

Supporting Information

Cr(III) Oxidation by Biogenic Manganese Oxides of Varying Structural Ripening

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Table S1. LCF fitting results of the unreacted Mn oxides at different age.

Mn oxide age (h)	δ-MnO₂ (hexagonal)	Na-birnessite (triclinic)	R factor*
4	1	0	0.08
31	0.87	0.13	0.08
96	0.864	0.136	0.04
211	0.559	0.441	0.02

*R factor represents the goodness of fit.

Table S2. Summary of Mn K-edge EXAFS fitting parameters using the full multiple scattering model for reference compounds and bioMnOx before and after interaction with Cr(III).

Sample *	R	f_{occ}	β (a-axis)	β (b-axis)	Shell	CN	Distance (Å)		σ^2		
<i>Unreacted bioMnOx</i>											
4 h oxide	0.0354	0.64 (3)	0 (1)	0	Mn-O	4	1.89	+/-0.08	0.014	+/-0.004	
					Mn-O	2	1.90	+/-0.04	0.003		
					Mn-Mn edge	2	2.83	+/-0.03	0.005	+/-0.004	
					Mn-Mn edge	4	2.89	+/-0.03			
					Mn-O	4	3.64	+/-0.22	0.004	+/-0.002	
					Mn-O	2	4.48	+/-0.41			
					Mn-Mn corner	3.2	+/-0.1	3.51	+/-0.11	0.005	
					Mn- interlayer	0.9	+/-0.3	4.04	+/-0.30	0.006	
					Mn-O	4	4.77	+/-0.31	0.014	+/-0.044	
					Mn-O	8	4.77				
					Mn-Mn diag	4	4.97	+/-0.26	0.005	+/-0.019	
					Mn-Mn diag	2	5.13	+/-0.45			
					Mn-Mn next	2	5.67		0.424		
					Mn-Mn next	4	5.78				
31 h oxide	0.0359	0.92 (4)	2 (4)	0	Mn-O	4	1.89	+/-0.11	0.008	+/-0.005	
					Mn-O	2	1.91	+/-0.10	0.003		
					Mn-Mn edge	2	2.83	+/-0.03	0.007	+/-0.004	
					Mn-Mn edge	4	2.89	+/-0.03			
					Mn-O	4	3.71	+/-0.10	0.005	+/-0.011	
					Mn-O	2	4.48	+/-0.30			
					Mn-Mn corner	3.2	+/-1.5	3.56	+/-0.07	0.005	
					Mn- interlayer	2.9	+/-0.8	4.11	+/-0.13	0.006	
					Mn-O	4	4.76	+/-0.20	0.011	+/-0.065	
					Mn-O	8	4.76				
					Mn-Mn diag	4	5.00	+/-0.30	0.010	+/-0.300	
					Mn-Mn diag	2	5.06	+/-0.43			
					Mn-Mn next	2	5.67		0.424		
					Mn-Mn next	4	5.78				
96 h oxide	0.0134	0.88 (3)	7 (4)	0	Mn-O	4	1.88	+/-0.11	0.006	+/-0.008	
					Mn-O	2	1.91	+/-0.15	0.003		
					Mn-Mn edge	2	2.82	+/-0.02	0.005	+/-0.003	
					Mn-Mn edge	4	2.90	+/-0.02			
					Mn-O	4	3.63	+/-0.25	0.012	+/-0.064	
					Mn-O	2	4.39	+/-0.75			
					Mn-Mn corner	1.7	+/-0.9	3.52	+/-0.11	0.005	
					Mn- interlayer	1.3	+/-0.8	4.05	+/-0.20	0.006	
					Mn-O	4	4.75	+/-0.20	0.016	+/-0.036	
					Mn-O	8	4.75				
					Mn-Mn diag	4	4.97	+/-0.12	0.006	+/-0.014	
					Mn-Mn diag	2	5.13	+/-0.25			
					Mn-Mn next	2	5.63		0.424		
					Mn-Mn next	4	5.80				

211h oxide	0.0318	0.66 (3)	7 (3)	0	Mn-O	4	1.88	+/-0.09	0.009	+/-0.006	
					Mn-O	2	1.91	+/-0.07	0.003		
					Mn-Mn edge	2	2.83	+/-0.03	0.004	+/-0.004	
					Mn-Mn edge	4	2.90	+/-0.03			
					Mn-O	4	3.65	+/-0.26	0.006	+/-0.047	
					Mn-O	2	4.42	+/-0.46			
					Mn-Mn corner	1.4	+/-1.0	3.50	+/-0.15	0.005	
					Mn- interlayer	2.4	+/-1.5	4.07	+/-0.24	0.006	
					Mn-O	4	4.75	+/-0.36	0.023	+/-0.114	
					Mn-O	8	4.75				
					Mn-Mn diag	4	4.99	+/-0.52	0.011	+/-0.371	
					Mn-Mn diag	2	5.03	+/-0.27			
					Mn-Mn next	2	5.65		0.424		
					Mn-Mn next		5.80				

Reacted bioMnOx

4 h-K-L	0.0119	0.80 (5)	13 (2)	0	Mn-O	4	1.87	+/-0.06	0.006	+/-0.006	
					Mn-O	2	1.92	+/-0.07	0.001		
					Mn-Mn edge	2	2.82	+/-0.04	0.004	+/-0.003	
					Mn-Mn edge	4	2.91	+/-0.02			
					Mn-O	4	3.45	+/-0.10	0.008	+/-0.014	
					Mn-O	2	4.26	+/-0.72			
					Mn-Mn corner	1.4	+/-1.1	3.75	+/-0.07	0.005	
					Mn- interlayer	1.5	+/-1.6	4.38	+/-0.45	0.006	
					Mn-O	4	4.60	+/-0.26	0.000	+/-0.031	
					Mn-O	8	4.80	+/-0.13			
					Mn-Mn diag	4	5.02	+/-0.12	0.000	+/-0.021	
					Mn-Mn diag	2	5.20	+/-0.22			
					Mn-Mn next	2	5.64		0.424		
					Mn-Mn next	4	5.83				

4 h-ASW-D	0.0203	0.78 (5)	24 (5)	0	Mn-O	4	1.89	+/-0.07	0.006	+/-0.008	
					Mn-O	2	1.93	+/-0.08	0.001		
					Mn-Mn edge	2	2.88	+/-0.13	0.006	+/-0.005	
					Mn-Mn edge	4	2.92	+/-0.06			
					Mn-O	4	3.53	+/-0.15	0.009	+/-0.020	
					Mn-O	2	4.14	+/-0.92			
					Mn-Mn corner	1.8	+/-0.7	3.80	+/-0.15	0.005	
					Mn- interlayer	1.5	+/-1.5	4.34	+/-0.34	0.006	
					Mn-O	4	4.68	+/-0.17	0.001	+/-0.030	
					Mn-O	8	4.87	+/-0.16			
					Mn-Mn diag	4	5.08	+/-0.18	0.000	+/-0.025	
					Mn-Mn diag	2	5.24	+/-0.26			
					Mn-Mn next	2	5.75		0.424		
					Mn-Mn next	4	5.83				

4 h-ASW-L	0.008	0.99 (7)	22 (7)	0	Mn-O	4	1.87	+/-0.04	0.006	+/-0.005	
					Mn-O	2	1.92	+/-0.05	0.001		
					Mn-Mn edge	2	2.86	+/-0.32	0.007	+/-0.013	
					Mn-Mn edge	4	2.91	+/-0.13			
					Mn-O	4	3.53	+/-0.08	0.009	+/-0.013	
					Mn-O	2	4.42	+/-2.00			
					Mn-Mn corner	0.3	+/-0.9	3.80	+/-0.07	0.005	
					Mn- interlayer	1.2	+/-1.0	4.40	+/-0.33	0.006	
					Mn-O	4	4.60	+/-0.23	0.000	+/-0.022	
					Mn-O	8	4.79	+/-0.10			
					Mn-Mn diag	4	5.01	+/-0.11	0.002	+/-0.016	
					Mn-Mn diag	2	5.17	+/-0.18			
					Mn-Mn next	2	5.72		0.424		
					Mn-Mn next	4	5.83				

4 h-K-D	0.0113	0.95 (6)	27 (7)	0	Mn-O	4	1.88	+/-0.05	0.007	+/-0.005	
					Mn-O	2	1.92	+/-0.05	0.001		
					Mn-Mn edge	2	2.87	+/-0.06	0.008	+/-0.003	
					Mn-Mn edge	4	2.91	+/-0.03			
					Mn-O	4	3.53	+/-0.10	0.009	+/-0.016	
					Mn-O	2	4.38	+/-4.37			
					Mn-Mn corner	0.9	+/-0.8	3.79	+/-0.09	0.005	
					Mn- interlayer	1.1	+/-1.3	4.42	+/-0.41	0.006	
					Mn-O	4	4.62	+/-0.45	0.002	+/-0.042	
					Mn-O	8	4.81	+/-0.11			
					Mn-Mn diag	4	5.02	+/-0.15	0.000	+/-0.022	
					Mn-Mn diag	2	5.20	+/-0.17			
					Mn-Mn next	2	5.74		0.424		
					Mn-Mn next	4	5.82				
					31 h-K-L	0.0099	0.89 (7)	16 (3)	0	Mn-O	4
Mn-O	2	1.92	+/-0.06	0.001							
Mn-Mn edge	2	2.84	+/-0.05	0.005						+/-0.004	
Mn-Mn edge	4	2.91	+/-0.03								
Mn-O	4	3.51	+/-0.07	0.007						+/-0.003	
Mn-O	2	4.37	+/-2.75								
Mn-Mn corner	0.0	+/-1.0	3.79	+/-0.08						0.005	
Mn- interlayer	1.2	+/-1.1	4.46	+/-0.65						0.006	
Mn-O	4	4.57	+/-0.57	0.000						+/-0.034	
Mn-O	8	4.79	+/-0.23								
Mn-Mn diag	4	5.01	+/-0.17	0.000						+/-0.013	
Mn-Mn diag	2	5.18	+/-0.20								
Mn-Mn next	2	5.68		0.424							
Mn-Mn next	4	5.83									
31 h-ASW-D	0.0162	0.82 (8)	27 (6)	0						Mn-O	4
					Mn-O	2	1.92	+/-0.07	0.001		
					Mn-Mn edge	2	2.87	+/-0.07	0.006	+/-0.004	
					Mn-Mn edge	4	2.91	+/-0.03			
					Mn-O	4	3.54	+/-0.12	0.010	+/-0.004	
					Mn-O	2	4.31	+/-1.38			
					Mn-Mn corner	1.2	+/-1.3	3.80	+/-0.10	0.005	
					Mn- interlayer	1.1	+/-1.3	4.38	+/-0.80	0.006	
					Mn-O	4	4.62	+/-0.42	0.000	+/-0.036	
					Mn-O	8	4.82	+/-0.22			
					Mn-Mn diag	4	5.04	+/-0.16	0.000	+/-0.020	
					Mn-Mn diag	2	5.20	+/-0.22			
					Mn-Mn next	2	5.74		0.424		
					Mn-Mn next	4	5.83				
					211 h-K-L	0.0127	0.80 (5)	16 (4)	0	Mn-O	4
Mn-O	2	1.92	+/-0.05	0.001							
Mn-Mn edge	2	2.81	+/-0.05	0.004						+/-0.005	
Mn-Mn edge	4	2.92	+/-0.02								
Mn-O	4	3.49	+/-0.21	0.015						+/-0.048	
Mn-O	2	4.23	+/-2.63								
Mn-Mn corner	1.8	+/-1.3	3.76	+/-0.20						0.005	
Mn- interlayer	0.9	+/-1.4	4.40	+/-0.56						0.006	
Mn-O	4	4.64	+/-0.81	0.001						+/-0.062	
Mn-O	8	4.82	+/-0.36								
Mn-Mn diag	4	5.03	+/-0.25	0.000						+/-0.037	
Mn-Mn diag	2	5.21	+/-0.32								
Mn-Mn next	2	5.63		0.424							
Mn-Mn next	4	5.84									

211 h-ASW-D	0.0132	0.80 (7)	17 (4)	0	Mn-O	4		1.88	+/-0.05	0.006	+/-0.006
					Mn-O	2		1.92	+/-0.06	0.001	
					Mn-Mn edge	2		2.83	+/-0.06	0.004	+/-0.005
					Mn-Mn edge	4		2.92	+/-0.02		
					Mn-O	4		3.53	+/-0.12	0.012	+/-0.026
					Mn-O	2		4.23	+/-1.10		
					Mn-Mn corner	2.5	+/-1.3	3.82	+/-0.14	0.005	
					Mn- interlayer	1.2	+/-0.8	4.43	+/-0.55	0.006	
					Mn-O	4		4.66	+/-0.42	0.001	+/-0.062
					Mn-O	8		4.83	+/-0.23		
					Mn-Mn diag	4		5.03	+/-0.18	0.000	+/-0.045
					Mn-Mn diag	2		5.19	+/-0.29		
					Mn-Mn next	2		5.66		0.424	
					Mn-Mn next	4		5.84			

Reference compounds (as described in detail by Webb et al, 2005)

δ -MnO ₂	0.0097	0.77 (8)	0 (4)	0 (4)	Mn-Mn corner	0.6	+/-1.0	3.42	+/-0.05	0.005	+/-0.004
Triclinic birnessite	0.0145	0.90 (8)	15 (5)	0 (5)	Mn-Mn corner	0.8	+/-0.8	3.36	+/-0.09	0.006	+/-0.003

* Samples are labeled as bioMnOx age-organic carbon content-light condition. Organic carbon contents include carbon-replete (K) and -deplete (ASW) conditions. Light conditions include light (L) and dark (D).

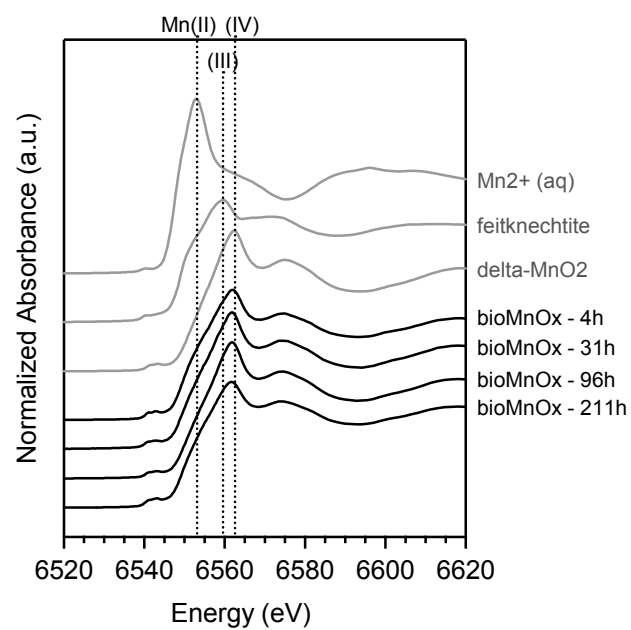


Figure S1. Mn K-edge XANES spectra of reference compounds in grey lines and unreacted Mn oxides (4, 31, 96, and 211 h old) in black lines.

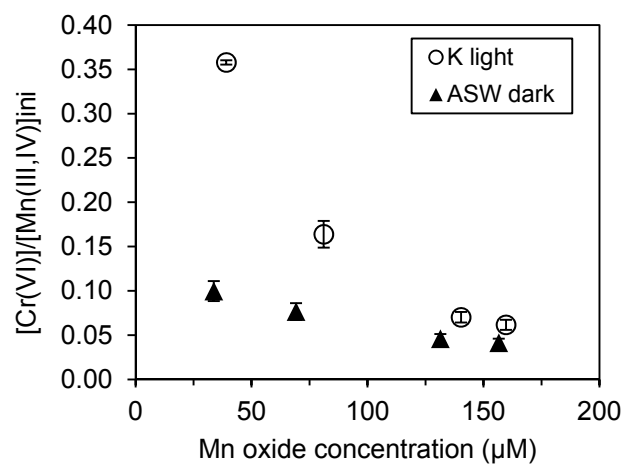


Figure S2. Cr oxidation capacity as a function of biogenic Mn oxide concentration in K medium-light or ASW-dark conditions. Reaction conditions: 4 h bioMnOx, pH 7.2.