5.7 Supporting Information

References

(1) Bilinski, H. and Morgan, J. J. Complex formation and oxygenation of manganese (2) in pyrophosphate solutions. *Preprints of Papers Presented at National Meeting, Division Water, Air and Waste Chemistry, American Chemical Society* **1969**, April14-18, 32-38.

(2) Bozor, I. and Simandi, L. I. Oxidation of tiron by (pyrophosphato) manganese(III). Kinetics and mechanism. *J. Chem. Soc., Dalton Trans.* **2002**, 3226-3233.

(3) Farmer, R. M. and Popov, A. I. Electron-spin-resonance study of manganese(II) complexes in aqueous-solutions. *Inorg. Chim. Acta* **1982**, 59, 87-91.

(4) Wang, Y. and Stone, A. T. The citric acid-$Mn^{III,IV}O_2$(birnessite) reaction. Electron transfer, complex formation, and autocatalytic feedback. *Submitted to Geochim. Cosmochim. Acta* **2005**.

(5) Martell, A. E., Smith, R. M., and Motekaitis, R. J. *NIST Critically Selected Stability Constants of Metal Complexes Database*. 2004, US Department of Commerce, National Institute of Standards and Technology: Gaithersburg, MD.

Table S5.1. logK Values Used to Perform Equilibrium Calculations.

Reactions	log ^{c}K[1]	Ionic Str. (M)	T (^{o}C)
<u>Reactions Involving PP</u>			
$H^{+} + L^{4-} = HL^{3-}$	8.91	0.01	25
$2H^{+} + L^{4-} = H_2L^{2-}$	15.34	0.01	25
$3H^{+} + L^{4-} = H_3L^{-}$	17.44	0.01	25
$4H^{+} + L^{4-} = H_4L^{0}$	18.25	0.01	25
$Mn^{2+} + L^{4-} = MnL^{2-}$	6.12 *(1)*	0.01	25
$Mn^{3+} + H^{+} + L^{3-} = MnHL^{+}$	18.99	3.0	25
$Mn^{3+} + 2H^{+} + L^{3-} = MnH_2L^{2+}$	19.78	3.0	25
$[Mn^{III}(HL)(H_2L)_2]^{4-} + H^{+} = [Mn^{III}(H_2L)_3]^{3-}$	3.41 *(2)*	0.5	25
<u>Reactions Involving MDP</u>			
$H^{+} + L^{4-} = HL^{3-}$	10.96	0	25
$2H^{+} + L^{4-} = H_2L^{2-}$	18.36	0	25
$3H^{+} + L^{4-} = H_3L^{-}$	21.32	0	25
$4H^{+} + L^{4-} = H_4L^{0}$	23.14	0	25
<u>Reactions Involving PAA</u>			
$H^{+} + L^{3-} = HL^{2-}$	8.33	0.01	25
$2H^{+} + L^{3-} = H_2L^{-}$	13.26	0.01	25
$3H^{+} + L^{3-} = H_3L^{0}$	14.47	0.01	25
$Mn^{2+} + L^{3-} = MnL^{-}$	6.80 *(3)*	0.01	25
$Mn^{2+} + H^{+} + L^{3-} = MnHL^{0}$	12.17 *(3)*	0.01	25
<u>Metal Ion Hydrolysis Reactions</u>			
$Mn^{2+} + H_2O = Mn(OH)^{+} + H^{+}$	-10.69	0.01	25
$Mn^{2+} + 3H_2O = Mn(OH)_3^{-} + 3H^{+}$	-34.80	0.01	25
<u>Metal (Hydr)oxide Solubility-Controlling Phases</u>			
$Mn^{2+} + 2H_2O = Mn(OH)_2(s) + 2H^{+}$	-15.09	0.01	25
$Mn^{3+} + 2H_2O = MnOOH(s, manganite) + 3H^{+}$	-1.2 *(4)*	0.0	25

[1] Unless otherwise noted, log^{c}K values from electronic database CRITICAL *(5)*, and referred to 25^{o}C, values not originally at ionic strength = 0.01 M corrected using the Davies Equation.

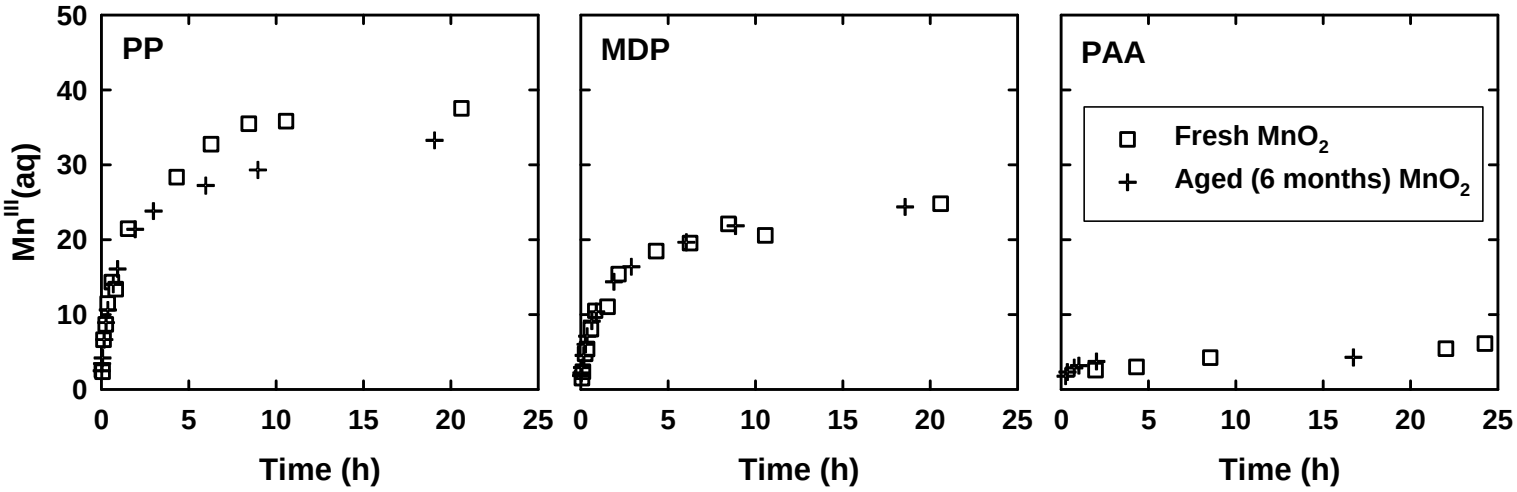

Figure S5.1. MnO_2 aging effect on time course plots for reaction of 200 mM MnO_2 with 5.0 mM PP, MDP and PAA at pH 7.0. For reactions with MDP and PAA, a pH stat was employed. For reaction with PP, self-buffering was sufficient to maintain constant pH.

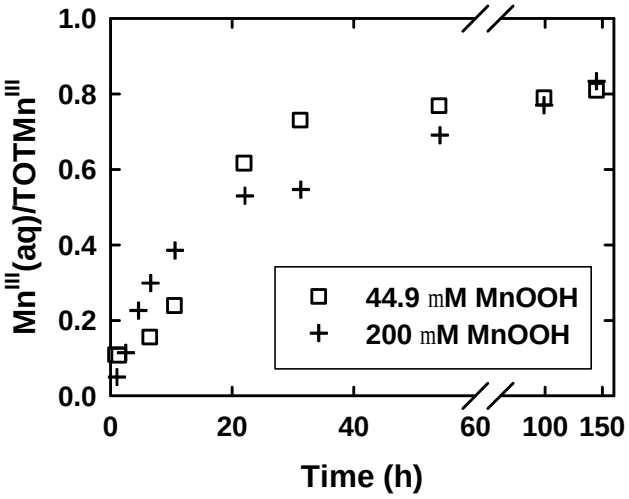

Figure S5.2. Time course plot for reaction of MnOOH with 5.0 mM PP at pH 6.0. Self-buffering was sufficient to maintain constant pH.