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Determination of manganese valence states in (Mn^{3+}, Mn^{4+}) minerals by electron energy-loss spectroscopy

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Abstract

Various manganese valence quantification methods using manganese $L_{2,3}$ and oxygen K electron energy loss near-edge spectra (ELNES) were applied to determine the relative portions of individual valence state in a mixed (Mn^{3+}, Mn^{4+}) valence system. Multiple linear least-squares (MLLS) fitting of Mn $L_{2,3}$ ELNES using reference spectra and Gaussian peak fitting of Mn L_3 edge are newly developed and the feasibility of these methods was tested on a set of cryptomelane minerals with different valence states. The selection of appropriate standards is crucial to the success of the MLLS method. The O K-edge structures for manganese oxides can provide valuable guidance in the selection of appropriate reference spectra for quantitative determination of Mn valence state. Gaussian peak fitting, however, failed to determine the Mn valence for (Mn^{3+}, Mn^{4+}) minerals due to the small separation between the primary L_3 peaks from Mn^{4+} and Mn^{3+} valence. As to the methods based on calibration curves, the energy difference between Mn L_3 and oxygen K, i.e., ΔE (L_3-O K) vs. valence, is the most valence-sensitive method in the range of Mn^{3+} and Mn^{4+} and yields good agreement with the actual values.

Keywords: EELS, valence determination, manganese oxides, cryptomelane