Aberration-Corrected STEM Characterization of Glass Analogs for Regolith Grains on Airless Bodies

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Space weathering of regolith particles on airless bodies leads to formation of nanophase Fe metal and amorphization of silicate minerals in the top ~100 nm of the grain surfaces [1]. Such changes can have a drastic effect on the optical properties of these bodies, in effect masking their true mineralogy and composition. Making a quantitative link between the atomic-to-nanoscale effects on the particles, and the macroscale properties is essential for maximizing the science return from exploration of airless bodies and returned samples. As part of the RIS4E collaboration, we are performing aberration-corrected scanning transmission electron microscopy (STEM) on analog samples to determine the atomic-scale structural and chemical effects of space weathering. We will utilize the new Nion UltraSTEM 200 currently being installed at the Naval Research Laboratory, which will permit single atom detection for energy dispersive spectroscopy (EDS) and spectral resolution of 0.3 eV for electron energy loss spectroscopy (EELS). These nanoscale measurements will be coordinated with synchrotron X-ray absorption near-edge structure (XANES) spectroscopy of the same samples to extend the analyzed volume to the macroscale.

Background

One effect of space weathering is the reduction and mobilization of Fe to form nanoscale beads within a ~100 nm amorphous surface layer [1, 2]. Aberration-corrected TEM is a perfect technique to characterize these changes with both high spatial and spectral resolution. As the oxidation state of Fe changes, so do the energy levels of the valence *d*-shell electrons. By measuring the amount of electrons in the transmitted beam that lose energy as they interact inelastically with the sample, known as electron energy-loss spectroscopy (EELS), this shift in Fe oxidation state can be directly observed [3], as shown in **Figure 1**. Therefore, this measurement can be used as both a proxy for the amount of space weathering in the sample (as Fe is reduced to Fe^0) and as an indicator for changes in infrared spectroscopy of the surfaces of airless bodies.

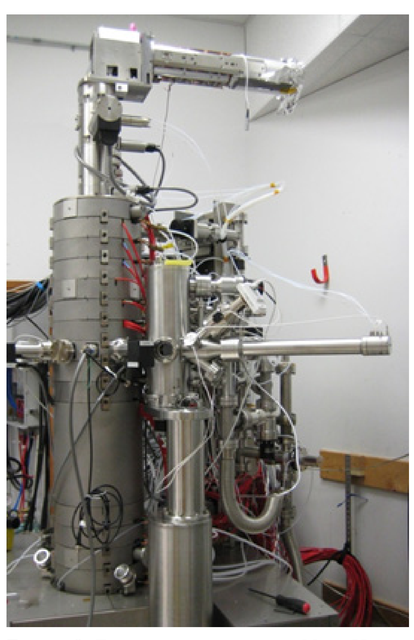

Figure 2. Exposed column of the Nion UltraSTEM 200 under construction at the Nion factory, April 2014.

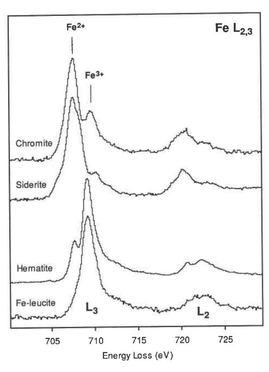

Figure 1. Fe L-edge EELS from various minerals with different Fe valence oxidation states. Figure taken from [3].

The energy splitting between the Fe^{2+} and Fe^{3+} peaks is 1.7 eV, which is not resolved by most EELS-enabled TEM instruments with energy resolutions of ~1 eV. However, the new Nion UltraSTEM 200 [**Figure 2**], currently being installed at NRL, will have an energy resolution of 0.3 eV, and will be used to independently measure the ratio of Fe valence states in both mineral standards, regolith analogs, and returned samples.

Samples and Methods

The initial sample analog suite consists of 132 glasses synthesized with chemical compositions matching all major igneous rock types under four different oxygen fugacity conditions. For our preliminary examination, we selected six basaltic glasses synthesized under atmospheric oxygen fugacity. The bulk Fe^{2+}:Fe^{3+} ratio has been measured for three of these samples by Mossbauer spectroscopy [**Table 1**].

Table 1. Glass samples in this study

Sample	Rock Type	$t_{microtome}$	$t_{measured}$	wt.% Fe	% Fe^{3+}
BAS-1	Basalt	70 nm	110 nm	7.07	87
BAS-2	Basalt	40 nm	57 nm	10.54	--
BAS-3	Basalt	40 nm	84 nm	11.66	89
BAS-4	Basalt	40 nm	65 nm	10.24	85
BAS-5	Basalt	40 nm	235 nm	10.14	--
BAS-6	Basalt	60 nm	93 nm	11.24	--

Single grains (< 1 mm) were embedded in epoxy and sectioned using an ultramicrotome with a 45° diamond knife and placed on Quantifoil holey carbon TEM grids. Since the UltraSTEM requires very thin samples, 30-40 nm sections were desired, rather than typical 70-100 nm sections. Because the glasses are brittle, all of the sections contained "chattered" shards [**Figure 3**], although this is acceptible for the present analog study. Thinner sections may be achievable using a 35° diamond knife.

Preliminary analyses were performed with a JEOL 2200FS TEM at NRL. This microscope includes an in-column imaging filter, which can be used to disperse transmitted electrons according to their energy, generating EELS spectra. The cold field emission electron gun in this microscope gives an achievable energy resolution of 1.0-1.2 eV. The EELS resolution was measured by the full-width half-maximum of the zero-loss peak as 1.19 eV [**Figure 4**]. Spectra were acquired using a 250 eV/mm dispersion field on the in-column filter and an entrance aperture limiting the convergence semi-angle to 10 mrad (giving an effective analysis spot size of 150 nm). Smaller spot sizes are achievable by aquiring spectra at higher magnification.

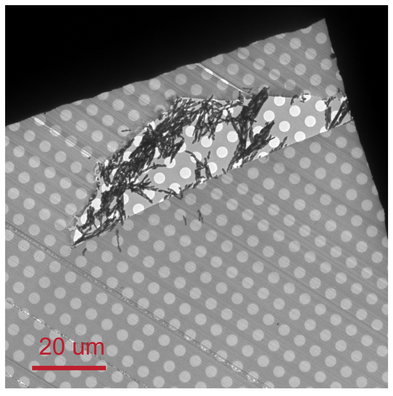

Figure 3. TEM image of sample BAS-3. Although the glass is chattered and dispersed, there is enough material spanning holes in the support film to perform EELS analysis.

Valence State Measurement

All six basaltic glass samples contain similar Fe $L_{2,3}$ absorption edge features in their EELS spectra [**Figure 5**]. The position of the L_3 peak is located at higher energy loss (~709 eV) indicating a predominance of Fe^{3+}. Some intensity is present at lower energy loss (~708 eV) due to Fe^{2+}, but the spectral resolution of the measurement is low enough that the two peaks cannot be robustly distinguished (compare with the hematite spectrum in **Figure 1**). Using the new Nion UltraSTEM, the two peaks can be resolved, and the peak splitting can be modeled with two Gaussian distributions, giving a measurement of the local Fe oxidation state at the nm scale.

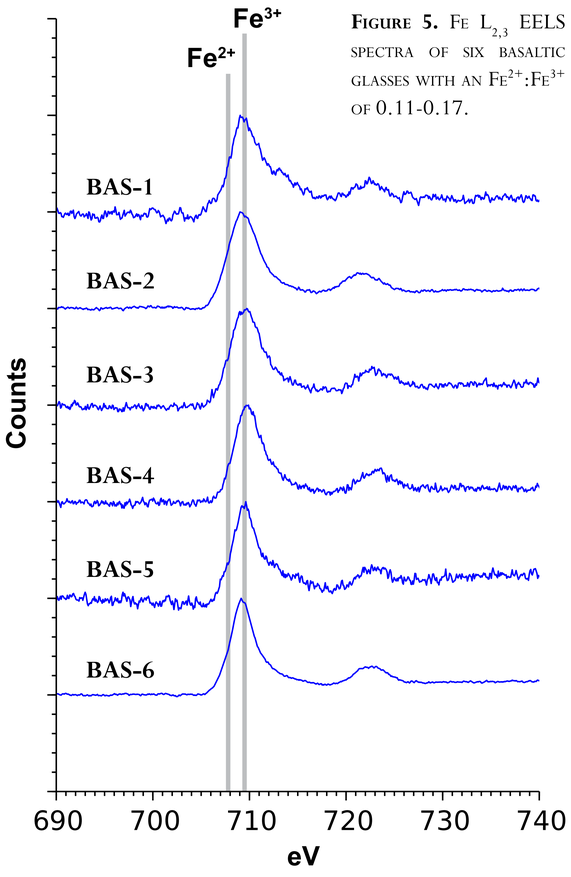

Figure 5. Fe $L_{2,3}$ EELS spectra of six basaltic glasses with an Fe^{2+}:Fe^{3+} of 0.11-0.17.

Sample Thickness Measurement

Actual thickness of individual shards of ultramicrotome samples can vary considerably. Thickness was estimated by acquiring a low-loss EELS spectrum including the zero-loss, unscattered beam [**Figure 4**]. The ratio of the total intensity of the complete spectrum I_t to the intensity in the zero-loss peak I_0 is related to the thickness of the sample t and the average "mean free path" λ.

$$t/\lambda = \ln(I_t/I_0)$$

The mean free path length of a material can be estimated from its bulk composition and microsope parameters [4]. For basaltic glass under illumination by 200 keV electrons, λ = 134 nm, which gives sample thicknesses slightly larger than the expected thickness [**Table 1**]. However, any thickness less than the average mean free path will be adequate for EELS analysis.

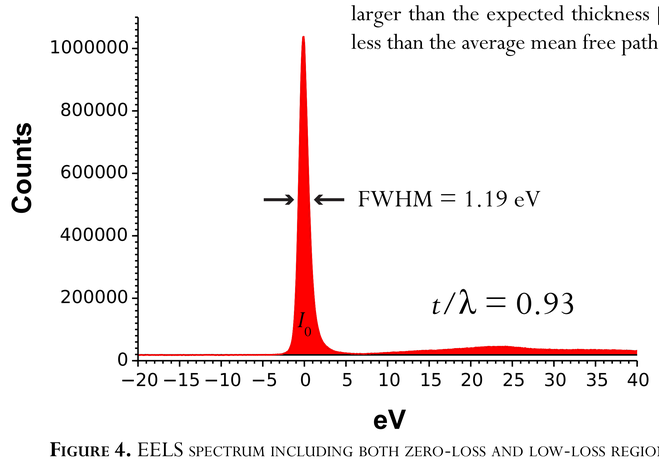

Figure 4. EELS spectrum including both zero-loss and low-loss regions.

Electron energy-loss spectroscopy with the new aberration-corrected Nion UltraSTEM 200 will allow direct and accurate measurement, at the sub-100 nm scale, of the oxidation state of Fe in synthetic igneous glasses, which are analogs for amorphous surfaces on space-weathered regolith particles. This technique will be applied to mineral standards, artificially space-weathered samples, and lunar/asteroidal particles.

References:
[1] Keller and McKay (1997) *Geochimica et Cosmochimica Acta* 61, 2331-2341.
[2] Thompson and Zega (2014) *Lunar and Planetary Science Conference XLV*, abstract 2834.
[3] Garvie, Craven, and Brydson (1994) *American Mineralogist* 79, 411-425.
[4] Egerton (1992) *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd ed., Plenum Press.