Supporting Information

for

"A Hydrous Manganese Oxide Doped Gel Probe Sampler for Measuring *In Situ* Reductive Dissolution Rates: I. Laboratory Development"

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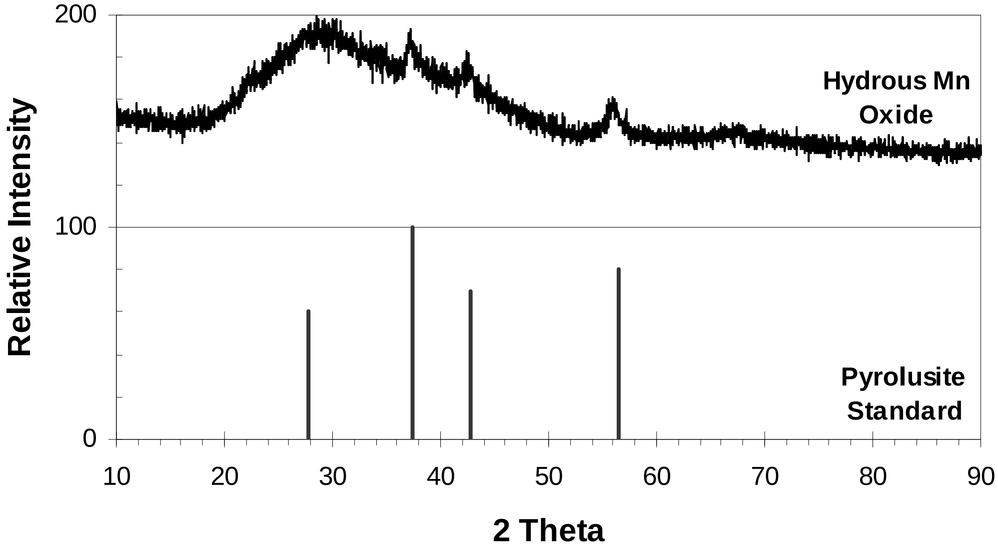

Figure S1. X-ray diffractogram for synthesized HMO with the pyrolusite (β-MnO_2) standard, the best match for the small peaks. The broad, ill-defined peak is indicative of an amorphous solid.

Table S1. Final mass balance in abiotic miniprobe reductive dissolution experiments.

Reductant, pore size	(1) Total Lost from Gels	(2) Storage Soln. before Expt.[a]	(3) Reduced from Gels[b]	(4) Bulk Soln.	% Unaccounted[c]
Ascorbate 0.45 µm	7.39	3.68	3.71	3.55	2.2%
1.0 µm	7.50	3.68	3.81	3.70	1.5%

Listed data are µmoles of Mn.

[a] The percentage of Mn lost to the gel storage solution (50%) is relatively high in this example. Typically ≤ 20% of Mn leached into the storage solution.

[b] The amount of Mn reduced from the gels (3) is equal to the difference between the total Mn lost from the gels (1) and the Mn lost to the gel storage solution before the experiment (2).

[c] Perfect mass balance would lead to the amount of Mn reduced from the gels (3) equaling the amount of Mn measured in the bulk solution at the end of the experiment (4). The percentage is given as: $[(3) – (4)]\cdot(1)^{-1}$.

Table S2. Basic components of MR-1 minimal medium[a]

Chemical	Concentration (mM or given)
Sodium Lactate	6
PIPES	3
Sodium Hydroxide	7.5
Ammonium Chloride	28.0
Potassium Chloride	1.34
Sodium Phosphate (monobasic)	4.35
Sodium Fumarate	30
Vitamins:	(nM)
d-biotin	81.9
folic acid	45.3
pyridoxine-HCl	486
riboflavin	133
thiamine-HCl· H_2O	141
nicotinic acid	406
d-pantothenic acid, hemicalcium salt	210
B12	0.74
p-aminobenzoic acid	365
thioctic acid	242
Amino Acids:	(mg l^{-1})
L-glutamic acid	2
L-arginine	2
DL-serine	2

[a] In addition, 10 ml of Wolfe's Mineral Solution (which comprises trace amounts of Mg, Mn, Na, Fe, Ca, Co, Zn, Cu, Al, B, and Mo salts) were added to this medium.

Although direct reduction of Mn oxide by the MR-1 medium was not tested, previous studies of the individual compounds suggest this would have a negligible effect on the measured rates. Fumarate, lactate, and ammonia do not appear to reduce Mn oxide when present in excess (1, 2). Only DL-lactic acid reduced MnO_2, at an average rate of 0.47 μmol m^{-2} h^{-1} at pH 5 (3), which corresponds to a range of $3.4\text{-}20\times10^{-11}$ M s^{-1} for the conditions of our study; even at the maximum estimated rate, this would account for less than 5% of our measured HMO reduction rate.

Table S3. Parameters input to or solved by AQUASIM model.

Experiment		$[C_6H_7O_6^-]_{0,\text{ bulk}}$ or $[Red]_{0,\text{ bulk}}$ (mM)	$[HMO]_{0,\text{ gel}}$ (mM)[a]	k ($M^{-1}\,s^{-1}$)	k″ (s^{-1})	A ($m^2\,l^{-1}$)	D_{Mn} ($cm^2 s^{-1}$)	$D_{A,\text{ bulk}}$ or $D_{Red,\text{ bulk}}$ ($cm^2 s^{-1}$)	$D_{A,\text{ gel}}$ or $D_{Red,\text{ gel}}$ ($cm^2 s^{-1}$)	V_{bulk} (ml)	χ^2
Abiotic	HMO gels	2.0	7.77	4.2	---	33.1	6.88e-6	3.0e-6	4.28e-7[b]	10	2.3
	MP 1.0 um	2.0	6.68	4.2	---	28.5	6.88e-6	3.0e-6	1.03e-6[b]	25	2.0
Microbially-mediated	HMO	1.182	0.360[d]	3.5e-3	7.5e-6 [b]	1.53	---	---	---	55	2.6
	HMO gels	1.182[c]	10.2	3.5e-3[b]	---	25.0	6.88e-6	3.0e-6	4.28e-7	10	1.2
	MP 1.0 um	1.182	6.59	3.5e-3[b]	---	28.1	6.88e-6	3.0e-6	1.03e-6	25	1.4

[a] This concentration is normalized to the volume of pore space in the gel, which is approximately 92.3% × 0.225 g × 1 ml g^{-1}, or 0.208 ml.
[b] Denotes a fitted parameter.
[c] Assumed to be 5 times Mn_T for this system.
[d] In this case, the HMO was added to the bulk solution, and no gel compartment was necessary. Consequently, no diffusion coefficients were needed for this simulation.

Table S4.a. [Mn(II)] release over time:
HMO-doped gels and ascorbate. (184 μM Mn_T)

Time (hrs)	0.5	1	2	3	4
$[Mn]_{diss}$ (μM)	38	64	116	132	145
Std Dev (μM)	7	1	16	27	8

Table S4.b. [Mn(II)] release over time:
Miniprobes, 0.45-μm membrane, and ascorbate. (52 μM Mn_T)

Time (hrs)	0.6	1.7	3.25	4.75
$[Mn]_{diss}$ (μM)	4.0	12	20	25
Std Dev (μM)	1	1	2	2

Table S4.c. [Mn(II)] release over time:
Miniprobes, 1.0-μm membrane, and ascorbate. (52 μM Mn_T)

Time (hrs)	0.6	1.7	3.25	4.75
$[Mn]_{diss}$ (μM)	5.7	14	21	25
Std Dev (μM)	1	1	2	2

Table S4.d. [Mn(II)] release over time:
HMO and *S. oneidensis* MR-1. (360 μM Mn_T)

Time (hrs)	0.25	0.5	0.75	1	1.5	2	3	4
$[Mn]_{diss}$ (μM)	0.5	8.1	4.8	3.7	24	34	39	60
Std Dev (μM)	4	13	11	10	4	35	21	39

Table S4.e. [Mn(II)] release over time:
HMO-doped gels and *S. oneidensis* MR-1. (295 μM Mn_T)

Time (hrs)	4.5	8	16	25	36
$[Mn]_{diss}$ (μM)	13	23	43	65	86
Std Dev (μM)	2	4	7	6	12

Table S4.f. [Mn(II)] release over time:
Miniprobes, 1.0-μm membrane, and *S. oneidensis* MR-1. (62 μM Mn_T)

Time (hrs)	7.9	14	20	26	38.8	63
$[Mn]_{diss}$ (μM)	-0.4	2.2	5.5	8.1	14	27
Std Dev (μM)	1	2	1	3	4	6

Table S4.g. [Mn(II)] release over time:
Miniprobes, 5.0-μm membrane, and *S. oneidensis* MR-1. (60 μM Mn_T)

Time (hrs)	7.9	14	20	26	38.8	63
$[Mn]_{diss}$ (μM)	0.6	4.1	7.4	10	17	29
Std Dev (μM)	1	1	2	3	4	7

Table S5. AQUASIM mass balance at steady state.

Experiment		t_{ss} (h)	HMO_0 (μmol)	$Mn_{T,t}$ (μmol)	% Error[a]	Red_0[b] (μmol)	Red_{red}[c] (μmol)	$Red_{T,t}$ (μmol)	% Error[a]
Abiotic	HMO gels	6	1.794	1.792	0.07%	20	1.792	18.25	0.2%
	MP 1.0 um	25.1	1.542	1.541	0.04%	50.03	1.541	48.6	0.2%
Microbially-mediated	HMO	150	19.8	19.8	0.01%	65.01	6.91[d]	58.25	0.2%
	HMO gels	360	2.364	2.362	0.06%	11.82	2.362	9.48	0.2%
	MP 1.0 um	420	1.521	1.520	0.09%	29.55	1.520	28.01	0.08%

[a] % Error is the absolute value of either the difference between HMO_0 and $Mn_{T,t}$ divided by HMO_0, or the difference between Red_0 and the sum of Red_{red} and $Red_{T,t}$ divided by Red_0.
[b] Red denotes the reductant, either ascorbate (abiotic) or the generic reductant (microbially mediated).
[c] Amount of Red that is reduced is equal to the amount of Mn(II) produced.
[d] Amount of Red that is reduced is equal to 35% of the amount of Mn(II) produced.

References

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