

EFFECT OF SPACE RADIATION PROCESSING ON LUNAR SOIL SURFACE CHEMISTRY: X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES.

C. Dukes¹, R. Christoffersen^{2,3}, L. Keller³, M.J. Loeffler¹ and R. Baragiola¹. ¹Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA 22902. E-mail: car8r@virginia.edu. ²Jacobs Technology, ESCG, Mail Code JE23, Houston, TX, 77058. ³Mail Code KR, ARES, NASA Johnson Space Center, Houston, TX 77058

Introduction: Current understanding of the chemistry and microstructure of the surfaces of lunar soil grains is dominated by a reference frame derived mainly from electron microscopy observations [e.g. 1,2]. These studies have shown that the outermost 10-100 nm of grain surfaces in mature lunar soil finest fractions have been modified by the combined effects of solar wind exposure, surface deposition of vapors and accretion of impact melt products [1,2]. These processes produce surface-correlated nanophase Fe⁰, host grain amorphization, formation of surface patinas and other complex changes [1,2]. What is less well understood is how these changes are reflected directly at the surface, defined as the outermost 1-5 atomic monolayers, a region not easily chemically characterized by TEM. We are currently employing X-ray Photoelectron Spectroscopy (XPS) to study the surface chemistry of lunar soil samples that have been previously studied by TEM. This work includes modification of the grain surfaces by *in situ* irradiation with ions at solar wind energies to better understand how irradiated surfaces in lunar grains change their chemistry once exposed to ambient conditions on earth.

Results and Discussion: Baseline XPS analyses of 10084 mare soil in both "bulk" (< 1 mm grain size) and ≤ 20 μm dry-sieved size fractions dispersed on high-purity oriented graphite substrates detects Ti: 1.5%, Mg: 2.8%, Ca: 3.4%, Fe: 4.2%, Al: 4.8%, Si: 18.3%, and O: 65.1%. These results are quite similar, although not identical, to previous measurements [3]. High-resolution scans of the Fe 2p peak show Fe is completely in the 3+ oxidation state, suggesting that at least on XPS depth scales (1-5 nm), both metallic Fe and Fe²⁺ in the bulk grains is completely oxidized at the surface, likely by atmospheric reactions. This oxidation is yet to be evident in our analytical TEM studies of the outer margins of ≤ 20 μm 10084 grains prepared by ultramicrotomy. Irradiation of the bulk 10084 soil in the XPS chamber with 4 keV He⁺ ions results in the Fe 2p photoelectron peak shifting to 707 eV characteristic of predominantly metallic Fe on the surface at an ultimate dose of 1×10^{17} He⁺/cm². Exposure of this irradiated sample to ambient laboratory conditions for only 5 minutes, followed by re-analysis, shows only Fe³⁺ on the surface, consistent with complete re-oxidation. A more detailed progressive *in situ* irradiation study of the ≤ 20 μm 10084 sample using 4 keV Ar⁺ to sputter clean the sample shows metallic Fe appearing at only 4.4×10^{14} Ar⁺/cm², where a monolayer or less has been removed. By comparison, a much larger fluence, $\sim 10^{16}$ Ar⁺/cm², was needed to form metallic Fe on olivine surfaces [4], a material that has no metallic Fe in the bulk. This suggests that the observed metallic Fe on the irradiated lunar grains is intrinsic Fe⁰ of lunar origin, and that irradiation mainly removes surface oxidation.

References: [1] Keller L. P. and McKay D. S. 1993. Science 261:1305-1307. [2] Keller L. P. and Christoffersen R. 2005. 68th Meteoritical Society Meeting, 40: 5244. [3] R.M Housley and R.W. Grant (1976) Proceeding of the 7th Lunar Science Conference, 881-888. [4] Loeffler M. J. et al. 2009. Journal of Geophysical Research 114.