Phyllosilicates, phyllomanganates, and iron oxyhydroxides are redox active and play a major role in the geochemistry of contaminated soils and waters. Our recent work has centered on using EELS to probe valence of Fe, Mn, and U in natural samples to deduce reaction mechanisms of toxic metals in experimental systems.

Actinide valence determination has previously been based on determination of variation in $M_{4.5}$ white-line ratios in second-difference spectra [1]. We now use background corrected spectra; however, the small scattering cross-sections and high energy losses of the $M_{4.5}$ edges of U make the work difficult and particularly susceptible to problems associated with beam damage. Uranium $O_{4.5}$ edges would seem to offer an attractive alternative, but overlap with Si $L_{2.3}$ renders them impractical in many geological materials. Alternatively, U $N_{6.7}$ edges have no critical overlaps and are less affected by screening complications. Uranium $N_{6.7}$ have been shown by XPS to have fine structure sensitive to valence and bonding environment. In U $N_{6.7}$ EELS spectra, major challenges include correcting for the large background contribution from the C-K edge and resolving the fine structure. New generation spectrometers and monochromated electron guns promise significant breakthroughs for the use of EELS in actinide research.

We have also followed previous work [2, 3, 4] on calibrations of $L_{2.3}$ intensity ratios for Fe and Mn valence and largely verified the “universal curve” of van Aken and Liebscher [4]. Deviations at the extremes of the calibration suggest inter-laboratory differences are to be expected. As pointed out by Garvie, et al. [5], transition metal valence can reduce or increase with beam damage. In beam altered biotite, maximum Fe$^{3+}/(\Sigma\text{Fe})$ is 2/3, corresponding to oxiannite (K(Fe$^{2+}$Fe$^{3+}$)$_2$(Si$_3$Al)O$_{12}$) and supporting the conclusion of Garvie et al. [5] that deprotonation is associated with oxidation. Like Fe, many workers have shown that the $L_{2.3}$ intensity ratio for Mn correlates with mean oxidation state. Unlike Fe, however, Mn in soil minerals may exist in three valences. A calibration curve to determine mean oxidation state of Mn in a range of minerals is proposed. ELNES fingerprinting is required, however, to identify the specific species accounting for the mean valence.

Nitrogen in clay minerals is associated with the occurrence of gas and oil in both source and reservoir shales. EELS of clay minerals allows simultaneous collection of K-L and N-K edges to establish the K/N ratio. Quantification of N can then be calculated from an EDS analysis of the K. This affords the first direct method of N analysis in minerals on the nm scale.

References