

## Quantification of Manganese Valence States Using Mn L<sub>2,3</sub> Electron Energy-Loss Near-Edge Spectra

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Manganese orbital configuration, [Ar]4s<sup>2</sup>3d<sup>5</sup>, allows for a wide variety of possible valence states. Among the various oxidation states, ranging from Mn<sup>3-</sup> through Mn<sup>0</sup> to Mn<sup>7+</sup>, the most prevalent in nature are Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup>. EELS in a transmission electron microscope has been widely used to determine the oxidation state and bonding environment of metals [1,2]. In this paper, we demonstrate several independent methods, including calibration curves generated from standards of known valence, Gaussian peak fitting method, and linear least squares method, which have been used in Fe system (Fe<sup>2+</sup>, Fe<sup>3+</sup>) for quantification of the Fe valence [2,3], and test their feasibility for the quantification of Mn valence using the observed Mn L<sub>2,3</sub> ELNES.

The EELS experiments were performed with a Philips/FEI CM300-FEG TEM equipped with a Gatan Imaging Filter (GIF 200). The field emission gun operating at 297 kV produces a typical energy width of 1 eV measured as full width at half maximum (FWHM) of the zero-loss peak at nominal 0.2 eV/channel energy dispersion and 2mm GIF entrance aperture.

The multiple linear least squares method yields the best results for the quantification of manganese valence in any energy-loss range. The quality of the fitting depends on the selection of appropriate reference spectra for Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup>. It seems that the crystal structure and Mn site symmetry have only minor effects on the shapes of the Mn<sup>2+</sup> and Mn<sup>3+</sup> L<sub>3</sub> edges. However, different polymorphs of MnO<sub>2</sub> display quite different L<sub>3</sub> edge structures for Mn<sup>4+</sup> (Fig.1), which consequently gives different results for the mathematical fitting. Here we rely on manganese O K edges (Fig.2) to select the optimum reference spectra, since they are especially sensitive to the octahedral arrangement in MnO<sub>2</sub> polymorphs. The O K spectra, however, hardly vary with different amounts of Mn<sup>3+</sup> and Mn<sup>4+</sup> in cryptomelane, for example. It turns out that using pyrolusite (1×1) for Mn<sup>4+</sup> reference spectra is more appropriate for fitting cryptomelane with its 2×2 tunnel structure than using ramsdellite (1×2) (Figure 3). Further application to Mn oxides with different tunnel sizes, such as romanechite (3×2), todorokite (3×3), and woodruffite (3×4), will be investigated in the near future.

### References:

- [1] L. A. J. Garvie and A. J. Craven, *Phys Chem Minerals*. 21 (1994)191.
- [2] P. A. van Aken and B. Liebscher, *Phys Chem Minerals*. 29 (2002)188.
- [3] C. C. Calvert et al., *J Electron Spectrosc*. 143 (2005) 173.

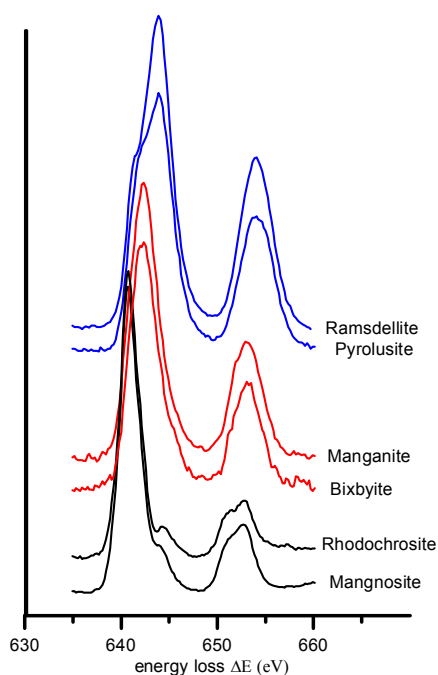


Fig.1. Series of EEL spectra illustrating the structures of Mn L<sub>2,3</sub> edges in Mn-containing minerals with with a single valence state: 2+, 3+, and 4+, respectively.

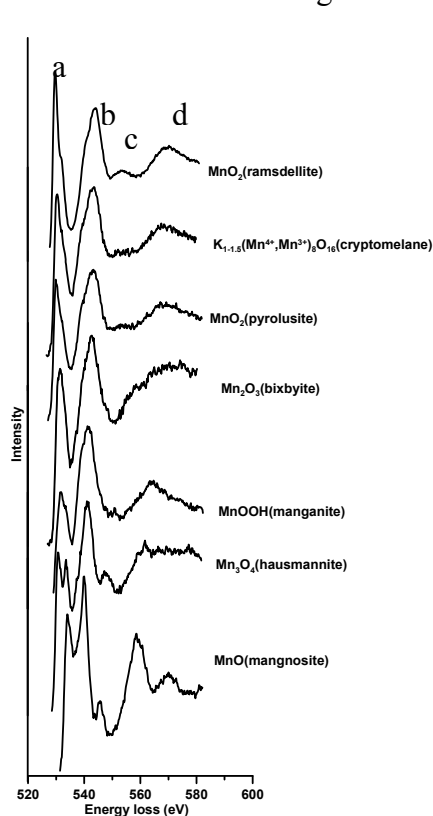


Fig.2. Comparison of O K edges among Mn-bearing minerals. Peaks of a, b, c, and d reflect crystal structure differences among them.

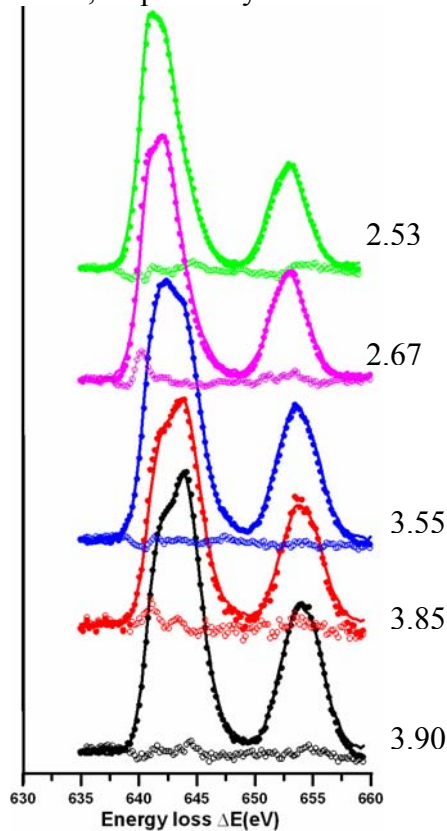


Fig.3. Multiple linear least squares fitting of Mn oxides with mixed valence. Selection of reference spectra is based on Fig.2.