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Physical and Chemical Speciation of Iron in the Polar Oceans

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Chapter 1

Introduction

1. Iron and ligands

Iron (Fe) is a transition metal and is the fourth most abundant element in the Earth's crust (5.6%, Taylor, 1964; Turner *et al.*, 2001) after oxygen (O), silicon (Si) and aluminium (Al). This abundance is due to its very stable nucleus ^{56}Fe which represents 91.66% of the six Fe isotopes (from ^{54}Fe to ^{59}Fe ; Turner *et al.*, 2001). In contrast, in the modern ocean Fe is present at very low concentrations. It is such a scarce element, that it is limiting phytoplankton growth in 40% of the world ocean in region known as HNLC (High Nutrient, Low Chlorophyll, De Baar *et al.*, 1990; Martin *et al.*, 1991; De Baar and De Jong, 2001). Despite its very low concentration, Fe is essential for phytoplankton in the euphotic zone of the surface ocean where solar irradiance is present. Phytoplankton is the base of the food web and is responsible for fixation of dissolved carbon dioxide via photosynthesis in the upper euphotic. Photosynthesis is the process that transforms water (H_2O) and carbon dioxide (CO_2) into carbohydrates ($\text{C}_6\text{H}_{12}\text{O}_6$ or CH_2O) and dioxygen (O_2) with presence of light (photons). Microbial communities comprising the bacteria and archaea also need Fe for their functioning. These organisms are, in contrast to phytoplankton, present throughout the whole water column (Tortell *et al.*, 1999; Reinthaler *et al.*, 2006) and are responsible for degradation and remineralisation of sinking organic matter. Part of the organic matter and the products issued from its breakdown constitute an interesting mixture of molecules with a potentially high affinity to bind Fe. These molecules that are able to bind Fe are called ligands and are crucial to keep Fe dissolved in seawater. Due to their strong binding properties, these ligands enhance the solubility of Fe in seawater (as explained in paragraph 3) and thus its bioavailability to micro-organisms.

2. Evolution of the biogeochemistry of iron in the ocean and appearance of the ligands: from the primitive to the modern ocean

During the Archean Era (>2.5 billion years ago), oxygen was absent from the ocean. However, sulphur was dominant, hence governed the redox potentials in the ocean instead of oxygen. Under these conditions, due to the higher solubility, Fe

was abundant (Da Silva and William, 1991) between 10 and 100 μM (Saito *et al.*, 2003). Later in this period, photoautotroph cyanobacteria appeared (Saito *et al.*, 2003; Hunter and Boyd, 2007) and they evolved relying on the most abundant, available and suitable transition metal as an electron mediator for their metabolism.

Iron allows an easy electron transfer in enzymes because of a low energy requirement. Iron has a standard redox potential of 0.77V ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$; $E^0 = 0.77 \text{ V}$; Hunter and Boyd, 2007). Iron is used in 1) metallo-enzymes (ATP synthase, nitrogen fixation and reduction of nitrate, nitrite and sulphate), 2) in vital processes of living entities, notably for respiration and photosynthesis (Photosystems I and II, cytochromes; Sunda *et al.*, 1991 and 2001; Timmermans *et al.*, 2001 and 2005), and for 3) oxygen transport in higher organisms.

Cyanobacteria evolved during a transition period between the primitive and the modern ocean, the Proterozoic Era (2.5-0.5 billion years ago). At this time, the ocean was even more sulfidic than during the Archean Era (Saito *et al.*, 2003; Hunter and Boyd, 2007) and photosynthesis by the cyanobacteria caused a gradual oxygenation of the oceans, from the surface to the deep followed by transfer of oxygen into the atmosphere. Concentrations of Fe decreased to about 0.1 μM in the ocean (Saito *et al.*, 2003). Eukaryotes also appeared during the Proterozoic; they evolved and diversified through the geological times in a wide range of living entities, from unicellular phytoplankton to multicellular complex organisms, all of them using Fe. The multiplication and diversification of the living entities lead to the increasing production of organic ligands. The gradual ocean oxygenation led to massive precipitation of Fe, such that concentrations in seawater decreased to nano-molar values. This massive precipitation formed large and worldwide Fe deposits (Banded Iron Formation, BIF; De Baar and La Roche, 2003). This resulted in a dramatic change in Fe availability over the geological time (Saito *et al.*, 2003), with organic complexation of Fe controlling its availability to the living organisms.

3. The biogeochemistry of iron in the modern ocean

Iron exists in several physical-chemical states in seawater. These states are classified as species and the complete assembly of several species is known as the speciation of Fe (or another trace metal) in seawater. Iron has two oxidation states: the soluble ferrous form Fe(II), which is oxidised into the ferric form Fe(III) under oxic conditions. Under oxic conditions, the ferric form has a low solubility at normal seawater pH~8 (Kuma *et al.*, 1996; Millero, 1998), of 0.08 to 0.2 nM Fe (Liu and Millero, 2002; Wu *et al.*, 2001). However, thanks to the presence of organic molecules (*i.e.* ligands), Fe is found at higher concentrations than expected by its solubility. These ligands form strong Fe(III)-complexes allowing to keep Fe in the dissolved phase, hence enhance Fe solubility, as already mentioned in paragraph 1. The existence of Fe-binding ligands was proven first by Gledhill and Van Den Berg (1994). In oxic seawater, Fe(III) forms strong complexes with donor ligands containing oxygen, nitrogen (N) and fluor (F), whereas in anoxic conditions, Fe(II) forms strong complexes with donor ligands containing phosphorus (P) and sulphur (S) (Ussher *et al.*, 2004).

In seawater, up to 99.9% of dissolved Fe(III) (DFe) is bound to organic ligands (Gledhill and Van Den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995; Nolting *et al.*, 1998; Hutchins *et al.*, 1999a and 1999b; Powell and Donat, 2001; Gerringa *et al.*, 2006 and 2007), which are mainly originating from living organisms (Dissolved Organic Matter, DOM; Hirose, 2007). These ligands are either originating from the degradation of organic matter, like algae and fecal pellets, or other biologic products, like sugars and siderophores. Siderophore are molecules produced by prokaryotes and enhance the availability of Fe under Fe-stress conditions (Butler, 1998 and 2005; Barbeau *et al.*, 2001; Maldonado *et al.*, 2005). Recent studies allowed assigning a large variety of molecules as being Fe-binding ligands like humic substances, which seem to be very refractory in the deep oceans (Laglera *et al.*, 2007). Among others, siderophores (Rue and Bruland, 1995; Lewis *et al.*, 1995; Hudson, 1998; Hutchins *et al.*, 1999; Witter *et al.*, 2000; Macrellis *et al.*, 2001; Martinez *et al.*, 2007; Gledhill *et al.*, 2004; Haygood *et al.*, 1993; Reid *et al.*, 1993; Wilhelm and Trick, 1994; Wilhelm, 1995; Wilhelm *et al.*,

1996 and 1998), transparent exopolymer particles (TEP, Logan *et al.*, 1995), and saccharides (Van Der Merwe *et al.*, 2009; Hassler *et al.*, 2009 and 2011) have proven to be of importance in the Fe binding ligand pool and having a potential to enhance Fe bioavailability.

Under the term “ligand”, one should read “ligand soup” since there may actually be hundreds, thousands yet more different ligands in seawater over a wide size spectrum of size classes and Fe-binding functional groups (Buffle and Leppard, 1995a and 1995b). In oceanography, this metal complexation is commonly measured using voltammetric methods (Gledhill and Van Den Berg, 1994; Wu and Luther, 1995; Rue and Bruland, 1995 and 1997; Lewis *et al.*, 1995; Nolting *et al.*, 1998; Hutchins *et al.*, 1999a and 1999b; Witter *et al.*, 2000; Barbeau *et al.*, 2001; Boye *et al.*, 2001; Powell and Donat, 2001; van Leeuwen and Raewyn, 2005; van Leeuwen and Jansen, 2005; Gerringa *et al.*, 2006, 2007 and 2008). The ligands are described using one ligand class (Gledhill and Van Den Berg, 1994; Wu and Luther, 1995; Boye *et al.*, 2001; Powell and Donat, 2001; Gerringa *et al.*, 2006, 2007 and 2008) or two classes of ligands (Rue and Bruland, 1995 and 1997; Lewis *et al.*, 1995; Nolting *et al.*, 1998; Hutchins *et al.*, 1999a and 1999b; Barbeau *et al.*, 2001), the distinction between one or two ligand classes also depending on the method of measurement. In the case of two ligand classes, most authors discuss a relatively strong class L1 (siderophore like) mainly found in surface waters. This L1 ligand is attributed to bacterial/microbial activity, but exists at lower concentrations than the second class of ligands L2. This second class of L2 ligands is relatively weak but found in the whole water column and originates from degradation of organic matter (breakdown of biological material) in sinking particles (dying plankton, fecal pellets) and terrestrial organic matter transported from the shelves. Moreover, Rijkenberg *et al.* (2008b) measured weaker ligands in surface waters which were attributed to bacterial breakdown of phytoplankton blooms.

Nevertheless, Fe is not only bound to organic ligands, but also forms inorganic complexes (Fe-oxy(hydr)-oxides) defining the inorganic Fe speciation (Millero, 1998; Hudson *et al.*, 2003). The main inorganic complexes may be the oxy-oxide

$[\text{Fe}(\text{CO}_3)_2]^{2-}$ for Fe(II) and the hydr-oxides $[\text{Fe}(\text{OH})]^{2+}$, $[\text{Fe}(\text{OH})_2]^+$, $[\text{Fe}(\text{OH})_3]^0$, $[\text{Fe}(\text{OH})_4]^-$ and $[\text{FeCl}]^{2+}$ for Fe(III). At normal seawater pH, about 60% of inorganic dissolved Fe may be in the $[\text{Fe}(\text{OH})_3]^0$ form as predicted by a model for inorganic Fe(III) speciation in seawater (Liu and Millero, 2002; Millero *et al.*, 1995). This chemical species is very sensitive to precipitation.

4. Processes controlling the fate of iron in the ocean: the main parameters of the Fe cycle

The distribution of Fe is controlled by the competition between stabilisation and removal processes within the oceans and by the presence of external sources of Fe to the ocean (De Baar and De Jong, 2001).

The external sources of Fe to the oceans are predominantly inputs from the river runoff and continental margin, sediment re-suspension and upwelling (Johnson *et al.*, 1997; De Baar and De Jong, 2001; Moore and Braucher, 2008; Klunder *et al.*, 2011), aerosols deposition at the surface (Duce and Tindale, 1991; Jickells *et al.*, 2005), ice melting (Lannuzel *et al.*, 2007, 2008 and 2010) and hydrothermal vents (Klunder *et al.*, 2011). The residence time of Fe has been estimated from 20 to 200 days in surface waters, where mixing and biologic activity are very dynamic, to 70-200 yr in deep waters (Ussher *et al.*, 2004). Stabilisation of Fe in seawater is ensured by organic complexation with natural ligands, which increases the residence time of Fe in seawater, hence enhances its potential bioavailability. Iron can be removed from the water column by precipitation as oxy-hydroxides and by adsorption and scavenging on settling particles ($>0.2 \mu\text{m}$). In seawater, the majority of Fe is actually present in the particulate phase (Cullen *et al.*, 2006; Vraspir and Butler, 2009). Terrigenous particles from lands (*i.e.* earth crust) are very rich in Fe but only release a small percentage of metals (*e.g.* Fe) in seawater (Desboeufs and Losno, 2001; Bonnet and Guieu, 2004; Journet *et al.*, 2008) and have a short residence time in the water column. Fine colloids are known to be very reactive (Wells *et al.*, 1993 and 2000; Nishioka *et al.*, 2001 and 2005) and can have a long residence time in seawater.

These fine colloids can be the first step in the removal of Fe in the deep ocean by next forming larger aggregates that by Stokes Law can sink more rapidly (Kepkay *et al.*, 1994; Logan *et al.*, 1995; Wu *et al.*, 2001; Cullen *et al.*, 2006).

5. Physical and chemical speciation of Fe in this study

Since size fractionation gives information on the concentrations of Fe and ligands and on the conditional stability constant of the ligands with Fe, it informs us on the processes controlling the distribution of Fe in the Ocean, for example solubilisation of Fe via organic complexation and Fe removal via colloid aggregation, export via scavenging and precipitation.

The speciation of Fe comprises the investigation of the different forms of Fe in seawater within a size spectrum. Different size fractions are separated by means of filtrations (*i.e.* physical speciation). In each of the size fractions, chemical analyses are used to determine different parameters which characterize the Fe binding ligands (*i.e.* chemical speciation).

Three size fractions were studied during this thesis: 1) the total fraction using unfiltered samples, which contains the particulate fraction ($>0.2 \mu\text{m}$), 2) the dissolved fraction ($<0.2 \mu\text{m}$); and 3) a fraction smaller than 1000 kDa which contains the truly soluble ($<10 \text{kDa}$) and the small colloidal fraction. Upon such size fractionation, one or more fractions were subjected to voltammetric analyses in order to obtain results on the concentrations and conditional stability constant of the Fe-binding ligands in seawater. The filtrations and analytical procedures involved here are described in Chapter 2.

The physical and chemical speciation of Fe was investigated first in the Eastern North Atlantic Ocean at a station off the coast of Portugal (Chapter 3). Following this cruise, three polar cruises were completed: the first one in the Arctic Ocean in 2007 (Chapter 6); a second one in the Atlantic sector of the Southern Ocean in 2008 (Chapter 4 and 5) along the Zero Meridian from Cape Town to the Antarctic continent, through the Weddell Sea and through the Drake Passage; and the third one in the Amundsen Sea (Southern Ocean), west of the Antarctic Peninsula in 2009 during the phytoplankton blooms (Chapter 7). The major findings and an

overview of the processes involved in the cycling of Fe regarding the organic complexation, as well as recommendations for future research, are summarised in the final synthesis (Chapter 8).

6. Importance and objectives of the GEOTRACES program during the International Polar Year

Geotraces is an international program which aims to study the large-scale distribution of the key trace elements and isotopes in order to understand their biogeochemical cycles in the oceans in relation to a changing environment (GEOTRACES Science Plan). The key trace elements are iron (Fe), aluminium (Al), manganese (Mn), zinc (Zn), cadmium (Cd) and copper (Cu). These metals can either be essential (Fe, Mn, Zn) and/or toxic (Cd and Cu) for the marine organisms and thus directly influencing their ecosystems, hence the global carbon cycle. Moreover Al and some other trace elements show intriguing correlations with the overall ocean biological cycle (Middag *et al.*, 2009) that deserve further unraveling by investigation. The cycling of the trace elements depends on the sources to the oceans (notably continental runoff, sediments, atmosphere, ocean crust, hydrothermal activity), on internal processes taking place within the ocean (uptake, regeneration, burial, and circulation), and on their chemical speciation.

The International Polar Year (IPY) is a scientific framework aiming to study the Arctic and Antarctic regions. The fourth IPY, after those in 1882-1883, 1932-1933 and 1957-1958, took place between March 2007 and March 2009 in order to cover 2 complete annual cycles. Very diverse social, physical, biological and chemical subjects were investigated by over 60 nations. The Arctic and the Antarctic Peninsula regions are among the most affected by the warming climate. These sensitive polar ecosystems are therefore are threatened by the rapid changing environment. It is therefore of our duty to observe, understand and explain the mechanisms involved in order to predict future changes and limit the negative effects on our planet.

