Nanoscale Measurement of Manganese Valence in Mn-oxides

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Manganese (Mn) oxides are among the strongest mineral oxidants in the environment and impose significant influence on mobility and bioavailability of redox-active substances, such as arsenic, chromium, and pharmaceutical products, through oxidation processes. Oxidizing potentials of Mn oxides are determined by Mn valence states (II, III, IV). In this study, the effects of beam damage during Electron Energy-Loss Spectroscopy (EELS) measurement in the Transmission Electron Microscope have been investigated to determine the "safe dose" of electrons [1]. Time series analyses demonstrate that some Mn-oxide minerals experience a reduction of Mn valence during intense or prolonged electron beam exposure. We have determined the safe dose fluence (electrons/nm^2) for todorokite (10^6 e/nm^2), acid birnessite (10^5), triclinic birnessite (10^4), randomly-stacked birnessite (10^3) and δ-MnO_2 (<10^3) at 200 kV. The results show that precise measurements of the mean Mn valence can be acquired by EELS if proper care is taken. EELS anayses are shown to be as precise as chemical titration analyses, but with twelve orders of magnitude less volume (~5 attoliters, 10^{-18}).

The value of EELS analysis is demonstrated by two applications: 1) Analysis of run products from experiments reacting 1 mM dissolved Mn^{2+} with δ-MnO_2 in the presence of other cations (Na^+, Ca^{2+} Zn^{2+} and Ni^{2+},). These experiments, designed to determine reaction rates of the reduction of Mn(IV) in poorly-crystalline Mn-oxides by Mn^{2+}, produce mixtures of phases with variable mean valence. Unlike bulk chemical tiration or X-ray absorption spectroscopy, EELS, in concert with energy-dispersive X-ray analysis (EDS), can determine the individual phase valences and their mineral formulae (including other divalent cations). 2) Analysis of todorikite in a Mn-oxide crust from the Pacific ocean floor. This natural todorokite includes Fe(II,III) and other minor elements. EELS is capable of measuring the mean valence for both Mn and Fe, while simulaneously acquiring quantitative EDS analyses.

[1] Livi et al. (2012) *Environmental Science & Technology* **46,** 970-976.