

DETERMINING THE OXIDATION STATE OF IRON NANOPARTICLES IN MATURE LUNAR SOIL THROUGH ELECTRON ENERGY-LOSS SPECTROSCOPY. M. S. Thompson¹ and T. J. Zega¹, ¹Lunar and Planetary Laboratory, Department of Planetary Sciences, University of Arizona, 1629 E. University Blvd, Tucson, AZ 85721, mst@lpl.arizona.edu.

Introduction: The alteration of the optical properties of surface grains on airless bodies has been attributed to the production of reduced iron nanoparticles (npFe⁰) in surface soils through the processes known collectively as space weathering [1,2]. In lunar soils, npFe⁰ particles occur both as vapor-deposited rims on surface grains and as inclusions in agglutinitic glass particles produced by micrometeorite impact events [3]. npFe⁰ particles vary in size, averaging 3 nm in diameter in the vapor deposited rims and 7 nm in diameter as inclusions in agglutinitic glass in mature mare soils [4]. The size and distribution of these grains has important implications for the optical characteristics of lunar soil, with grains >10 nm acting to darken and grains <5 nm acting to redden spectral slopes [5,6].

The conditions of formation of these nanoparticles, particularly in the presence of a reducing environment, is important for understanding the nature of space weathering mechanisms across the inner solar system. The oxidation state of Fe in these nanoparticles can provide insight into the processes governing space weathering and the consequent alteration of surface particles. In order to measure the oxidation state of individual npFe⁰ particles in lunar soil, we used electron energy-loss spectroscopy (EELS) coupled to a transmission electron microscope (TEM). Previous analyses [4] employed similar methods but lacked the spatial resolution to resolve and measure individual particles from matrix material. With the introduction of aberration-corrected TEMs, we now have the capability to probe individual nanoparticles. We report here analyses of six isolated particles, both in vapor deposited rims and inclusions in agglutinate grains.

Samples and Methods: We embedded grains from Apollo sample 79221 in epoxy and created ultramicrotomed TEM sections for analysis. Soil sample 79221 is a <1 mm size fraction of a mature (Is/FeO = 81.0) mare lunar soil. The soil is reported as having a high agglutinate content and npFe⁰ particles were abundant as both inclusions in agglutinate grains and in vapor deposited rims.

To complete the EELS analysis we used the 100 keV monochromated and aberration-corrected Nion UltraSTEM at Arizona State University equipped with a Gatan Enfium spectrometer. We used a 0.2 nm probe (convergence semiangle is 30 mrad), 3 mm spectrometer entrance aperture and a collection angle of 45 mrad. We obtained EELS spectra from line profiles for individual particles with an energy resolution

between 200 to 300 meV and a dispersion of 0.1 eV/channel. Dwell time varied for each measurement, ranging between 0.01s/px to 0.5 s/px.

EELS spectra were collected at the Fe L_{2,3} core-loss edge for several nanoparticles and compared to Fe⁰ and Fe²⁺ standards previously acquired [4] to determine the oxidation state of the particles. Prior measurements of Fe standards reveal a ~1.5 eV chemical shift between Fe⁰ and Fe²⁺ [4], which can be used to assess qualitatively the oxidation state of Fe in the npFe.

Results and Discussion: We collected EELS spectra for six individual nanoparticles. Their spectra are shown, along with spectra from Fe²⁺ and Fe⁰, in Fig. 1. The spectra from Fe⁰ and Fe²⁺ exhibit different near-edge structure. Both edges appear asymmetric relative to a Gaussian shape. However, the L₃ edge for Fe²⁺ is asymmetric with a slight shoulder on the high-energy side of the peak, whereas the L₃ edge for Fe⁰ lacks a resolved shoulder. When compared to these reference standards, the L₃ near-edge structure acquired for the nanoparticles appears intermediate between the Fe⁰ and Fe²⁺ end members. These data indicate that each nanoparticle contains a mixture of Fe⁰ and Fe²⁺ oxidation states, in varying proportions. Spectra a-c contain a greater proportion of Fe²⁺ than Fe⁰, as the primary peak is shifted to higher energies and aligned with the Fe²⁺ standard. Spectra e-g contain relatively higher amounts of Fe⁰ with peak positions shifted to lower energies.

Figure 2 shows a typical particle that we analyzed and the location and length of the Fe L_{2,3} line profile (Fig. 1e) acquired from it. The particle occurs on the edge of a soil grain and is likely part of a vapor-deposited rim. Spectra from other particles containing similar near-edge structure are shown as g and f in Fig. 1. Each of these spectra contain a significant contribution from Fe⁰. It also appears there is a lesser but noticeable proportion of their spectra that can be attributed to Fe²⁺ content.

Keller and Clemett [4] predicted that Fe nanoparticles in vapor-deposited rims would contain only Fe⁰, because the Fe condensed from the vapor phase under highly reducing conditions. In comparison, our observations suggest mixed oxidation states within the particles, which could suggest that conditions were not completely reducing during vapor deposition. We note however, that the size of the nanoparticles (<10 nm) is generally smaller than the average thickness of the ultramicrotomed slice at ~60 nm. Although we meas-

ured particles at the very edges of grains where the thinnest regions of the grain occur, we cannot entirely rule out contributions to the Fe L_{2,3} edges from the surrounding material, which may contain oxidized Fe. The contribution of such matrix effects to the spectra from the nanoparticles will need to be taken into account before a more definitive conclusion on their oxidation state(s) can be made.

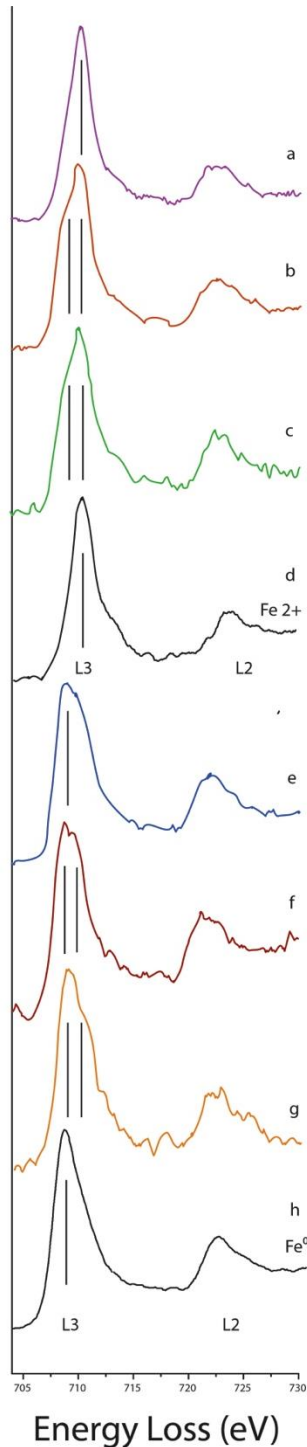


Figure 1: Fe L_{2,3} EELS spectra of six individual nanoparticles (a-c and e-g) and reference spectra for Fe²⁺ (d) and Fe⁰ (h) from [4]. Peak positions are indicated by vertical lines. Peaks with shoulders (most notably b, c, g, f) likely have contributions from both oxidation states.

Fig. 3 shows a typical agglutinate grain and the individual Fe nanoparticles measured within these grains. The spectrum collected from this grain is displayed in Fig. 1c. This particle may have formed in the micrometeorite melting event that generated the agglutinate grain. This Fe may not have entered the vapor phase and as such did not experience the same reducing formation conditions as a vapor deposit, predicting a higher proportion of Fe²⁺ in these grains.

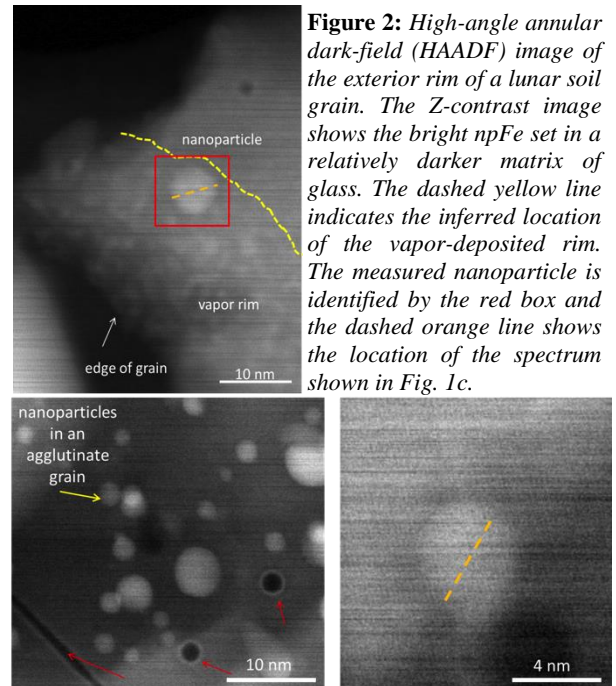


Figure 2: High-angle annular dark-field (HAADF) image of the exterior rim of a lunar soil grain. The Z-contrast image shows the bright npFe set in a relatively darker matrix of glass. The dashed yellow line indicates the inferred location of the vapor-deposited rim. The measured nanoparticle is identified by the red box and the dashed orange line shows the location of the spectrum shown in Fig. 1c.

Figure 3: Left: HAADF image of a typical agglutinate grain interior with several Fe nanoparticles present. Red arrows indicate dark circles and linear features caused by damage from the probe. Right: HAADF image of an individual nanoparticle, showing the transect for the EELS spectrum displayed as c in Fig. 1.

High-resolution and monochromated EELS spectrum imaging has been performed for the first time on Fe nanoparticles from lunar soils. The data suggest a mixture of oxidation states exist within the Fe nanoparticles, which may reflect such conditions during vapor deposition. We plan to test this possibility with future measurements. If confirmed, the results would appear to suggest that space weathering processes may not be able to completely reduce Fe to Fe⁰, despite long exposure times.

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.