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Iron Cycle in Oceans

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Preface

This book aims to present the multiple facets of the study of iron cycling in the ocean. The modern age of marine iron biogeochemistry started in the late 1980s concomitantly with the emergence of trace-metal clean techniques. At that time, only a few groups were able to produce data with the analytical quality required to reveal the first consistent distributions of iron concentrations in seawater and to begin identifying the underlying biogeochemical processes at work. After approximately four decades, there is now a considerable scientific effort underway by a growing community of "iron researchers". Their research covers numerous fields where iron is studied from the gene level to the Earth system, from the atmosphere to the deep ocean, from a timescale of seconds to millennia.

This book is organized into seven chapters. The main topic of the book, iron, is presented in Chapter 1 "Iron Speciation in Seawater", where the essential physicochemical properties and definitions (e.g. solubility, bioavailability) are introduced. This chapter is followed by the presentation of the available tools for investigating iron biogeochemistry in the ocean. This includes Chapter 2 that describes the "Analytical Methods" and Chapter 3 related to the "Modeling Methods". With this background in hand, Chapter 4 "Iron Sources" presents the different pathways by which iron enters into the ocean. Once in the ocean, iron will continue to experience a multitude of transformations that are presented in Chapter 5 "Iron Cycling in the Ocean".

The methods described in Chapters 2 and 3 together with the processes presented in Chapters 4 and 5 lay the foundation for understanding of processes controlling the distributions of iron in the ocean, which are described in Chapter 6 “Dissolved Iron Distributions in the Ocean”. Finally, Chapter 7 presents “The Iron Hypothesis”, the major trigger of the research field of marine iron biogeochemistry. This hypothesis is presented from the historical perspective that led to the design of small-scale artificial iron fertilization experiments and investigations of naturally iron-fertilized ocean regions. The implications of large-scale fertilization of the ocean in the context of climate engineering are presented and discussed.

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Iron Speciation in Seawater

1.1. The chemical element

The nucleus of iron is composed of 26 protons and 30 neutrons. Formed in the heart of stars, iron is dispersed in the interstellar space following a supernova explosion. Within the iron nucleus, the binding forces between protons and neutrons balance the repulsive forces between protons, resulting in the most stable nucleus in the universe. A total of 28 isotopes of iron are known. Among the stable isotopes, only ^{54}Fe and ^{57}Fe with the respective abundance of 5.8 and 2.1% are of interest in biogeochemistry. Among the radioactive isotopes, two are used to investigate iron biogeochemical reactions: ^{55}Fe, which disintegrates by electron capture into ^{55}Mn via the production of X-rays, and ^{59}Fe, which disintegrates into ^{59}Co via the production of electrons and gamma photons. The addition of 26 electrons to the iron nucleus leads to the formation of the iron atom. The formation of the Earth 4.6 billion years ago resulted in a large accumulation of iron, making it an iron planet. Iron is now mainly concentrated in the core of Earth, but it is also the third most abundant metal in the Earth's crust. Two or three electrons of the electronic cloud of the iron atom are easily exchanged during chemical reactions, leading to the formation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions. This redox speciation plays a major role in the understanding of iron biogeochemistry. For example, it contributes to answering two basic questions: why is iron so scarce in the modern ocean and why is iron so essential for life? However, in addition to redox speciation, other basic or operational definitions of speciation also exist. This chapter aims to present the different views of iron speciation in the ocean and show how iron speciation affects biogeochemical properties.

1.2. Iron speciation

As we will see in this chapter, the speciation of iron in seawater is an extremely complex issue for which there is no ideal logical presentation. We propose here a chemical species-based approach that has the advantage of starting with well-defined chemical concepts, such as oxidation states, organic and inorganic domains, thermodynamics and kinetic laws. However, throughout this chapter, we also introduce *a priori* the distinction between dissolved and solid phases and related terms such as precipitation or solubility. As will be discussed later in the chapter, this separation relies on operational definitions that make this distinction unclear. This should be kept in mind when reading the following sections.

1.2.1. *Inorganic speciation*

The inorganic speciation of iron in ionic media is primarily controlled by hydrolysis:

$$Fe^{3+} + nH_2O \overset{\beta_n^*}{\leftrightarrow} Fe(OH)_n^{(3-n)+} + nH^+ \; with\, n \in [1,4] \qquad [1.1]$$

with subsequent precipitation of amorphous oxo ferric oxyhydroxide ($Fe_{n/2}(OH)_{3-n}$ xH_2O). These forms evolve over time to more stable forms, including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH).

The precise calculation of the dissolved iron speciation should also consider the complexation with major anions such as F^- or SO_4^{2-}, for example:

$$Fe^{3+} + nF^- \overset{\beta_{Fn}^*}{\leftrightarrow} FeF_n^{(3-n)+} + (n-1)H^+ \; with\, n \in [1,2], \qquad [1.2]$$

where β^* are the conditional stability constants that depend on ionic strength (I) of the media, which can be calculated using the equation

$$I = \frac{19.922S}{(1000 - 1.005S)},$$

where S is the salinity.

These constants can be determined experimentally or derived from thermodynamic constants (at I = 0), and the activity coefficient of the different ions in a ionic media can be estimated by different models [MIL 95].

Therefore, the inorganic speciation of both Fe(III) and Fe(II) as a function of pH has been calculated for artificial seawater at a given salinity. The variations of β^* with temperature have also been studied experimentally and fitted with the equation $log\beta_n^* = A - \frac{B}{T}$ [LIU 02].

1.2.2. *Organic speciation*

The inorganic speciation of iron in seawater, described in section 1.2.1, has been essentially studied in artificial seawater, with one of the goals being to determine iron solubility [LIU 02]. In this context, it has been found that the solubility of iron in natural seawater is higher than that in NaCl solution or ultraviolet (UV)-irradiated natural seawater, leading to the conclusion that the occurrence of organic ligands must increase iron solubility. This conclusion has given support to the field observations made with electrochemical techniques showing that up to 99% of dissolved iron is present as organic complexes [VAN 95]. Moreover, these methods suggest that two different classes of ligands exist with different binding strengths: strong ligands (class L1) and weak ligands (class L2). The most recent compilation [GLE 12] of published values of conditional stability constants reports a range of 11.1–13.9 for $logK^{cond}_{FeL_1,Fe'}$ and a range of 9.7–11.95 for $logK^{cond}_{FeL_2,Fe'}$. In fact, there is an overlap between the two classes because of the absence of a standardized definition. The authors recommend adopting in the future a clear operational definition of the different classes of ligands. They propose to use “L1” for $logK^{cond}_{FeL_1,Fe'} > 12$, “L2” for $logK^{cond}_{FeL_1,Fe'}$, in the range of 11–12, and L3 for $logK^{cond}_{FeL_2,Fe'} < 11$. The four orders of magnitude of difference in the stability constant can only result from large differences in the nature of the ligands. This leads us to the next question: what are the chemical structures of these ligands?

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There are a large variety of organic molecules that are able to bind Fe(III) and, to a lesser extent, Fe(II). The complexation by a ligand can greatly modify the thermodynamic and kinetic properties of iron.

It is therefore critical for our understanding of iron biogeochemistry to acquire knowledge about the nature and physicochemical properties of these iron complexing molecules.

One of the most popular ligands in iron aquatic chemistry is ethylene diamine tetraacetic acid (EDTA). This ligand is not present in natural seawater; however, due to its binding capacity, it has been used in early iron speciation studies to prevent precipitation in seawater and to increase iron bioavailability. Currently, it is also widely used to control iron speciation in artificial culture media [MOR 79] (see section 1.3.3). Considering the natural organic ligands in seawater, different categories have been identified.

Siderophores are molecules produced by terrestrial and marine heterotrophic and cyanobacteria to acquire iron, and depending on the functional groups that chelate Fe(III), they are commonly classified into three categories: catechol group, hydroxamic acid group and α-hydrocarboxylic acid group [SAN 09]. These siderophores exhibit extremely high stability constants (e.g. proton-independent stability constant of 10^{47} for enterobactin belonging to the tris-catecholate siderophore). Among the tris-hydroxamate category, desferrioxamine B (DFOB), a terrestrial siderophore, has been widely used to induce iron limitation in culture experiments with phytoplankton and heterotrophic bacteria.

Many marine siderophores have been isolated and characterized. The elucidation of their chemical structures shows that half are amphiphilic (e.g. amphibactin). They are composed of a head group, the binding iron group that is ligated to one or two fatty acid chains. The nature of the head group and the length and degree of saturation of the chain lead to a suite of siderophores with various degrees of amphiphilicity. Therefore, such amphiphilic siderophores are able to form miscelles or cell wall associations [MAR 00]. It has been suggested that the production of a suite of siderophores with different degrees of amphiphilicity could be an advantageous strategy for iron acquisition in the aquatic environment compared with the production of freely diffusive hydrophilic siderophores [MAR 03] that are rapidly entrained away from the cell [VÖL 99].

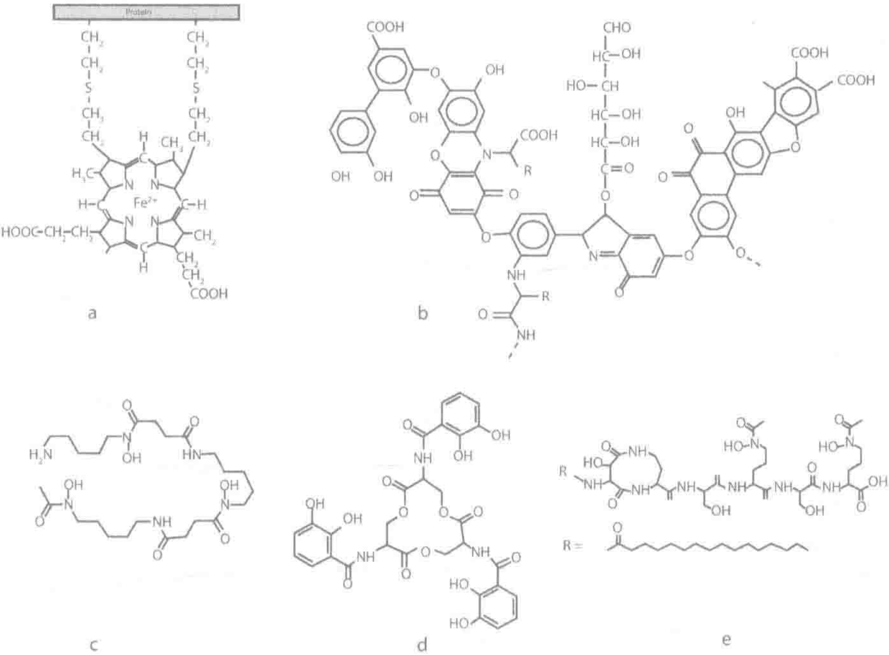


Figure 1.1. *Examples of different categories of ligands in seawater. a) Important enzyme in photosynthetic or respiration chains that contain a porphyrin binding Fe(II). b) Example of different functional groups with iron binding capacity found in humic acid. c, d, e) Siderophores. In marinobactin (e) the complexing site is bound to an aliphatic chain of variable composition R*

In addition to siderophores, other molecules with iron-binding capacity are synthesized by living organisms. These molecules, regardless of whether complexed or not with iron, are released in seawater following bacterial degradation, viral lysis or grazing. Porphyrins are a good example of this category of molecules. These molecules are ubiquitous in marine organisms as the reacting center of numerous enzymes, which do not always include iron. Moreover, they have conditional stability constants for iron complexation, which are in the range of L_2 class ligands and stable enough to persist in the environment after the degradation of cell material. Although they have been detected in the environment and some heterotrophic bacteria have the capability to directly assimilate the Fe–porphyrin complex

[ROE 13], porphyrins are not thought to be a large part of the dissolved organic iron pool in the ocean.

In contrast to the chemically well-characterized ligands described above, with relatively high iron-binding capacity, but very low concentrations in seawater, it has been suggested that other molecules with lower binding capacity but relatively higher concentrations may contribute significantly to the organic iron speciation. Saccharides represent an important fraction of dissolved and colloidal organic matter [BEN 92]. They are a diverse class of molecules containing a variety of functional groups with the potential to bind Fe(III), for example, uronic acids [HAS 11], a dominant component of exopolysaccharides. Humic substances are another class of poorly defined components present in the marine environment. They are partitioned into humic and fulvic acids. The latter are known to form complexes with Fe(III) and the same property is exhibited by humic acids. This property has been used to determine their concentrations [LAG 11]; however, little is known about the contribution of humic substance to the natural pool of organic iron complexes in the marine environment.

The dominant role of iron organic complexes in the ocean has important implications for key biogeochemical issues such as solubility, bioavailability and redox speciation of iron.

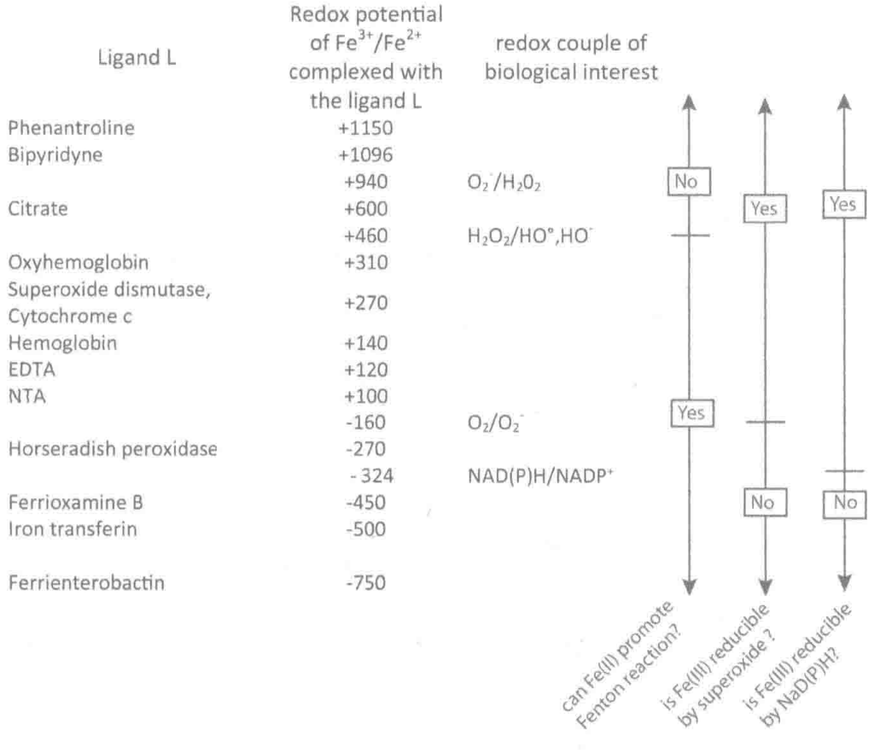
1.2.3. *Redox speciation*

Fe(II) and Fe(III) are the reducer (electron donor) and oxidizer (electron acceptor), respectively, of the redox couple Fe(III)/Fe(II) characterized by the standard potential $E^0 = 0.771$ V. In the presence of a redox couple with the appropriate redox potential, the exchange of one electron converts one form to the other as follows:

$$Fe(III) + e^- \leftrightarrow Fe(II).$$

The reduction of Fe(III) is thermodynamically feasible in the presence of any reducer belonging to a redox couple with a potential lower than $E_{Fe^{3+}/Fe^{2+}}$, and the oxidation of Fe(II) is possible in the presence of any oxidizer belonging to a redox couple with a potential higher than $E_{Fe^{3+}/Fe^{2+}}$.

Therefore, comparing redox potentials provides an easy way to predict the possible oxido-reduction reactions. However, the knowledge of the standard potentials is not adequate, as the standard conditions are usually very different from those prevailing in natural seawater or in intracellular environments. In the case of iron, the complexation by a ligand modifies the redox potential. Therefore, the capability of iron to form complexes with a large number of different ligands results in a wide range of redox potentials for the Fe(III)L/Fe(II)L couple (Figure 1.2).



Ligand L	Redox potential of Fe^{3+}/Fe^{2+} complexed with the ligand L	redox couple of biological interest
Phenantroline	+1150	
Bipyridyne	+1096	
	+940	O_2^{-}/H_2O_2
Citrate	+600	
	+460	$H_2O_2/HO^{\circ},HO^{-}$
Oxyhemoglobin	+310	
Superoxide dismutase, Cytochrome c	+270	
Hemoglobin	+140	
EDTA	+120	
NTA	+100	
	-160	O_2/O_2^{-}
Horseradish peroxidase	-270	
	-324	NAD(P)H/NADP^{+}
Ferrioxamine B	-450	
Iron transferin	-500	
Ferrienterobactin	-750	

No
Yes
Yes
Yes
No
No
can Fe(II) promote Fenton reaction?
is Fe(III) reducible by superoxide ?
is Fe(III) reducible by NaD(P)H?

Figure 1.2. *Redox potential of the couple Fe(II)/Fe(III) as a function of the nature of the ligand and implication for their reactivity*

It is this ability to fine-tune its redox potential that makes iron an essential element in living organisms, as it can reduce or oxidize a large number of chemical species involved in cellular electron transfer reactions (photosynthesis, respiration, nitrogen fixation).

However, examining the potentials shown in Figure 1.2 also reveals the "dark side" of iron redox speciation with the possible reaction between Fe(III) and the superoxide produced in the intracellular environment (in water, the superoxide ion O_2^- is in equilibrium with the radical HOO°; thus, in this book, we will use the notation O_2^-* to represent the sum of the two species [ROS 12]). The following equations, called the Haber–Weiss cycle, show how this yields OH° radicals, with high oxidative power leading to reactive oxygen species (ROS) potentially deleterious for cells:

$$O_2^{-*} + Fe(III) \rightarrow O_2 + Fe(II) \qquad (superoxide\,is\,a\,reductant)$$

$$O_2^{-*} + Fe(II) + 2H^+ \rightarrow H_2O_2 + Fe(III) \qquad (superoxide\,is\,an\,oxidant)$$

$$H_2O_2 + Fe(II) \rightarrow HO^{\circ} + HO^- + Fe(III) \qquad (Fenton\,reaction)$$

At neutral pH and ambient O_2 concentrations of the surface ocean, Fe(II) is more soluble than Fe(III). However, Fe(II) is also rapidly oxidized by O_2 and H_2O_2 (the role of O_2^- is still unclear [ROS 12]).

Thus, the occurrence of Fe(II) at detectable levels in oxygenated seawater requires continuous input and the kinetics of the different chemical reactions emerge as a critical factor of control [CRO 12]. Fe(II) production can result from Fe(III) reduction by a variety of pathways such as photoreduction or thermal reduction, reaction with O_2^-* of biological or photochemical origin, reduction at the surface of phytoplankton cells and reduction in localized anoxic environments (fecal pellet aggregates).

When the oxidation of organic material reduces oxygen concentrations at levels typical of suboxic or anoxic environments, other oxidizers are used for the microbial respiration of organic matter in the following sequence: NO_3^-, MnO_2, FeOOH, SO_4^{2-}. This can be observed in the pore waters of sediments or in anoxic layers in the ocean with important consequences for iron speciation. At low O_2 concentrations, Fe(II) becomes the dominant form for dissolved iron. In these reducing environments, the redox chemistry is mainly dominated by the redox couple sulfate/sulfide. Therefore, the solubility of iron is controlled by the precipitation of Fe(II)-sulfide.

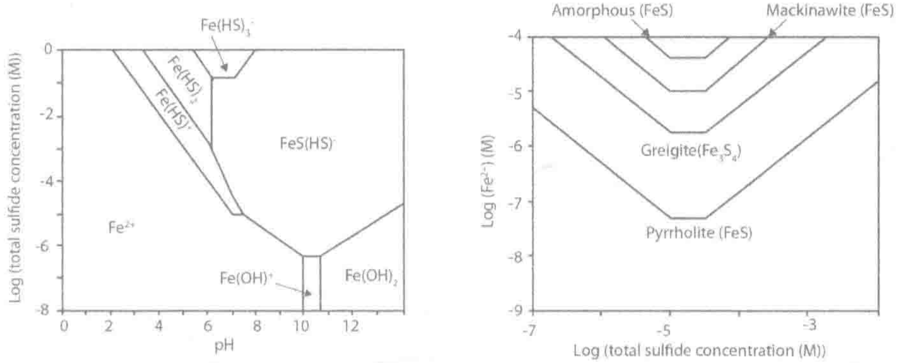


Figure 1.3. *Speciation of iron in anoxic environments (data from [LAN 88])*

High Fe(II) environments such as sediment, rainwater, hydrothermal vents and anoxic layers can also contribute to Fe(II) supply in the ocean. In addition, any decrease in the oxidation rate of Fe(II), caused by low pH, low temperature or complexation by ligands, may also act to enhance Fe(II) concentrations.

In the solid phase, the oxidation state of iron, related to mineralogy, is also a critical characteristic that may influence the solubility and bioavailability of particulate iron. We have already mentioned (section 1.2.1) that precipitation of hydrated forms of Fe(III) leads to amorphous oxide-oxyhydroxides that evolve in the crystal forms of iron oxide-oxyhydroxides and oxides; however, a large variety of other minerals containing Fe(III), Fe(II) or both oxidation states exit and may be transported into or produced in the ocean.

Table 1.1 lists the minerals of lithogenic or authigenic origin that may play a significant role in the ocean. They have served as model minerals to shed light on marine particulate iron speciation [LAM 12]. This illustrates the diversity of the minerals and therefore the difficulty that we face in linking the chemical composition of solid phases to their biogeochemical properties.

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