

**REFLECTANCE SPECTROSCOPY OF ILMENITE: NEW CONSTRAINTS FROM APOLLO SAMPLE MEASUREMENTS.** P. J. Isaacson<sup>1</sup>, C. M. Pieters<sup>1</sup>, T. Hiroi<sup>1</sup>, Y. Liu<sup>2</sup>, D. Dhingra<sup>1</sup>, R. L. Klima<sup>3</sup>, L. A. Taylor<sup>2</sup>, <sup>1</sup>Dept. Geological Sciences, Brown Univ., Providence RI, 02912 [Peter\_Isaacson@Brown.edu], <sup>2</sup> Planetary Geosciences Inst., Dept. Earth & Planetary Science, Univ. Tennessee, Knoxville TN, 37996, <sup>3</sup>Planetary Exploration Group, Space Department, Johns Hopkins University Applied Physics Lab, Laurel MD, 20723.

**Introduction:** The presence of abundant ilmenite ( $\text{FeTiO}_3$ ) in lunar mare basalts is one of the major properties that distinguish some lunar basalts from other basalts in the solar system [1-6]. The  $\text{TiO}_2$  content of the bulk rock is the primary means of classification for mare basalts.  $\text{TiO}_2$  is largely hosted in Fe-Ti spinels in low-Ti basalts and by ilmenite in high-Ti basalts [4, 5]. Therefore, identifying the abundance of ilmenite offers a first-order approximation of basalt type and thus clues to mare basalt source regions and their evolution over time [e.g., 7, 8]. The importance of ilmenite and the spatial limitations of returned samples have led to major efforts to estimate its abundance through remote sensing, largely through optical measurements in the visible to near-infrared (VNIR), although gamma ray spectroscopy can also provide measurements of Ti abundance, albeit at substantially lower spatial resolution [e.g., 9]. As the lunar surface is dominated by optically mature lunar soils, efforts with VNIR reflectance data have focused on analysis of soil samples. As modal mineralogy is difficult to estimate for soil samples, remote evaluations of ilmenite abundance have instead focused on chemical parameters like  $\text{TiO}_2$  abundance, which are much easier laboratory measurements. However, it is important to recall that  $\text{TiO}_2$  does not correlate directly with ilmenite, especially for lunar soils (low-Ti basalt soils in particular due to the ilmenite/spinel issues discussed above). In the case of more mature soils, ilmenite tends to be melted and incorporated into agglutinitic glass (and potentially at rates different from other minerals), meaning that the soil loses its ilmenite mineralogy but retains its  $\text{TiO}_2$  content [10, 11].

Most techniques for remote estimation of  $\text{TiO}_2$  abundance [e.g., 12-17] center on an empirical correlation between soil  $\text{TiO}_2$  content and the spectral slope across ultraviolet to visible (UV-Vis) wavelengths (with Ti-rich soils being relatively flat or “blue”) first recognized by Charrette et al. [12]. However, this correlation is purely empirical and not linked directly to ilmenite abundance, and may be at least partially related to other properties of soils such as nanophase or microcrystalline weathering properties. Regardless of the source, this empirical correlation is difficult to link directly to understanding of mineralogy and mineral structures, making it difficult to use for quantitative assessments of ilmenite abundance.

**Ilmenite Spectroscopy:** While our understanding of the optical properties of ilmenite is still evolving, the

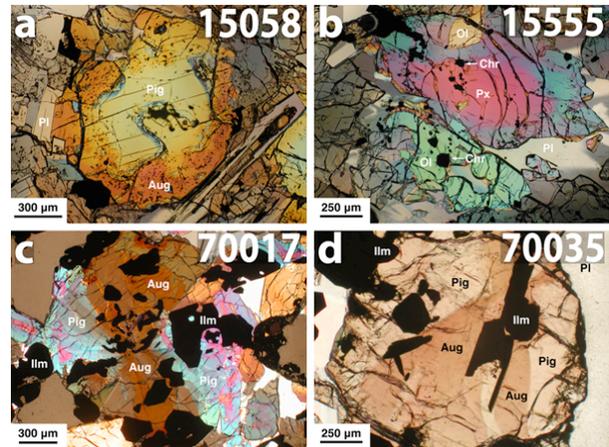


Fig. 1: Photomicrographs of LRMCC thin sections of low-Ti and high-Ti samples. Images were acquired with cross-polarized transmitted light (a, b, c) and plane-polarized transmitted light (d). (c) and (d) demonstrate the complex pyroxene compositional zonation and the intergrowth of ilmenite and pyroxene (largely of augite composition) grains.

highly absorbing nature of ilmenite across UV-Vis wavelengths has largely been attributed to a variety of charge transfer absorptions, including metal-metal (e.g. Fe-Ti), metal-oxygen (e.g. Fe-O, Ti-O) and intervalence (e.g.  $\text{Ti}^{3+}$ - $\text{Ti}^{4+}$ ) charge transfers [17-21]. Ilmenite also demonstrates a broad absorption centered near 600-700 nm, a relative reflectance peak around 1  $\mu\text{m}$ , and a substantial increase in reflectance across NIR wavelengths [22, 23]. While the general reflectance properties of ilmenite have been recognized, the nature in which opaque minerals contribute to bulk spectra in mixtures (i.e. rocks and particulate bulk samples) is poorly understood and appears to be strongly influenced by sample texture (grain size and interrelationships between opaques and ferromagnesian silicates) [e.g., 23, 24].

**New Sample Constraints:** The Lunar Rock and Mineral Characterization Consortium (LRMCC) conducted coordinated mineralogy/petrography and reflectance spectroscopy analyses of a suite of mare basalt samples, two low-Ti (15058, 15555) and two ilmenite-rich high-Ti samples (70017, 70035) [23]. These analyses included careful characterization of modal mineralogy and sample texture through thin section analyses, and also involved the preparation of mineral separates and particulate bulk sample splits for reflectance spectroscopy measurements. All of the samples are coarse-grained (Fig. 1), as they were selected to facilitate the preparation of mineral separates by hand

picking. In the case of the high-Ti samples, ilmenite is commonly found intergrown with pyroxene grains, which themselves typically exhibit complex sector zonation (Fig. 1). These samples and the acquired reflectance measurements represent important new constraints on the spectral properties of ilmenite for crystalline materials, for which the traditional UV-Vis correlation may not be completely appropriate. Prior to the LRMCC results, the only lunar sample in which the presence of ilmenite has been suggested from spectral reflectance properties is the Apollo 17 black beads (74001) [25], although the presence of microcrystalline ilmenite is strongly suspected in a suite of recently-analyzed lunar impact melt samples [26].

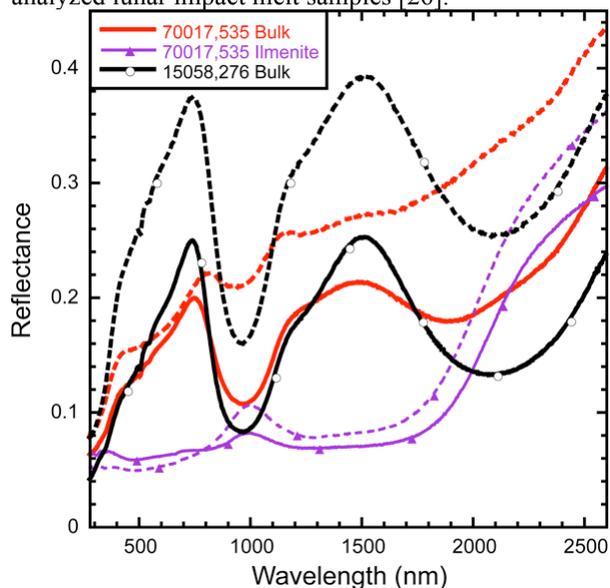


Fig. 2: Bidirectional reflectance spectra of particulate bulk samples (low-Ti and ilmenite-rich high-Ti) and ilmenite separates at two particle size ranges. Coarse-particle samples are in solid lines, and fine-particle samples are in dashed lines.

**LRMCC Reflectance Measurements:** The VNIR reflectance spectra of selected LRMCC mineral separates and particulate bulk samples are illustrated in Fig. 2. The particulate bulk samples (red and black lines) are comparable in texture and mineralogy apart from ilmenite abundance. The overall spectral properties of ilmenite (purple lines) include a generally dark, flat nature across visible wavelengths, although substantial spectral structure is apparent. The “positive” inflection near 1  $\mu\text{m}$  can be noted, as well as a pronounced increase in reflectance beyond  $\sim 1.7 \mu\text{m}$ . The low-Ti bulk sample spectra (black lines) show the classic 1 and 2  $\mu\text{m}$  absorptions diagnostic of pyroxene, due to the pyroxene-rich composition of these basalts. In comparing the black (low-Ti basalt) to the red (high-Ti, ilmenite-rich basalt) spectra, in which the only substantial difference in the samples is ilmenite abundance, several important distinctions are apparent, most of which are

more apparent in the fine-particle spectra (dotted lines). The high-Ti basalt spectra are substantially darker overall and exhibit relatively weak and in some cases distorted 1 and 2  $\mu\text{m}$  absorptions. The high-Ti basalt spectra also exhibit an enhanced absorption across visible wavelengths centered near 600 nm, a flattened long wavelength “shoulder” of the 1  $\mu\text{m}$  band (from  $\sim 1.2 \mu\text{m}$  to 1.5  $\mu\text{m}$ ), and a pronounced “red” spectral slope, especially at longer wavelengths.

**Current Status and Needed Future Work:** There are complications to the interpretation of each of the properties of ilmenite-rich basalts discussed above and ilmenite contributes to bulk mixture spectra in highly nonlinear and poorly-understood ways, although efforts are underway to use these properties to evaluate VNIR reflectance signatures of high-Ti basalts [e.g., 27]. The LRMCC data represent important constraints, but effectively offer limited data for the understanding of ilmenite’s contribution to bulk mixture reflectance spectra, as both high-Ti samples have comparable ilmenite abundances and textures and all samples are of large particle size. Additional laboratory work across a range of sample compositions, textures, and particle sizes (both real samples and laboratory mixtures) is required in order to address quantitatively the effect of spectrally complex opaques such as ilmenite on bulk mixture spectra. However, such work is essential for the extraction of ilmenite abundance from remote VNIR reflectance spectroscopy measurements, as the currently-available approaches are likely to have difficulty producing accurate estimations of ilmenite abundance for crystalline materials [e.g., 24].

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