Contextualizing the Compositional Variation within Apollo 17 Core Sample 73002/73001: X-ray Photoelectron and Energy-Dispersive X-ray Spectroscopic Measurements.

C.A. Dukes[1], J. Maxson[1], T. Ho[1], L. Ziamanesh[1], M. Jones[1], J. Oraegbu[1], K. Stelmach[1], A.W. Woodson[1], R. V. Morris[2], L. P. Keller[2], R. Christoffersen[3], C. K. Shearer[4], and the ANGSA Science Team[5]. [1]University of Virginia, Charlottesville, VA 22902 (cdukes@virginia.edu), [2]NASA JSC, Houston, TX, [3]Jacobs, NASA JSC, Houston, TX, , [4]University of New Mexico, Albuquerque, NM, [5]ANGSA Science Team list at https://www. lpi.usra.edu/ ANGSA /teams/. (cshearer@unm.edu).

Introduction: Half-a-century after the Apollo 11 manned-landing on the lunar surface, several previously unexamined core samples were released by NASA for analysis by new or improved scientific methodologies. Double-drive tube regolith core samples from Apollo 17: 73002 (upper ~22 cm) and the 73001 (lower ~22 cm) were collected at the lunar surface within landslide material near Station 3 in the Taurus-Littrow Valley on the southeastern edge of Mare Serenitatis [1-3]. Native stratigraphy of the collected material has remained preserved in the tubes, allowing analyses of grain composition, volatile content, and the effects of the space environment to be evaluated as a function of depth.

Experiment: "Pass 2" of regolith material from Apollo Core sample 73002 was dissected in 5 mm intervals and subsequently dry-sieved to < 1 mm size fractions within an N_2-purged lunar sample cabinet at Johnson Space Center. An allocation of 1-2 mg per interval for 15 intervals over the 18 mm closest to the surface was provided to UVa from the JSC Allocation Team general allotment (~235 mg). The UVa allocation can be directly correlated to additional stratigraphic analyses, such as Mossbauer maturity indices [6], Vis-NIR reflectance [6,7], electron microscopy cosmic-ray track analysis [8].

Lunar samples were transported to UVa in aluminum containers, double-bagged under N_2. Because grains were typically 50 - 200 um dia. and few in number, they were prepared in air using a Zeiss Stereo Microscope with cross-polarizer for mineralogical separation. For each depth interval, two to five grains were selected on a clean glass slide, both dark (glassy/agglutinate or isotropic minerals) and bright (anisotropic) under cross-polarized light. Grains were then gently pressed into an indium (99.9975%) foil for X-ray photoelectron spectroscopy (XPS) and subsequent energy-dispersive X-ray analysis (EDAX) in a desktop Phenom XLG2 scanning electron microscope (SEM). No adhesives were used to preserve the integrity of the surface material.

XPS is a non-destructive near-surface (< 10 nm) analytical technique based on the photoelectric effect that provides quantitative elemental composition, as well as chemical-bond/oxidation state characterization, for species with Z > 2. We used a PHI Versaprobe III XPS microprobe (~6 x 10^{-8} Pa) with a monochromatic X-ray source ($Al_{K\alpha}$: 1486.6 eV) and hemispherical electron energy analyzer to collect survey spectra (1400–0 eV; 0.5 eV/step; ΔE = 2.7 eV) for species identification; high-resolution spectra (0.2 eV/step; ΔE = 0.25 eV) were acquired to understand Fe-oxidation surface chemistry. An X-ray beam spot (20, 50 or 100 µm) appropriate to the individual grain size was used, as determined by secondary electron (SXI) imaging. All data was acquired at room temperature. Charge neutralization from an electron flood-gun was utilized during analysis to eliminate variation or change in surface potential during analysis. Data was processed using PHI Multipak, with binding energy scales calibrated to the C-1s peak at 284.8 eV.
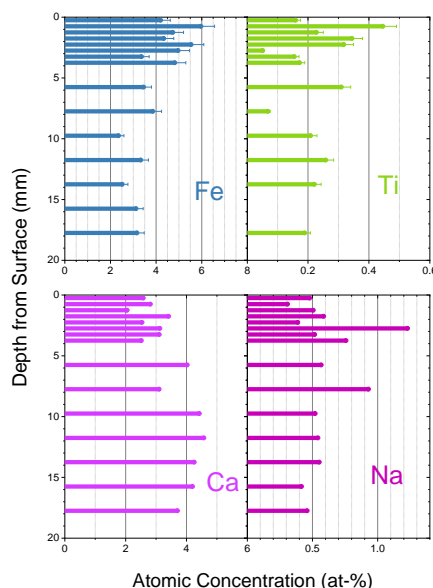

Fig. 1. XPS surface (< 10 nm) elemental composition for 73002 lunar grains from a distribution of depths suggests enrichment in the grain rims of Fe and Ti and near-surface depletion of Na and Ca with distance from the lunar surface.

Quantitative elemental concentrations were acquired by EDAX with an Oxford 50 mm Silicon drift detector (SDD) sensitive for Z > 5. Compositions were determined using the Phenom proprietary software after benchmarking the system to a NIST-traceable glass standard. Because our interest was in comparing

"bulk" composition to surface (XPS), spectra and images (mag. ~1000×) were acquired at 15 kV over the entire grain. No conductive coating was necessary. At least 10^6 X-rays were collected per grain.

Results and Discussion: XPS shows all grains contain: O, Si, Al, Mg, Ca, Fe, Na, C, and F, with many grains also retaining Ti, K, & S throughout the entire 73002 core. Identified species are similar to elemental bulk compositions as measured by EDAX, which additionally noted Cr, Mn, and Mo in low concentrations in some particles. F was not noted in the bulk analysis and is likely the result of vapor deposition from heat-sealing under the N_2-hood (JSC curation) of the PTFE bags used for transport.

Preliminary analysis of XPS measurements (Fig. 1) describe trends in elemental surface (< 10 nm) concentrations with stratigraphy using the average composition of all grains within each 5 mm interval. We find that volatile species (Na, K, S) and Ca are depleted in the surface segments relative to their concentrations deeper in the core, while Fe and Ti are conversely enriched over the near-surface intervals. Si and O content appear relatively constant throughout the 73002 core. C was also identified, generally adventitious in nature, rather than endogenous to the Moon.

The Fe-content for grain surfaces can be separated into three general regions within the 73002 core: ≤ 10 mm (5.8 at-%); 15 - 40 mm (4.2 - 4.9 at-%); and ≥ 55 mm (3.0 - 3.7 at-%). Oxidation state information for the iron can be derived from the HR XPS spectra (Fig. 2), and preliminary data suggest an enhancement in metallic-component relative to the native (typically Fe^{2+}) chemistry for grains that lie close to the core surface. This result is consistent with measurements of I_s/FeO maturity index, which decreases with depth, identifying mature material within the topmost 30 mm and immature soil for intervals
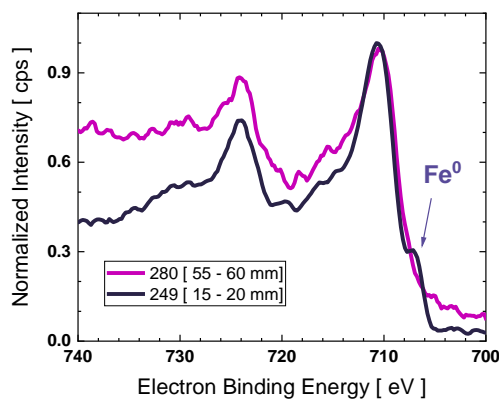

Fig. 2. Comparison of XPS Fe-2p photoelectron feature from near-surface grains (249; 15-20 mm) and from deeper (280; 55-60 mm) into the core show subtle

differences in oxidation state suggestive of a metallic Fe component closer to the surface.

below ~70 mm [6]. Vis-NIR reflectance measurements for both dissection Pass 1 and Pass 2 find significant darkening (~ 0.22) in the near surface regions (< 30 mm) at 750 nm, relative to material from depth > 10 mm (reflectance ~0.36) [6, 7]. While brightening with depth can signal possible variation in interval mineralogy, it may also suggest the presence of opaque mineral phases, such as nFe^0, which can reduce overall material reflectance [5]. The potential presence of nFe^0 would be indicative of enhanced weathering for the 73002 near-surface intervals, with detailed studies ongoing.

Comparison of grain composition with nearby soil samples (Fig. 3) suggests mineralogical similarity with bulk surface composition of landslide materials acquired in other nearby locations, including near the South Massif.
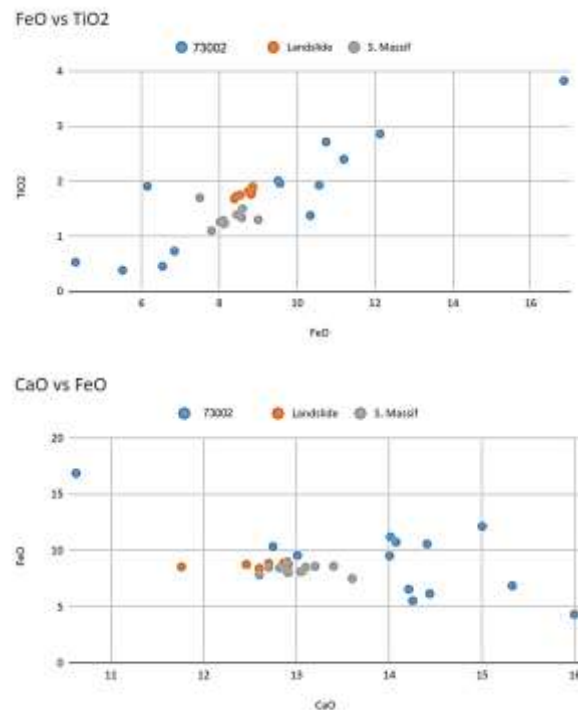

Fig. 3. EDAX grain compositions for 73002 over a distribution of depths compared to surrounding landslide surface mineralogies at nearby locations.

References. [1] Shearer *et al*., 2020, *LPSC51*, abs1181; [2] Koorotev and Kremser, LPSC22, 275-301; [3] Shearer *et al.*, 2022, *LPSC53*. [4] Keller and McKay, 1997, GCA 61, 11, 2331-2341. [5] Pieters & Noble, (2016). JGR Planets, 121(10), 1865–1884. [6] Morris et al., 2022, *LPSC53*. [7] Sun *et al.*, 2021, *M&PS, 56*, 1574. [8] Mcfadden *et al.*, 2022, *LPSC53*.