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Iron Cycle in Oceans

Stéphane Blain
Alessandro Tagliabue

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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.

1

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.

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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.