

Siderophores and the Dissolution of Iron-Bearing Minerals in Marine Systems

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INTRODUCTION

Scope of this review

Metal ions have critical functions in biological processes and provided important biological feedbacks with the environment throughout earth history. For example, Fe, Ni, Mg, Mn, Mo, Cu, W, V, and Zn play an essential role as catalysts in key compounds involved in respiration, photosynthesis, nitrogen fixation, and many other enzymatic processes (da Silva and Williams 2001). It is likely that some of these metal bearing enzymes evolved early in the history of life. However, the availability of metal ions has changed dramatically in the last 3.8 billion years due to changes in atmospheric and marine chemistry (Canfield 1998; Anbar and Knoll 2002; Saito et al. 2003). Homeostasis of metal ions (i.e., the maintenance of an approximately constant intracellular concentration) became a major problem over geologic time scales and in contemporary environments.

Iron is an essential nutrient for almost all known organisms due to its important role in important enzymatic processes. While iron is the fourth most abundant element in the Earth crust, its low bioavailability limits primary production in various terrestrial and marine environments. The limitation of primary production in important ecosystems has significant implications for the global carbon cycle and the world climate. This review focuses on geochemical aspects of biological iron acquisition in iron limited “high nutrient low chlorophyll” (HNLC) ocean regions. The purpose of this review is to discuss the effect of biogenic iron specific ligands, the so called siderophores, on the iron speciation, and the dissolution of iron-bearing minerals in the presence of siderophores in these marine systems.

Important iron sources for algal growth in HNLC ocean regions are the upward mixing of iron rich subsurface waters to the euphotic zone and the atmospheric deposition of dust particles on the sea surface followed by the dissolution of iron from these particles into the surface water. Iron sinks include the scavenging of iron onto inorganic and organic particles in the water and subsequent settling and sedimentation of these particles out of the water column. A number of thermodynamically or kinetically controlled processes influence the redistribution of iron among various chemical species in the water and on the water-solid interfaces along the water column. Among those processes are dissolution and formation of iron-bearing minerals, iron adsorption on and desorption from inorganic and organic particles, (photo-) reduction of Fe(III) and oxidation of Fe(II), and iron complexation by organic and inorganic ligands. Marine micro-organisms and phytoplankton may influence or even regulate these processes through 1) the biological exudation of iron binding ligands; 2) reduction of Fe(III) at the cell surface or Fe(III) photo reduction in the presence of biogenic chromophores which may change the redox speciation of iron; 3) transformation of colloidal iron to more bioavailable forms in the digestive system of grazers; 4) biological recycling of iron from sinking biomass. In iron limiting environments, such biogeochemical processes are critical to enhance iron uptake and/or to decrease iron bioavailability for competing species.

Unfortunately, very little is known about the kinetics and fluxes associated with many of these processes. An important impediment to field research in this area is the astoundingly low iron concentration in the HNLC surface waters. Dissolved iron in these ocean areas have a nutrient-like vertical distribution with average sea surface concentrations in the sub-nanomolar range and increasing concentrations with depth (Johnson et al. 1997). Considering the tremendous problems involved in contamination free sampling and chemical analysis in this concentration range, a remarkable range of information has been gathered on dissolved organic and inorganic iron speciation.

A key process of iron cycling in HNLC ocean regions and the focus of this review is the dissolution of iron from dust as part of biological iron acquisition strategies. We will summarize pertinent information from field and laboratory studies and discuss important dissolution mechanisms. For in-depth discussion of related issues the reader is referred to a number of excellent review articles (Jickells 1999; Boyd 2002; Morel and Price 2003).

The iron limitation hypothesis

Over glacial/interglacial time scales, CO₂ levels in the earth atmosphere are strongly influenced by phytoplanktonic photosynthesis in the oceans. In HNLC ocean areas phytoplankton productivity and consequently the efficiency of the biological CO₂ pump is not limited by macronutrients such as phosphate or nitrate, since their concentrations at the HNLC sea surface waters are high. Martin and Fitzwater (1988) proposed that primary productivity in these ocean areas is limited by the low availability of the micronutrient iron. Iron fertilization experiments in the Equatorial Pacific (IRONEX I and II), the Southern Ocean (SOIREE, EisenEx, SOFeX-N and SOFeX-S) and the Sub-Arctic North Pacific (SEEDS, SERIES) have decisively supported this hypothesis (Martin et al. 1994; Coale et al. 1996, 2004; Boyd and Law 2001; Gervais et al. 2002; Tsuda et al. 2003; Boyd et al. 2004). Vast ocean areas are affected by iron limitation and it may be as important as nitrogen and phosphorous limitation of global marine phytoplankton productivity (Moore et al. 2002).

BIOLOGICAL IRON ACQUISITION STRATEGIES

Iron acquisition by bacteria

Considering the importance of iron as a limiting nutrient, biological iron acquisition is a key factor determining the ecology of HNLC ocean regions. An important iron acquisition

strategy among both freshwater and marine cyanobacteria and heterotrophic bacteria involves the production of siderophores under iron limiting conditions (Gonye and Carpenter 1974; Trick 1989; Wilhelm and Trick 1994; Wilhelm 1995; Granger and Price 1999). Siderophores are low molecular weight organic ligands (0.5–1.5 kDa) with high affinity and specificity for iron. The siderophore mediated uptake of iron involves the recognition of the siderophore complex and the transport of the ferric siderophore complex across the cell membrane (Reid and Butler 1991; Butler 1998; Murakami et al. 2000; Guan et al. 2001; Armstrong et al. 2004). Although siderophore exudation is an important bacterial response to iron limitation, not all cyanobacteria and heterotrophic bacteria produce siderophores. While some cyanobacteria have been reported to produce multiple siderophores (Wilhelm and Trick 1994), other strains produce none (Wilhelm 1995). Similar results are reported for heterotrophic bacteria. In a recent study, from a total of 421 strains of heterotrophic marine bacteria which were isolated from marine sponges and seawater, 223 strains were observed not to produce siderophores under iron limiting conditions (Guan et al. 2001). However, the growth of 134 strains out of the total non-siderophore producing strains was stimulated by both cross-streaking of siderophore producing strains and by the addition of siderophores. Similarly, Trick (1989) showed that some marine bacteria produced siderophores which promoted growth of unrelated isolates, while other siderophores only satisfied the iron requirements of the strains that produced them. Granger and Price (1999) isolated strains of heterotrophic bacteria and found that not all of them produced siderophores under the assay conditions, but all took up Fe bound to siderophores. The utilization of ferric siderophore complexes by non-siderophore producing bacterial strains may be a typical pattern in iron limited aquatic systems, since siderophore excretion is considered to be metabolically expensive (Völker and Wolf-Gladrow 1999). However, siderophore production may simply also be a “survive at all cost” response to low iron availability and the high metabolic costs are offset by the potential for survival (Wilhelm 1995).

Iron acquisition by eukaryotic phytoplankton

Fe(III)-siderophore complexes may not only be an essential iron source for heterotrophic and phototrophic bacteria (prokaryotes), but also for eukaryotic phytoplankton. It has been reported that some eukaryotic species are able to acquire iron from various iron complexes and siderophores (Allnut and Bonner 1987; Soria-Dengg and Horstmann 1995; Kuma et al. 2000; Maldonado and Price 2001), even if they generally do not produce siderophores themselves (for exceptions see Trick et al. 1983; Benderliev and Ivanova 1994; Benderliev 1999). An important process in this context is the reduction of organically bound Fe(III) by a plasma membrane ferrireductase, which promotes the dissociation of Fe(II) from the siderophore complex (Jones et al. 1987; Weger 1999). The inorganic iron is then taken up by membrane transporters.

However, the acquisition of iron from iron-siderophore complexes by eukaryotic phytoplankton (e.g., diatoms) is controversially discussed in literature. It has been shown that ferric organic complexes, including model Fe-siderophore complexes like Fe-DFOB are utilized as iron sources by some eukaryotic phytoplankton species (Soria-Dengg and Horstmann 1995; Maldonado and Price 1999, 2001). Several studies found that uptake of iron is largely inhibited by DFO-B additions or at least insufficient to satisfy cellular requirements of eukaryotic phytoplankton (Hutchins et al. 1999; Wells 1999; Timmermans et al. 2001; Eldridge et al. 2004). It is important to note in this context that adaptation of former iron-replete eukaryotic phytoplankton to artificially induced iron limitation may require the activation of membrane bound ferric chelate reductases or high-affinity transport systems over timescales that are longer than typical shipboard incubation experiments (Maldonado and Price 2001; Wells and Trick 2004). Hutchins et al. (1999) observed iron uptake from weaker complexes (e.g., Fe-porphyrin). In contrast to most siderophores, the Fe(III)-porphyrin complex exhibits a tetradentate structure, so that iron bound to porphyrin may be

more accessible to surface reductase of eukaryotic plankton and may be reduced more easily. Consequently, the complexation of iron by siderophores may increase the bioavailability of iron for bacterial species, but also may reduce iron availability for eukaryotic phytoplankton (depending on the nutritional status), unless the iron-siderophore complexes are transformed by secondary processes (e.g., by photochemical processes).

Marine algae can change iron speciation by excretion of low and high molecular weight organic substances (Lancelot 1984; Fuse et al. 1993; Mykkestad 1995). In iron-limited cultures of the coccolithophore *Emiliania huxleyi*, the release of strong iron-chelating ligands (with conditional stability constants comparable to those of siderophores) was observed under iron-limiting conditions and increased after inorganic iron was added to the cultures (Boye and van den Berg 2000). These observations suggest that the observed ligands were not siderophores (where the release is triggered by iron limitation). An increase of the concentrations of iron binding ligands was also observed as a response to iron fertilization in mesoscale experiments (Rue and Bruland 1997). Potential sources of strong Fe-chelators from phytoplankton in seawater are exudation or the rupture of intact cells. Cell rupture could lead, for example, to the release of compounds with porphyrin-type moieties with a high affinity for binding iron (Witter et al. 2000).

Role of protozoan grazers in the cycling of iron

Radiotracer studies indicate that iron is rapidly cycled within the planktonic community by linked biological processes such as grazing, excretion, viral lysis, and bacterial respiration of organic matter (Hutchins et al. 1993). Regeneration of iron among the phytoplankton community does not necessarily require grazing of phytoplankton by heterotrophic protozoan grazers. Regeneration of iron is also accomplished by the grazing of bacteria through photosynthetic protozoan grazers, so called mixotrophs. Mixotrophy—defined as the ability to assimilate organic compounds as carbon sources while using inorganic compounds as electron donors for energy metabolism (Madigan et al. 2000)—is a widespread phenomenon in aquatic habitats and is observed in many ciliates and flagellates (Stoecker 1998). It has been suggested that phagotrophic ingestion of bacteria may be an adaptive strategy for photosynthetic algae to obtain iron for growth in iron limited regions of the sea. In a recent study, it has been shown that the photosynthetic flagellate *Ochromonas sp.* can obtain iron directly by ingesting bacteria (Maranger et al. 1998). As *Ochromonas* also excretes some of the Fe it ingests, phagotrophic phytoflagellates may in general play an important role in the Fe cycle by regenerating Fe for themselves and for other microorganisms.

Heterotrophic protozoan grazers may also generate bioavailable iron by digestion of refractory iron phases in the acidic food vacuoles. Barbeau et al. (1996) have demonstrated several grazer mediated effects on colloidal ferrihydrite, including a decrease in colloid size, an increase in colloid lability as determined by competitive ligand exchange techniques, and an increase in the bioavailability of colloids to iron limited diatoms. These results indicate that protozoan grazers may significantly enhance the supply of iron to marine phytoplankton from terrestrial sources. It has been estimated that protozoan grazing of colloidal particles (e.g., ferrihydrite) may equal or exceed photoreductive dissolution in increasing iron availability to phytoplankton (Barbeau et al. 1996; Barbeau and Moffett 2000). The effect of grazing on more crystalline iron oxides is not known.

SOURCES OF IRON IN HNLC OCEAN REGIONS

The most important iron sources in HNLC ocean areas are upwelling and atmospheric deposition of iron derived from continental dust (Archer and Johnson 2000; Moore et al. 2002, 2004). The atmospheric flux of iron to the remote HNLC ocean areas is relatively low.

However, iron deficiency is not only triggered by low total iron concentrations but also by the low bioavailability of iron from atmospheric inputs. As a consequence of its low bioavailability, only a small fraction of the iron input by atmospheric aerosol is solubilized before sedimentation (Zhuang et al. 1990; Fung et al. 2000). The bioavailability of iron is strongly influenced by the mineralogy of aerosol particles which in turn is influenced by the characteristics of soils in the source area of the particles. Iron speciation can further be modified by the chemical environment during atmospheric transport (Jickells 1999). Iron-bearing minerals can be dissolved by proton-promoted and photoreductive dissolution and re-precipitated during drying cycles (Spokes et al. 1994; Siefert et al. 1999; Johansen et al. 2000).

Atmospheric dust as a source of iron

A strong link between dust deposition and primary production has been established by observations of increased chlorophyll and particulate organic carbon concentrations at the sea surface during episodic dust deposition events (Ditullio and Laws 1991; Lenes et al. 2001; Bishop et al. 2002). The most important source for atmospheric dust are the arid or semiarid regions of the continents (Duce et al. 1980; Duce and Tindale 1991; Tegen and Fung 1995; Mahowald et al. 1999; Perry et al. 1999; Ginoux et al. 2001). The iron content of atmospheric dust is roughly related to the average crustal abundance of iron (3.5%; Taylor 1964) and depends on the continental source area (Hand et al. 2004) and on size fractionation during transport (Claquin et al. 1999; Jickells 1999). A number of researchers have estimated aeolian iron fluxes to the oceans based on measurements or models of atmospheric dust distributions over the oceans (Duce and Tindale 1991; Tegen and Fung 1995; Mahowald et al. 1999) and on global assumptions or databases of local measurements of the iron content in dust (Archer and Johnson 2000; Gao et al. 2001; Moore et al. 2002).

Iron mineralogy of atmospheric dust

The distribution of iron among iron-bearing mineral phases has an important effect on its solubility and lability (Cornell and Schwertmann 2003). The fate of iron during atmospheric transport and after deposition at the sea surface will therefore strongly depend on the mineralogy of aerosol particles. Nanoparticulate hematite (11–170 nm) was observed in Mössbauer studies of atmospheric aerosols collected in a rural area of Poland (Kopcewicz and Kopcewicz 1994, 1998). Reid et al. (2003) report single particle analysis of aerosol particles of Saharan origin collected at Puerto Rico. They found most iron associated with particles with elemental abundances corresponding to illite. The elemental composition of a smaller fraction of high Fe particles suggested kaolinite aggregated with iron oxides. However, the authors noted the difficulty of assigning mineralogical structures to aggregates based on elemental abundances. Falkovich et al. (2001) used SEM-EDS and XRD to analyze individual dust particles of North African origin collected over Israel. They found most iron on particle surfaces and suggested that hematite aggregated with clay minerals were coating particle surfaces. Direct evidence of the presence of hematite and goethite was provided by diffuse reflectance spectrometry of aerosol particles collected from Bermuda, Barbados, and Izaña (Arimoto et al. 2002). Crystalline iron oxides of primarily aeolian origin were also found in deep sea sediments (Bloemendal et al. 1992; Balsam et al. 1995).

Transformation of iron-bearing minerals during atmospheric transport

The bioavailability of iron is strongly influenced by its speciation in the aerosol particles. Iron-bearing minerals can be transformed by proton-promoted and photoreductive dissolution as well as precipitation during drying cycles (Spokes et al. 1994; Siefert et al. 1998). The observation of significant concentrations of dicarboxylic acids in marine aerosols may promote ligand-controlled and photoreductive dissolution mechanisms (Stephanou and Stratigakis 1993; Sempere and Kawamura 2003).

Reduction of Fe(III) to Fe(II) dramatically increases its solubility. Reduced iron species are thermodynamically unstable under atmospheric conditions, but photoredox reactions can lead to the significant transient Fe(II) concentrations, particularly in acidic aerosols (Behra and Sigg 1990). Even though Fe(II) is rapidly reoxidized in seawater (Millero et al. 1987; Millero and Sotolongo 1989; King et al. 1995; King 1998), the precipitating Fe(III)-polymers are expected to be thermodynamically and kinetically less stable than iron-bearing minerals of the atmospheric dust. For these reasons, the redox speciation of iron in aerosols is a subject of ongoing research. Most studies of iron redox speciation show that the fraction of Fe(II) in acid extracts of aerosols represents only a small fraction of the total iron (Zhuang et al. 1990; Zhu et al. 1993, 1997; Siefert et al. 1999; Johansen et al. 2000; Chen and Siefert 2004). Large variations of Fe(II) fractions in aerosols collected over the Atlantic and Pacific Oceans were observed by Hand et al. (2004), with significantly higher Fe(II) fractions in fine aerosols (<2.5 μm) compared to coarse particles. A study of the redox speciation of soluble iron extracted from aerosols collected at Barbados by acid extraction showed diel variations of the Fe(II)/Fe(III) ratio (Zhu et al. 1997). This is consistent with photo reduction of iron during irradiation of the aerosols with sunlight. However, no correlation between the ratio of soluble iron to total iron in the aerosol (on the average 6.2%) and the redox speciation in the soluble iron was found. Hence, it was uncertain if the photo redox reactions lead to a net mobilization of iron from aerosol.

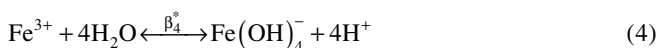
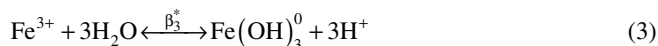
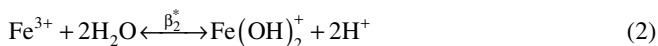
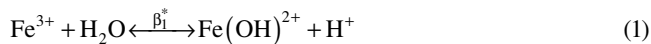
CONCENTRATIONS, SPECIATION AND SOLUBILITY OF IRON IN SEAWATER

Iron concentrations as a function of depth in HNLC regions

Iron is strongly depleted at the sea surface due to uptake by phytoplankton and downward flux of iron tied to settling biomass. Increasing dissolved iron concentrations with depth and a maximum coinciding with an oxygen minimum are consistent with release of iron from organic complexes by bacterial degradation of organic matter and are similar to nutrient-like concentration profiles of other essential trace metals (Martin et al. 1989). Johnson et al. (1997) measured iron concentration profiles in 30 stations in the Pacific, North Atlantic and Southern Ocean and found average dissolved iron concentrations of 0.07 nmol/kg in the mixed layer and 0.6 nmol/kg in depth. Surface water iron concentrations can vary over time (Wu and Luther 1996). Moore et al. (2002) calculated mixed layer dissolved iron concentrations using a global marine ecosystem model and predicted depletion of iron in the summer (<0.1 nmole/kg) relative to winter iron concentrations, in agreement with observations. Also, increasing iron concentrations have been observed in surface water of the Northeast Pacific Ocean after episodic deposition of dust from Asia (Johnson et al. 2003).

Inorganic iron species

In the absence of organic ligands, the speciation of Fe(III) in seawater in the neutral to slightly alkaline pH range is dominated by hydroxo complexes (Millero et al. 1995). The hydrolysis of iron can be defined by the following reactions:



The equilibrium species distribution of hydrolysis species can be calculated using the appropriate mass laws and stability constants β_n :

$$\beta_n = \frac{\{\text{Fe}(\text{OH})_n^{(3-n)+}\} \{\text{H}^+\}^n}{\{\text{Fe}^{3+}\} \{\text{H}_2\text{O}\}} = \frac{[\text{Fe}(\text{OH})_n^{(3-n)+}] [\text{H}^+]^n}{[\text{Fe}^{3+}]} \cdot \frac{\gamma_{\text{Fe}(\text{OH})_n} \gamma_{\text{H}^+}^n}{\gamma_{\text{Fe}} \{\text{H}_2\text{O}\}} \quad (5)$$

where $[\text{Fe}^{3+}]$ and $[\text{Fe}(\text{OH})_n^{(3-n)+}]$ are the concentrations of the iron hexaquo species and the hydrolysis species respectively, expressed in units of mole/kg. γ are activity coefficients. $[\text{H}^+]$ is defined on the free hydrogen ion molality scale (Byrne and Kester 1976). Equation (5) requires the calculation of activity coefficients in order to correct for non-ideality effects arising from the high ionic strength of seawater. Alternatively, conditional stability constants β_n^* can be defined, that are only valid for the ionic strength and composition of seawater:

$$\beta_n^* = \frac{[\text{Fe}(\text{OH})_n^{(3-n)+}] [\text{H}^+]^n}{[\text{Fe}^{3+}]} \quad (6)$$

so that

$$\beta_n = \beta_n^* \cdot \frac{\gamma_{\text{Fe}(\text{OH})_n} \gamma_{\text{H}^+}^n}{\gamma_{\text{Fe}} \{\text{H}_2\text{O}\}} \quad (7)$$

The use of conditional stability constants is convenient and appropriate for speciation in open ocean water where small variations of salinity have only a minor effect on activities. Iron hydrolysis has been under investigation for several decades (Baes and Mesmer 1976; Byrne and Kester 1976; Millero et al. 1995; Liu and Millero 1999). However, the determination of conditional hydrolysis constants in seawater has been problematic and considerable uncertainty remains. The principal problems include the analysis of total iron or iron species at trace concentrations dictated by the low solubility of iron in seawater (sub-nanomolar at pH 8!); and by the difficulty to distinguish the mononuclear hydrolysis species from polymeric and colloidal iron (Byrne et al. 2000). For the model calculations presented in this paper, hydrolysis constants by Liu and Millero (1999) have been used (see Table 1). Using these constants it can be predicted that the dominant inorganic iron species in seawater (pH of 8.1) are $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3^0$, and $\text{Fe}(\text{OH})_4^-$ at thermodynamic equilibrium and under aerobic conditions. If the iron speciation is dominated by hydrolysis species, the total dissolved iron concentration $[\text{Fe}(\text{III})_T]$ equals the sum of all inorganic species $[\text{Fe}']$ and is related to the iron hexaquo complex by the following relationship (Byrne and Kester 1976):

$$[\text{Fe}(\text{III})_T] = [\text{Fe}'] = [\text{Fe}^{3+}] \cdot \left(1 + \beta_1^* [\text{H}^+]^{-1} + \beta_2^* [\text{H}^+]^{-2} + \beta_3^* [\text{H}^+]^{-3} + \beta_4^* [\text{H}^+]^{-4} \right) \quad (8)$$

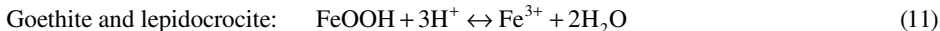
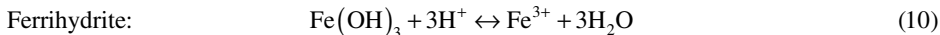
or

$$[\text{Fe}(\text{III})_T] = [\text{Fe}'] = [\text{Fe}^{3+}] \cdot \alpha_{\text{Fe}'} \quad (9)$$

where $\alpha_{\text{Fe}'}$ is the inorganic side reaction coefficient.

Solubility of iron in the presence of iron oxides

Some of the most important Fe(III) oxide phases in aerobic systems are ferrihydrite, lepidocrocite ($\gamma\text{-FeOOH}$), goethite ($\alpha\text{-FeOOH}$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$). Ferrihydrite is a poorly ordered phase with variable composition (Cornell and Schwertmann 2003). We report dissolution reactions and corresponding solubility constants based on the simplifying assumption of a $\text{Fe}(\text{OH})_3$ stoichiometry. The dissolution reactions are:



With the conditional solubility constants K^*_{oxide} in seawater defined as:

$$K_{\text{Fe}(\text{OH})_3} = \frac{\{\text{Fe}^{3+}\}\{\text{H}_2\text{O}\}^3}{\{\text{H}^+\}^3} = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^3} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^3}{\gamma_{\text{H}}^3} = K^*_{\text{Fe}(\text{OH})_3} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^3}{\gamma_{\text{H}}^3} \quad (13)$$

$$K_{\text{FeOOH}} = \frac{\{\text{Fe}^{3+}\}\{\text{H}_2\text{O}\}^2}{\{\text{H}^+\}^3} = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^3} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^2}{\gamma_{\text{H}}^3} = K^*_{\text{FeOOH}} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^2}{\gamma_{\text{H}}^3} \quad (14)$$

$$K_{\alpha\text{-Fe}_2\text{O}_3} = \frac{\{\text{Fe}^{3+}\}\{\text{H}_2\text{O}\}^{1.5}}{\{\text{H}^+\}^3} = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^3} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^{1.5}}{\gamma_{\text{H}}^3} = K^*_{\alpha\text{-Fe}_2\text{O}_3} \cdot \frac{\gamma_{\text{Fe}}\{\text{H}_2\text{O}\}^{1.5}}{\gamma_{\text{H}}^3} \quad (15)$$

where [...] and {...} are species concentrations and activities respectively, γ are activity coefficients and K^*_{oxide} are the solubility constants at infinite dilution. The activity of ocean water (with a total mass of dissolved salts per kg seawater of 35 parts per thousand at 20–40 °C) is 0.9813 mole/kg (Millero and Leung 1976). The total dissolved iron concentration in equilibrium with the solid can be calculated combining Equations (13) to (15) with Equation (8):

Ferrihydrite:

$$[\text{Fe(III)}_T] = K^*_{\text{Fe}(\text{OH})_3} [\text{H}^+]^3 \cdot \left(1 + \beta_1^* [\text{H}^+]^{-1} + \beta_2^* [\text{H}^+]^{-2} + \beta_3^* [\text{H}^+]^{-3} + \beta_4^* [\text{H}^+]^{-4} \right) \quad (16)$$

or

$$[\text{Fe(III)}_T] = K^*_{\text{Fe}(\text{OH})_3} [\text{H}^+]^3 \cdot \alpha_{\text{Fe}'} \quad (17)$$

Goethite: $[\text{Fe(III)}_T] = K^*_{\text{FeOOH}} [\text{H}^+]^3 \cdot \alpha_{\text{Fe}'} \quad (18)$

Hematite: $[\text{Fe(III)}_T] = K^*_{\alpha\text{-Fe}_2\text{O}_3} [\text{H}^+]^3 \cdot \alpha_{\text{Fe}'} \quad (19)$

The determination of conditional solubility constants are subject to the same difficulties as the determination of conditional hydrolysis constants. Indeed, both types of conditional constants are often derived from measurements of the total iron concentrations in seawater (or analogous synthetic media) in equilibrium with the corresponding solid phase. The uncertainties in the prediction of mineral solubilities do not only arise from experimental difficulties. Solubility constants are functions of the mineral properties. Solubilities increase with decreasing particle sizes (also see chapter by Gilbert and Banfield, which discusses other size-dependent phenomena in nanoparticles) and increasing bulk lattice energies of iron oxides. Size and lattice energy are influenced by ageing and isomorphous substitution by metal ions such as Al(III). The solubility of ferrihydrite is usually orders of magnitude larger than the solubility of goethite and hematite. However, with decreasing crystal sizes the solubilities of goethite and hematite increase and approach the solubility of ferrihydrite at particle sizes below 10 nm (Langmuir 1969; Trolard and Tardy 1987). Particle diameters of soil goethite and hematites are in the nanometer range (10–150 nm; Cornell and Schwertmann 2003). Hematite particles in aerosols

collected at a mountain peak in rural Poland had a size range of 5.5 to 8.5 nm (Kopcewicz and Kopcewicz 1991). In these size ranges, the solubilities of crystalline iron oxides are orders of magnitude larger than predicted from bulk mineral solubilities (see Table 2). It is therefore important to note that the solubility constants used in this paper (Table 2) are provisional, a fact that needs to be considered in the interpretation of solubility calculations.

Table 1. Conditional iron hydrolysis constants used for speciation calculations in this publication.

Reaction	$\log \beta_n^{* (a)}$	
$\text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})^{2+} + \text{H}^+$	β_1^*	-2.52
$\text{Fe}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	β_2^*	-6.5
$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_3^0 + 3\text{H}^+$	β_3^*	-15
$\text{Fe}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_4^- + 4\text{H}^+$	β_4^*	-22.8

^(a) (Liu and Millero 1999), $I = 0.7 \text{ M (NaCl)}$; $T = 25 \text{ }^\circ\text{C}$.

Table 2. Solubility of iron oxides in seawater.

Oxide	$\log K_s^{(a)}$	$\log K_s^*$	$[\text{Fe}]_{\text{tot}}$ seawater ⁽ⁱ⁾ [M]
hematite			
$\alpha\text{-Fe}_2\text{O}_3$ (bulk)	-0.53 ^(b)	0.11 ^(h)	7.1×10^{-15}
crystal size 100 nm ^(d)	-0.28 ^(c)	0.36 ^(h)	1.3×10^{-14}
crystal size 10 nm ^(d)	1.79 ^(c)	2.43 ^(h)	1.5×10^{-12}
crystal size 6 nm ^(d)	3.64 ^(c)	4.28 ^(h)	1.0×10^{-10}
goethite			
$\alpha\text{-FeOOH}$ (bulk)	0.36 ^(b)	1.01 ^(h)	5.6×10^{-14}
crystal size 100 nm ^(d)	0.63 ^(c)	1.28 ^(h)	1.0×10^{-13}
crystal size 10 nm ^(d)	3.09 ^(c)	3.74 ^(h)	3.0×10^{-11}
crystal size 8 nm ^(d)	3.77 ^(c)	4.42 ^(h)	1.5×10^{-10}
ferrihydrate	3.55 ^(e)	4.2 ^(f)	8.7×10^{-11}
lepidocrocite	2.5 ^(g)	3.1 ^(h)	6.9×10^{-12}

^(a) $K_s = \text{Fe}^{3+}/\{\text{H}^+\}^3$ at infinite dilution and 298.15 K

^(b) Parker and Khodakovskii 1995

^(c) calculated according to Langmuir (1969) using bulk $\log K_s$

^(d) cube edge length [nm]

^(e) $I = 3 \text{ M (NaClO}_4\text{)}$ (Schindler et al. 1963)

^(f) $I = 0.7 \text{ M (NaClO}_4\text{)}$, (Liu and Millero 1999)

^(g) (Hashimoto and Misawa 1973)

^(h) estimated for seawater using Equations (13) to (15) with γ_{Fe} estimated for $I = 0.7$ (NaClO_4) using the Pitzer parameters from Millero et al. (1995), γ_{H} in seawater from Millero (1986), and $\{\text{H}_2\text{O}\}$ in seawater from Millero and Leung (1976).

⁽ⁱ⁾ calculated using conditional hydrolysis constants on Table 2, not considering organic complexation

Colloidal iron in marine systems

The foregoing discussion on the solubility of iron-bearing minerals distinguished conceptually between soluble and particulate iron. For practical reasons, dissolved concentrations in seawater are operationally defined as iron fractions below a certain particle size as determined by filtration, ultrafiltration, or centrifugation. For example, iron fractions can be defined as “dissolved” ($<0.2 \mu\text{m}$), “colloidal” ($0.2\text{--}0.4 \mu\text{m}$), and “particulate” ($>0.4 \mu\text{m}$) (Wu and Luther 1994; 1996). Wu and Luther (1994) found that colloidal iron significantly (20–40%) contributed to the total iron pool $< 0.4 \mu\text{m}$ in the top 500 m of the water column of the western North Atlantic Ocean. However, abundant colloidal particles have been found in a size range below 120 nm, often with primary particle sizes in the low nanometer range (McCave 1984; Wells and Goldberg 1991) and iron has been found in small colloids ($<0.2 \mu\text{m}$) (Nishioka et al. 2001). Iron can be present as iron oxides or hydroxides, in primary silicates, in living cells or bound by organic matter (Price and Morel 1998). Iron is usually a minor component of marine colloidal particles that consist to a large part of organic material (Koike et al. 1990; Wells and Goldberg 1991).

An important mechanism for removal of small colloids is aggregation to larger aggregates that sink to depth (Wells and Goldberg 1993). Sinking of iron-bearing organic colloids from the euphotic zone leads to export of iron to the subsurface. Aggregation and sinking of iron-bearing colloids is consistent with observations of decreasing colloidal iron and increasing particulate iron concentrations with depth (Wu and Luther 1994). Iron release upon microbial decomposition of the organic material is partly responsible for elevated iron concentrations in deep water (Bruland et al. 1994). Also, the decomposition of the organic colloids leads to the generation of fluorescent humic type substances in intermediate and deep water (Tani et al. 2003). These humic substances have a high affinity for iron and increase the solubility ($<0.025 \mu\text{m}$ filtered) of Fe(III) hydroxide, contributing to the regulation of soluble iron concentrations along the water column.

Photochemistry and redox speciation of iron

Considering the much higher solubility of Fe(II) over Fe(III), any process that facilitates the reduction of Fe(III) to Fe(II) and prevents reoxidation and precipitation will increase the solubility of iron. Changes in the redox state of iron are induced by several processes, of which photo reduction and thermal oxidation are assumed to play major roles. Photochemical Fe reduction has been suggested as an important process leading to high observed Fe(II) concentrations in the SOIREE iron enrichment experiment (Croot et al. 2001). Photochemical redox cycling of iron in the marine system may therefore increase the iron availability to aquatic microorganisms (Wells and Mayer 1991; Miller and Kester 1994). The thermodynamics and kinetics of these processes are highly dependent on the speciation of both Fe(II) and Fe(III). For example, the redox potential of iron can be altered through chelation by organic or inorganic ligands. Carboxylic acids, which are ubiquitous in aquatic systems, are assumed to accelerate the effective oxidation rate of Fe(II) by oxygen via the formation of complexes that react faster than corresponding aquo complexes (Voelker and Sulzberger 1996). However, even among structurally similar carboxylic acid ligands, a broad range of effects on the oxidation rate of Fe(II) has been observed, including the inhibition of Fe(II) oxidation (Santana-Casiano et al. 2000, 2004). Polyphenolic compounds including tannic acids also inhibit Fe(II) oxidation by forming stable complexes with Fe(II) (Theis and Singer 1974; Lopes et al. 1999). Without significant concentrations of such Fe(II) stabilizing ligands, oxidation of Fe(II) in oxygen saturated sea- and freshwater at near neutral pH is expected to be fast, resulting in very small Fe(II) concentrations. However, detectable Fe(II) concentrations as well as diel Fe(II) cycles in surface seawater and freshwater have been reported (Hong and Kester 1986; King et al. 1991; O’Sullivan et al. 1991; Kuma et al. 1992; Johnson et al. 1994; Waite et al. 1995; Emmenegger

et al. 2001; Rijkenberg et al. 2005). Diel Fe(II) cycles have been explained by photo reduction of dissolved or colloidal Fe(III) during irradiation and reoxidation of photo produced Fe(II) by reactive oxygen species in the dark. Photo reduction of Fe(III)-organic ligand complexes may occur through light-induced ligand-to-metal charge transfer or through reduction by secondary photolysis products (Voelker and Sedlak 1995).

ORGANIC LIGANDS AND IRON SOLUBILITY AND SPECIATION

Speciation of soluble iron in the presence of organic ligands

Organic iron complexing ligands are ubiquitous in marine systems and the dominant dissolved iron species are organic iron complexes (Gledhill and van den Berg 1994, 1995; Rue and Bruland 1995, 1997; van den Berg 1995; Wu and Luther 1995; Luther and Wu 1997; Gledhill et al. 1998; Nolting et al. 1998; Witter and Luther 1998; Powell and Donat 2001; Boye et al. 2003). Iron binding compounds include siderophores (as discussed below), non-siderophore ligands released by eukaryotic phytoplankton, or compounds that are released by bacterial lysis (Poorvin et al. 2004). Correlations of iron solubility and fluorescence from humic matter in intermediate and deep waters suggest iron binding by marine humic substance originating from biodegradation of sinking organic matter (Tani et al. 2003). Lateral changes in iron oxide solubility (Nakabayashi et al. 2002) and changes in ligand concentration and iron affinity with depth (Rue and Bruland 1995) may therefore reflect variations in ligand structure and origin.

Reported concentrations of the iron binding ligands in seawater (0.3–12 nM) usually equal or exceed the total dissolved iron concentrations. Conditional stability constants of the iron complexes were determined by competitive ligand equilibration - cathodic stripping voltammetry (CLE-CSV) and by observation of the complex formation and dissociation kinetics. Without consideration of the (usually unknown) exact stoichiometry of the complexation reaction and the resulting complex, or of the full speciation of the ligand in ocean water, the conditional stability constants can be defined as:

$$K_{\text{Fe}^{3+}L}^* = \frac{[\text{Fe}L]}{[\text{Fe}^{3+}][L']} \quad (20)$$

where $[L']$ is the concentration of ligand not complexed to iron and $[\text{Fe}L]$ is the concentration of the complex. These conditional constants are only valid for the conditions (P , T , pH, salinity, concentration of competing trace metals, etc.) under which they have been determined. To avoid uncertainties in the calculation of $[\text{Fe}^{3+}]$, the stability constant is often expressed in terms of the total iron that is not complexed by the organic ligand $[\text{Fe}']$:

$$K_{\text{Fe}'L}^* = \frac{[\text{Fe}L]}{[\text{Fe}'][L']} \quad (21)$$

Combining Equations (20), (21), and (9) shows the relationship between the two constants:

$$K_{\text{Fe}^{3+}L}^* = K_{\text{Fe}'L}^* \cdot \alpha_{\text{Fe}'} \quad \text{or} \quad \log K_{\text{Fe}^{3+}L}^* = \log K_{\text{Fe}'L}^* + \log \alpha_{\text{Fe}'} \quad (22)$$

In this manuscript we have recalculated all conditional stability constants for organic iron complexes in terms of $\log K_{\text{Fe}^{3+}L}^*$ using $\log \alpha_{\text{Fe}'} = 10$, as calculated using the hydrolysis constants in Table 1.

The total iron concentration in seawater (pH = 8.1) in the presence of organic ligands L_1 to L_n is the sum of organic complexes and hydrolysis species:

$$\begin{aligned}
 [\text{Fe(III)}_T] &= [\text{Fe}'] + \sum_{i=1}^n [\text{Fe}L_i] \\
 &= [\text{Fe}^{3+}] \cdot \left(1 + \beta_1^* [\text{H}^+]^{-1} + \beta_2^* [\text{H}^+]^{-2} + \beta_3^* [\text{H}^+]^{-3} + \beta_4^* [\text{H}^+]^{-4} + \sum_{i=1}^n K_{\text{Fe}^{3+}}^* [L'_i] \right) \quad (23)
 \end{aligned}$$

or

$$[\text{Fe(III)}_T] = [\text{Fe}^{3+}] \cdot \left(\alpha_E + \sum_{i=1}^n K_{\text{Fe}^{3+}L}^* [L'_i] \right) \quad (24)$$

Observed $\log K_{\text{Fe}^{3+}L}^*$ in seawater range between 18 and 24. Rue and Bruland (1995) found two ligand classes L_1 and L_2 in a depth profile in the Central North Pacific. The stronger ligand L_1 ($\log K_{\text{Fe}^{3+}L}^* \approx 23$, $[L_{\text{tot}}] = 0.37\text{--}0.6$ nmole/kg) was found only in depth between 0 and 300 m. The weaker ligand L_2 ($\log K_{\text{Fe}^{3+}L}^* \approx 21.5$, $[L_{\text{tot}}] = 1.9\text{--}2.8$ nmole/kg) was distributed over the whole water column. On the other hand, Wu and Luther (1995) found one ligand class.

Marine siderophores

Siderophores are biogenic organic ligands with a high affinity and specificity for binding iron (Neilands 1957; Takagi 1976; Winkelmann 1992). Examples of siderophores from marine and terrestrial organisms produced in iron limited culture is shown in Figure 1 and Table 3. Observations of siderophore exudation by iron limited marine bacteria have lead to the hypothesis that strong iron binding organic ligands include siderophores in iron limiting marine environments. Indeed, Witter et al. (2000) have determined $K_{\text{Fe}^{3+}L}^*$ for known marine and terrestrial siderophores in seawater and found that their affinity for iron corresponds to $K_{\text{Fe}^{3+}L}^*$ of strong iron binding ligands in seawater. However, in order to identify marine strong iron binding ligands as siderophores, it would be necessary to demonstrate not only their affinity but also their specificity for iron and their biological function in iron acquisition; or to show that their chemical structure corresponds to a known marine siderophore. This is difficult due to their low concentrations in seawater.

Siderophores are structurally diverse. The structures of almost 500 siderophores from culturable organisms have been elucidated to date (Boukhalfa and Crumbliss 2002) but important marine siderophores may not be known. However, siderophores seem to share some common properties including their molecular mass range between 0.5–1.5 kDa (Matzanke et al. 1989) and their metal binding groups which include α -hydroxycarboxylate, hydroxamate, catecholate, and less frequently carboxylate groups. Macrellis et al. (2001) have extracted iron binding ligands from large volumes of seawater in the Central Californian coastal upwelling zone by solid phase extraction. In the photic zone of the water column they found iron binding ligands in the mass range of 0.3–1 kDa containing hydroxamate and catecholate functional groups. Siderophores including ferrioxamine B and G, Amphibibactin D, and E were also found and characterized in nutrient enriched seawater incubations (Gledhill et al. 2004). These observations are consistent with siderophores as important iron binding ligands in seawater. This is further supported by a strong correlation between iron solubility and cell counts of heterotrophic bacteria in surface water of the northwestern North Pacific Ocean (Takata et al. 2004). As siderophore production is highly regulated and depends on the iron status of the originating organism, the types of siderophores and their concentrations in seawater will be influenced by local biological community structures and by the chemical environment and may vary both horizontally and with depth. However, at the present time no direct evidence of the presence of siderophores and their relative importance as iron binding ligand in marine systems is available.

An important characteristic of siderophores is their specificity for iron. This is of critical importance in marine waters, where the concentrations of major sea salt cations can be many orders of magnitude higher than soluble iron concentrations. It has been found empirically

that ligands with negative oxygen donor groups such as siderophores typically form metal complexes with increasing stability constants in the order $\text{Ca}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+}$ (Evers et al. 1989). For example the 1:1 formation constants ($I = 0.1 \text{ M}$) of Ca^{2+} , Al^{3+} and Fe^{3+} DFO-B complexes are $10^{2.64}$, $10^{24.14}$ and $10^{30.7}$ respectively (Martell et al. 2001). The specificity of siderophores for iron(III) complexation is illustrated by experiments where Cu or Zn additions to coastal water had no effect on iron solubility, whereas UV irradiation (before Fe, Cu, or Zn additions) strongly decreased iron solubility (Chen et al. 2004). Low affinities of siderophores for Fe(II) stabilizes the Fe(III) redox state in solution (Dhungana and Crumbliss 2005). Exceptions to the specificity of siderophores for Fe(III) are tetravalent actinides. For example, Th^{IV} and Pu^{IV} form DFO-B complexes with 1:1 formation constants of $10^{26.6}$ and $10^{30.8}$ respectively (Whisenhunt et al. 1996). The presence of siderophores could therefore have an important effect on the speciation of actinides in the ocean.

Photo reduction of iron and redox cycling in the presence of siderophores

Processes leading to the formation of inorganic Fe(II) or photolysis of organic ligands can increase the bioavailability of iron by increasing the iron solubility and by facilitating the biological uptake of iron from organic complexes. Barbeau et al. (2003) have investigated the photo reactivity of Fe(III)-siderophore complexes based on characteristic Fe(III)-binding groups. Siderophores carrying α -hydroxycarboxylic acid groups such as petrobactin (Barbeau et al. 2002; Bergeron et al. 2003; Hickford et al. 2004), aquachelin (Barbeau et al. 2001), and aerobactin (Borer et al. 2005) have been found to form photo reactive iron complexes. Upon

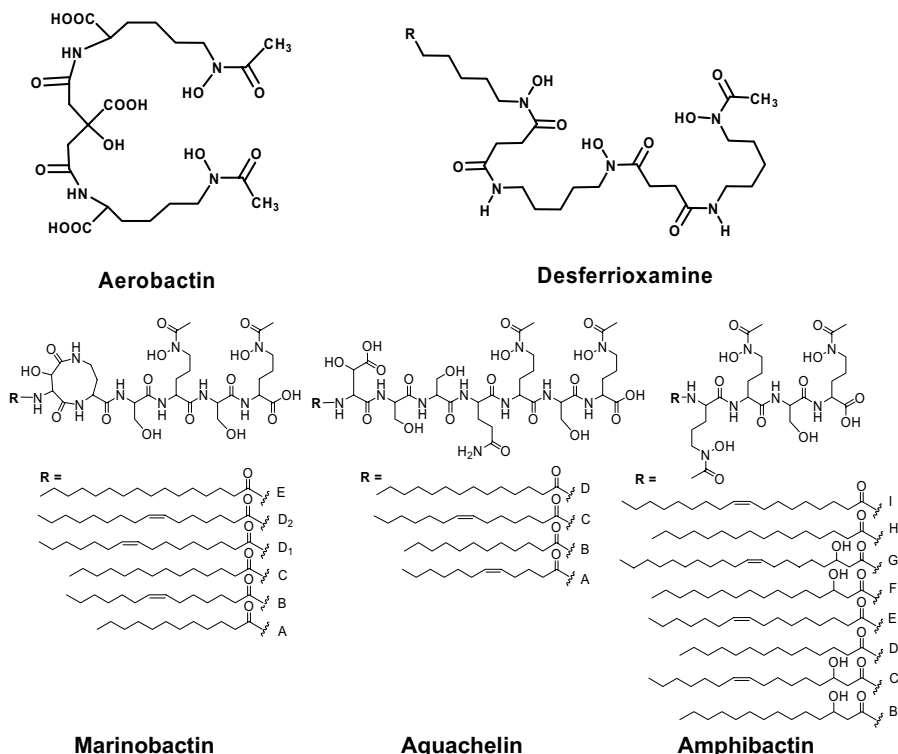


Figure 1. Examples of siderophores including amphiphilic marine siderophores structures (Martinez et al. 2000, 2003).

Table 3. A selection of siderophores by marine and terrestrial organisms.

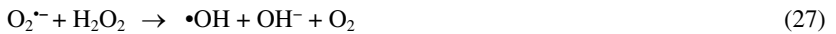
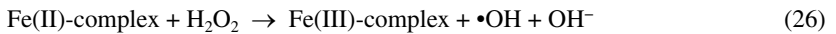
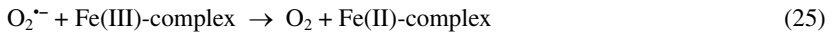
<i>Ligand</i>	<i>Ligating Groups</i>	<i>Organism</i>	$\log K_{\text{Fe}^{3+}\text{L}}^*$	$\log K_{\text{FeL}}$	<i>Ref.</i>
<u><i>Siderophores Originating from Marine Bacteria</i></u>					
Alterobactin A	catecholate hydroxycarboxylate	<i>Alteromonas luteoviolacea</i>	23.9 ^(a)	49-53	(1)
Alterobactin B	catecholate carboxylate	<i>Alteromonas luteoviolacea</i>	>24 ^(a)	43.6 ^(b)	(1)
Anguibactin	catecholate hydroxamate	<i>Vibrio anguillarum</i>			(2)
Aquachelin	hydroxamate α -hydroxycarboxylate	<i>Halomonas aquamarina</i>			(3)
Bisucaberin	hydroxamate	<i>Alteromonas haloplanktis</i>			(4)
Marinobactin	hydroxamate	<i>Marinobacter sp.</i>			(3)
Petrobactin	catecholate α -hydroxycarboxylate	<i>Marinobacter hydrocarbonoclasticus</i>			(5)
Amphibactin	hydroxamate	<i>Vibrio sp.</i>			(6)
Vulnibactin	catecholate	<i>Vibrio vulnificus</i>			(7)
n.n.	catecholate	<i>Synechococcus sp.</i>		38.1 – 42.3	(7)
<u><i>Siderophores Originating from Marine and Terrestrial Bacteria</i></u>					
Aerobactin	hydroxamate α -hydroxycarboxylate	<i>Vibrio sp.</i>		22.93 ^(c)	(8)
Desferrioxamine B	hydroxamate	<i>Streptomyces pylosus</i>	21.6 ^(a)	30.6	(9)(10)
Desferrioxamine G	hydroxamate carboxylate	<i>Vibrio sp.</i>			(10)(11)
<u><i>Strong Iron Binding Ligands Originating from Algae</i></u>					
n.n.	?	<i>Emiliana huxleyi</i>	20.7–21.5		(12)
Procentrin	?	<i>Prorocentrum minimum</i>			(13)
n.n.	?	<i>Scenedesmus incrassatulus</i>			(14)
<u><i>Siderophores from Terrestrial Bacteria and Fungi</i></u>					
Enterobactin	catecholate	<i>Pseudomonas aeruginosa</i>	20.8 ^(d)	49	(15)
Ferrichrome	hydroxamate	<i>Ustilago spaerogena</i>	21.6 ^(a)	29.1	(16)

^(a) determined by CLE-CSV (Witter et al. 2000)^(b)(Lewis et al. 1995) I = 0.1 M, pH = 8.3^(c)(Harris et al. 1979)^(d) determined by the kinetic method (Witter et al. 2000)

References: (1) Reid et al. 1993; (2) Jalal et al. 1989; (3) Martinez et al. 2000; (4) Takahashi et al. 1987; (5) Barbeau et al. 2002; (6) Martinez et al. 2003; (7) Okujo et al. 1994; (8) Haygood et al. 1993; (9) Schwarzenbach and Schwarzenbach 1963; (10) Gledhill et al. 2004; (11) Martinez et al. 2001; (12) Boye and van den Berg 2000; (13) Trick et al. 1983; (14) Benderliev and Ivanova 1994; (15) Loomis and Raymond 1991; (16) Wong et al. 1983

irradiation, Fe(III) complexed to these siderophores is reduced and the α -hydroxycarboxylic group is oxidized. This leads to the loss of an iron binding group. Even so, the photolyzed siderophores still retain a relatively high binding affinity to Fe(III). Interestingly, measured conditional binding constants of Fe(III)-aquachelin complexes and Fe(III)-photoproduct complexes are consistent with values reported in field studies for the class of strong Fe(III)-binding ligands L_1 and the weaker class of Fe(III)-binding ligands L_2 in seawater, respectively (Barbeau et al. 2001). Furthermore, Barbeau et al. (2001) have demonstrated the bioavailability of iron bound to aquachelin photoproducts to a natural assemblage of planktonic organisms. In contrast, non-photolyzed and intact Fe(III)-aquachelin complexes were largely unavailable.

Where non-photo-reactive Fe(III)-siderophores determine dissolved Fe(III) speciation, siderophore bound Fe(III) will be stabilized against reduction by superoxide and many other reductants. For example, it has been shown that desferrioxamine B (DFOB), a terrestrial trihydroxamate siderophore, is able to hinder the redox cycling of iron in natural aquatic systems (Gao and Zepp 1998) and to prevent the formation of hydroxyl radicals (\bullet OH) in the iron catalyzed Haber-Weiss reaction (Eqn. 27) by keeping iron in the trivalent state (Gutteridge et al. 1979):



Gao and Zepp (1998) have studied the role of iron in the photo-oxidation of CDOM (photo-bleaching) in a coastal river by adding fluoride ions or DFOB to the water. The addition of DFOB led to a decrease in CDOM photo-oxidation, which was explained by the inhibition of iron redox cycling in the presence of DFOB. For aquatic systems in which speciation of dissolved iron is determined by strong complexing agents like siderophores, photoredox cycling of iron may either be initiated by siderophores (Barbeau et al. 2001) or at the other extreme be completely inhibited, depending on the photo-reactivity or photo-stability of the iron binding groups in these siderophores.

In addition to their inhibitory effect on the Haber-Weiss reaction, siderophores can also reduce free radical concentrations by radical scavenging. For example, it has been reported that DFOB reacts with hydroxo-radicals (Sinaceur et al. 1984) and semiquinone radicals (Zhu et al. 1998) via formation of DFO-nitroxide radical. It should be noted that these observations may have been influenced by the fact that DFOB is usually supplied and used as mesylate salt and that mesylate (methylsulfonate) is an efficient radical scavenger as well (Zhu et al. 2003). However, pyoverdins have also been shown to act as hydroxyl and peroxy radical scavengers (Morel et al. 1992).

Effect of organic ligands on the solubility of iron oxides

Due to their high affinity for iron, organic ligands such as siderophores can have a strong effect on the solubility of iron oxides. Expressions for the total iron concentrations in equilibrium with iron oxides can be derived from Equations (17) to (19) and (24):

$$\text{Ferrihydrite} \quad [\text{Fe(III)}_T] = K_{\text{Fe(OH)}_3}^* [H^+]^3 \cdot \left(\alpha_{\text{Fe}'} + \sum_{i=1}^n K_{\text{Fe}^{3+L}}^* [L'_i] \right) \quad (28)$$

$$\text{Goethite} \quad [\text{Fe(III)}_T] = K_{\text{FeOOH}}^* [H^+]^3 \cdot \left(\alpha_{\text{Fe}'} + \sum_{i=1}^n K_{\text{Fe}^{3+L}}^* [L'_i] \right) \quad (29)$$

$$\text{Hematite} \quad [\text{Fe(III)}_T] = K_{\alpha\text{-Fe}_2\text{O}_3}^* [H^+]^3 \cdot \left(\alpha_{\text{Fe}'} + \sum_{i=1}^n K_{\text{Fe}^{3+L}}^* [L'_i] \right) \quad (30)$$

As Equations (28) to (30) indicate, dissolved iron concentrations in equilibrium with an iron oxide increase as a function of the ligand concentrations $[L_i]$ and of the conditional stability constant $K^*_{Fe^{3+}L}$. This is illustrated in Figure 2 where the soluble iron concentrations in equilibrium with ferrihydrite or goethite in the presence of two siderophores with different affinities for iron are plotted as a function of the siderophore concentrations. At ligand concentrations below 0.1 nmole/kg, the solubility of ferrihydrite is controlled by hydrolysis species and is not affected by organic ligands. At higher ligand concentrations its solubility is a linear function of the organic ligand concentration. The different affinity of the two siderophores is not affecting the solubility of ferrihydrite because siderophores are quantitatively present as iron complexes. In equilibrium with goethite, the iron speciation is dominated by siderophore complexes. Therefore the soluble iron concentration increases linearly with the siderophore concentration over the whole concentration range shown here. Also, the affinity of the siderophores for iron has a stronger effect on equilibrium iron concentrations.

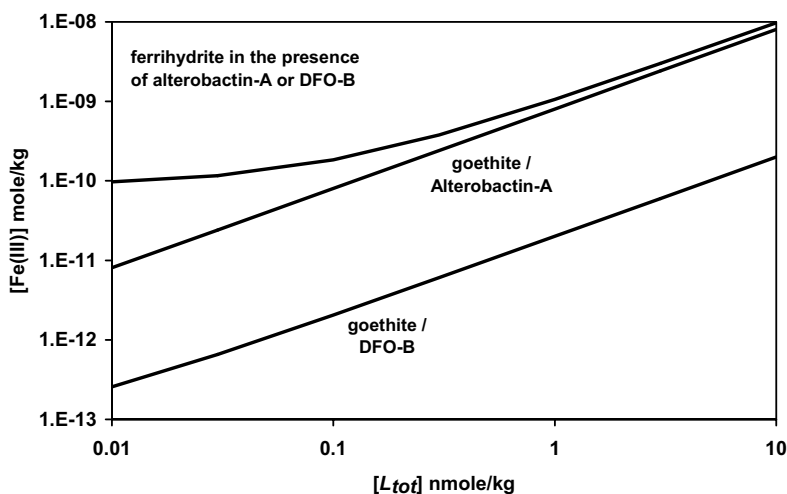


Figure 2. Calculated soluble iron concentrations in equilibrium with ferrihydrite and goethite in seawater (pH 8) as a function of soluble siderophore concentrations. The siderophores are DFO-B ($\log K^*_{Fe^{3+}L} = 21.6$) or alterobactin-A ($\log K^*_{Fe^{3+}L} = 23.9$).

Figure 3 further illustrates the effect of the conditional stability constant of the organic complex on the solubility of ferrihydrite and goethite. For this model calculation the ligand concentration was kept constant at one nmole/kg and the $\log K^*_{Fe^{3+}L}$ was varied between 18 and 25. At $\log K^*_{Fe^{3+}L} < 19$ an organic ligand concentration of 1 nM has little effect on iron oxide solubilities and the soluble iron speciation is dominated by hydrolysis species. The soluble iron concentration in equilibrium with ferrihydrite increases with increasing complex stabilities until at $\log K^*_{Fe^{3+}L} > 21$ effectively all siderophore is complexing iron and the iron concentrations are limited by the total ligand concentration of 1 nM. The solubility of goethite increases linearly with increasing conditional stability constant until it approaches the solubility of ferrihydrite at $\log K^*_{Fe^{3+}L} > 24$.

It has been suggested that in the deep sea soluble iron may be in equilibrium with ferrihydrite (Johnson et al. 1997). It is difficult to deduce from observations of iron speciation in seawater if soluble iron concentrations are controlled by equilibria with minerals or by steady state kinetics of the various source and sink terms. However, calculations of the solution

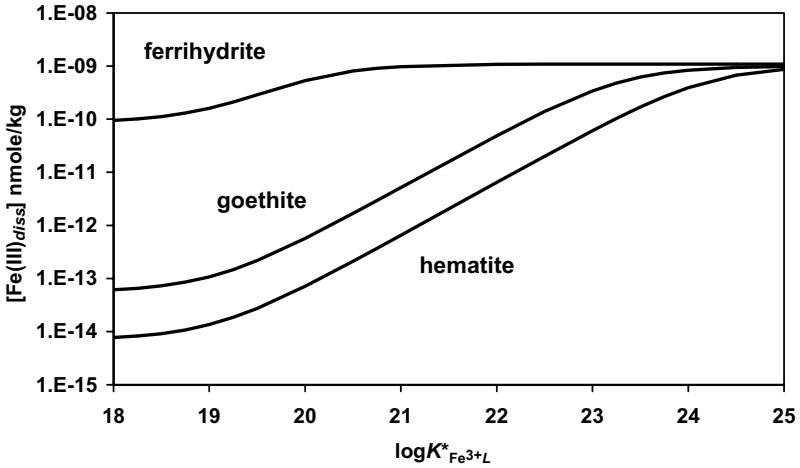


Figure 3. Calculated soluble iron concentrations in equilibrium with ferrihydrite, goethite, or hematite and $[L_{tot}] = 1 \text{ nM}$ as a function of the conditional equilibrium constant of the metal organic complex $K_{Fe^{3+}L}^*$ in seawater (pH 8.1).

saturation state of seawater with respect to iron oxides helps to constrain models including iron-bearing minerals as sources or sinks of iron. Many marine iron speciation studies report total iron and ligand concentrations as well as conditional stability constants of the metal organic complex. In these cases, the solution saturation state with respect to a mineral phase expressed as Gibbs free energy change of reaction ΔG can be calculated using

$$\Delta G = RT \ln \frac{\{Fe^{3+}\} \{H_2O\}^3 \{H^+\}^{-3}}{K_{Fe(OH)_3}} \quad (31)$$

$$= RT \ln \frac{[Fe^{3+}] \{H_2O\}^3 [H^+]^{-3}}{K_{Fe(OH)_3}} \cdot \frac{\gamma_{Fe^{3+}}}{\gamma_{H^+}^3} \quad (32)$$

$$= RT \ln \frac{[Fe^{3+}] [H^+]^{-3}}{K_{Fe(OH)_3}^*} \quad (33)$$

where $[Fe^{3+}]$ is the concentration of the iron hexaquo complex; R is the gas constant and T is the temperature in K. The equation is correct only if it can be assumed that the activity coefficients and the activity of seawater are not influenced by the disequilibrium. This is certainly true in the case of iron in seawater where the disequilibrium leads to variations of iron concentrations in or below the nanomolar range. Equation (33) can be combined with Equation (24) for an expression that takes into account iron hydrolysis and complexation:

$$\Delta G = RT \ln \frac{[Fe(III)]_T [H^+]^{-3}}{\left(\alpha_{Fe'} + \sum_{i=1}^n K_{Fe^{3+}L}^* [L_i'] \right) K_{Fe(OH)_3}^*} \quad (34)$$

ΔG is negative if the solution is under-saturated with respect to the mineral phase and $\Delta G = 0$ at equilibrium.

DISSOLUTION OF AEROSOLS AND DEFINED IRON OXIDES IN SEAWATER

Dissolution mechanisms

Iron oxide dissolution mechanisms involve the breaking of coordinative bonds between surface Fe(III) and the crystal structure. Various processes can labilize these bonds and accelerate the dissolution reaction, including the protonation of lattice O or OH groups in the inner coordination sphere of surface Fe(III) ions; the deprotonation of OH₂ or OH groups in the inner coordination sphere; the reduction of Fe(III) to Fe(II); and the coordination of surface Fe(III) by organic or inorganic ligands. The corresponding mechanisms are proton-promoted dissolution, alkaline dissolution, reductive dissolution (including photoreductive dissolution), and ligand-controlled dissolution. Under the assumption that these mechanisms are independent of each other, the overall rate law of dissolution is:

$$R = \frac{d[\text{Fe(III)}_T]}{dt} = (R_H + R_{OH} + R_{red} + \sum R_{L_n}) f(\Delta G) \quad (35)$$

where R_H and R_{OH} are the rates of proton-promoted and alkaline dissolution respectively, R_{red} is the rate of reductive dissolution and R_{L1} to R_{Ln} are the rates of ligand-promoted dissolution in the presence of ligands L_1 to L_n , including siderophore ligands, and $f(\Delta G)$ is a function of the solution saturation state with respect to the dissolving mineral (Furrer and Stumm 1986; Kraemer and Hering 1997). $f(\Delta G)$ is 1 at strong under-saturation of the dissolving mineral phase and goes to 0 at solubility equilibrium (i.e., the dissolution rates are 0 at equilibrium). A more detailed discussion of the effect of the solution saturation state on dissolution rates follows below. Dissolution experiments are often conducted far from equilibrium where Equation (35) simplifies to:

$$R = R_H + R_{OH} + R_{red} + \sum R_{L_n} \quad (36)$$

Proton-promoted dissolution rates of iron oxides are related to surface excess of adsorbed protons relative to the protonation state at the point of zero net proton charge:

$$R_H = k_H [H_{ads}]^n \quad (37)$$

where k_H is the rate constant of proton-promoted dissolution and n is the reaction order (3.25 for goethite according to Zinder et al. 1986). If the surface protonation state is not known, the rate law can be written as a function of the H⁺ activity in solution and the specific surface area of the mineral:

$$R = k'_H (\text{surface} - \text{area}) \cdot \{H^+\}^n \quad (38)$$

where $(\text{surface} - \text{area})$ is expressed as m²/kg_{water}. It is important to note that the H⁺ activity in solution {H⁺} is non-linearly related to the surface protonation state so that rate constants and reaction orders in Equations (37) and (38) are not identical. Kuma et al. (1992) further simplified Equation (38) to express the mineral concentration in terms of a conveniently measurable quantity in seawater, the particulate iron concentration [Fe(III)_p]:

$$R = -\frac{d[\text{Fe(III)}_p]}{dt} = k_{H2} [\text{Fe(III)}_p] \quad (39)$$

where k_{H2} is a rate constant conditional to the seawater pH, crystal structure, and specific surface area of the iron oxide. This has to be taken into consideration when comparing k_{H2} with other published rate constants of proton-promoted dissolution.

Natural and anthropogenic ligands have an important influence on the weathering kinetics of oxide minerals (Furrer and Stumm 1986; Casey and Ludwig 1996; Kraemer and Hering 1997). A generalized mechanism of ligand-controlled dissolution has been proposed (Furrer and Stumm 1986) which includes three steps 1) fast surface complex formation by a ligand exchange mechanism, 2) slow, rate determining detachment of the surface metal center, and 3) fast regeneration of the surface. The rate of ligand-controlled dissolution R_L is a function of the surface excess of adsorbed ligands (Furrer and Stumm 1986):

$$R_L = k_L [L]_{ads} \quad (40)$$

where k_L is a pseudo first order rate coefficient [h^{-1}] and $[L]_{ads}$ is the surface excess of adsorbed ligands [mole m^{-2}]. The rate constant of ligand-controlled dissolution k_L is influenced by changes in surface speciation of the ligand. The surface speciation can potentially be influenced by factors such as pH, surface coverage and the adsorption of other inorganic ligands (Kraemer et al. 1998). The rate coefficient is therefore conditional and depends on the geochemical environment. Alkaline dissolution can be seen as a special case of ligand-controlled dissolution with the deprotonation of adsorbed water or hydroxyl leading to an increase of their labilizing effect.

The combined proton-promoted and alkaline dissolution rates have a minimum in the same pH range in which iron oxides have a minimum solubility, i.e., near the average pH of seawater. This means that in the absence of complexing ligands or reducing agents, iron acquisition in marine systems is not only limited by the low solubility of iron oxides, but also by their slow dissolution kinetics.

Common to reductive dissolution and ligand-promoted dissolution is the formation of surface complexes which weaken the oxo bonds of the coordinated iron ions. For reductive dissolution, destabilization of the oxo bonds is achieved by the transfer of electron(s) from thermally or photo-excited ligands to the coordinated iron ion. Photo-reductive dissolution may also occur by other mechanisms (photolysis of surface hydroxo groups or reduction of surface sites by a bulk semiconductor mechanism). Typically ligands containing carboxylic and α -hydroxycarboxylic groups have been shown to form photo-reactive complexes with Fe(III) in solution and at the mineral surface. Upon irradiation in the near UV range, ligand to metal charge transfer (LMCT) within the surface complex leads to the reduction of Fe(III) and to the concomitant oxidation of the ligand. The reduction of Fe(III) to Fe(II) strongly weakens the oxo bonds and facilitates bond breaking. The detachment of reduced Fe(II) rather than the reduction of Fe(III) to Fe(II) is the rate determining step in the overall dissolution reaction (Banwart et al. 1989; Siffert and Sulzberger 1991). Due to the slow detachment of Fe(II), reoxidation of Fe(II) and thus restabilization of the oxo bonds may occur. Overall dissolution rates are then determined by two competing processes: (i) detachment of Fe(II) from the surface and (ii) reoxidation of Fe(II). Detachment rates of Fe(II) depend highly on the iron oxide structure. Detachment rates of Fe(II) are likely to decrease with increasing thermodynamic stability (and increasing crystallinity) of the various iron oxide phases, (Sulzberger and Laubscher 1995). However, in analogy to Fe(III), detachment of Fe(II) from the surface is also facilitated by proton-promoted and ligand-promoted destabilization of the oxo bonds (Banwart et al. 1989; Borer et al. 2005; Sulzberger and Laubscher 1995). Therefore, the overall photo-reductive dissolution rate expression must include surface complex formation, photo-excitation and charge transfer within the surface complex, detachment as well as reoxidation of Fe(II). For an in-depth discussion of photo-reductive mechanisms and dissolution kinetics we refer to (Siffert and Sulzberger 1991).

Experimentally observed dissolution rates of aerosol and defined minerals

The observation of iron oxide dissolution kinetics under ambient seawater conditions is a non-trivial task. As discussed above, dissolution rates are approaching zero near the solubility limit of the dissolving minerals. However, the solubilities of iron oxide minerals in seawater are extremely low. To overcome the analytical difficulties involved in measuring dissolution rates at such low concentration ranges, Kuma et al. (1992) have devised a setup in which the dissolution rates have been obtained from the decrease of a small mass of isotopically labeled iron oxides in a dialysis tube which was immersed in a large volume of seawater at constant pH. The advantage of this setup is that it is not necessary to measure soluble iron concentrations which are kept at concentration levels below the oxide equilibrium solubility. Using this method rate constants k_2 in autoclaved seawater were determined for the dissolution of ferrihydrite, lepidocrocite, and goethite of 0.015, 0.005, and 0.00012 day⁻¹ (Kuma et al. 1992; Kuma et al. 1993; Kuma and Matsunaga 1995). They also observed growth rates of red tide marine flagellates and a marine diatom in the presence of Fe(III)-EDTA complex and various iron oxides. Growth rates decreased in the order Fe(III)-EDTA > ferrihydrite > lepidocrocite > goethite (Kuma and Matsunaga 1995).

Iron dissolution from aerosol samples in seawater shows more complex dissolution behaviour than pure mineral phases for several reasons. Aerosols can consist of more than one iron-bearing mineral phase with corresponding variations in solubilities and dissolution rates. Moreover, minerals are undergoing extensive transformations due to the harsh conditions during atmospheric transport, leading to the labilization of some fraction of iron from primary minerals including dissolved Fe(II) and Fe(III) as discussed above. Zhuang et al. (1990) have observed fast dissolution of up to 50% of the total iron from aerosol samples immersed into seawater at ambient pH (see corrected value in Yhu et al. 1993). A labile Fe(II) pool of between 0.3–2.2% of the total aerosol iron was quantified by extraction in acidic solutions (Zhu et al. 1993; Zhu et al. 1997; Siefert et al. 1999; Johansen et al. 2000).

Photo-reductive dissolution in seawater

Typically, iron oxide photolysis in the laboratory has been investigated by measuring the photo-production of Fe(II). Quantification of iron oxide photolysis in seawater by this methodological approach is constrained by fast reoxidation of photo-produced surface Fe(II) as well as fast reoxidation of Fe(II) that has eventually been released to the solution. Thus, the formation of Fe(II) may not be used as a reliable quantitative measure of photo-reductive iron oxide dissolution in seawater.

In recent years other approaches have been taken to quantify iron oxide photolysis in seawater samples. Barbeau and Moffett (2000) have used a novel inert tracer technique to investigate the photo-dissolution of a model iron oxide. Colloidal ferrihydrite uniformly impregnated with an inert tracer (¹³³Ba) was spiked to seawater and the release and accumulation of this tracer in solution was measured under irradiated conditions (natural sunlight). According to these authors, iron oxide photo-dissolution was directly related to the release and accumulation of ¹³³Ba, regardless of the fate of iron. During irradiation of ¹³³Ba and ⁵⁹Fe impregnated ferrihydrite, only release and accumulation of ¹³³Ba was observed (Barbeau and Moffett 2000) while iron was most likely re-oxidized.

Wells and Mayer (1991) investigated the photo-dissolution of colloidal ferrihydrite and goethite in spiked seawater of pH 8 by measuring the labile portion of total iron as determined by extraction with the complexing agent 8-hydroxyquinoline. The lability of these colloidal iron oxides was found to increase upon irradiation with artificial and natural sunlight, and this was assigned to the rapid cycling of photo-reductive dissolution, rapid reoxidation in solution and precipitation in the presence of unknown chromophores. Pre-irradiation of the

seawater prior to addition of colloidal Fe(III) eliminated the photoreaction, confirming the role of natural organic chromophores in photo-dissolution of iron oxides. The labile portion of iron in seawater was further shown to correlate positively with its availability to marine algae (Wells and Goldberg 1991). Thus it seems that photo-reductive dissolution of colloidal iron may generate an iron pool that is bioavailable to marine algae, either by generating dissolved Fe(II) of highly labile colloidal Fe(III).

ORGANIC LIGANDS AND IRON OXIDE DISSOLUTION IN SEAWATER

Siderophore-promoted dissolution mechanisms

Siderophores can influence iron oxide dissolution by acceleration of the dissolution reaction via ligand-controlled and light induced dissolution mechanisms (Kraemer et al. 1999; Borer et al. 2005) and by modifying the solution saturation state of the seawater with respect to the iron oxide (Cheah et al. 2003; Kraemer 2004). A model calculation was performed to illustrate the effect of the concentration of a strong marine siderophore (alterobactin A) on the solution saturation state in the presence of various model iron oxides and a total concentration of 0.1 nM dissolved iron in seawater (Fig. 4). Under these conditions, a small concentration of the siderophore is required to maintain solubility equilibrium ($\Delta G = 0$ kJ/mole). Obviously the equilibrium siderophore concentration increases with increasing thermodynamic stability of the iron oxide. A further increase of the siderophore concentration leads to under-saturation ($\Delta G < 0$ kJ/mole).

A quantitative treatment of the effect of the solution saturation state on dissolution rates as derived from the activated complex theory (Lasaga 1981; Aagaard and Helgeson 1982) has been applied to ligand-controlled dissolution (Kraemer and Hering 1997) resulting in an empirical rate law:

$$R_{net} = k_L [L]_{ads} f(\Delta G) = k_L [L]_{ads} \left[1 - \exp\left(\frac{\Delta G}{2RT}\right) \right] \quad (41)$$

where k_L is the rate constant of ligand-controlled dissolution, $[L]_{ads}$ is the adsorbed ligand concentration; ΔG is the Gibbs free energy of reaction (kJ mole⁻¹); R is the gas constant, and T is the absolute temperature (K).

Figure 5 illustrates the effect of the solution saturation state expressed as Gibbs free energy change on the net dissolution rate represented as $f(\Delta G) = [1 - \exp(\Delta G/(2RT))]$. At a $\Delta G \leq -3$ kJ/mole, $f(\Delta G) \geq 0.5$, i.e., net dissolution rates are more than half of the maximum dissolution rates. In the model calculation presented in Figure 4, $\Delta G \approx -3$ kJ/mole at a total siderophore concentration between 0.25 nM (ferrihydrite) and 1 nM (hematite) which is in the range of observed strong ligand concentrations in marine surface water. Based on these considerations, it seems likely that the maintenance of small free siderophore concentrations by marine bacterial exudation may provide the driving force for dissolution mechanisms including ligand-controlled dissolution.

Adsorbed siderophores can also accelerate iron oxide dissolution by a ligand-controlled dissolution mechanism (Holmen and Casey 1998; Kraemer et al. 1999; Kalinowski et al. 2000; Maurice et al. 2000, 2001; Cervini-Silva and Sposito 2002; Coccozza et al. 2002; Cheah et al. 2003; Kraemer 2004). As indicated in the rate law for ligand-controlled dissolution (Eqn. 41) the effect of adsorbed siderophores on dissolution rates is linearly related to their adsorbed concentrations. Adsorbed concentrations are non-linearly related to soluble siderophore concentrations via adsorption isotherms (Kraemer et al. 1999, 2002; Coccozza et al. 2002; Neubauer et al. 2002; Cheah et al. 2003). At extremely low dissolved siderophore

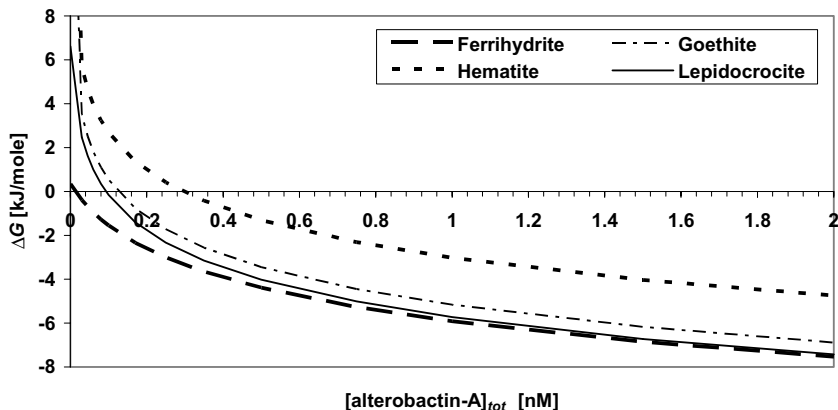


Figure 4. Calculated solution saturation state of various iron oxides as a function of the alterobactin-A concentration, assuming a total soluble iron concentrations $[\text{Fe(III)}]_{\text{tot}} = 0.1 \text{ nM}$ in seawater. The solution saturation state is expressed as Gibbs free energy change ΔG as calculated by Equation (34) using conditional hydrolysis constants as listed in Table 1. Positive ΔG indicates super-saturation, negative ΔG under-saturation. At equilibrium $\Delta G = 0$. $\text{pH} = 8.1$; $\log K_{\text{FeL}}^{\circ} = 23.9$.

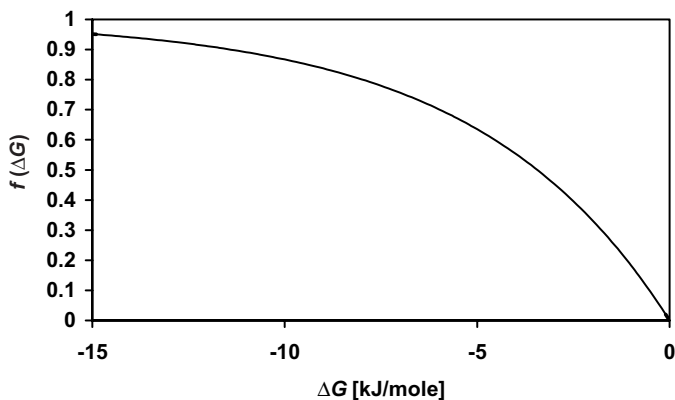


Figure 5. The effect of the solution saturation state expressed as Gibbs free energy change ΔG on net dissolution rates where $f(\Delta G) = [1 - \exp(\Delta G / (2RT))]$. At equilibrium, $f(\Delta G) = 0$, i.e., the net dissolution rate $R_{\text{net}} = 0$. With decreasing Gibbs free energy changes, $f(\Delta G)$ approaches unity, i.e., the net dissolution rates approach a constant maximum value.

concentrations reported in literature, adsorbed siderophore concentrations are also expected to be low. Based on this consideration Kraemer (2004) has suggested that direct siderophore-controlled dissolution mechanisms are insignificant at low siderophore concentrations typically found in natural environments compared to other dissolution mechanisms including proton-promoted dissolution, alkaline dissolution or ligand-promoted dissolution mechanisms driven by other adsorbed ligands. In this context, the more important function of siderophores in oligotrophic natural environments may be to increase the solubility of iron oxides and to drive other dissolution mechanisms by lowering the solution saturation state.

This hypothesis is supported by observations of siderophore-promoted dissolution rates of iron oxides in artificial seawater by Yoshida et al. (2002). They have demonstrated that

micromolar concentrations of a siderophore produced by a marine bacterium *Alteromonas haloplanktis* accelerate the dissolution rates of goethite and a poorly crystalline iron hydroxide. The dissolution rates increased with increasing siderophore concentrations in a roughly linear relationship at pH 4. Interpolating these results toward nanomolar concentrations suggests that the effect of the siderophores on dissolution rates is negligible at natural concentration levels.

Photo-reductive dissolution mechanisms in the presence of siderophores

Photo-reductive dissolution of iron oxides or other particulate iron forms is expected to be slow at seawater pH due to low adsorption of possible photo-reductive ligands (e.g., carboxylic and α -hydroxycarboxylic acids) to iron oxide surfaces, slow release of photo-produced surface Fe(II) to the solution and fast reoxidation of surface Fe(II). Waite et al. (1995) studied diel variations in iron speciation in northern Australian shelf waters and found no correlation between measured particulate iron concentrations and ferrozine active iron (Fe(II)). Therefore, they proposed that particulate iron does not appear to be the dominant source of Fe(II) in seawater. However, for seawater that is characterized by the presence of strong iron complexes (e.g., HNLC waters), dissolution of iron oxides by photo-reductive mechanisms may be enhanced considerably. Recently, Borer et al. (2005) have studied the photo-reduction of goethite and lepidocrocite in the presence of a typical organic photo-reductant (oxalate) and two model siderophores, desferrioxamine B (DFO-B) and aerobactin. They have observed that under irradiated and aerated conditions at pH 6, surface Fe(III) is reduced by oxalate, but only a minor part of surface Fe(II) is detached from the surface before reoxidation takes place. Due to the slow detachment of Fe(II) from iron oxide surfaces, in particular for higher crystalline and less soluble iron oxide phases, reoxidation of surface Fe(II) has been shown to limit the overall dissolution rate at circumneutral pH (Sulzberger and Laubscher 1995; Voelker et al. 1997). However, in the presence of siderophores, Fe(II) is efficiently detached from the surface and significant photo-reductive dissolution rates are observed (Borer et al. 2005). Due to the fact that Fe-siderophore complexes have very negative redox potentials at neutral pH, oxidation of dissolved Fe(II)-siderophore complexes is assumed to be very fast (Boukhalfa and Crumbliss 2002), and the trivalent iron state is stabilized against reduction by many ligands. For the reported case of DFOB, oxidation of Fe(II)-DFOB complexes is instantaneous (Welch et al. 2002). These combined observations indicate that siderophores potentially enhance photo-reductive dissolution without contributing to the formation of measurable Fe(II).

Amphiphilic siderophores

In addition to the preponderance of α -hydroxycarboxylic-acid-containing siderophores characterized to date from open ocean bacterial isolates, amphiphilic siderophores are also prevalent and many also contain both an α -hydroxycarboxylic-acid, in the form of β -hydroxyaspartic acid, as well as a fatty acid that confers the amphiphilicity (e.g., marinobactins and aquachelins, see Fig. 1). The wide diversity of marine bacteria from which amphiphilic siderophores have been isolated suggests this property evolved as a common iron acquisition strategy for marine bacteria (Martinez et al. 2003). Not only could the amphiphilic character of the siderophores function to keep siderophores in close contact with the bacteria (Xu et al. 2002), but importantly this amphiphilicity will increase surface reactivity. The enhanced surface reactivity of photo-reactive siderophores on iron-containing particles may well further promote dissolution of iron minerals; these investigations are in progress. The aquachelins, marinobactin and amphibactins are all produced as suites of siderophores. The amphiphilic siderophores with shorter fatty acids (e.g., C12) partition into vesicle membranes far less than the longer chained fatty acids (C18). The decreased partitioning however increases the availability of particle interactions.

CONCLUSIONS

Understanding the cycling of iron in marine systems and how it relates to biological nutrient acquisition processes remains a challenge for biogeochemical research. This challenge has been met with impressive vigor and success, considering the difficulty to measure iron concentrations, solubilities, and speciation at sub-nanomolar levels. However, some important information is missing. For example, while it is well known that iron in marine surface waters is bound to strongly complexing ligands, their characterization and identification is difficult. However, indirect evidence suggests that biogenic ligands including microbial siderophores play an important role in marine iron speciation. A further challenge will be the understanding of trace nutrient cycling and the indications of trace nutrient limitation in the geological record, considering the potential importance of iron and other trace nutrients for the global climate and for biological evolution in the past.

In this chapter we reviewed the coordination chemistry and redox-/photoredox chemistry of soluble siderophore iron complexes as well as the effect of siderophores on the solubility of iron-bearing minerals, and their dissolution mechanisms and rates. We hope that the discussion of these processes may help to appreciate the complexity of biological influences on marine iron cycling.

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