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Manganese valence imaging in Mn minerals at the nanoscale using STEM-EELS

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ABSTRACT

Electron energy loss spectroscopy (EELS) was used with scanning transmission electron microscopy (STEM) to quantify the average Mn valence in natural minerals at the nanometer scale. A method was developed to calibrate the energy-loss scale accurately, providing a comparison between STEM-EELS and the X-ray absorption spectroscopy methods that investigate the *L*-edge chemical shift as Mn valence changes. The chemical-shift measurements were consistent with data reported by previous researchers from both X-ray and electron energy-loss spectroscopy. The L_3/L_2 white-line intensity ratios also were consistent with previous work. A calibration curve for Mn valence was produced using the L_3/L_2 white-line intensity ratios from measurements of synthetic standards. The average Mn valence was determined because it is not possible to distinguish Mn^{3+} from mixtures of Mn^{2+} and Mn^{4+} using either method. The white-line intensity method was implemented in automated software that allows for rapid processing of point spectra, and 1-D and 2-D spectrum images. Point analyses of two natural pyrolusite samples indicated a Mn valence of 4.0, and point analyses of romanechite and manganite gave values of 3.8 and 3.4, respectively. An interface between braunite and bementite was used to illustrate 1-D and 2-D spectrum-imaging capabilities. The measured valence of Mn in the braunite and bementite was 2.9 and 2.0, respectively; both consistent with theoretical values. The braunite-bementite sample demonstrated the heterogeneity of Mn valence common to natural minerals and the advantages of acquiring quantitative valence information in a known spatial context.

Keywords: Electron microscopy, electron energy loss spectroscopy (EELS), scanning transmission electron microscopy (STEM), spectrum imaging, valence mapping, manganese, Mn valence, pyrolusite, manganite, romanechite, braunite, bementite