Supporting Information

Fate of Transition Metals in PO_4-based *in vitro* Assays: Equilibrium Modeling and Macroscopic Studies

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Table S1 Thermodynamic Data for Fe(III)

Name	H20	H+	CO3 2-	Fe 3+	PO4 3-	log k	delta H
Aqueous							
Fe3(OH)4 +5	4	-4	0	3	0	-6.288	15.593
Fe(OH) 4-	4	-4	0	1	0	-21.588	0
Fe(OH)3	3	-3	0	1	0	-12.56	24.809
Fe2(OH)2 +4	2	-2	0	2	0	-2.854	13.771
Fe(OH) 2+	2	2	0	1	0	-4.954	0
FeOH+2	1	-1	0	1	0	-2.187	9.993
FeHPO4+	0	1	0	1	1	22.292	-7.3
FeH2PO4 +2	0	2	0	1	1	23.852	0
Solids							
GOETHITE	2	-3	0	1	0	-0.491	14.48
LEPIDOCROCITE	2	-3	0	1	0	-1.371	0
HEMATITE	3	-6	0	2	0	1.418	30.829
FERRIHYDRITE	3	-3	0	1	0	-3.191	17.573
MAGHEMITE	3	-6	0	2	0	-6.386	0
STRENGITE	2	0	0	1	1	26.4	2.237

Table S2 Thermodynamic Data for Fe(II)

Name	H20	H+	CO3 2-	Fe 2+	PO4 3-	log k	delta H
Aqueous							
FeOH+	1	-1	0	1	0	-9.397	13.339
Fe(OH)2	2	-2	0	1	0	-20.494	28.59
Fe(OH) 3-	3	-3	0	1	0	-28.991	30.218
FeHCO3+	0	1	1	1	0	11.429	0
FeH2PO4+	0	2	0	1	1	22.273	0
FeHPO4	0	1	0	1	1	15.975	0
Solids							
WUSITE	1	-2	0	0.95	0	-11.688	24.842
Fe(OH)2	2	-2	0	1	0	-13.564	0
VIVIANITE	8	0	0	3	2	36	0
SIDERITE	0	0	1	1	0	10.24	3.824
Fe3(PO4)2	0	0	0	3	2	36	0

Table S3 Thermodynamic Data for Cu(II) and Cu(I)

Name	H20	H+	CO3 2-	Cu 2+	PO4 3-	log k	delta H
Aqueous							
Cu(OH)2	2	-2	0	1	0	-16.194	0
Cu2(OH)2 +2	2	-2	0	2	0	-10.594	18.313
Cu(OH)4 -2	4	-4	0	1	0	-39.98	0
Cu(OH)+	1	-1	0	1	0	-7.497	8.559
Cu(OH) 3-	3	-3	0	1	0	-26.879	0
CuHCO3 +	0	1	1	1	0	12.129	0
CuCO3	0	0	1	1	0	6.77	0
Cu(CO3)2 -2	0	0	2	1	0	10.2	0
CuHPO4	0	1	0	1	1	16.5	0
Solids							
AZURITE	2	-2	2	3	0	16.906	22.758
MALACHITE	2	-2	1	2	0	5.306	-18.255
TENORITE	1	-2	0	1	0	-7.644	15.504
Cu(OH)2	2	-2	0	1	0	-8.674	13.485
Cu3(PO4)2 :3H2O	3	0	0	3	2	35.12	0
CuCO3	0	0	1	1	1	11.5	0
Cu3(PO4)2	0	0	0	3	2	36.85	0
Cu(I)	**H20**	**H+**	**CO3 2-**	**Cu 1+**	**PO4 3-**	**log k**	**delta H**
CUPRITE	1	-2	0	S	0	1.406	29.642

Table S4 Thermodynamic Data for Mn(II), Mn(III) and Mn(IV)

Name	**H20**	**H+**	**CO3 2-**	**Mn 2+**	**PO4 3-**	**log k**	**delta H**
Aqueous							
Mn(OH)4 -2	4	-4	0	1	0	-48.28	0
MnOH+	1	-1	0	1	0	-10.597	13.339
Mn(OH) 3-	3	-3	0	1	0	-34.8	0
MnHCO 3+	0	1	1	1	0	11.629	-2.534
MnCO3	0	0	1	1	0	4.7	0
MnHPO4	0	1	0	1	1	15.8	0
Solids							
PYROCHROITE	2	-2	0	1	0	-15.194	23.186
MnHPO4	0	1	0	1	1	25.4	0
RHODOCHROSITE	0	0	1	1	0	10.58	0.449
Mn3(PO4)2	0	0	0	3	2	23.827	-2.12
Mn(III)	**H20**	**H+**	**CO3 2-**	**Mn 3+**	**PO4 3-**	**log k**	**delta H**
BIXBYITE	3	-6	0	2	0	0.644	29.754
Mn(IV)	**H20**	**H+**	**CO3 2-**	**Mn 2+**	**PO4 3-**	**log k**	**delta H**
MANGANITE	2	-3	0	1	0	-25.34	0

Table S5. Modeling Procedures for Each Task Based on the Steps Employed in *MINEQL*.

Steps		Precipitate Type and Resulting Solubility
1	Select components:	Metal ion, PO4(3-), CO3(2-), H(+), H2O
2	Scan Thermo	
3	Wizard	
4	Totals:	PO4(3-)= 0.1M or 0 M, Metal: fixed solid
	pH:	pH is supplied by user =7.4
	CO2:	closed to the atmosphere TOTCO3= 1.4e-4M
	Fixed ions:	no selection
	Solids mover:	each solid is individually chosen as 'fixed solid' and others are 'not considered'
	Redox:	
5	Ionic Strength corrections:	Fixed= 0.22 µ (molar)
	Temperature corrections:	On= 37 ˚C
6	Run	Single

Steps		Effect of pH
1	Select components:	Metal ion, PO4(3-), CO3(2-), H(+), H2O
2	Scan Thermo	
3	Wizard	
4	Totals:	PO4(3-)= 0.1M, Metal= 5e-6M; (use 50e-6M for Fe(2+) and Fe(3+) only)
	pH:	pH is supplied by user =7.4
	CO2:	closed to the atmosphere TOTCO3= 1.4e-4M
	Fixed ions:	no selection
	Solids mover:	Chosen solids as 'dissolved solids' and others are 'not considered'
		all as 'not considered' for no solids
	Redox:	
5	Ionic Strength corrections:	Fixed= 0.22 µ (molar)
	Temperature corrections:	On= 37 ˚C
6	Run	Multirun: pH 5-10, 51points

Table S5, Continued

Steps		Effect of PO4
1	Select components:	Metal ion, PO4(3-), CO3(2-), H(+), H2O
2	Scan Thermo	
3	Wizard	
4	Totals:	PO4(3-)= 0.1M, Metal= 5e-6M; (use 50e-6M for Fe(2+) and Fe(3+) only)
	pH:	pH is supplied by user =7.4
	CO2:	closed to the atmosphere TOTCO3= 1.4e-4M
	Fixed ions:	no selection
	Solids mover:	Chosen solids as 'dissolved solids' and others are 'not considered'
		all as 'not considered' for no solids
	Redox:	
5	Ionic Strength corrections:	Fixed= 0.22 μ (molar)
	Temperature corrections:	On= 37 ˚C
6	Run	Multirun: PO4 concentration 1e-5-0.5M, 255 points

Steps		Redox (controlled by pO2)
1	Select components:	Metal ions (couple), PO4(3-), CO3(2-), H(+), H2O, e(-)
2	Scan Thermo	
3	Wizard	
4	Totals:	PO4(3-)= 0.1M, Metal= 5e-6M; (use 50e-6M for Fe(2+) and Fe(3+) only), Metal couple= 1e-23M
	pH:	pH is supplied by user =7.4
	CO2:	closed to the atmosphere TOTCO3= 1.4e-4M
	Fixed ions:	no selection
	Solids mover:	Chosen solids as 'dissolved solids' and others are 'not considered'
		all as 'not considered' for no solids
	Redox:	Check gases and ion pairs
		O2 (g): -0.677; redox couple
5	Ionic Strength corrections:	Fixed= 0.22 μ (molar)
	Temperature corrections:	On= 37 ˚C
6	Run	Multirun: logPO2 -0.699 to -50 , 100 points

Table S5, Continued

Steps		Adsorption
1	Select components:	Metal ion, PO4(3-), CO3(2-), H(+), H2O, e(-), Surface Opts: Two Layer Model: HFO, Both: weak and strong bonds
2	Scan Thermo	
3	Wizard	
4	Totals:	PO4(3-)= 0.1M, Metal= 5e-6M
	pH:	pH is supplied by user =7.4
	CO2:	closed to the atmosphere TOTCO3= 1.4e-4M
	Fixed ions:	no selection
	Solids mover:	all solids as 'not considered'
	Redox:	
5	Ionic Strength corrections:	Fixed= 0.22 μ (molar)
	Temperature corrections:	On= 37 ˚C
6	Run	Multirun: Fe(III) 5e-6 - 5e-4 M, 100 points

Table S6. Results from Triplicates of Macro-Studies

		%, Precipitation	
Fe(III), µM	PO4,M	Average	STD
5	0.1	78.6	5.1
50	0.1	76.4	2.9
500	0.1	95.2	0.8
5000	0.1	97.2	1.9
5000	0.1	95.8	0.5
5000	0.01	97.8	3.0
5000	0.00001	99.9	0.1
5000	0	98.0	3.1
		AVG STD	**2.2**

		%, Precipitation	
Mn(II), uM	PO4, M	Average	STD
50	0.1	5.9	1.5
500	0.1	83.2	1.7
5000	0.1	98.6	0.2
5000	0.1	95.3	5.5
5000	0.01	99.0	0.1
5000	0.00001	26.0	1.7
5000	0	33.4	1.3
		AVG STD	**1.8**

		% Precipitated		% Fe(II)		% Fe(III)	
Fe(II), µM	PO4, M	Average	STD	Average	STD	Average	STD
5	0.1	69.6	2.5	0.00	0.0	30.36	2.5
50	0.1	94.1	0.8	0.48	0.5	5.71	0.5
500	0.1	84.5	6.2	0.32	0.3	15.14	6.2
5000	0.1	93.5	4.3	0.22	0.0	6.28	4.3
5000	0.1	91.9	1.6	0.22	0.0	7.87	1.7
5000	0.01	83.5	3.3	0.28	0.0	16.19	3.3
5000	0.00001	82.5	0.6	14.95	2.3	2.55	1.8
5000	0	81.0	2.0	14.60	0.7	4.38	2.1
		AVG STD	**2.7**	**AVG STD**	**0.5**	**AVG STD**	**2.8**

		%, Precipitation	
Cu(II), uM	PO4, M	Average	STD
50	0.1	65.3	2.7
500	0.1	91.0	0.5
5000	0.1	99.3	0.6
5000	0.01	99.6	0.0
5000	0.00001	99.5	0.1
5000	0	99.5	0.1
		AVG STD	**1.01**

Table S7. Dominant Species at pH = 7.4 with and without Precipitation

Precipitation Not Allowed			Precipitation Allowed	
Metal	**Dominant species**	**% Total**	**Dominant species**	**% Total**
Fe(II)	$FeHPO_{4(aq)}/FeH_2PO_4^+$	85/15	$Fe_3(PO_4)_{2(s)}$	96
Fe(III)	$Fe(OH)^{2+}$/ $Fe(OH)_{3(aq)}$	50/50	Strengite ($FePO_4$-$2H_2O$)	100
Cu(I)	Cu^+	100	Cuprite	100
Cu(II)	$CuHPO_{4(aq)}$	98	$CuHPO_{4(aq)}/Cu_3(PO_4)_{2(s)}$	88/12
Mn(II)	$MnHPO_{4(aq)}/Mn^{2+}$	95/5	$MnHPO_{4(s)}$	100
Mn(III)	Mn^{3+}	100	$MnO(OH)_{(s)}$	100
Mn(IV)	Mn^{4+}	100	$MnO_{2(s)}$	100

(a)

(b)

(c)

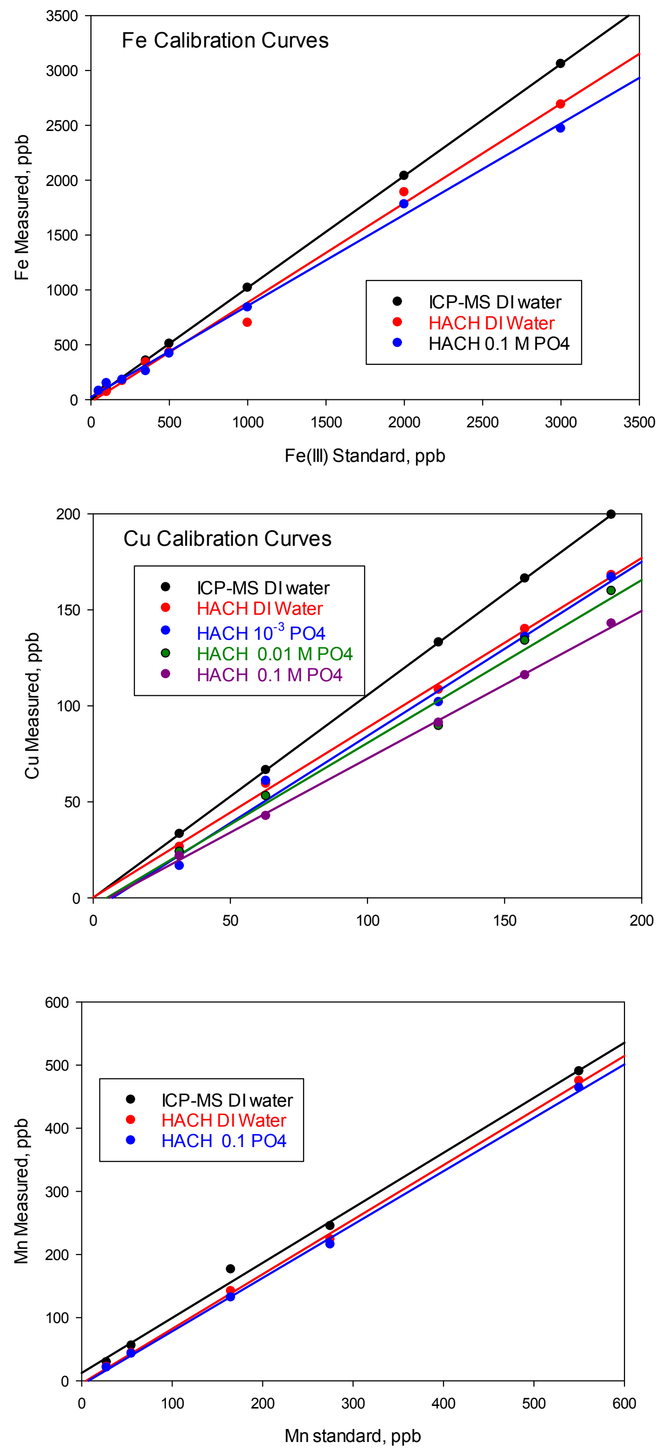


Figure S1. HACH calibration curves for (a) Fe, (b) Cu and (c) Mn

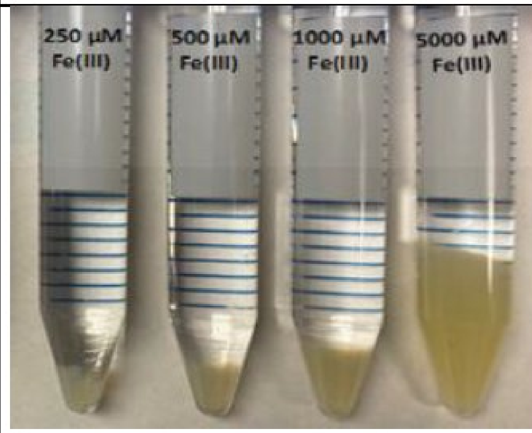
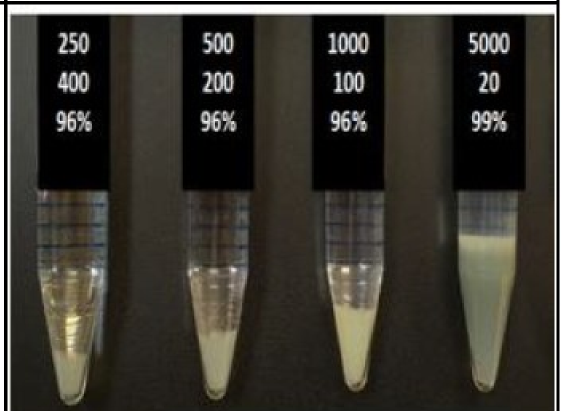
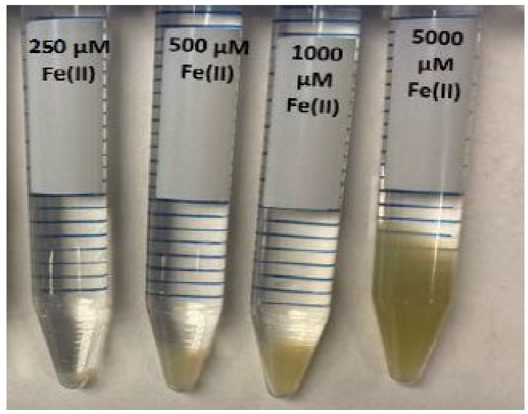
Metal = Fe(III) pH = 7.4 T = 37 ˚C	Effect of metal concentration in 0.1M phosphate buffer:
In the presence of Dithiothreitol	
In the absence of Dithiothreitol	

Figure S2. Fe(III) macroscopic experiments with and without DTT.

<table>
<tr><td>Metal = Fe(II)
pH = 7.4
T = 37 °C</td><td>Effect of metal concentration in 0.1M phosphate buffer:</td></tr>
<tr><td>In the presence of Dithiothreitol</td><td>
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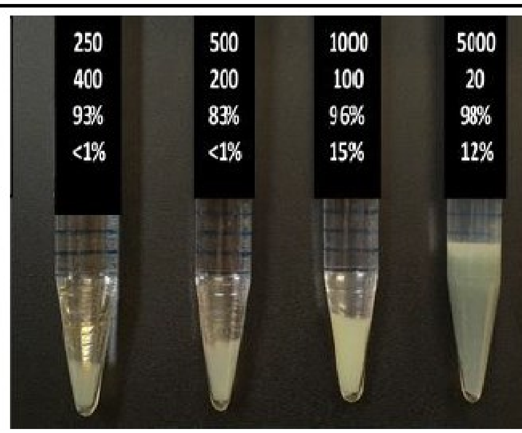
<tr><td>In the absence of Dithiothreitol</td><td>
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Figure S3. Fe(II) macroscopic experiments with and without DTT.

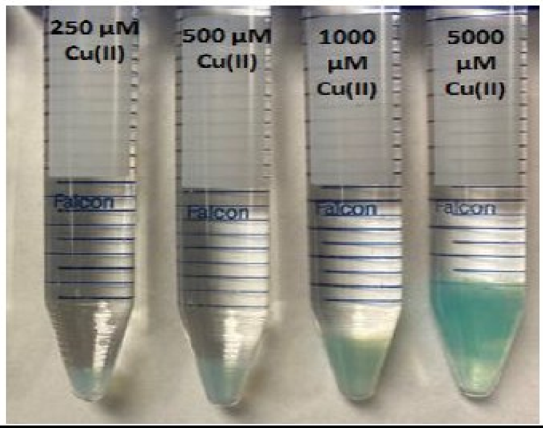
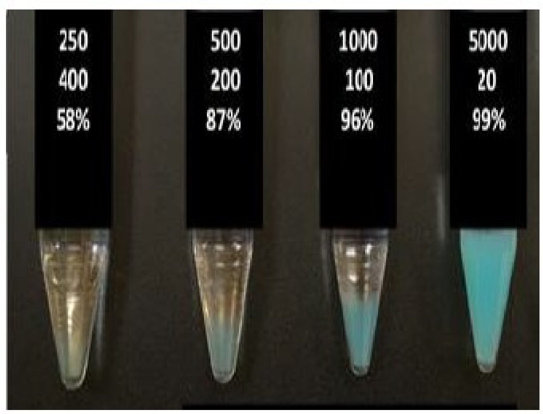
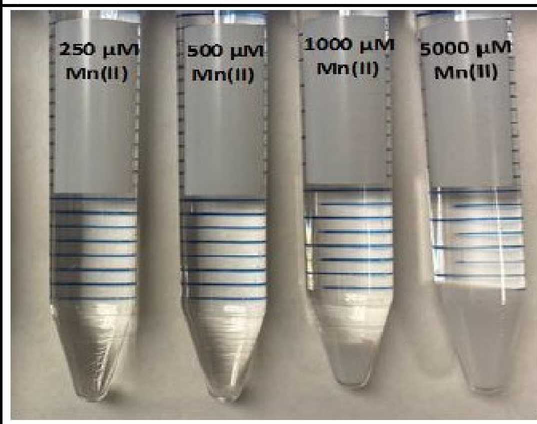
Metal = Cu(II) pH = 7.4 T = 37 ˚C	Effect of metal concentration in 0.1M phosphate buffer:
In the presence of Dithiothreitol	
In the absence of Dithiothreitol	

Figure S4. Cu(II) macroscopic experiments with and without DTT.

<table>
<tr><td>Metal = Mn(II)
pH = 7.4
T = 37 ˚C</td><td>Effect of metal concentration in 0.1M phosphate buffer:</td></tr>
<tr><td>In the presence of Dithiothreitol</td><td>
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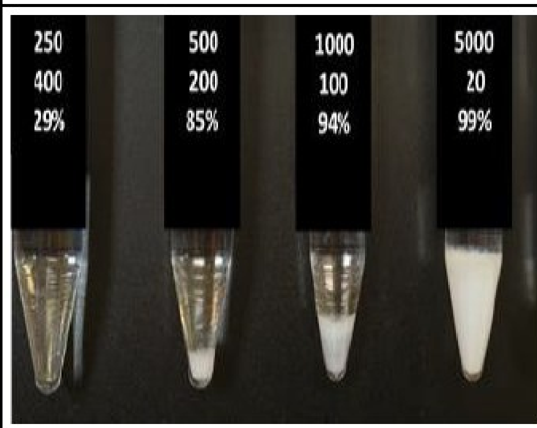
<tr><td>In the absence of Dithiothreitol</td><td>
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Figure S5. Mn(II) macroscopic experiments with and without DTT.

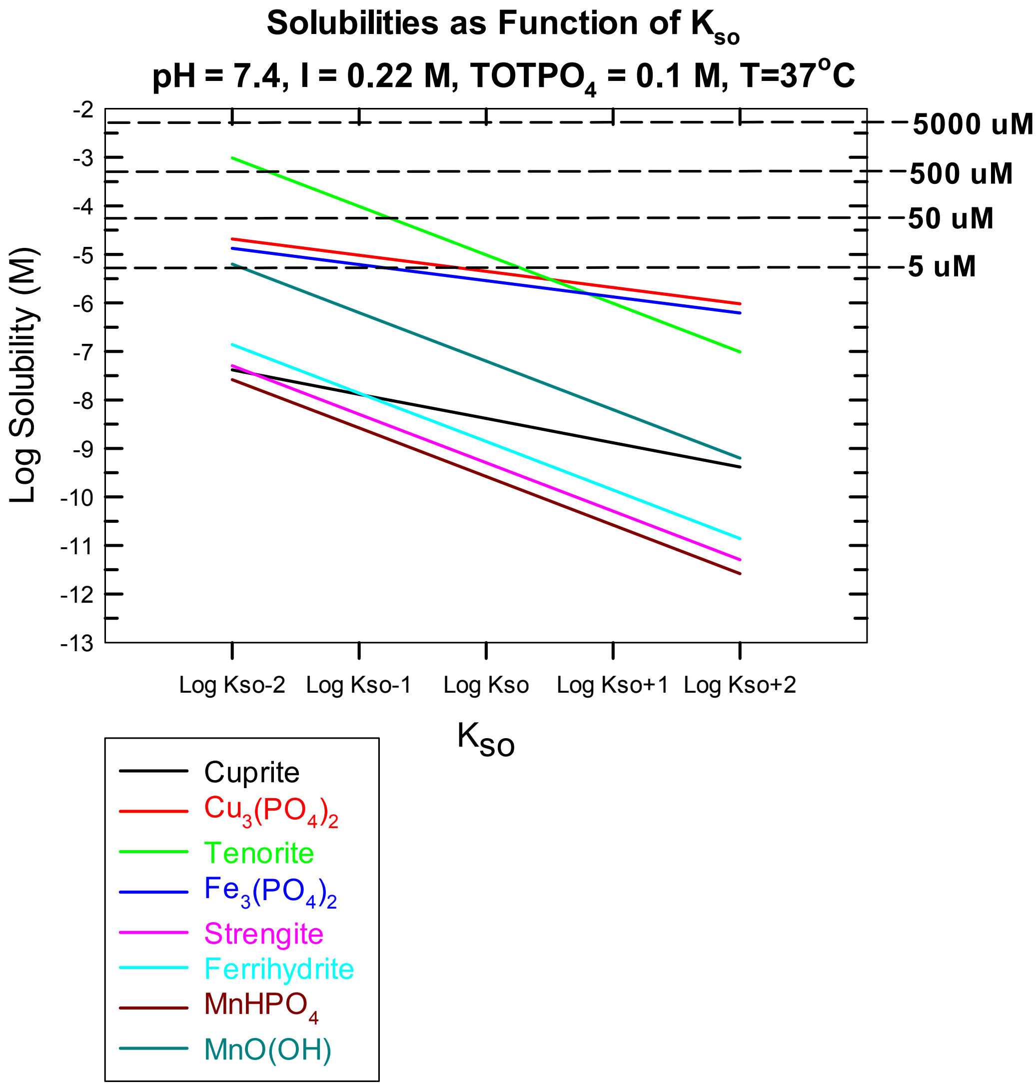

Figure S6. Effect of K_{so} on metal solubilities on selected precipitates.

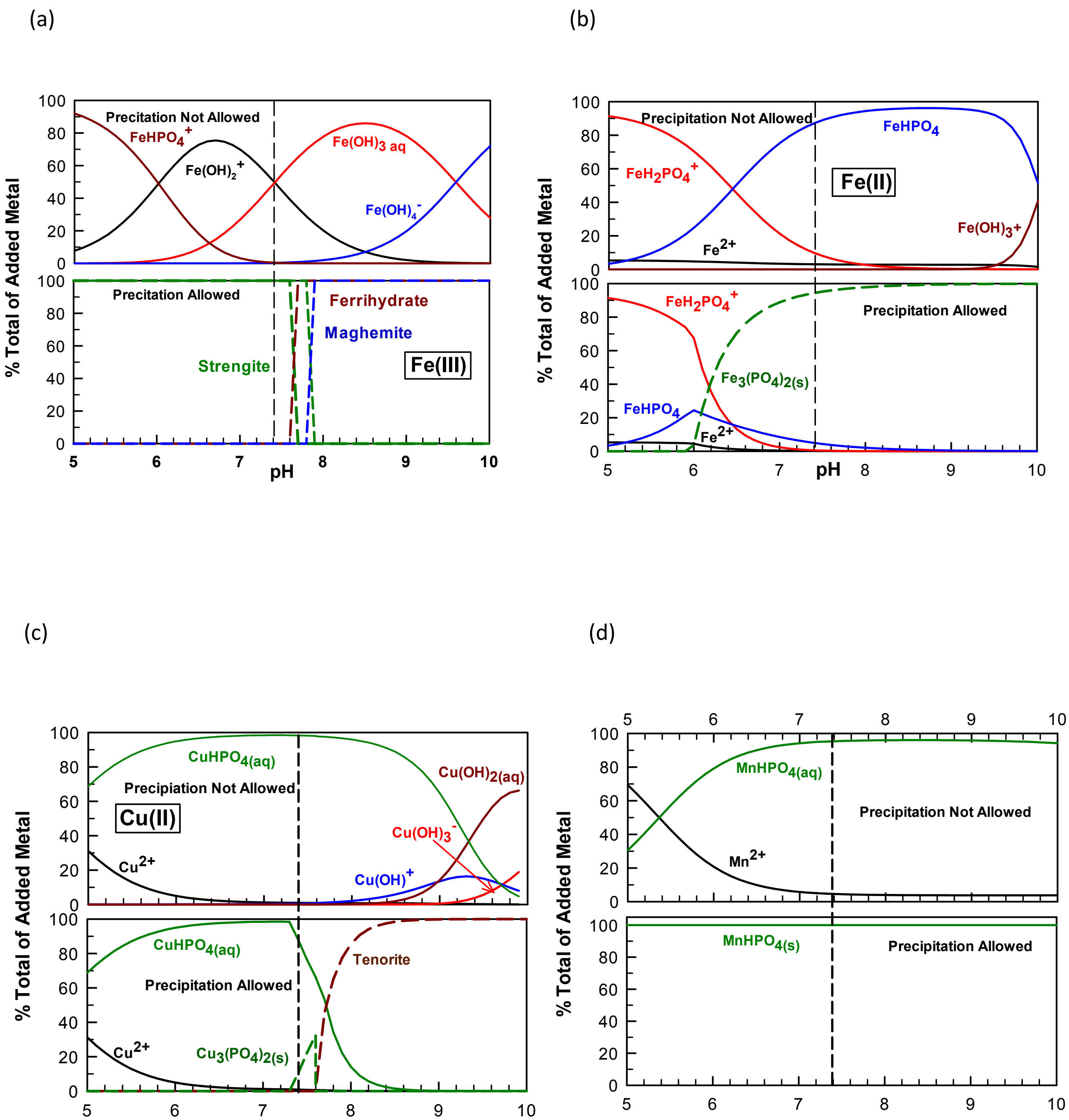

Figure S7. Effect of pH on metal speciation (a) Fe(III), (b) Fe(II), (c) Cu(II) and (d) Mn(II)

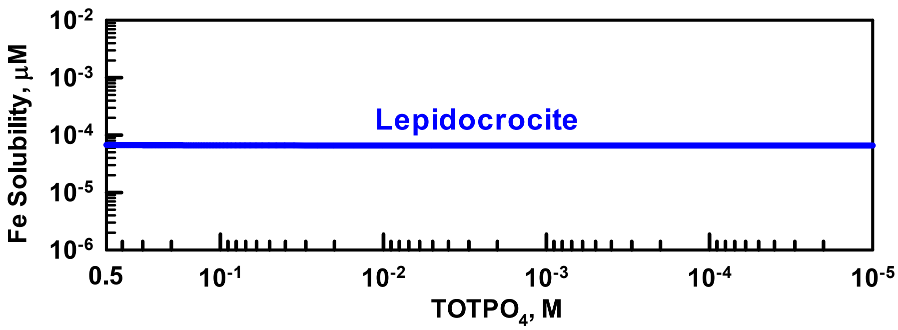

Figure S8. Fe(III) solubility versus $TOTPO_4$ for strengite- lepidocrocite

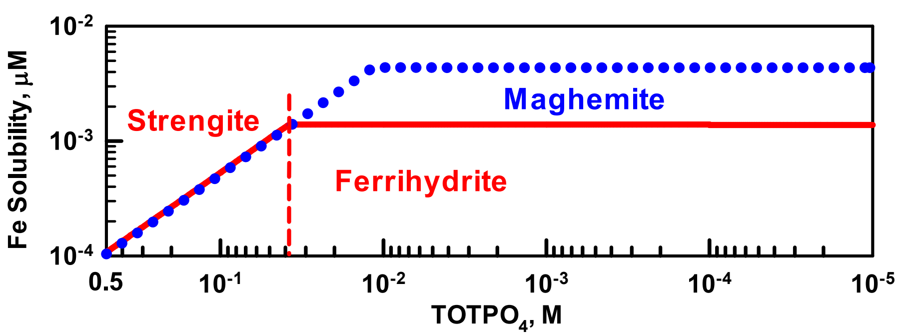

Figure S9. Fe(III) solubility versus $TOTPO_4$ for strengite-ferrihydrite (red) and strengite-maghemite (blue)

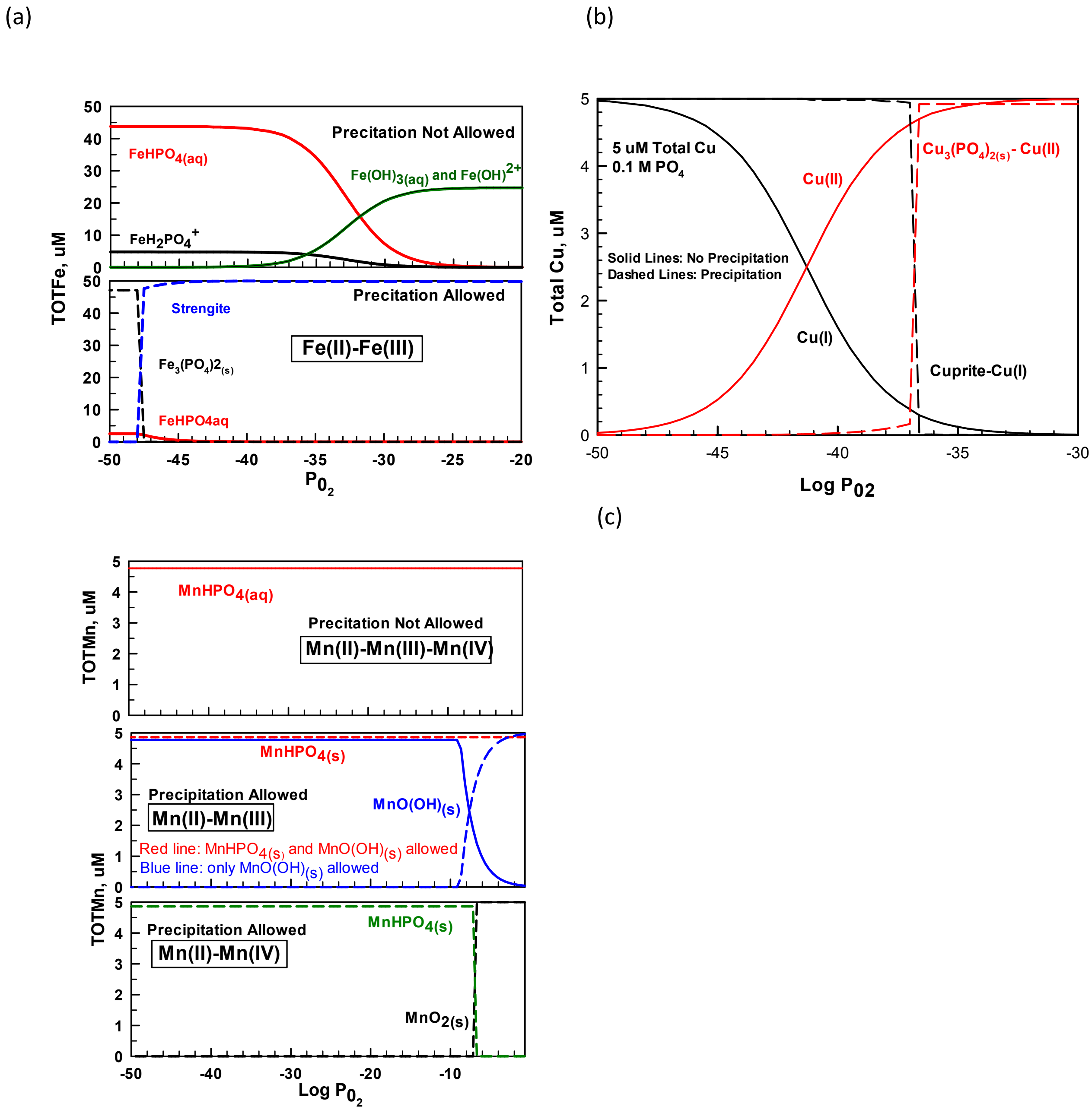

Figure S10. Effect of P_{O2} on metal speciation: (a) Fe(II)-Fe(III), (b) Cu(I)-Cu(II) and (c) Mn(II)-Mn(III)-Mn(IV)

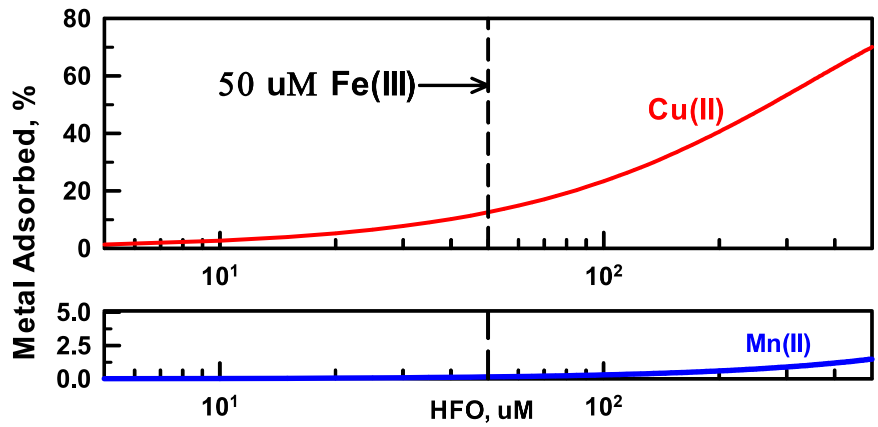

Figure S11. Adsorption of Cu(II) and Mn(II) by HFO: Function of Fe(III) concentration. TOTCu(II) = TOTMn(II) = 5 µM