

## The Oxidation State of Nanophase Fe Particles Produced by Space Weathering as Revealed Through Aberration-Corrected Transmission Electron Microscopy

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Mineral grains on the surfaces of planetary bodies such as the Moon and near-Earth asteroids are continuously modified by collisional processes such as micrometeorite impacts and radiation processing from solar energetic ions. These processes are collectively known as space-weathering and they alter the microstructural and microchemical characteristics of minerals on planetary surfaces [1]. These features were first identified in lunar soils returned by the Apollo missions e.g., [2].

Modification of crystal chemistry and structure results in changes to optical properties of materials. Space weathering has occurred over the history of the solar system and so has progressively altered surface optical properties of the moon and other airless bodies. Understanding the nature of such alteration and how it occurs is important for determining the mineralogy of planetary bodies from remote sensing data and understanding the processes operating on their surfaces [3].

A primary characteristic of space weathering is the development of iron nanoparticles, termed npFe. The npFe particles are typically <10 nm in size and occur in the amorphous rims of mineral grains and within glassy agglutinate grain interiors. Prior studies have shown that the glassy agglutinates contain Fe in multiple oxidation states [4], but the individual nanoparticles have been assumed to contain only metallic Fe, i.e., Fe<sup>0</sup>.

Here we use electron energy-loss spectroscopy (EELS) coupled to a monochromated and aberration-corrected transmission electron microscope (TEM) to analyze the oxidation state of npFe particles in several lunar soils. Understanding the oxidation state of Fe in the npFe can provide insight into the formation conditions of the nanoparticles and the evolution of space weathering processes on airless body surfaces.

We embedded <1 mm grains of three Apollo lunar soils in low-viscosity epoxy and prepared them for TEM analysis via ultramicrotomy. EELS analysis was performed with the 100 keV monochromated and aberration-corrected Nion UltraSTEM at Arizona State University, equipped with a Gatan Enfium spectrometer. We used a convergence semi-angle of 30 mrad, a 0.2 nm probe size, 3 mm spectrometer entrance aperture, and a collection angle of 45 mrad. With the monochromator on, we achieved an energy resolution between 200 to 300 meV. We measured individual nanoparticles via line profiles with a 0.1 eV/channel dispersion and dwell times between 0.01s/px to 0.5 s/px.

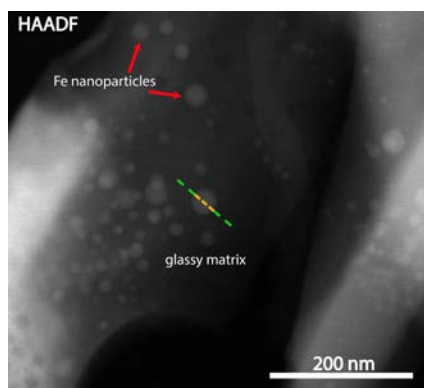
EELS spectra were collected at the Fe L<sub>2,3</sub> core-loss edge and were compared to metal (Fe<sup>0</sup>), wüstite (FeO), and hematite (Fe<sub>2</sub>O<sub>3</sub>) standards for reference to Fe<sup>0</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>, respectively. We quantified the oxidation state of Fe in the npFe particles using a flux-weighted linear, least-squares fitting routine programmed in MatLab. Fitting over the L<sub>3</sub> edge, which exhibits edge-onset and multiplet structure that is indicative of oxidation state, e.g., [5], the routine generated Fe<sup>0</sup>/Fe<sub>total</sub>, Fe<sup>2+</sup>/Fe<sub>total</sub>, and Fe<sup>3+</sup>/Fe<sub>total</sub> ratios for each measured spectrum.

We acquired line profiles from >120 individual particles, over 40 from each of our three samples, as shown in Figure 1. An example of an extracted spectrum is shown in Figure 2. Spectral processing included removal of background and deconvolution of the zero loss peak using the Fourier-Ratio method. Once the core-loss edge was isolated from the background continuum (using a straight line from 702 to 725 eV), the Matlab code was used to simulate the experimental spectra from the standards. We quantified each fit by assessing the residual intensity, expressed as  $R^2$ , after subtraction of the simulation from the experimental spectrum. Fits having an  $R^2 > 0.9$  are presented here.

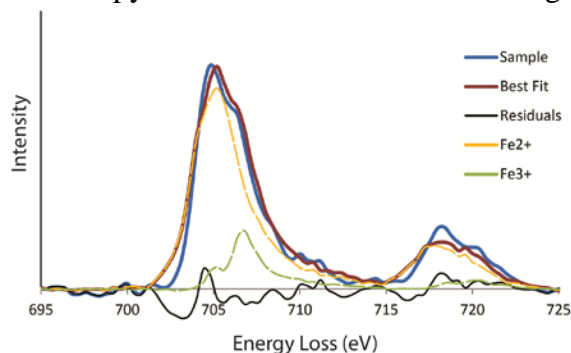
The EELS data reveal that Fe occurs in multiple oxidation states in these lunar soils. The immature soil, which is the sample with the shortest exposure time to interplanetary space, contains nanoparticles composed primarily of  $\text{Fe}^0$ . The submature soil, which is the sample with intermediate exposure time, contains nanoparticles with mixtures of  $\text{Fe}^0$  and  $\text{Fe}^{2+}$  in varied ratios. Moreover, the EELS spectrum images show that several individual particles in this submature soil contain an oxidized ( $\text{Fe}^{2+}$ ) rim surrounding a reduced  $\text{Fe}^0$  core. In comparison, the most mature sample contains nanoparticles composed of mixtures of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Structural measurements were used to corroborate the EELS data, e.g., Fig. 3. These results indicate there is increasing oxidation of Fe in the nanoparticles in soils with increasing maturity. This trend suggests that space weathering products such as Fe nanoparticles are evolving microchemically and microstructurally after their formation. The mechanisms for oxidation of the nanoparticles and the implications for reflectance spectroscopy will be discussed at the meeting.

### References:

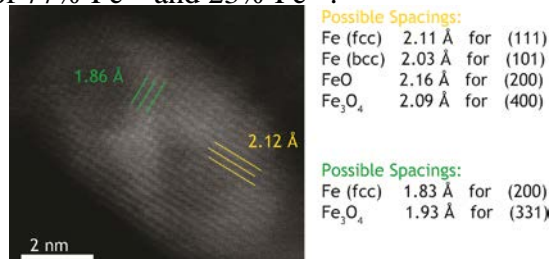
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 [4] Keller L. P and Clemett S. J. *Lunar and Planetary Science Conference Proceedings* (2001), p. 2097.  
 [5] Zega T. J. *et al*, *American Mineralogist* **88** (2003), p. 1169.



**Figure 1:** High-angle annular dark field (HAADF) image of bright npFe particles in a darker glassy matrix. The green dashed line represents the locations where matrix spectra were collected; orange shows those of the nanoparticle spectra.



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



**Figure 3:** HRTEM image of a nanoparticle in lunar soil sample 79221. Spacing measurements and possible identifications are shown for two directions.