S4

Quantification of average Mn valence based on pre-edge peaks

The pre-edge peak at the K-edge of Mn (~6537-6548 eV) is related to electronic transitions from the 1*s* core levels to the empty 3*d* levels, more or less 4*p* hybridized by the Mn ligands (Farges, 2005). It has been demonstrated that the pre-edge peak is much less affected by the medium- and long-range structure than the main edge region (Chalmin et al., 2009; Farges, 2005). In particular, for minerals with a constant geometry of Mn (i.e. 4-, 5-, or 6-fold coordinated by O in the first shell), the energy position of the pre-edge peak correlates linearly with Mn oxidation state (Farges, 2005; Schulze et al., 1995). A simlar linear dependence has been also reported for Fe (Prietzel et al., 2007; Wilke et al., 2001). Our Mn XANES data (Fig. 8) indicate that Mn in the natural deposit (YBS_1, YBS_2, and YBS_3) and in one of the bacterial cultures (*Hydrogenophaga* sp.) predominantly occurs as birnessite- or todorokite-like phases, but with small contributions of Mn(II) and possibly Mn(III) in the natural samples. The remaining cultures were mainly associated with Mn(II) bound to humic acid combined with low amounts of Mn(III), possibly present as feitknechtite, manganite, or groutite. All these phases have the same geometry of Mn (octahedrally coordinated by six O atoms in the first shell), meaning that the energy position of the pre-edge peak for these samples varies linearly as a function of Mn valence.

The pre-edge peaks on the XANES spectra of the samples and the four octahedrally coordinated Mn references were subtracted by fitting a spline base-line through the region 6537-6548 eV. The baseline-subtracted pre-edge peak was fitted with pseudo-Voigt functions (50% Gaussian and 50% Lorentzian) constrained to have the same width and line-shape (Fig. S4.1). Consistent with previous observations (Chalmin et al., 2009; Farges, 2005), two pseudo-Voigt functions were required to fit the pre-edge peaks for the two Mn(II) references, while the pre-edge peaks for the Mn(III) and Mn(VI) oxide references are more intense and need to be modeled by three pseudo-Voigt functions. The obtained pre-edge peak characteristics for each sample and reference compound are reported in Table S4.1. The centroid energy for each sample and reference was calculated as the intensity-weighted average of the energy position of the two or three pseudo-Voigt components. Mn oxidation states in the samples were estimated by establishing a standard curve using the octahedrally coordinated Mn references of known Mn valences.

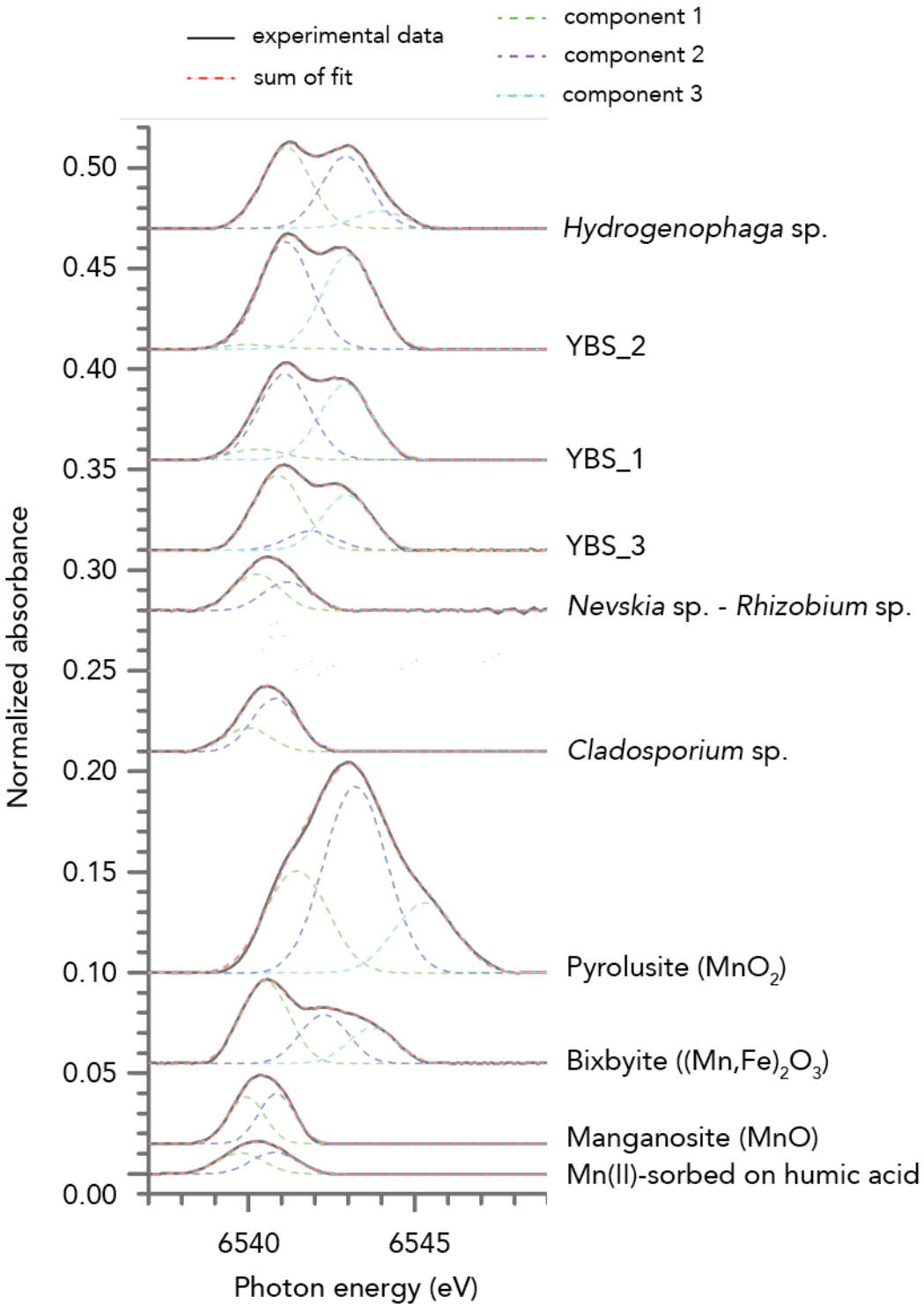

Figure S4 Pre-edge peaks isolated from the XANES spectra of samples and selected reference compounds as well as their best fit with pseudo-Voigt components (fitting parameters are given in Table S4). The samples and reference compounds from bottom to top displayed increasing centroid energies.

Table S4. Pre-edge peak characteristics for reference compounds and samples. Estimated average Mn oxidation state for each of the samples is also indicated.

		Pre-edge components and fitting parameters					Integrated area	Centroid (eV)	Estimated Mn valence
		Components	Position (eV)	Area	Half-width	Weighted sum of squared			
Reference	Mn(II)-sorbed on humic acid	C1	6539.77	0.017	0.80	3.7×10^{-7}	0.035	6540.28	-
		C2	6540.78	0.018					
	MnO	C1	6539.95	0.031	0.63	8.5×10^{-6}	0.064	6540.41	-
		C2	6540.85	0.033					
	Mn_2O_3	C1	6540.50	0.070	0.85	1.3×10^{-5}	0.142	6541.30	-
		C2	6542.27	0.041					
		C3	6543.72	0.030					
	MnO_2	C1	6541.45	0.116	1.10	1.3×10^{-4}	0.405	6543.12	-
		C2	6543.22	0.211					
		C3	6545.31	0.079					
Samples	*Cladosporium*	C1	6539.98	0.019	0.80	7.7×10^{-6}	0.062	6540.55	2.49
		C2	6540.80	0.043					
	Nevskia and Rhizobium	C1	6540.25	0.031	0.83	8.8×10^{-4}	0.056	6540.65	2.56
		C2	6541.16	0.024					
	YBS_3	C1	6540.88	0.067	0.90	7.9×10^{-6}	0.133	6541.77	3.37
		C2	6541.89	0.017					
		C3	6542.96	0.049					
	YBS_1	C1	6540.27	0.010	0.92	9.4×10^{-6}	0.162	6541.85	3.43
		C2	6541.09	0.081					
		C3	6542.93	0.071					
	YBS_2	C1	6540.00	0.004	0.91	1.8×10^{-6}	0.196	6541.97	3.51
		C2	6541.12	0.102					
		C3	6543.01	0.090					
	Hydrogenophaga	C1	6541.14	0.073	0.85	8.9×10^{-6}	0.153	6542.19	3.67
		C2	6542.93	0.065					
		C3	6543.94	0.016					

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