

SPECTRAL INTERPRETATION OF MAGMATIC EVOLUTION, OXIDATION, AND CRYSTALLINITY IN A VOLCANIC PLANETARY ANALOG SYSTEM. N. A. Scudder¹, B. Horgan¹, E. B. Rampe², R. J. Smith³, and A. M. Rutledge¹, ¹Dept. Earth, Atmospheric, & Planetary Sciences, Purdue University (nscudder@purdue.edu), ²NASA Johnson Space Center, ³Stony Brook University.

Introduction: Volcanic surfaces are common and varied throughout the terrestrial planets. Remote spectroscopy is often the only method for determining surface chemistry and mineralogy of such provinces, and is thus critical for understanding petrologic processes and constraining planetary interior evolution and chemistry. Natural volcanic systems exhibit variability in magmatic chemical evolution, crystallinity, oxidation, and eruption-related alteration (e.g. hydrothermal). The extent to which spectroscopy can identify these characteristics alongside each other is thus a key question for interpreting volcanic processes from orbit. While the effects of each of these on visible/near-infrared (VNIR) and thermal infrared (TIR) spectra of igneous rocks has been studied separately to varying degrees, their combined spectral effects (and interpretability of such spectra) are understudied.

To test how well VNIR and TIR spectra can quantify volcanic variability in a natural system, we collected ~140 rock samples from 12 volcanic units at the North and Middle Sister Volcanoes in Oregon. The 43 representative samples discussed here range from basaltic andesite to rhyolite, tephra to massive lava flow, and exhibit variable degrees of crystallinity and oxidation.

Methods: All rocks were crushed and sieved to <125 μm before further analysis. TIR (5-50 μm) emission spectra of pelletized samples were acquired at Arizona State University using a Nicolet iS50R FT-IR spectrometer modified to measure emitted energy. To analyze mineral abundances, we compiled a new volcanic environment-oriented TIR emission spectral library using spectra from previously published studies and the ASU SpecLib [1]. We deconvolved sample spectra using the non-negative least squares technique of [2] between 325-1250 cm⁻¹ to retrieve modal mineral abundances. VNIR (0.35-2.5 μm) reflectance spectra of powders were collected using an ASD QualitySpec Trek spectrometer at Purdue University. Samples were prepared for X-ray diffraction (XRD) analysis by adding an internal standard (20 wt.% Al₂O₃). XRD patterns were measured at Purdue University and NASA/JSC using PANalytical X'Pert Pro MPD diffractometers outfitted with Co-Kα X-ray sources. The X'Pert HighScorePlus software was used to derive quantitative mineral and X-ray amorphous abundances via the Rietveld method [3] and average plagioclase feldspar chemistry via unit cell refinement [4]. Mineral chemistries for 10 samples were also measured using a

Cameca SX100 electron microprobe (EMPA) at JSC.

Magmatic evolution: VNIR: Fe-bearing mineral signatures indicative of magmatic evolution overlap in VNIR, and Fe-poor primary silicates (e.g. quartz, feldspars) exhibit little to no VNIR signature, hindering petrologic interpretation when multiple phases are present. Previous studies have created parameters for assessing the spectrally dominant phases in ferrous mineral mixtures [5], but nonlinear mixing, spectrally bland phases, and non-uniqueness make petrologic interpretation or modal abundance retrieval difficult and imprecise. In our samples, highly similar 1.1-1.3 μm shoulders often attributed to olivine also arise from Fe-bearing glass [5], Fe-bearing plagioclase [6], and/or rapidly cooled Fe-bearing pyroxene [7] (Fig. 1).

TIR: Previous studies have retrieved modal primary mineral abundances from TIR spectra of relatively crystalline, unoxidized igneous material to within ~5-

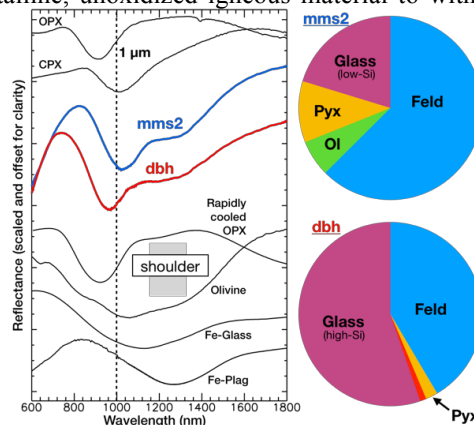


Fig. 1. Basaltic andesite (mms2) and dacite (dbh) VNIR spectra compared to primary mineral spectra (RELAB/USGS), with XRD abundances. The spectra are highly similar despite large differences in modal mineralogy.

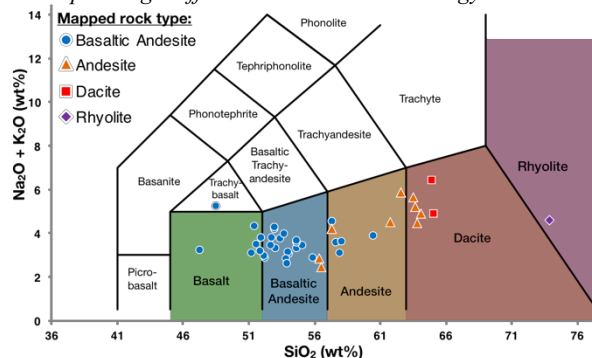


Fig. 2. TAS diagram of TIR-derived sample chemistries, colored by their mapped rock type from Hildreth et al. (2012). TIR correctly identifies most samples.

15% [8-10]. We successfully reproduce these results with our sample suite, and a total-alkali vs. silica classification based on TIR-derived chemistry correctly classifies most rock types (Fig. 2). Furthermore, we show that TIR deconvolutions can successfully estimate plagioclase composition (i.e. An#) to within 15% across a wide range of igneous lithologies (Fig. 3). We are moderately more successful at estimating average pyroxene composition than previous studies [10].

Oxidation and alteration: *VNIR*: Syn-eruptive oxidation or later hydrothermal alteration has oxidized some samples without further alteration. In some of these oxidized samples, strong hematite signatures overwhelm spectra even when little or no hematite is observed in EMPA or in XRD. Samples that are petrologically identical, except for minor Fe-oxide phases, exhibit significantly different spectral shapes. Spectra of relatively unoxidized samples are dominated by ferrous primary mineral absorptions, while oxidized sample spectra are completely dominated by hematite absorptions (Fig. 4). Thus, igneous rocks with only minor oxidation may appear as spectrally pure hematite in VNIR remote sensing applications. We observe minor hydrothermal clays to have a similar effect.

TIR: XRD and EMPA analyses show that iron oxides occur below about 5% in all samples, and in agreement with standard TIR detection limits of 5-10%, our models fail to accurately retrieve abundance or oxide type. Compared to XRD and EMPA identifications, our models consistently overestimate ferric oxides such as hematite and goethite, and underestimate magnetite and ilmenite. Alteration phases such as clay minerals and zeolites are also typically overestimated in TIR, perhaps due to spectral similarity to some glasses [11].

Crystallinity: *VNIR*: Previous studies place the confident detection limit of glass in ferrous mineral mixtures at around 50-70% abundance [5]. This limit holds for our spectra. Our most glassy (55%), unaltered sample displays a $\sim 1.2\text{-}\mu\text{m}$ glass shoulder, but the spectral shape is nearly identical to that of a more crystalline olivine-bearing sample (Fig. 1). In VNIR spectra of moderately crystalline mafic material, glass is unlikely to be uniquely detectable and may actually confound olivine interpretation (and vice versa).

TIR: Unlike previous studies that overestimate amorphous abundance at low fractions [12], we successfully estimate amorphous abundance to within 15% below about 30% abundance. Above this, we observe a slight overestimation of amorphous abundance also observed in tephra samples [13]. We also observe an increasing error in modeled plagioclase composition with increased amorphous abundance.

Conclusions: VNIR is very sensitive to oxidation

and alteration, but petrologic interpretations even of pristine volcanic rocks can be difficult. In contrast, TIR spectra can estimate mineral abundances, rock type, and plagioclase composition across a range of chemistry and crystallinity. We find that increased glass and/or ferric oxides tend to worsen models and interpretations in both VNIR and TIR spectra. Nevertheless, when used together, we find that VNIR and TIR spectroscopy can estimate rock type, plagioclase composition, oxidation, and crystallinity of planetary lavas, providing information on emplacement and interior processes.

References: [1] Christensen P. et al. (2000) *JGR:P*, 105(E4), 9735-39. [2] Rogers A. D. et al. (2008), *JGR*, 113(E6), E06S14-19. [3] Bish D. et al. (1993) *Am. Min.*, 78(9-10), 932-40. [4] Morrison S. et al. (2018) *Am. Min.*, 103(6), 848-56. [5] Horgan B. et al. (2014) *Icarus*, 234, 132-154. [6] Adams J. et al. (1978) *LPSC IX*, 2901-9. [7] Klima R. et al. (2007) *Met. & Planet. Sci.*, 42(2), 235-253. [8] Feely K. et al. (1999) *JGR:SE*, 104(E10), 24195-210. [9] Hamilton V. et al. (2000) *JGR:P*, 105(E4), 9717-33. [10] Wyatt M. et al. (2001) *JGR:P*, 106(E7) 14711-32. [11] Koepfen W. et al. (2005) *JGR:P*, 110(E8) E08006. [12] Thorpe M. et al. (2015) *JGR:P*, 120(11), 1956. [13] McBride et al., *in prep.*

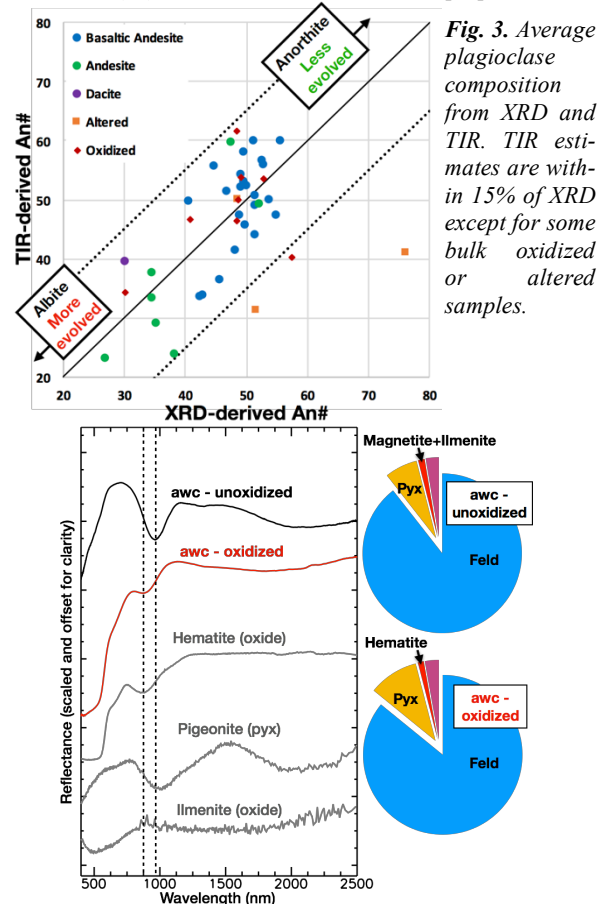


Fig. 4. VNIR spectra of two andesites from the same unit, having \sim identical XRD mineralogy except for oxides. Pyroxene and a $1.3\ \mu\text{m}$ band are apparent in the unoxidized spectrum, but only hematite is apparent in the oxidized spectrum.