



Supplementary Figure 2. Results of PCA analysis using Mn XANES spectra between 6540 and 6570 eV. All micro XANES spectra collected at ALS 10.3.2. (energy shifted to match to SSRL) and SSRL 2-3, bulk Mn XANES spectra collected at SSRL 11-2, and Mn standards reference spectra were used for the analysis. PC1, PC2, and PC3 explain 99.5% of variance in the data. Samples are shown in circles and Mn standards (KBi = synthetic K-rich birnessite, Mn-POC = Mn(II) sorbed to POC) in squares. Filled squares represent pyroxmangite, feitknechtite, and δ -MnO₂ that were used as Mn(II), Mn(III), and Mn(IV) model compounds in this study. Most sample Mn XANES appear in a shaded area where they can be well modeled with the three model compounds. Several XANES spectra appear to have an unknown component other than the three. Those include six XANES spectra from GT8435qp and GT8436st whose EXAFS spectra also could not be identified with the Mn reference spectra used in this study (section 3.3 and Supp. Fig. 5).