A kinetic approach to assess the strengths of ligands bound to soluble Mn(III)

George W. Luther, III[1], Andrew S. Madison[1], Alfonso Mucci[2], Bjørn Sundby[2,3] and Veronique E. Oldham[1]

[1] School of Marine Science and Policy, University of Delaware, Lewes, DE 19958 USA.

[2] GEOTOP and Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec H3A 0E8, Canada.

[3] Institut des sciences de la mer de Rimouski, Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada.

Corresponding Author: George W. Luther, III, 1-302-645-4208; luther@udel.edu

Abstract

The soluble porphyrin ligand [α, β, γ, δ -tetrakis(4-carboxyphenyl)porphine (T(4-CP)P)] was used as a competitive complexing ligand to study Mn speciation in the sediment porewaters of four stations in the Laurentian Trough. Both Mn(II) and Mn(III) concentrations were determined simultaneously. The rate of recovery of Mn(II) complexes by the porphyrin shows similar kinetics, but Mn(III)-ligand complexes give different values for the kinetics of recovery, which can be used along with the steady-state approximation to determine the dissociation rate constant, k_d, of the Mn(III)L complex(es). Dissociation rate constants for the recovery of inorganic Mn′ as the Mn(III)-porphyrin complex ranged from 2.28×10^{-3} to 7.20×10^{-3} s^{-1}. The k_d values reflect the dissociation of ligand from natural Mn(III)L complexes, which are slower to dissociate than Mn(III) bound to pyrophosphate but faster than desferrioxmaine-B bound to Mn(III). A comparison of the k_d values of natural Mn(III)L and Fe(III)L complexes from previous studies indicates that Mn(III)L complexes dissociate faster than Fe(III)L complexes. Because $K_{cond} = k_f / k_d$, we estimate K_{cond} at 1.39 to 4.35×10^{11} M^{-1} for these Mn′L complexes [where Mn′ is defined as all inorganic forms of Mn(III)] from the diffusion controlled rate of water exchange (k_{ex}) for $Mn(H_2O)_6^{3+}$ and its hydroxo species, which is the upper limit for the value of k_f for Mn′ reacting with ligands. These K_{cond} values for Mn′L complexes are similar to those found for Fe′L in open ocean waters.

Highlights:

We determine the strength of natural Mn(III)-ligand complexes
Mn(III)-ligand complexes are faster to dissociate than Fe(III)-ligand complexes

Keywords: absorption spectroscopy, metal-ligand complexes, kinetics, thermodynamics, soluble manganese(III), porewater, St. Lawrence estuary

1. Introduction

During the last decade, there have been several reports of the presence of soluble Mn(III) in the suboxic water column of the Black Sea, the Baltic Sea and the Chesapeake Bay (Dellwig et al., 2012; Schnetger and Dellwig, 2012; Trouwborst et al., 2006; Yakushev et al., 2009) as well as in the sediment porewaters of the Laurentian Trough (Madison et al., 2011 and 2013). Soluble Mn(III), stabilized by complexation to unknown, natural organic ligands, can potentially serve as both oxidant and reductant in one-electron transfer reactions with other redox species. It is likely ubiquitous in sediment porewaters and suboxic water columns, where it would facilitate key electron transfer processes in global biogeochemical cycles. On the other hand, the nature of the ligands that stabilize Mn(III) in solution and the stability of the Mn(III) complexes are unknown.

Different analytical methods have been used to determine soluble Mn(III) in natural waters. Trouwborst et al. (2006) used the competitive ligand desferrioxamine-B (DFOB) to outcomplex the natural ligands originally bound to Mn(III) in Black Sea and Chesapeake Bay suboxic waters; the resulting Mn(III)-desferrioxamine-B complex was measured by voltammetry and the reaction with the seawater sample occurred within 30 seconds. Yakushev et al. (2009) measured manganese before and after UV irradiation of Baltic Sea water samples; the difference was assumed to be soluble Mn(III) since Mn(II) normally does not form strong organic complexes. Schnetger and Dellwig (2012) measured the dissolved Mn concentration in aliquots of samples recovered from the redoxcline of the Black Sea. One aliquot was analyzed immediately upon filtration through 0.45 μm filters. A second filtered aliquot was exposed for 48h to an oxygenated atmosphere and was then analyzed after another filtration through 0.45 μm filters to remove MnO_x that precipitated. The concentration difference between these two measurements was termed reactive Mn, which was similar in concentration to the Mn(III) measurements made by Trouwborst et al. (2006). The spectrophotometric method, developed by Madison et al. (2011), determines both soluble Mn(II) and Mn(III) using a competitive chelate, a soluble porphyrin. The rate of Mn(II) reacting with the porphyrin is faster than that of Mn(III) bound to chelates such as pyrophosphate (PP) and desferrioxamine-B (DFOB) as well as unknown chelates in seawater.

The thermodynamic stability constants (K_{Therm}, based on the activities of the chemical species) of known Mn(III)-ligand complexes are similar to or slightly greater than the equivalent Fe(III)-ligand complexes (Harrington et al., 2012), indicating that they have a similar ratio for the kinetic formation and dissociation constants, k_f and k_d. This ratio of the kinetic constants gives the conditional stability constant ($K_{cond} = k_f / k_d$, based on the concentrations of the chemical species), which can be corrected for the side-reaction coefficients of the metal and ligand to give K_{Therm}. For most metals, the side-reaction coefficients are known, but the side reactions of the natural ligands are unknown. Thus, K_{cond} are reported as $K_{M'L}$ when no side-reaction coefficients are known or $K_{M(n+)L}$ when the metal side-reaction coefficients are known. There is a large body of information on the conditional stability constants of Fe(III) bound to unknown natural ligands (see review by Gledhill and Buck, 2012) derived from competitive ligand exchange-adsorption cathodic stripping voltammetry (CLE-CSV) titrations (Wells et al., 2013). Conversely, there are no reports on the stability of Mn(III) with unknown natural ligands using either competitive ligand thermodynamic or kinetic techniques.

Wu and Luther (1995) and Witter and Luther (1998) showed that the competitive ligand [1-nitroso-2-naphthol or 1N2N] method of van den Berg (1995) could be used to obtain both conditional stability constants and kinetic constants (k_f and k_d) for Fe(III)-ligand complexes. The conditional stability constant (K_{cond}), obtained by the kinetic method was the same as the conditional stability constant obtained by the more traditional competitive ligand titration method. In the kinetic method, Fe′ (inorganic Fe) is added to a seawater sample at natural pH; aliquots of the sample are then taken over time and analyzed with the competitive ligand 1N2N. The formation rate constant k_f is derived from the decreasing Fe′ concentration as it binds with the unknown ligands in seawater to form Fe′L. Once the Fe′ is completely bound to the unknown natural ligands, it is recovered using the competitive ligand 1N2N. The kinetics of the recovery using the steady-state approximation for Fe′ (i.e., $d[\mathrm{Fe'}]/dt = 0$) yields the dissociation rate constant k_d. This approach was used successfully by Gerringa et al. (2007) and Jones et al. (2009), indicating the merit of the kinetic approach. An additional valuable piece of information that is obtained from the kinetic approach is the half-life, $t_{1/2}$, of the metal-ligand complex to dissociation, which is related to the estimated residence time of iron in seawater (Luther and Wu, 1997). In these thermodynamic and kinetic studies, much of the information on Fe(III) bound to natural ligands focused on ligands whose total concentration was in excess of the total iron concentration in the seawater sample as the Fe(III) already bound to organic ligands could not be recovered.

The method of Madison et al. (2011) provides direct kinetic information on the recovery of Mn(III) from the actual ligand bound to the manganese. In this paper, we describe how to extract k_d and $t_{1/2}$ data from this information. We compare the kinetic data for the unknown Mn(III)-ligand complexes in sediment porewaters of the St. Lawrence Estuary (an organic matter decomposition zone) with those determined previously for the unknown Fe(III)-ligand complexes encountered throughout the water column of the Atlantic Ocean and the Arabian Sea (including its suboxic zone). We show that the unknown Fe(III)-ligand complexes dissociate more slowly than the Mn(III) complexes. The half-life of the Mn(III) complexes determined here indicates that they are less stable to dissociation.

At present, it is not possible to obtain accurate information on the formation constant, k_f, of natural-ligand complexes reacting with Mn' to form the Mn(III)- ligand complex as the unknown ligand must be isolated. Therefore, an accurate determination of the conditional stability constant cannot be obtained. Nevertheless, an estimate of the formation constant can be derived from the kinetic method of Madison et al (2011), which gives k_d, and knowledge of the water exchange rates (k_{ex}) of Mn(III), which is a measure of k_f. $Mn(H_2O)_6^{3+}$ is a $t_{2g}^3 e_g^{*1}$ ion exhibiting Jahn-Teller distortion from octahedral geometry (Atkins et al, 2010). $Cr(H_2O)_6^{2+}$ has the same electron configuration and has a diffusion-controlled water exchange rate of 10^9 s^{-1} (Helm and Merbach, 2005). The $Mn(H_2O)_6^{3+}$ water exchange rate is so fast that it has not yet been measured. In comparison, $Fe(H_2O)_6^{3+}$ is a $t_{2g}^3 e_g^{*2}$ ion with a water exchange rate of 1.6 x 10^2 s^{-1} whereas $Fe(H_2O)_5OH^{2+}$ has a water exchange rate of 1.2 x 10^5 s^{-1}. The OH^- permits more lability as it stabilizes a five-coordinate intermediate better than water does as a ligand. Furthermore, the second order rate constant for metal cations reacting with ligands rarely is faster than the value of the water exchange rate but is near the value of the water exchange rate (Margerum et al, 1978), so we assume the rate constant for these forward metal-ligand reactions of $Mn(H_2O)_6^{3+}$ and Mn′ to be 10^9 M^{-1} s^{-1}. Using this value for k_f and the k_d data, we can estimate K_{cond}.

2. Experimental

2.1 Field stations and sample processing

Undisturbed sediment cores were recovered in July 2010 at four stations along the Laurentian Trough in the Lower St. Lawrence Estuary (Figure1; Station 23) and the Gulf of St. Lawrence (Station CE, Station Cabot, Station 16) using a 0.12 m^2 Ocean Instruments Mark II box corer. With the exception of Station 16, duplicates cores were collected at each station. Upon recovery, the vertical distribution of dissolved O_2 in the first core was measured by in situ high-resolution micro-electrode voltammetry (Brendel and Luther, 1995). The second 40 cm+ long core was immediately sectioned at various depth intervals in a glove box purged with nitrogen gas (Edenborn et al., 1986). The sampled depth intervals were 0 – 0.5 cm, 0.5 – 1 cm, 1 – 2 cm, 2 – 3 cm, 4 – 5 cm, 5- 7 cm, 7 – 9 cm, 9 – 11 cm, 11 – 13 cm, 13 – 15 cm, 15 – 18 cm, 18 – 21 cm, 21 – 24 cm, 24 – 28 cm, 28 – 32 cm, 32 – 36 cm, and 36 – 40 cm. Up to 50 - 100 ml of porewater were extracted from each depth interval using Reeburgh-type squeezers, modified to filter the water through a glass microfiber pre-filter and 0.45 μm Type HA Millipore® filter as it passed directly into a 50-ml pre-cleaned syringe (Mucci et al., 2003). To preserve the anoxic integrity of the porewater and prevent oxidation of dissolved Mn, the porewaters destined for Mn speciation determinations were sub-sampled from the syringes in a glove bag under a steady stream of argon after approximately 20 ml of porewater had been extracted from each depth interval. These sub-samples were then filtered, in the glove bag under an argon atmosphere, through a 0.2 μm acid-cleaned Nuclepore® polycarbonate track etched filter into acid-cleaned 15-ml centrifuge tubes to remove any particles that passed through the original 0.45 μm filter. The porosity of the sediment was calculated for each depth interval from the water content (difference in weight of wet and freeze-dried sediments), salinity (of bottom water) and a solid-sediment density of 2.71 g cm^{-3}.

Figure 1 here

2.2 Mn speciation analyses

The porewater samples were immediately analyzed by the method of Madison et al. (2011) in duplicate to determine soluble Mn(II) and Mn(III) concentrations using the soluble porphyrin ligand [α, β, γ, δ -tetrakis(4-carboxyphenyl)porphine (T(4-CP)P)]. The detection limit for Mn(II) and Mn(III) was 0.1 μM. Briefly, a porewater sample (typically 100 μl) was injected into a clean spectrophotometric quartz cell containing the cadmium-porphyrin complex, imidazole catalyst, and borate buffer (total volume 3 ml). The absorbance of the resulting Mn-porphyrin complex was measured over time against a blank with a Hewlett Packard 8452B diode array spectrophotometer (2-nm wavelength resolution) controlled by Olis, Inc. Globalworks software. The signal was measured for 15 minutes, or until a steady-state signal was attained. To confirm the accuracy of the method, a Mn(II) standard was added to approximately one-third of the porewater samples and these samples were analyzed in duplicate. Hence, these specific samples were analyzed in quadruplicate. The reproducibility of all Mn(II) and Mn(III) measurements was better than 5%. The rate of Mn(II) complexation by the porphyrin was $0.0250 \pm 0.007\ s^{-1}$, whereas the average for the unknown Mn(III) complexes detected in the porewaters was $4.76 \times 10^{-3} \pm 1.39 \times 10^{-3}\ s^{-1}$. The root mean square error of the kinetic model fits to the measured absorbance was below 0.04 and the r^2 values were greater than 0.99 for all curves indicating accurate simulation of Mn(II) and Mn(III) complexation with the porphyrin. We note that colloidal Mn does not react with the porphyrin, as reported in Madison et al. (2011).

3. Results and Discussion

3.1 Mn speciation determined from the kinetic curves

The addition of the porphyrin ligand [α, β, γ, δ -tetrakis(4-carboxyphenyl)porphine (T(4-CP)P)] permits the simultaneous determination of Mn(II) and Mn(III)L complexes in the porewater samples. Figure 2 shows a plot of the formation of the Mn-porphyrin complex with time for a known mixture of Mn(II) [2.52 μM] and Mn(III)pyrophosphate [1.90 μM] in de-ionized (DI) water.

Figure 2 here

The kinetic equation that describes the formation of the porphyrin complexes is given by eq. 1, where $[Mn]_{total}$, $Mn(II)_0$ and $Mn(III)_0$ are, respectively, the total Mn , Mn(II) and Mn(III) concentrations in the sample.

$$[Mn]_{total} = Mn(II)_o(1 - e^{-k_1 t}) + Mn(III)_o(1 - e^{-k_2 t}) \quad (1)$$

As shown in Madison et al (2011), the plot of Mn concentration (absorbance) with time can be resolved as a two component system where k_1 is the observed rate constant for Mn(II) going into the porphyrin, and k_2 is the observed rate constant for the Mn(III) from Mn(III)L going into the porphyrin. The recovery of each species in Figure 2 is quantitative.

3.2 Kinetics of dissociation of unknown Mn(III)L complexes in the Laurentian Trough sediment porewaters

The porphyrin kinetic method can be described as a ligand exchange reaction (eq. 2) for the unknown Mn(III)L complex(es) with ***excess*** porphyrin ligand, hereafter abbreviated as POR. The reaction is run under pseudo-first order conditions, and the greater the excess of the POR, the faster the reaction will proceed.

$$Mn(III)L + POR \xrightarrow{k_{obs}} Mn(III)(POR) + L \quad (2)$$

The k_2 rate constant in eq. 1 is related to k_{obs} for the formation of Mn(III)POR in eq. 2, as derived from the growth curve of the kinetics plot used to determine the concentration of Mn(II) and Mn(III). For simplicity, Mn(III) is abbreviated hereafter as Mn′ to be consistent with previous terminology used for the Fe system (e.g., Wu and Luther, 1995). The rate expression for the dissociation (or loss) of Mn′L and the formation of Mn′POR in eq. 2 is given in eq. 3.

$$-\frac{d}{dt}[Mn'L] = \frac{d}{dt}[Mn'POR] = k_{obs}[Mn'L][POR] \quad (3)$$

On integrating this expression, we have eq. 4, which shows how the first order rate constant k_2 from eq. 1 is related to k_{obs}, a second order rate constant.

$$\ln[Mn'L] = -\,k_{obs}[POR]\,t \;=\; -\,k_2 t \quad (4)$$

The dissociation rate constant of a Mn′L complex can be determined using the steady-state approximation (Wilkins, 1991) from the associative reaction (eq. 2), which can be broken into ***two elementary reaction steps***. First, the ***dissociation*** of the natural organic ligand complex to form Mn′ (eq. 5, which leads to K_{cond} for Mn′L in eq. 6), where Mn′ represents all inorganic forms of Mn(III) in seawater at ambient pH; and second, the ***reaction*** of Mn′ with the soluble porphyrin (POR; eq. 7):

$$Mn'L \underset{k_f}{\overset{k_d}{\rightleftarrows}} Mn' + L \quad (5)$$

$$where\ K_{cond} = K_{M\prime L} = \frac{k_f}{k_d} \quad (6)$$

K_{cond} in eq. 6 is a conditional equilibrium constant based on Mn′ as the inorganic side-reaction coefficients for Mn(III) bound to Cl^-, OH^-, etc. are not currently known.

$$Mn' + POR \overset{k_{2a}}{\longrightarrow} Mn'(POR) \quad (7)$$

The rate expression for eq. 7 is eq. 8.

$$\frac{d}{dt}[Mn'(POR)] = k_{2a}[Mn'][POR] \quad (8)$$

The Mn′ concentration will always be very small and, thus, applying the ***steady-state approximation*** to equations 5 and 7, we can write eq. 9:

$$\frac{d}{dt}[Mn'] = 0 = k_d[Mn'L] - k_f[Mn'][L] - k_{2a}[Mn'][POR] \quad (9)$$

Rearranging and solving for Mn′ gives eq. 10.

$$[Mn'] = \frac{k_d[Mn'L]}{k_f[L] + k_{2a}[POR]} \quad (10)$$

Substituting [Mn′] from eq. 10 into eq. 8 gives eq. 11.

$$\frac{d}{dt}[Mn'(POR)] = -\frac{d}{dt}[Mn'L] = \frac{k_d[Mn'L]k_{2a}[POR]}{k_f[L] + k_{2a}[POR]} \quad (11)$$

Although we do not have data on k_{2a} [POR] for the formation of Mn′(POR) and k_f [L] for the formation of Mn′L, the Mn′L complexes react completely with POR so that k_{2a} [POR] >> k_f [L]. Thus, eq. 11 reduces to eq. 12.

$$\frac{d}{dt}[Mn'(POR)] = -\frac{d}{dt}[Mn'L] = k_d[Mn'L] \quad (12)$$

On integrating this expression, we obtain eq. 13.

$$\ln[Mn'L] = -k_d t \quad (13)$$

Substituting for ln[Mn′L] with eq. 13 into eq. 4, gives eq. 14 and that k_d is equal to k_2 (eq. 15).

$$\ln[Mn'L] = -k_d t = -k_{obs}[POR]\,t = -k_2 t \qquad (14)$$

$$k_d = k_2 \quad \text{eq. (15)}$$

The half-life, eq. 16, for the Mn′L complex dissociation (or its residence time) is:

$$t_{1/2} = \frac{0.693}{k_d} = \frac{0.693}{k_2} \quad (16)$$

Lastly, the second order rate constant (k_{obs}) from eqs. 2 and 3 can be evaluated from eq. 17.

$$k_{obs} = \frac{k_2}{[POR]} \quad (17)$$

Table 1 shows the k_d (s^{-1}) and Mn(III) concentration values derived from the kinetics curves and obtained from the Mn speciation determinations in the Laurentian Trough porewaters. ***These data are for the actual or natural, unknown ligand(s) or chelate(s) bound to Mn(III) in the porewaters.*** Figure 3 shows the variation of k_d in graphical form. In general, the most stable Mn′L complexes were isolated from station CE, and the most prone to dissociation are from station Cabot. The k_{obs} values vary by only a factor of about 3.5. The highest k_d values were obtained at station Cabot and 23 where, of the sampled stations, the sedimentary organic carbon is most reactive (Alkhatib et al., 2012; Silverberg et al., 2000).

Table 1 here.

Figure 3 here.

Table 2 gives the k_{obs} values obtained from eq. 17. The k_{obs} values range from 95.8 to 300 M^{-1} s^{-1} and indicate that the complexes react quickly with the porphyrin in an associative reaction. The k_{obs} values for Mn′PP and Mn′DFOB are 1040 M^{-1} s^{-1} and 2.31 M^{-1} s^{-1}, respectively .

Table 2 here.

Table 3 gives the half-life for Mn′L dissociation in minutes. Longer half-lives reflect the stability of the complexes, their potential diffusion to the overlying water and transport to the overlying waters of the Laurentian Trough. Sundby et al. (1981) have demonstrated that Mn is released from the bottom sediments in the Laurentian Trough, transported landward with the bottom current and ultimately exported to the ocean with surface waters. In this scenario, Mn′L originating from the microbially-mediated dissolution of MnO_2 or the oxidation of Mn(II) diffusing up from the anoxic sediments, may escape the sediment by diffusion to the overlying waters where it would be transported some distance before being precipitated following the dissociation of Mn′L. In comparison, the half-lives for Fe′L complexes found in the open ocean are longer as they range from 2 to 1900 hours (Witter and Luther, 1998; Witter et al, 2000a). Because Wu and Luther (1997) showed that the half-lives of Fe′L dissociation were related to the Fe residence times in the ocean calculated by Johnson et al. (1997), these Mn′L half-lives are assumed to reflect the Mn′L residence time in the porewaters.

Table 3 here.

3.3 Comparison with known ligands

Using the porphyrin method, we determined the values of k_d ($2.83 \times 10^{-4}\ s^{-1}$) and the half-life (40.8 min) for the dissociation of the Mn′DFOB complex (eq. 18):

$$\mathrm{Mn'DFOB} \rightarrow \mathrm{Mn'} + \mathrm{DFOB} \quad (18)$$

The k_d values for the porewater Mn′L complexes reveal that the natural complexes dissociate more slowly than Mn(III) complexed to pyrophosphate (Figure 3) but are faster to dissociate than Mn(III) complexed with desferrioxmaine-B.

3.4 Comparison with known Fe(III) ligand kinetics

Figure 4 shows a comparison of the k_d values obtained for Mn′L complexes in Laurentian Trough sediment porewaters with k_d data for Fe′L complexes obtained from the western Atlantic Ocean (Witter and Luther, 1998; Wu and Luther, 1995) and the OMZ waters of the Arabian Sea (Witter et al 2000a). These data indicate that Mn′L complexes typically dissociate over a hundred times faster than Fe′L complexes, as indicated in Figure 4. The k_d data show that the Fe′L complexes approach a lower value of $1.0 \times 10^{-7}\ s^{-1}$ and appear to become more stable to dissociation with depth (and in the OMZ). These zones are characterized by higher organic matter decomposition with the release of nutrients and micronutrients to the water column. The faster k_d values for Mn′L complexes indicate that the unknown ligands cannot stabilize Mn(III) in an octahedral geometry. Mn(III) has a $t_{2g}^{3}\ e_g^{*1}$ electron configuration, which is known to exhibit tetragonal distortion as explained by the Jahn – Teller theorem (Atkins et al, 2010). Thus, the two axial positions in an octahedral environment are prone to ligand dissociation. In contrast, Fe(III) has a $t_{2g}^{3}\ e_g^{*2}$ electron configuration and does not exhibit tetragonal distortion.

The k_d values reported in Figure 4 are for ‘weaker’ Fe′L complexes and not the actual ligand bound to Fe(III) because the competitive ligand 1-nitroso 2-naphthol (1N2N) could not recover Fe(III) already bound to natural ligands in the original samples. Fe(III) added to the samples reacted with ligand(s) in excess of the original Fe(III) content, and the Fe(III) could only be recovered from the excess ligand upon the addition of the 1N2N ligand. Hence, k_f and k_d could only be obtained for Fe(III) bound to excess natural ligands.

Figure 4 here.

3.5 Estimate of the conditional equilibrium constant for Mn′ with ligands

The general reaction for inorganic Mn′ as Mn(III) reacting with ligands was described by eq. 5 from section 3.2 as

$$Mn'L \underset{k_f}{\overset{k_d}{\rightleftarrows}} Mn' + L \quad (5) \qquad where\ K_{cond} = K_{Mn'L} = \frac{k_f}{k_d}$$

We now demonstrate two ways to estimate a k_f value and derive an equilibrium constant for any Mn′L complex. First, we used the easily prepared Mn′PP complex as a proxy for Mn′ (eq. 5). Although we do not have k_f data for the unknown natural ligand bound to Mn′, we have determined k_f to be $3.97 \times 10^2\ M^{-1}\ s^{-1}$ for the formation of Mn′DFOB from the following reaction (eq. 19) where PP = pyrophosphate and DFOB = desferrioxamine-B.

$$\text{Mn'PP} + \text{DFOB} \rightarrow \text{Mn'DFOB} + \text{PP} \quad (19)$$

As $K = \frac{k_f}{k_d}$; we use the k_f value determined from eq. 19 and the k_d values from Table 1 to estimate conditional K values. Thus, the Mn′L complex with the smallest k_d value (Table 1) gives the highest $K_{(20)}$ value as in eq. 20.

$$K_{(20)} = \frac{3.97\ x\ 10^2 M^{-1} s^{-1}}{2.28\ x\ 10^{-3}\ s^{-1}} = 1.74\ x\ 10^5\ \ M^{-1} \quad (20)$$

Adopting the value of k_f from eq. 19 for all unknown natural ligands and the range of k_d values reported in Table 1, we estimate a conditional equilibrium constant, $K_{(20)}$, analogous to eq. 5 that ranges from $5.51 \times 10^4\ M^{-1}$ to $1.74 \times 10^5\ M^{-1}$. We believe that these values are low because, unlike Fe(III), we do not currently have an inorganic Mn(III) solution to test for known ligands as $[Mn(H_2O)_6]^{3+}$ is prepared by the comproportionation reaction of permanganate with excess Mn^{2+}. In fact, $[Mn(H_2O)_6]^{3+}$ is unstable even at low pH as it is prone to disproportionation even in the presence of excess Mn^{2+} (Davies, 1968). Furthermore, the actual natural ligand(s) is unknown, and its properties cannot be investigated unless it is isolated from the sample matrix.

From the k_d data in section 3.3 for Mn′DFOB ($2.83 \times 10^{-4}\ s^{-1}$; eq. 18) and the k_f of $3.97 \times 10^2\ M^{-1}\ s^{-1}$ from eq. 19, we calculate that $K_{(20)}$ is $1.40 \times 10^6\ M^{-1}$. We note that this estimate of the equilibrium constant for Mn′DFOB is also likely low, perhaps by as much as 4 orders of magnitude or more, because we used the k_f determined from eq. 19. For example, the k_f for Fe(III) reacting with DFOB to form Fe(III)-DFOB is $\sim 1 \times 10^6\ M^{-1}\ s^{-1}$ (Witter et al, 2000b) compared to the value of $3.97 \times 10^2\ M^{-1}\ s^{-1}$ noted above for the formation of Mn′DFOB from Mn′PP and DFOB, which does not use Mn′ for the calculation.

A better second estimate of k_f and hence K_{cond} can be made by comparing the kinetics and thermodynamics for Fe(III) and Mn(III) ligand complexes. We note that the water exchange rate (k_{ex}) for $Fe(H_2O)_6^{3+}$ is $1.6 \times 10^2\ s^{-1}$ and $1.2 \times 10^5\ s^{-1}$ for $Fe(OH_2)_5(OH)^{2+}$ (Helm and Merbach, 2005). Although k_{ex} for $Mn(H_2O)_6^{3+}$ has not yet been determined, the value of k_{ex} for the tetragonally distorted $Cr(H_2O)_6^{2+}$, which has the same electron configuration as $Mn(H_2O)_6^{3+}$, was determined to be 10^9 s^{-1} (Helm and Merbach, 2005). Thus, as discussed in the introduction, $Mn(H_2O)_6^{3+}$ and $Mn(OH_2)_5(OH)^{2+}$ should have at least the minimum diffusion-controlled k_f value of 10^9 M^{-1} s^{-1} for reaction with a ligand as in eq. 5. Using this value for $k_{f,}$ for all unknown ligands, instead of 3.97 x 10^2 M^{-1} s^{-1} from eq. 19, gives a range of K_{cond} from 1.39 x 10^{11} M^{-1} to 4.35 x 10^{11} M^{-1} for Mn′L complexes (Table 4), which is within the known range for Fe′L complexes of 10^{10} to 10^{14} M^{-1}. The k_f multiplication factor of 2.5 x 10^6 (1 x 10^9 / 3.97 x 10^2) accounts for the difference in reactivity of DFOB between Mn′ and Mn′PP. Likewise, Mn′DFOB would have a K_{cond} value of 3.53 x 10^{12} M^{-1}, similar to the value of 1.25 x 10^{12} M^{-1} for Fe′DFOB determined by Witter et al (2000b) using the kinetic and CLE-CSV methods. The similarity of the conditional equilibrium constants for Mn′L and Fe′L is consistent with the similarity of the thermodynamic constants (K_{Therm}) reported by Harrington et al (2012) for known ligands bound to Mn(III), indicating that our second estimate for k_f of 10^9 M^{-1} s^{-1} is reasonable. Furthermore, these data indicate that the inorganic side-reaction coefficients for Mn′ and Fe′ may be of the same order of magnitude.

Table 4 here.

4. Conclusions

The dissociation constant and half-life data for unknown, natural ligands bound to Mn(III) in Laurentian Trough sediment porewaters indicate that the Mn′L complexes are stable to dissociation with half-lives as long as 5 minutes. It should be noted that the data were determined at room temperature rather than at the ambient bottom-water temperature of about 5°C. Thus, the half-lives to dissociation would approach 20 minutes (two-fold increase in half-life for every 10°C decrease, Atkins (1982) at 5°C. For the Mn′DFOB complex, the half-life is 40.8 minutes at 25°C and 163 minutes at 5°C.

Our kinetic data indicate that K_{cond} values for Mn′L are likely similar to K_{cond} values for Fe′L because, based on comparison of their water exchange rates, the k_f for Mn′L complexes should be faster than Fe′L complexes thus compensating for the faster k_d data for Mn′L complexes. Note that the K_{cond} values determined in this study are for "weak" complexes as all Mn(III) could be recovered by the porphyrin method. As determined by Witter et al (1998, 2000b) for Fe(III), stronger ligands are likely present in natural waters. Although k_f for Mn′L formation is at the diffusion controlled limit, it would be useful to determine the actual k_f for the unknown, natural ligands with Mn(III) to better evaluate K_{cond}. In order to accomplish this, it would be necessary to remove the unknown ligand from the Mn(III), and then trap it via chromatographic or other methods. The unknown, natural ligand could then be reacted with Mn′ and Mn(III)-PP as in eq. 18. However, to form Mn′, a 100-fold excess of Mn^{2+} would be required to prevent disproportionation of $Mn(H_2O)_6^{3+}$ (Davies, 1968).

Unlike competitive ligand titration experiments, the kinetic approach does not add any form of manganese, including Mn(III), to the sample. In other words, the competitive ligand only binds with the Mn(III) bound to the actual ligand in the sample. Therefore, the k_d data derived from this method reflect the binding strength of the *actual ligand* to Mn(III).

5. Acknowledgments

This work was funded by grants from the Chemical Oceanography Division of the National Foundation to G.W.L. (OCE-1155385 and OCE-1031272) and from the Natural Sciences and Engineering Research Council of Canada (NSERC) through Discovery and Ship-time grants to A.M. and B.S. We thank B. Voelker, and D. Di Toro for helpful discussions, and two anonymous journal reviewers for constructive comments.

References

Alkhatib, M., Schubert, C.J., del Giorgio, P. A., Gelinas, Y., Lehmann, M.F. 2012. Organic matter reactivity indicators in sediments of the St. Lawrence Estuary. Estuar. Coast. Shelf Sci. 102-103, 36–47.

Atkins, P. W. 1982. *Physical Chemistry*, 2nd ed. W. H. Freeman and Co., San Francisco.

Atkins P, Overton, T., Rourke, J., Weller, M., Armstrong F. and Hagerman, M. 2010. *Inorganic Chemistry,* 2nd edition. New York: W. H. Freeman and Co. 824 p.

Brendel, P. J, Luther, G. W.. 1995. Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O_2, and S(-II) in porewaters of marine and freshwater sediments. Environ. Sci. Technol. 29, 751–761.

Davies, G. 1968. Some aspects of the chemistry of manganese(III) in aqueous solution. Coord. Chem. Rev. 4, 199-224 .

Dellwig, O., Schnetger, B., Brumsack, H. J., Grossart, H. P., Umlauf, L. 2012. Dissolved reactive manganese at pelagic redoxclines (part II): Hydrodynamic conditions for accumulation. J. Mar. Systems 90, 31-41.

Edenborn H.M., Mucci A., Belzile N., Lebel J., Silverberg N. and Sundby B. 1986. A glove box for the fine-scale subsampling of sediment box cores. Sedimentology **33:** 147-150.

Gerringa L. J. A., Rijkenberg M. J. A., Wolterbeek H. T., Verburg T. G., Boye M., de Baar H. J. W. 2007. Kinetic study reveals weak Fe-binding ligand, which affects the solubility of Fe in the Scheldt estuary. Mar. Chem. 103, 30–45.

Gledhill, M., Buck, K. N. 2012. The organic complexation of iron in the marine environment: a review. Front. Microbio. 3, article 69. doi: 10.3389/fmicb.2012.00069

Harrington, J. M., Parker, D. L., Bargar, J. R., Jarzecki, A. A., Tebo, B. M., Sposito, G., Duckworth, O. W. 2012. Structural dependence of Mn complexation by siderophores: Donor group dependence on complex stability and reactivity. Geochim. Cosmochim. Acta 88, 106-119.

Helm, L. and Merbach, A. E. (2005) Inorganic and Bioinorganic Solvent Exchange Mechanisms. *Chemical Reviews* 105, 1923-1959.

Johnson, K. S., Gordon, R. M., Coale, K. H. 1997. What controls dissolved iron concentrations in the world ocean? – a comment. Mar. Chem. 57, 137-161.

Jones, A. M., Ninh Pham, A., Collins, R. N., Waite, T. D. 2009. Dissociation kinetics of Fe(III)– and Al(III)–natural organic matter complexes at pH 6.0 and 8.0 and 25 ^{0}C. Geochim. Cosmochim. Acta 73, 2875-2887.

Luther, III, G.W. 2005. Manganese(II) oxidation and Mn(IV) reduction in the environment– two one-electron transfer steps versus a single two-electron step. Geomicrobio. J. 22, 195-203.

Luther, III, G. W. 2010. The role of one and two electron transfer reactions in forming thermodynamically unstable intermediates as barriers in multi-electron redox reactions. Aquat. Geochem. 16, 395-420.

Luther, G. W. and Wu, J. 1997. What controls dissolved iron concentrations in the world ocean? – a comment. Mar. Chem. 57, 173-179.

Madison, A. S., Tebo, B. M., Luther, G. W. 2011. Simultaneous determination of soluble manganese(III), manganese(II) and total manganese in natural (pore)waters. Talanta 84, 374–81.

Margerum, D. W., Cayley, R., Weatherburn, D. C. and Pagenkopf, G. K. 1978. Kinetics and mechanisms of complex formation and ligand exchange. In *Coordination Chemistry* Volume 2 (Martell, A. E., ed.) ACS Monograph 174. ACS, Washington, D. C. p. 1-221.

Morgan J. J. 2005. Kinetics of reaction between O_2 and Mn(II) species in aqueous solution. Geochim Cosmochim Acta 69, 35–48.

Mucci, A., B. Boudreau, C. Guignard. 2003. Diagenetic mobility of trace elements in sediments covered by a flash flood deposit: Mn, Fe and As. Appl. Geochem. 18, 1011–1026.

Rue, E.L., Bruland, K.W. 1997. The role of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. Limnol. Oceanogr. 42, 901-910.

Schnetger, B., Dellwig. O. 2012 Dissolved reactive Manganese at pelagic redoxclines (part I): A method for determination based on field experiment. J. Mar. Systems 90, 23-30.

Silverberg N., Sundby B., Mucci A., Zhong S., Arakaki T., Hall P., Landen A., Tenberg A. 2000. Remineralization of organic carbon in Eastern Canadian margin sediments. Deep-Sea Res. 47, 699-731.

Sundby, B., Silverberg, N., Chesselet, R. 1981. Pathways of manganese in an open estuarine system, Geochim. Cosmochim. Acta 45, 293–307.

Trouwborst, R. E., Clement, B. G., Tebo, B. M., Glazer, B. T., Luther III, G. W. 2006. Soluble Mn(III) in suboxic zones. Science 313, 1955–1957.

van den Berg, C.M.G. 1995. Evidence for organic complexation of iron in seawater. Mar. Chem. 50, 139–157.

Wells, M., Buck, K. N., Sander, S. G. 2013. New approach to analysis of voltammetric ligand titration data improves understanding of metal speciation in natural waters. Limnol. Oceanogr. Methods 11, 450-465.

Wilkins, R. G. 1991. Kinetics and mechanism of reactions of transition metal complexes (2nd edition) VCH, Weinheim, pp. 465.

Witter, A. E., Luther, G. W. 1998. Variation in Fe(III)-organic complexation with depth in the Northwestern Atlantic Ocean as determined using a kinetic approach. Mar. Chem. 62, 241-258.

Witter, A. E., Lewis, B. L., Luther, G. W. 2000a. Iron speciation in the Arabian Sea. Deep Sea Res.47, 1517-1539.

Witter, A. E., Hutchins, D. A., Butler, A., Luther, G. W. 2000b. Determination of conditional stability constants and kinetic constants for strong Fe-binding ligands in seawater, Mar. Chem. 69, 1-17.

Wu, J., Luther, G. W. 1995. Complexation of iron(III) by natural organic ligands in the Northwest Atlantic Ocean by a competitive ligand equilibration method and a kinetic approach. Mar. Chem. 50, 159-177.

Yakushev, E., Pakhomova, S., Sørenson, K., Skei, J. 2009. Importance of the different manganese species in the formation of water column redox zones: Observations and modeling. Mar. Chem. 117, 59–70.

Table 1. The k_d (or k_2 from eq. 1; s^{-1}) values from the Laurentian Trough sediment porewaters. Mn(III) concentrations (μM) are in parentheses; for depths above 0.5 cm and below 4 cm, Mn(III) was not detectable (ND).

Depth (cm)	**St CE**	**St 16**	**St 23**	**St Cabot**
0.5 - 1	0.00298 (3.45)	ND	ND	0.00550 (1.07)
1 - 2	0.00477 (41.4)	ND	0.00517 (3.45)	0.00720 (27.9)
2 - 3	0.00228 (29.9)	0.00387 (11.7)	0.00410 (41.4)	0.00602 (81.5)
3- 4	ND	0.00394 (43.4)	0.00609 (29.9)	0.00521 (57.6)

Table 2. The k_{obs} values (M^{-1} s^{-1}) derived from Laurentian Trough sediment porewaters.

depth	**St CE**	**St16**	**St 23**	**St Cabot**
0.5-1	125			229
1.0-2	200		217	300
2.0-3	95.8	163	171	250
3.0-4		163	254	217

Table 3. Half-lives in minutes for Mn′L dissociation.

Depth (cm)	**St CE**	**St 16**	**St 23**	**St Cabot**
0.5-1	3.85			2.10
1.0-2	2.41		2.22	1.60
2.0-3	5.02	2.96	2.82	1.93
3.0-4		2.96	1.89	2.22

Table 4. Estimated conditional equilibrium constants (M^{-1}) for the Mn′L natural complexes in Laurentian Trough sediment porewaters.

Depth (cm)	**St CE**	**St 16**	**St 23**	**St Cabot**
0.5-1	3.33×10^{11}			1.82×10^{11}
1.0-2	2.08×10^{11}		1.92×10^{11}	1.39×10^{11}
2.0-3	4.35×10^{11}	2.56×10^{11}	2.44×10^{11}	1.67×10^{11}
3.0-4		2.56×10^{11}	1.64×10^{11}	1.92×10^{11}

Figure Legends.

Figure 1. Map outlining the 200-m isobath of the Laurentian Trough with station locations.

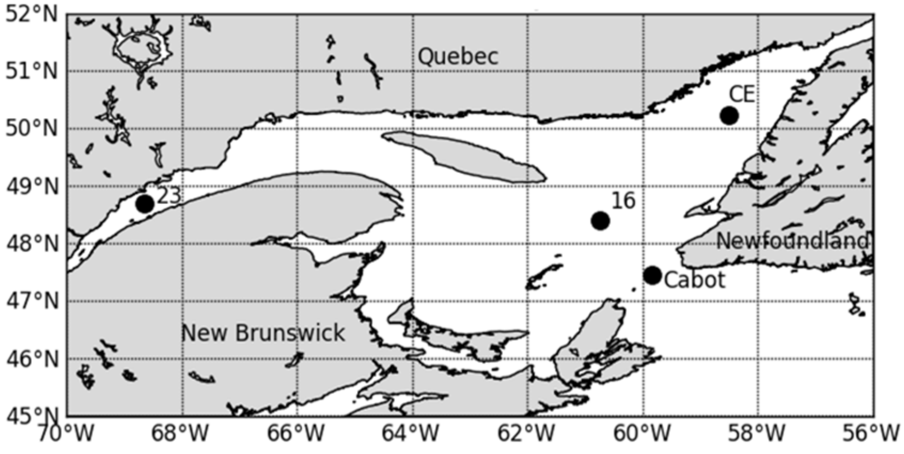

Figure 2. Kinetic curve for a mixture of Mn(II) and Mn(III)pyrophosphate in DI water.

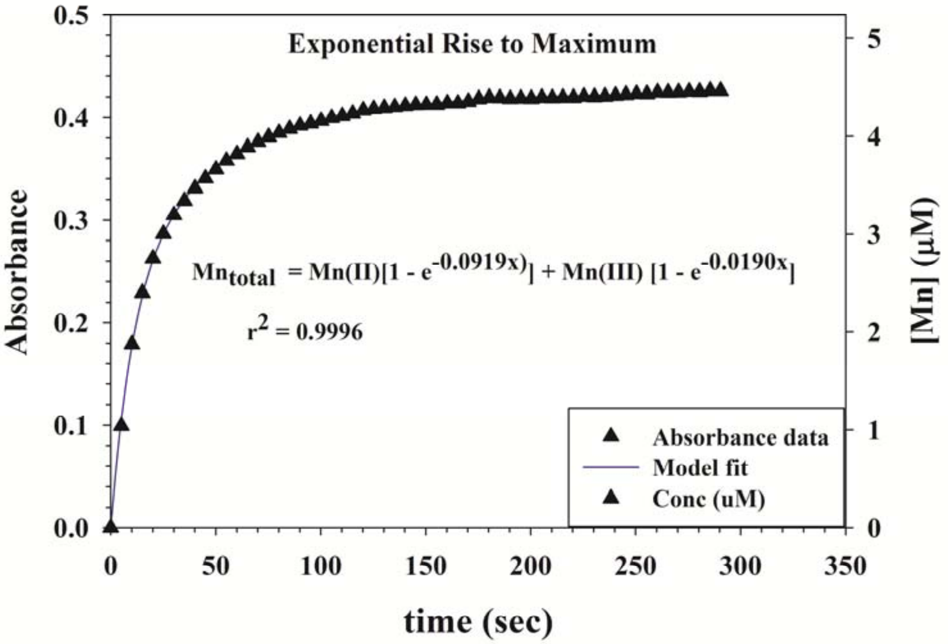

Figure 3. The k_d (or k_2) values for porewater samples with measurable Mn(III). The value of Mn(III)-pyrophosphate in seawater is given for comparison.

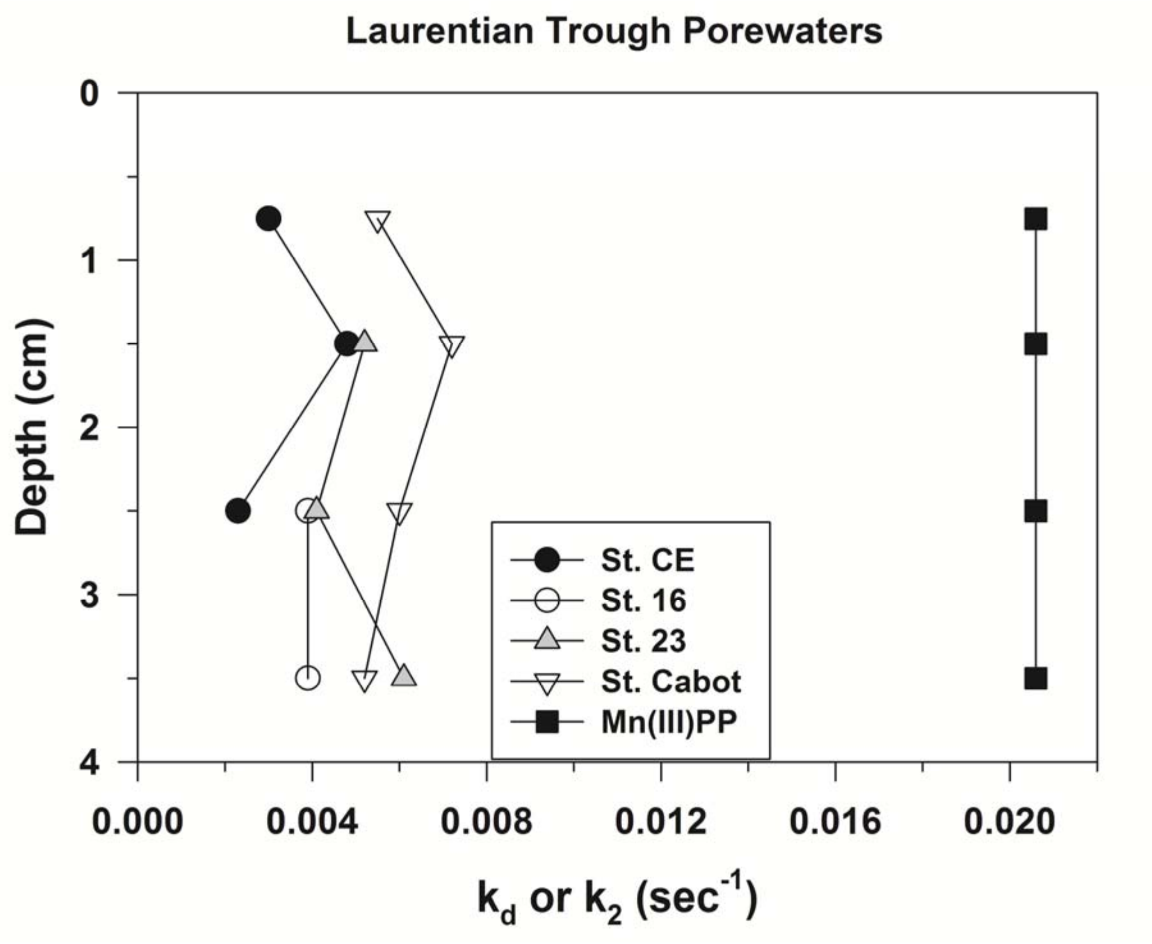

Figure 4. Top) Calculated k_d values for Mn′L complexes measured in Laurentian Trough porewater samples (Table 1); Bottom) Calculated k_d values for Fe′L complexes with excess ligands from water column data (Atlantic Ocean and Arabian Sea). All data were obtained using the same kinetic approach.