Determining the Volcanic Eruption Style of Tephra Deposits From Infrared Spectroscopy

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Abstract

Orbital imagery and spectroscopy at Mars have identified a variety of deposits potentially consistent with volcanic tephra formed during explosive volcanic eruptions, and some of these deposits may have formed due to water- or ice-magma interactions during phreatomagmatic eruptions. If this is the case, these deposits could serve as an additional record of past water on Mars. Previous work has demonstrated that phreatomagmatic tephra is characterized by much lower crystallinities than tephras from other types of eruptions. We hypothesize that crystallinity could be inferred remotely using spectroscopy; however, tephra spectral properties have not been directly linked to their mineralogy. Here, we use Mars analog tephra samples to investigate if eruption styles and the past presence of water during the eruption of possible volcanic deposits on Mars can be determined using orbital spectroscopy. Visible/near-infrared (VNIR) reflectance and thermal infrared (TIR) emission spectra were collected of basaltic volcanic tephra sourced from a range of eruption styles and deposit types on Earth. Our research demonstrates that, TIR and VNIR data are both sufficient to detect increased glass abundances in volcanic deposits, potentially indicating volatile interactions during an eruption, and that glass-poor tephra have distinct TIR properties that can be used to infer tephra type (e.g., ignimbrite vs. scoria). Combining VNIR and TIR orbital data for analysis based on our new laboratory spectral endmember library may allow a reevaluation of Martian volcanic and volatile histories using current and future planetary orbital and in situ spectral datasets.

Plain Language Summary

Volcanism is a common process across the solar system. Eruptions can become explosive after interactions with water, and the search for current or past water is critical to planetary exploration. Collecting planetary samples to understand what types of eruptions created the volcanic rocks present is not always possible, so we investigate a method for determining volcanic eruption styles that could be completed from orbit. Spectrometers are common instruments on orbiters and can measure the reflection and emission of light from surface materials, including glass. Glass forms in volcanic eruptions when magma quickly cools before minerals can form. We demonstrated that, volcanic deposits from eruptions that were explosive due to interaction with water were glass-rich and could be distinguished from deposits created in other types of eruptions using data similar to those collected by satellites at Mars. Alteration due to water in the local environment just after eruption is also detectable from orbit. Applying these results to existing or future satellite datasets will provide insight into volcanic eruption styles and environments on planets like Mars.

1. Introduction

Explosive volcanism is driven by volatiles, either sourced from the magma or encountered during ascent and eruption. On Earth, different volatile sources and contents are a significant cause of variations in eruption styles that produce distinct surface deposits (Byrne, 2020). Volcanism is also a common process across the solar system, including on Mars, and these extraterrestrial volcanic deposits can provide a record of the history of interior and surface volatiles on other planets. Mars has likely experienced explosive volcanicism throughout the planet’s history, as indicated by mineralogy and geomorphology (e.g., Bandfield et al., 2012; Head & Wilson, 1979; B. Horgan and Bell, 2012; Robbins et al., 2011; Squyres et al., 2007). However, the causes of explosive eruptions on Mars are poorly constrained due to uncertainty in the abundance, composition, and evolution of surface and interior volatile reservoirs (Wilson & Head, 2007). On Mars, explosive volcanic deposits produced by interactions with both magmatic and surface volatile reservoirs are critical...
targets of investigation for both landed and orbital missions. Magmatic volatiles place constraints on the composition and evolution of planetary interiors, while detecting magma-water or magma-ice interactions can help constrain past surface environments and climates (National Research Council, 2011).

Thus, a method is needed for differentiating volcanic deposits produced by these two types of explosive eruptions. Previous studies have shown that the crystallinity of volcanic tephra, as determined by X-ray diffraction (XRD), can be used to infer eruption style (Wall et al., 2014); however, this technique is only applicable to landed investigations (Blake et al., 2012). Here, we propose a method for distinguishing eruption styles in volcanic deposits using laboratory visible/near-infrared (VNIR; 0.3–2.5 μm) reflectance spectra and thermal infrared (TIR; 8–25 μm) emission spectra that is analogous to orbital datasets from Mars. Identifying explosive eruption styles from orbital data of volcanic deposits would provide significant insight into Mars’ volcanic and volatile history.

2. Background

Glass forms by numerous natural processes, including impacts, tectonics, and volcanic eruptions (Glass, 2016). Glasses form via quenching of molten material, where rapid cooling prevents the crystallization of minerals. Rapid cooling can occur due to interaction with water (e.g., mid-ocean ridge eruptions), air (e.g., Plinian eruptions), or the vacuum of space (e.g., lunar pyroclastic eruptions). In explosive eruptions, volatiles like water can enhance this process by driving explosive fragmentation (smaller particles cool more efficiently) and direct cooling (during magma-water interactions). Glass can form in magmas of any composition, from mafic to felsic. More interactions with volatiles during eruption generally leads to glassier pyroclastic deposits.

Explosive eruptions can be divided into two categories: magmatic (volatile-limited) and phreatomagmatic (volatile-rich; e.g., Cashman & Sparks, 2013; Wall et al., 2014). In “magmatic” eruptions (e.g., Plinian and Strombolian eruption styles), volatiles dissolved in the magma are decompressed during ascent, increasing the volume fraction of gas and causing fragmentation. The pyroclasts formed by magmatic eruptions cool relatively slowly, either due to prolonged residence time within a warm plume or larger clast sizes, resulting in more crystalline tephras. Phreatomagmatic eruptions, during which magma encounters external water or ice, are more explosive than magmatic eruptions of similar magma volumes. Vapourization of meteoric water causes rapid fragmentation of magma into smaller pyroclasts that are quickly quenched to create glass-rich deposits. Phreatomagmatic eruptions favor glass production because the interaction with surface or subsurface water causes a cooling rate of >10^6 K/s, while the airfall deposits from magmatic eruptions cool at rates ≤10 K/s (Szramek et al., 2010; Wallace et al., 2003; Zimanowski et al., 1997).

Eruption properties other than water interaction can lead to explosive eruptions and glass-rich tephra. For example, one exception to the general observation that explosive magmatic eruptions produce glass-poor tephra is the high glass content of cinder cone tephras (a form of low-density scoria) formed during Strombolian cinder cone eruptions. Cinder cones form when magma works its way slowly through a crack in the surface and erupts subaerially. Dissolved magmatic gasses exsolve into bubbles within the magma before breaking through the surface, resulting in a very explosive localized eruption. As degassing progresses, cinder cone eruptions can transition to effusive lava flows. The explosiveness of this type of eruption is initially determined by volatile content and then increases by external factors such as interaction with water, conduit specifications, and clogging of the vent (Walker, 1973).

Explosive volcanic eruptions are thought to have been common on Mars. Water and/or ice have been present at the surface and in the subsurface from the Noachian to the present day (e.g., Carr & Head, 2010) and have been hypothesized to cause phreatomagmatic eruptions (e.g., Ghatan & Head, 2002). Lower atmospheric pressure in the Hesperian and Amazonian would have enhanced eruptions’ explosivity even in basaltic magmas with lower volatile contents (Wilson & Head, 2007). Under low atmospheric pressures, tephra and ash would have dispersed onto the surface at distances much greater than on Earth (Wilson & Head, 1994); thus, explosive eruptions may have emplaced many of the regional-scale sedimentary deposits on Mars (Kerber et al., 2012).

Deposits potentially consistent with volcanic tephra as well as explosive volcanic edifices have been identified on Mars based on morphological and thermophysical properties (Carr et al., 1973; Edgett, 1997; Hynek...
et al., 2003; McCoy et al., 2008; Robbins et al., 2011; Wilson & Head, 1994). Previous investigations used orbital VNIR spectra as well as orbital and in situ TIR spectra to identify possible tephra deposits on Mars, based on the presence of glass-rich sand and altered sediments that could both be attributed to explosive volcanism (Cannon et al., 2017; B. Horgan & Bell, 2012; Edwards & Ehlmann, 2015). However, it is unclear from these studies whether these possible explosive volcanic deposits formed from phreatomagmatic or magmatic eruptions. This study aims to develop new techniques using spectroscopy applied to differentiate these two eruption styles. Understanding the history of water and habitable environments on Mars is one of the primary goals of the Mars Exploration Program, and the ability to detect signs of possible water-magma interactions in the geologic record would be a novel way to place constraints on the history of water at the surface (MEPAG, 2020).

Previous work suggests the crystallinity of volcanic tephra may be related to eruption styles. A study by Wall et al. (2014) investigated a suite of 16 volcanic tephras and 14 lavas from globally distributed basaltic sources on Earth and developed a method using X-ray diffraction (XRD) to estimate their crystallinity. Their results showed that crystallinity could be used to distinguish tephra from phreatomagmatic and magmatic eruptions, as phreatomagmatic tephras exhibit a lower groundmass crystallinity (<35%) than slower cooling magmatic eruptions (>44%). Applying their results to analyses by the CheMin XRD instrument on the Mars Curiosity rover showed that the moderate crystallinity (>50%; Bish et al., 2013) of the Rocknest aeolian sediment sample is consistent with magmatic tephra of Strombolian or Plinian origin.

Here, we seek to develop similar analysis techniques to constrain tephra crystallinity using spectroscopy. Orbital spectroscopy is used extensively to study the Martian surface’s mineralogy (e.g., Bandfield, 2002; Murchie et al., 2009). Previous studies showed that glass is distinguishable from crystalline minerals in both VNIR and TIR spectra (Adams et al., 1974; Cloutis et al., 1990; Crisp et al., 1990; Dyar & Burns, 1981; B. H. N. Horgan et al., 2014; Minitti & Hamilton, 2010), but a survey of the spectral properties of natural tephra samples from different eruption styles has not yet been conducted.

3. Materials and Methods

In this study, we use a suite of basaltic tephra samples to test the ability of VNIR and TIR spectra, typical data acquired from planetary orbital and landed missions, to infer eruption styles from explosive volcanic deposits. To “ground truth” these datasets, we compare the VNIR and TIR results to XRD crystallinity measurements as well as to VNIR, TIR, and XRD data from physical mixtures of glass and crystalline igneous minerals.

3.1. Sample Suite

Basaltic tephra samples (Table 1, Figure 1) were collected by Wall et al. (2014; and references therein) from a range of tephra types (hydrovolcanic sand, lapilli, tuff, scoria, and ignimbrites) attributed to a range of eruption styles (phreatomagmatic, Plinian, and Strombolian). All phreatomagmatic samples in this study result from magmatic interaction with groundwater (with the exception of Surtsey, which was a submarine eruption). These samples may also be referred to as hydrovolcanic, but we maintain the usage of the term “phreatomagmatic” for consistency with previous literature and with the Wall et al. (2014) study. Two cinder samples from Craters of the Moon (CotM) National Monument (Kuntz et al., 1992) and Tseax Cone (Wuorinen, 1978) were added to the collection for this study. The cinders have a lower density and smaller clast size than other scorias in our study. Possible cinder cones have been identified on the martian surface (Brož et al., 2015; Hauber et al., 2015; McCauley, 1967; Wood, 1979) and represent a distinct tephra type that was not considered by Wall et al. (2014). We created a physical mixture set with glasses and crystalline minerals to compare the tephra samples to well-characterized samples of known crystallinity (Section 3.4). To minimize the effects of grain size and surface area on the spectra, all samples and mixtures were crushed to <150 μm, the same size fraction examined by CheMin on the Curiosity rover (Blake et al., 2012). For spectral analysis, all samples were pressed into ~1g pellets to reduce pore space and increase spectral contrast. This preparation step compares tephra of different densities and grains sizes more consistently, which is appropriate for our study. These properties can vary widely for a given eruption and do not indicate eruption style as bulk composition. However, it should be noted that these properties may significantly affect the spectral properties of tephra deposits, particularly in the TIR.
3.2. X-Ray Diffraction

Crystallinities for the tephra samples were derived from XRD patterns by comparing the area of the broad hump due to X-ray amorphous phases, including glass, to the area of peaks due to crystalline minerals (Wall et al., 2014). This “relative crystallinity” was then calibrated to a quantitative measure using a series of known standards. Thus, these crystallinities are not just a measure of the glass content but also the presence of other X-ray amorphous phases, including assemblages like palagonite (S. E. Ackiss et al., 2018a). Palagonite is an assemblage of largely amorphous phases that forms due to hydrothermal alteration of glass during or shortly after an eruption (S. E. Ackiss et al., 2018a; Allen et al., 1981; Drief & Schiffman, 2004; Farrand et al., 2018; Pauly et al., 2011; Stroncik & Schmincke, 2001, 2002). Bulk crystallinity (groundmass/phenocrysts), as well as groundmass crystallinity (phenocrysts removed by hand) for our samples, were inferred from XRD models by Wall et al. (2014). While bulk crystallinity is more likely to be measured during orbital spectroscopy, groundmass crystallinity is more closely related to late-stage magma cooling history. In our study, the spectroscopic analyses were compared to both the bulk and groundmass crystallinities where

| Sample name | Deposit location | Eruption style | Deposit type | Wall et al. (2014) bulk crystallinity | Wall et al. (2014) groundmass crystallinity | Thermal infrared modeled crystallinity ±15% |
|-------------|-----------------|---------------|--------------|---------------------------------------|------------------------------------------|-------------------------------------------|
| Phreatomagmatic                               |                |               |              |                                       |                                          |                                           |
| SA-1       | Surtsey, Iceland| Phreatomagmatic| Hydrovolcanic Sand | 35                                    | 34                                       | 29.2                                     |
| 98WN6/NL E | Newberry Volcano, OR | Phreatomagmatic | Accretionary Lapilli | N/A                                   | 31–33                                   | 28.4                                     |
| FR-12-91A  | Fort Rock, OR   | Phreatomagmatic | Tuff          | 22                                     | 9–22                                     | 18.2                                     |
| FR-12-97B  | Fort Rock, OR   | Phreatomagmatic | Tuff          | 47                                     | 11                                       | 34.1                                     |
| LSC/Tuff 1-1m | Columbia River Basalt | Phreatomagmatic | Hyaloclastite Tuff | 27–30                                 | 8                                        | 65.4                                     |
| Volatile-rich magmatic                        |                |               |              |                                       |                                          |                                           |
| CotM       | Craters of the Moon, ID | Cinder Cone | Cinder | 17.8                                   | N/A                                      | 12.4                                     |
| Tsx-s3     | Teseax Cone, BC, Canada | Cinder Cone | Cinder | N/A                                   | N/A                                      | 12.1                                     |
| Magmatic                                           |                |               |              |                                       |                                          |                                           |
| T13-5      | Mt. Tarawera, NZ | Plinian | Scoria      | 60–79                                  | 47–78                                    | 31.4                                     |
| 122 BC 1   | Mt. Etna, Italy  | Plinian | Scoria      | 47–61                                  | N/A                                      | 56.5                                     |
| 122 BC 2   | Mt. Etna, Italy  | Plinian | Scoria      | 51–68                                  | N/A                                      | 43.8                                     |
| TB 1       | Trailbridge, OR  | Plinian | Ignimbrite Densely Welded | 98                                 | 95                                       | 83.7                                     |
| TB 2       | Trailbridge, OR  | Plinian | Ignimbrite Mod Welded | 91                                 | 86                                       | 89.4                                     |
| TB 3       | Trailbridge, OR  | Plinian | Ignimbrite Lightly Welded | 95                                 | 74                                       | 93.3                                     |
| LP13-1     | Lake Pupuke, NZ  | Strombolian | Scoria | 75–79                                  | 72–79                                    | 29.1                                     |

Figure 1. Tephra samples used in this study (not including Tseax cinders) before being crushed, sieved, and pressed into pellets for spectral analysis.
available. We applied this same technique to determine bulk XRD crystallinities for the CotM, Tseax, and physical mixture samples, using XRD patterns we acquired following sample preparation and analytical procedures as described by Zorn et al. (2018) at the University of Auckland X-ray Centre on a PANalytical Empyrean XRD. Crystallinity was calculated using the AMORPH program (Rowe & Brewer, 2018), calibrated against physical glass-mineral mixtures (Wall et al., 2014). All XRD crystallinities are reported here as vol. %.

3.3. Visible/Near-Infrared Spectra

VNIR reflectance spectroscopy is sensitive to electronic absorptions, vibrational overtones, and element combinations (e.g., Hunt, 1977), as demonstrated by the laboratory reference spectra shown in Figure 2. An ASD FieldSpecPro3 spectroradiometer with a contact probe attachment collected the VNIR spectra of pelletized samples from 0.35 to 2.5 μm at standard incidence/emission angles of 0°/30° and as an average of 100 individual spectra with respect to a white reference. In the VNIR spectral range, glasses exhibit a characteristic broad absorption due to crystal field effects in iron centered between 1.08 and 1.15 μm and often exhibit a second broad band near 2 μm (Cannon et al., 2017; Dyar & Burns, 1981; B. H. N. Horgan et al., 2014). These absorption bands have been used to infer the presence of glass on Mars (B. Horgan & Bell, 2012; B. H. N. Horgan et al., 2014); however, they are easily obscured by other Fe-bearing minerals like olivine and pyroxene that exhibit similar bands centered between 0.9 and 1.08 μm. As such, glass absorptions only dominate VNIR spectra for abundances >70–80 wt.% (B. H. N. Horgan et al., 2014).

Figure 2. Laboratory reference spectra of minerals common in volcanic environments in the (a) visible/near-infrared (VNIR) (Horgan et al., 2017; Kokaly et al., 2017) and (b) thermal infrared (TIR) (see citations in Table 2).
VNIR spectra can also infer aqueous alteration. Narrow hydration bands at \(1.9 \mu m\) in tephra may imply formation or alteration in a wet environment (Farrand et al., 2016). Absorption bands near 2.2–2.3 \(\mu m\) are often attributed to Si-OH bonds in hydrated silicates like glass or Fe/Mg/Al-OH bonds in phyllosilicates (Bishop et al., 2008; Rice et al., 2013). Glass that has been devitrified, or partially reordered as a result of thermal alteration (Marshall, 1961), loses the 1.1 \(\mu m\) glass band and gains an iron oxide band closer to 1 \(\mu m\) (S. E. Ackiss et al., 2018a; Farrand et al., 2016). Palagonite can be identified by narrow VNIR absorption bands at 1.78 \(\mu m\) (hydration in zeolites), 1.9 \(\mu m\) (hydration in zeolites and smectites), and 2.2–2.3 \(\mu m\) (smectites), and post-eruptive weathering can also cause the development of smectites on tephra (S. E. Ackiss et al., 2018a; Allen et al., 1981; Drief & Schiffman, 2004; Pauly et al., 2011). Thus, the presence of these absorptions in VNIR spectra may indicate that amorphous and/or crystalline endmembers replace some glass in the deposit through the processes of devitrification, palagonization, and/or surface weathering. These types of alteration are spectrally distinct from magmatic volatiles in the glass, which in glasses, e.g., obsidian, can result in only a 2.2 \(\mu m\) absorption band without an accompanying 1.9 \(\mu m\) hydration band (B. H. N. Horgan et al., 2014). Absorption bands due to these alteration minerals have also been detected on Mars using VNIR spectral parameter maps (Viviano-Beck et al., 2014), but glass detections have required more detailed analysis (e.g., B. H. N. Horgan et al., 2014).

### 3.4. Thermal-Infrared Spectra

TIR emission spectroscopy is sensitive to molecular bending and stretching vibrational modes present in nearly all geologic materials (Thomson & Salisbury, 1993), as shown in Figure 2. TIR spectra (8–25 \(\mu m\)) of tephra and mixture pellet samples actively heated to 80°C were acquired at Arizona State University using a Nicolet iS50R FT-IR spectrometer modified to measure emitted energy, then calibrated to emissivity (Christensen & Harrison, 1993; Ruff et al., 1997). Spectra were measured between 200 and 2,000 \(cm^{-1}\) with a resolution of 2 \(cm^{-1}\) as an average of 512 scans.

TIR spectra are sensitive to the fundamental \(\sim 10 \mu m\) Si-O absorption, and crystalline silicates exhibit a composite \(10 \mu m\) absorption band with many sharp features due to modification of the Si-O bond by variations in mineral structure. In contrast, glass exhibits a rounded \(\sim 10 \mu m\) absorption band indicative of a substantial degree of disorder of the silicate units (Crisp et al., 1990; Dufresne et al., 2009; Minitti et al., 2002; Minitti & Hamilton, 2010). TIR spectra show that devitrified glass is spectrally and thus structurally distinct from crystalline minerals. During devitrification, the rounded band changes to a doublet, with a narrow band minimum at 9.5–9.6 \(\mu m\) and a broad shoulder at 10.9–11.3 \(\mu m\), caused by the development of sheet and chain structures, respectively (Crisp et al., 1990; Farrand et al., 2016). These bands are distinct from the more complex bands expected for common crystalline igneous minerals like olivine and pyroxene, suggesting that early devitrification does not necessarily lead to crystallization. The \(\sim 10 \mu m\) silicate band’s position and shape can be used to infer relative crystallinity and silica content (Michalski et al., 2005).

Quantitative mineralogy was determined from TIR spectra using standard nonnegative linear least-squares deconvolution with a suite of laboratory mineral endmember spectra (Ramsey & Christensen, 1998; Rogers & Christensen, 2007). Our library (Table 2) includes spectral endmembers relevant to volcanic environments, including mafic to silicic volcanic glasses (Michalski et al., 2005; Minitti et al., 2002; Minitti & Hamilton, 2010) and devitrified glass (Farrand et al., 2016), as well as pyroxenes, olivines, plagioclases, high silica alteration phases, oxides, zeolites, and clays (e.g., Christensen et al., 2000; Rogers & Christensen, 2007). Corrective spectra listed in Table 2 were used to normalize the spectra models. All TIR abundances and crystallinities are reported in vol.%. TIR linear deconvolution models of our tephra samples and physical mixtures produce RMS errors in the range 0.11–0.79 and 0.19–0.81, respectively.

Crystallinity was determined from TIR linear deconvolution models by subtracting from 100 the fraction of unambiguously amorphous phases (glass, devitrified glass, partially to fully amorphous silica phases) as well as clay, oxide, and zeolite phases that are difficult to quantify using XRD and/or may be poorly crystalline when present in palagonites (S. E. Ackiss et al., 2018a; Farrand et al., 2018). Previous studies of crystalline igneous rocks suggested that TIR-derived abundances are accurate within 15 vol.% (Feely & Christensen, 1999). This estimate of crystallinity from TIR linear deconvolution models likely differs somewhat from XRD modeled crystallinity. While both datasets produce models of bulk mineralogy, XRD detects re-
peating crystal structure while TIR detects molecular bonds. Thus, materials that are X-ray amorphous and challenging to distinguish in XRD may be detected and quantified in TIR. However, this difference should be small in samples with minimal alteration products, as glass dominates their amorphous component in

| Mineral library composed of mineral spectra from the Arizona State University’s (ASU) spectral library^a |
|---|
| **Glass** | **Pyroxene** | **Clay** |
| Andesite interstitial glass (MEM-5) | Augite (BUR-620)^12,24 | Antigorite (MINUN-30) |
| Dacite interstitial glass (MEM-4) | Augite (NMNH-119)^24 | Beidellite [pellet] (Shb-1)^16 |
| K-rich glass^3 | Bronzite (BUR-1920)^12,24 | Biotite (BUR-840) |
| Martian meteorite basalt proxy glass (MEM-3)| Diopside (HS-15.4 B)^12,24 | Chlorite (WAR-1924) |
| TES andesite proxy glass (MEM-2) | Enstatite (HS-9.4 B)^12,24 | Illite <0.2 um (Imt-1)^16 |
| TES basalt proxy glass (MEM-1) | Hedenbergite (Manganano) (DSM-HED01)^13,24 | Ilmenite (WAR-419) |
| Hypersthene (NMNH-B182)^12 | | Kaolinite (Kga-1b)^17,18 |
| Devitrified Glass | **Feldspar** | |
| NMB12-14 (cut_surface_average)^3 | Albite (WAR-0244)^12 | Montmorillonite (Sca-3)^18 |
| NMB12-14 bulk (uncut surface average)^3 | Albite (WAR-0612)^12 | Montmorillonite (Stx-1)^18 |
| Obsidian-Devitrified^4 | Albite (WAR-0235) | Montmorillonite (Swy-2)^18 |
| CH-02^1 | Andesine (BUR-240) | Muscovite (WAR-5474) |
| Other Poorly Crystalline | Andesine (WAR-0024)^12 | Nontronite (Nau-1)^18 |
| Allophane Si:Al 0.44 (ALLO044)^3 | Anorthite (BUR-340)^12 | Saponite (Eb-1) |
| Allophane Si:Al 0.92 (ALLO092)^3 | Anorthoclase (WAR-0579) | Serpentine (HS-8.4 B) |
| Aluminosilicate Gel Si:Al 5.6 (ALLO560)^5 | Bytownite (WAR-1384) | |
| Hydrated Silica | Labradorite (WAR-4524) | Goethite (GTS4)^14,20 |
| Opal-Aluminous^6,7 | Labradorite (BUR-3080A)^12 | Goethite-Derived Hematite (GTSH4-300)^15,20 |
| Opal-A^4 | Microcline (BUR-3460)^12 | Hematite (BUR-2600) |
| opal-CT (02-031)^8 | Microcline (BUR-3460A)^12 | Magnetite (MTS4)^16,20 |
| Cristobalite^8 | Mircocline (Perthite) (WAR-5802) | Zeolites |
| Olivine | Oligoclase (WAR-3680) | Analcime (WAR49-0672) |
| Olivine Fo10 (KI 3008)^9,10,11 | Oligoclase (BUR-060)^12 | Clinoptilolite (27031)^18,21 |
| Olivine Fo25 (KI 3352)^9,10,11 | Oligoclase (WAR-5804)^12 | Heulandite (agu_heu)^12 |
| Olivine Fo39 (KI 4143)^9,10,11 | Orthoclase (WAR-RGSAN01)^12 | Corrections |
| Olivine Fo60 (KI 3362)^9,10,11 | **Other Crystalline** | Basalt Substrate w/473 micron^23 |
| Olivine Fo68 (KI 3115)^9,10,11 | Anhydrite (S9) | Heater Spectrum 2 |
| Fayalite (WAR-FAY01)^11 | Gypsum (S8)^14,15 | Slope_250/247 |
| Forsterite (AZ-01) | Hornblende (NMF-R720) | |
| The 291 minerals are Categorized as they appear in the Figure 5 pie charts. |
| ^aExcept where indicated, all library spectra are from the ASU spectral library: Christensen et al., 2000. ^bMinitti & Hamilton, 2010; ^cWyatt et al., 2001; ^dFarrand et al., 2016; ^eWards Samples; ^fRampe et al., 2012; ^gMichalski et al., 2006; ^hGlotch et al., 2006; ^iMichalski et al., 2003; ^jMorse, 1996; ^kHamilton, 2010; ^lKoeppen & Hamilton, 2008; ^mHamilton & Christensen, 2000; ^nLane & Christensen, 1997; ^oLane & Christensen, 1998; ^pLane, 2007; ^qClay Mineral Society samples; ^rPruett et al., 1993; ^sMorris et al., 1985; ^tGlotch, 2004; ^uSheppard & Gude, 1982; ^vRuff, 2004; ^wMorrison et al., 1986; ^xHamilton, 2000. |
both XRD and TIR. Because VNIR is highly sensitive to alteration products, altered samples that may cause divergence in the models can be identified using VNIR.

3.5. Mixture Study

Previous studies have examined glass-mineral mixtures and partially crystalline basalts in the VNIR and TIR (e.g., B. H. N. Horgan et al., 2014; Minitti et al., 2002), but none has examined the accuracy of TIR spectral models for these mixtures. Thus, the accuracy of TIR spectral deconvolutions is unclear when amorphous phases are present. Some previous studies have proposed that TIR linear deconvolution models may overestimate the abundance of amorphous endmembers because of their nonunique shape (e.g., Thorpe et al., 2015). To evaluate the effect on our tephra models, we include a study of the VNIR and TIR properties of physical glass-mineral mixtures.

To compare spectra of the tephra samples to spectra of samples of known crystallinity, we acquired VNIR and TIR spectra of a set of physical mixtures of glasses and crystalline minerals, analogous to the XRD calibration set created by Wall et al. (2014). Three mixture sets were created using three different glass compositions: a high-silica microscope glass slide used in Wall et al. (2014), Craters of the Moon basaltic cinders, and obsidian from a rhyolitic eruption. While the basaltic cinders are the best compositional analog for our basaltic tephra samples, the other endmembers provide insight into the effects of glass composition on their detection in VNIR and TIR spectra. Each glass was mixed in 10 wt.% increments (20 wt.% glass mixtures were skipped due to a lack of available sample during the experiment) with a crystalline mixture of San Carlos olivine and pyroxene of the same grain size (82 wt.% olivine and 18 wt.% pyroxene). Each endmember was additionally analyzed by XRD to determine the endmember crystallinity. The endmember crystallinities were used to interpolate the expected crystallinity for each mixture for comparison to VNIR and TIR derived crystallinity.

4. Results

4.1. VNIR Spectra and Mineral Interpretations

The VNIR reflectance spectra for the tephra samples are shown in Figure 3a. We have classified the tephra spectra into four spectrally distinct categories, as shown in Table 3: (1) Unaltered glass-dominated spectra; (2) Altered glass-dominated spectra; (3) Alteration-dominated spectra; (4) Glass-poor spectra. Unaltered glass-dominated spectra (CotM, Tseax, Surtsey) are characterized by two broad absorption bands centered between 1.05 and 1.12 and 1.9 μm consistent with significant glass and do not display any additional absorption bands. These spectra correspond to magmatic cinder and hydrovolcanic sand samples.

Altered glass-dominated spectra (Newberry, Fort Rock A) also exhibit a broad glass band centered between 1.05 and 1.12 μm, but the broad 1.9 μm glass band is obscured by additional much narrower bands attributed to alteration, including bands at 1.42, 1.78, and 1.92 μm due to hydration in zeolites and smectites. Complex bands between 2.2 and 2.3 μm are consistent with various phases. The asymmetric band shape and band minimum near 2.21 μm is most consistent with hydrated glass or silica (e.g., Rice et al., 2010), but could also be due to Al-smectites. Shoulders on this band near 2.23 and 2.27–2.29 μm are likely due to complex Al/Fe/Mg-smectites. These spectra correspond to phreatomagmatic tuff and lapilli samples.

Alteration-dominated spectra exhibit strong alteration bands at 1.42, 1.78, 1.92, and 2.2–2.3 μm (Fort Rock B, Columbia River Basalt). Compared to the altered glass-dominated spectra, the 2.2–2.3 μm region exhibits stronger 2.3 μm bands, consistent with Fe/Mg-smectites. These spectra also exhibit a broad band centered between 0.92 and 0.97 μm, which could be consistent with low-Ca pyroxenes (Adams, 1974; Cloutis & Gaffey, 1991) some iron oxides like goethite or lepidocrocite (e.g., Morris et al., 1985), partial recrystallization of nanophase ferric oxides in palagonite, or devitrified glass (Adams, 1974; Cloutis & Gaffey, 1991; Farrand et al., 2016). Crystallinity should generally increase with decreasing band center (e.g., B. H. N. Horgan et al., 2014), and this trend is observed in most of the samples with 1 μm iron bands (Figure 4). However, the phreatomagmatic samples with band centers below 1 μm have the same low crystallinity as the samples with the highest band centers. This suggests that the band shift is not due to the formation of additional
crystalline phases like pyroxene and is more likely due to either devitrified glass or the addition of a small amount of pigmentary and thus spectrally dominant crystalline iron oxides. These spectra correspond to phreatomagmatic tuffs.

Glass-poor spectra do not exhibit glass or alteration bands (Tarawara, Etna, Trailbridge, Lake Pupuke). Instead, a strong blue and concave up slope dominates these spectra. This lack of bands is most likely due to very small grain sizes for the crystalline components, potentially formed during rapid cooling, consistent with previous studies showing that aphanitic or microcrystalline basalts do not exhibit strong VNIR absorption bands (Carli et al., 2014). The narrower ~1 μm pyroxene-like absorption without a corresponding 2 μm absorption present in the magmatic Trailbridge 1 spectrum is consistent with an aphanitic basalt (Carli et al., 2014). These spectra correspond to magmatic scoria and ignimbrites.

4.2. TIR Spectra and Deconvolution Models

The TIR emission spectra for all tephra samples are shown in Figure 3b. All spectra exhibit an absorption near the fundamental Si-O band at 10 μm. A well-rounded 10 μm band as visible in Surtsey is consistent
with glass (Crisp et al., 1990; Minitti et al., 2002; Minitti & Hamilton, 2010). The low-density scoria/cinders (CotM, Tseax) exhibit a broad V-shape, while tuff and accretionary lapilli (Fort Rock A/B, Newberry) exhibit a weak doublet in this region, composed of a narrow band near 9.6–9.8 µm and a weak shoulder near 10.9–11.3 µm, which is consistent with partial reordering of the glass structure due to devitrification (Far rand et al., 2016). As crystallinity increases, the 10 µm band narrows and exhibits a more complex shape, consistent with absorption bands due to crystalline silicates like feldspar and pyroxene (Trailbridge 2/3). At longer wavelengths, four spectra (CotM, Tseax, Newberry, Fort Rock (b) exhibit broad bands near 21 µm.

**Table 3**

| Tephra type                  | VNIR spectral class       | TIR assemblage                                      |
|------------------------------|---------------------------|----------------------------------------------------|
| **Phreatomagmatic**          |                           |                                                    |
| Hydrovolcanic sand           | Unaltered glass-dominated | Glass and devitrified glass-rich with minor alteration |
| Accretionary lapilli         | Altered glass-dominated   |                                                    |
| Tuff                         | Altered glass-dominated or alteration-dominated* |                                                    |
| **Volatile-rich magmatic**   |                           |                                                    |
| Low-density scoria/Cinders   | Unaltered glass-dominated | Glass and devitrified glass dominated              |
| **Magmatic**                 |                           |                                                    |
| Scoria                       | Glass-poor                | Glass and devitrified glass with variable feldspar |
| Ignimbrite                   | Glass-poor                | Igneous crystalline dominated                      |
| **Post-eruption alteration** |                           |                                                    |
| Weathered samples            | Alteration-dominated      | Mostly alteration minerals                         |

*The Columbia River Basalt hyaloclastite tuff was altered by post-eruptive surface weathering.

Abbreviations: TIR, thermal infrared; VNIR, visible/near-infrared.

![Figure 4](image-url)  
**Figure 4.** Comparison of bulk (open symbol) and groundmass (closed symbol) X-ray diffraction (XRD) crystallinities of the tephra to the position of their 1 µm band center in VNIR spectra. The phreatomagmatic and cinder cone tephras display clear 1 µm bands with two distinct groups of band centers: near 1.08 µm, interpreted as due to glass, and 0.95 µm, interpreted as due to either devitrified glass or spectrally dominant iron oxides in palagonite. Most magmatic tephra samples (e.g., scoria) do not exhibit clear 1 µm bands and are omitted.
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These four spectra correspond to the glass-rich phreatomagmatic and cinder samples, as well as the glass-dominated VNIR spectral class.

In general, TIR linear deconvolution models (hereafter, TIR models) are able to accurately predict the lower crystallinity characteristic of phreatomagmatic tephra previously identified based on XRD crystallinity, as well as the high crystallinity of magmatic ignimbrites. Figure 5 shows TIR models calculated using our spectral library (Table 2), and the crystallinities derived from these TIR models are compared to their XRD counterparts in Figure 6. Crystallinities from TIR models (11%–46%) typically agree with XRD crystallinities (9%–35%) of samples from deposits formed in phreatomagmatic or cinder cone eruptions (Figure 6), and TIR models also agree with XRD measurements of ignimbrites (85%–95% for both techniques). One exception is the highly weathered Columbia River Basalt hyaloclastite tuff, but we attribute the mismatch to the high percentage of phyllosilicate and other alteration minerals in this sample that may be difficult to characterize in XRD. However, TIR models of some scoria samples (e.g., Tarawara, Lake Pupuke) with moderate XRD crystallinity (∼50%–80%) predict much lower crystallinities (up to 45% less) than determined from XRD. Previous studies of other rock types (e.g., sedimentary rocks; Thorpe et al., 2015) have

Figure 5. Tephra mineralogies modeled from linear deconvolution of thermal infrared (TIR) spectra, separated by eruption style and tephra type. Red/pink indicates X-ray amorphous phases, blues indicate alteration minerals, and green/yellow indicate crystalline igneous minerals.

(465 cm⁻¹), consistent with amorphous silicates (Ruff & Christensen, 2007).
also observed higher than expected TIR models of amorphous phases in some samples and postulated that this could occur if the smooth and broad TIR absorptions of amorphous phases were used to better fit other poorly modeled spectral features. However, this may not be true for igneous samples where significant glass is present, as demonstrated by our mixing study.

### 4.3. Mixture Study

VNIR spectra of our physical mixtures of crystalline minerals and glasses confirm that low abundances of glass cannot be easily identified in VNIR spectra, but high abundances of glass exhibit a unique spectral character (Figure 7; Cannon et al., 2017; B. H. N. Horgan et al., 2014). When glass of any composition is added to our crystalline endmember mixture, it dampens and broadens the 1 µm band compared to the fully crystalline mixture's deep and narrow absorption band. However, the band center is not clearly affected until the crystallinity is reduced to 30–40 wt.% in the Fe-bearing glasses (Figure 8a), and Fe-poor glasses like the glass slide do not exhibit 1 μm bands and thus do not change the band center.

In some TIR models of the magmatic tephra samples, glass is over-modeled in TIR at intermediate to high crystallinities, >45%, while some consistent over-modeling of glass in Craters of the Moon and obsidian mixtures is observed for crystallinities 50%–60%; however, it is typically within the 15% error expected for TIR models (Figure 8b). The opposite trend occurs for the glass slide mixture, as the TIR crystallinity is never modeled below 28%, even for the slide endmember sample, although the sample is nearly totally amorphous (1.8% XRD crystallinity). This discrepancy is likely due to a lack of a high-silica glass endmember that best matches this type of glass in our spectral library. In contrast, the other mixtures are modeled well at low crystallinities because the obsidian glass is an endmember of our library, and the Craters of the Moon sample is similar to basaltic glass samples in the library. However, the significant over-modeling of glass seen in some of our tephra samples (up to 45% above that predicted by XRD) is not observed in these physical mixtures. Thus, the mismatch between TIR and XRD crystallinity in some scoria samples may be due to other physical or compositional effects, as discussed in the next section.

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**Figure 6.** Comparison of thermal infrared (TIR) modeled crystallinity to bulk (open symbol) and groundmass (closed symbol) X-ray diffraction (XRD) crystallinities. Horizontal lines indicate the range of measured XRD crystallinities for each sample. Dotted trendlines represent standard errors in TIR measurements.
5. Discussion

5.1. Detecting Eruption Styles in VNIR, TIR, and XRD Data

Phreatomagmatic deposits are consistently poorly crystalline (glass- and/or palagonite-rich) based on XRD and TIR models and are distinctive in VNIR spectra as glass or palagonite-rich. It is particularly notable that most phreatomagmatic deposits exhibit glass-rich signatures in VNIR spectra because previous VNIR spectral studies have shown that glass is only confidently detected when present in mixtures with crystalline minerals at abundances higher than 70–80 wt.% (B. H. N. Horgan et al., 2014). This is confirmed by our VNIR observations, which only exhibit clear glass bands centered between 1.08 and 1.15 μm for XRD and TIR glass abundances >70% (Figure 4). Thus, the presence of a clear glass band centered between 1.08 and 1.2 μm in volcanic deposits implies that the deposit is either phreatomagmatic tephra or a cinder/scoria cone, which should be straightforward to differentiate based on geomorphology. However, several of our glassy samples exhibit band centers below 1.08 μm, which could be misinterpreted due to crystalline end-members such as olivine and pyroxene (Figure 2). In this case, glass can still be identified based either on the position of the 2 μm band or based on strong palagonite signatures. Additionally, TIR models of phreatomagmatic tephras consistently show glass abundances >50% (Figures 5 and 6), so possible VNIR indicators of glass could be confirmed by high glass abundances from TIR models and vice versa.

Other than the cinder samples, magmatic deposits are distinct from the phreatomagmatic deposits in VNIR spectra as they do not exhibit strong 1 and 2 μm glass bands. Instead, they exhibit a strong concave up blue spectral slope consistent with aphanitic basalt (Cheek & Pieters, 2014), but this spectral shape is challenging...
Figure 8. Analysis of physical mixture spectra. (a) The position of the 1 µm band center with respect to the expected crystallinity in the mixing study. As the amount of glass in the mixture decreased, the band center also decreased and can be used to determine relative glass abundance and potentially eruption style. (b) Comparison of the thermal infrared (TIR) crystallinities of the mixtures to their expected X-ray diffraction (XRD) crystallinities. The glass slide endmember did not have a representative glass type in the spectral library, which could account for the diversion from the trendline at low crystallinities. This mixing study does not display the over-modeling of glass seen in the tephra samples.
to differentiate from other causes of similar slopes, like leaching rinds on glass that often form in arid volcanic environments (Minitti & Hamilton, 2010).

In TIR models, the crystallinity and composition of magmatic deposits vary between specific deposit types. Samples from Etna, Tarawara, and Lake Pupuke were collected as scoria deposits. Scoria can be highly vesicular and thus cool relatively quickly, preventing extensive crystal growth. TIR and XRD crystallinities of the scoria samples are generally moderate, but some scoria TIR crystallinities are much lower than their XRD crystallinities. Some of the mismatch may be due to materials with complex crystallinities, such as hydrated silica (Figure 5), but may also be due to variability in crystallinity within each sample. Wall et al. (2014) suggested that the large range of XRD crystallinities observed within each scoria sample is due to clast size, as larger pyroclasts would cool more slowly, allowing for more crystal growth than small pyroclasts, where the glass-rich cinders are an endmember of this trend. While TIR appears to undermodel the crystallinity of scoria, this could be due to local variability (e.g., phenocryst density within the samples due to variations in clast size or vesicularity). This may be further exacerbated by TIR sample prep techniques—phenocrysts may be challenging to mix throughout otherwise fine-grained crushed samples evenly.

In contrast, both TIR and XRD models of ignimbrites (Trailbridge 1/2/3) predict similar crystallinities, >70%. Ignimbrites are deposited as dense layers and cool more slowly, increasing crystallization. TIR models of the ignimbrites show a trend of increasing crystallinity with the degree of welding (Trailbridge 3, lightly welded, to Trailbridge 1, densely welded; Figure 5), consistent with crystallization during the sustained higher temperatures of higher degrees of welding (Keating, 2005). The glass in the samples is entirely modeled as devitrified, also consistent with welding. Therefore, the geologic context of the pyroclasts from the magmatic eruptions strongly influences the resulting crystallinity (Table 3), and both the abundance of glass and overall assemblage can be used to infer eruption style.

5.2. Strategies for Determining Eruption Styles on Mars

A combination of VNIR and TIR spectra, along with high-resolution imagery, would be the most definitive method to determine volcanic eruption style of possible volcanic deposits on Mars from orbit. Phreatomagmatic tephras and cinders would exhibit both VNIR and TIR spectra consistent with high abundances of glass and/or palagonite (Figure 3), and geomorphology from visible imagery could help to distinguish between specific eruption styles (e.g., S. Ackiss et al., 2018b; Ghatan & Head, 2001). Magmatic eruptions can produce a wide range of crystallinities that are modeled to varying levels of accuracy with TIR, but the crystallinity is high enough that the spectra consistently show no clear evidence of glass in VNIR. So, for example, in cases where VNIR spectra of a deposit are indistinguishable as glass or olivine, TIR spectra could provide the resolving factor, as TIR models with high crystallinities would indicate magmatic tephra.

In cases with ambiguous moderate crystallinities like our scoria samples, TIR would predict moderate to high glass abundances, and VNIR should be able to confirm that these are magmatic deposits based on their strong blue slope and lack of glass absorption bands.

Ultimately, neither TIR nor VNIR can reproduce the quantitative XRD models' accuracy for estimating the crystallinity of volcanic tephras. This partly because standard lab XRD utilizes an internal standard to calibrate the results, but this step requires extensive sample preparation that is not possible in XRD instruments flown on planetary missions like CheMin (Blake et al., 2012). However, previous work has shown that even without an internal standard, amorphous abundances from XRD refinements are consistently accurate (Smith et al., 2018). Thus, for landed missions, XRD still provides the gold standard for bulk assemblage analysis. However, sample acquisition for XRD analysis is labor and resource intensive, leading to a small number of total samples analyzed (e.g., 19 drilled samples by Curiosity in 6.5 years; (Rampe et al., 2020). In contrast, remote sensing via VNIR or TIR spectroscopy can be deployed from orbit and allows rapid analysis of all visible outcrops from a landed mission, so the lack of accuracy of these techniques is often balanced by their ability to acquire significantly more data.

Another advantage of VNIR and TIR spectra over XRD is that they can identify and differentiate specific amorphous phases and constrain their origin. For example, VNIR is sensitive to alteration products, even when they are poorly crystalline, which can then be used to constrain the nature of syn-eruptive alteration environments (Ackiss et al., 2018; Farrand et al., 2016). Devitrified glass can be differentiated from glass in
TIR spectra and indicates distinct thermal conditions after emplacement (Farrand et al., 2016). TIR models of both welded ignimbrites and hydrovolcanic tephra are dominated by devitrified glass, indicating prolonged thermal alteration, but the hydrovolcanic tephra often also exhibits strong clay mineral absorptions, allowing us to specifically infer hydrothermal alteration (Ehmann & Mustard, 2012; Farrand et al., 2018). Similarly, accretionary lapilli exhibit evidence for aqueous alteration in the VNIR but are dominated by glass in both VNIR and TIR, suggesting that alteration occurred under cooler and more water-limited conditions. Thus, spectroscopy of tephra deposits can be used not only to characterize eruption style but also to constrain the nature of phreatomagmatic volatiles and post-eruption alteration processes.

5.3. Differentiating Impact and Volcanic Glasses

This study provides a framework for using spectroscopy to constrain the origin and aqueous history of possible volcanic tephra deposits on Mars. However, additional work is needed before the spectral properties of deposits can confidently infer a volcanic origin without clear supporting evidence from morphology or geologic context. In particular, while explosive volcanism is a likely hypothesis for the origin of glass-rich deposits, on other planets, impact processes could also produce these deposits, and the mineralogical and spectral properties of impact products are not yet well understood. Studies conducted to date suggest that impact and volcanic glasses are both highly variable but may exhibit some consistent compositional or spectral differences. Hydration may be one good indicator of volcanic glass. On Earth, volcanic glasses tend to have higher water contents than glasses formed by impacts due to differences in temperature of formation, and the difference in water content can constrain formation processes (Glass, 2016; Zhang, 1999). However, some impact melts formed underwater may also be hydrated (Osinski et al., 2019). Some TIR studies suggest that the narrow or broad shape of the SiO$_4$ bending feature between 21.3 and 22.2 µm could distinguish between impact and volcanic glasses, respectively (Farrand et al., 2016; Wright et al., 2011). Many synthetic impact glasses are broadly spectrally similar to our unaltered glass-rich phreatomagmatic tephra in the VNIR (Cannon et al., 2017; Moroz et al., 2009), but it is unclear if these synthetic impact glasses are analogous to actual impact deposits. As our study has demonstrated for volcanic tephras, understanding the spectral properties of impact glass alone is insufficient because glass abundance, macro- and micro-textures, and syn- or post-emplacement alteration can modify both the TIR and VNIR spectral properties of the actual deposits significantly. Further work is needed on the spectral properties of impact deposits, but a combination of spectral properties and geologic context would likely be the most effective method to distinguish impact deposits and pyroclastic deposits from orbit.

6. Conclusions

Explosive volcanic deposits are records of local environmental conditions and the internal volatile content of planetary bodies. Wall et al. (2014) showed that XRD-derived crystallinity of a tephra deposit is a good indicator of the source of volatiles—magmatic volatiles produce highly crystalline tephra compared to the external volatiles that produces glass-rich (>50%) tephra during phreatomagmatic eruptions. For planetary exploration, XRD measurements would require landed missions or sample return, while VNIR and TIR spectra are far easier to collect and can be acquired from orbit over a far larger set of samples/targets or in situ. Our study suggests that high glass abundances identified using TIR and VNIR spectra of possible volcanic deposits can infer interactions with external volatiles during eruption. VNIR spectra can detect glass at high abundances and alteration minerals, both of which form during water-magma interactions. VNIR spectra are unable to detect moderate glass abundances typical of magmatic deposits and instead show featureless spectra consistent with fine-grained basalt. TIR spectral models can detect glass at all abundances; however, texture, grain size, and compositional variability of the sample influence the accuracy of TIR models. Thus, it would be ideal to use multiple remote sensing datasets as well as geomorphic context to characterize the origin of volcanic deposits. Detections of high abundance of glass (>50%) in both VNIR and TIR suggest a phreatomagmatic tephra (or a cinder cone, if present in visible imagery), while no glass detection in VNIR and moderate to low abundances of glass in TIR would suggest a magmatic tephra. These interpretations could be bolstered by the specific phases detected, where devitrified glass detected in TIR but little alteration or glass in VNIR is more likely to indicate an ignimbrite, and strong alteration and/or glass in VNIR would indicate water- or ice-magma interactions. Combining VNIR and TIR orbital data for...
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Data Availability Statement
All spectral data and unmixing results are included in a supplementary document. The spectral library used for the deconvolutions is publicly available on the ASU TES spectral library site under the name mhenderson_2019.

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