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Aberration-Corrected STEM-EELS Measurements in Fe-bearing Silicate Glasses

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Space-weathered materials exhibit a wide range of complex nanometer-scale features caused by solar wind irradiation and micrometeorite impacts, such as nanophase iron metal particles ($npFe^0$) and amorphous rims [1,2]. The high brightness and focused probe of the aberration-corrected STEM enable fast acquisition of data and low detection limits in EELS, and aberration-corrected STEM measurements of the oxidation state of individual nanoparticles have been reported [3]. However, the highly focused beam can cause significant damage to sensitive samples, including breaking bonds, which can change valence or coordination states of atoms, or cause loss of material [4]. Returned space-weathered planetary samples are of limited availability. Thus, prior determination, on analog samples, of the best experimental conditions, such as accelerating voltage, beam current, scan speed, and exposure time, is necessary for obtaining high-quality data with minimal beam damage to the returned samples.

We have a large number of homogenous, well-characterized (e.g., using microprobe, x-ray diffraction, Mössbauer, x-ray absorption spectroscopy), synthetic glasses prepared for EELS measurement. The glasses range in composition from komatiite to rhyolite (43-78 wt% SiO_2) and have been equilibrated in atmospheres buffered at iron-wüstite (IW), quartz-fayalite-magnetite (QFM), in air, and in CO_2. Small pieces of each sample have been embedded in epoxy and microtomed, then placed on Quantifoil carbon support film TEM grids. The thinnest regions (usually less than ~50 nm) of the glass shards are used in the measurements. To collect EELS data, we use PRISM, the NION UltraSTEM at the Naval Research Laboratory equipped with a Gatan Enfinium ER EEL spectrometer (0.3 eV energy resolution) at a range of conditions including 60 kV, 100 kV and 200 kV, and 0.01-1.5 nA.

The glass samples measured here are easily affected by the electron beam, both from knock-on damage and radiolysis; for measurements at 200 kV, knock-on damage and field-induced migration and phase separation occur quickly [5]. Scans shown here were done using a 40 pA probe current and dwell times between 0.001 and 0.1 s dwell for core-loss measurements. Depending on total electron dose and dose-rate, an O pre-peak at 528 eV appears, then disappears at higher dose (Fig. 1a). Sequential scans (0.01 s dwell) over the same region causes the Fe L_2 peak to shift from 706 eV to slightly higher energy, indicating oxidation from Fe^{2+} to Fe^{3+} (Fig. 1b). A peak at ~5 eV related to the presence of C π^* transitions [6] in the sample decreases (Fig. 1c), and loss of C could cause the oxidation of the Fe. Fig. 2 illustrates the changes over regions with different acquisition parameters; integrated signals for the final scan at 0.001 s/pixel show correlations between O pre-peak intensity, Fe concentration and low-loss C π^* intensity. Additional measurements at lower accelerating voltages (60 kV and 100 kV), where radiolysis should dominate over knock-on damage and carbon losses may be minimized, are planned for comparison.

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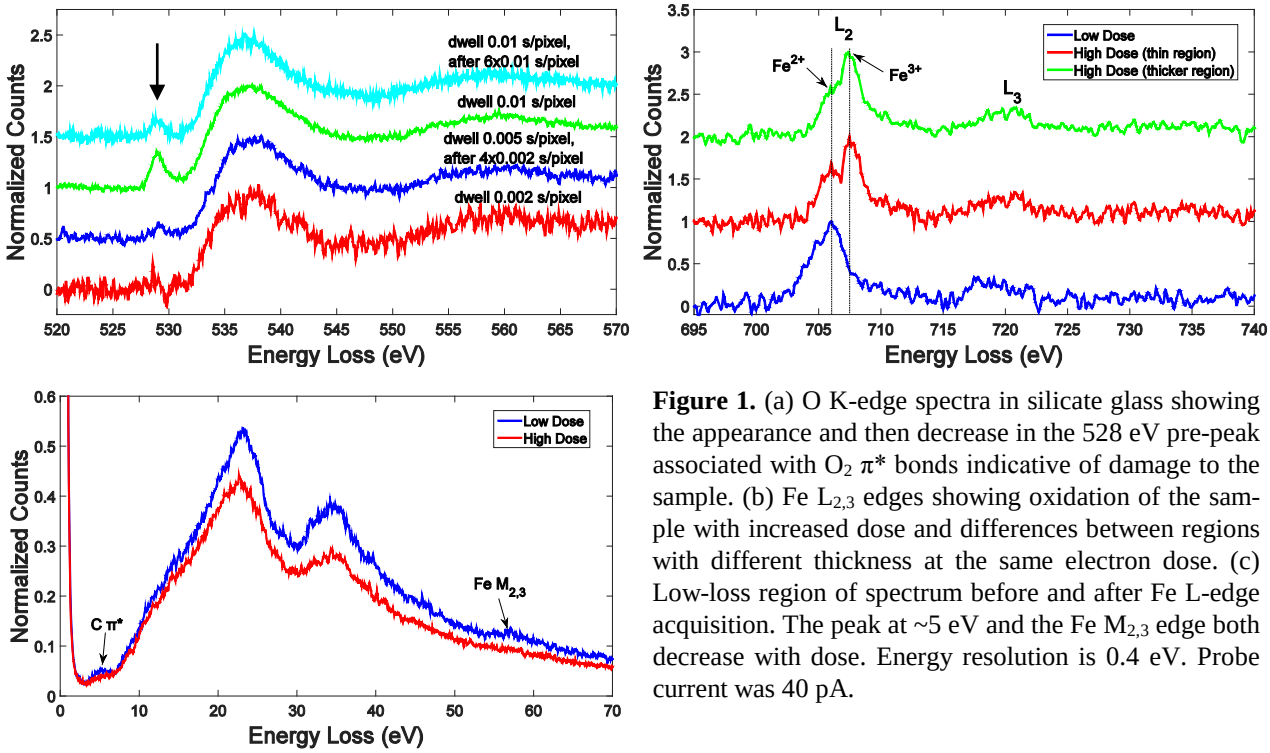

Figure 1. (a) O K-edge spectra in silicate glass showing the appearance and then decrease in the 528 eV pre-peak associated with O_2 π^* bonds indicative of damage to the sample. (b) Fe $L_{2,3}$ edges showing oxidation of the sample with increased dose and differences between regions with different thickness at the same electron dose. (c) Low-loss region of spectrum before and after Fe L-edge acquisition. The peak at ~5 eV and the Fe $M_{2,3}$ edge both decrease with dose. Energy resolution is 0.4 eV. Probe current was 40 pA.

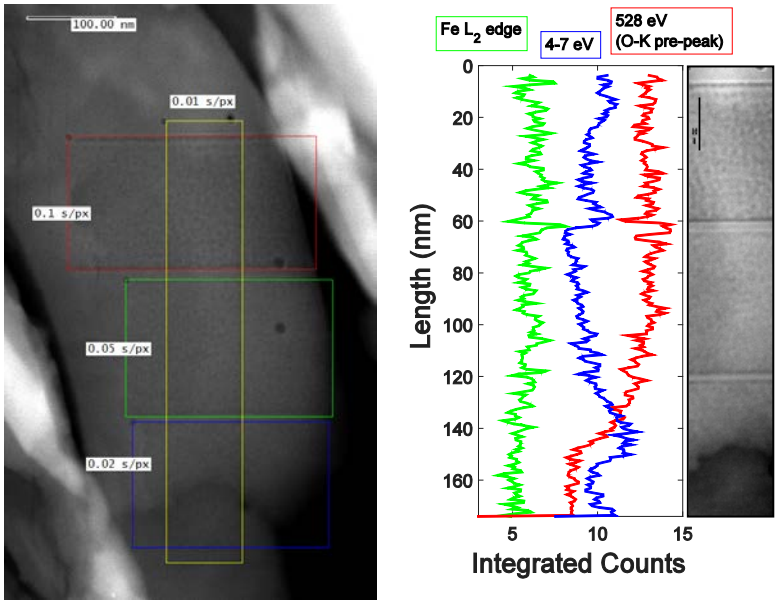

Figure 2. (a) HAADF image of the silicate glass sample showing Spectrum Imaging regions. (b) Integrated line profiles for the Fe L_2 edge (705-708 eV), C c (4-7 eV), and the O K-edge pre-peak at 528 eV. The final scan was done with a dwell of 0.01 s/px. The small regions between the scanned areas have increased Fe and a larger π^* peak. The region scanned at 0.02 s/px also has a larger π^* peak prior to the thickness change. The HAADF image to the right is from the yellow box in (a) and shows phase separation in the regions with the highest electron doses.

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