

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/225507214>

The Role of One- and Two-Electron Transfer Reactions in Forming Thermodynamically Unstable Intermediates as Barriers in Multi-Electron Redox Reactions

ARTICLE *in* AQUATIC GEOCHEMISTRY · JUNE 2009

Impact Factor: 1.23 · DOI: 10.1007/s10498-009-9082-3

CITATIONS

39

READS

63

1 AUTHOR:



George W Luther

University of Delaware

318 PUBLICATIONS 12,832

CITATIONS

SEE PROFILE

The Role of One- and Two-Electron Transfer Reactions in Forming Thermodynamically Unstable Intermediates as Barriers in Multi-Electron Redox Reactions

George W. Luther III

Received: 24 July 2009 / Accepted: 9 November 2009 / Published online: 1 December 2009
© Springer Science+Business Media B.V. 2009

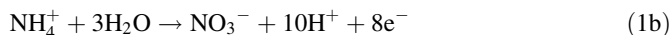
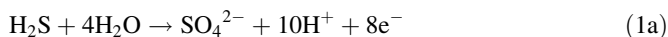
Abstract In the aquatic geochemical literature, a redox half-reaction is normally written for a multi-electron process ($n > 2$); e.g., sulfide oxidation to sulfate. When coupling two multi-electron half-reactions, thermodynamic calculations indicate possible reactivity, and the coupled half-reactions are considered favorable even when there is a known barrier to reactivity. Thermodynamic calculations should be done for one or two-electron transfer steps and then compared with known reactivity to determine the rate controlling step in a reaction pathway. Here, thermodynamic calculations are presented for selected reactions for compounds of C, O, N, S, Fe, Mn and Cu. Calculations predict reactivity barriers and agree with one previous analysis showing the first step in reducing O_2 to O_2^- with Fe^{2+} and Mn^{2+} is rate limiting. Similar problems occur for the first electron transfer step in these metals reducing NO_3^- , but if reactive oxygen species form or if two-electron transfer steps with O atom transfer occur, reactivity becomes favorable. H_2S and NH_4^+ oxidation in a one-electron transfer step by O_2 is also not favorable unless activation of oxygen can occur. H_2S oxidation by Cu^{2+} , Fe(III) and Mn(III, IV) phases in two-electron transfer steps is favorable but not in one-electron steps indicating that (nano)particles with bands of orbitals are needed to accept two electrons from H_2S . NH_4^+ oxidation by Fe(III) and Mn(III, IV) phases is generally not favorable for both one- and two-electron transfer steps, but their reaction with hydroxylamine and hydrazine to form N_2O and N_2 , respectively, is favorable. The anammox reaction using hydroxylamine via nitrite reduction is the most favorable for NH_4^+ oxidation. Other chemical processes including photosynthesis and chemosynthesis are considered for these element–element transformations.

Keywords Thermodynamics of electron transfer · Oxygen · Nitrogen · Sulfur · Iron · Manganese · Copper

G. W. Luther III (✉)
School of Marine Science and Policy, College of Earth, Ocean and Environment,
University of Delaware, Lewes, DE 19958, USA
e-mail: luther@udel.edu

1 Introduction

Thermodynamic calculations are important in indicating that a reaction is favorable or possible even though kinetically inhibited. In most aquatic environmental and geochemical redox studies, thermodynamic calculations are used to describe reactions in which one or more of the reactants undergo an electron transfer of many electrons ($n > 2$) from most reduced to most oxidized chemical species (e.g., [Beal et al. 2009](#)) as in Eqs. 1a and 1b for the oxidation of hydrogen sulfide and ammonium ion to sulfate and nitrate, respectively.



However, most reactions proceed in several discrete one- or two-electron transfer steps along the entire reaction coordinate or pathway of eight electrons. To better understand how an element may cycle in the environment, thermodynamic calculations should be performed considering only one- or two-electron transfer steps over an entire pathway as in the eight-electron oxidations shown in Eqs. 1a and 1b. These calculations would show whether a particular electron transfer step is thermodynamically unfavorable and hence a rate controlling step with a barrier to reactivity for forming a (meta)stable species with another intermediate oxidation state. [These calculations are not to be confused with transition state theory where the kinetics of a reaction and its activation energy ($\neq \Delta G$) can indicate how much energy is needed to be overcome to form an intermediate in the transition state of the reaction prior to it decomposing and forming products.]

The above-mentioned points may seem obvious for metals such as Fe, which transforms between +2 and +3 oxidation states, and Mn, which transforms between +2, +3 and +4 oxidation states, but it is less obvious for non-metals such as N and S that have nine possible oxidation states (including 0 as N_2 and S_8). Thus, the stability of all possible intermediates, which may form, can be assessed. When the formation of an intermediate is not thermodynamically favored, then another pathway, not previously considered, is necessary to have the full multi-electron reaction pathway proceed. The new pathway could require another reactant, which could be produced by photochemical means or be produced in an enzymatic or a microbial process, for the reaction to proceed.

In this paper, I look at several possible transformations in the elemental cycles of C, N, O, S, Fe, Mn and Cu using common environmental oxidants and reductants. The transformations include (1) the oxidation of Fe^{2+} and Mn^{2+} by O_2 and NO_x species to Fe(III) and Mn(III, IV) solid phases, (2) the oxidation of NH_4^+ to N_2 and N_2O by oxygen species as well as Fe(III) and Mn(III, IV) solid phases and (3) the reduction of Fe(III) and Mn(III, IV) solid phases by H_2S to Fe^{2+} and Mn^{2+} . Thus, I use the common environmental oxidants [O_2 , Fe(III) solid phases and Mn(III, IV) solid phases], and the common reductants [Fe^{2+} , Mn^{2+} and $\text{H}_2\text{S}/\text{HS}^-$] in the analysis. Because oxygen reduction to water requires four electrons to break the O–O bond, reactive oxygen species (ROS) can be produced in some of these reactions and are also considered. Because the N cycle has an eight electron swing from fully reduced to fully oxidized chemical species, some N intermediates can also interact with other N compounds as has been shown in the anaerobic oxidation of ammonia (anammox) reaction ([Kuypers et al. 2003](#)). In the stepwise processes presented, there are some important reaction steps that are thermodynamically unfavorable. To affect the desired chemical transformation may require that oxidants/reductants other

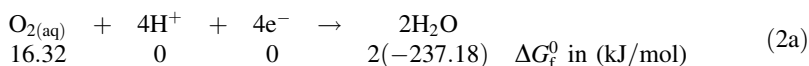
than the common or traditionally available ones need to be formed and used or another reaction must occur. Several of these are also presented, and some are actually used by organisms. Thus, this process of looking at 1–2 electron transfer steps can lead us to predict what enzymes an organism might use when confronted with a thermodynamically unfavorable process along a given pathway.

The reactions shown can occur in oxic photosynthetically active areas to suboxic and anoxic waters and porewaters as well as at their interfaces. Because the pH range considered is from 0 to 10 (and 14 by extrapolation), the calculations pertain to diverse environmental systems ranging from acid mine drainage areas, acid rain to the open ocean and alkaline lakes. Lastly, the analysis will show where appropriate how the calculations compare with available kinetic data, some of which is due to Frank J. Millero to whom this paper and issue are dedicated.

2 Experimental Procedure

2.1 Thermodynamic Calculations

Thermodynamic data used (at 25°C and 1 atm) are from Stumm and Morgan (1996) and other sources (e.g., Maloy 1985; Stanbury 1989). The value used for the Gibbs free energy for Fe^{2+} ($-90.53 \text{ kJ mole}^{-1}$) is that discussed in Rickard and Luther (2007). The basic mathematical approach has been fully developed in standard textbooks and used in previous publications (Luther et al. 1997; Anschutz et al. 2000). First, a reduction half-reaction for each redox couple is written as for the case of aqueous oxygen reduction to water in Eq. 2a. From the known Gibbs free energies or standard redox potentials, a $p\epsilon^0$ ($=\log K$) is calculated at the standard state conditions for each half-reaction (Eqs. 2b and 2c), which is normalized to a one-electron reaction. For example, Eq. 2a is normalized to become Eq. 2d.

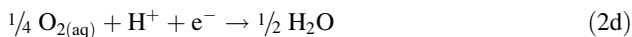


The standard state ΔG^0 for the reaction $= -490.68 \text{ kJ/2 mole H}_2\text{O}$ or 4 mole of electrons. The equilibrium constant (K_4^0) is given in Eq. 2b where $\{\}$ indicates activity for each chemical species. $\log K_4^0 = \Delta G/[-(2.303)RT] = 86.00$ for 4 mole of electrons or 21.50 for 1 mole of electrons where

$$K_4^0 = \frac{\{\text{H}_2\text{O}\}_2}{\{\text{O}_2\}\{\text{H}^+\}^4\{\text{e}^-\}^4} \text{ so } \log K_4^0 = 86.00 = \log \frac{\{\text{H}_2\text{O}\}_2}{\{\text{O}_2\}\{\text{H}^+\}^4\{\text{e}^-\}^4}. \quad (2b)$$

$$\text{or } \log K_4 = -\log\{\text{O}_{2(\text{aq})}\} - \log\{\text{H}^+\}^4 - \log\{\text{e}^-\}^4 \quad (2c)$$

For a one-electron reaction, we have



and Eq. 2c becomes Eq. 2e

$$\frac{1}{4} \log K_4^0 = -\frac{1}{4} \log\{\text{O}_{2(\text{aq})}\} - \log\{\text{H}^+\} - \log\{\text{e}^-\} = -\frac{1}{4} \log\{\text{O}_{2(\text{aq})}\} + \text{pH} + p\epsilon \quad (2e)$$

which is rearranged to Eq. 2f

$$pe = 1/4 \log K_4^0 + 1/4 \log \{O_{2(aq)}\} - pH \quad (2f)$$

From the Nernst Equation, $pe^0 = 1/4 \log K_4^0 = 21.50$ (standard state value).

$$\text{Thus, } pe = pe^0 + 1/4 \log \{O_{2(aq)}\} - pH = 21.50 + 1/4 \log \{O_{2(aq)}\} - pH \quad (2g)$$

At 250 $\mu\text{M } O_2$ ($250 \times 10^{-6} \text{ M}$; 100% saturation at $\sim 25^\circ\text{C}$), this expression becomes

$$pe = 21.50 + 1/4 \log \{250 \times 10^{-6} \text{ M}\} - pH = 20.60 - pH \quad (2h)$$

and at 1 $\mu\text{M } O_2$ (10^{-6} M), this expression becomes

$$pe = 21.50 + 1/4 \log \{10^{-6} \text{ M}\} - pH = 20.00 - pH \quad (2i)$$

At unit activity for all reagents, $pe = pe^0$. At unit activity of all reagents other than the H^+ , we can calculate the approximate pH dependence for all reactions. In the O_2 example, Eq. 2f becomes Eq. 2j, which we will use for all calculations in this paper.

$$pe = pe^0 - pH = 21.50 - pH \quad (2j)$$

A $pe(pH)$ for a half-reaction at a given pH can then be calculated and some common ones are presented in Table 1. The calculated value for each half-reaction is given as a function of pH as in the examples in Table 1, and these can easily be entered into spreadsheets for quick calculations of full reactions from two half-reactions (see next section). [When H^+ or OH^- is not in a balanced equation for a half-reaction, there is no pH dependence on the half-reaction.] The pe calculated is termed $pe(pH)$ that provides a $\log K$ for each half-reaction at a given pH. Concentration dependence for the other reactants are not considered in the calculation; thus, these are considered standard state calculations (note that Eqs. 2i and 2j show a 1.50 log change for an oxygen concentration range from 1 μM to unity activity so the calculations could vary an order of magnitude or more in either direction when concentration dependence is included). However, comparisons can be more easily made when combining different half-reactions at a given pH. This permits an assessment of which combined half-reactions are thermodynamically favorable and thus more likely to react in a given environmental setting.

2.2 Coupling Half-Reactions

As an example of coupling two half-reactions to determine whether a reaction is favorable, I use the data in Table 1 for the reaction of O_2 (Eq. A) and Mn^{2+} (Eq. E) to form H_2O and MnO_2 at $pH = 7$. In this case, $\log K$ [for the complete reaction] = $pe(O_2) - pe(Mn^{2+}) = 14.50 - (6.8) = 7.70$. The negative sign in front of $pe(Mn^{2+})$ indicates that the half-reaction is now an oxidation half-reaction. This calculation is for the full reduction of O_2 to water (4 electrons); however, as to be shown here, this reaction is thermodynamically unfavorable at the first electron transfer step where superoxide ion, O_2^- , would be formed.

For this work, I list in Table 2 the $pe(pH)$ values for Mn, Fe, Cu, N, S and N species for the relevant one- and two-electron transfer reactions considered. Dissolved Fe(II) and Mn(II) are primarily hexaquo species until the pH is >7 , where hydroxo complexes start to become important. The latter are not considered in this analysis, but I will show that the present calculations are consistent with an analysis using hydroxo complexes performed for Fe(II) oxidation with O_2 as described in Stumm and Morgan (1996).

Table 1 Important half-reactions for calculated as per Stumm and Morgan (1996)Selected half-reactions and $p\epsilon(\text{pH}) = p\epsilon^0 (\log K^0) - n \text{ pH}$

(A)	$\frac{1}{4}\text{O}_{2(\text{aq})} + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - \text{pH} = 21.50 - \text{pH}$
(B)	$\frac{1}{5}\text{NO}_3^- + \frac{6}{5}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{10}\text{N}_2 + \frac{3}{5}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - 1.2\text{pH} = 21.05 - 1.2\text{pH}$
(C)	$\frac{1}{8}\text{NO}_3^- + \frac{5}{4}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{8}\text{NH}_4^+ + \frac{3}{8}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - 1.25\text{pH} = 14.9 - 1.25\text{pH}$
(D)	$\frac{1}{6}\text{N}_2 + \frac{4}{3}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{3}\text{NH}_4^+$	$p\epsilon = p\epsilon^0 - 1.33\text{pH} = 4.65 - 1.33\text{pH}$
(E)	$\frac{1}{2}\text{MnO}_{2(\text{s})} + 2\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{Mn}^{2+} + \text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - 2\text{pH} = 20.8 - 2\text{pH}$
(F)	$\text{FeOOH}_{(\text{s})} + 3\text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - 3\text{pH} = 13.37 - 3\text{pH}$
(G)	$\frac{1}{2}\text{S} + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2\text{S}$	$p\epsilon = p\epsilon^0 - \text{pH} = 2.44 - \text{pH}$
(H)	$\frac{1}{6}\text{IO}_3^- + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{6}\text{I}^- + \frac{1}{2}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^0 - \text{pH} = 18.5 - \text{pH}$
(I)	$\frac{1}{2}\text{I}_2 + \text{e}^- \rightarrow \text{I}^-$	$p\epsilon = p\epsilon^0 - \text{pH} = 10.8 - \text{pH}$

 $p\epsilon(\text{pH}) = \text{Log } K(\text{pH})$ for half-reactions A through F at a given pH

pH	$p\epsilon$ [A]	$p\epsilon$ [B]	$p\epsilon$ [C]	$p\epsilon$ [D]	$p\epsilon$ [E]	$p\epsilon$ [F]
0	21.50	21.05	14.9	4.65	20.8	13.37
1	20.50	19.85	13.65	3.32	18.8	10.37
2	19.50	18.65	12.4	1.98	16.8	7.37
3	18.50	17.45	11.15	0.65	14.8	4.37
4	17.50	16.25	9.90	-0.68	12.8	1.37
5	16.50	15.05	8.65	-2.02	10.8	-1.63
6	15.50	13.85	7.4	-3.35	8.8	-4.63
7	14.50	12.65	6.15	-4.7	6.8	-7.63
8	13.50	11.45	4.9	-6.02	4.8	-10.63
9	12.50	10.25	3.65	-7.35	2.8	-13.63
10	11.50	9.05	2.4	-6.7	0.8	-16.63

The $p\epsilon^0 (\log K^0)$ is the standard state condition (activity of unity in all species including H^+)

3 Results and Discussion

3.1 Oxygen Transformations

3.1.1 Fe^{2+} and Mn^{2+} Oxidation by Oxygen Species

The oxidation reactions of Fe^{2+} and Mn^{2+} by O_2 have received much attention in the literature. It is well known that the oxidation of Fe^{2+} by O_2 occurs at lower pH than that for Mn^{2+} . Stumm and Morgan (1996) noted that the one-electron reduction of O_2 by Fe^{2+} leads to the ROS, superoxide (O_2^-), which is unstable (see reaction O6 in Table 2). In their analysis, they used the iron species Fe^{2+} at $\text{pH} = 1$, $\text{Fe}(\text{OH})^+$ at $\text{pH} = 4$ and $\text{Fe}(\text{OH})_2$ at $\text{pH} = 7$. Their data showed that the first electron transfer from Fe^{2+} to O_2 is a key step and controls the reaction progress and rate at a $\text{pH} > 5$.

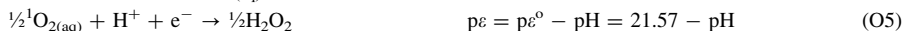
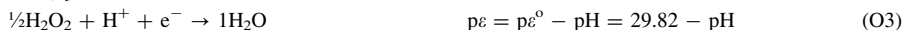
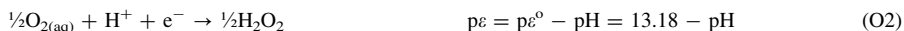
In Fig. 1, I show that the same predictions can be made over the pH range from 1 to 10 but without specifying the Fe(II) species. In fact, Fig. 1a shows that depending on the Fe(III) species formed that the one-electron oxidation of Fe^{2+} by O_2 will begin to occur at a pH value as low as 5. Figure 2a shows the kinetic data from Millero et al. (1987a) over the pH range from 4 to 10 as well as the calculated thermodynamic data for the first

Table 2 Reduction reactions for relevant O, N, S, Fe and Mn reactions normalized to one electron—all soluble species are aqueous forms*Oxygen reactions*

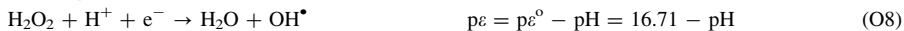
Four-electron reaction normalized to one electron



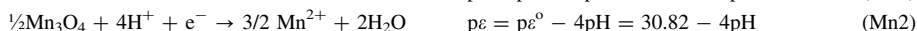
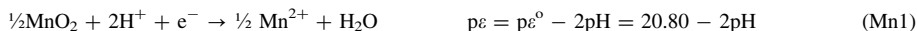
Two-electron reactions normalized to one electron



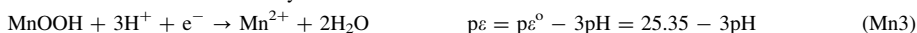
One-electron transfer reactions only

*Manganese reactions*

Two-electron reactions normalized to one electron



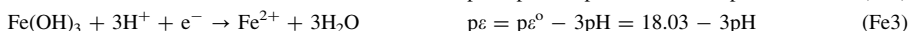
One-electron transfer reaction only

*Iron reactions*

Two-electron reaction normalized to one electron



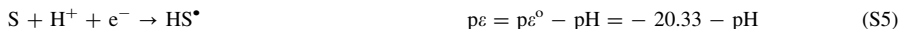
One-electron transfer reactions only

*Cu²⁺ Reduction**Sulfide reactions*

Two-electron reactions normalized to one electron



One-electron transfer reactions only

*Nitrogen reactions*

Two-electron reactions normalized to one electron

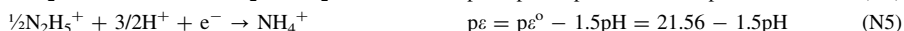
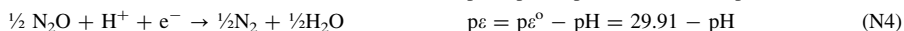
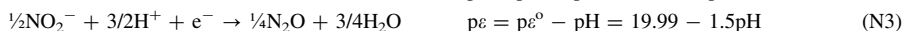
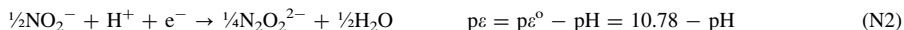
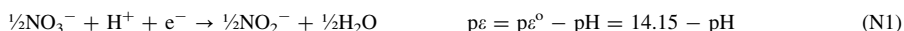


Table 2 continued

$\frac{1}{2}\text{NH}_3\text{OH}^+ + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{NH}_4^+ + \frac{1}{2}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - \text{pH} = 22.83 - \text{pH}$	(N6)
$\frac{1}{4}\text{N}_2 + 5/4 \text{H}^+ + \text{e}^- \rightarrow \frac{1}{4}\text{N}_2\text{H}_5^+$	$p\epsilon = p\epsilon^\circ - 1.25\text{pH} = -3.89 - 1.25\text{pH}$	(N7)
$\frac{1}{4}\text{N}_2\text{O} + \frac{1}{4}\text{H}_2\text{O} + 3/2 \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{NH}_3\text{OH}^+$	$p\epsilon = p\epsilon^\circ - 1.5\text{pH} = -0.92 - 1.5\text{pH}$	(N8)
$\text{NH}_3\text{OH}^+ + \frac{1}{2}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{N}_2\text{H}_5^+ + \text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - 0.5\text{pH} = 24.02 - 0.5\text{pH}$	(N9)
One-electron transfer reactions only		
$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - 2\text{pH} = 13.07 - 2\text{pH}$	(N10)
$\text{NO}_2 + \text{e}^- \rightarrow \text{NO}_2^-$	$p\epsilon = p\epsilon^\circ = 15.6$	(N11)
$\text{NO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - 2\text{pH} = 19.87 - 2\text{pH}$	(N12)
$2\text{NO} + 2\text{e}^- \rightarrow \text{N}_2\text{O}_2^{2-}$	$p\epsilon = p\epsilon^\circ = 3.04$	(N13)
Hydrolysis decomposition reaction to form N_2O		
$\text{N}_2\text{O}_2^{2-} + 2\text{H}^+ \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - 2\text{pH} = 25.13 - 2\text{pH}$	(N14)
<i>Methane oxidation</i>		
$\frac{1}{2}\text{CH}_3\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{CH}_4 + \frac{1}{2}\text{H}_2\text{O}$	$p\epsilon = p\epsilon^\circ - \text{pH} = 9.94 - \text{pH}$	(C1)

Activities of all reactants other than H^+ are at unity

electron transfer in Fig. 1a. The linearity of the rate and thermodynamic data over pH up to 8 indicates that the rate of the reaction is controlled by the first electron accepted by O_2 to form O_2^- . The linear free energy relationship in Fig. 2a indicates that the reaction can be described as an outer sphere electron transfer by Marcus theory (Wehrli 1990). Because Fe^{2+} and O_2 have highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of π character, these reactants are ideal for an outer sphere electron transfer process (Luther 2005). Deviation of the kinetics from linearity at high pH suggests an inner sphere electron transfer process may also occur. Because this reaction is thermodynamically favorable, it is possible to create ROS in deep waters where light does not penetrate.

For the other one-electron oxidations of Fe^{2+} by superoxide (O_2^- , Fig. 1b) and peroxide (H_2O_2 ; the Fenton reaction in Fig. 1c) and OH radical ($\cdot\text{OH}$; Fig. 1d), there is no thermodynamic barrier to reaction over the pH range 0–10 and higher. Thus, these reactions do not control the rate of Fe^{2+} oxidation and are not rate limiting.

Figure 1a–d also shows the data for the oxidation of Mn^{2+} by O_2 . Again the reaction is controlled by the first electron accepted by O_2 to form O_2^- , and the reaction may start to occur at a pH as low as 8, which is substantially higher than that for Fe^{2+} and which has been noted by Stumm and Morgan (1996). Recent kinetic data (Von Langen et al. 1997; Morgan 2005) indicate that oxidation of Mn^{2+} by O_2 is slow at a pH near 8, the pH of surface seawater. Mn^{2+} oxidation by O_2 is an inner sphere process as the HOMO of Mn^{2+} is a σ orbital (not π) and an outer sphere process is symmetry forbidden (Luther 2005). Thus, Marcus theory cannot be used to describe the first electron transfer process. The kinetics of the reactions of O_2^- with $\text{Mn}(\text{II})$ bound to sulfate, phosphate and pyrophosphate have been shown to have high rate constants that exceed $10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Barnese et al. 2008).

Figure 2b shows a plot of the calculated free energies for these Fe^{2+} and Mn^{2+} reactions at pH = 7 for each electron transferred as O_2 accepts four successive electrons from four separate Fe^{2+} and Mn^{2+} ions to break the $\text{O}=\text{O}$ bond to eventually form water (Eq. 3). It is clear that the first electron transfer for Mn^{2+} oxidation by O_2 is thermodynamically unfavorable and a barrier to reaction. The corresponding Fe^{2+} reaction has an energy of activation to overcome, but is thermodynamically favorable.

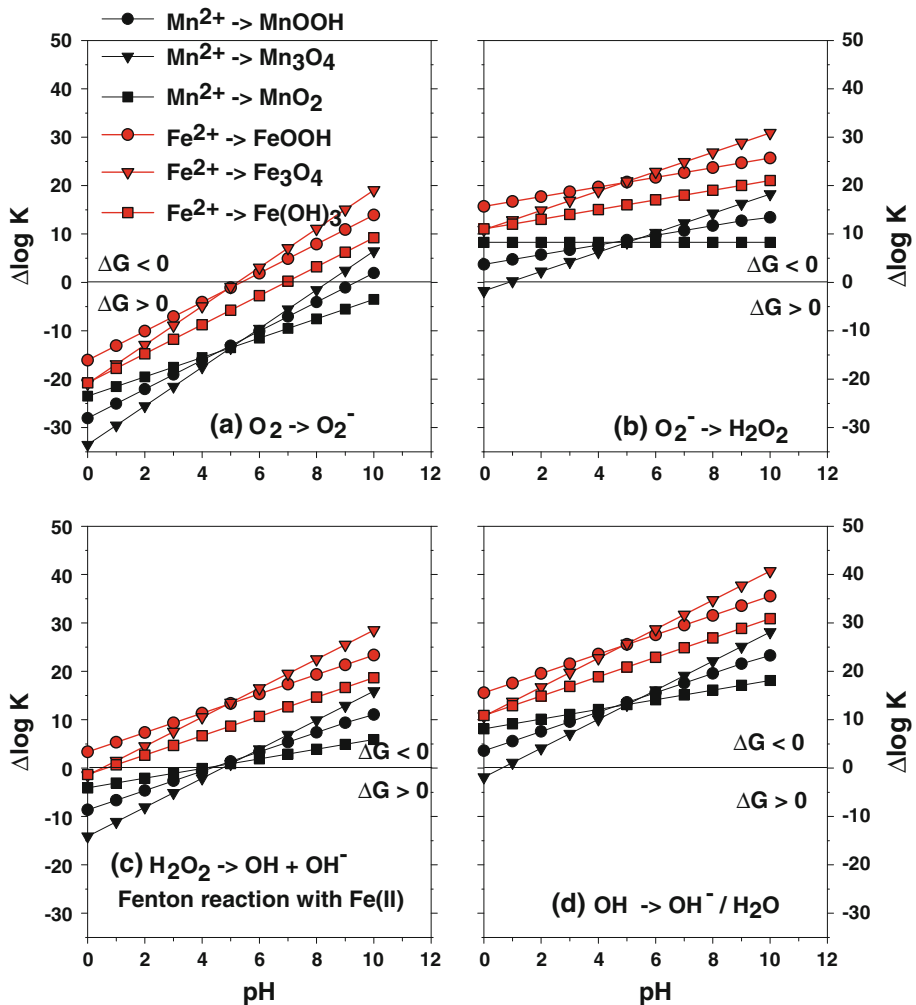


Fig. 1 One-electron transfer reactions of Fe^{2+} and Mn^{2+} with oxygen species from Table 2; the $+\Delta\log K$ on the y-axis indicates a favorable complete reaction and $-\Delta\log K$ indicates an unfavorable reaction as $\Delta G^\circ = -RT \ln K = -2.303 RT \log K$. **a** reaction O6 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **b** reaction O7 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **c** reaction O8 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **d** reaction O9 coupled with reactions Mn1–Mn3 and Fe1–Fe3

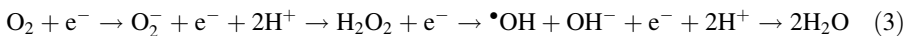


Figure 3 also shows molecular orbital diagrams for O_2 , O_2^- and H_2O_2 where the left part of the figure is the ground state for O_2 , known as triplet oxygen $^3\text{O}_2$. The reactivity of O_2^- is apparent because of the one singly occupied orbital; it is more likely to gain an electron and form the stable H_2O_2 . The ROS have almost no thermodynamic barrier to reaction and these can be formed in a variety of ways in the environment. For example, Nico et al. (2002) reported rapid photo-oxidation of Mn(II) mediated by humic substances via O_2^- . Thus, it is possible for either photochemical processes or the dark Fe(II) oxidation to produce O_2^- which could then oxidize Mn^{2+} .

Fig. 2 **a** Kinetic and thermodynamic data for the first electron transfer step in O_2 oxidation of Fe^{2+} . **b** Thermodynamics of stepwise oxidation reactions (O6–O9) in O_2 oxidation of Fe^{2+} and Mn^{2+} . At zero electrons transferred, ΔG^0 is the sum of the standard state ΔG^0 values before a reaction occurs

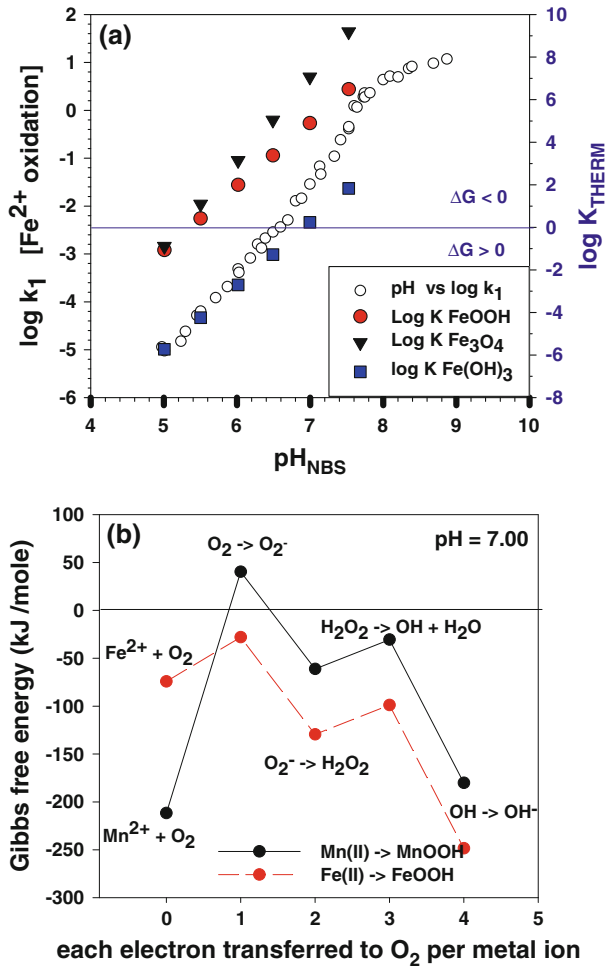
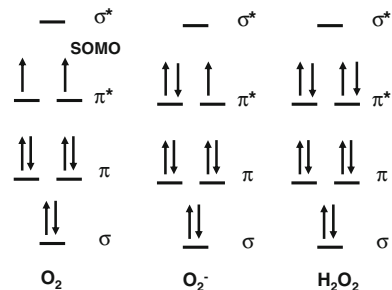


Fig. 3 Simplified molecular diagrams for oxygen species. O_2 and O_2^- have singly occupied molecular orbitals (SOMO)



Although O_2 is the primary oxidant for these metals in aquatic systems, superoxide (O_2^-), hydrogen peroxide, hydroxyl radical and ozone are produced either in water or in the gas phase with subsequent dissolution in surface and/or deep waters. Figure 4 shows the thermodynamic data for the four-electron reduction of O_2 to water (Fig. 4a), the two-electron

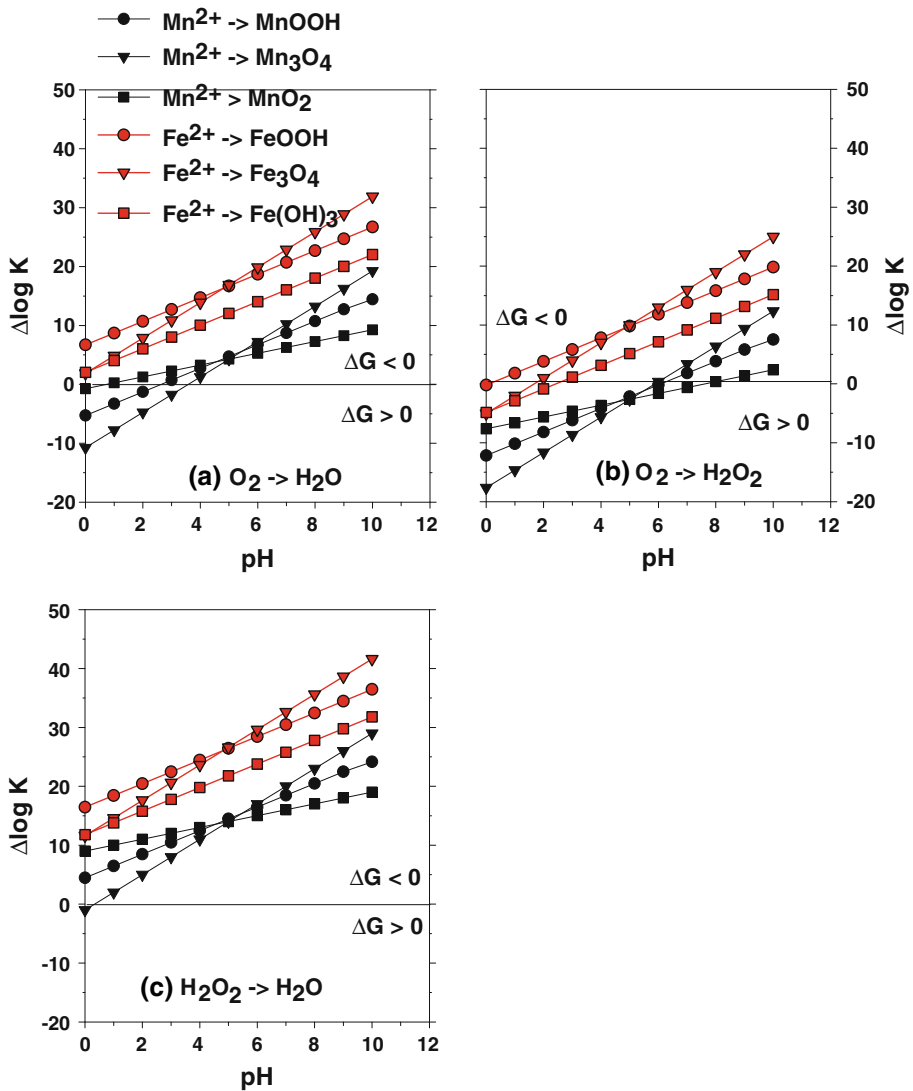
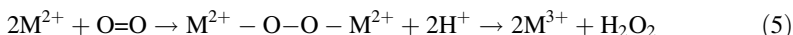
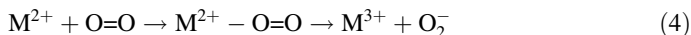


Fig. 4 Multi-electron transfer reactions of Fe^{2+} and Mn^{2+} with oxygen species from Table 2. **a** four-electron transfer reaction O1 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **b** two-electron transfer reaction O2 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **c** two-electron transfer reaction O3 coupled with reactions Mn1–Mn3 and Fe1–Fe3

reduction of O_2 to H_2O_2 (Fig. 4b) and the two-electron reduction of H_2O_2 to water (Fig. 4c). The thermodynamic barrier to reaction is for the two-electron reduction of O_2 to H_2O_2 (Fig. 4b), but at a lower pH than that found in Fig. 1 for the one-electron transfer reactions. Thus, it is possible to oxidize Fe^{2+} and Mn^{2+} at lower pH in environmental waters if H_2O_2 is present. The reaction of Fe^{2+} with H_2O_2 shows a linear increase in rate constant with pH (González-Davila et al. 2005) consistent with the thermodynamic data in Fig. 4b.

Figures 1 and 4 indicate Fe^{2+} and Mn^{2+} oxidation by O_2 is a complex process as both inner and outer sphere mechanisms are available. For inner sphere mechanisms, there are several possible intermediates as indicated in Eqs. 4 and 5.



Equation 4 indicates a one-electron transfer via a $[\text{M}^{2+}-\text{O}=\text{O}]$ intermediate, which would have a bent $\text{M}-\text{O}-\text{O}$ bond. Equation 5 indicates two metals in a one-electron transfer each via a $[\text{M}^{2+}-\text{O}-\text{O}-\text{M}^{2+}]$ intermediate with a peroxo bridge ($\text{O}-\text{O}$), which could have the $\text{O}-\text{O}$ entity linear or side-on (e.g., Karlsson et al. 2003) between the two metals.

So far, the discussion has not indicated anything about organic complexes bound to the metal and how these complexes may affect the reactivity of Fe^{2+} and Mn^{2+} . Ligands in metal ligand complexes can donate electrons to Fe^{2+} and Mn^{2+} and enhance the loss of electrons to O_2 and other electron acceptors so that Fe^{2+} and Mn^{2+} oxidation can occur at lower pH values (Duckworth and Sposito 2005; Luther et al. 1992; Wallar and Lipscomb 1996). In addition, bacteria can facilitate metal oxidation as both direct (enzymatic) and indirect (e.g., non-enzymatic bacterial spore coat mediation) processes are well documented for Mn^{2+} oxidation (Tebo et al. 2004).

Equation 6 indicates another inner sphere oxidation where a single metal in a two-electron transfer forms a M(IV)=O bond with the metal having an oxidation state of +4. This happens for Mn to form MnO_2 but also occurs for Mn and Fe in macrocyclic ligand complexes such as porphyrin or heme type compounds (Suslick and Watson 1991). Recently, non-heme related compounds have been shown to form highly reactive Fe(IV)=O species (Rohde et al. 2003). M(IV)=O metalloenzyme species are known to oxidize CH_4 to CH_3OH (Wallar and Lipscomb 1996) and naphthalene (Karlsson et al. 2003) as well as other organic substrates in a two-electron O atom transfer process (Eq. 7). At present, the thermodynamic quantities for these compounds are not available for calculations.

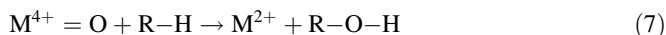


Figure 5 compares thermodynamic data for triplet oxygen ($^3\text{O}_2$; Fig. 5a; the normal state for oxygen discussed earlier) with singlet oxygen ($^1\text{O}_2$; Fig. 5b) and O_3 (Fig. 5c is one-electron reduction and Fig. 5d is two-electron reduction). Again the oxidations of Fe^{2+} and Mn^{2+} occur at lower pH values for $^1\text{O}_2$ than for $^3\text{O}_2$. This is due to the pairing of the two electrons into one of the upper $^3\text{O}_2$ orbitals (left hand side of Fig. 3) to create a vacant orbital in $^1\text{O}_2$, which can accept one electron or a pair of electrons without any electron repulsions, compared to the singly occupied orbitals for $^3\text{O}_2$, which can only accept a single electron and must overcome electron repulsions. The one-electron reduction of O_3 has a thermodynamic barrier at low pH whereas the two-electron reduction has no thermodynamic barrier over any pH. Thus, a concerted two-electron transfer process is likely for O_3 reduction by Fe(II) .

The reverse reactions can also be considered in these figures. For example, Fig. 1d is a proxy for *photosynthesis* since the first step in oxidizing water is to form a hydroxyl radical (Armstrong 2008) from two separate water molecules so that a linear peroxo complex can be formed as in Eq. 5. Subsequently, the peroxo complex is oxidized to form O_2 . These transformations use light harvesting with a $[\text{Mn}_3\text{O}_4\text{Ca}]\text{Mn}$ cluster in photosystem center II (PSII) that contains Mn(III, IV and V) ions with a $\text{Mn}=\text{O}$ bond. Consistent with the

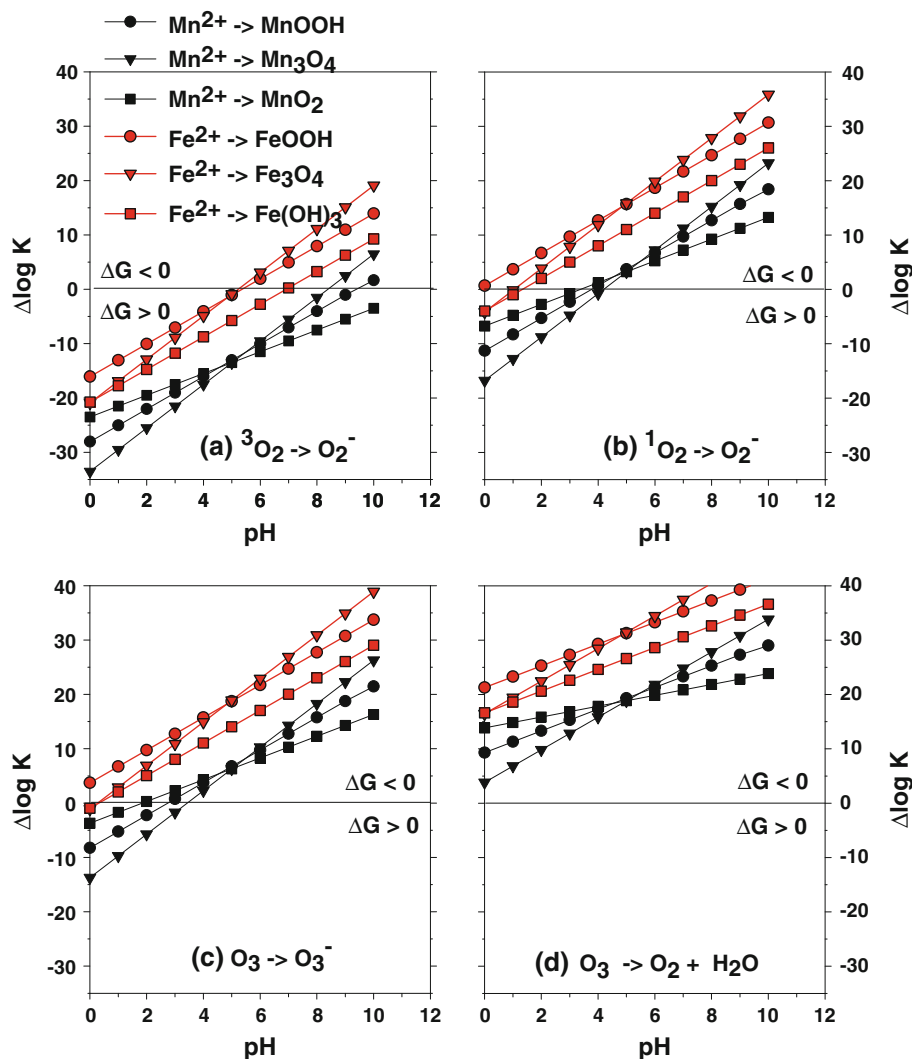


Fig. 5 Electron transfer reactions of Fe^{2+} and Mn^{2+} with oxygen species from Table 2. **a** one-electron transfer reaction O6 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **b** one-electron transfer reaction O10 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **c** one-electron transfer reaction O11 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **d** two-electron transfer reaction O4 coupled with reactions Mn1–Mn3 and Fe1–Fe3

photosynthetic pathway, Fig. 1d shows that Mn(III, IV) and not Fe(III) species are likely best for the reverse reaction.

3.1.2 H_2S Oxidation by Oxygen Species (Chemosynthesis)

Another important environmental reaction is the oxidation of H_2S eventually to sulfate by O_2 . For the one-electron transfer reaction, unstable O_2^- would need to be formed. In addition, H_2S would need to form the HS radical ($\cdot\text{HS}$), and Table 2 (Eqs. S3, S4) indicates that $\cdot\text{HS}$ is a thermodynamically unstable species. Figure 6a shows data for the

one-electron reaction of H_2S with oxygen species to form $\bullet\text{HS}$. Note that the reaction of H_2S with O_2 is thermodynamically unfavorable over all pH so both species can co-exist (Luther and Ferdelman 1993; Millero et al. 1987b). Only $\bullet\text{OH}$ should react with H_2S in an one-electron transfer over all pH whereas O_2^- will only react at low pH. If $\bullet\text{HS}$ could form, it would readily react with any oxygen species to form S(0) sulfur (Fig. 6b). The one-electron reactions of oxygen species to react with H_2S to form S(0) (Fig. 6c) are favorable but not likely as two oxygen species would need to react with each H_2S .

The two-electron reactions of oxygen species to react with H_2S to form S(0) (Fig. 6d) are favorable. *Chemosynthetic* organisms use the energy from O_2 to oxidize H_2S and fix CO_2 into biomass, and the calculations indicate that there is not a likely advantage for these organisms to convert triplet oxygen to singlet oxygen prior to reaction with sulfide. It may be possible that chemosynthetic organisms use Fe(II) catalysis to oxidize sulfide as described by Vazquez et al. (1989) in their study of sulfide oxidation with a variety of common transition metal cations. Once formed, H_2O_2 has no kinetic barrier to reaction (Luther et al. 1995). It is not clear whether these organisms use a process as in Eq. 6 with M=O bond formation to oxidize sulfide in a two-electron process.

3.2 Sulfide Transformations

3.2.1 Fe(III) and Mn(III, IV) Reduction by Sulfide

Just as the formation of $\bullet\text{HS}$ leads to a thermodynamic barrier in the oxidation of H_2S by O_2 , a similar barrier occurs with the one-electron reduction of oxidized metal species by sulfide [Fig. 7a; note MnO_2 would have to be reduced to Mn(III)]. If $\bullet\text{HS}$ could form, it would react quickly with metals to reform H_2S or lose an electron to form S(0) (Fig. 7b). Figure 7c shows that the two-electron reduction of Fe(III) and Mn(III, IV) phases by H_2S to S(0) is favorable but decreases with increasing pH as observed by Yao and Millero (1993, 1996) and dos Santos Afonso and Stumm (1992). However, there is a thermodynamic barrier to Fe(III) reduction at a $\text{pH} \geq 8$ whether H_2S (Fig. 7c) or HS^- (Fig. 7d) is the reductant. Mn(III, IV) phases have no apparent thermodynamic barrier until $\text{pH} > 10$. These Fe and Mn reactions are solid phase reactions and are surface controlled (Herszage and dos Santos Afonso 2003; Yao and Millero 1993, 1996). The transition state also varies with increasing pH as the zero point of charge of the metal oxide phases changes from positive to negative at the same time that H_2S loses a proton to form HS^- . Thus, two negative species that would repel each other are involved in the transition state at high pH. For H_2S to give two electrons to an Fe(III) or Mn(III) phase would require that each H_2S donate the electrons to a band containing several orbitals that are empty or partially occupied so that two Fe(III) or Mn(III) ions would accept the electrons. These calculations indicate that clusters or nanoparticles of oxidized metals would be important environmental oxidants. In addition to solid phases, many soluble Mn(III) complexes oxidize Fe^{2+} and HS^- rapidly (Kostka et al. 1995; Trouwborst et al. 2006) and Fe(III) complexes oxidize sulfide (Martell et al. 1996) perhaps via M–S–M bridges.

3.2.2 Cu(II) Reduction by Sulfide

Cu^{2+} is an interesting case as an oxidant with sulfide as it is a soluble entity in aquatic systems. The one-electron reduction of Cu^{2+} to form $\bullet\text{HS}$ and Cu^+ is also unfavorable (Fig. 7a) but a two-electron reduction to form S(0) and 2 Cu^+ cations is favorable (Fig. 7c). These latter data indicate that Cu^{2+} should form a Cu-sulfide cluster or

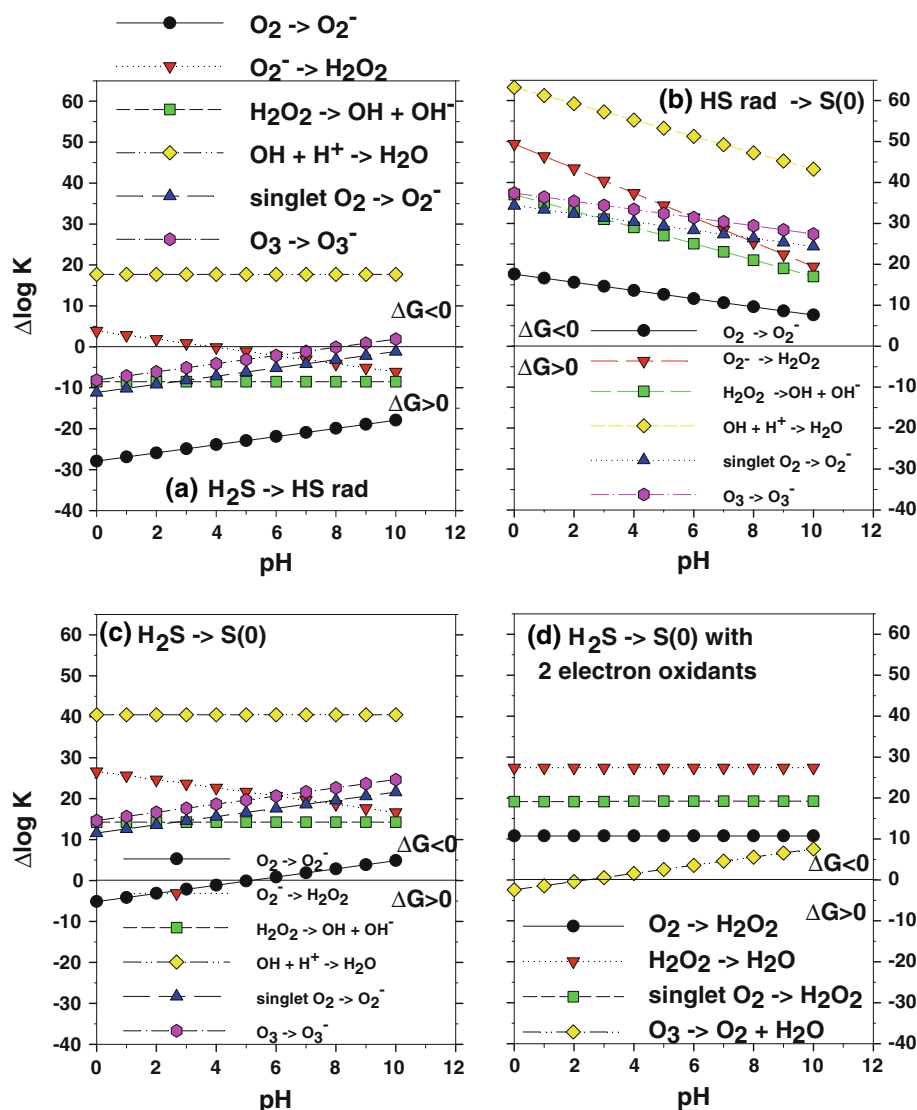


Fig. 6 Reactions of H_2S with oxygen species from Table 2. HS^- reactions are not included but are in Fig. 7 to show the similarity in reactivity between each sulfide species (note pK of $\text{H}_2\text{S} \sim 7$ and depends on salinity and temperature). **a** one-electron transfer reactions O6–O11 coupled with reaction S4. **b** one-electron transfer reactions O6–O11 coupled with reaction S5. **c** one-electron transfer reactions O6–O11 coupled with reaction S1. **d** two-electron transfer reactions O2–O5 coupled with reaction S1

nanoparticle prior to reduction so that there are several Cu^{2+} ions in contact with sulfide, which could then donate two electrons to two Cu^{2+} ions (Fig. 7c, d). This behavior has been observed by Luther et al. (2002), who used NMR and EPR spectroscopy to demonstrate that all Cu^{2+} is reduced to Cu^+ when copper and sulfide are reacted. The initial reaction phase indicates that Cu^{2+} binds with sulfide and that some Cu^{2+} can be released to

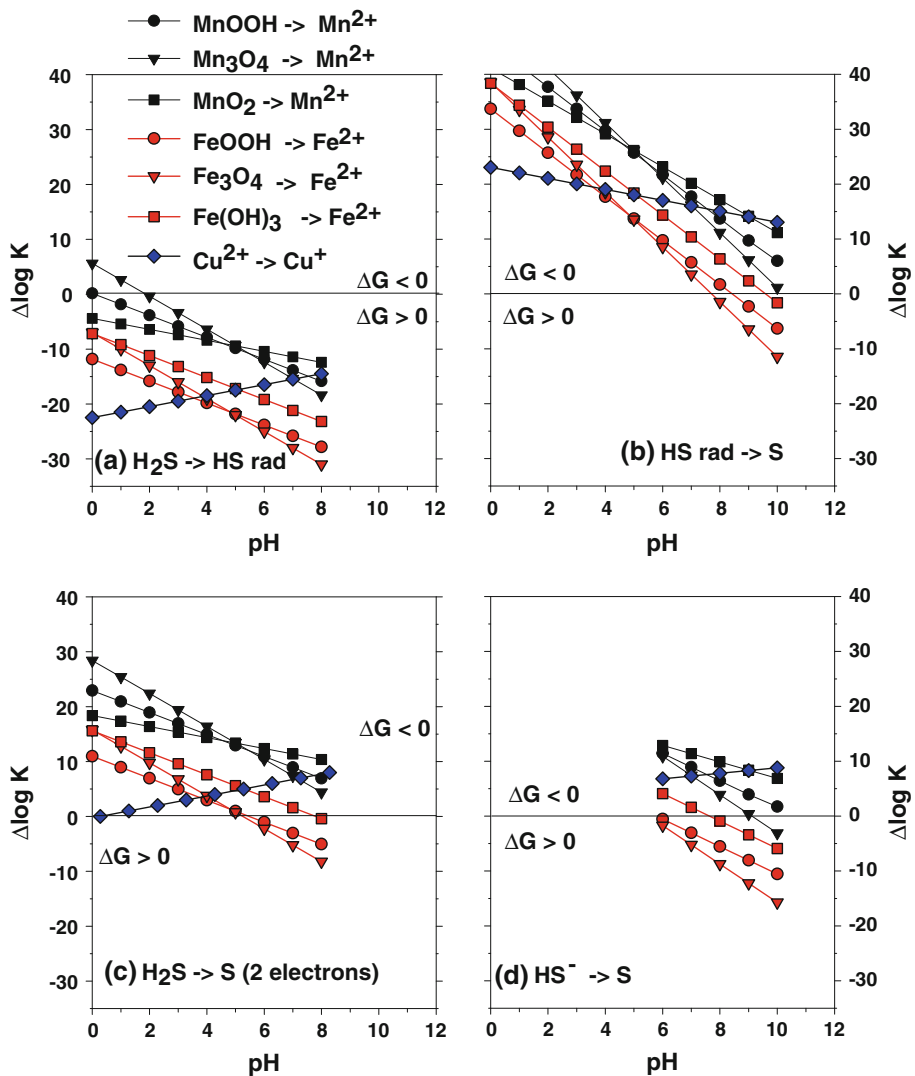


Fig. 7 Reactions of H_2S and HS^- with Fe, Mn and Cu species from Table 2. **a** reactions Mn1–Mn3, Fe1–Fe3 and Cu1 coupled with reaction S4. **b** reactions Mn1–Mn3, Fe1–Fe3 and Cu1 coupled with reaction S5. **c** reactions Mn1–Mn3, Fe1–Fe3 and Cu1 coupled with reaction S1. **d** reactions Mn1–Mn3, Fe1–Fe3 and Cu1 coupled with reaction S2

the solution. Over time, the copper and sulfide that remain bound undergo redox reactions to form Cu^+ and S_2^{2-} that leads to covellite formation. Cu isotope studies by Ehrlich et al. (2004) show the feasibility of this reaction sequence.

3.3 Oxidation of Methane by Fe(III) and Mn(III, IV) Phases

A recent report by Beal et al. (2009) indicates that the anaerobic oxidation of methane can be accomplished with oxidized Fe and Mn phases, and they performed multi-electron

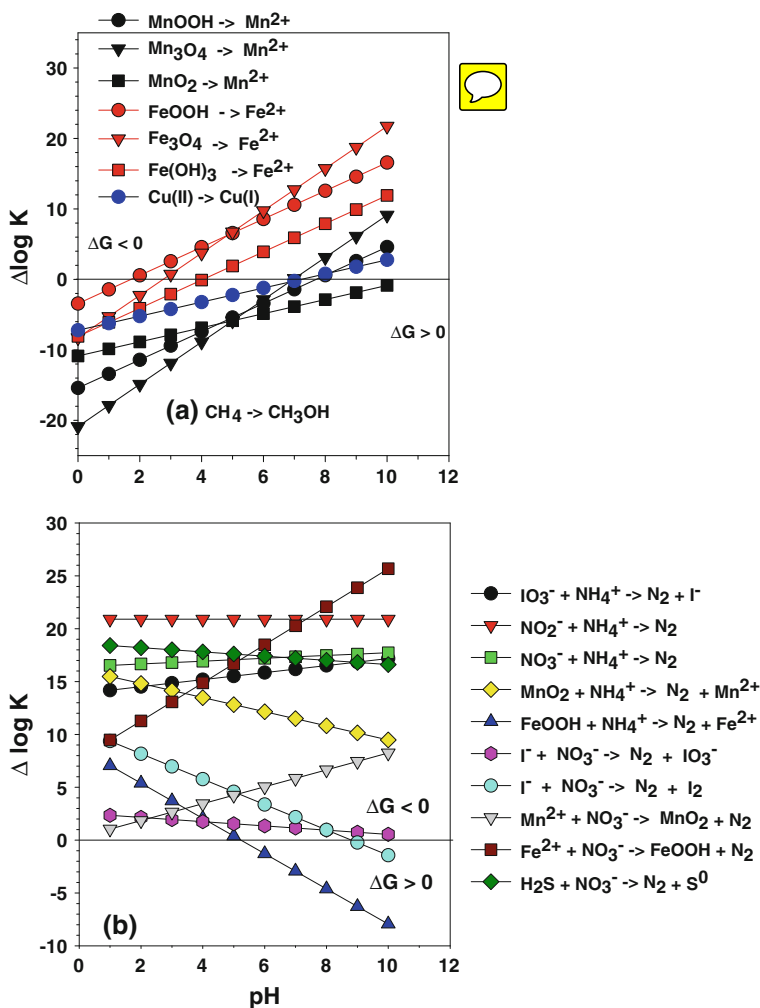


Fig. 8 **a** Reactions of iron (FeI–Fe3), manganese (MnI–Mn3) and copper (CuI) species with methane (C1) to produce methanol. **b** some of the possible multi-electron reactions that can result in N_2 formation

thermodynamic calculations to support the process. Figure 8a investigates the thermodynamics of the first two-electron transfer step for the oxidation of methane to methanol. Data for Cu(II) oxidation are also included because Cu has been found to be important for membrane bound mono-oxygenases (Hakemian and Rosenzweig 2007). The Fe(III) phases are predicted to be oxidants above $\text{pH} = 3$, but Cu(II) and the Mn(III, IV) phases are predicted to be important at $\text{pH} > 7$. Thus, enzyme catalysis may be important for methane oxidation. In most methane mono-oxygenases, Cu and Fe are the likely metals used in oxidation of methane to methanol and a $\text{Fe}^{(\text{IV})}_2\text{O}_2$ core as in Eq. 5 has been identified as a key intermediate (Shu et al. 1997). These catalysts also activate the C–H bond for O atom insertion. A terpyridine complex that stabilizes high oxidation states of Mn in a $\text{Mn}^{\text{III}}(\mu\text{-O}_2)\text{Mn}^{\text{IV}}$ core has also been shown to insert O atoms into C–H bonds with a high degree of selectivity and high catalytic turnover (Das et al. 2006).

3.4 Nitrogen Transformations

3.4.1 General Considerations

The nitrogen system is complex as the reduction of NO_3^- to form N_2 and NH_4^+ can occur via many reaction pathways. Loss of fixed nitrogen to gaseous N_2 is an important part of the N cycle which is poorly understood (Hulth et al. 2005) and Fig. 8b shows some possible N_2 formation reactions based on the multi-electron transformations and data in Table 1. The reactions in Fig. 8b show a variety of known environmental chemical species that could produce N_2 but which have not been documented or considered in previous work. Prior to discussing some of the possible reduction pathways, Fig. 9 shows with Lewis structures the one-electron (Eq. 8) and two-electron (Eq. 9) transfer pathways possible from NO_3^- to NO^- before eventual formation of N_2O and N_2 . Equation 8 indicates the formation of neutral radical compounds [nitrogen dioxide, NO_2 , and nitric oxide, NO] along the pathway whereas Eq. 9 shows direct formation of NO^- . Figure 9 also indicates that formation of the neutral species N_2O_2 is not considered as this species does not exist in solution but is a low temperature van der Waals species that can be observed in the gas phase using spectroscopic techniques at 120°K (Ewing 1975). Instead NO^- can dimerize to form the hyponitrite anion ($\text{N}_2\text{O}_2^{2-}$ for which there are thermodynamic data available) and a N–N bond that is necessary to eventually form either N_2 or N_2O . Hydrolysis of $\text{N}_2\text{O}_2^{2-}$ leads to N_2O , which can lose an O atom to form N_2 .

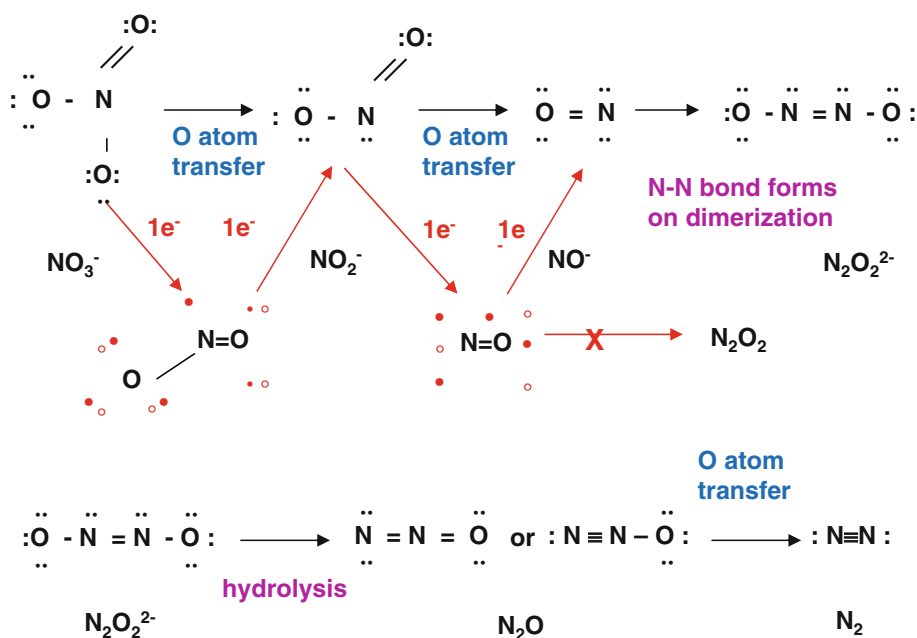
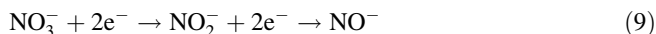
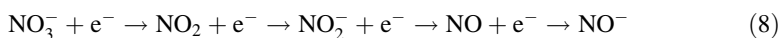


Fig. 9 Possible one-electron and two-electron nitrogen transformations. O atom transfers are two-electron processes

Also, the oxidation of $\text{NH}_3/\text{NH}_4^+$ to N_2 or N_2O by aerobic and anaerobic processes is particularly interesting because other reactions such as anammox (Kuypers et al. 2003) would provide a direct pathway to N_2 , thus short-circuiting the traditional coupled nitrification-denitrification pathway in sediments and suboxic zones (Hulth et al. 2005). Another alternative to N_2 formation is the bacterially mediated oxidation of organic matter by MnO_2 (Froelich et al. 1979). In chemical reactions, MnO_2 can also oxidize organic-N compounds with the immediate formation of N–N and N=N bonds (Laha and Luthy 1990), which is necessary to eventually form N_2 or N_2O .

3.4.2 Reduction of Oxidized Nitrogen Species by H_2S , Fe^{2+} and Mn^{2+}

Figure 10 shows the one-electron transfer thermodynamic calculations of NO_3^- reduction with Fe^{2+} and Mn^{2+} for the first four single-electron transfer steps. The pattern here for the first electron transfer from NO_3^- to form NO_2 (Fig. 10a) is remarkably similar to that found for O_2 in Fig. 1a so the first electron transfer for NO_3^- is a thermodynamic barrier to reaction and thus a rate controlling and pH-dependent step. The second (Figs. 10b vs. 1b) and third (Figs. 10c vs. 1c) electron transfers are also favorable, but Mn^{2+} reactions are not as favorable over all pH as the Fe^{2+} reactions are. Also, the formation of Mn(III) solids is more favored than Mn(IV) solids as pH increases. The fourth electron transfer, which accounts for dimerization of NO^- to $\text{N}_2\text{O}_2^{2-}$, also has some similarities to Fig. 1a but not Fig. 1d for the corresponding O_2 reactions. The similarities for these nitrogen reactions with Fe^{2+} and Mn^{2+} (Fig. 10) with the corresponding oxygen reactions (Fig. 1) can be related to the π like LUMO orbitals for both the nitrogen and oxygen species (Gimarc 1979). For one-electron transfer reactions, an outer sphere mechanism is available for Fe^{2+} but not Mn^{2+} . The one-electron transfer reactions of any of the NO_x species with H_2S are not thermodynamically favorable at any pH.

Figure 11a, b shows the two-electron transfer thermodynamic calculations of NO_3^- reduction with Fe^{2+} and Mn^{2+} for the first two transfer steps. Figure 11b describes the reduction of nitrite to NO^- (Eq. 9) as well as its dimerization to $\text{N}_2\text{O}_2^{2-}$. These have similar pH dependence as found for O_2 reduction to water via two-electron steps (Fig. 4). Thus, it is possible to oxidize Fe^{2+} and Mn^{2+} at lower and acidic pH in environmental waters with nitrate and nitrite. The figures also show that the two-electron transfer reactions of any of the NO_x species with H_2S are thermodynamically favorable.

The Fe^{2+} reaction with NO_3^- has been documented to eventually form ammonium ion in laboratory (Postma 1990; Hansen et al. 1994) and pure culture experiments (Straub et al. 1996). Although the formation of N_2O and N_2 with Fe^{2+} and Mn^{2+} has not yet been documented in the environment, complexed Fe^{2+} reacts with NO in a one-electron transfer to form Fe(III) (Wanat et al. 2002) and porphyrin complexes with Mn=O and Fe=O species reduce both nitrate and nitrite in O atom transfer reactions (Suslick and Watson 1991).

The conversion of NO_2^- to N_2O is a four-electron transfer that includes the formation and hydrolysis of $\text{N}_2\text{O}_2^{2-}$ to N_2O and H_2O , and Fig. 11c indicates that both Fe^{2+} and Mn^{2+} can be oxidized by NO_2^- over a wide range of pH. Figure 11d indicates that there is no thermodynamic barrier for the reduction of N_2O to N_2 by Fe^{2+} and Mn^{2+} . Interestingly, the reactions to form Mn(III) solids is more favored than Mn(IV) solids for all the reactions shown in Fig. 11a–d.

The reverse reactions can also be considered in these figures. Figure 11a indicates that the oxidation of Mn^{2+} by NO_3^- is not favorable at $\text{pH} \leq 6$. Thus, the reverse reaction Eq. 10, which is the anaerobic nitrification of nitrite by MnO_2 , is predicted to be favorable.

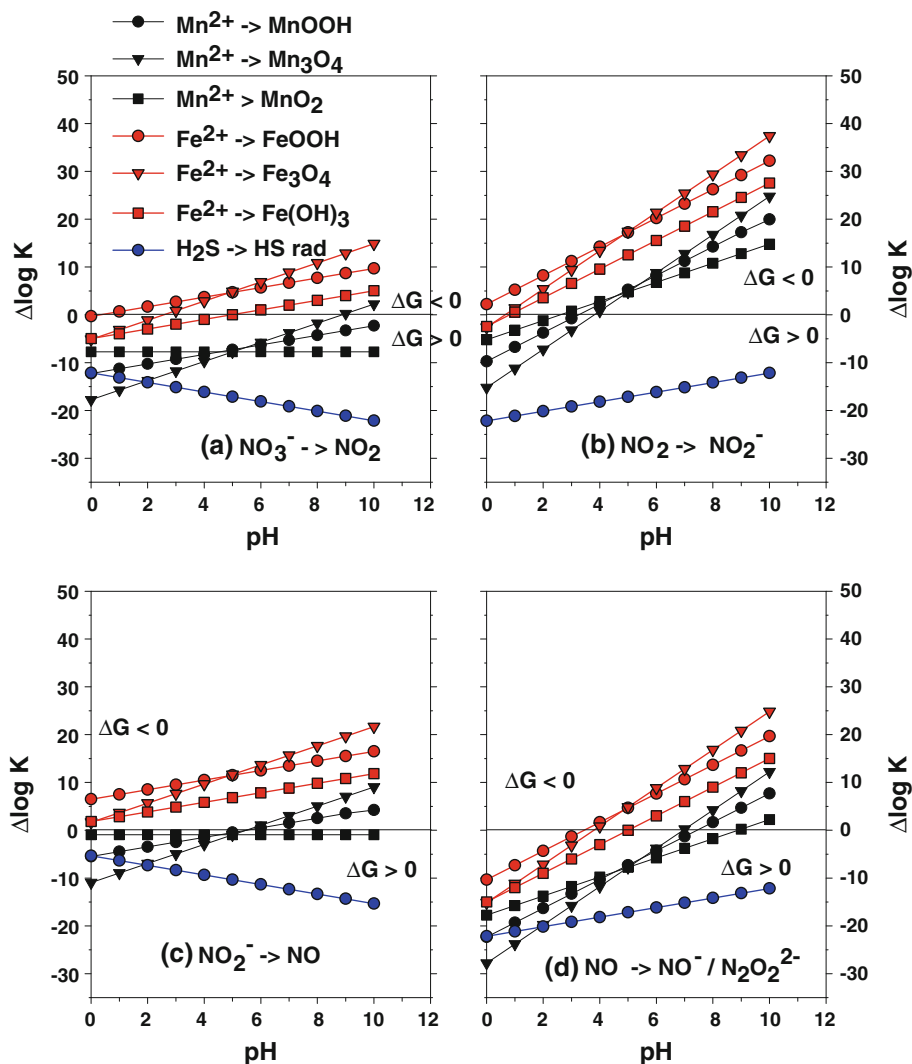


Fig. 10 One-electron transfer reactions of Fe^{2+} and Mn^{2+} with oxidized nitrogen species from Table 2. **a** reaction N10 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **b** reaction N11 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **c** reaction N12 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **d** reaction N13 coupled with reactions Mn1–Mn3 and Fe1–Fe3

In a kinetic study, [Luther and Popp \(2002\)](#) showed that Eq. 10 did not occur in laboratory solutions above a pH of 6 in agreement with the thermodynamic calculations.



3.4.3 Oxidation of Reduced Nitrogen Species Including Ammonium Ion by ROS

The oxidation of ammonium ion, which is the dominant form of ammonia over the pH range 0–10, to N_2 , N_2O and eventually to NO_3^- is an important process. The first electron

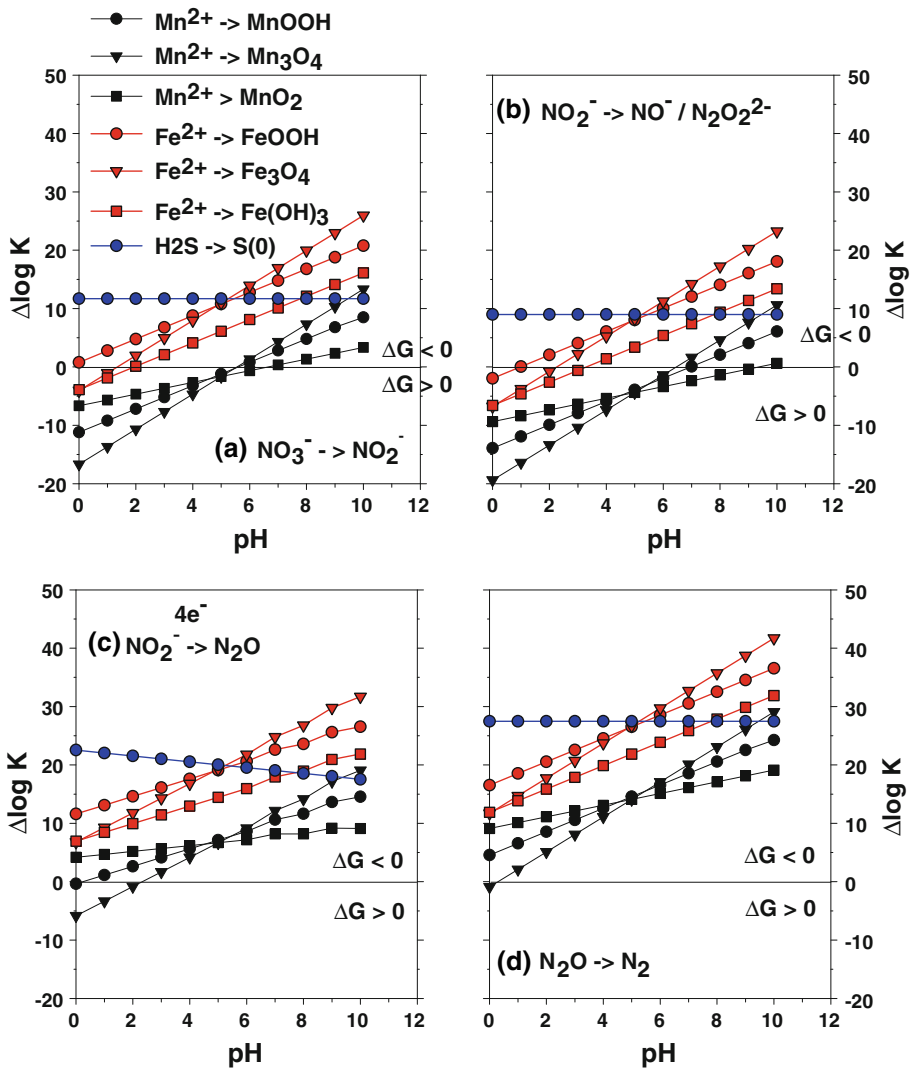


Fig. 11 Two-electron transfer reactions of Fe^{2+} and Mn^{2+} with oxidized nitrogen species from Table 2. **a** reaction N1 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **b** reaction N2 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **c** reaction N3 coupled with reactions Mn1–Mn3 and Fe1–Fe3. **d** reaction N4 coupled with reactions Mn1–Mn3 and Fe1–Fe3

transfer step is complicated by the poor thermodynamics for the formation of NH_3^+ (Stanbury 1989). Figure 12 shows possible one-electron and two-electron transfer steps. In the oxidation of NH_4^+ , either hydroxylamine (NH_2OH) or hydrazine ($\text{H}_2\text{N}-\text{NH}_2$) are the first (meta)stable species that can be formed. In the case of $\text{H}_2\text{N}-\text{NH}_2$ formation, two NH_4^+ ions are required whereas in NH_2OH formation only one NH_4^+ is required. The pK_a values for N_2H_5^+ and NH_3OH^+ are 7.93 and 5.82, respectively, so they are largely protonated at environmental pH values.

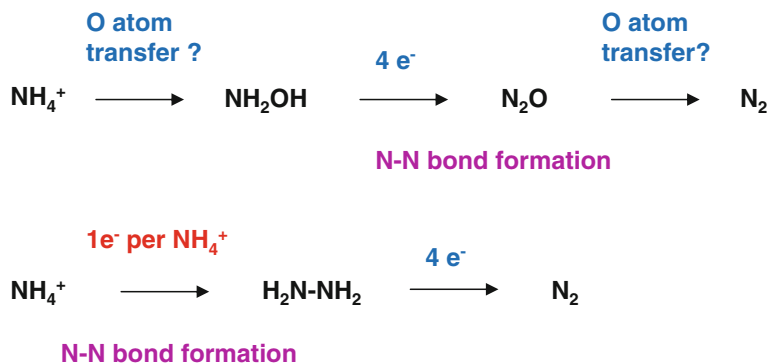


Fig. 12 Possible one-electron and two-electron nitrogen transformations for the oxidation of ammonia to hydrazine and hydroxylamine. O atom transfers are two-electron processes

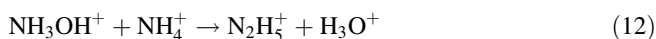
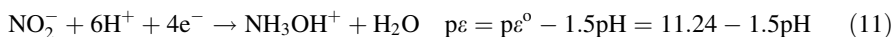
Figure 13a, c show thermodynamic calculations for N_2H_5^+ and NH_3OH^+ formation when one-electron oxidants (O_2 plus ROS) react with NH_4^+ . Both figures show that O_2 must be *activated* to oxidize ammonium. Calculations indicate that there are more possible favorable reactions to form N_2H_5^+ than NH_3OH^+ , and the predicted reactivity is in the order $\text{O}_2 < \text{H}_2\text{O}_2 < {}^1\text{O}_2 < \text{O}_3 < \text{O}_2^- < {}^\bullet\text{OH}$. Because O_2^- can be formed by many pathways including Fe^{2+} oxidation by O_2 (Fig. 1a), ammonia oxidation to N_2H_5^+ could occur in the presence of metals and oxygen in a possible *catalytic cycle*.

Figure 13b, d shows thermodynamic calculations for N_2H_5^+ and NH_3OH^+ formation when two-electron oxidants (O_2 , H_2O_2 , ${}^1\text{O}_2$, O_3) react with NH_4^+ . Again O_2 must be activated for reaction to cause ammonium oxidation. There is predicted an increasing reactivity in the order $\text{O}_2 < {}^1\text{O}_2 < \text{H}_2\text{O}_2 < \text{O}_3$ with formation of N_2H_5^+ favored over NH_3OH^+ .

As in the case of methane mono-oxygenases, nitrifying bacteria produce ammonia monooxygenases, which use metals including copper to activate oxygen (Keener et al. 1998; Shiemke et al. 2004; Whitaker et al. 2000). Ammonia, NH_3 , is the physiological substrate.

3.4.4 Oxidation of Reduced Nitrogen Species Including Ammonium Ion by N, Fe(III), Mn(III, IV) Phases

Anaerobic oxidation of ammonia has received much attention since it was documented in the Black Sea by Kuypers et al. (2003). A biochemical process was described which indicated that $\text{H}_2\text{N-NH}_2$ is formed within a hydrophobic part of a cell called the anammoxosome and is then oxidized to N_2 . However, to form $\text{H}_2\text{N-NH}_2$, nitrite must be reduced to NH_2OH (Eq. 11), which then reacts with ammonium ion (Eq. 12). Figure 14a shows that the reaction of NH_3OH^+ with NH_4^+ is favorable over all pH, and this is the key step in the anammox reaction described by Kuypers et al. (2003).



Luther et al. (1997) performed multi-electron thermodynamic calculations that showed oxidized Mn solids could react with ammonium ion to form N_2 . Figure 14a, c

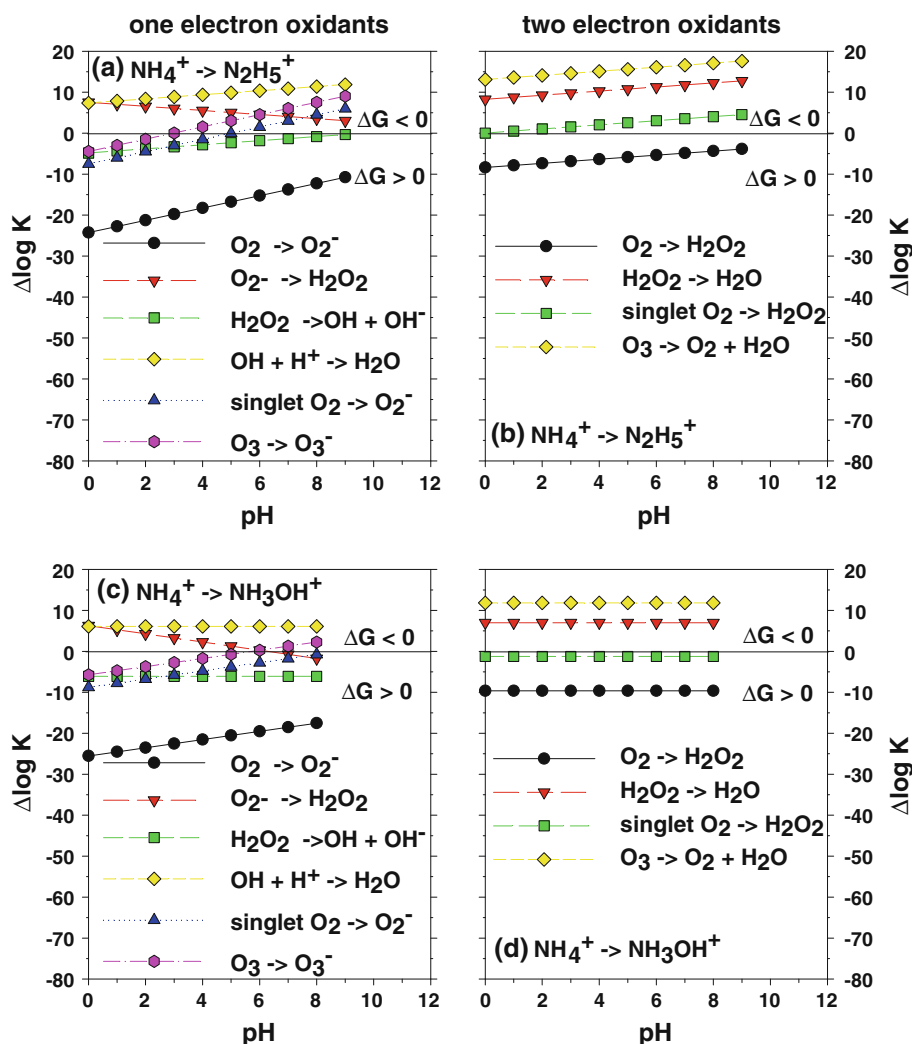


Fig. 13 Reactions of oxygen species with reduced nitrogen species from Table 2. **a** one-electron transfer reactions of O6–O11 coupled with reaction N5. **b** two-electron transfer reactions of O2–O5 coupled with reaction N5. **c** one-electron transfer reactions of O6–O11 coupled with reaction N6. **d** two-electron transfer reactions of O2–O5 coupled with reaction N6

show one- and two-electron thermodynamic calculations for N_2H_5^+ and NH_3OH^+ formation, respectively; when Fe(III) and Mn(III, IV) oxide phases are used as oxidants. Only at pH values below 4 and for reaction with the Mn(III, IV) phases is the formation of these intermediates predicted. These calculations do not consider the possibility of $\text{M}=\text{O}$ or $\text{M}(\text{O}_2)\text{M}$ formation and catalysis (Eqs. 5, 6) and subsequent oxidation of ammonium ion as has been shown for methane nor do they consider the possibility that the $[\text{Mn}_3\text{CaO}_4]\text{Mn}$ photosynthetic cluster in photosystem center II (PSII) could be an oxidant for NH_4^+ . Recent research shows that NH_4^+ as well as methanol binds to PSII and is toxic to both higher plants (Britto and Kronzucker 2002) and cyanobacteria (Drath et al. 2008). The

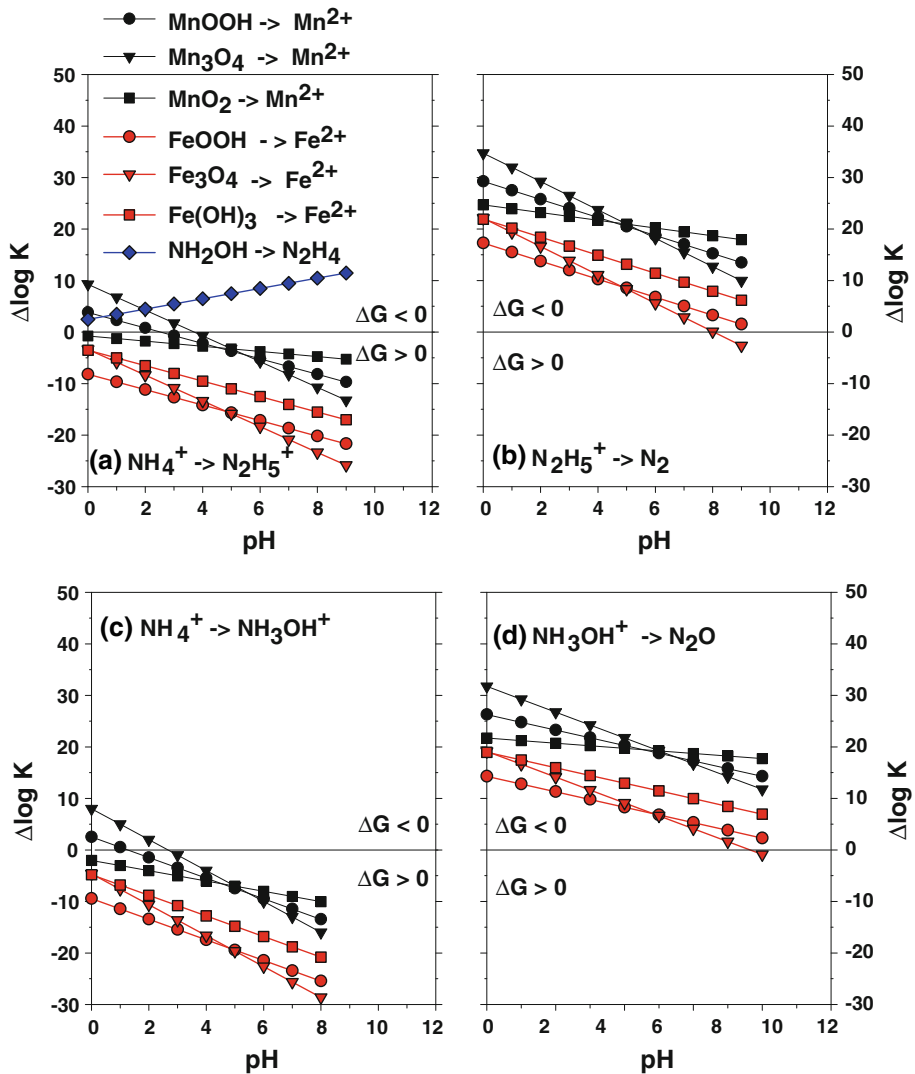


Fig. 14 Reactions of iron and manganese species with reduced nitrogen species from Table 2. **a** reactions Mn1–Mn3, Fe1–Fe3 and N9 coupled with reaction N5. **b** reactions Mn1–Mn3 and Fe1–Fe3 coupled with reaction N7. **c** reactions Mn1–Mn3 and Fe1–Fe3 coupled with reaction N6. **d** reactions Mn1–Mn3 and Fe1–Fe3 coupled with reaction N8

binding triggers damage to PSII, which is more pronounced under higher light conditions (Britto and Kronzucker 2002). Research is not clear about the final nitrogen end-product of the interaction.

Figure 14b, d show thermodynamic calculations for the reaction of N_2H_5^+ and NH_3OH^+ with Fe(III) and Mn(III, IV) oxide phases as oxidants to form N_2 and N_2O , respectively. The Mn reactions are more favorable than the corresponding Fe reactions. These reactions are well known and have been described (Cotton and Wilkinson 1999; Luther et al. 1997; M. Westley, personal communication).

4 Conclusions

The thermodynamic analysis of common environmental oxidants reacting with common reductants indicate that one-electron transfers to O_2 and NO_3^- are often thermodynamically unfavorable and rate limiting in reactions with Fe^{2+} and Mn^{2+} but the corresponding two-electron transfers are not rate limiting over most pH values considered. Mn(III) formation is favored over Mn(IV) formation.

One-electron oxidations of H_2S with NO_x , all ROS except for $\bullet OH$, Fe(III) and Mn(III, IV) species are also not thermodynamically favorable over all pH, but corresponding two-electron transfer reactions are favorable. For Fe(III) and Mn(III, IV) reactions, (nano)particles with bands of partially occupied orbitals are likely important reactants.

One-electron oxidations of NH_4^+ with O_2 and Fe(III) species are thermodynamically unfavorable over all pH and are rate limiting whether hydroxylamine or hydrazine are the first by-products of the reactions. One-electron oxidations of NH_4^+ with O_3 , O_2^- and $\bullet OH$ are thermodynamically favorable over most pH whereas Mn(III, IV) species are favorable at $pH < 4$. Two-electron oxidations of NH_4^+ with O_3 and H_2O_2 are thermodynamically favorable over most pH to form hydroxylamine or hydrazine; however, 1O_2 should only lead to hydrazine formation. The reactions of Fe(III) and Mn(III, IV) species with hydroxylamine or hydrazine lead to N_2O and N_2 formation, respectively.

Of the common environmental oxidants, ROS and Mn(III, IV) species are the best thermodynamically. Although common environmental oxidants may be involved in rate controlling or limiting electron transfer steps, ROS and reactive metal species with organically complexed metals containing $M(IV)=O$ or $Fe(O-O)Fe$ peroxo linkages can be found in the environment or in enzymes produced by organisms. Many of these reactive species activate oxygen, C–H bonds, N–H bonds and the metals while facilitating two-electron transfers so are more effective oxidants than O_2 , Fe(III) and Mn(III, IV) species. It is not clear whether the PSII Mn cluster oxidizes methanol and ammonia as well as water.

Acknowledgments This work was supported by grants from the U.S. National Science Foundation (DEB-0516121; OCE-00963635; OCE-0732439; MCB-0919682), from the U.S. National Oceanic and Atmospheric Administration Sea Grant program (NA09OAR4170070) and from a subcontract to the University of Delaware from the NASA Astrobiology grant to University of California, Berkeley NASA (NCC2-1056 and NAG2-1523). I thank two anonymous reviewers for their constructive comments. The statements, findings, conclusions, and recommendations are those of the author and do not necessarily reflect the views of the granting agencies. The author also wishes to express his gratitude and appreciation to Frank Millero for his encouragement and friendship.

References

- Anschutz P, Sundby B, Lefrançois L, Luther GW, Mucci A (2000) Interactions between metal oxides and species of nitrogen and iodine in bioturbated marine sediments. *Geochim Cosmochim Acta* 64:2751–2763
- Armstrong FA (2008) Why did nature choose manganese to make oxygen? *Philos Trans R Soc B Biol Sci* 363:1263–1270
- Barnese K, Gralla EB, Cabelli DE, Valentine JS (2008) Manganous phosphate acts as a superoxide dismutase. *J Am Chem Soc* 130:4604–4606
- Beal EJ, House CH, Orphan VJ (2009) Manganese- and iron-dependent marine methane oxidation. *Science* 325:184–187
- Britto DT, Kronzucker HJ (2002) NH_4^+ toxicity in higher plants: a critical review. *J Plant Physiol* 159: 567–584
- Cotton FA, Wilkinson G (1999) *Advanced inorganic chemistry*. Wiley, New York

- Das S, Incarvito CD, Crabtree RH, Brudvig GW (2006) Molecular recognition in the selective oxygenation of saturated C–H bonds by a dimanganese catalyst. *Science* 312:1941–1943
- dos Santos Afonso M, Stumm W (1992) Reductive dissolution of iron(III) (hydr)oxides by hydrogen sulfide. *Langmuir* 8:1671–1675
- Drath M, Kloft N, Batschauer A, Marin K, Novak J, Forchhammer K (2008) Ammonia triggers photo-damage of photosystem II in the cyanobacterium *Synechocystis* sp. Strain PCC 6803. *Plant Physiol* 147:206–215
- Duckworth OW, Sposito G (2005) Siderophore–Manganese(III) interactions. I. Air oxidation of manganese(II) promoted by desferrioxamine B. *Environ Sci Technol* 39:6037–6044
- Ehrlich S, Butler I, Halicz L, Rickard D, Oldroyd A, Matthews A (2004) Experimental study of the copper isotope fractionation between aqueous Cu(II) and covellite, CuS. *Chem Geol* 209:259–269
- Ewing G (1975) Structure and properties of van der Waals molecules. *Acc Chem Res* 8:185–192
- Froelich PN, Klinkhammer GP, Bender ML, Luedtke NA, Heath GR, Cullen D, Dauphin P, Hammond D, Hartman B, Maynard V (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim Cosmochim Acta* 43:1075–1090
- Gimarc BM (1979) Molecular structure and bonding: the qualitative molecular orbital approach. Academic Press, New York
- González-Davila M, Santana-Casiano JM, Miller FJ (2005) Oxidation of iron (II) nanomolar with H₂O₂ in seawater. *Geochim Cosmochim Acta* 69:83–93
- Hakemian AS, Rosenzweig AC (2007) The biochemistry of methane oxidation. *Annu Rev Biochem* 76:223–241
- Hansen HCB, Boorgaard OK, Sorensen J (1994) Evaluation of the free energy of formation of Fe(II)–Fe(II) hydroxide-sulphate (green rust) and its reduction of nitrite. *Geochim Cosmochim Acta* 58:2599–2608
- Herszage J, dos Santos Afonso M (2003) Mechanism of hydrogen sulfide oxidation by manganese(IV) oxide in aqueous solutions. *Langmuir* 19:9684–9692
- Hulth S, Aller RC, Canfield DE, Dalsgaard T, Engström P, Gilbert F, Sundbäck K, Thamdrup B (2005) Nitrogen removal in marine environments: recent finding and future research challenges. *Mar Chem* 94:125–145
- Karlsson A, Parales JV, Parales RE, Gibson DT, Eklund H, Ramaswamy S (2003) Crystal structure of naphthalene dioxygenase: side-on binding of dioxygen to iron. *Science* 299:1039–1042
- Keener WK, Russell SA, Arp DJ (1998) Kinetic characterization of the inactivation of ammonia monooxygenase in *Nitrosomonas europaea* by alkyne, aniline and cyclopropane derivatives. *Biochim Biophys Acta* 1388:373–385
- Kostka JE, Luther GW, Nealson KH (1995) Chemical and biological reduction of Mn(III)–pyrophosphate complexes: potential importance of dissolved Mn(III) as an environmental oxidant. *Geochimica Cosmochimica Acta* 59:885–894
- Kuypers MMM, Sliker AO, Lavik G, Schmid M, Jorgensen BB, Kuenen JG, Sinninghe Damsté JS, Strous M, Jetten MSM (2003) Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature* 422:608–611
- Laha S, Luthy RG (1990) Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environ Sci Technol* 24:363–373
- Luther GW (2005) Manganese(II) oxidation and Mn(IV) reduction in the environment—two-one-electron transfer steps versus a single two-electron step. *Geomicrobiol J* 22:195–203
- Luther GW, Ferdelman TG (1993) Voltammetric characterization of iron (II) sulfide complexes in laboratory solutions and in marine waters and porewaters. *Environ Sci Technol* 27:1154–1163
- Luther GW, Popp JI (2002) Kinetics of the abiotic reduction of polymeric manganese dioxide by nitrite: an anaerobic nitrification reaction. *Aquat Geochem* 8:15–36
- Luther GW, Kostka JE, Church TM, Sulzberger B, Stumm W (1992) Seasonal iron cycling in the salt marsh sedimentary environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively. *Mar Chem* 40:81–103
- Luther GW, Wu J, Cullen J (1995) Redox chemistry of iodine in seawater: frontier molecular orbital theory considerations. In: Huang CP, O'Melia CR, Morgan JJ (eds) *Aquatic chemistry: interfacial and interspecies processes*, Advances in Chemistry Series, American Chemical Society, Washington, DC, vol 244, 135–155
- Luther GW, Sundby B, Lewis BL, Brendel PJ, Silverberg N (1997) Interactions of manganese with the nitrogen cycle: alternative pathways to dinitrogen. *Geochim Cosmochim Acta* 61:4043–4052
- Luther GW, Theberge SM, Rozan TF, Rickard D, Rowlands C, Oldroyd A (2002) Aqueous copper sulfide clusters as intermediates during copper sulfide formation. *Environ Sci Technol* 36:394–402
- Maloy JT (1985) Nitrogen chemistry. In: Bard AJ, Parsons R, Jordan J (eds) *Standard potentials in aqueous solution*, 1st edn. M. Dekker, New York, pp 127–139

- Martell AE, Motekaitis RJ, Chen D, Hancock RD, McManus D (1996) Selection of new Fe(III)/Fe(II) chelating agents as catalysts for the oxidation of hydrogen sulfide to sulfur by air. *Can J Chem* 74:1872–1879
- Millero FJ, Sotomlongo S, Izaguirre M (1987a) The oxidation kinetics of Fe(II) in seawater. *Geochim Cosmochim Acta* 51:793–801
- Millero FJ, Hubinger S, Fernandez M, Garnett S (1987b) Oxidation of H₂S in seawater as a function of temperature, pH, and ionic strength. *Environ Sci Technol* 21:439–443
- Morgan JJ (2005) Kinetics of reaction between O₂ and Mn(II) species in aqueous solution. *Geochim Cosmochim Acta* 69:35–48
- Nico PS, Anastasio C, Zasoski RJ (2002) Rapid photo-oxidation of Mn(II) by humic substances. *Geochim Cosmochim Acta* 66:4047–4056
- Postma D (1990) Kinetics of nitrate reduction by detrital Fe(II)-silicates. *Geochim Cosmochim Acta* 54:903–908
- Rickard D, Luther GW (2007) Chemistry of iron sulfides. *Chem Rev* 107:514–562
- Rohde JU, In JH, Lim MH, Brennessel WW, Bukowski MR, Stubna A, Munck E, Nam W, Que L (2003) Crystallographic and spectroscopic characterization of a nonheme Fe(IV) = O complex. *Science* 299:1037–1039
- Shiemke AK, Arp DJ, Sayavedra-Soto LA (2004) Inhibition of membrane-bound methane monooxygenase and ammonia monooxygenase by diphenyliodonium: implications for electron transfer. *J Bacteriol* 186:928–937
- Shu L, Nesheim JC, Kauffmann K, Münck E, Lipscomb JD, Que L (1997) An Fe₂^{IV}O₂ diamond core structure for the key intermediate Q of methane monooxygenase. *Science* 275:515–518
- Stanbury D (1989) Reduction potentials involving inorganic free radicals in aqueous solution. In: Sykes AG (ed) *Advances in inorganic chemistry*, vol 33. Academic Press, New York, pp 69–138
- Straub KL, Benz M, Schink B, Widdel F (1996) Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. *Appl Environ Microbiol* 62:1458–1460
- Stumm W, Morgan JJ (1996) *Aquatic chemistry*, 3rd edn. Wiley, New York
- Suslick KS, Watson RA (1991) Photochemical reduction of nitrate and nitrite by manganese and iron porphyrins. *Inorg Chem* 30:912–919
- Tebo BM, Bargar JR, Clement BG, Dick GJ, Murray KJ, Parker D, Verity R, Webb SM (2004) Biogenic manganese oxides: properties and mechanisms of formation. *Annu Rev Earth Planet Sci* 32:287–328
- Trouwborst RE, Clement BG, Tebo BM, Glazer BT, Luther GW (2006) Soluble Mn(III) in suboxic zones. *Science* 313:1955–1957
- Vazquez FG, Zhang J, Millero FJ (1989) Effect of metals on the rate of the oxidation of H₂S in seawater. *Geophys Res Lett* 16:1363–1366
- Von Langen PJ, Johnson KS, Coale KH, Elrod VA (1997) Oxidation kinetics of manganese (II) in seawater at nanomolar concentration. *Geochim Cosmochim Acta* 61:4945–4954
- Waller BJ, Lipscomb JD (1996) Dioxxygen activation by enzymes containing binuclear non-heme iron clusters. *Chem Rev* 96:2625–2657
- Wanat A, Schnepfensieper T, Stochel G, van Eldik R, Bill E, Wieghardt K (2002) Kinetics, mechanism, and spectroscopy of the reversible binding of nitric oxide to aquated iron(II): an undergraduate text book reaction revisited. *Inorg Chem* 41:4–10
- Wehrli B (1990) Redox reactions of metal ions at mineral surfaces. In: Stumm W (ed) *Aquatic chemical kinetics*. Chapter 11. Wiley, New York, pp 311–336
- Whitaker M, Bergmann D, Arciero D, Hooper AB (2000) Electron transfer during the oxidation of ammonia by the chemolithotrophic bacterium *Nitrosomonas europaea* (2000). *Biochim Biophys Acta* 1459:346–355
- Yao W, Millero FJ (1993) The rate of sulfide oxidation by δ MnO₂ in seawater. *Geochim Cosmochim Acta* 57:3359–3365
- Yao W, Millero FJ (1996) Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Mar Chem* 52:1–16