

DEVELOPMENT OF AN FE-MG COMPOSITIONAL CALIBRATION FOR THE ILMENITE – GEIKIELITE SOLID-SOLUTION USING XRD AND REFLECTIVE SPECTROSCOPY. L. Tokle¹, K.M. Robertson¹, and R.E. Milliken¹, ¹Dept. of Earth, Environmental, and Planetary Sciences, Brown University, 324 Brook St., Providence, RI 02912. Leif_Tokle@brown.edu

Introduction: Ilmenite ($\text{Fe}^{2+}\text{TiO}_3$) is a Ti-bearing mineral observed on Earth as well as in lunar samples and martian (SNC) meteorites [1,2,3]. Ilmenite found in returned lunar samples has played an important role in shaping our understanding of magmatic processes that lead to the formation of lunar mare basalts [2]. Though global mapping of high-Ti basalts on the lunar surface is of interest for science and *in situ* resource utilization, achieving this through reflectance spectroscopy can be difficult due to the complex spectral behavior of ilmenite when it is present in mixtures [4].

An important consideration with any spectral mixing model that relies on mineral endmembers is whether or not the chosen endmembers are representative of the surface being studied. This is particularly true with ilmenite, where small amounts of Mg substitution can result in large changes in the spectral properties.

At high temperatures ilmenite forms a solid-solution with geikielite (MgTiO_3) and pyrophanite (MnTiO_3) [5]. Analysis of terrestrial and returned lunar samples show that Mg commonly substitutes for Fe^{2+} in ilmenite [1,2]. Therefore, improving our understanding of the physical and spectral properties of the ilmenite-geikielite solid solution and relating observed variations to crystal chemistry will aid in the characterization and modeling of ilmenite-bearing basalts.

In this study we use X-ray Diffraction (XRD) and visible-near-mid-infrared (VNIR & MIR) reflectance spectroscopy to measure different spectral properties of synthesized samples covering the ilmenite – geikielite solid solution. Varying the cation ratio of Fe to Mg is expected to affect a variety of properties in the XRD patterns (unit cell dimensions, diffraction peak positions and areas) and spectra (albedo, slopes, band depths and positions). Variations in these features are compared with the Fe content in ilmenite, focusing on features that are diagnostic of composition. We then compare our calibration with Apollo 17 high-Ti lunar basalt samples and one synthetic basalt sample to illustrate the robustness of our compositional calibration.

Methods: All synthetic ilmenite and geikielite powders utilized in this study were synthesized from reagent grade oxides in a 1 atmosphere $\text{CO}:\text{CO}_2$ furnace at 1573K for at least 30 hours. Powders were mechanically ground and sieved to a grain size of 10-20 μm . Fe contents for all powders were determined by wavelength-dispersive spectroscopy (WDS) on an electron microprobe. Microprobe analysis also shows

impurities in all powders are $< 1\%$.

XRD patterns for all powder samples were measured on a Bruker D2 Phaser XRD from 10 to 90° with a 15 second time step (Fig. 1). All XRD samples were mechanically mixed with quartz to create a common peak position reference to avoid any sample bias. VNIR and MIR data (0.35 – 25 μm) were collected on an ASD FieldSpec3 portable spectroradiometer and iS50 FTIR, respectively (Figs. 2,4).

Three Apollo 17 high-Ti lunar basalt samples were analyzed in this study (70017, 70215, 71055). Thin sections were measured on an electron microprobe to obtain modal mineralogy, ilmenite chemistry, and textural information, and corresponding powders for each thin section were ground and sieved to $< 45 \mu\text{m}$ for analysis on the XRD. One high-Ti basalt sample was also synthesized from oxides in a one-atmosphere furnace at an f_{O_2} of IW-2 for comparison with the lunar samples.

Results: The XRD data for the complete ilmenite-geikielite solid solution (Fig. 1) illustrate a systematic shift in the unit cell parameters with Mg substitution. Mg^{2+} has a smaller atomic radius than Fe^{2+} , thus an increase in Mg content results in a contraction of the unit cell and a shift to larger 2θ for all reflections. Peak intensities for all reflections systematically decrease, and peak intensities for (003) and (012) reflections disappear when ilmenite has at least 80% Fe.

A compositional calibration for Fe content based on the XRD data was generated by calculating the relative difference between two diffraction peaks ($\Delta 2\theta$) for a given composition (Fig. 3). We chose the (104) and (110) reflections because these are easily identifiable and have minimal peak overlap with other phases that are common in high-Ti basalts (Fig. 3). Using this XRD parameter, we find that the Apollo 17 high-Ti basalt and synthetic basalt samples fall along the

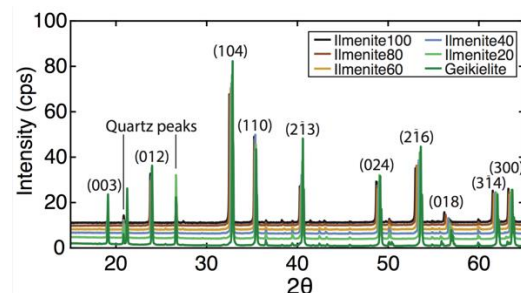


Figure 1. XRD of the synthetic ilmenite-geikielite suite.

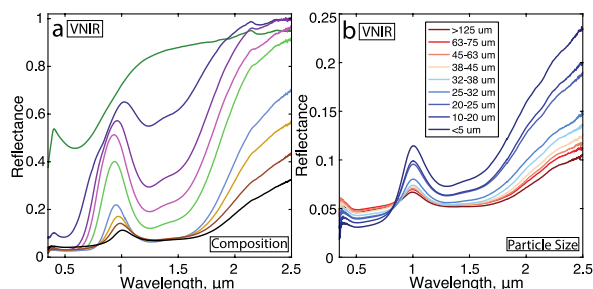


Figure 2. NIR reflectance spectra for a) the ilmenite-geikielite suite (colors as in Fig. 1) and b) different particle sizes of Ilm100 [4].

calibration curve (Fe content from probe data) and that ilmenite composition of the latter is indeed similar to lunar values (Fig. 3).

VNIR reflectance spectra exhibit several important trends based on composition as well as particle size (Fig. 2) [4]. Increasing Mg in ilmenite results in an increase in the slope at longer wavelengths and a decrease in the strength of Fe absorptions at 0.7, 1.25 and 1.5 μm . The rate of change in strength of these absorptions is not uniform, resulting in an apparent shift in a local reflectance maximum at $\sim 1 \mu\text{m}$. These features are observed with as little as 1-5% Fe.

The apparent shift in the peak at $1 \mu\text{m}$ may be a diagnostic feature that can be related to composition. Particle size has an effect on the slopes at VNIR wavelengths, but the position of the $1 \mu\text{m}$ 'peak' remains fixed at a single wavelength regardless of particle size (Fig. 2). As Mg% increases, the peak generally shifts to shorter wavelengths as the strength of the Fe absorptions weaken. Spectra of samples with low Fe content exhibit weak shoulders near $\sim 0.86 \mu\text{m}$ that may indicate partial oxidation of Fe and being studied in more detail. For most planetary and terrestrial applications however, ilmenite will rarely possess $<40\%$ Fe, mak-

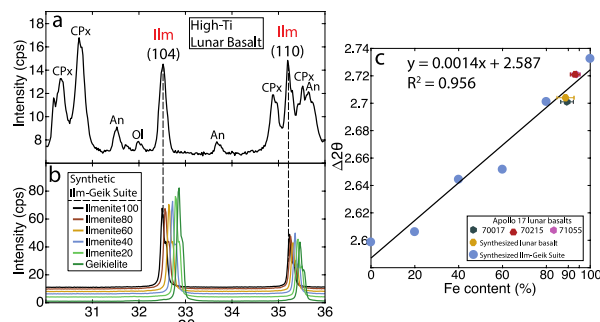


Figure 3. a) XRD of a high-Ti lunar basalt. Peaks are labeled with their respective mineral group with ilmenite highlighted in red (CPx – clinopyroxene, An – Anorthite, Ol – olivine, and Ilm – Ilmenite). b) XRD patterns of the synthetic ilm-geik solid solution. Dashed lines indicate the agreement of two different ilmenite peaks in both the natural and synthetic samples. c) plot of Fe content vs. the $\Delta 2\theta$ for the ilmenite diffraction peaks (104) and (110). High-Ti lunar basalt samples and our synthetic lunar basalt sample are plotted against the trend with error bars of one standard deviation.

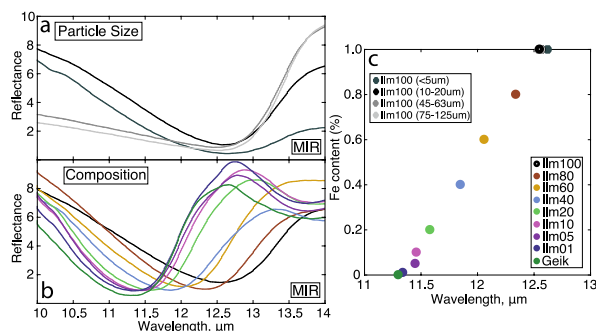


Figure 4. Plots of wavelength vs. reflectance for a) different particle sizes of synthesized Ilm100 and b) different compositions of the ilmenite-geikielite suite c) A plot illustrating position of reflectance minimum as a function of both particle size and composition.

ing the observed shift in the $1 \mu\text{m}$ peak a potential useful proxy for ilmenite Fe content.

The MIR data, like the VNIR data, are complicated because of the influences of both composition and particle size on absorption features. However, we observed a diagnostic feature at $\sim 12.55 \mu\text{m}$ that is sensitive only to composition and not particle size (Fig. 4). The wavelength position of this feature shifts to shorter values with increasing Mg substitution but remains fixed for different particle sizes at a given composition.

Conclusions: It is shown here that a compositional calibration for the Ilm-Geik solid solution based on XRD patterns will allow for rapid determination of the Mg-/Fe-content of ilmenite in basalts for both terrestrial and lunar samples. A suite of synthetic Ti-bearing basalts with different Fe content is being generated to further assess the robustness of our XRD-derived calibration at both moderate and low Fe content. Ongoing work is focused on measuring additional high-Ti lunar basalts (70035, 75075, and 74275) on the XRD and microprobe to continue ilmenite characterization.

These results also highlight the variability of Mg content in lunar ilmenite and the potential effects on spectral properties, which must be reconciled when performing spectral modeling of lunar samples or surfaces. Small changes in the Mg# of ilmenite result in significant changes in spectral shape, thus using a single ilmenite endmember for spectral unmixing may not be a sufficient representation of the compositional variability in naturally occurring ilmenite. The observed shifts in the both the $1 \mu\text{m}$ peak and the $12.55 \mu\text{m}$ absorption may provide useful proxies for estimating ilmenite Fe content via reflectance spectroscopy.

Reference: [1] Agar & Lloyd, (1997) *Proc. Ocean Drilling Prog. Scientific Results*, 153, 123-141. [2] Neal and Taylor, (1992) *Geochim. Cosmochim. Acta*. 79. [3] Rull F. et al. (2004) *J. Raman Spectros.*, 35, 497-503. [4] Robertson et al. (2017) *LPSC #2127*. [5] Lifervich & Mitchell (2005) *Phys Chem Minerals*, 32, 442-449.