

Supplementary materials

Fe^{II}_{aq}-Fe^{III}_{oxide} electron transfer and Fe exchange: effect of organic carbon

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Table S1. Selected physical and chemical characteristics of natural organic matter isolates used for electron transfer and Fe exchange experiments

Elliott Soil Humic Acid data are from the International Humic Substances Society^[1] and Thorn et al.^[2] Suwannee River Fulvic Acid data are from the International Humic Substances Society^[1] and Ravichandran et al.^[3] n/a, not available

Organic matter	Elemental Composition (%)						Avg molecular weight (Da)	Aromatic C (% total C)	Carboxy groups (meq (g C) ⁻¹)	Phenol Groups
	C	H	O	N	S	Ash				
Elliott Soil Humic Acid	58.13	3.68	34.08	4.14	0.44	0.88	n/a	50	8.28	1.87
Suwannee River Fulvic Acid	54.2	3.92	38	0.72	0.35	0.19	1360	22.9	11.17	2.84

Table S2. Recipes for growth media used to culture *Shewanella oneidensis* MR-1 for cell materials to use in electron transfer experiments

Listed quantities are per litre of growth medium

LB medium, Miller Composition	
Tryptone	10.0 g
Yeast extract	5.0 g
Sodium chloride	10 g
Defined <i>Shewanella</i> medium	
Dipotassium phosphate	0.225 g
Monopotassium phosphate	0.225 g
Ammonium sulfate	0.225 g
Sodium chloride	0.46 g
HEPES buffer	4.77 g
Vitamin mix	5 mL
Wolfe's mineral mix	5 mL
60 % D,L-lactate syrup	9.37 g

Table S3. Mass and Fe isotope data for enriched ^{57}Fe isotope tracer experiments between aqueous Fe^{II} and goethite with various forms of organic carbon present

$$f^{57}\text{Fe} = (^{57}\text{counts} / ^{54+56+57+58}\text{counts}), f^{56}\text{Fe} = (^{56}\text{counts} / ^{54+56+57+58}\text{counts}),$$

$$f^{54}\text{Fe} = (^{54}\text{counts} / ^{54+56+57+58}\text{counts}); \text{DOPA, 1,2-dioleoyl-sn-glycero-3-phosphate}$$

Time (days)	Aqueous Fe^{II}					Residual solids			Recovery (%)		
	Fe^{II} (μmoles)	$f^{57}\text{Fe}$	$f^{56}\text{Fe}$	$f^{54}\text{Fe}$	Fe exchange (%)	Fe^{II} (μmoles)	Total Fe (μmoles)	$f^{57}\text{Fe}$	Fe^{II}	Fe^{III}	Total Fe
Carbon free											
0.00	18.9 (0.5)	0.423 (0.036)	0.537 (0.035)	0.029 (0.0023)	0.0	1.1 (0.2)	323.7 (13.6)	0.025 (0.0005)	100.0	100.0	100.0
0.03	9.6 (0.8)	0.248 (0.010)	0.707 (0.019)	0.038 (0.0009)	2.4	49.1 (7.4)	592.9 (10.0)	0.030 (0.001)	294.3	168.5	175.9
0.35	8.7 (1.4)	0.151 (0.010)	0.801 (0.010)	0.043 (0.0005)	7.5	0.0 (0.0)	379.3 (15.6)	0.034 (0.004)	54.9	117.6	114.6
3.91	11.2 (2.6)	0.068 (0.018)	0.882 (0.017)	0.048 (0.001)	30.6	87.8 (17.1)	312.0 (9.8)	0.034 (0.0008)	495.9	69.5	94.3
6.96	8.5 (1.1)	0.056 (0.019)	0.892 (0.012)	0.048 (0.001)	44.1	18.6 (6.0)	317.5 (30.3)	0.036 (0.0004)	135.8	92.6	95.1
14.06	6.4 (0.2)	0.041 (0.013)	0.914 (0.024)	0.048 (0.0004)	89.5	17.5 (3.5)	250.4 (6.8)	0.034 (0.002)	119.8	72.2	75.0
Elliott Soil humic acid											
0	14.8 (0.1)	0.774 (0.0043)	0.198 (0.041)	0.010 (0.0003)	0.0	1.1 (0.2)	323.7 (13.6)	0.024 (0.0002)	100.0	100.0	100.0
6.81	6.0 (0.9)	0.118 (0.0008)	0.831 (0.002)	0.048 (0.0012)	28.5	32.4 (11.4)	506.8 (163.3)	0.053 (0.0004)	240.9	147.1	151.6
60.91	5.7 (3.0)	0.027 (0.004)	0.920 (0.003)	0.057 (0.0038)	100.0	7.8 (1.7)	256.2 (16.3)	0.038 (0.0011)	85.1	77.0	77.4
Suwanee River fulvic acid (8 mg L ⁻¹)											
0.00	14.8 (0.1)	0.857 (0.028)	0.117 (0.027)	0.007 (0.001)	0.0	1.1 (0.2)	323.7 (13.6)	0.024 (0.0002)	100.0	100.0	100.0
1.05	7.4 (1.7)	0.278 (0.0066)	0.677 (0.009)	0.041 (0.0023)	10.4	8.8 (0.6)	324.1 (15.6)	0.059 (0.0052)	101.4	97.7	97.9
6.80	2.5 (0.3)	0.180 (0.0066)	0.770 (0.006)	0.046 (0.0007)	19.8	7.9 (1.4)	307.1 (1.1)	0.056 (0.0020)	65.6	92.8	91.5
31.00	4.5 (0.8)	0.096 (0.0148)	0.853 (0.015)	0.048 (0.0011)	48.1	9.0 (0.1)	414.8 (21.9)	0.065 (0.0015)	84.9	125.9	123.9
65.8	4.1 (1.1)	0.095 (0.0019)	0.853 (0.002)	0.051 (0.0004)	48.8	8.7 (1.0)	299.0 (14.1)	0.065 (0.0001)	80.7	90.2	89.7
DOPA											
0	14.8 (0.1)	0.911 (0.0013)	0.064 (0.001)	0.004 (0.0001)	0.0	1.1 (0.2)	323.7 (13.6)	0.024 (0.0002)	100.0	100.0	100.0
29.89	1.9 (0.2)	0.791 (0.022)	0.180 (0.021)	0.011 (0.0005)	0.71	15.1 (0.9)	304.1 (2.1)	0.073 (0.0005)	106.9	89.6	90.5
61.77	1.0 (0.0)	0.744 (0.009)	0.226 (0.008)	0.014 (0.0008)	1.06	14.7 (1.1)	455.3 (25.2)	0.074 (0.0003)	98.2	136.7	134.9

Table S4. Mass and Fe isotope data for Fe isotope tracer experiments between aqueous Fe^{II} and magnetite with various forms of organic carbon present

$$f^{57}\text{Fe} = (^{57}\text{counts} / ^{54+56+57+58}\text{counts}), f^{56}\text{Fe} = (^{56}\text{counts} / ^{54+56+57+58}\text{counts}),$$

$$f^{54}\text{Fe} = (^{54}\text{counts} / ^{54+56+57+58}\text{counts}); \text{DOPA, 1,2-dioleoyl-sn-glycero-3-phosphate}$$

Time (days)	Aqueous Fe ^{II}				Fe exchange (%)	Fe ^{II} (μmoles)	Residual solids Total Fe (μmoles)	<i>f</i> ⁵⁷ Fe	Recovery (%)		
	Fe ^{II} (μmoles)	<i>f</i> ⁵⁷ Fe	<i>f</i> ⁵⁶ Fe	<i>f</i> ⁵⁴ Fe					Fe ^{II}	Fe ^{III}	Total Fe
Carbon free											
0.00	14.8 (0.1)	0.774 (0.044)	0.198 (0.041)	0.010 (0.003)	0.0	124.5 (19.9)	357.2 (1.7)	0.021 (3 × 10 ⁻⁵)	100.0	100.0	100.0
0.05	14.7 (0.4)	0.570 (0.046)	0.395 (0.045)	0.022 (0.002)	2.2	158.2 (28.9)	407.5 (32.3)	0.039 (0.0004)	124.0	107.1	113.5
6.67	11.3 (0.2)	0.232 (0.020)	0.723 (0.019)	0.038 (0.001)	12.3	128.8 (10.2)	363.2 (34.7)	0.045 (0.001)	100.6	100.7	100.7
62.95	7.5 (0.5)	0.196 (0.032)	0.762 (0.031)	0.037 (0.002)	15.7	175.7 (32.1)	428.8 (119.3)	0.052 (0.002)	131.5	108.8	117.3
Elliot Soil humic acid											
0.00	14.8 (0.1)	0.774 (0.044)	0.198 (0.041)	0.010 (0.003)	0.0	124.5 (19.9)	357.2 (1.7)	0.021 (3 × 10 ⁻⁵)	100.0	100.0	100.0
0.05	13.8 (1.3)	0.479 (0.102)	0.483 (0.010)	0.027 (0.005)	2.1	112.7 (20.4)	306.4 (46.6)	0.037 (0.001)	90.8	83.2	86.1
6.92	9.6 (1.5)	0.236 (0.007)	0.716 (0.007)	0.043 (0.0007)	9.1	222.9 (0.6)	485.2 (1.5)	0.045 (0.002)	166.9	112.7	133.0
62.68	7.2 (1.2)	0.108 (0.008)	0.840 (0.008)	0.050 (0.001)	28.6	95.9 (9.8)	258.5 (3.9)	0.038 (0.0007)	74.0	69.9	71.4
Suwanee River fulvic acid (8 mg L ⁻¹)											
0.00	14.8 (0.1)	0.774 (0.044)	0.198 (0.041)	0.010 (0.003)	0.0	124.5 (19.9)	357.2 (1.7)	0.021 (3 × 10 ⁻⁵)	100.0	100.0	100.0
1.18	10.0 (0.5)	0.429 (0.033)	0.532 (0.031)	0.030 (0.003)	4.4	137.6 (18.2)	384.2 (63.1)	0.049 (0.0016)	105.9	106	105.9
7.00	5.9 (0.2)	0.309 (0.015)	0.647 (0.015)	0.037 (0.001)	7.9	134.4 (1.5)	415.5 (111.4)	0.048 (0.0002)	100.7	120.8	113.3
30.94	7.0 (0.5)	0.279 (0.028)	0.675 (0.027)	0.038 (0.002)	9.3	112.4 (4.2)	332.8 (4.3)	0.051 (0.0002)	85.7	94.7	91.4
65.03	6.9 (0.3)	0.292 (0.019)	0.661 (0.019)	0.040 (0.001)	8.6	138.5 (11.0)	368.3 (12.9)	0.055 (0.0003)	104.3	98.8	100.8
DOPA											
0.00	14.8 (0.1)	0.911 (0.001)	0.064 (0.001)	0.004 (0.0001)	0.0	124.5 (19.9)	357.2 (1.7)	0.021 (3 × 10 ⁻⁵)	100.0	100.0	100.0
29.98	5.3 (0.5)	0.709 (0.007)	0.259 (0.007)	0.016 (0.0006)	1.2	127.3 (9.6)	387.5 (4.8)	0.054 (0.0005)	95.2	111.8	105.6
61.84	4.9 (0.1)	0.698 (0.016)	0.271 (0.017)	0.017 (0.0006)	1.3	166.7 (62.6)	479.5 (31.0)	0.058 (0.0006)	123.1	134.4	130.2

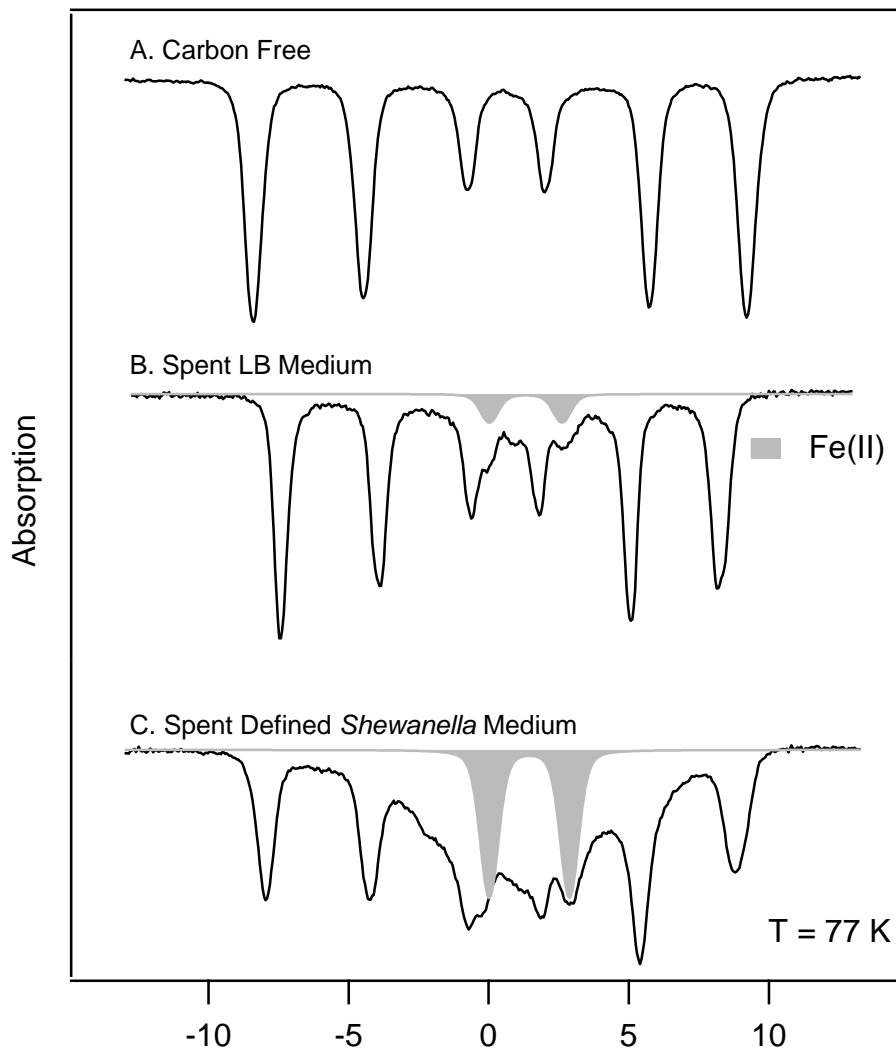


Fig. S1. ^{57}Fe Mössbauer spectra of 1 mM $^{57}\text{Fe}^{\text{II}}$ reacted with ^{56}Fe goethite and organic carbon in spent growth medium from *Shewanella oneidensis* MR-1 cultures. ^{56}Fe goethite was pre-equilibrated with (a) no carbon source, (b) a 1:10 dilution of spent Luria-Bertani medium, (c) a 1 : 10 dilution of spent defined medium. Samples were reacted with Fe^{II} for 24 h before analysis.

References

- [1] *Elemental Compositions and Stable Isotopic Ratios of IHSS Samples 2008* (International Humic Substances Society). Available at <http://www.humicsubstances.org/elements.html> [Verified 20 October 2014].
- [2] K. A. Thorn, D. W. Folan, P. MacCarthy, *Characterization of the International Humic Substances Society Standard and Reference Fulvic and Humic Acids by Solution State Carbon-13 (^{13}C) and Hydrogen-1 (^1H) Nuclear Magnetic Resonance Spectrometry 1989* (US Geological Survey: Denver, CO, USA).
- [3] M. Ravichandran, G. R. Aiken, M. M. Reddy, J. N. Ryan, Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. *Environ. Sci. Technol.* **1998**, 32, 3305.
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