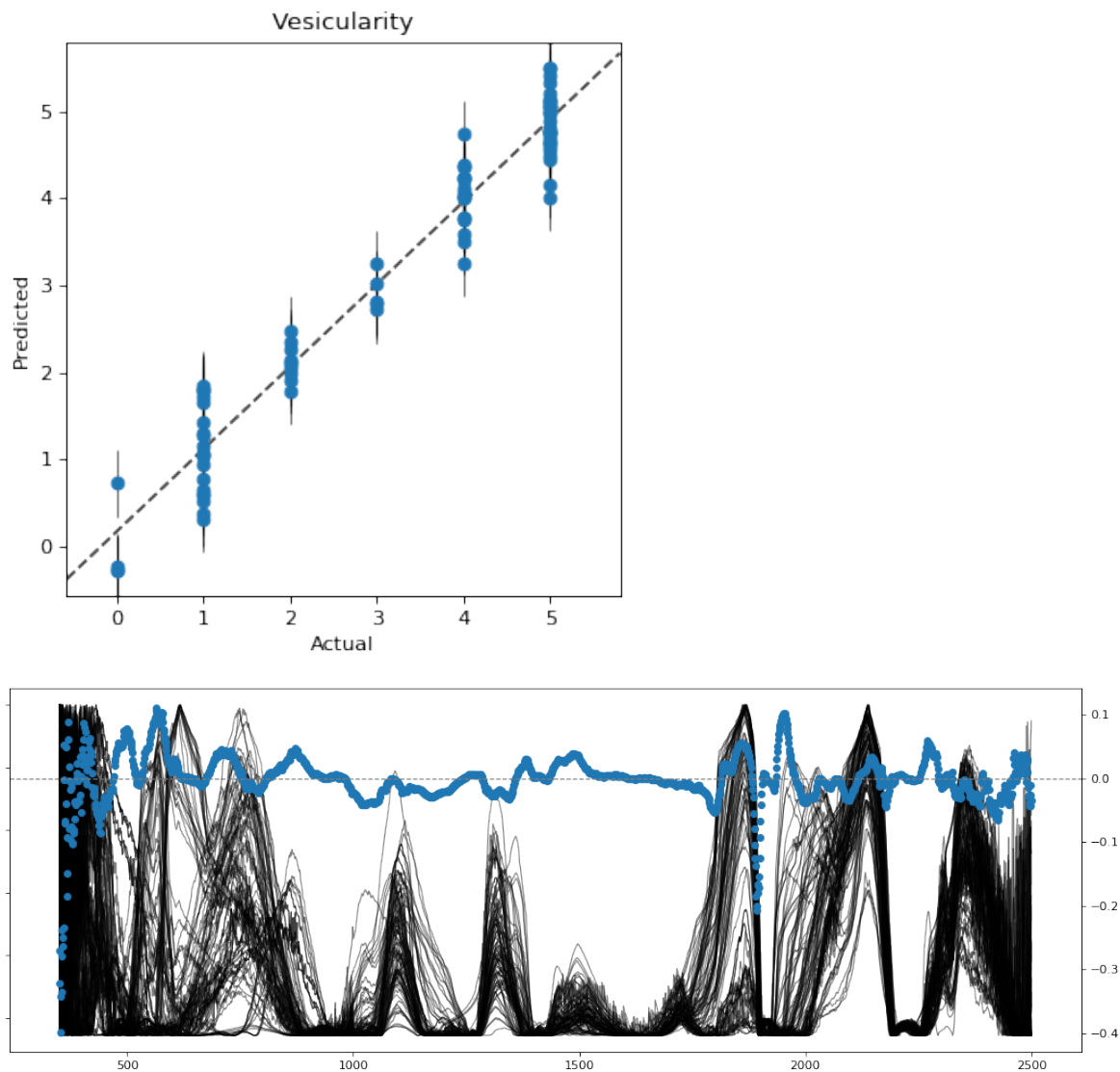


Figure 6.5. 4 VNIR vesicularity PLS model

Figure 6.5.4. Top, VNIR PLS model of vesicularity. Error in predictions shown by black lines. Bottom, PLS model parameters (blue dots) plotted over VNIR spectra. PLS coefficients are unitless.

Appendix B: Tables

Table 1. Samples

Sample	Abbreviation	Locality	Eruption Date, If Relevant	Size Fractions
Cima 1	Cima 1	Cima Volcanic field, Mojave Desert, CA		>500 μm , 500–250 μm 250–125 μm , 125–63 μm , <63 μm
Cima 2	Cima 2	Cima Volcanic field, Mojave Desert, CA		>500 μm , 500–250 μm 250–125 μm , 125–63 μm , <63 μm
Cima 3	Cima 3	Cima Volcanic field, Mojave Desert, CA		>500 μm , 500–250 μm 250–125 μm , 125–63 μm , <63 μm
CraterFlats Unit 1	CFU 1	Crater Flats Volcanic field, Nevada		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
CraterFlats Unit 2	CFU 2	Crater Flats Volcanic field, Nevada		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
CraterFlats Unit 4	CFU 4	Crater Flats Volcanic field, Nevada		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Crater Flats Southwest				
Little Cone	CFSWLC	Crater Flats Volcanic field, Nevada		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Heimaey	Hei	Heimaey Island	1973	>500 μm , 500–250 μm 250–125 μm , 125–63 μm , <63 μm
Vesuvius	Ves	Mount Vesuvius, Campania, Italy	1631	>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Summerland Sample 1	SS 1	Mt. Rainier, WA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Summerland Sample 2	SS 2	Mt. Rainier, WA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Summerland Sample 3	SS 3	Mt. Rainier, WA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Summerland Sample 4	SS 4	Mt. Rainier, WA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
R8D1	R8D1	Mt. Rainier, WA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Okmok AD	OAD	Okmok volcano, Aleutian Islands, AK		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Okmok Ashishik Point	OAP	Okmok volcano, Aleutian Islands, AK		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Pinatubo S2	PS 2	Mt. Pinatubo, Philippines	1991	>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Pinatubo S3	PS 3	Mt. Pinatubo, Philippines	1991	>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Hotlum Ash	HLA	Mt. Shasta, CA		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Mount St. Helens	MSH	Mt. St. Helens, WA	1980	>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm
Bishop Tuff	BT	California		>2 mm, 2 mm–250 μm , 250–125 μm , 125–63 μm , <63 μm

Table 2. Sample phase assemblages

Sample	Glass	Pyroxene	Feldspar	Amphibole	Apatite	Quartz	Oxides	Olivine	Total
Cima_1	0.456	0.086	0.384	0.000	0.010	0.000	0.016	0.048	1.000
Cima_2	0.541	0.335	0.100	0.000	0.008	0.000	0.002	0.014	1.000
Cima_3	0.403	0.242	0.259	0.000	0.004	0.000	0.018	0.074	1.000
CFU_1	0.598	0.043	0.278	0.000	0.000	0.000	0.023	0.057	1.000
CFU_2	0.408	0.111	0.425	0.000	0.002	0.000	0.034	0.020	1.000
CFU_4	0.408	0.000	0.388	0.000	0.000	0.000	0.061	0.142	1.000
CFSWLC	0.525	0.057	0.335	0.000	0.006	0.000	0.055	0.022	1.000
Hei	0.902	0.000	0.092	0.002	0.000	0.000	0.004	0.006	1.000
Ves	0.655	0.033	0.296	0.000	0.010	0.000	0.006	0.000	1.000
SS_1	0.667	0.127	0.175	0.000	0.004	0.000	0.026	0.000	1.000
SS_2	0.743	0.075	0.176	0.000	0.000	0.000	0.006	0.000	1.000
SS_3	0.824	0.036	0.131	0.000	0.000	0.000	0.010	0.000	1.000
SS_4	0.776	0.044	0.170	0.002	0.000	0.000	0.008	0.000	1.000
R8D1	0.675	0.062	0.247	0.000	0.000	0.000	0.016	0.000	1.000
OAD	0.722	0.042	0.226	0.000	0.002	0.000	0.008	0.000	1.000
OAP	0.910	0.008	0.061	0.000	0.000	0.000	0.020	0.000	1.000
PS_2	0.702	0.173	0.086	0.000	0.014	0.012	0.014	0.000	1.000
PS_3	0.628	0.156	0.171	0.000	0.008	0.002	0.035	0.000	1.000
HLA	0.510	0.241	0.239	0.000	0.000	0.000	0.010	0.000	1.000
MSH	0.815	0.063	0.085	0.000	0.008	0.000	0.030	0.000	1.000
BT	0.796	0.004	0.142	0.000	0.000	0.050	0.008	0.000	1.000

Table 3. Sample bulk compositions

	Cima 1	Cima 2	Cima 3	CFU 1	CFU 2	CFU 4	CFSWLC
P ₂ O ₅	0.57 (0.09)	1.12 (0.14)	0.52 (0.07)	1.37 (0.06)	1.23 (0.23)	1.23 (0.04)	1.44 (0.11)
SiO ₂	48.17 (0.91)	47.00 (0.30)	48.65 (0.73)	48.78 (0.47)	49.54 (0.92)	46.99 (0.84)	48.81 (0.37)
SO ₂	0.02 (0.01)	0.07 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)	0.01 (0.01)
TiO ₂	2.39 (0.33)	0.99 (0.03)	2.00 (0.22)	2.03 (0.08)	1.82 (0.26)	1.96 (0.06)	2.12 (0.10)
Al ₂ O ₃	13.51 (1.74)	14.04 (0.36)	12.62 (1.66)	16.46 (0.41)	17.33 (1.08)	16.57 (0.35)	16.39 (0.39)
Cr ₂ O ₃	0.04 (0.02)	0.02 (0.01)	0.09 (0.02)	0.01 (0.01)	0.00 (0.00)	0.01 (0.01)	0.01 (0.01)
MgO	8.12 (1.10)	6.61 (0.17)	11.35 (1.18)	5.08 (0.33)	4.77 (0.47)	4.69 (0.10)	4.65 (0.22)
CaO	10.61 (0.71)	12.35 (0.25)	8.45 (0.50)	8.45 (0.18)	8.30 (0.29)	9.70 (0.12)	9.12 (0.19)
MnO	0.18 (0.02)	0.13 (0.01)	0.19 (0.02)	0.17 (0.01)	0.16 (0.01)	0.17 (0.01)	0.17 (0.02)
FeO	9.95 (0.70)	7.60 (0.18)	10.73 (0.96)	9.94 (0.51)	9.12 (0.79)	9.70 (0.20)	9.73 (0.42)
Na ₂ O	3.51 (0.34)	1.66 (0.07)	3.24 (0.34)	3.29 (0.08)	3.65 (0.16)	2.87 (0.09)	3.38 (0.12)
K ₂ O	1.27 (0.17)	5.00 (0.20)	1.31 (0.21)	1.88 (0.10)	2.02 (0.14)	1.64 (0.06)	2.26 (0.11)
Mo	0.16 (0.26)	1.27 (0.22)	0.21 (0.41)	0.56 (0.47)	0.01 (0.02)	0.85 (0.49)	0.36 (0.28)
Total	98.51 (0.35)	97.87 (0.29)	99.38 (0.27)	98.03 (0.55)	97.95 (1.00)	96.40 (1.28)	98.46 (0.24)

	Hei	Ves	SS 1	SS 2	SS 3	SS 4	R8d1
P ₂ O ₅	0.74 (0.07)	0.84 (0.47)	0.23 (0.06)	0.16 (0.04)	0.30 (0.14)	0.48 (0.20)	0.17 (0.04)
SiO ₂	49.54 (0.86)	50.94 (1.34)	53.77 (0.56)	56.89 (0.49)	56.37 (1.90)	60.44 (2.55)	60.32 (0.38)
SO ₂	0.04 (0.05)	0.04 (0.03)	0.03 (0.01)	0.02 (0.01)	0.05 (0.02)	0.01 (0.01)	0.02 (0.01)
TiO ₂	2.79 (0.33)	0.63 (0.07)	1.56 (0.07)	1.54 (0.12)	1.75 (0.27)	0.81 (0.40)	1.40 (0.06)
Al ₂ O ₃	16.30 (0.71)	19.82 (0.68)	24.70 (0.23)	22.18 (0.22)	21.58 (0.64)	18.06 (2.38)	20.30 (0.28)
Cr ₂ O ₃	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
MgO	3.55 (0.22)	1.56 (0.23)	2.22 (0.05)	2.43 (0.11)	2.49 (0.24)	1.69 (0.46)	2.02 (0.06)
CaO	7.25 (0.18)	6.67 (0.83)	6.08 (0.17)	6.38 (0.10)	5.92 (0.38)	5.21 (0.98)	5.50 (0.13)
MnO	0.26 (0.02)	0.15 (0.02)	0.07 (0.01)	0.08 (0.01)	0.08 (0.01)	0.09 (0.02)	0.08 (0.01)
FeO	12.44 (0.69)	5.20 (0.51)	6.83 (0.43)	4.62 (0.27)	5.23 (0.89)	5.37 (1.15)	4.95 (0.23)
Na ₂ O	4.84 (0.17)	4.54 (0.15)	3.34 (0.17)	3.68 (0.09)	4.12 (0.25)	3.99 (0.30)	3.55 (0.15)
K ₂ O	1.37 (0.07)	7.57 (0.40)	0.89 (0.04)	1.26 (0.05)	1.47 (0.14)	3.10 (0.36)	1.60 (0.07)
Mo	0.30 (0.43)	0.40 (0.26)	0.05 (0.05)	0.01 (0.02)	0.01 (0.01)	0.01 (0.02)	0.01 (0.01)
Total	99.41 (0.37)	98.37 (1.39)	99.78 (0.74)	99.26 (0.53)	99.37 (2.06)	99.25 (0.85)	99.91 (0.40)

Table 3. Cont.

	OAD	OAP	PS 2	PS 3	HLA	MHS	BT
P ₂ O ₅	0.22 (0.04)	0.18 (0.03)	0.20 (0.08)	0.10 (0.15)	0.06 (0.03)	0.11 (0.08)	0.03 (0.01)
SiO ₂	60.86 (1.38)	68.51 (0.92)	67.56 (0.97)	70.79 (3.51)	57.46 (2.01)	74.03 (2.43)	73.46 (1.83)
SO ₂	0.02 (0.01)	0.01 (0.01)	0.02 (0.01)	0.00 (0.00)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
TiO ₂	1.23 (0.09)	0.63 (0.05)	0.40 (0.06)	0.20 (0.14)	0.91 (0.20)	0.54 (0.31)	0.10 (0.03)
Al ₂ O ₃	15.16 (0.29)	14.98 (0.78)	15.31 (0.43)	16.70 (1.86)	24.92 (1.59)	13.32 (1.77)	15.18 (1.28)
Cr ₂ O ₃	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.00 (0.00)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
MgO	2.20 (0.15)	0.76 (0.23)	2.20 (0.10)	1.18 (0.50)	3.92 (0.99)	1.00 (0.90)	0.39 (0.12)
CaO	5.12 (0.29)	2.76 (0.30)	4.37 (0.21)	3.16 (0.89)	4.94 (0.70)	2.09 (0.31)	1.11 (0.19)
MnO	0.19 (0.02)	0.16 (0.03)	0.09 (0.01)	0.06 (0.03)	0.10 (0.02)	0.05 (0.03)	0.05 (0.01)
FeO	8.47 (0.48)	5.00 (0.65)	3.06 (0.26)	1.62 (0.56)	3.60 (0.82)	3.00 (1.85)	0.93 (0.18)
Na ₂ O	3.35 (0.11)	3.49 (0.14)	3.98 (0.22)	4.23 (0.15)	2.71 (0.35)	3.86 (0.36)	2.79 (0.20)
K ₂ O	1.89 (0.12)	3.27 (0.13)	2.04 (0.09)	2.51 (0.18)	0.99 (0.12)	2.24 (0.19)	4.33 (0.26)
Mo	0.60 (0.17)	0.01 (0.02)	0.21 (0.18)	0.03 (0.02)	0.15 (0.16)	0.02 (0.02)	0.13 (0.08)
Total	99.34 (0.24)	99.77 (0.35)	99.45 (0.60)	100.60 (1.18)	99.80 (0.84)	100.28 (0.83)	98.51 (1.41)

Table 4. Sample glass compositions

	Cima 1	Cima 2	Cima 3	CFU 1	CFU 2	CFU 4	CFSWLC
P ₂ O ₅	1.41 (0.35)	1.09 (0.45)	1.31 (0.09)	1.86 (0.43)	1.76 (0.59)	1.71 (0.12)	1.52 (0.18)
SiO ₂	54.43 (1.38)	47.99 (1.28)	52.53 (1.16)	51.40 (0.84)	53.47 (0.86)	51.25 (0.57)	50.17 (0.36)
TiO ₂	2.84 (0.40)	1.17 (0.32)	2.99 (0.18)	3.15 (0.60)	3.44 (0.34)	2.80 (0.10)	2.55 (0.22)
Al ₂ O ₃	17.93 (1.04)	18.82 (2.72)	17.19 (0.72)	14.19 (1.53)	13.52 (0.65)	13.96 (0.43)	15.17 (0.69)
Cr ₂ O ₃	0.01 (0.01)	0.00 (0.01)	0.01 (0.01)	0.00 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
MgO	2.32 (0.65)	3.53 (1.59)	2.70 (0.62)	2.90 (0.76)	2.34 (0.33)	3.90 (0.25)	4.36 (0.96)
CaO	4.84 (1.30)	10.36 (2.52)	5.08 (1.08)	7.86 (1.31)	6.90 (1.10)	7.84 (0.36)	7.92 (0.64)
MnO	0.15 (0.05)	0.19 (0.07)	0.16 (0.03)	0.20 (0.04)	0.24 (0.04)	0.21 (0.02)	0.20 (0.02)
FeO	7.24 (1.46)	8.86 (2.10)	7.44 (0.67)	11.10 (2.14)	10.64 (0.91)	11.43 (0.40)	10.15 (0.36)
Na ₂ O	4.50 (0.62)	2.89 (1.00)	5.21 (0.55)	3.48 (0.46)	3.68 (0.29)	3.13 (0.25)	4.27 (0.24)
K ₂ O	5.35 (1.66)	4.21 (2.79)	5.13 (0.92)	3.27 (0.84)	3.81 (0.51)	2.78 (0.17)	3.16 (0.47)
S	0.02 (0.01)	0.03 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.00 (0.01)
Total	101.05 (0.92)	99.15 (1.60)	99.76 (1.08)	99.42 (1.52)	99.80 (1.01)	99.03 (0.85)	99.49 (0.67)
	Hei	Ves	SS 1	SS 2	SS 3	SS 4	R8D1
P ₂ O ₅	0.91 (0.03)	0.27 (0.34)	0.35 (0.04)	0.28 (0.08)	0.26 (0.15)	0.32 (0.03)	0.31 (0.08)
SiO ₂	49.89 (0.27)	53.52 (1.72)	60.33 (1.94)	69.18 (1.24)	57.94 (3.21)	57.81 (0.92)	58.50 (1.12)
TiO ₂	3.29 (0.10)	0.56 (0.06)	1.18 (0.17)	1.10 (0.09)	0.77 (0.48)	1.02 (0.05)	0.98 (0.29)
Al ₂ O ₃	14.43 (0.21)	21.46 (0.80)	17.12 (1.27)	14.23 (0.99)	21.28 (4.51)	18.33 (0.90)	18.93 (2.52)
Cr ₂ O ₃	0.01 (0.01)	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
MgO	3.26 (0.09)	0.71 (0.20)	2.74 (0.74)	0.95 (0.12)	2.19 (1.75)	3.55 (0.24)	2.84 (0.90)
CaO	7.16 (0.07)	4.98 (0.97)	5.97 (0.85)	3.08 (0.52)	7.90 (2.34)	6.75 (0.38)	6.77 (1.14)
MnO	0.32 (0.02)	0.17 (0.04)	0.11 (0.02)	0.07 (0.02)	0.08 (0.05)	0.12 (0.02)	0.10 (0.03)
FeO	13.91 (0.20)	4.93 (0.71)	6.10 (0.55)	4.10 (0.35)	4.63 (2.43)	6.44 (0.40)	5.78 (1.46)
Na ₂ O	4.37 (0.57)	7.31 (0.88)	3.91 (0.38)	4.51 (0.21)	4.25 (0.63)	3.76 (0.32)	4.16 (0.54)
K ₂ O	1.81 (0.09)	6.13 (0.95)	1.86 (0.35)	3.13 (0.20)	1.13 (0.73)	1.50 (0.21)	1.38 (0.46)
S	0.05 (0.01)	0.04 (0.02)	0.02 (0.02)	0.01 (0.01)	0.02 (0.02)	0.04 (0.01)	0.02 (0.02)
Total	99.39 (0.59)	100.09 (3.63)	99.68 (0.79)	100.65 (1.22)	100.45 (2.32)	99.64 (1.06)	99.78 (1.88)

Table 4. Cont.

	OAD 1	OAD 2	OAP	PS 2	PS 3	HLA	MSH
P ₂ O ₅	0.03 (0.02)	0.31 (0.03)	0.17 (0.05)	0.03 (0.01)	0.04 (0.02)	0.13 (0.08)	0.04 (0.01)
SiO ₂	73.21 (0.92)	56.84 (0.93)	66.75 (2.74)	76.82 (1.66)	75.84 (2.22)	73.63 (2.40)	79.20 (0.60)
TiO ₂	0.27 (0.05)	1.52 (0.15)	0.57 (0.13)	0.14 (0.03)	0.18 (0.10)	0.79 (0.22)	0.38 (0.04)
Al ₂ O ₃	13.28 (0.24)	15.12 (0.66)	16.33 (2.86)	12.89 (0.40)	14.16 (1.41)	13.22 (1.04)	12.13 (0.32)
Cr ₂ O ₃	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)	0.01 (0.01)
MgO	0.07 (0.06)	2.93 (0.40)	0.60 (0.18)	0.22 (0.06)	0.48 (0.65)	0.45 (0.78)	0.20 (0.02)
CaO	1.44 (0.14)	6.89 (0.62)	2.98 (1.33)	1.14 (0.07)	1.22 (0.32)	1.87 (1.21)	0.92 (0.09)
MnO	0.12 (0.02)	0.22 (0.03)	0.13 (0.03)	0.03 (0.02)	0.04 (0.01)	0.03 (0.02)	0.03 (0.02)
FeO	3.42 (0.24)	10.28 (0.81)	4.50 (1.11)	0.82 (0.10)	0.92 (0.31)	1.94 (0.47)	1.60 (0.05)
Na ₂ O	4.03 (0.65)	3.74 (0.28)	4.99 (0.48)	2.63 (0.88)	4.14 (0.25)	4.09 (0.31)	2.57 (0.30)
K ₂ O	3.69 (0.35)	1.41 (0.26)	2.93 (0.63)	3.11 (0.16)	3.02 (0.20)	2.76 (0.98)	2.86 (0.09)
S	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.00 (0.00)
Total	99.58 (1.24)	99.29 (0.64)	99.97 (1.53)	97.84 (1.81)	100.06 (2.87)	98.93 (0.61)	99.95 (0.95)
	BT						
P ₂ O ₅	0.02 (0.01)						
SiO ₂	75.09 (0.96)						
TiO ₂	0.07 (0.02)						
Al ₂ O ₃	12.42 (0.18)						
Cr ₂ O ₃	0.01 (0.01)						
MgO	0.04 (0.01)						
CaO	0.43 (0.03)						
MnO	0.03 (0.01)						
FeO	0.66 (0.04)						
Na ₂ O	3.27 (0.21)						
K ₂ O	5.20 (0.22)						
S	0.01 (0.01)						
Total	97.24 (1.18)						

Table 5. Cima mineral compositions

Cima_1						
	Feldspar, Labradorite	Pyroxene, Augite	Pyroxene, Pigeonite	Olivine	Oxide	
SiO ₂	52.72 (0.95)	48.96 (0.44)	52.34 (0.54)	39.44 (0.23)	0.11 (0.03)	
TiO ₂		1.24 (0.11)	0.35 (0.03)		49.12 (1.79)	
Al ₂ O ₃	28.41 (1.61)	5.99 (0.24)	3.42 (0.10)	0.05 (0.04)	0.43 (0.05)	
V ₂ O ₃					0.02 (0.03)	
Cr ₂ O ₃		0.15 (0.02)	0.07 (0.01)	0.02 (0.01)	0.35 (0.07)	
MgO		13.16 (0.25)	24.63 (0.62)	44.53 (0.93)	6.26 (0.48)	
CaO	11.74 (1.13)	19.45 (0.09)	1.20 (0.09)	0.21 (0.09)	0.05 (0.03)	
MnO		0.18 (0.01)	0.31 (0.01)	0.27 (0.07)	0.39 (0.06)	
FeO	1.21 (0.97)	8.87 (0.07)	17.31 (0.74)	15.41 (0.99)	37.78 (1.86)	
NiO				0.22 (0.03)		
ZnO					0.02 (0.01)	
Na ₂ O	4.59 (0.55)	0.89 (0.03)	0.08 (0.03)			
K ₂ O	0.28 (0.20)	0.01 (0.01)	0.01 (0.01)			
Total	98.96 (0.93)	98.89 (0.54)	99.73 (0.31)	100.15 (0.39)	94.54 (0.54)	

Cima_2						
	Feldspar, Labradorite	Feldspar, Othoclase	Pyroxene, CPX	Apatite	Olivine	Oxide
P ₂ O ₅				41.59 (0.24)		
SiO ₂	47.05 (0.68)	55.01 (0.70)	46.73 (1.43)	0.36 (0.02)	38.13 (0.41)	0.24 (0.11)
TiO ₂			1.51 (0.34)	0.01 (0.03)	0.02 (0.01)	7.40 (1.38)
Al ₂ O ₃	33.34 (0.48)	22.74 (0.43)	7.42 (1.26)	0.01 (0.01)	0.06 (0.07)	4.33 (3.43)
V ₂ O ₃						0.22 (0.20)
Cr ₂ O ₃			0.04 (0.05)	0.01 (0.01)	0.00 (0.01)	0.03 (0.03)
MgO			12.41 (0.81)	0.32 (0.01)	36.77 (0.80)	2.65 (1.68)
CaO	16.89 (0.56)	0.33 (0.46)	23.00 (0.45)	53.70 (0.34)	0.52 (0.06)	0.23 (0.10)
MnO			0.15 (0.02)	0.05 (0.01)	0.50 (0.02)	0.35 (0.06)
FeO	0.53 (0.02)	0.75 (0.39)	8.13 (0.75)	0.37 (0.03)	24.65 (0.72)	74.55 (6.16)
NiO					0.07 (0.01)	
ZnO						0.05 (0.03)
Na ₂ O	1.67 (0.27)	0.13 (0.11)	0.32 (0.09)	0.05 (0.05)	0.01 (0.01)	
K ₂ O	0.31 (0.08)	20.63 (0.78)	0.04 (0.05)	0.02 (0.02)	0.03 (0.07)	
Total	99.78 (0.32)	99.58 (0.93)	99.75 (0.39)	96.51 (0.53)	100.71 (0.80)	90.05 (0.84)

Table 5 cont.

Cima 3

	Feldspar, Labradorite	Feldspar, Plagioclase	Pyroxene, Augite 1	Pyroxene, Augite 2	Olivine	Oxide
SiO ₂	53.76 (1.01)	59.02 (0.47)	48.74 (1.61)	53.68 (0.27)	38.15 (0.68)	0.23 (0.09)
TiO ₂			2.32 (1.00)	0.23 (0.10)	0.06 (0.04)	2.37 (1.98)
Al ₂ O ₃	28.54 (1.12)	25.69 (0.24)	4.55 (0.79)	2.78 (0.29)	0.06 (0.08)	4.39 (2.05)
V ₂ O ₃						0.33 (0.11)
Cr ₂ O ₃			0.09 (0.13)	0.19 (0.04)	0.01 (0.01)	3.93 (4.84)
MgO			13.78 (0.87)	27.18 (0.74)	36.74 (1.92)	3.26 (2.39)
CaO	11.42 (0.81)	7.57 (0.26)	21.21 (0.40)	1.24 (0.63)	0.25 (0.12)	0.14 (0.08)
MnO			0.20 (0.04)	0.32 (0.11)	0.54 (0.11)	0.73 (0.48)
FeO	1.01 (0.74)	0.27 (0.02)	8.24 (0.82)	15.05 (0.98)	24.86 (2.60)	77.33 (7.66)
ZnO						0.11 (0.07)
Na ₂ O	4.89 (0.46)	6.81 (0.14)	0.65 (0.09)	0.06 (0.04)	0.01 (0.01)	
K ₂ O	0.32 (0.14)	0.83 (0.07)	0.04 (0.03)	0.00 (0.00)	0.01 (0.01)	
Total	99.94 (0.85)	100.20 (0.47)	99.83 (0.49)	100.73 (0.27)	100.69 (1.11)	92.82 (1.59)

Table 6. Crater Flats mineral compositions

CFU 1				
	Feldspar, Bytownite	Olivine	Oxide	
SiO ₂	51.27 (0.84)	37.53 (0.62)	0.31 (0.30)	
TiO ₂		0.12 (0.03)	11.59 (1.28)	
Al ₂ O ₃	29.62 (0.80)	0.13 (0.07)	6.41 (0.70)	
V ₂ O ₃			0.30 (0.04)	
Cr ₂ O ₃		0.00 (0.00)	1.37 (1.26)	
MgO		36.15 (1.67)	5.08 (0.60)	
CaO	13.18 (0.23)	0.56 (0.32)	0.16 (0.07)	
MnO		0.44 (0.02)	0.36 (0.03)	
FeO	1.18 (0.73)	25.14 (1.55)	69.13 (1.25)	
ZnO			0.08 (0.03)	
Na ₂ O	3.79 (0.22)	0.03 (0.02)		
K ₂ O	0.33 (0.08)	0.03 (0.01)		
Total	99.36 (1.37)	100.13 (0.71)	94.66	1.10
CFU 2				
	Feldspar, Labradorite	Pyroxene, Augite	Olivine	Oxide
SiO ₂	51.94 (0.83)	49.08 (0.69)	38.41 (0.80)	0.15 (0.05)
TiO ₂		1.84 (0.26)	0.02 (0.01)	11.98 (1.11)
Al ₂ O ₃	29.52 (0.69)	3.54 (0.66)	0.03 (0.01)	6.20 (1.00)
Cr ₂ O ₃		0.00 (0.00)	0.01 (0.01)	2.16 (1.46)
MgO		13.93 (0.66)	40.12 (0.98)	5.09 (0.56)
CaO	12.82 (0.55)	19.52 (1.43)	0.16 (0.02)	0.08 (0.09)
MnO		0.30 (0.03)	0.31 (0.01)	0.36 (0.03)
FeO	1.15 (0.18)	10.56 (0.78)	20.98 (0.25)	67.94 (1.16)
NiO			0.17 (0.03)	
Na ₂ O	3.97 (0.32)	0.46 (0.07)	0.00 (0.00)	
K ₂ O	0.34 (0.08)	0.15 (0.21)	0.00 (0.00)	
Total	99.74 (0.91)	99.40 (0.56)	100.14 (1.75)	93.96 (0.92)

Table 6 Cont.

	CFU 4			CFSWLC		
	Feldspar, Labradorite	Olivine	Oxide	Feldspar, Labradorite	Pyroxene, Augite	Oxides
SiO ₂	51.32 (0.85)	38.18 (0.77)	0.20 (0.11)	51.35 (0.91)	46.25 (1.55)	0.13 (0.05)
TiO ₂		0.07 (0.05)	14.39 (1.17)		2.44 (0.65)	11.23 (5.28)
Al ₂ O ₃	28.42 (1.33)	0.21 (0.44)	4.38 (0.71)	29.64 (0.87)	6.23 (1.55)	5.67 (4.39)
V ₂ O ₃			0.42 (0.04)			0.19 (0.04)
Cr ₂ O ₃		0.01 (0.01)	1.38 (1.56)		0.00 (0.00)	1.55 (2.80)
MgO		37.68 (2.53)	4.90 (0.48)		13.14 (0.88)	7.65 (2.87)
CaO	12.73 (0.46)	0.32 (0.24)	0.13 (0.05)	12.72 (0.68)	21.25 (0.34)	0.10 (0.04)
MnO		0.39 (0.08)	0.39 (0.01)		0.18 (0.02)	0.47 (0.21)
FeO	1.77 (0.88)	23.39 (2.51)	68.91 (1.47)	1.23 (0.89)	8.78 (0.38)	65.13 (3.20)
ZnO			0.09 (0.02)			0.09 (0.07)
Na ₂ O	3.91 (0.19)	0.04 (0.06)		3.95 (0.18)	0.46 (0.09)	
K ₂ O	0.49 (0.19)	0.03 (0.04)		0.35 (0.05)	0.04 (0.03)	
Total	98.65 (1.44)	100.29 (1.47)	94.92 (1.15)	99.25 (1.69)	98.77 (1.53)	92.18 (1.62)

Table 7. Heimaey mineral compositions

	Hei		
	Feldspar, Andesine	Olivine	Oxide
SiO ₂	55.63 (1.06)	36.48 (0.57)	0.22 (0.06)
TiO ₂		0.21 (0.20)	21.87 (0.47)
Al ₂ O ₃	26.65 (1.25)	0.20 (0.52)	4.24 (0.31)
V ₂ O ₃			0.31 (0.04)
Cr ₂ O ₃		0.00 (0.01)	0.03 (0.01)
MgO		29.19 (1.47)	4.03 (0.14)
CaO	9.73 (0.76)	0.42 (0.18)	0.11 (0.03)
MnO		0.70 (0.07)	0.60 (0.03)
FeO	1.49 (1.35)	33.72 (1.41)	65.47 (0.31)
ZnO			0.08 (0.02)
Na ₂ O	5.53 (0.35)	0.10 (0.42)	
K ₂ O	0.36 (0.11)	0.02 (0.03)	
Total	99.38 (0.83)	101.04 (0.74)	96.96 (0.34)

Table 8. Vesuvius mineral compositions

	Ves					
	Feldspar, Anorthite	Feldspar, Leucite	Pyroxene, Augite	Biotite	Biotite	Oxide
P2O5						
SiO2	53.40 (0.73)	55.50 (0.41)	44.11 (1.86)	38.08 (0.88)	34.95 (1.19)	0.10 (0.02)
TiO2		0.03 (0.02)	1.71 (0.34)	2.92 (0.06)	3.68 (0.12)	5.27 (0.16)
Al2O3	29.65 (0.45)	23.37 (0.22)	9.15 (1.27)	16.52 (0.42)	16.40 (0.35)	4.92 (0.15)
V2O3						0.45 (0.02)
Cr2O3			0.01 (0.02)	0.08 (0.05)	0.05 (0.01)	0.06 (0.02)
MgO			9.91 (2.01)	21.28 (0.67)	14.91 (1.35)	2.09 (0.15)
CaO	11.67 (0.61)	0.01 (0.02)	23.45 (0.49)	0.03 (0.01)	0.03 (0.02)	0.10 (0.01)
MnO		0.01 (0.01)	0.21 (0.12)	0.04 (0.01)	0.16 (0.02)	0.57 (0.02)
FeO	0.50 (0.02)	0.28 (0.05)	11.14 (2.81)	7.05 (0.20)	14.84 (1.03)	81.18 (0.36)
ZnO						0.06 (0.01)
BaO					0.30 (0.08)	
H2O				4.19 (0.09)	3.97 (0.11)	
Na2O	4.21 (0.18)	0.94 (0.07)	0.39 (0.19)	0.26 (0.10)	0.38 (0.04)	
K2O	0.87 (0.12)	20.25 (0.22)	0.01 (0.01)	9.55 (0.72)	9.38 (0.35)	
Total	100.30 (0.18)	100.36 (0.53)	100.10 (0.81)	100.00 (2.15)	98.92 (2.18)	94.81 (0.68)

Table 9. Summerland mineral compositions

	SS 1			SS 2		
	Feldspar, Plagioclase	Pyroxene, Augite	Pyroxene, Pigeonite	Feldspar, Plagioclase	Pyroxene, Pigeonite	Oxide
SiO ₂	57.02 (1.18)	51.77 (1.84)	52.14 (0.59)	55.04 (1.56)	53.02 (1.01)	0.29 (0.10)
TiO ₂		0.63 (0.07)	0.31 (0.06)		0.31 (0.07)	12.74 (0.15)
Al ₂ O ₃	26.88 (0.74)	4.13 (0.18)	0.93 (0.14)	27.95 (1.54)	0.96 (0.55)	2.94 (0.49)
V ₂ O ₃						0.42 (0.02)
Cr ₂ O ₃		0.10 (0.05)	0.02 (0.01)		0.01 (0.01)	0.13 (0.04)
MgO		15.89 (0.28)	21.70 (0.42)		22.65 (1.96)	2.81 (0.12)
CaO	9.38 (0.64)	19.61 (5.54)	1.64 (0.04)	10.91 (1.17)	1.76 (0.31)	0.06 (0.02)
MnO		0.16 (0.02)	0.51 (0.03)		0.50 (0.05)	0.37 (0.01)
FeO	0.50 (0.04)	7.85 (3.36)	22.30 (0.22)	0.87 (0.64)	21.18 (2.39)	74.78 (0.62)
NiO						0.03 (0.01)
ZnO						0.09 (0.02)
Na ₂ O	5.60 (0.32)	0.37 (0.07)	0.04 (0.01)	4.91 (0.52)	0.04 (0.01)	
K ₂ O	0.42 (0.06)	0.09 (0.26)	0.00 (0.00)	0.35 (0.47)	0.02 (0.09)	
Total	99.80 (1.35)	100.59 (0.79)	99.59 (0.98)	100.03 (2.01)	100.44 (0.65)	94.66 (0.44)

	SS 3				SS 4		
	Feldspar, Plagioclase	Pyroxene, Pigeonite 1	Pyroxene, Pigeonite 2	Oxide	Feldspar, Plagioclase	Pyroxene, Pigeonite	Pyroxene, Augite
SiO ₂	56.13 (1.28)	53.83 (0.75)	51.81 (0.55)	0.11 (0.03)	57.25 (1.17)	52.78 (1.12)	42.66 (0.20)
TiO ₂		0.31 (0.03)	0.32 (0.07)	42.33 (0.41)		0.59 (0.17)	2.75 (0.02)
Al ₂ O ₃	27.35 (0.81)	1.26 (0.44)	0.84 (0.23)	0.58 (0.58)	27.47 (0.66)	1.08 (0.37)	12.74 (0.07)
V ₂ O ₃				0.11 (0.03)			
Cr ₂ O ₃		0.02 (0.01)	0.01 (0.01)	0.08 (0.01)		0.01 (0.01)	0.02 (0.01)
MgO		26.29 (0.88)	21.38 (0.43)	3.47 (0.09)		23.29 (2.32)	15.61 (0.08)
CaO	10.13 (0.82)	1.52 (0.11)	1.70 (0.19)	0.07 (0.04)	9.60 (0.73)	3.57 (3.76)	11.43 (0.05)
MnO		0.40 (0.05)	0.54 (0.02)	0.35 (0.01)		0.45 (0.02)	0.11 (0.01)
FeO	0.63 (0.10)	16.54 (0.93)	22.45 (0.70)	49.55 (0.49)	0.59 (0.08)	17.80 (1.45)	9.79 (0.07)
NiO				0.02 (0.01)			
ZnO				0.04 (0.01)			
Na ₂ O	5.36 (0.42)	0.04 (0.02)	0.04 (0.01)		5.76 (0.44)	0.08 (0.08)	2.38 (0.03)
K ₂ O	0.33 (0.05)	0.02 (0.03)	0.00 (0.00)		0.40 (0.06)	0.02 (0.01)	0.42 (0.01)
Total	99.93 (0.87)	100.23 (1.03)	99.08 (0.70)	96.70 (0.40)	101.07 (0.97)	99.66 (0.79)	97.90 (0.31)

Table 9 Cont.

R8D1

	Feldspar	Pyroxene, Augite	Pyroxene, Pigeonite	Oxide
SiO ₂	56.14 (1.77)	51.85 (0.77)	52.11 (0.67)	0.32 (0.17)
TiO ₂		0.46 (0.22)	0.29 (0.08)	40.39 (0.67)
Al ₂ O ₃	26.72 (0.89)	1.50 (0.76)	0.94 (0.59)	0.44 (0.09)
V ₂ O ₃				0.26 (0.08)
Cr ₂ O ₃		0.01 (0.01)	0.01 (0.01)	0.22 (0.06)
MgO		17.94 (3.54)	21.48 (0.84)	3.29 (0.50)
CaO	9.67 (0.85)	11.09 (9.26)	1.69 (0.08)	0.07 (0.05)
MnO		0.40 (0.13)	0.53 (0.03)	0.28 (0.04)
FeO	0.55 (0.08)	16.12 (5.96)	22.11 (1.03)	51.69 (0.97)
NiO				0.03 (0.02)
ZnO				0.03 (0.02)
Na ₂ O	5.40 (0.49)	0.21 (0.17)	0.04 (0.01)	
K ₂ O	0.38 (0.06)	0.01 (0.01)	0.01 (0.01)	
Total	98.87 (1.77)	99.59 (1.17)	99.22 (1.11)	97.02 (0.49)

Table 10. Okmok mineral compositions

OAP						
	Feldspar, Plagioclase	Pyroxene, CPX	Olivine	Oxide		
P2O5			0.04 (0.01)			
SiO2	55.11 (1.52)	50.20 (1.12)	33.14 (0.18)	0.16 (0.09)		
TiO2		0.25 (0.05)		19.81 (0.63)		
Al2O3	27.16 (0.98)	0.61 (0.40)	0.01 (0.01)	1.93 (0.31)		
V2O3				0.00 0.00		
Cr2O3		0.00 (0.00)	0.01 (0.01)	0.01 (0.01)		
MgO		13.30 (1.51)	17.23 (0.13)	1.32 (0.25)		
CaO	9.85 (0.97)	5.94 (5.20)	0.23 (0.02)	0.04 (0.04)		
MnO		1.28 (0.20)	1.36 (0.02)	0.75 (0.05)		
FeO	0.40 (0.05)	27.34 (4.30)	47.19 (0.19)	69.84 (0.78)		
NiO			0.01 (0.01)	0.01 (0.01)		
ZnO				0.13 (0.02)		
Na2O	5.67 (0.59)	0.13 (0.14)				
K2O	0.38 (0.08)	0.03 (0.03)				
Total	98.58 (1.54)	99.08 (1.69)	99.22 (0.40)	94.00 (0.94)		
OAD						
	Feldspar, Plagioclase	Feldspar, Labradorite	Pyroxene, CPX 1	Pyroxene, CPX 2	Olivine	Oxide
P2O5					0.07 (0.02)	
SiO2	58.14 (0.96)	55.52 (1.91)	47.45 (1.10)	47.36 (1.14)	37.36 (0.34)	0.14 (0.03)
TiO2			2.19 (0.17)	1.54 (0.10)		21.88 (0.21)
Al2O3	22.46 (1.08)	26.83 (0.72)	6.50 (0.74)	4.77 (0.67)	0.03 (0.01)	1.05 (0.06)
V2O3						0.01 (0.01)
Cr2O3			0.01 (0.01)	0.00 (0.00)	0.01 (0.01)	0.01 (0.01)
MgO			12.02 (0.99)	7.15 (0.32)	34.85 (0.31)	0.25 (0.01)
CaO	8.50 (0.69)	10.87 (0.79)	16.22 (1.25)	15.82 (1.05)	0.23 (0.01)	0.01 (0.01)
MnO			0.44 (0.04)	0.82 (0.04)	0.49 (0.01)	1.03 (0.03)
FeO	3.07 (0.62)	1.60 (0.20)	14.97 (0.62)	21.08 (0.57)	27.42 (0.16)	72.18 (0.34)
NiO					0.03 (0.01)	
ZnO						0.23 (0.02)
Na2O	5.37 (0.33)	4.98 (0.48)	0.43 (0.08)	0.41 (0.09)		
K2O	0.69 (0.13)	0.34 (0.08)	0.11 (0.09)	0.15 (0.11)		
Total	98.23 (0.57)	100.14 (1.38)	100.33 (0.79)	99.10 (0.52)	100.50 (0.67)	96.79 (0.46)

Table 11. Pinatubo mineral compositions

PS 2

	Feldspar, Andesine	Feldspar, Labradorite	Pyroxene, CPX 1	Pyroxene, CPX 2	Amphibole	Amphibole	Apatite	Oxide	Oxide
P2O5							40.85 (0.22)		
SiO2	59.03 (1.17)	54.77 (0.98)	47.38 (1.06)	42.06 (0.91)	41.60 (0.56)	47.27 (0.84)	0.12 (0.02)	0.04 (0.05)	0.09 (0.02)
TiO2			0.93 (0.10)	2.14 (0.12)	2.35 (0.13)	0.95 (0.08)	0.01 (0.02)	28.86 (0.75)	4.99 (0.85)
Al2O3	25.28 (0.50)	27.52 (0.94)	7.46 (0.81)	12.28 (0.40)	12.36 (0.27)	7.62 (0.47)	0.01 (0.01)	0.31 (0.04)	1.50 (0.24)
V2O3								0.33 (0.02)	0.37 (0.07)
Cr2O3			0.01 (0.01)	0.06 (0.04)	0.03 (0.03)	0.02 (0.02)	0.01 (0.01)	0.07 (0.02)	0.16 (0.06)
MgO			15.33 (0.67)	15.41 (0.62)	14.31 (1.13)	14.96 (0.46)	0.15 (0.02)	1.00 (0.22)	1.07 (0.07)
CaO	7.29 (0.62)	10.28 (0.98)	10.39 (0.20)	11.63 (0.20)	11.61 (0.17)	10.66 (0.13)	52.79 (0.29)	0.06 (0.08)	0.04 (0.02)
MnO			0.52 (0.05)	0.12 (0.01)	0.15 (0.03)	0.53 (0.03)	0.19 (0.01)	0.42 (0.55)	0.70 (0.15)
FeO	0.16 (0.02)	0.30 (0.09)	12.85 (0.65)	9.89 (0.46)	11.75 (1.57)	13.23 (0.37)	0.55 (0.05)	63.28 (0.97)	84.04 (0.90)
ZnO								0.03 (0.02)	0.14 (0.02)
H2O	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	2.02 (0.02)	2.03 (0.02)	0.00 0.00	0.00 0.00	0.00 0.00
Na2O	7.06 (0.41)	5.39 (0.48)	1.23 (0.12)	2.37 (0.14)	2.41 (0.18)	1.27 (0.08)	0.11 (0.05)		
K2O	0.32 (0.05)	0.24 (0.08)	0.25 (0.05)	0.41 (0.03)	0.77 (0.12)	0.28 (0.04)	0.01 (0.01)		
S							0.04 (0.01)		
Total	99.15 (0.73)	98.49 (0.89)	96.36 (1.08)	96.37 (1.96)	99.36 (0.23)	98.81 (1.07)	94.85 (0.50)	94.19 (0.83)	93.09 (0.60)

Table 11. Cont.

PS 3

	Feldspar, Andesine	Feldspar, Labradorite	Pyroxene, Pigeonite	Pyroxene, CPX	Amphibole	Oxide	Oxide
SiO ₂	59.51 (0.95)	54.20 (1.30)	53.61 (1.05)	48.06 (1.07)	48.47 (0.61)	0.03 (0.04)	0.06 (0.02)
TiO ₂			0.36 (0.13)	0.96 (0.12)	0.96 (0.13)	28.64 (0.37)	4.25 (0.02)
Al ₂ O ₃	25.54 (0.51)	28.84 (0.84)	2.81 (0.81)	7.48 (0.80)	7.23 (0.46)	0.33 (0.03)	1.89 (0.05)
V ₂ O ₃						0.34 (0.01)	0.47 (0.01)
Cr ₂ O ₃			0.01 (0.01)	0.04 (0.03)	0.02 (0.01)	0.07 (0.01)	0.25 (0.03)
MgO			20.40 (0.56)	15.52 (0.64)	15.82 (0.28)	0.95 (0.09)	1.07 (0.02)
CaO	7.42 (0.60)	11.53 (1.01)	2.99 (1.26)	10.48 (0.39)	10.51 (0.11)	0.01 (0.02)	0.01 (0.01)
MnO			0.85 (0.08)	0.53 (0.04)	0.49 (0.05)	0.23 (0.01)	0.41 (0.01)
FeO	0.17 (0.03)	0.31 (0.06)	16.06 (0.70)	12.95 (0.45)	12.66 (0.21)	64.55 (0.35)	85.03 (0.40)
ZnO						0.03 (0.02)	0.12 (0.03)
H ₂ O					2.06 (0.01)	0.00 0.00	0.00 0.00
Na ₂ O	6.92 (0.38)	4.86 (0.54)	0.43 (0.15)	1.19 (0.13)	1.19 (0.09)		
K ₂ O	0.31 (0.08)	0.15 (0.03)	0.06 (0.04)	0.24 (0.05)	0.23 (0.03)		
Total	99.88 (0.54)	99.89 (0.23)	97.58 (0.90)	97.45 (0.46)	99.64 (0.35)	94.90 (0.74)	93.56 (0.37)

Table 12. Hotlum Ash mineral compositions

HLA

	Feldspar, Labradorite	Pyroxene, Pigeonite	Quartz
SiO ₂	53.67 (2.40)	54.74 (1.37)	96.87 (0.55)
TiO ₂		0.18 (0.07)	
Al ₂ O ₃	29.55 (1.47)	1.10 (0.33)	2.10 (0.08)
Cr ₂ O ₃		0.12 (0.12)	
MgO		28.27 (3.08)	
CaO	12.41 (1.45)	1.31 (0.32)	0.06 (0.02)
MnO		0.34 (0.12)	
FeO	0.67 (0.06)	14.31 (4.11)	0.12 (0.02)
Na ₂ O	4.57 (0.90)	0.02 (0.01)	1.16 (0.04)
K ₂ O	0.14 (0.05)	0.01 (0.01)	0.03 (0.01)
Total	101.01 (1.70)	100.40 (1.06)	100.35 (0.63)

Table 13. Mt St Helens mineral compositions

MHS						
	Feldspar, Labradorite	Feldspar, Andesine	Pyroxene, Pigeonite	Oxide	Oxide	Apatite
P2O5						41.69 (0.38)
SiO2	54.37 (1.38)	57.17 (1.35)	51.60 (1.01)	0.15 (0.03)	0.24 (0.10)	0.44 (0.29)
TiO2			0.17 (0.04)	42.24 (0.50)	10.39 (0.43)	0.01 (0.01)
Al2O3	28.75 (0.91)	26.87 (0.85)	0.97 (0.34)	0.24 (0.01)	1.91 (0.10)	0.01 (0.01)
V2O3				0.21 (0.02)	0.53 (0.03)	
Cr2O3			0.01 (0.01)	0.01 (0.01)	0.07 (0.02)	0.01 (0.01)
MgO			22.09 (1.96)	2.14 (0.08)	1.44 (0.04)	0.25 (0.12)
CaO	11.49 (1.03)	9.06 (0.69)	1.78 (3.99)	0.10 (0.08)	0.05 (0.04)	53.51 (0.74)
MnO			0.68 (0.06)	0.44 (0.02)	0.37 (0.02)	0.09 (0.02)
FeO	0.37 (0.10)	0.37 (0.15)	21.56 (0.52)	52.02 (0.62)	79.54 (0.49)	1.05 (0.13)
ZnO				0.05 (0.02)	0.11 (0.02)	
Na2O	4.86 (0.56)	6.01 (0.41)	0.01 (0.01)			0.04 (0.03)
K2O	0.12 (0.03)	0.20 (0.04)	0.00 (0.00)			0.01 (0.01)
S						0.01 (0.01)
Total	99.96 (0.35)	99.68 (0.54)	98.87 (1.45)	97.60 (0.22)	94.65 (0.44)	97.11 (0.99)

Table 14. Bishop Tuff mineral compositions

	BT			
	Feldspar, Sanidine	Feldspar, Albite	Quartz	Oxide
SiO ₂	65.82 (0.29)	64.57 (1.08)	99.45 (1.80)	0.08 (0.01)
TiO ₂			0.00 0.00	8.26 (0.07)
Al ₂ O ₃	18.94 (0.10)	22.01 (0.76)	0.38 (0.98)	1.01 (0.01)
V ₂ O ₃				0.01 (0.01)
Cr ₂ O ₃			0.03 (0.01)	0.00 (0.00)
MgO			0.00 (0.00)	0.34 (0.01)
CaO	0.15 (0.02)	3.42 (0.72)	0.02 (0.03)	0.01 (0.01)
MnO			0.01 (0.00)	0.74 (0.02)
FeO	0.08 (0.01)	0.17 (0.05)	0.03 (0.06)	84.17 (0.22)
ZnO				0.17 (0.01)
Na ₂ O	3.94 (0.07)	8.59 (0.62)	0.13 (0.34)	
K ₂ O	11.52 (0.15)	1.52 (0.24)	0.12 (0.34)	
Total	100.45 (0.25)	100.28 (0.56)	100.14 (0.12)	94.79 (0.19)

Table 15. Reststrahlen band minimum wavenumbers

Sample	Size Fraction	Minimum wnb 1	Minimum wnb 2	Minimum wnb 3	Number of Minima
Cima 1	500 250um	966	1089	0	2
Cima 1	250 125um	960	1091	0	2
Cima 1	125 63um	1002	0	0	1
Cima 1	63um	825	881	0	2
Cima 2	500 250um	920	1071	0	2
Cima 2	250 125um	920	1071	0	2
Cima 2	125 63um	920	2071	0	2
Cima 2	63um	900	1075	0	2
Cima 3	500 250um	970	1060	1090	3
Cima 3	250 125um	970	1060	1090	3
Cima 3	125 63um	967	1060	1090	3
Cima 3	63um	941	1055	0	2
CFU 1	2mm-250um	1040	0	0	1
CFU 1	250-125um	1040	0	0	1
CFU 1	125-63um	1040	0	0	1
CFU 1	63um	828	1035	0	2
CFU 2	2mm-250um	1036	0	0	1
CFU 2	250-125um	1036	0	0	1
CFU 2	125-63um	1036	0	0	1
CFU 2	63um	820	0	0	1
CFU 4	2mm-250um	1033	0	0	1
CFU 4	250-125um	1033	0	0	1
CFU 4	125-63um	1037	0	0	1
CFU 4	63um	1037	842	0	2
CFSWLC	2mm-250um	1037	0	0	1
CFSWLC	250-125um	1037	0	0	1
CFSWLC	125-63um	1037	0	0	1
CFSWLC	63um	817	1040	0	2
Hei	2mm-250um	1037	0	0	1
Hei	250-125um	1037	0	0	1
Hei	125-63um	1037	0	0	1
Hei	63um	871	1037	0	2
Ves	2mm-250um	1035	0	0	1
Ves	250-125um	1035	0	0	1

Table 15 con't. Reststrahlen band minimum wavenumbers

Sample	Size Fraction	Minimum wnb 1	Minimum wnb 2	Minimum wnb 3	Number of Minima
Ves	125-63um	1035	0	0	1
Ves	63um	840	1035	0	2
SS 1	2mm-250um	1041	0	0	1
SS 1	250-125um	1041	0	0	1
SS 1	125-63um	1041	0	0	1
SS 1	63um	860	1041	0	2
SS 2	2mm-250um	1055	0	0	1
SS 2	250-125um	1055	0	0	1
SS 2	125-63um	1055	0	0	1
SS 2	63um	858	1055	0	2
SS 3	2mm-250um	1022	0	0	1
SS 3	250-125um	1022	0	0	1
SS 3	125-63um	877	1022	0	2
SS 3	63um	877	1022	0	2
SS 4	2mm-250um	1025	0	0	1
SS 4	250-125um	1025	0	0	1
SS 4	125-63um	871	1004	1164	3
SS 4	63um	871	1004	1164	3
R8D1	2mm-250um	1051	0	0	1
R8D1	250-125um	1020	0	0	1
R8D1	125-63um	1020	0	0	1
R8D1	63um	871	1007	0	2
OAD	2mm-250um	1070	863	0	2
OAD	250-125um	1070	863	0	2
OAD	125-63um	856	1060	1203	3
OAD	63um	856	1060	1203	3
OAP	2mm-250um	1070	0	0	1
OAP	250-125um	1070	850	0	2
OAP	125-63um	1070	850	0	2
OAP	63um	850	1070	0	2
PS 2	2mm-250um	1087	0	0	1
PS 2	250-125um	860	1087	0	2
PS 2	125-63um	860	1087	0	2
PS 2	63um	860	1087	0	2

Table 15 con't. Reststrahlen band minimum wavenumbers

Sample	Size Fraction	Minimum wnb 1	Minimum wnb 2	Minimum wnb 3	Number of Minima
PS 3	2mm-250um	1091	0	0	1
PS 3	250-125um	997	0	0	1
PS 3	125-63um	875	1080	1204	3
PS 3	63um	875	1080	1204	3
HLA	2mm-250um	1090	0	0	1
HLA	250-125um	1090	0	0	1
HLA	125-63um	1090	0	0	1
HLA	63um	1090	0	0	1
MSH	500 250um	1091	871	0	2
MSH	250 125um	1091	871	0	2
MSH	125 63um	1091	871	0	2
MSH	63um	871	1091	0	2
BT	2mm-250um	1075	866	0	2
BT	250-125um	1075	866	0	2
BT	125-63um	1075	866	0	2
BT	63um	1075	866	1203	3

Table 16. Christiansen feature position

Sample	Size Fraction	Wavenumber	Sample	Size Fraction	Wavenumber	Sample	Size Fraction	Wavenumber
Cima 1	500-250um	1632	Ves	125-63um	1630	PS 3	2mm-250um	1628
Cima 1	250-125um	1641	Ves	63um	1630	PS 3	250-125um	1630
Cima 1	125-63um	1641	SS 1	2mm-250um	1585	PS 3	125-63um	1630
Cima 1	63um	1643	SS 1	250-125um	1630	PS 3	63um	1626
Cima 2	500-250um	1591	SS 1	125-63um	1595	HLA	2mm-250um	1630
Cima 2	250-125um	1589	SS 1	63um	1630	HLA	250-125um	1626
Cima 2	125-63um	1599	SS 2	2mm-250um	1579	HLA	125-63um	1632
Cima 2	63um	1551	SS 2	250-125um	1599	HLA	63um	1630
Cima 3	500-250um	1632	SS 2	125-63um	1603	MSH	500-250um	1626
Cima 3	250-125um	1632	SS 2	63um	1601	MSH	250-125um	1624
Cima 3	125-63um	1632	SS 3	2mm-250um	1597	MSH	125-63um	1630
Cima 3	63um	1632	SS 3	250-125um	1599	MSH	63um	1630
CFU 1	2mm-250um	1659	SS 3	125-63um	1597	BT	2mm-250um	1628
CFU 1	250-125um	1595	SS 3	63um	1603	BT	250-125um	1635
CFU 1	125-63um	1591	SS 4	2mm-250um	1626	BT	125-63um	1626
CFU 1	63um	1591	SS 4	250-125um	1639	BT	63um	1626
CFU 2	2mm-250um	1599	SS 4	125-63um	1610			
CFU 2	250-125um	1641	SS 4	63um	1630			
CFU 2	125-63um	1630	R8D1	2mm-250um	1606			
CFU 2	63um	1626	R8D1	250-125um	1606			
CFU 4	2mm-250um	1632	R8D1	125-63um	1606			
CFU 4	250-125um	1632	R8D1	63um	1605			
CFU 4	125-63um	1632	OAD	2mm-250um	1585			
CFU 4	63um	1632	OAD	250-125um	1630			
CFSWLC	2mm-250um	1632	OAD	125-63um	1595			
CFSWLC	250-125um	1632	OAD	63um	1601			
CFSWLC	125-63um	1632	OAP	2mm-250um	1628			
CFSWLC	63um	1632	OAP	250-125um	1622			
Hei	2mm-250um	1641	OAP	125-63um	1632			
Hei	250-125um	1630	OAP	63um	1630			
Hei	125-63um	1639	PS 2	2mm-250um	1624			
Hei	63um	1630	PS 2	250-125um	1626			
Ves	2mm-250um	1558	PS 2	125-63um	1626			
Ves	250-125um	1552	PS 2	63um	1630			

Table 17. Normalization and baseline removal techniques

Normalization Techniques

Maximum	scales the maximum value of the spectrum to 1*
Minimum	scales the minimum value of the spectrum to 0*
L ₂	scales by the sum of squared values*
Cumulative	scales by the cumulative intensity value of the spectrum*

* Carey et al., (2017)

Baseline Removal Techniques

Asymmetric Least Squares (ALS)	utilizes Whittaker smoothing corrected by weighting points above the baseline, and iterating until convergence
Morphologically weighted penalized least squares (MPLS)	approximates the baseline by altering the spectra to produce flat regions where spectral peaks are, and adjusting with a penalized least squares procedure **
Tophat	a morphological correction, correcting to a flat baseline with a top-hat transformation to preserve spectral feature width ***
Kajifosz and Kwiatek	fits a set of polynomials to the spectra and takes the maximum values from the polynomials as the baseline
Median Filter	approximates the baseline by applying a moving window (501 channels across) filter to the spectra, and replacing the value at the center of the window with the median of the intensities within the window **

Dyar et al., (2016) * Perez-Pueyo et al., (2010)

Table 18. VNIR and MIR PLS model parameters

	Predicted Value	Normalization	Baseline Correction	Components	R ²	Error
VNIR	Glass Phase %	Max	Kaijfoszkwiatak	2c	0.607	0.135 %
	Glass wt % SiO ₂	L2	ASL	5c	0.847	6.053 wt%
	Bulk wt % SiO ₂	Max	ASL	9c	0.960	4.307 wt%
	Vesicularity	Cumulative	ASL	8c	0.950	1.029
	Size Fraction	Min	None	7c	0.546	0.992
MIR	Glass Phase %	Cumulative	Tophat	4c	0.771	0.119 %
	Glass wt % SiO ₂	Cumulative	MedianFilter	9c	0.935	4.021 wt%
	Bulk wt % SiO ₂	Cumulative	ASL	5c	0.983	3.388 wt%
	Vesicularity	Cumulative	None	10c	0.983	0.980
	Size Fraction	Cumulative	MPLS	10c	0.982	0.565

VITA

CJ Leight was born and raised in Austin, Texas. They received their B.A. in Astronomy with a minor in Geology from Mount Holyoke College in May 2018. While at Mount Holyoke, CJ worked with Dr. Caleb Fassett on crater degradation rate on the Moon and Mercury, and assisted in Dr. Darby Dyar's Mineral Spectroscopy Laboratory with the Mossbauer and Raman spectrometer. They completed two REUs, one at the Arecibo Observatory studying impact simulations of Rhea's surface with Dr. Edgard Rivera-Valentin, and one at the USGS Astrogeology Division conducting analysis of melt features in Mercurian craters with Dr. Lillian Ostrach. CJ is graduating with a Master's of Science in geology in August 2020, and will be staying at the University of Tennessee to pursue their Ph.D in geology.