Table SI-1. Thermodynamic data used to calculate thermodynamic equilibrium constants to construct phase diagrams.

	ΔG^o kJ/mol *at* 25 °C [a]	ΔG^o kJ/mol at 31.25 °C [a]	ΔG^o kJ/mol at 100 °C [a]	Density (g / cm^3) 25 °C	Molar Surface Area for 10 nm (m^2 / mol) [c]	Surface energy [d]		† $\ddot{A}H_{Surface}$ [e]	
						Hydrous (J / m^2)	Anhydrous (J / m^2)	Hydrous (kJ /mol)	Anhydrous (kJ /mol)
H_2O	-237.1 ± 0.1	-237.10 ± 0.1							
CO_2	-394.4 ± 0.2	-394.78 ± 0.2							
$Mn^{2+}_{(aq)}$	-228.1 ± 0.5	-228.20 ± 0.5							
$MnCO_{3(s)}$	-819.1 ± 0.6	-816.64 ± 0.6	-799.63± 0.6	3.7	18640.04	0.64 ± 0.08	0.94 ± 0.12	11.93	17.52
$Mn_3O_{4\ (s)}$	-1288.3± 1.4 [b]	-1286.1 ± 1.4[b]	-1263.4± 1.4[b]	4.84	28364.88	0.96 ± 0.08	1.62 ± 0.08	27.23	45.95

[a] $\Delta G_f{}^o$ (25 and 31.25 °C) values except for Mn_3O_4 are taken from Robie and Hemingway (Robie et al., 1978)

[b] $\Delta Gf_{(Mn3O4)}$ (25 – 707 °C) = -333.592 - (3.672E-3)T LnT + (0.331E-6) T^2 + 123.300/T + (109.543E-3) T (Pankratz, 1982)

[c] Molar surface area for spherical particle size D = (6 * molar mass * 1000) / (density* D)

[d] Surface energy values of Mn_3O_4 are from Birkner and Navrotsky_ENREF_37 and $MnCO_3$ are from this work.

[e] Free energy shift due to surface energy ($\ddot{A}H_{surface}$) = Molar surface area for 10 nm X surface energy/1000.

Table SI-2. Chemical reactions and thermodynamic calculations used to construct Eh- pH and Oxygen-CO_2 fugacity diagrams.

Reaction No	Half reactions for phase boundaries in Eh-pH diagrams	
1. Mn^{2+} /$MnCO_3$	***0.5 $MnCO_{3(s)}$ → 0.5 $Mn^{2+}_{(aq)}$ + 0.5CO_3^{2-}*** $\Delta G_r(1)$-bulk = 0.5 $\Delta G_f(Mn^{2+})$ + 0.5$\Delta G_f(CO_3)$ – 0.5 $\Delta G_f(MnCO_3)$ $\Delta G_r(1)$-nano = 0.5 $\Delta G_f(Mn^{2+})$ + 0.5$\Delta G_f(CO_3)$ – 0.5 $\Delta G_f(MnCO_3)$-0.5$\Delta H_{surface}$ ($MnCO_3$)	pH = [-ΔG_r (1)/2.303RT] - 0.5Log [Mn^{2+}] - 0.5Log [CO_2] + 9.05
2. Mn^{2+} / Mn_3O_4	***0.5 $Mn_3O_{4\,(s)}$ + 4H^+ + e → 1.5 Mn^{2+} + 2 H_2O*** $\Delta G_r(2)$-bulk = 1.5$\Delta G_f(Mn^{2+})$ +2$\Delta G_f(H_2O)$ – 0.5$\Delta G_f(Mn_3O_4)$ $\Delta G_r(2)$-nano = 1.5$\Delta G_f(Mn^{2+})$ +2$\Delta G_f(H_2O)$ – 0.5$\Delta G_f(Mn_3O_4)$-0.5$\Delta H_{surface}(Mn_3O_4)$	Eh = E^o - 2.303RT/nF (1.5 log[Mn^{2+}] + 4pH) where E^o = -$\Delta G_r(2)$/ n F
3. Mn_3O_4/ $MnCO_3$	**0.5 $Mn_3O_{4(s)}$ + 1.5CO_3 + 4 H^+ + e → 1.5 $MnCO_{3(s)}$ + 2 H_2O** $\Delta G_r(3)$- bulk = 1.5$\Delta G_f(MnCO_3)$ + 2$\Delta G_f(H_2O)$ – 0.5$\Delta G_f(Mn_3O_4)$-1.5$\Delta G_f(CO_3)$ $\Delta G_r(3)$ - nano = 1.5$\Delta G_f(MnCO_3)$ + 1.5$\Delta H_{surface}$ ($MnCO_3$) + 2$\Delta G_f(H_2O)$ – 0.5$\Delta G_f(Mn_3O_4)$-0.5$\Delta H_{surface}(Mn_3O_4)$ - 1.5$\Delta G_f(CO_3)$	Eh = E^o - 2.303RT/nF (-1.5 log[CO_3] + 4pH) where E^o = -$\Delta G_r(3)$/ n F
	Equilibrium reactions for Oxygen-CO_2 fugacity diagrams	
4. Mn_3O_4/ $MnCO_3$	***6 $MnCO_{3(s)}$ + O_2 → 2 $Mn_3O_{4\,(s)}$ + 6 $CO_{2(g)}$*** $\Delta G_r(4)$-bulk =2$\Delta G_f(Mn_3O_4)$ + 6$\Delta G_f(CO_2)$ - 6$\Delta G_f(MnCO_3)$ $\Delta G_r(4)$ -nano = 2$\Delta G_f(Mn_3O_4)$ + 2$\Delta H_{surface}(Mn_3O_4)$ + 6$\Delta G_f(CO_2)$ - 6$\Delta G_f(MnCO_3)$ - 6$\Delta H_{surface}$ ($MnCO_3$)	log[P_{O2}] = [($\Delta G_r(4)$ /2.303RT) + 6 Log [P_{CO2}]

Where Log[CO_3^{2-}] = -18.1 + Log [CO_2] + 2 pH
Eh = Potential of a solution relative to the SHE
pE = - log [e] = (nF/2.303 RT) Eh