

Supporting Information

To accompany the manuscript entitled

Reactivity of inorganic Mn and Mn Desferrioxamine B with O_2 , O_2^- and H_2O_2 in seawater

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Comprising :

32 Pages

3 Tables

11 Figures

Supplementary Information:

Cautionary Tales for comparing O_2^- decay rates: The published literature for the reactivity of Mn complexes with O_2^- is littered with apparently contradictory results, some of which is related to the choice of buffer and the detection system employed ¹, ². Problems may also occur through other redox reactions involving probe compounds (e.g. oxidation of ferrocytochrome, reduction of nitroblue tetrazolium (NBT)). In our evaluation of the literature we also came across two other critical problems:

- (1) The frequent use of the piperazine ring containing Good's buffer ³ HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) without apparent recognition that this buffer is known to react with O_2^- producing HEPES radicals ⁴. It has also been shown that H_2O_2 oxidizes HEPES ⁵. Indeed a number of studies have recommended that HEPES should not be used for O_2^- quantification ^{6,7}.
- (2) The reporting of reaction rates for different Mn species but without consideration of the complexation effects of the buffer. In many cases where phosphate buffers have been used results are interpreted in terms of a synergistic effect of phosphate on the rates however a closer examination of the Mn speciation may reveal it is simply the reactivity of the Mn phosphate complexes in solution.

Seawater sampling

Sampling Stations. The seawater used in this study was collected during three research expeditions with the German research vessels RV Meteor and RV Maria S. Merian. The first cruise was performed in the Eastern Tropical North Atlantic (ETNA) during M83/1 (Las Palmas, Gran Canaria, Spain – Mindelo, Cape Verde),

from 14 October - 13 November 2010. The second expedition took place in the ETNA during MSM17/4 (Dakar, Senegal to Las Palmas, Spain) from 10 March to 12 April, 2011. The final cruise was in the Eastern Tropical South Pacific (ETSP) during M90 (Colon, Panama – Callao, Peru), from October 26 – 26 November 2012.

Field Sample collection. All analytical work at sea was performed in an over-pressurized ISO class 5 clean container, inside of which analysts wore the appropriate clean room apparel; overalls with hood (Tyvek), shoes (Abeba) and plastic gloves (Carl Roth). Seawater samples in this work were obtained from the whole water column using modified Teflon coated PVC General Oceanics (Miami, FL, USA) GoFlo bottles of 8 L in which the original drain cock was replaced by a Teflon stop cock. These bottles were deployed on a Kevlar line from the side of the ship. Immediately upon recovery of the bottles, samples were filtered in-line through 0.2 μm filter cartridges (Sartorius Sartobran filter capsule 5231307H5) by N_2 overpressure into acid cleaned 1 L Teflon bottles (Nalgene).

Overview of the FeLume chemiluminescence system: This system comprises a light tight box equipped with a Plexiglas spiral flow cell mounted below a photon counter (Hamamatsu HC-135-01) linked to a laptop computer via a Bluetooth connection controlled through a purpose built LabviewTM (National Instruments) virtual instrument. For O_2^- determination we ran the sample and the MCLA reagent directly into the flow cell using a peristaltic pump (Gilson Minipuls 3, operating at 18 rpm,) with the sample line being pulled through the flow cell as this leads to the smallest amount of dead time in the system (typically 2 – 3 s). The overall flow rate through the cell was 8.25 mL min^{-1} , comprising 5.0 mL min^{-1} from the MCLA and

3.25 mL min⁻¹ from the sample. The transit time through the optical cell (300 μL) was therefore 2.18 s. For the precision and accuracy of the method, please, see assessment in Heller and Croot⁸. For more information on specific calibration issues and impurities for O₂⁻ the reader is referred to Heller and Croot⁹.

Calculation of rate data for superoxide. The raw chemiluminescence signal for the reaction between MCLA and O₂⁻ recorded by the computer was processed using a specially designed LabviewTM VI constructed for this purpose using standard kinetic fitting procedures to determine both the 1st (k_{obs}) and 2nd order (k_2) rates simultaneously. The photon counter has a base counting period of 10 ms, for the present work we used average counts of an integration time of 200 ms. Dark background counts for this detector were typically 60 – 120 counts s⁻¹. Apparent reaction rates for Mn complexes with O₂⁻ were calculated via linear regression of k_{obs} versus the total metal added. Using our experimental setup the minimum values for k_{obs} that we can determine is estimated at 1 x 10⁶ mol L⁻¹ s⁻¹.

Model Calculations for O₂⁻ kinetics. Numerical modeling of O₂⁻ reactions in seawater was performed using a fully explicit model written in C++. Rate constants for the key reactions involved were compiled from those already published in the literature (see Table S2 in our companion paper¹⁰).

Water exchange rates for Mn(II) and Mn(III) complexes:

Water exchange rates for the d^5 Mn(II) aquo ion have been determined, $k_{ex} = 2.1 \times 10^7 \text{ s}^{-1}$ ¹¹. Measurements for the rate of water exchange for the d^4 Mn(III) aquo ion do not exist as yet, but have been recently estimated by comparison with Fe at $k_{ex} \sim 10^2 - 10^3 \text{ s}^{-1}$ ¹². Ligand exchange rates for the fluoride complexation of the aquo Mn(III) ion ($k_{ex} = 1 \times 10^4 \text{ s}^{-1}$, 10° C) and Mn(OH)²⁺ ion ($k_{ex} \sim 10^4 - 10^5 \text{ s}^{-1}$, 10° C) have been reported and the fast rates ascribed to a strong Jahn-Teller effect¹³. The water loss kinetics of Mn(OH)₂⁺ and Mn(OH)₃ are not determined but we would predict greater rates of water exchange in which water loss rates increase as the charge to radius ratio of the metal ion decreases analogous to that for Fe(III)¹⁴. Data for Mn(III) porphyrins indicates that exchange of axial ligands is rapid $k_{ex} = 0.4 - 2.8 \times 10^7 \text{ s}^{-1}$ due to the charge density of the metal centre and the steric decompression of the complex¹².

Reactions of O₂⁻ with Mn(II) organic complexes

There are only a limited number of published data sets on the reactions of other Mn(II) organic complexes with O₂⁻¹⁵. Fisher and colleagues¹⁶ using O₂⁻ detection with NBT reported a value of $k = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of Mn(II) EDTA with O₂⁻, while a more recent study could only place an upper bound for this reaction of $k < 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ using spectrophotometry/stopped flow¹. It is noted however that other studies have found no evidence for this reaction¹⁷⁻²⁰.

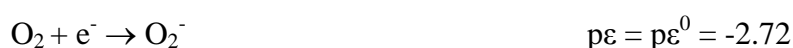
Thermodynamic calculations used in Figures S3-S5

Reduction reactions for relevant oxygen and Mn reactions normalized to one electron.

All species are in aqueous form except for MnOOH. Activities of all reactants other than H^+ are at unity.

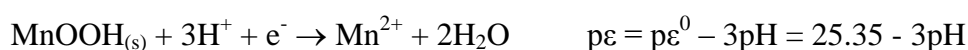
Oxygen Reactions

One electron transfer reactions only



Manganese Reactions

One electron transfer reactions only



References: Oxygen reactions ^{21, 22} MnDFB ²³

Determination of required binding strength for Mn(III)L for spontaneous oxidation of Mn(II)L by O₂ using the Nernst equation.

$$pE^{\circ}_{Mn(III)L/Mn(II)L} = pE^{\circ}_{Mn(III)/Mn(II)} + \log \left(\frac{{}^cK_{[Mn(II)L]}}{{}^cK_{[Mn(III)L]}} \right)$$

where cK is the conditional stability constant for the complex of the form



electron potential. $pE = E / 0.059$.

If $\Delta G < 0$ for the 1 electron oxidation by O_2 to proceed then $pE > 0$ for the combination of the two $1 e^-$ transfers, this condition is reached when $pE^{\circ}_{Mn(III)L/Mn(II)L} < -2.72$. Then using $pE = 25.3$ for the $Mn^{3+} + e^- \rightarrow Mn^{2+}$ results in $\log(^cK_{[Mn(II)L]}/^cK_{[Mn(III)L]}) < -28.02$. Thus $^cK_{[Mn(III)L]}/^cK_{[Mn(II)L]} > 10^{28.02}$.

Notes: Complexation by Ca and Mg will result in the same lowering of the conditional stability constant for both Mn(II) and Mn(III) complexes if their stoichiometry is the same.

Table S1: Mn(II), Mn(III) and Mn(IV) reactivity with O₂, HO₂, O₂⁻ and H₂O₂

Reactant	Products	Forward reaction k_f	Reverse reaction k_r	pH	Ionic Strength	Tempe- rature	Ref.
O ₂ + MnOH ⁺		1.66 x 10 ⁻² M ⁻¹ s ⁻¹		8.03-9.30	Ammonia- C _T - P _{CO2} - seawater	25°C	²⁴
O ₂ + Mn(OH) ₂		2.09 x 10 ⁻¹ M ⁻¹ s ⁻¹		8.03-9.30	Ammonia- C _T - P _{CO2} - seawater	25°C	²⁴
O ₂ + Mn(CO ₃) ₂ ²⁻		8.13 x 10 ⁻² M ⁻¹ s ⁻¹		8.03-9.30	Ammonia- C _T - P _{CO2} - seawater	25°C	²⁴
O ₂ + Mn ^(III) (Glu)	Mn(III)Glu + X	2.8 x 10 ⁴ M ⁻¹ s ⁻¹			0.3M NaOH+0.1M	25°C	²⁵

					NaGlu		
$\text{H}_2\text{O}_2 + \text{Mn}^{3+}$	$\text{MnO}_2^+ + 2\text{H}^+$	$2.8 \pm 0.3 \times 10^3 \text{ M}^{-1}$ s^{-1}		0-2 at higher pH, the rate increases due to the presence of $\text{Mn}(\text{OH})_2^+$	3.2 - 3.5	22°C	²⁶
$\text{H}_2\text{O}_2 + \text{Mn}^{3+}$	$\text{Mn}^{2+} + \text{HO}_2 + \text{H}^+$	$2.8 \pm 0.3 \times 10^3 \text{ M}^{-1}$ s^{-1}	(see below)	0-2		0.5-40°C	²⁷
$\text{H}_2\text{O}_2 + 2\text{Mn}^{3+}$	$2\text{Mn}^{2+} + \text{O}_2 + 2\text{H}^+$	$80 \pm 3 \text{ s}^{-1}$ with			4.00	25°C	²⁸

		initial Mn(III) 1.94-5.57 x 10 ⁴ M and H ₂ O ₂ 0.41-8.20 x 10 ⁴ M					
H ₂ O ₂ + Mn ^(IV)	Mn ²⁺ + 2H ⁺ + O ₂	$k > 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$					27
H ₂ O ₂ + MnO ₂	Mn ³⁺ + O ₂ ⁻ + 2H ⁺	$7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		10	Alkaline solutions		29
H ₂ O ₂ + Mn ^(III) gluconate		$2.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		10	1.82 - 18.2 mM NaGlu	room temperature	30
HO ₂ + Mn ²⁺	MnO ₂ ⁺ + H ⁺	$1.1 \pm 0.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$6.5 \pm 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		3.2 - 3.5	22°C	26
HO ₂ + Mn ²⁺ (Pyrophosphate)	Mn ^(III) Pyrophosphate + H ₂ O ⁻	$\sim 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$		0.1		25°C	31

$O_2^- + Mn^{2+}$	MnO_2^+	$1.5 \pm 0.2 \times 10^8 M^{-1} s^{-1}$	$6.5 \pm 1.0 \times 10^3 s^{-1}$ 1		3.2 - 3.5	22°C	²⁶
$O_2^- + Mn^{2+}$ (Sulfate)	MnO_2^+ (Sulfate)	$4.0 \pm 0.5 \times 10^7 M^{-1} s^{-1}$	$8.5 \pm 2.0 \times 10^3 s^{-1}$ 1		3.2 - 3.5	22°C	²⁶
$O_2^- + Mn^{2+}$ (Formate)	MnO_2^+ (Formate)	$4.6 \times 10^7 M^{-1} s^{-1}$		7 5?			^{32 33}
$O_2^- + Mn^{2+}$ (Sulfate)	MnO_2^+ (Sulfate)	$5.4 \times 10^7 M^{-1} s^{-1}$		7			³²
$O_2^- + Mn^{2+}$ (Phosphate)	MnO_2^+ (Phosphate)	$2.8 \times 10^7 M^{-1} s^{-1}$		7			³²
$O_2^- + Mn^{2+}$ (Pyrophosphate)	$Mn^{(III)}$ Pyrophosphate + H_2O^-	$\sim 2 \times 10^7 M^{-1} s^{-1}$		7		25°C	³¹
$O_2^- + Mn^{2+}$	MnO_2^+	$1.7 \times 10^7 M^{-1} s^{-1}$		7			³²

(Pyrophosphate)	(Pyrophosphate)						
$O_2^- + Mn^{2+}$ (Citrate)	MnO_2^+ (Citrate)	$1.3 \times 10^7 M^{-1} s^{-1}$	$< 10 s^{-1}$	7			34
$O_2^- + MnHCO_3^+$	MnO_2HCO_3	$1.4 \times 10^8 M^{-1} s^{-1}$	$7 s^{-1}$	7			34
$O_2^- + MnHPO_4$	$MnO_2(HPO_4)^-$	$2.3 \times 10^7 M^{-1} s^{-1}$	$10 s^{-1}$	7			34
$O_2^- + MnNTA$		$4 \times 10^8 M^{-1} s^{-1}$		5			35
$O_2^- + MnEDTA$		$7.5 \times 10^6 M^{-1} s^{-1}$		5			35
$O_2^- + Mn^{2+}$		$k_{cat} = 1.3 \times 10^6 M^{-1} s^{-1}$ (a)		7.8	0.05 M Potassium phosphate	25°C	20
$O_2^- + Mn^{2+}$	MnO_2^+	$k_{cat} = 8.9 \times 10^6 M^{-1} s^{-1}$ (b)		7	0.05 M phosphate medium	25°C	32
$O_2^- + Mn^{2+}$		$k_{cat} = 4 \times 10^6 M^{-1} s^{-1}$ (c)		6.5		22-25°C	18

$\text{O}_2^- + \text{Mn}^{2+}$		$k_{\text{cat}} = 2.7 \pm 0.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ (d)}$		7.8	0.111M	21°C	1
		$k_{\text{cat}} = 4.5 \pm 0.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ (e)}$		7.4			
		$k_{\text{cat}} = 6.9 \pm 0.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ (f)}$		7.0			
$\text{HO}_2 + \text{Mn}^{3+}$		$k < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$			3.2-3.5	22°C	26
$\text{O}_2^- + \text{Mn}^{3+}(\text{OAc}^-)_3$		No activity		8.1	0.026M	21°C	1
$\text{O}_2^- + \text{Mn}^{(\text{III})}\text{DFB}$		$k_{\text{cat}} = 1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (g)}$		7		37°C	36
MnO_2^+L (L=Pyrophosphate)	$\text{Mn}^{3+}\text{L} + \text{H}_2\text{O}_2$	$> 2 \times 10^4 \text{ s}^{-1}$		7		25°C	33

MnO ₂ ⁺ L (L=Phosphate)	Mn ³⁺ L + H ₂ O ₂	2 x 10 ³ s ⁻¹		5		25°C	33
MnO ₂ ⁺ L (L=NTA)	Mn ³⁺ L + H ₂ O ₂	3 x 10 ³ s ⁻¹		5			35
MnO ₂ ⁺ L (L=EDTA)	Mn ³⁺ L + H ₂ O ₂	9 x 10 ¹ s ⁻¹		5			35
MnO ₂ ⁺ L (L=Formate)	Mn ³⁺ L + H ₂ O ₂	< 5 s ⁻¹		5.9		25°C	33
MnO ₂ ⁺ L (L=Sulfate)	Mn ³⁺ L + H ₂ O ₂	< 1.4 s ⁻¹		5.6		25°C	33
MnO ₂ ⁺ + MnO ₂ ⁺ (+2H ⁺)	2Mn ²⁺ + H ₂ O ₂ + O ₂	6.0 ± 1.0 x 10 ⁶ M ⁻¹ s ⁻¹			3.2-3.5	22°C	26
MnO ₂ ⁺ L + MnO ₂ ⁺ L (L= HCO ₃ ⁻)	2Mn ²⁺ L + H ₂ O ₂ + O ₂	1.5 x 10 ⁶ M ⁻¹ s ⁻¹		7			34
MnO ₂ ⁺ L + MnO ₂ ⁺ L (L= HPO ₄ ²⁻)	2Mn ²⁺ L + H ₂ O ₂ + O ₂	8.9 x 10 ⁶ M ⁻¹ s ⁻¹		7			32, 34

$\text{HO}_2 + \text{MnO}_2^+ (+\text{H}^+)$	$\text{Mn}^{2+} + \text{H}_2\text{O}_2 + \text{O}_2$	$1.0 \pm 0.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$			3.2-3.5	22°C	²⁶
$\text{O}_2^- + \text{MnO}_2^+(\text{sulfate})$ (+2H ⁺)	$\text{Mn}^{2+} + \text{H}_2\text{O}_2 + \text{O}_2$	$3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$		5.5-6.5		25°C	³³

Notes: (a) Pulse radiolysis. (b) ⁶⁰Co gamma irradiation. (c) Xanthine oxidase/Xanthine. (d) DMSO/KO₂ Phosphate buffer pH 7.8, no apparent activity in HEPES at pH 7.8 or 8.1 (e) DMSO/KO₂ Phosphate buffer pH 7.4, (f) DMSO/KO₂ Phosphate buffer pH 7.0. (g) Xanthine oxidase/Xanthine, Cytochrome c.

Table S2: Table: Mn(II) and Mn(III) Speciation in Seawater

Reactant			Ref.
$\text{Mn}^{2+} + \text{H}_2\text{O}$	$\text{MnOH}^+ + \text{H}^+$	$\text{Log } K_1 = -10.6$	37
$\text{Mn}^{2+} + 2\text{H}_2\text{O}$	$\text{Mn}(\text{OH})_2 + 2 \text{H}^+$	$\text{Log } \beta_2 = -22.2$	37
$\text{Mn}^{2+} + 3\text{H}_2\text{O}$	$\text{Mn}(\text{OH})_3^- + 3 \text{H}^+$	$\text{Log } \beta_3 = 34.8$	37
$\text{Mn}^{2+} + 4\text{H}_2\text{O}$	$\text{Mn}(\text{OH})_4^{2-} + 4 \text{H}^+$	$\text{Log } \beta_4 = -48.3$	37
$\text{Mn}^{2+} + \text{CO}_3^{2-}$	MnCO_3	$\text{Log } K = 4.4$	38
$\text{Mn}^{2+} + 2\text{CO}_3^{2-}$	$\text{Mn}(\text{CO}_3)_2^{2-}$	$\text{Log } K = 5.7$	38
$\text{Mn}^{2+} + \text{CO}_3^{2-} + \text{H}^+$	MnHCO_3^+	$\text{Log } K = 11.6$	38
$\text{Mn}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	MnOHCO_3^-	$\text{Log } K = -6.1$	38
$\text{Mn}^{2+} + \text{NH}_3$	MnNH_3^{2+}	$\text{Log } K = 1.0$	38
$\text{Mn}^{2+} + 2\text{NH}_3$	$\text{Mn}(\text{NH}_3)_2^{2+}$	$\text{Log } K = 1.5$	38
$\text{Mn}^{2+} + \text{Cl}^-$	MnCl^-	$\text{Log } K = 0.66$	38
$\text{Mn}^{2+} + \text{SO}_4^{2-}$	MnSO_4	$\text{Log } K = 2.3$	38
$\text{Mn}^{2+} + \text{F}^-$	MnF^-	$\text{Log } K = 1.3$	38
$\text{Mn}^{2+} + \text{O}_2$	$\text{Mn}^{3+} + \text{O}_2^-$	$\text{Log } K = -17.82$	38
$\text{MnOH}^+ + \text{O}_2$	$\text{MnOH}^{2+} + \text{O}_2^-$	$\text{Log } K = -9.2$	38
$\text{Mn}(\text{OH})_2 + \text{O}_2$	$\text{Mn}(\text{OH})_2^+ + \text{O}_2$	$\text{Log } K = -3.12$	38
$\text{Mn}^{3+} + \text{H}_2\text{O}$	$\text{MnOH}^{2+} + \text{H}^+$	$K_1 = 1.0 \pm 0.2$	39
$\text{Mn}^{3+} + \text{H}_2\text{O}$	$\text{MnOH}^{2+} + \text{H}^+$	* $K_1 = 0.4 \pm 0.1$	40
$\text{Mn}^{3+} + 2\text{H}_2\text{O}$	$\text{Mn}(\text{OH})_2^+ + 2 \text{H}^+$	* $\beta_2 = 0.1 \pm 0.1$	40
$\text{MnOH}^{2+} + \text{H}_2\text{O}$	$\text{Mn}(\text{OH})_2^+ + \text{H}^+$	$K_2 = 5.0 \pm 0.1$	29
$\text{Mn}^{3+} + \text{H}_2\text{O}$	$\text{MnOH}^{2+} + \text{H}^+$	$\text{Log } K_1 = -0.12$	41

Mn(III) + OH ⁻	Mn(OH) ²⁺	Log K ₁ = 12.5	⁴²
Mn(III)+2OH ⁻	Mn(OH) ₂ ⁺	Log β ₂ = 24.0	⁴²
Mn(III)+3OH ⁻	Mn(OH) ₃	Log β ₃ = 35.6	⁴²
2Mn(III) (+2H ₂ O)	MnO ₂ + 4H ⁺ + Mn ²⁺	Log K ~ 8.4	⁴⁰

Notes: 95% CI listed for lower data. Data in reference 43 was estimated from uptake of ⁵⁴Mn onto particles.

Table S3: Dissociation constants (pK) for Desferrixamine B and overall stability constants ($\log \beta_{pqr}$) Thermodynamic data for Mn(II) DFB Speciation in Seawater

Metal		pK Lab ^a	pK Seawater ^b	Reference
H ⁺	H ⁺ +L ³⁻	10.84	10.85	⁴³
	H ⁺ +HL ²⁻	9.46	9.47	⁴³
	H ⁺ +H ₂ L ⁻	9.00	9.00	⁴³
	H ⁺ +H ₃ L	8.30	8.30	⁴³
Metal	M _p L _q H _r	Log β_{pqr}	Log β_{pqr}	Reference
	p q r	(Lab) ^a	(seawater) ^b	
Mn ²⁺	1 1 0	6.81	6.83	⁴⁴
	1 1 1	17.39	17.41	⁴⁴
	1 1 2	25.51	25.53	⁴⁴
	1 1 3	32.6	32.62	⁴⁴
Mn ³⁺	1 1 1	36.5	36.53	⁴⁴
	1 1 1	39.56 ^c	39.24	²³
Mg ²⁺	1 1 0	2.8	2.82	⁴³
	1 1 1	14.66	14.68	⁴³
	1 1 2	23.85	23.87	⁴³
Ca ²⁺	1 1 0	3.03	3.05	⁴³
	1 1 1	13.25	13.27	⁴³
	1 1 2	22.41	22.43	⁴³

Notes: ^aConditions: I = 0.2 mol dm⁻³ KCl, 25 °C. ^bConditions: I = 0.7 mol dm⁻³, 25 °C (seawater), corrected using the Davies Equation. ^cCalculated from $\beta_{111}=K_1K$ where $\log K = 28.6 \pm 0.5$, for $K = [\text{MnHDFB}]/[\text{Mn}][\text{HDFB}]$, conditions: I = 0.1 mol dm⁻³ NaCl, 25 °C. $\text{pKw} = -13.63$ (from Millero calculation at 25C and Ionic strength 0.7, equivalent to salinity 33.950).

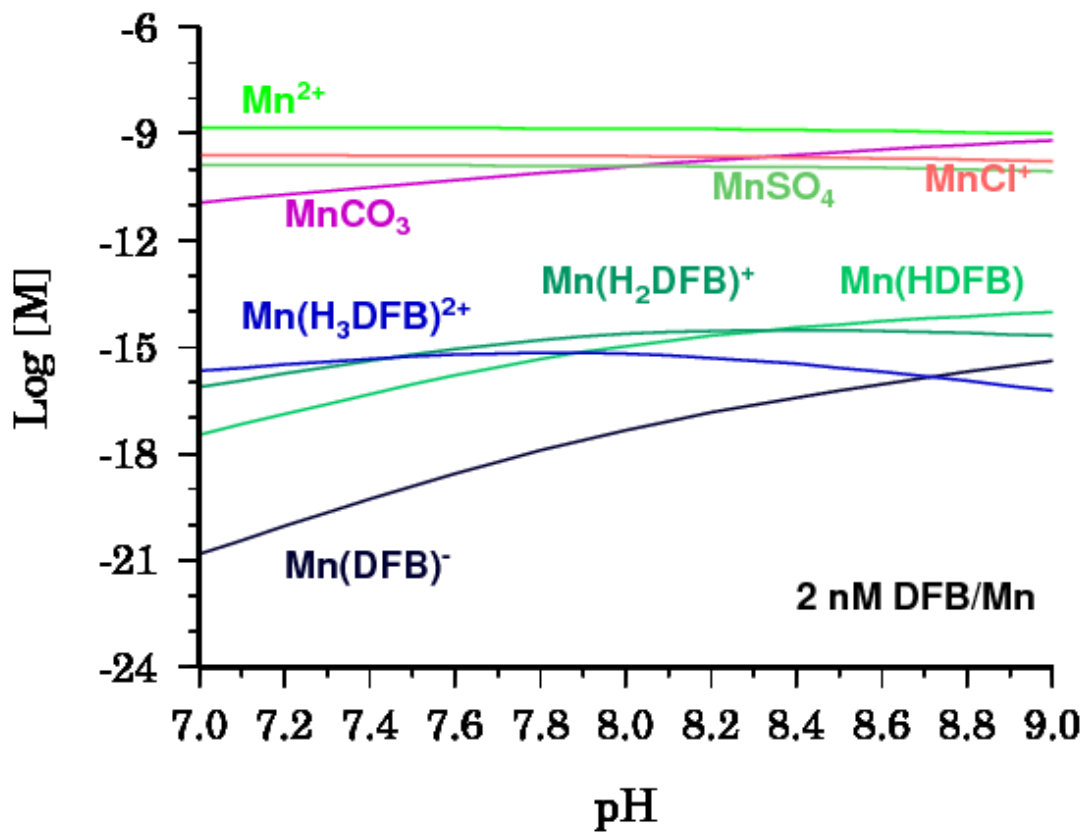


Figure S1: Calculated speciation of Mn(II) in seawater with 2 nM DFB.

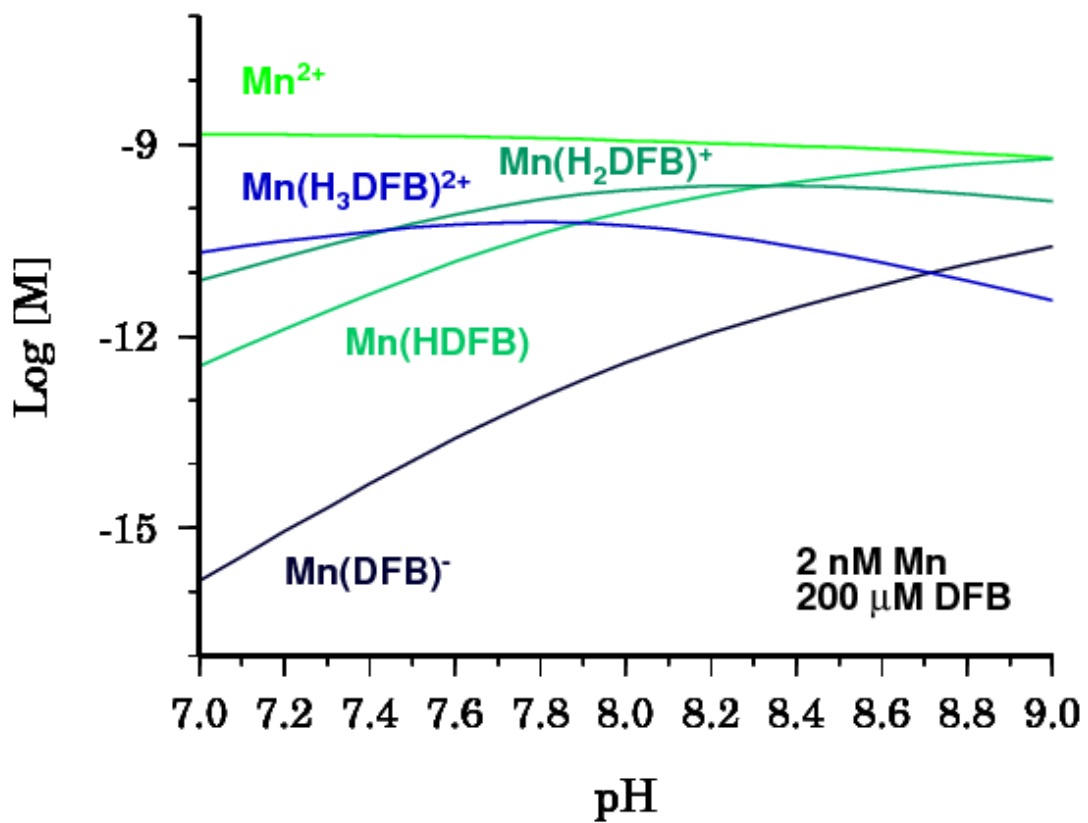


Figure S2: Calculated speciation of Mn(II) in seawater with 200 μM DFB. Other Mn inorganic species are not shown in order to highlight the Mn-DFB species.

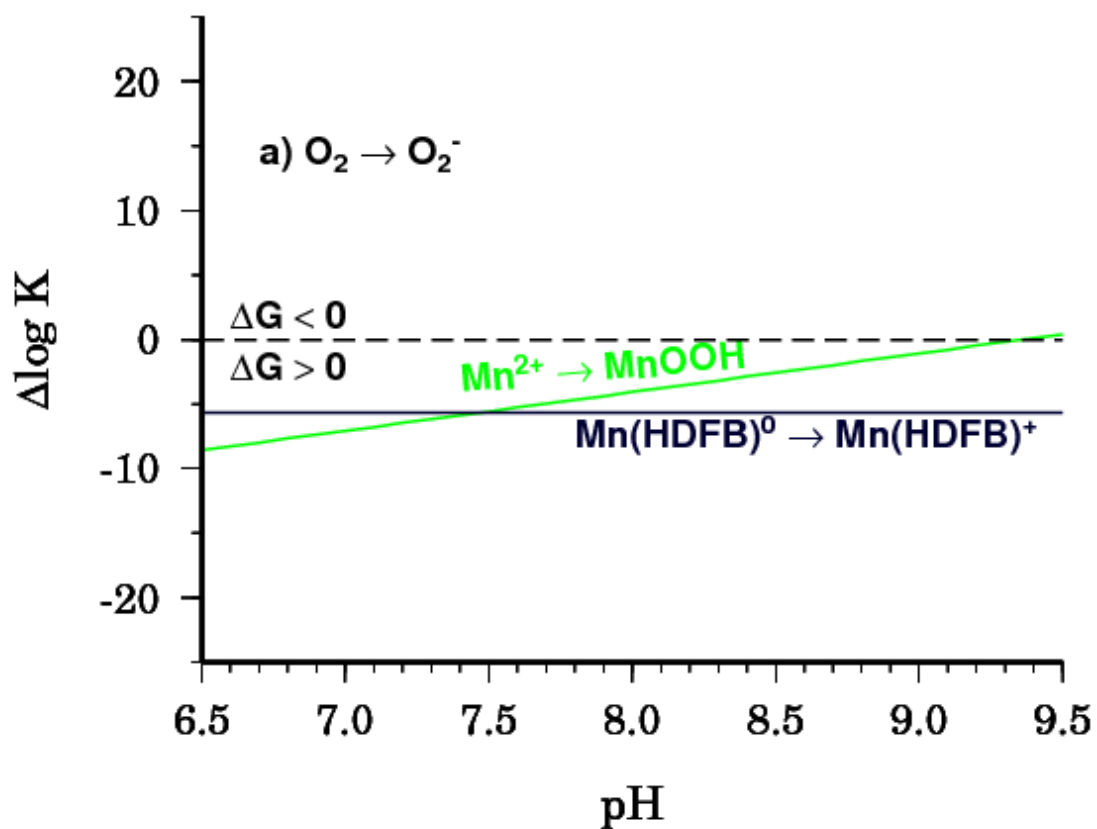


Figure S3: One-electron transfer reactions of Mn(II) and Mn(HDFB) in seawater with oxygen ($O_2 \rightarrow O_2^-$).

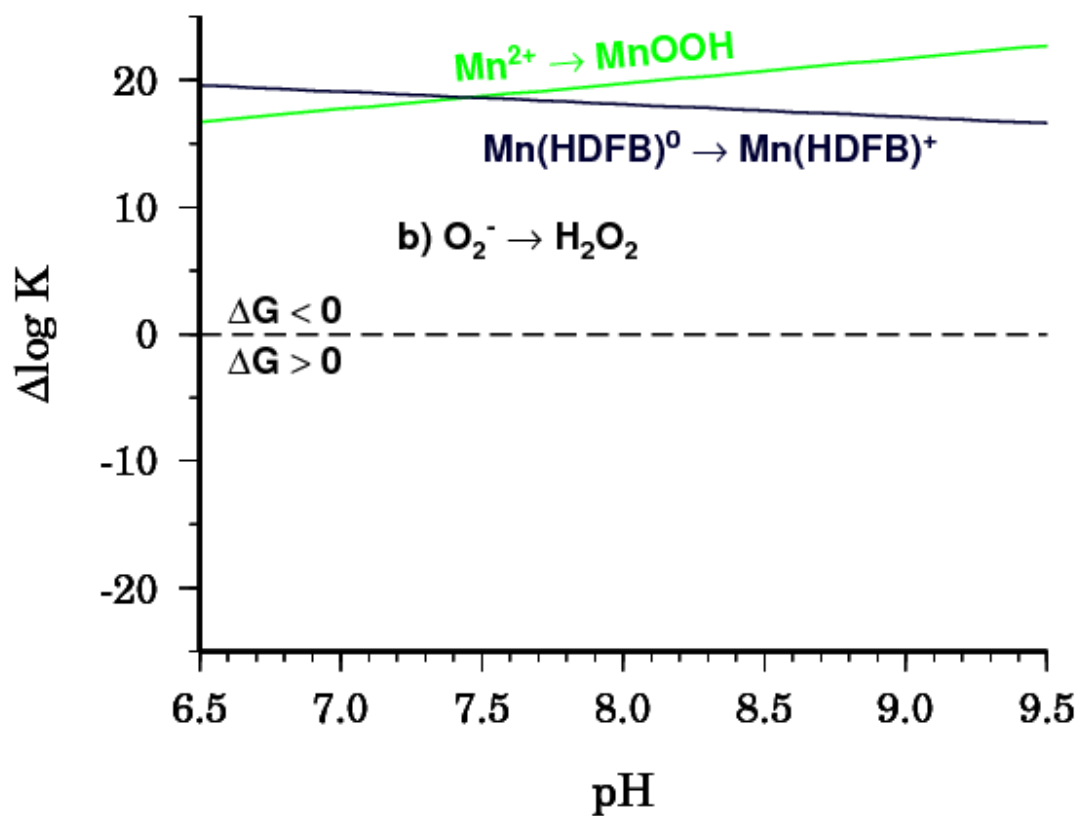


Figure S4: One-electron transfer reactions of Mn(II) and Mn(HDFB) in seawater with superoxide ($\text{O}_2^- \rightarrow \text{H}_2\text{O}_2$).

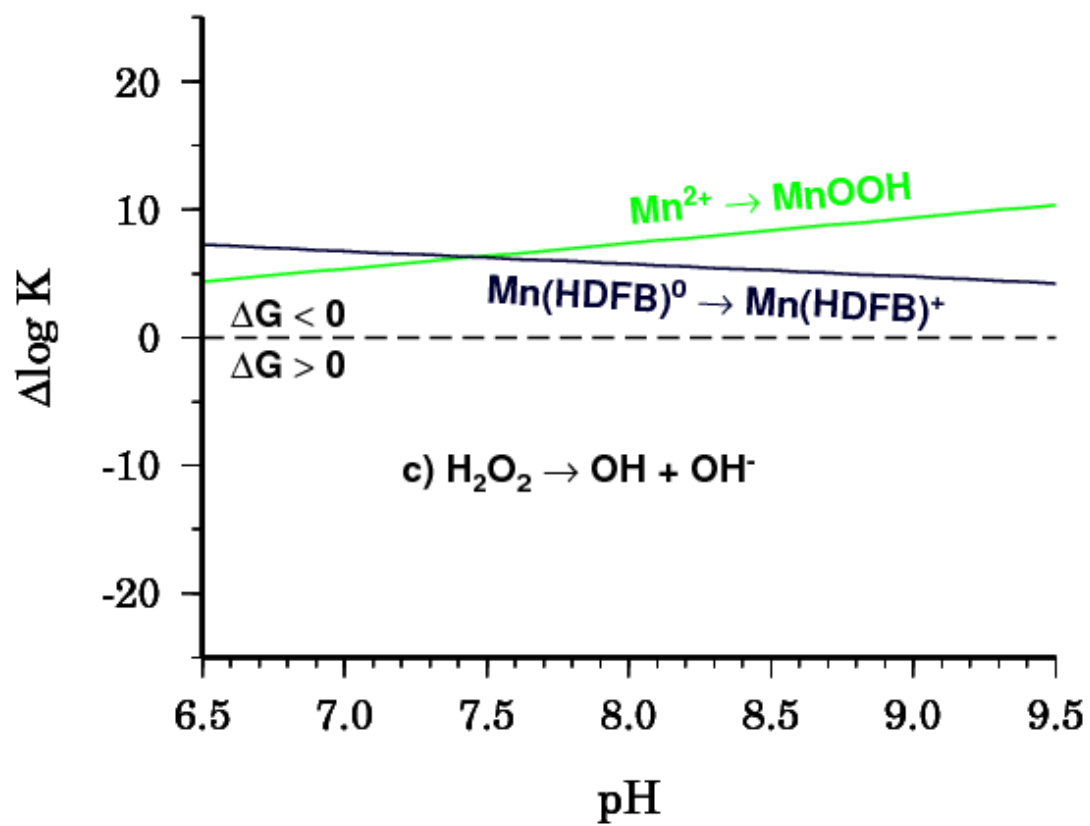


Figure S5: One-electron transfer reactions of Mn(II) and Mn(HDFB) in seawater with hydrogen peroxide ($\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$).

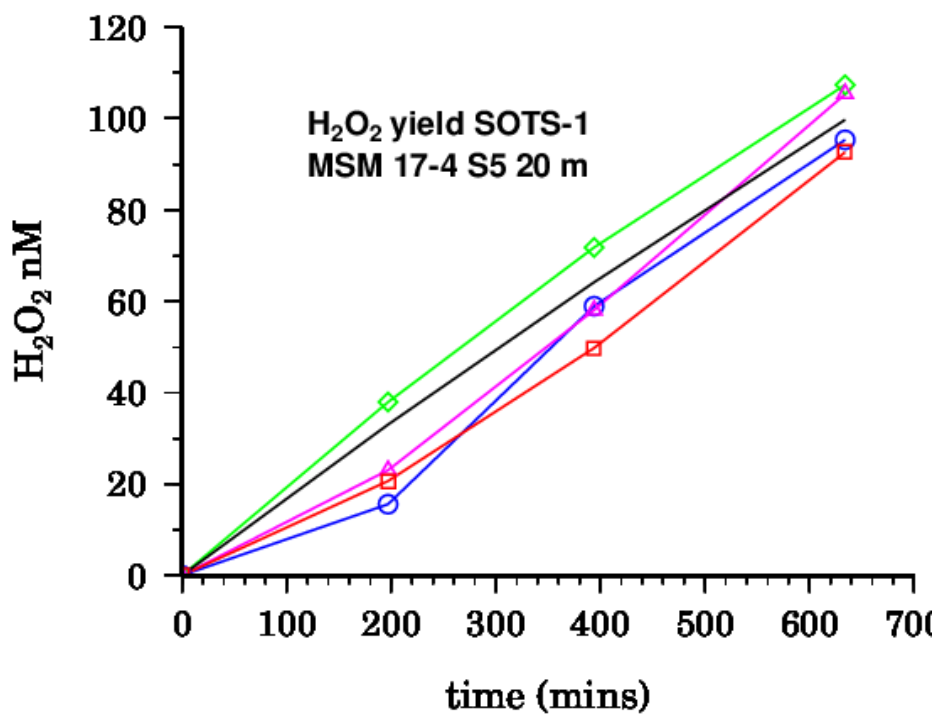
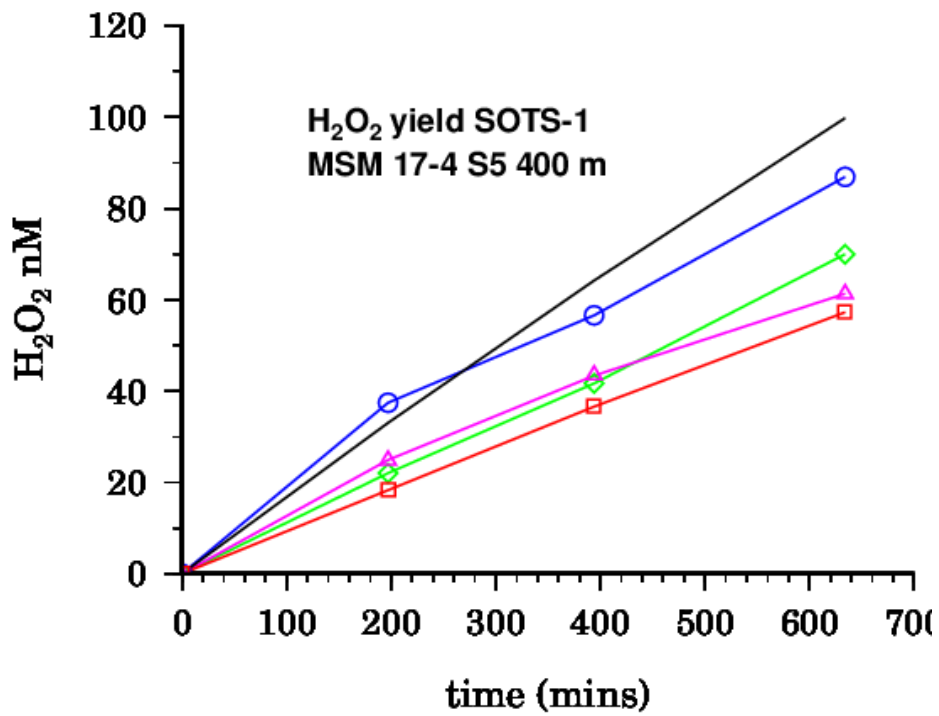


Figure S6: H₂O₂ (nM) yield of SOTS of two different depths versus the time (min).

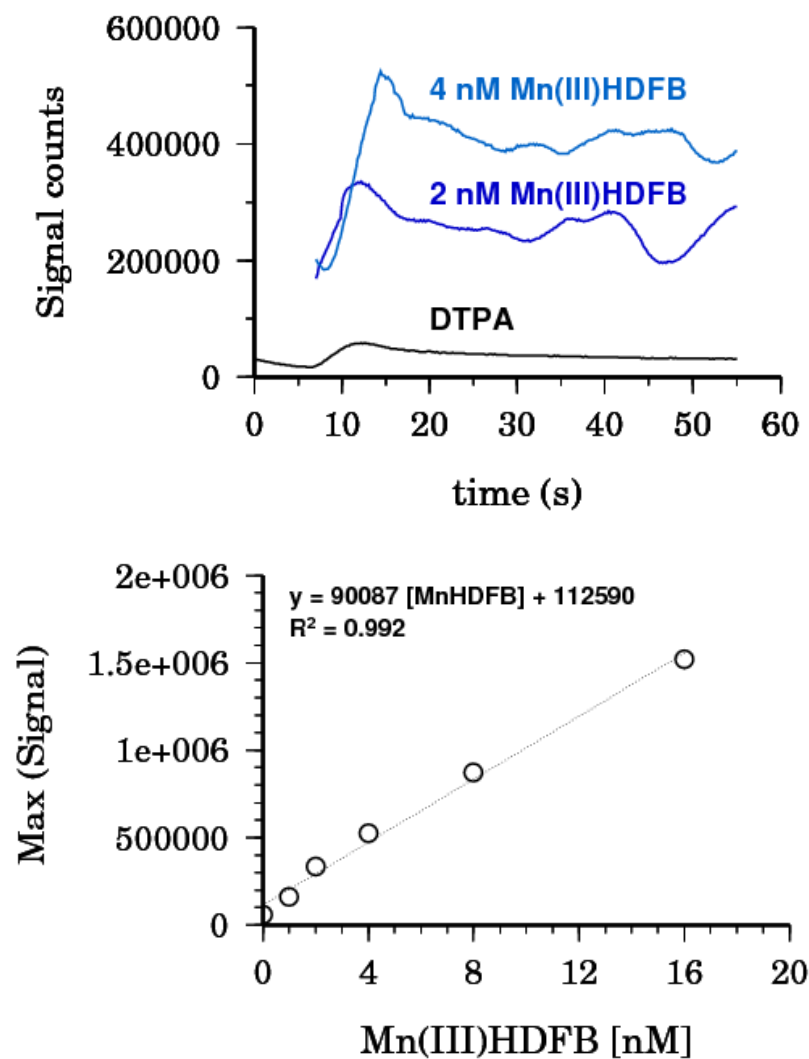


Figure S7: In the upper figure the signal counts of the O_2^- FIA versus the time (s) is shown for an aliquot containing (1) DTPA (black), (2) 2 nM Mn(III)HDFB and (3) 4 nM Mn(III)HDFB. In the lower figure the linearity of the maximum signal of the O_2^- FIA versus the Mn(III)HDFB (Mn) concentration is shown.

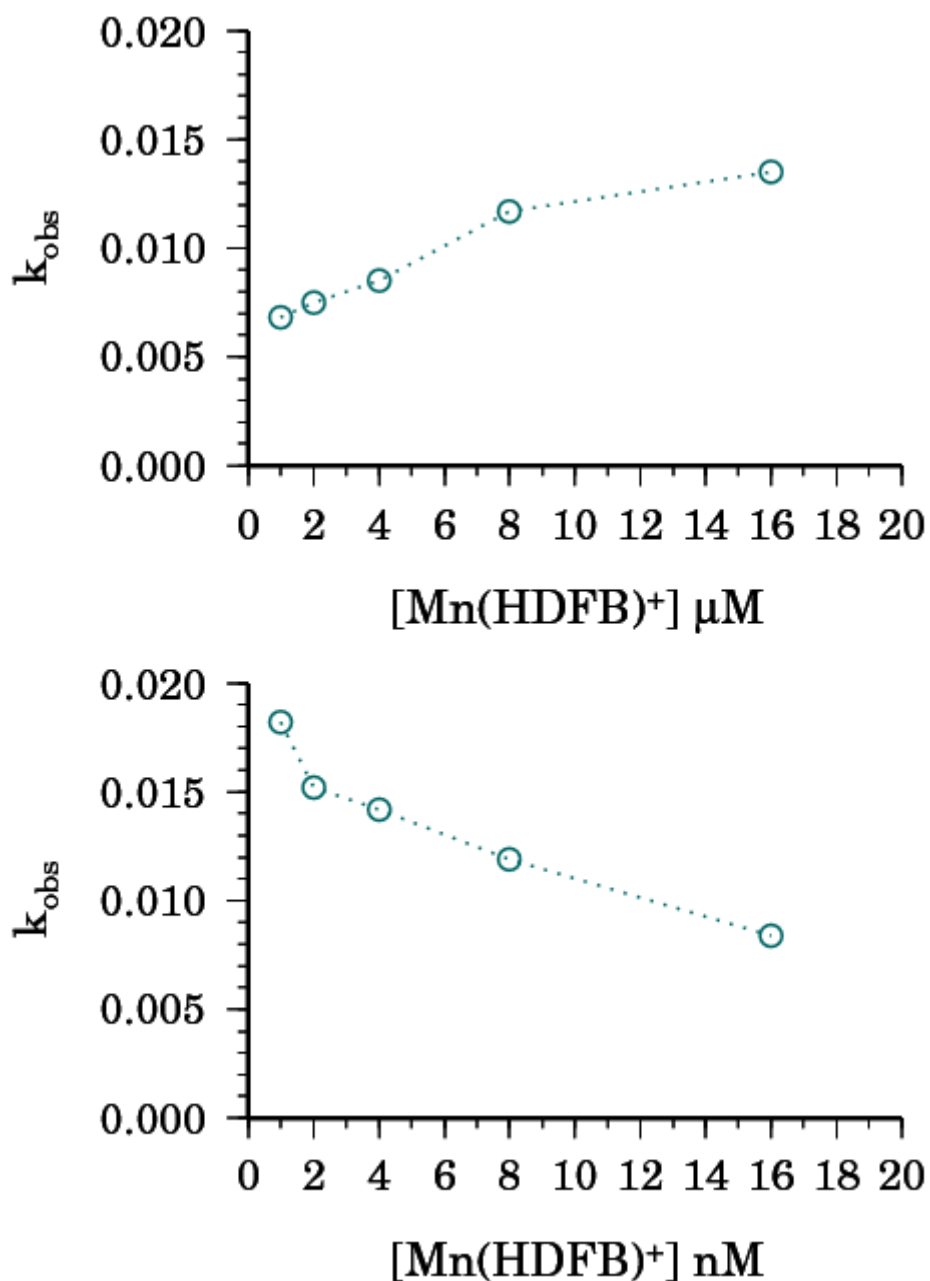


Figure S8: The observed loss rate of O_2^- (k_{obs}) versus $\text{Mn}(\text{HDFB})^+$ (nM) is plotted in the upper panel for μM level ($k_{\text{MnHDFB}^+} = 455 \pm 69 \text{ M}^{-1} \text{ s}^{-1}$) and in the lower panel for the nM level.

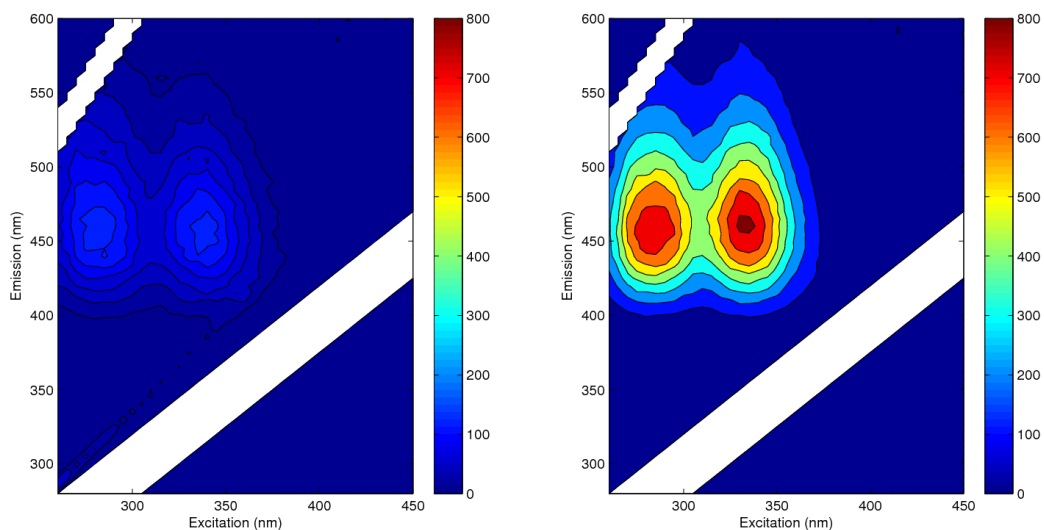


Figure S9: 3D Excitation Emission Matrix for (left) Mn(III)DFB and MCLA in seawater before and after (right) addition of H_2O_2 . The EEM spectra is identical to that of OxyMCLA^{45,46} (Max emission at 455 nm with excitation at 285 and 335 nm) the end product of the reaction between O_2^- and MCLA.

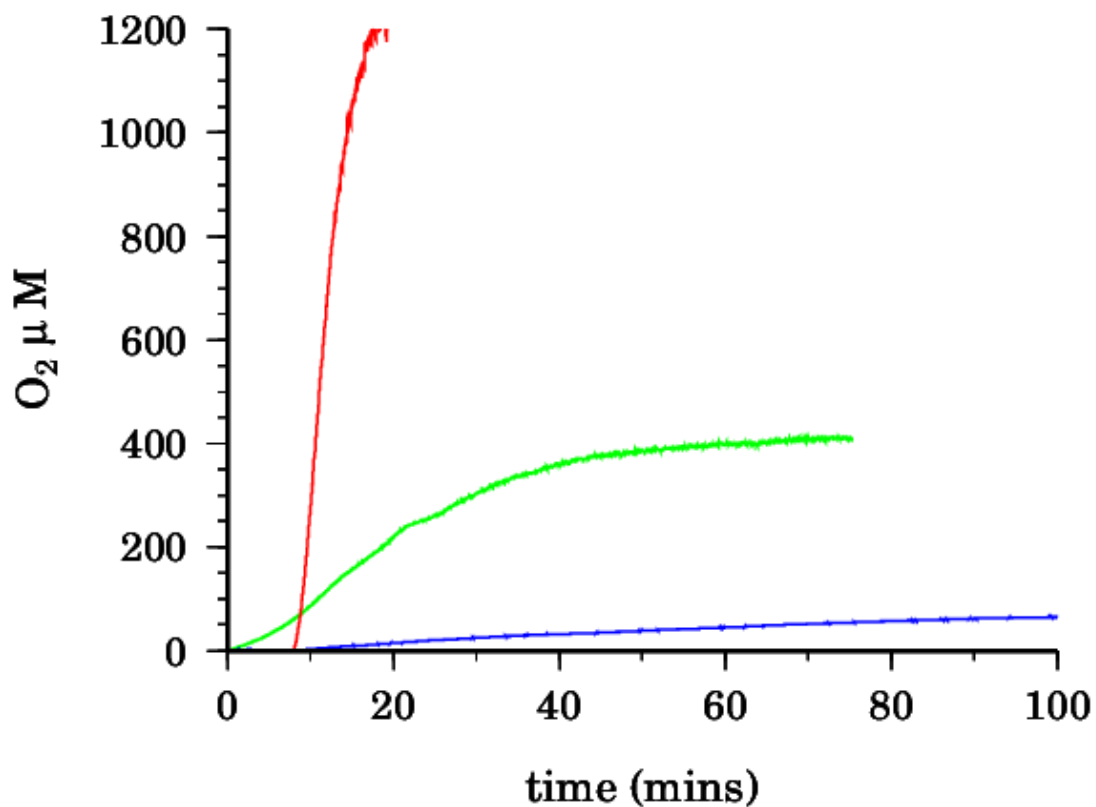


Figure S10: Production of O₂ from addition of H₂O₂ to Mn(HDFB)⁺ in seawater.

Red line – 98 μM Mn(HDFB)⁺ and 138 mM H₂O₂, Green line – 85.4 μM Mn(HDFB)⁺ and 27.9 mM H₂O₂ and Blue line – 28.5 μM Mn(HDFB)⁺ and 27.9 mM H₂O₂.

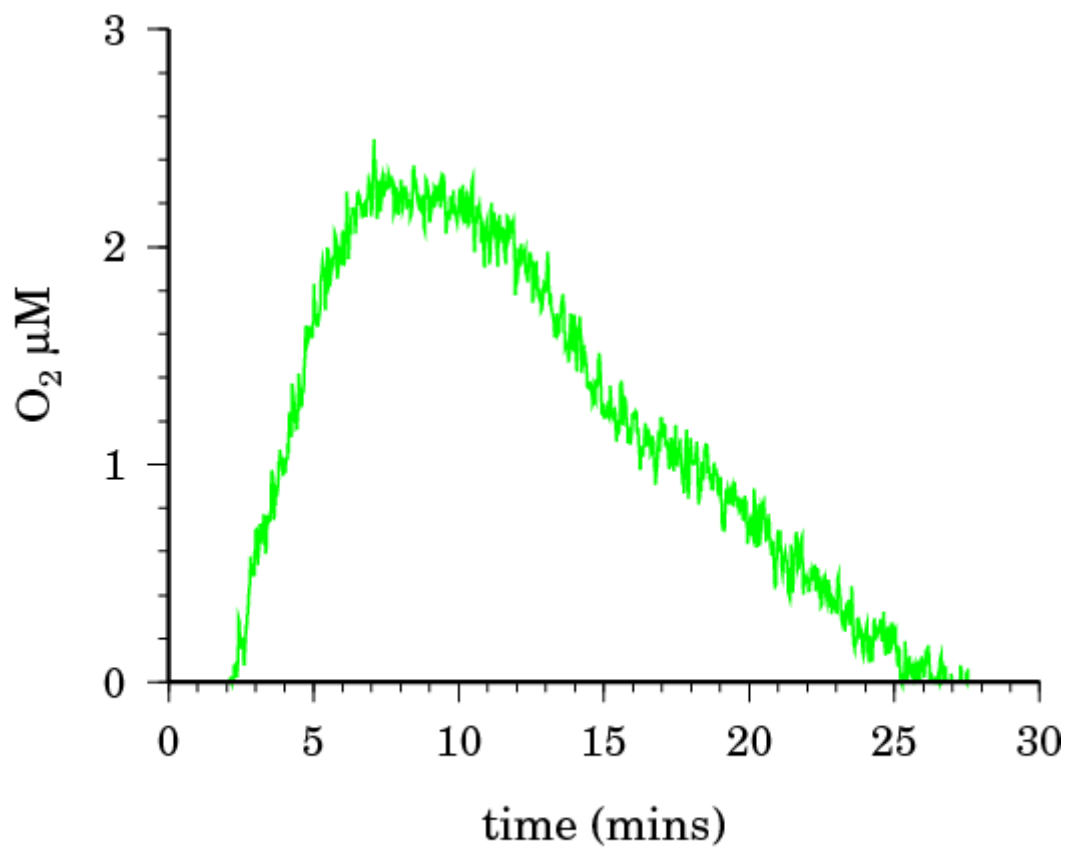


Figure S11: Production and consumption of O₂ from addition of 98 mM H₂O₂ to 10 µM Mn(II) and 10 µM DFB in deaerated seawater.

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