



Figure S13. Sensitivity of XANES spectra to the relative abundance of Mn³⁺, taking IRB20-1 (crosses) as an example. The fits shown in red on (a) were obtained by fixing the Mn³⁺ content (feitknechtite) successively from 0% to 35% (5% steps), and optimizing in each case the proportions of Mn⁴⁺ (chalcophanite) and Mn²⁺ (sorbed on fungal cells). b) Evolution of the fit quality (solid line) and of the proportions of Mn⁴⁺ (light grey bars) and Mn²⁺ (black bars) as a function of the fixed Mn³⁺ content (open bars). X-ray diffraction patterns of fungal Mn oxides compared with Ni-sorbed δ -MnO₂ (Grangeon et al. 2008). NibBi2-7 and NidBi177-7 contain respectively 0.1 and 0.2 “heavy” interlayer cations (Ni and Mn) at TC position. Solid arrows point out the intensity minimum appearing at $\sim 47^\circ 2\theta$ when the amount of interlayer Me cations at TC position increases from 0.1 to 0.2 per layer octahedron. When this number exceeds 0.2, a shoulder appears at $\sim 42^\circ 2\theta$ (dashed arrow).