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Coupled biogeochemical cycling of iron and manganese as mediated by microbial siderophores

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Abstract Siderophores, biogenic chelating agents that facilitate Fe(III) uptake through the formation of strong complexes, also form strong complexes with Mn(III) and exhibit high reactivity with Mn (hydr)oxides, suggesting a pathway by which Mn may disrupt Fe uptake. In this review, we evaluate the major biogeochemical mechanisms by which Fe and Mn may interact through reactions with microbial siderophores: competition for a limited pool of siderophores, sorption of siderophores and metal–siderophore complexes to mineral surfaces, and competitive metal-siderophore complex formation through parallel mineral dissolution pathways. This rich interweaving of chemical processes gives rise to an intricate tapestry of interactions, particularly in respect to the biogeochemical cycling of Fe and Mn in marine ecosystems.

Keywords Dissolution · Ligand exchange · Sorption · Siderophore · Iron · Manganese

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Introduction

Iron and manganese are the most abundant redox-active metals in the Earth's crust, with the chemistry of each element changing significantly with oxidation number (cf. Table 1). Both metals form a wide array of solid phases, with Fe and Mn (hydr)oxides in particular functioning as effective sorbents of organics, metals, and oxyanions (Cornell and Schwertmann 1996; Post 1999; Tebo et al. 2004). Because of their abundance and redox activity, both metals also are widely utilized in the enzyme systems of animals, plants, and microbes (da Silva and Williams 2001). Ferromanganese deposits contain intimate associations of Fe and Mn minerals and are common in both marine and terrestrial ecosystems.

In oxic environments, Fe exists primarily as solid Fe(III)-bearing mineral phases (Cornell and Schwertmann 1996). As a response to the low solubility of these phases, microbes and plants have developed specific strategies to increase Fe bioavailability. One is the production of siderophores, which are operationally defined as low-molecular-mass biogenic Fe(III)-binding compounds which may greatly increase the solubility and bioavailability of Fe in circumneutral oxic environments (Kraemer 2004). More than 500 siderophore structures are known (Kraemer et al. 2005). Although the above definition of siderophores emphasizes their biological function, the siderophore database reveals commonalities in the structures of these exudates. Microbial siderophores are typically

Table 1 Important chemical properties of Mn and Fe and their dissolved, particulate, and total concentrations in the environment

	IR[a]	LogK_{-w} (s^{-1})	$E_H{}^{\circ}$ (V)[d]	LogK_h	log $K_{M^{n+}HDFOB^{n-2}}$	LogK_{M-HPVD}	[Seawater]	[River] (μM)[k]	[Soil] (mg kg^{-1})[n]
Fe^{2+}	0.78 H 0.61 L	6.6[b]	–	−9.5[d]	11.09[f]	23.5[i]	–	–	–
Fe^{3+}	0.645 H 0.55 L	2.2[b]	Fe^{3+}/Fe^{2+}: 0.77	−2.19[d]	32.02[g]	44.6[j]	–	–	–
Fe_T	–	–	–	–	–	–	Total 0.02–1 nM[k]	Diss. 0.76 Part. 589	Total 26,000–40,000
Mn^{2+}	0.830 H 0.067 L	7.3[b]	–	−10.59[d]	7.7[h]	–	–	–	–
Mn^{3+}	0.645 H 0.58 L	5[c]	Mn^{3+}/Mn^{2+}: 1.51	−0.1[e]	29.9[h]	47.5[j]	Diss. up to 5 μM[l]	–	–
Mn^{4+}	0.530	−2[c]	MnO_2/Mn^{3+}: 1.07 MnO_2/Mn^{2+}: 1.29	<1[c]	–	–	–	–	–
Mn_T	–	–	–	–	–	–	Total 0.08–3 nM[i] Part. 0.035–0.87 nM[m]	Diss. 0.15 Part. 19.1	Total 550–1,000

[a] Octahedral coordination; IR = ionic radius; H = high spin; L = low spin; Data from Shannon (1976)

[b] K_{-w} = water exchange rate; Helm and Merbach (1999)

[c] Morgan (2000)

[d] $E_H{}^{\circ}$ = formal electrode potential from Stumm and Morgan (1996)

[e] Sisley and Jordan (2006)

[f] Kim et al. (2009)

[g] Kraemer (2004)

[h] Duckworth and Sposito (2005a)

[i] Estimated using cyclic voltammetry half-wave potential from Boukhalfa et al. (2006)

[j] Parker et al. (2004)

[k] Donat and Bruland (1995)

[l] Diss. = dissolved; In suboxic zones of the Black Sea and Chesapeake Bay (Trouwborst et al. 2006)

[m] Part. = particulate; Landing and Bruland (1980) and Yeats et al. (1992)

[n] Median concentrations from Sparks (2003)

tetradentate or hexadentate chelating ligands that contain some combination of hydroxamate, catecholate, and carboxylate binding moieties arranged in linear, tripodal, or cyclic configurations (Boukhalfa et al. 2006). Siderophores have been shown to be present at ca. 10–100 nanomolar concentrations in most oxic environments, including marine (Mucha et al. 1999) and fresh waters (Duckworth et al. 2009), and soils (Holmström et al. 2004; Essén et al. 2006). In the rhizosphere, the local concentration of siderophores around microbes and roots may be orders of magnitude higher than in the surrounding soil (Crowley 2006).

Recent work has shown that microbial siderophores have an affinity for Mn(III) that is near (Duckworth and Sposito 2005a), or can even exceed (Parker et al. 2004), the that for Fe(III). Because aqueous Mn(III) complexes may be widespread in soils (Bartlett 1988; Bartlett and James 1993) and natural waters (Trouwborst et al. 2006), these observations, as well as the typically fast dissolution kinetics of Mn minerals, have led to the suggestion that Mn may hinder siderophore-mediated Fe uptake (Duckworth and Sposito 2007). It is pertinent to note also that Fe and Mn have complicated relationships in microbial metabolism, e.g., as reflected in the behavior of Mn oxidizing bacteria (Parker et al. 2007). In this review, we explore the nature of the interactions between the biogeochemical cycles of Fe and Mn in soils and natural waters as mediated by microbial siderophores, drawing out of our findings several important implications for aquatic and soil biogeochemistry.

Stability and exchange of Mn and Fe siderophore complexes

Siderophores and their importance to Fe transport have been recognized for over a half century (Garibaldi and Neilands 1956). A common feature of these structurally diverse microbial chelating agents is a high binding constant with Fe(III) [$\log K_{\mathrm{Fe(III)-SID}} \approx 30$–$50$ for 1:1 complexes; (Kraemer 2004)]. In addition to what is imparted by multidentate binding, the stability of Fe(III)-siderophore complexes is rationalized by noting that the hard oxygen atoms in siderophore moieties interact strongly with the hard Fe(III) ion (Hernlem et al. 1999). Siderophore complexes with the softer Fe(II) ion generally have much lower stability constants, and Fe(II)-hydroxamate siderophore complexes in particular may be unstable with respect to oxidation or auto-oxidation (Farkas et al. 2001; Kim et al. 2009).

The Mn(III) ion is thought to be unstable in aqueous solution, undergoing disproportion or redox reactions (Morgan 2000); however, high-affinity ligands, including siderophores, may stabilize $\mathrm{Mn(III)_{(aq)}}$. Currently, Mn(III)-siderophore complexes are known only for the trihydroxamates, desferrioxamine B (DFOB) (Faulkner et al. 1994; Duckworth and Sposito 2005a) and desferrioxamine E (DFOE; Faulkner et al. 1994), and for a mixed-moiety pyoverdin (PVD) siderophore (Parker et al. 2004). However, the stability of Mn(III)-complexes formed with the above siderophores and with carboxylate ligands, including citrate (Klewicki and Morgan 1998), tartarate (Aitken and Irvine 1990), and aminopolycarboxylates (Hamm and Suwyn 1967), suggests that at least other hydroxamates and carboxylate siderophores may form stable Mn(III) complexes. It is not known if catecholate siderophores stabilize $\mathrm{Mn(III)_{(aq)}}$, although the (PVD) siderophore isolated by Parker et al. (2004) contains a catecholate moiety. Siderophore complexes with Mn(II) have significantly lower stability constants than with Mn(III) and may be converted by air-oxidation to Mn(III) complexes at $\mathrm{pH} > 7$ (Faulkner et al. 1994; Duckworth and Sposito 2005a; Parker et al. 2007). In turn, Mn(III)-siderophore complexes may degrade to Mn(II) by internal electron transfer at $\mathrm{pH} < 7$ (Duckworth and Sposito 2005a). Aqueous complexes with Mn(IV) are very uncommon (Morgan 2000), and there are no reports of stable Mn(IV)-siderophore complexes. To the authors' knowledge, siderophore-mediated Mn uptake by microbes has not been demonstrated; however, Mn(III)-siderophore complexes may mimic superoxide dismutase (Faulkner et al. 1994) and may play a role in bacterial Mn(II) oxidation (Parker et al. 2007).

In soils and natural waters, aqueous Mn and Fe may compete for a limited pool of siderophores. A number of (uncharacterized) ligands other than siderophores stabilize $\mathrm{Mn(III)_{(aq)}}$, and Mn(III)-complexes are thought to widespread in soils (Bartlett 1988; Bartlett and James 1993) and suboxic waters (Trouwborst et al. 2006). Thus, $\mathrm{Mn(III)_{(aq)}}$ could challenge Fe(III)-siderophore complexes by ligand exchange for a limited pool of siderophores, and vice versa.

From a kinetics perspective, the rates of ligand exchange (Table 1) for both metals suggest that these reactions would be reasonably rapid (ca. hours to days). A rigorous thermodynamic comparison is hindered by the limited database of stability constants for Mn(III)-complexes with siderophores and other common ligands. However, the Mn(III)–HPVD stability constant exceeds that of Fe(III)–HPVD by several orders of magnitude while the trend is reversed for DFOB (Table 1). Interestingly, predictors of stability constants based on logK_h, a proxy for metal hardness, suggest that the DFOB stability constant for Mn(III) should exceed those for Fe(III) (Hernlem et al. 1999; Duckworth and Sposito 2005a). These observations lead us to conclude that siderophores containing hydroxamate, carboxylate, and possibly catecholate moieties have the potential to form stable complexes with Mn(III) with binding constants similar to those of Fe(III) complexes, and thus Mn(III) may compete with Fe(III) for a limited pool of siderophores in the environment.

Sorption of metal-siderophore complexes

Despite interest in the effects of siderophores on sorption of contaminants to minerals, little is known about the sorption of Fe- and Mn-siderophore complexes to mineral surfaces. Sorption of Fe(III)HDfOB$^+$ to goethite and Pseudomonad cells was found to be negligible (Neubauer et al. 2002; Yoshida et al. 2004) over a wide range of pH; similarly, sorption was negligible on kaolinite at pH = 7.5 (Siebner–Freibach et al. 2004). However, Fe(III)HDFOB$^+$ sorbs strongly to Na- and Ca montmorrillonite (Siebner–Freibach et al. 2004); for the latter mineral, Fourier transform infrared spectroscopy revealed intercalation of the intact complex as the dominant mechanism of interaction (Siebner–Freibach et al. 2006).

Manganese and iron also interact by sorption of Fe(III)HDFOB$^+$ to Mn(III,IV) oxides. The Fe(III)HDFOB$^+$ complex was shown to sorb strongly to both synthetic [viz. c-disordered birnessite and δ-MnO$_2$; both are layer type predominantly Mn(IV) oxides] and a model biogenic Mn oxide (a mineral structurally similar to δ-MnO$_2$) at pH 8. X-ray absorption spectroscopy indicated that Fe(III) was stripped from the complex and directly sorbed to the surface, leading the authors to the hypothesis that sorption of Fe to Mn oxides may be important in marine environments (Duckworth et al. 2008). However, sorption of Fe(III) HDFOB$^+$ to Mn oxides occurs over a wide range of pH (Fig. 1) and so may occur in a wide range of natural environments. Additionally, batch experiments on DFOB-promoted Mn oxide dissolution suggest that the Mn(III)HDFOB$^+$ products may re-adsorb to Mn oxides, although the detailed mechanism is unknown (Duckworth and Sposito 2007; Peña et al. 2007). Thus Mn (hydr)oxides are potentially important sorbents of siderophore complexes and have the ability to affect the cycling of metal complexes, including high affinity complexes containing Mn(III) and Fe(III).

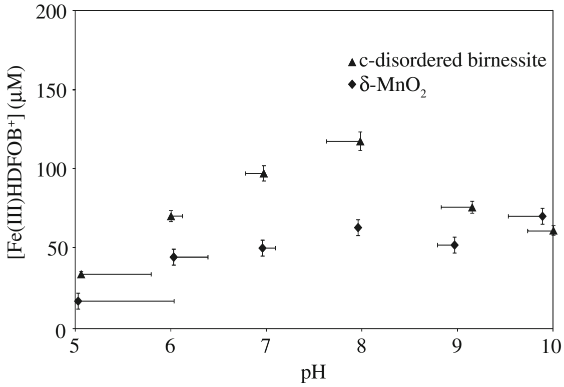


Fig. 1 Sorption of Fe(III)HDFOB$^+$ to layer type Mn(III,IV) oxides. Legend: *triangles*, δ-MnO$_2$ (AMON = 4.02); *squares*, c-disordered H$^+$-birnessite (AMON = 3.81). Conditions: 72 h incubation time, total 200 μM Fe(III)HDFOB$^+$, 20 mM buffer (acetate, MOPS, MES, HEPES, CHES, or CAPS), 0.1 M NaCl, and 2 g L^{-1} Mn oxide. The *x*-axis error bars indicate final pH arising from drift during the experiment. Data for pH = 8 are from and more details on experimental methods are available in Duckworth et al. 2008

Siderophore-promoted dissolution of Mn and Fe minerals

One of the primary biogeochemical functions of siderophores is to increase Fe bioavailability by promoting its dissolution from minerals. Consequently, understanding the linkages and antagonisms between Fe and Mn requires a detailed knowledge of the dissolution rates and mechanisms of minerals containing these elements. In comparison to Mn minerals, the siderophore-promoted dissolution of Fe minerals has been extensively studied. Dissolution rates of (hydr)oxides are generally pH independent over the environmentally relevant range (i.e., pH 5–9) and dissolution proceeds exclusively by a ligand-promoted reaction, producing Fe(III)-complexes (Lloyd 1999). Hydroxamate siderophore-promoted dissolution rates, compiled from a number of sources (Hersman et al. 1995; Lloyd 1999; Cocozza et al. 2002; Neubauer et al. 2002; Yoshida et al. 2002; Cheah et al. 2003; Carrasco et al. 2007; Wolff–Boenisch and Traina 2007; Carrasco et al. 2008) and spanning a large range of pH (3–9), concentration (1.3×10^{-5}–10^{-3} M), and solid phases [α-FeOOH, α-Fe_2O_3, and a poorly crystalline Fe(III)-hydroxide] vary by less than a factor of 20 ($R = 10^{-11.5}$–$10^{-12.8}$ mol m^{-2} s^{-1}), strongly suggesting commonalities among the mechanisms of hydroxamate siderophore-promoted dissolution. Desferrioxamine B promoted-dissolution of goethite appears to be surface-controlled (Cheah et al. 2003) and possibly mediated by the formation of dissolution-active bidentate mononuclear surface structures (Holmen et al. 1997; Cocozza et al. 2002). Interestingly, a number of low-molecular mass organic acids (LMMOAs; e.g., oxalate, citrate, malonate, succinate, and fumarate) have been shown to augment siderophore-promoted dissolution rates (Cheah et al. 2003; Reichard et al. 2007; Wolff–Boenisch and Traina 2007). These LMMOAs act catalytically, promoting Fe(III) dissolution from the surface and transporting it as an aqueous complex to be scavenged by aqueous siderophores. After the Fe(III) is removed from the LMMO complexes by siderophores, the LMMOAs are then free to react again with the surface, continuing the dissolution process (Cheah et al. 2003; Reichard et al. 2007).

For Mn minerals, DFOB-promoted dissolution rates have been measured for α-MnOOH (Lloyd 1999; Duckworth and Sposito 2005b), Mn_3O_4 (Peña et al. 2007), layer type Mn(III,IV) oxides (Duckworth and Sposito 2007), and MnO_2 (Lloyd 1999); the related siderophore DFOE also has been shown to promote the dissolution of MnO_2 (Faulkner et al. 1994). The rates of DFOB-promoted dissolution for these minerals (circumneutral pH, 0.1 M NaCl, 100 μM DFOB) decrease with increasing average Mn oxidation number (AMON) from ca. 10^{-9} mol m^{-2} s^{-1} for Mn_3O_4 (AMON = 2.76) to ca. $10^{-10.4}$ mol m^{-2} s^{-1} for layer type Mn(III,IV) oxides (AMON = 3.81–4.02) (Duckworth and Sposito 2007; Peña et al. 2007). Dissolution of α-MnOOH (AMON = 3.04) occurs via parallel reductive [producing Mn(II)] and ligand-promoted [producing Mn(III)HDFOB$^+$] pathways, with the former dominant at acidic and the latter dominant at alkaline pH. At pH = 8, the dissolution rate is proportional to surface excess, consistent with a surface controlled dissolution mechanism (Duckworth and Sposito 2005b). Although the mechanisms are more complicated than for DFOB-promoted α-MnOOH dissolution, the pH-dependent products are the same for the DFOB-promoted dissolution of several minerals [e.g., Mn_3O_4 and three different layer type Mn(III,IV) oxides] despite the differences in AMON (Duckworth and Sposito 2007; Peña et al. 2007). The commonalities in the pH-dependent dissolution products of Mn minerals with differing AMON suggest that the mechanisms of DFOB-promoted Mn (hydr)oxide dissolution may be controlled by a common factor [e.g., the stability of aqueous or surficial Mn(III)–DFOB complexes (Duckworth and Sposito 2007).] Although the dissolution of Mn (hydr)oxides promoted by LMMOAs has been widely studied [recently reviewed by Martin (2005)], currently no studies have probed the synergistic dissolution kinetics of Mn oxides with siderophore and LMMOAs.

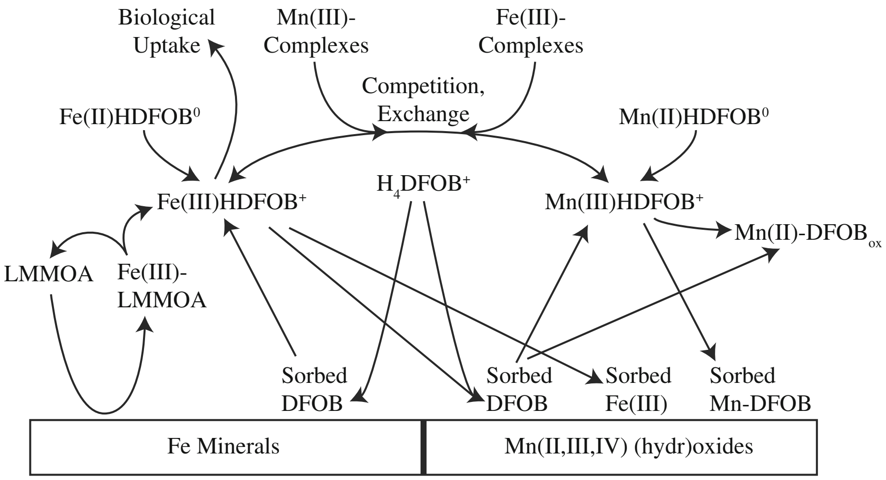
It is interesting to note that DFOB-promoted dissolution rates tends to be higher for Mn (hydr)oxides than for Fe (hydr)oxides, despite the fact that the stability constant for Mn(III)HDFOB$^+$ is ~2 orders of magnitude lower than for Fe(III)HDFOB$^+$ (Table 1). The maximum surface excess (n_{max}) for DFOB on manganite [$n_{max} = 32 \pm 5$ mmol kg^{-1} at pH = 8 (Duckworth and Sposito 2005b)] is significantly higher than on goethite [$n_{max} = 1.23 \pm 0.18$ mmol kg^{-1} at pH = 5 (Cheah et al. 2003)], although sorption of DFOB on goethite may increase at higher pH (Kraemer et al. 2002). Given that dissolution rates at corresponding conditions differ by >100-fold (Duckworth and Sposito 2005b), increased surface excess does not adequately explain the rapid dissolution rates of α-MnOOH relative to α-FeOOH. It has been previously noted that Mn (hydr)oxide dissolution rates generally exceed those of Fe (hydr)oxides (Martin 2005). For a number of mineral families, water- and proton- promoted dissolution rates correlate with water exchange rates, a relationship that is explained by noting the similarity between metal–oxygen bond-breaking in mineral structures and in hydration complexes (Casey 1991; Casey and Westrich 1992). Despite changes in structure and surface properties, the DFOB-promoted dissolution rates of Mn and Fe (hydr)oxides generally do trend with water exchange rates (Table 1). An exception to this trend is that Mn(IV) oxide dissolution rates exceed those of Fe(III) hydroxides. This difference may be related to the fact that Mn(IV) must be reduced to more labile Mn(II) or Mn(III) before dissolution may occur (Duckworth and Sposito 2007). In general, these observations suggest that fundamental differences in the chemistry of the cations in the mineral structures are dominant in controlling the rates and mechanisms of the siderophore-promoted dissolution of (hydr)oxides.

Outlook and conclusions

The interactions (summarized for DFOB in Fig. 2) described in this review have implications for the biogeochemical cycling and uptake of Fe, as well as for the cycling of Mn, in marine and terrestrial environments. In the ocean, Fe is typically considered to be a limiting nutrient (Behernfeld and Kolber 1999). The majority of soluble Fe in the ocean has been shown to be in the form of organic complexes (Rue and Bruland 1995; Powell and Donat 2001), and there is a growing consensus that siderophores are at least a major component of the pool of complexing ligands (Witter et al. 2000; Marcrellis et al. 2001; Kraemer et al. 2005). The concentration of particulate Mn is comparable to $[\mathrm{Fe}]_T$ in seawater (Table 1) suggesting that Mn (hydr)oxides may effectively compete with Fe for siderophores in the marine environment through sorption of existing Fe(III)-siderophore complexes, sorption of free siderophores to Mn (hydr)oxide surfaces, or siderophore-promoted dissolution of Mn (hydr)oxides. In addition, the recent discovery of Mn(III)-complexes in marine basins (Trouwborst et al. 2006) suggests that aqueous Mn(III)-complexes may directly compete with Fe(III) for siderophores via ligand exchange. Interestingly, biological oxidation of Mn(II), which is thought to be the dominant mechanism for Mn(III,IV) (hydr)oxide formation in many environments (Tebo et al. 2004), may be regulated in a complicated, non-linear manner by Fe, Mn, and siderophores (Parker et al. 2007), suggesting additional relationships beyond the competitive interactions described above.

The interactions depicted in Fig. 2 may also occur in soils. In the rhizosphere, microbial siderophores not only provide Fe to microbes but also plants (Crowley 2006). The presence of locally-abundant Mn (hydr)oxides as well as aqueous Mn(III)-complexes (Bartlett 1988; Bartlett and James 1993) suggests that the same antagonistic interactions described for the marine environment may occur in soils. However, in complicated soil systems many other factors affect metal cycling, which makes it difficult to enumerate with certainty specific interactions between Fe and Mn. Soils contain a wide range of minerals that may react with siderophores. The presence of graminaceous plant derived phytosiderophores (Kraemer et al. 2006) and high concentrations of LMMOAs (Jones 1998) further complicates these interactions by providing abundant chelating moieties that may encourage mineral dissolution or ligand exchange. Additionally,

Fig. 2 Schematic depicting the major DFOB-mediated mechanisms of interaction between Fe and Mn discussed in this article



abrupt temporal changes on the diurnal or seasonal scale may also affect these interactions (Crowley 2006; Kraemer et al. 2006).

In a review of siderophore effects on Fe (hydr)oxide dissolution and solubility, Kraemer (2004) noted the need to study both different types of siderophore that better represent the diversity of known structures and more complex, environmentally relevant systems. These topics are also key to understanding the reactivity of Mn with siderophores. Additionally, more information is needed about the environmental occurrence, chemical speciation, chemical reactivity, and biological roles of aqueous Mn(III). Finally, more biological and geochemical studies of the direct interactions between these metals will help clarify the relationship between, and the effect of siderophores on, Fe and Mn biogeochemical cycling. And finally, better understanding of the complicated nature of the biogeochemical interactions between these metals may aid in our understanding of the factors that influence the biological uptake of other important trace metals.

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