

THE OXIDATION STATE OF FE NANOPARTICLES IN LUNAR SOIL: IMPLICATIONS FOR SPACE WEATHERING PROCESSES. M. S. Thompson¹, T. J. Zega¹, J. T. Keane¹, P. Becerra¹, and S. Byrne¹. ¹Lunar and Planetary Laboratory, Department of Planetary Sciences, University of Arizona, 1629 E. University Blvd, Tucson, AZ 85721, mst@lpl.arizona.edu.

Introduction: Grains on the surfaces of airless bodies such as the Moon are continually modified by micrometeorite impacts and interactions with solar-wind ions, a process that is collectively known as space weathering. This phenomenon alters the optical properties of surface soils by darkening and reddening their reflectance spectra and by attenuating their characteristic absorption bands [1,2]. The change in optical properties has been attributed to the the production of Fe nanoparticles (npFe) in surface soils through space-weathering processes. In lunar soils, Fe nanoparticles occur as inclusions in agglutinitic glass grains and in vapor-deposited rims [3].

The nanoparticles in lunar soil samples are typically reported as containing Fe in the reduced metallic state, i.e., Fe⁰, and are widely referred to as npFe⁰ in the literature, e.g., [3-6]. However, previous work has shown a mixture of Fe oxidation states in agglutinitic glasses that contain Fe nanoparticles [4]. Here we expand on previous efforts and measure directly the oxidation state of individual nanoparticles. Understanding the oxidation state of these nanoparticles will provide insight into the conditions of their formation, and the nature and efficiency of space weathering mechanisms across the inner solar system.

Samples and Methods: We embedded <1 mm grains of three Apollo lunar soils in low-viscosity epoxy and prepared them through ultramicrotomy for analysis in an aberration-corrected transmission electron microscope (TEM). The samples include: 12033, an immature mare soil, 15071, a submature mare soil, and 79221, a mature mare soil. We measured over 100 individual nanoparticles from the three lunar soil samples building on our previous work [7,8]. Over 30 individual nanoparticles were measured in each lunar soil sample.

The oxidation state(s) of the npFe was measured with electron energy-loss spectroscopy (EELS) coupled to a TEM. All measurements were performed using the 100 keV monochromated and aberration-corrected Nion UltraSTEM at Arizona State University, equipped with a Gatan Enfium Spectrometer. We used a 3 mm spectrometer entrance aperture, a collection angle of 45 mrad, and a 0.2 nm probe size with a convergence semi-angle of 30 mrad. Line profiles for individual nanoparticles were collected with a dispersion of 0.1 eV/channel and an energy resolution between 200 to 300 meV. Each measurement had a variable dwell time, ranging from 0.01 s/px to 0.5 s/px.

EELS spectra were collected at the Fe L_{2,3} core-loss edge at energies ranging from 690 to 780 eV. All spectra were compared to measurements of Fe metal, FeO (wüstite), and Fe₂O₃ (hematite) standards for reference to Fe⁰, Fe²⁺, and Fe³⁺, respectively, using the same conditions. Spectral processing included background removal (AE⁻¹), subtraction of the continuum beneath the core-loss edge, and deconvolution of the zero loss peak. We also acquired spectra from the glass surrounding each nanoparticle and subtracted this ‘matrix’ spectrum from the nanoparticle component in order to isolate the contribution solely from the nanoparticle. For each sample spectrum, we determined the relative contribution of Fe⁰, Fe²⁺, and Fe³⁺ by performing a weighted non-negative least squares regression between the observed sample and the three respective standards. From this routine we obtained the Fe⁰/ΣFe, Fe²⁺/ΣFe, and Fe³⁺/ΣFe ratios for each nanoparticle.

Results and Discussion: We collected and successfully quantified (R²>0.90) EELS spectra for over 100 nanoparticles, with at least 30 from each sample. Fig. 1 shows an example nanoparticle spectrum that has been quantified from sample 12033. The measured spectrum is composed of 100% Fe⁰. In comparison, Fig. 2 shows a spectrum from sample 79221 that has been quantified. The measured spectrum is composed of 45% Fe²⁺ and 55% Fe³⁺. Spectra from each particle were quantified in this manner, and the results are shown in a ternary plot with Fe⁰, Fe²⁺, and Fe³⁺ end members in Fig. 3.

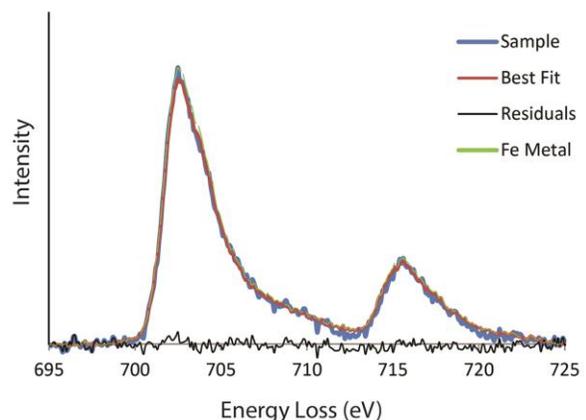


Fig. 1: EELS spectrum of a nanoparticle from immature soil sample 12033 showing Fe L_{2,3} edge. The measured sample (blue), the simulated best fit (red), the residuals (black), and the components fitting the spectrum, in this case Fe metal (green) are shown. This particle is composed of 100% Fe metal.

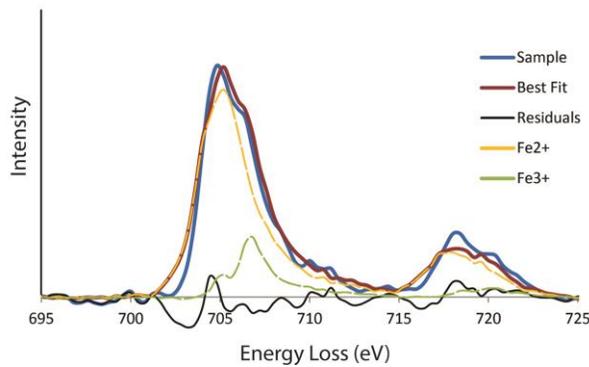


Fig. 2: EELS spectrum of a nanoparticle from mature soil sample 79221 showing Fe $L_{2,3}$ edge. The measured sample (blue), the simulated best fit (red), the residuals (black), and the components fitting the spectrum, in this case Fe^{2+} (gold) and Fe^{3+} (green) are shown. This particle is composed of 77% Fe^{2+} and 23% Fe^{3+} .

The data suggest that there is an increase in Fe oxidation state with an increase in maturity, i.e., Fe in nanoparticles in the immature soil are composed primarily of Fe^0 , whereas those in the submature are a mixture of Fe^0 and Fe^{2+} , and nanoparticles in the mature nanoparticles a mixture of Fe^{2+} and Fe^{3+} . We also made structural measurements using high resolution TEM (HRTEM) imaging of individual nanoparticles in each of the samples. An HRTEM image of a particle with measured d -spacings is shown in Fig. 4. Each of the HRTEM images acquired from these samples give d -spacings consistent with either Fe metal, or Fe oxide minerals such as wüstite or magnetite, further supporting our Fe EELS measurements.

Implications for Space Weathering Processes: Mature soils, which contain oxidized Fe nanoparticles, have significant exposure times on the lunar surface and are therefore subjected to prolonged weathering processes. We hypothesize that O in the silicate glass matrix could be a source of npFe oxidation. Supporting evidence for this pathway is provided by observations we made of individual nanoparticles in the submature soil sample 15071. Some nanoparticles in soil sample 15071 exhibit an oxidized rim surrounding a reduced, metallic nanoparticle core. We hypothesize that Fe metal in the nanoparticle shell was directly exposed to O in the surrounding silicate glassy matrix, and oxidation progressed into the particle interior over time. Observations of additional particles will verify whether this trend holds, nevertheless, these results suggest that space weathering products such as Fe nanoparticles are dynamic and their microchemical characteristics are evolving with time.

The optical effects of space weathering on surface samples has been investigated theoretically using spectral modeling techniques, e.g., [1]. These models aim to recreate reflectance spectra of space-weathered sur-

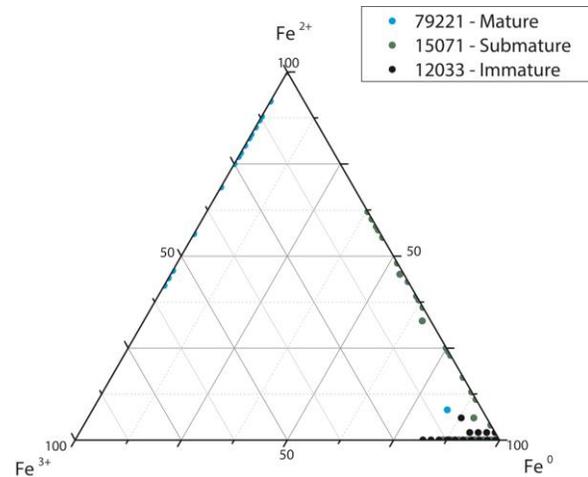


Fig. 3: Ternary plot showing compositions of nanoparticles in each of the lunar soil samples. Note the trend of increasing degree of oxidation with increasing maturity of the samples.

face materials by artificially adding metallic Fe^0 nanoparticles to a measured lunar soil matrix. However, the data presented here show that these nanoparticles are composed of Fe in multiple oxidation states. To under-

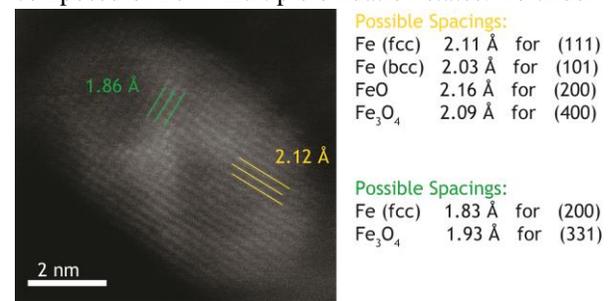


Fig. 4: HRTEM image of a nanoparticle in lunar soil sample 79221. Spacing measurements are shown in two directions, with possible identification listed on the right.

stand the effects that oxidized npFe have on the optical properties of lunar soil, we have begun modeling the reflectance spectra of lunar soils to include nanoparticles of variable oxidation states. Our data show differences in optical properties among nanoparticles with varied oxidation states, and the implications of these results will be discussed at the meeting.

References: [1] Hapke B. (2001) *J. Geophys. Res-Planet.*, 106, 10,039-10,073. [2] Pieters C. M. et al. (2000) *Meteorit. Planet. Sci.*, 35, 1101-1107. [3] Keller L. P. and McKay D. S. (1997) *Geochim. Cosmochim. Ac.*, 61, 2331-2341. [4] Keller L. P and Clemett S. J. (2001) *LPS XXXII*. [5] Keller et al. (1998) *LPS XXIX*. [6] Noble et al. (2007). *Icarus* 192, 629-642. [7] Thompson M. S. and Zega T. J. (2014) *LPS XXXV* Abstract #2834. [8] Thompson, M. S. and Zega T. J. *Microsc. and Microanal.* 20, p. 1672-1673.