

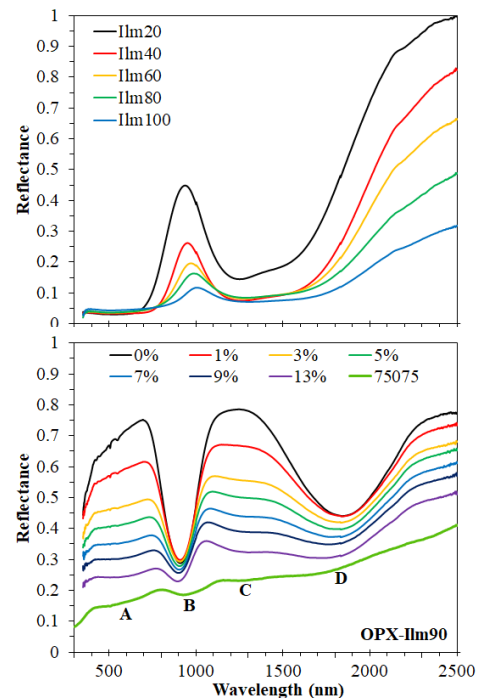
**SPECTRAL EFFECT OF ILMENITE ABUNDANCE AND COMPOSITION ON THE SPECTRAL PARAMETERS OF PYROXENE IN THE VIS-NIR WAVELENGTH RANGE.** K.M. Robertson<sup>1</sup>, L. Togle<sup>2</sup>, C.M. Pieters, and R.E. Milliken. <sup>1</sup>Dept. of Earth, Environmental and Planetary Sciences, Brown University, Providence, RI, 02912, <sup>2</sup>Geological Institute, ETH Zurich, Zurich, Switzerland.

**Introduction:** Ilmenite ( $\text{Fe,Mg}^{2+}\text{TiO}_3$ ) is a Ti-bearing oxide mineral observed in lunar basalts and regolith [1] that can be used to infer  $f\text{O}_2$  conditions and cooling rate during magma formation [2]. Thus, constraining the abundance, distribution, and Fe content of ilmenite on the Moon provides important scientific value in addition to helping assess lunar ilmenite as a potential *in-situ* resource for human exploration. Due to limited direct sampling of the lunar surface, visible-near infrared (VIS-NIR) orbital detections present the most efficient means of mapping oxide distribution at a global scale, but the opaque nature of oxide such as ilmenite results in complex, nonlinear spectral mixing properties [3] that can complicate ilmenite detection/quantification using reflectance spectroscopy.

Ilmenite forms a solid solution series (Fe-Mg) for which the Fe content significantly alters the spectral contrast of diagnostic absorptions, thereby influencing its spectral signature when mixed with other phases (e.g., in a basalt). For lunar basalts, the wavelength positions of diagnostic pyroxene absorptions centered near  $\sim 1 \mu\text{m}$  and  $\sim 2 \mu\text{m}$  are largely dictated by the pyroxene composition, but the presence of ilmenite and its associated  $\text{Fe}^{2+}$  absorptions can result in a shift of these features to shorter wavelengths [4,5]. Characterizing and quantifying these and other spectral effects associated with ilmenite can improve our ability to identify these phases in basalts and mare regolith from orbital spectral data, and potentially allow for estimates of ilmenite abundance and Fe#.

Here, we present VIS-NIR spectral data of samples for a synthetic ilmenite solid solution suite and their subsequent mixtures with a natural orthopyroxene. We assess the effect of ilmenite composition (Fe#) and overall abundance (wt%) on the  $1 \mu\text{m}$  and  $2 \mu\text{m}$  band parameters (position, shape, width) for 1) ilmenite-pyroxene mixtures, 2) Apollo 17 high-Ti basalts and 3) Apollo 17 mare soils.

**Methods:** Samples in the ilmenite-geikielite solid solution suite were synthesized as described in [6] in a 1 atmosphere  $\text{CO-CO}_2$  furnace at 1573K. Synthetic samples were ground and sieved to the  $10\text{-}32 \mu\text{m}$  size range. The ilm100 (Fe=100%), ilm80 (Fe=80%), and ilm60 (Fe=60%) synthetic samples were mixed with a natural orthopyroxene in abundances from 1 to 13 wt% in increments of 2 wt%. All endmembers and mixtures were measured using an ASD Fieldspec3 portable spectroradiometer from  $0.35$  to  $2.5 \mu\text{m}$  relative to a Spectralon standard. The spectra were processed using a convex hull continuum removal [7] prior to assessing the spec-

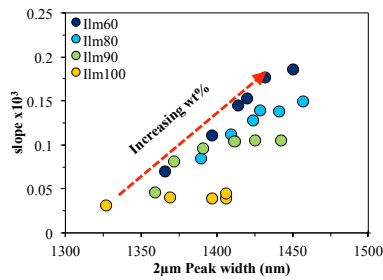


**Fig.1.** a) Ilmenite solid solution series. b) Ilm90-OPX mixtures showing the changes in band parameters (depth, position, slope) with increasing wt%. Lunar basalt sample 75075 is included with letters (A-D) as a means of comparing important spectral features.

tral parameters (band position, width, and shape/slope).

The correlation between ilmenite abundance, composition and spectral band parameters were evaluated for returned lunar basalts and mare soils from the Apollo 17 landing site. Apollo 17 lunar basalt samples (70035, 70017, 75075, and 71055) have been extensively characterized with regards to ilmenite abundance and composition [5]. Here we provide spectral parameter data for the  $<45 \mu\text{m}$  and  $>125 \mu\text{m}$  size fractions of those samples. Spectra of Apollo 17 mare soils ( $10\text{-}20 \mu\text{m}$ ,  $20\text{-}45 \mu\text{m}$  size fractions) were obtained from the lunar soil characterization consortium dataset along with their modal mineralogy and chemical compositions reported therein [8].

**Results:** Diagnostic spectral features of ilmenite include an increase in reflectance near  $1 \mu\text{m}$  and a sharp upturn in reflectance at NIR wavelengths ( $>1.7 \mu\text{m}$ ), features that can be attributed to the Fe absorptions at  $0.7$ ,  $1.25$  and  $1.5 \mu\text{m}$ . These absorptions become significantly stronger as  $\text{Fe}^{2+}$  is substituted for Mg, resulting in samples with lower Fe# exhibiting greater spectral contrast (Fig.1a). The dramatic increase in slope at longer wavelengths is expected to have a more pronounced



**Fig.2.** Width and slope plotted for the ilm-OPX mixtures of varying iron content. Decreasing the Mg content results in a greater change to the 2  $\mu\text{m}$  band shape.

effect on the 2  $\mu\text{m}$  pyroxene absorption when ilmenite is present in mare soils and basalts. This increased spectral contrast begins with as little as 5% Mg.

Spectra of the ilm90-OPX mixtures (Fig. 1b) show distinct spectral changes (points A, B, C, D) that can be attributed to the diagnostic features in ilmenite. With increasing ilmenite abundance, we observe an increase in the overall slope and a decrease in the band depths. Positions of the 1  $\mu\text{m}$  and 2  $\mu\text{m}$  band minima shift to shorter wavelengths and the bands develop an asymmetry that contributes to the ‘reddening’ of the overall spectrum. Additional features are observed at points A and C, which correspond to wavelength regions of strong absorption in the ilmenite spectrum. Comparison of this suite of data to the Apollo 17 sample (75075) shows very similar spectral properties.

The spectral changes to the 2  $\mu\text{m}$  band width and slope are compared for the differing ilmenite compositions in Fig. 2. As expected, decreasing the Fe content in the ilmenite leads to more substantial changes to the spectral parameters due to the increased spectral contrast of the Fe absorptions. Surprisingly, the ilm100 mixtures show little changes in spectral slope.

The 1  $\mu\text{m}$  and 2  $\mu\text{m}$  band centers are plotted in Fig. 3 for lunar basalts (High-Ti), mare soils (variable Ti) and ilm-OPX lab mixtures to evaluate any correlation with ilmenite abundance. The bulk of the deviations from the typical pyroxene trend are associated with the 2  $\mu\text{m}$  band because it is most strongly influenced by the steep slope of ilmenite at longer wavelengths. These data confirm that elevated ilmenite abundance will result in a shift of the 2  $\mu\text{m}$  band to shorter wavelengths

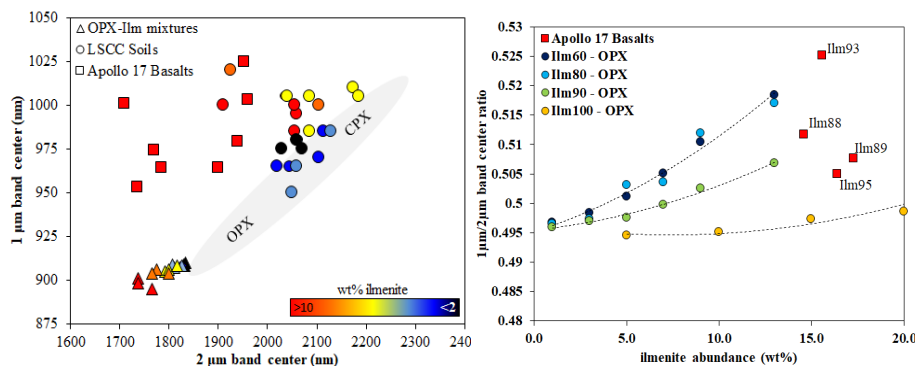
for all 3 data sets. This may be a useful means of inferring ilmenite presence in orbital data, although ilmenite abundances <3wt% will likely not be resolved.

Though plotting individual band centers indicates the presence of ilmenite, the compositions of the pyroxene with which it is mixed can make it difficult to compare the different data sets. Plotting the 1  $\mu\text{m}$ /2  $\mu\text{m}$  band ratio normalizes the data for direct comparison and allows for an additional spectral parameter to be plotted simultaneously. Plotting the 1  $\mu\text{m}$ /2  $\mu\text{m}$  band ratio as a function of ilmenite abundance (Fig. 3b) for the lab mixtures shows that the band centers are sensitive to both ilmenite abundance and composition. The Apollo 17 basalts plot roughly in the same parameter space and their Fe# correspond with the lab data.

**Conclusion:** Band center values for spectra of lab mixtures, lunar basalts and mare soils show that a systematic shift away from the ideal pyroxene band ratio trendline is related to ilmenite abundance. This relationship may provide a rapid method for ilmenite detection in orbital near-IR data. A distinct compositional effect was observed that is attributed to the increase in spectral contrast of diagnostic ilmenite features. The correlation between composition and spectral parameters for bulk basalt samples could be utilized to estimate ilmenite Fe# from orbital data, but additional work is needed to characterize the relationship over a wider range of pyroxene compositions. Future work will incorporate the synthesis of pyroxenes of variable compositions to span the entire range of possible spectral parameter space. We will explore these spectral parameters in orbital M<sup>3</sup> spectral data for various mare regions.

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**References:** [1] Haggerty, (1973), *Proc. Lunar Planet Sci.*, 4 [2] Neal and Taylor, (1992) *GCA* 79. [3] Isaacson et al., (2011) *Met. Plan. Sci.* 46 [4] Moriarty et al., (2016), *Met. Plan. Sci.* 51 [5] Robertson et al., (2019) *Icarus* (in review) [6] Tokle et al., (2019), *Eur. J. Min.*, 31 [7] Clark et al., (1984) *JGR*, 89 [8] Taylor, et al., (2001) *JGR* 106.



**Fig.3. a)** 1  $\mu\text{m}$  vs 2  $\mu\text{m}$  band center plot for OPX-ilm mixtures (ilm100, ilm90, ilm80, ilm60), lunar basalts and LSCC mare soils. Grey region shows the idealized band center plots for pure pyroxenes. **b)** 1  $\mu\text{m}$ /2  $\mu\text{m}$  band center ratio as function of ilmenite abundance for ilm60-ilm100. The ilmenite compositions are included for the lunar basalt samples (>125  $\mu\text{m}$ ).