MINERALOGY AND CHEMISTRY OF TI-BEARING LUNAR SOILS AND SIZE FRACTIONS.

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Introduction: Beginning with the Clementine mission, the possibility to map globally the distribution of Ti has been an objective of numerous investigations [e.g., 1-6]. The possibility stems from the Charette relationship [7], an empirical correlation between UV-VIS spectral ratios and TiO_2 concentrations in soils. Using Apollo and Luna landing site soils, with representatives from sample stations that could be observed with Clementine's ~100 m/pixel resolution, Blewett et al. [2] and numerous subsequent studies attempted to develop spectral algorithms to extract TiO_2 information. Although empirical correlations provide good results to first order in discriminating high-Ti soils from low-Ti soils, several of these studies [e.g., 4,5], have pointed out the difficulties and inaccuracies of the method.

If we knew everything about the petrographic and chemical characteristics of the soils and their quantitative effects on reflectance spectra, we could increase the accuracy of TiO_2 estimates from orbital reflectance spectroscopy. This effort is needed because of the importance of Ti content for basalt classification and studies of lunar crustal composition, surface volcanism, and spatial variations in mantle composition [7], and for improved mapping of ilmenite as a potential resource for extraction of oxygen and solar-wind gases [1].

Recently, the Lunar Reconnaissance Orbiter (LRO) Wide Angle Camera [8] has collected the first global UV coverage with two UV bands at nominally 400 m/pixel and these data have been photometrically well calibrated [9]. Using a UV/VIS ratio and correlating to landing site soils, the LRO WAC dataset offers an improved TiO_2 determination [10]. The purpose of this abstract is to report lab-based measurements aimed at further understanding this correlation and investigating some of the effects of parameters such as composition, soil maturity, and grain size.

Methods: We have analyzed a suite of 13 soils that represent the full range of TiO_2 concentrations, known from published compositions, and maturity as measured by Is/FeO [11,12]. We are analyzing bulk soils (<200 μm) and grain-size separates (100-200, 48-100, 20-48, and <20 μm). Here we focus on the bulk soil properties. We have also done electron petrography [13] for comparison to the extensive work of the Lunar Soil Characterization Consortium [14,15], but accurate bulk properties are difficult to obtain and that method is very labor intensive. In this work, we use powder X-ray diffraction (XRD) coupled with quantitative Rietveld refinement [cf 16], and reflection micro-X-ray fluorescence (μXRF) to measure small aliquots of soil powders. These techniques (and instruments) are both relatively new and they offer great promise for further investigation of lunar soils and size separates using small but representative (25 mg) subsamples that can also be measured with a UV-VIS laboratory spectrometer.

Analytical Procedures: Powder XRD analysis was performed on a Bruker d8 Advance using a Lynx-EyeXE position sensitive detector. A zero diffraction sample holder with 25 mg capacity was used sequentially for both XRD and μXRF analysis. The Bruker Topas program was used for Rietveld refinement and quantitative analysis using structure files for plagioclase, augite, pigeonite, ilmenite, olivine, troilite, and kamacite. The amorphous content was determined by refinement of a peak adjusted to match background curvature of the spectra. Particle size and preferred orientation effects were minimized by sample rotation and evaluated via replicate samples. The sensitivity for ilmenite by XRD is good because the main ilmenite diffraction peaks are not interfered by plagioclase and pyroxene.

An Edax Orbis μXRF with a silicon drift detector and a Rh X-ray tube was used to collect XRF data on the soils. Data were collected at 1 atm. using 40 kV and 350 μA tube current, and 10 replicates measured over the sample area were summed for data processing. The analytical sensitivity for Ti by μXRF is very good, and the soils were used to generate calibration curves using multi-element influence coefficients. This accurate calibration allows us to analyze a selected suite of elements in lunar soils which have similar matrix compositions.

Results: The key parameters that we focus on here are ilmenite content as measured by XRD and TiO_2 as measured by μXRF. We have analyzed size fractions for several samples, and although we observe trends, we present these results here as preliminary, pending additional measurements prior to generalization.

TiO_2 concentrations determined by μXRF are shown in Fig. 1. The high correlation (R^2=0.99) gives us confidence in the μXRF measured values. These values are in turn plotted against ilmenite proportions extracted from the XRD Rietveld refinements on the exact same subsamples (Fig. 2).

We include data for two sets of grain size separates in Figure 2, for 10084 and 70181. In both cases, the ilmenite content increases in the finer grain size fractions. This trend is counter to the trend obtained from electron petrography of grain mounts by [15] but consistent with results obtained for these two soils from analysis of grain mounts by [13]. In order for ilmenite content to increase at relatively constant bulk TiO_2, another Ti-bearing component must decrease. In the analysis of [13], the agglutinate content decreases as size fractions decrease from 100-48 µm, 48-20 µm, and <20 µm. In our Rietveld refinement, however, the amorphous component does not decrease in the finer fractions; it increases. Although the amorphous component generally correlates positively with Is/FeO, it is not solely related to agglutinates. It is also a function of other glasses in the soils and of amorphous rims, which are ubiquitous and likely occupy a greater proportion of the grain volume in the finer fractions [15]. This aspect of the work is preliminary; additional grain size separates must be analyzed.

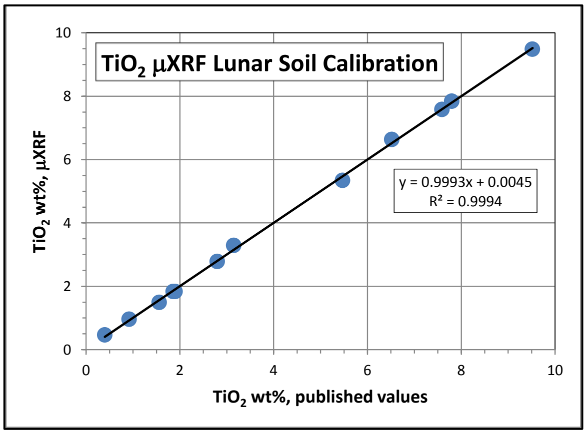

Figure 1. TiO_2 wt.% determined by µXRF compared to published values as collated primarily by [11,12].

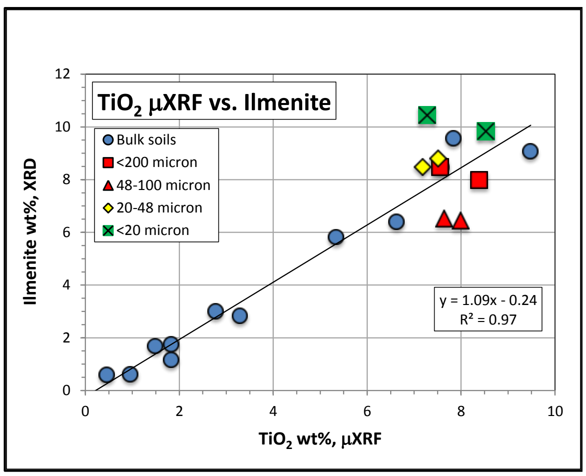

Figure 2. TiO_2, measured by µXRF vs. ilmenite content, wt.%, measured by XRD with Rietveld refinement. Deviations from perfect correlation reflect the fact that Ti, while dominantly hosted by ilmenite, is also hosted by other phases, including agglutinates, other impact glass, and volcanic glass.

Correlations with UV/VIS: As noted above, LRO WAC data provide an improved empirical correlation between the UV/VIS ratio (321 nm / 415 nm) for Apollo and Luna (sample return) landing site soils [10]. We are testing this relationship using a laboratory UV-VIS spectrometer (Ocean Optics). From preliminary results, we find that the correlation between TiO_2 or ilmenite content and 321/415 is not as good as for the LROC WAC orbital measurements. We find, however, that the correlation improves if the immature soil samples are omitted from the dataset. This result indicates that what we sense from orbit at a scale of 400 m/pixel (WAC UV data) is, on average, relatively mature soil. We continue to investigate the effects of specific components and variations with grain size as potential causes of variations in the relationship between spectral data and soil TiO_2 contents.

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