

MEASUREMENT OF FE OXIDATION STATE USING ABERRATION-CORRECTED SCANNING TRANSMISSION ELECTRON MICROSCOPY. K. D. Burgess¹, R. M. Stroud², B. T. De Gregorio³, M. D. Dyar⁴, and M. C. McCanta⁵, ¹ASEE Postdoctoral Fellow, Naval Research Laboratory, Washington, DC 20375 (kate.burgess.ctr@nrl.navy.mil), ²Naval Research Laboratory, Washington, DC 20375, ³Nova Research, Inc., Alexandria, VA 22308, ⁴Mount Holyoke College, South Hadley, MA 01075, ⁵Tufts University, Medford, MA 02155

Introduction: Space-weathered materials exhibit a wide range of complex nanometer-scale features, such as nanophase iron metal particles (npFe⁰), that contribute to the over-all alteration and changes in optical and spectral characteristics [1,2]. Analysis of such materials requires specialized techniques, and the development of electron energy-loss spectroscopy (EELS) in the aberration-corrected scanning transmission electron microscope (STEM) is leading to significant improvement in both the spatial and energy resolution available for the analysis of space-weathered materials. Aberration-corrected STEM measurements of the oxidation state of individual nanoparticles have been reported [3] and here are used to examine a suite of silicate glasses with varying Fe³⁺ contents [4].

Fe L-edges in EELS spectra are caused by the excitation of inner shell (2p) electrons to the unoccupied 3d orbitals. EEL spectra of Fe²⁺- and Fe³⁺- bearing minerals show distinct edge shapes and chemical shifts that depend on the oxidation state and the symmetry and coordination of the atom site. The shape of the spectrum obtained from mixed-valence materials can be approximated as a linear combination of end-member oxidation states. Thus, the oxidation state of the unknown material can be determined by a linear deconvolution of the observed L-edge [5-7]. EELS has been successfully used in Fe²⁺-Fe³⁺ valence determinations for a number of minerals, including those in meteorites [8-12]. However, because energy shifts are known to occur due to differences in chemistry as well as crystal structure, accurate interpretation of the oxidation state requires a detailed library of standard spectra at the same (or similar) energy resolution for use in the deconvolution.

The high brightness and focused probe of the aberration-corrected STEM enable fast acquisition of data and low detection limits in EELS. However, the highly focused beam can cause significant damage to sensitive samples, including loss of material or breaking of bonds, which can change valence or coordination states of atoms [13]. Returned planetary samples are of limited availability, making prior determination of the best experimental conditions, such as accelerating voltage, beam current, scan speed, and exposure time, necessary for obtaining high-quality data with minimal beam damage to the sample.

Studies of oxidation state utilizing EELS require robust measurement of end-member standards with well-characterized oxidation states and similar atom site symmetries to the unknown. Work is ongoing in our group to prepare well-characterized synthetic and natural samples for measurement in the STEM in order to determine precisely the effects of composition and structure variations in common minerals and create the reference spectra required for quantitative measurements. The present study focuses on silicate glasses.

Methods: More than 200 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% SiO₂) and have been equilibrated in atmospheres buffered at iron-wüstite (IW), quartz-fayalite-magnetite (QFM), in air, and in CO₂; a full discussion of their characterization is given in [4].

Small pieces of each sample were 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 were used in the measurements.

To collect EELS data, we use PRISM, the NION UltraSTEM at the Naval Research Laboratory equipped with a Gatan Enfimum ER EEL spectrometer (0.3 eV energy resolution) at a range of conditions including 60 kV, 100 kV and 200 kV, and 0.3-1.5 nA. Energy resolution and sample thickness are measured using the zero-loss and low-loss peaks from each sample region of interest.

Results and Discussion: The composition-specific valence end-member spectra produced by our measurements will be broadly useful in characterizing the oxidation state of terrestrial, planetary, and synthetic materials. Use of reference spectra in linear deconvolution of mixed-valence spectra results in the highest level of precision for oxidation state determination among commonly used methods [9].

The spectra displayed in Figure 1 are averages of several measurements from each of two basalt glass samples. Although containing some fixed noise, the data show a clear distinction between the two glasses equilibrated at different oxidation fugacities. We have begun assessing the samples for calibration of an oxi-

ation scale for silicate glasses, and it will be important to recognize the features that change with composition as well as those that follow oxidation state. Figure 2 shows the ratio of the height of a Gaussian curve centered at ~ 711 eV, assigned to Fe^{3+} , to the curve at ~ 708 eV (Fe^{2+}), fitted using a least squares method. They demonstrate the difference between samples with varying amounts of Fe^{2+} and Fe^{3+} . While there is overlap in the peak height ratio for the glasses at different buffers, there are also several high values for the oxidized glass equilibrated in air, indicating that the glass is more oxidized but is damaged quickly in the electron beam.

Glass samples are easily affected by the electron beam, both from knock-on damage and radiolysis. For these measurements at 200 kV, knock-on damage occurs quickly and a stationary beam easily creates holes in the sample. The precise effect of the damage is not known, but it likely contributes to the overlap of the peak ratios between the samples and the broad range in ratios within a nominally homogeneous sample. The damage here appears to reduce the glass samples. However, mechanisms of both oxidation [8,14] and reduction [15,16] due to effects of the electron beam have been measured in transition metal-bearing materials. Additional measurements at lower accelerating voltages (60 kV and 100 kV), where radiolysis should dominate over knock-on damage, are planned for comparison.

Both energy resolution and signal to noise are improved by the use of thin samples with uniform thickness over the region of measurement. Future work will explore focused ion beam (FIB) preparation of samples for EELS measurements to assess ion beam damage during preparation of site-specific samples versus our ability to control sample thickness and prepare adequately thin specimens.

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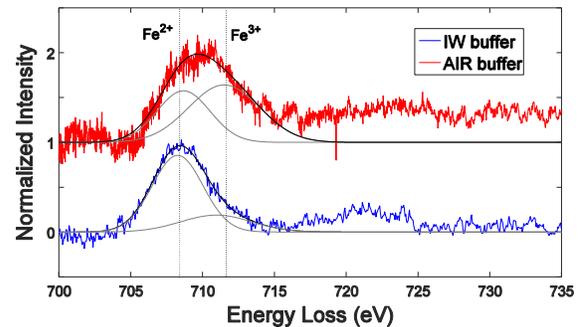


Figure 1. EEL spectra of two basaltic glasses equilibrated in air (red) and at the IW buffer (blue) acquired at 200 kV. The basalt glass equilibrated at IW has a much lower proportion of Fe^{3+} than the glass run in air. Spectra have been normalized and offset for clarity. The measured energy resolution is 0.45 eV.

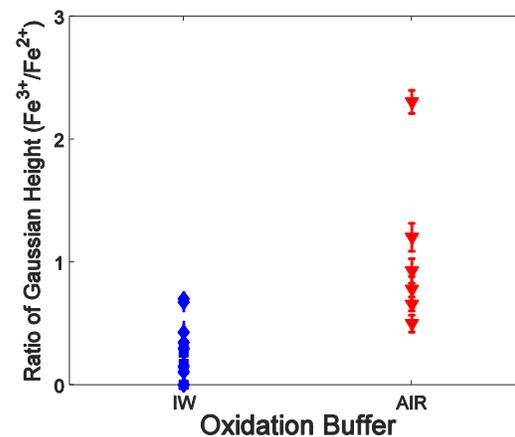


Figure 2. Ratio of height of two Gaussian curves fitted to the Fe L_3 edge, centered at ~ 708 eV and ~ 711 eV. In Mossbauer measurements for these glasses, the % Fe^{3+} is ~ 87 and ~ 13 for the samples equilibrated in air or at the IW buffer, respectively. The broad range in peak height ratios seen here indicates significant beam damage, although the air samples extend to more oxidized values. Error bars are standard deviation of the fit residual.