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## Photochemistry and organic complexation of iron

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## *Chapter 1*

### Introduction and objectives

#### **1.1 Iron, the case for the Southern Ocean**

Iron (Fe) is the fourth most abundant element in the earth crust (~ 5.6%) and was present in high concentrations in seawater during the anoxic past of the earth (Sternberg, 1974; Fallows and Raven, 1997; Turner et al., 2001). Given its abundance and capacity to transfer electrons, Fe evolved into a key element in many biochemical reactions, e.g. nitrogen fixation and photosynthesis (Reuters and Ads, 1987; Guider et al., 1993; de Bar and la Roche, 2003). With the oxygenation of the atmosphere and oceans (Holland, 1984) the Fe was removed from the oceans by precipitation, resulting in the Precambrian “banded iron formations” as have been found in North America, Asia and Australia (Evans, 1980). Fe became a “hard to get essential” (Gran, 1931; Martin and Fitzwater, 1988) inducing the evolution of specialized Fe harvesting strategies in biology (Price and Morel, 1998).

The Southern Ocean, making up 17% of the world oceans, is together with the Northeast Pacific and the Equatorial Pacific, known as a high-nutrient low-chlorophyll (HNLC) area. In HNLC areas the major nutrients such as phosphate, nitrate and silicate are in ample supply and apparently cannot be fully used by phytoplankton (Martin and Fitzwater, 1988; de Baar et al., 1990; Martin et al., 1990; Martin et al., 1994). The extremely low Fe concentrations (de Baar et al., 1990; Martin et al., 1990) together with factors such as irradiance and grazing (Mitchell et al., 1991; Nelson and Smith, 1991; Sunda and Huntsman, 1997; de Baar et al., 1999; de Baar and Boyd, 2000; Lancelot et al., 2000) limit and thus regulate primary production, species composition (Buma et al., 1991) and carbon cycling within Southern Ocean planktonic communities.

The Fe concentrations as measured in surface waters of the open Southern Ocean ranged from 0.05 – 0.4 nM as measured in 1996 in the Polar Front in the eastern part of the Atlantic sector (de Jong et al., 1998). Low Fe concentrations are the result of low Fe input rates. Sources of Fe for the open Southern Ocean surface waters were suggested to be: i) contact of waters with continental margin sediments of e.g. the Argentine Basin (de Baar et al., 1995) or archipelagos like the Kerguelen Islands (Blain et al., 2001), ii) aeolian sources of Fe originating from e.g. the South American continent (Duce and Tindale, 1991), iii) transport by melting sea-ice (Sedwick and DiTullio, 1997), iv) upwelling (de Baar and de Jong, 2001; Hoppema et al., 2003) and v) extraterrestrial dust (Johnson, 2001). Next to the above described sources of “new” Fe, regeneration and recycling of biological Fe may be very important in supporting the primary production in an open ocean Fe limited environment such as the Southern Ocean (Hutchins and Bruland, 1994; Hutchins et al., 1995).

In the austral spring, phytoplankton has to deal with significantly increased levels of ultraviolet B radiation (UVB: 280-315 nm) due to stratospheric ozone depletion (Frederick and Snell, 1988; Solomon, 1990), this in addition to limiting factors such as Fe. In the clear Southern Ocean waters UVB penetrates to significant depths (60 m) (Smith et al., 1992). Biological effects of enhanced UVB, detected to maximum depths of 20-30 m (Karentz and Lutze, 1990; Smith et al., 1992), negatively affect the marine Antarctic primary producers. It has been demonstrated that enhanced UVB increases photoinhibition (Neale et al., 1998), by decreasing photosystem II efficiency (Schofield, 1995), and modifying the RUBISCO pool (Lesser et al., 1996). Also much information is available on UVB-related accumulation of DNA damage, as demonstrated by the formation of cyclobutane pyrimidine dimers (CPD) in marine phytoplankton (Buma et al., 1996; Buma et al., 2001). So far, research mainly focused on evaluating the potentially harmful effects of enhanced UVB radiation on biological systems in this region. However, little is known about the effects of UVB on marine chemistry, in particular the iron photochemistry.

Ever since the onset of the industrial revolution, large scale burning of fossil fuels due to human activities causes a rapid rise of atmospheric carbon dioxide concentration. Carbon dioxide, acting as a global blanket, prevents the heat transport from the atmosphere into space, thereby increasing the temperature and largely determining the climate on earth. The Southern Ocean plays an important role in controlling this CO<sub>2</sub> concentration in the atmosphere (Hoppema et al., 1999). Here biological fixation of CO<sub>2</sub> by phytoplankton in surface waters (de Baar and Boyd, 2000) exceeds the expected outgassing of CO<sub>2</sub>-rich upwelling waters.

Past global climate changes as correlated with dust input (and hence iron) in the Southern Ocean coincide with lower temperatures and lower atmospheric CO<sub>2</sub> concentrations (Jouzel et al., 1993; Edwards et al., 1998). The "Iron hypothesis" (Martin, 1990) suggests that high Fe-rich dust input, as a result of a dry climate and strong winds in combination with a weakened hydrological cycle (Yung et al., 1996), enhanced primary production and consequently the drawdown of atmospheric CO<sub>2</sub> during glacial maxima. It is not known as yet whether these correlations are an indirect result of Southern Ocean Fe enrichment, subsequent phytoplankton bloomforming, resulting in enhanced CO<sub>2</sub> sequestration, or that other mechanisms play a role (Arimoto, 2001; Ridgwell, 2002). Model calculations show that only about a third of the glacial-interglacial CO<sub>2</sub> change can be explained by dust deposition (Popova, 2000; Ridgwell and Watson, 2002; Fennel et al., 2003).

Large scale Fe enrichment experiments have been performed to investigate the possibility of climate regulation via the induction of phytoplankton blooms in the Southern Ocean (Boyd et al., 2000; Gervais et al., 2002; Boyd et al., 2004; Coale et al., 2004; de Baar et al., 2005). Biological sequestration of CO<sub>2</sub> into the deep ocean, via the sinking of particulate material (the biological pump), may prevent CO<sub>2</sub> from entering the atmosphere for

a long period of time. Recently, two Fe enrichment experiments, one in the Gulf of Alaska (Boyd et al., 2004) and one in the Southern Ocean (Buesseler et al., 2004) demonstrated that organic material resulting from an Fe induced phytoplankton bloom is exported to the deep ocean. Yet, the results suggest that the carbon export to the deep ocean was small and that the majority of the particulate organic carbon (POC) was remineralized by bacteria. The remineralization of POC results in an increase in pCO<sub>2</sub> in the surface seawater which eventually might lead to outgassing of the previously biologically fixed CO<sub>2</sub> back to the atmosphere. Minor carbon sequestration and export and subsequently the amount of Fe needed to add to the ocean in order to have an impact on the annual anthropogenic CO<sub>2</sub> released would make Fe enrichment an expensive tool (Buesseler and Boyd, 2003). Moreover, Fe enrichment as a tool for climate regulation should not be used until ecological consequences and possible unintended climatic feedbacks are investigated (Buesseler and Boyd, 2003; Turner et al., 2004).

Nevertheless, Fe is the dominant limiting nutrient of the ecosystem in the Southern Ocean. Not only phytoplankton, but also organisms higher up in the hierarchy of the foodchain will suffer the consequences. Hence a detailed knowledge of the chemistry of Fe in seawater and its biological availability is important to address the many questions relating with Fe metabolism in high nutrient low chlorophyll regions.

## **1.2 Fe chemistry in seawater**

The chemistry of Fe in seawater is very complex (Figure 1). Fe(III) is the thermodynamically stable form in oxygenated waters. It has a very low solubility in seawater (Millero, 1998; Liu and Millero, 2002). The inorganic speciation of Fe(III) is dominated by its hydrolysis behavior (Waite, 2001). The Fe(III) has a low solubility product: ~ 0.07 nM in seawater of 4°C (pH = 8, S =36) (Liu and Millero, 1999). It tends to form particulate iron oxyhydroxides. Little is known about the kind of particulate iron oxyhydroxides present in seawater or formed upon addition of low concentrations of Fe(III). Moffett (2001) suggests, based on model studies, that in aqueous alkaline media Fe(III) polymerizes into amorphous Fe(III) hydroxides. With aging, these solids loose water and develop crystalline structures leading to two principal products, lepidocrocite ( $\gamma$ -FeOOH) (Tipping et al., 1989) and a more amorphous solid, ferrihydrite (Fe<sub>5</sub>HO<sub>8</sub> · 4H<sub>2</sub>O) (Schwertmann and Thalmann, 1976). The final crystalline form is depending on the chemical environment of the Fe, e.g. in the presence of relatively high concentrations of Si(OH)<sub>4</sub> (Si/Fe ratios > 0.05), as found in the

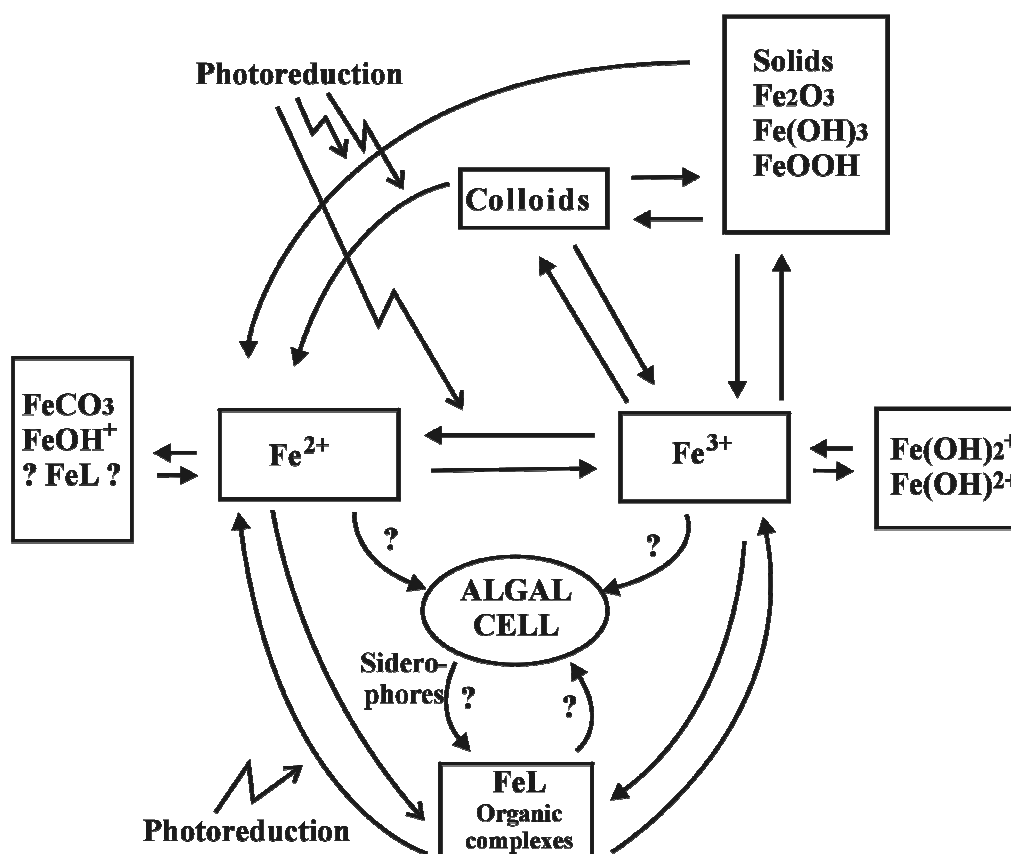


Figure 1. Model of the chemistry of Fe in seawater (Gerringa *et al.*, 2000).

Southern Ocean, Fe will form ferrihydrite (Schwertmann and Thalmann, 1976; Tipping *et al.*, 1989). Ultimately these oxyhydroxide minerals will lose additional water with aging, and become more refractory minerals such as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and goethite ( $\alpha$ -FeOOH) (Schwertmann and Taylor, 1972; Schwertmann and Fischer, 1973; Cornell and Schwertmann, 1996).

Organic complexation of iron in seawater increases the Fe solubility (Kuma *et al.*, 1996; Johnson *et al.*, 1997). Over 99% of the dissolved iron in the ocean is organically complexed (Gledhill and van den Berg, 1994; van den Berg, 1995). These organic ligands are found in excess over the dissolved Fe pool (Boye *et al.*, 2001). The organic ligands are presumed to be of biological origin (Johnson *et al.*, 1997; Hutchins *et al.*, 1999). Nevertheless, the identity, origin, and chemical characteristics of the organic Fe binding ligands in the oceans are largely unknown. The conditional stability constants of FeL complexes range in magnitude between  $10^{18}$  and  $10^{23}$  as measured in the North Atlantic (Gledhill and van den Berg, 1994; Wu and Luther, 1995; Witter and Luther, 1998), the North Sea (Gledhill *et al.*, 1998), the Mediterranean Sea (van den Berg, 1995), the Arabian Sea (Witter *et al.*, 2000), the North Central and equatorial Pacific Ocean (Rue and Bruland, 1995;

Rue and Bruland, 1997) and the Southern Ocean (Nolting et al., 1998; Boye et al., 2001; Boye, in press). Although there is five orders of magnitude difference in the  $K'_{\text{FeL}}$  of organic complexes between different ocean regions, it has not been possible to use the  $K'_{\text{FeL}}$  to identify organic ligands using the  $K'_{\text{FeL}}$  of known model ligands (Witter et al., 2000). However, comparison of formation- and dissociation rate constants between model ligands and field samples suggests that most of the unknown ligands in seawater originate from porphyrin and siderophore-like compounds (Witter et al., 2000). Siderophores are low-molecular weight, high affinity Fe(III) binding ligands, which are secreted by e.g. Fe limited marine cyanobacteria and heterotrophic bacteria to scavenge and transport Fe (Wilhelm and Trick, 1994; Martinez et al., 2000; Barbeau et al., 2002). Siderophores have shown to be present in the marine environment: hydroxamate and catecholate Fe-binding functional groups, characteristic for siderophores, were present in different size classes of samples taken along the Californian coast (Macrellis et al., 2001). Furthermore, Gledhill et al. (2004) confirmed the presence of siderophores in coastal seawater by detecting 7 siderophore type compounds among which one was identified as desferrioxamine B.

For a long time it was thought that organic iron binding ligands were not photodegradable. There were no reports of vertical gradients in depth profiles of Fe(III) chelators (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995), i.e. exhibiting minima within the shallow mixed layer, or any other feature which would suggest a surface/photochemical sink (Moffett, 2001). However, recently, a surface low ligand concentration followed by higher ligand concentrations at depth suggested photochemical breakdown, as observed by (Boye et al., 2001) in the Southern Ocean. Powell and Wilson-Finelli (2003) reported that photodegradation of ligands appears to occur in a size class smaller than 1 kDa in the Gulf of Mexico. The hydroxamate and catecholate Fe-binding functional groups found by Macrellis et al. (2001) and present in the low molecular weight classes (< 300 Da) was suggested to be caused by UV induced degradation of larger Fe-binding siderophores in surface waters. Furthermore, Barbeau et al. (2001) showed for the first time the direct photolysis of marine Fe(III)-siderophore complexes (Trick, 1989; Wilhelm and Trick, 1994; Granger and Price, 1999) leading to the formation of lower-affinity Fe(III) ligands and the reduction of Fe(III) to Fe(II).

The Fe(II) is better soluble in seawater than Fe(III). However, the Fe(II) concentration is always the result of the reduction of Fe(III) counteracted by the oxidation of Fe(II). There are several possible mechanisms for the production of Fe(II) within oxic seawater: i) photochemical reduction of inorganic oxyhydroxides (Waite and Morel, 1984; Wells and Mayer, 1991) and organically complexed Fe (Barbeau et al., 2001), ii) dark reduction of Fe by superoxide (Voelker and Sedlak, 1995) or free radical organic ligand species (Ross and Neta, 1982; Faust, 1994), iii) reduction of Fe by intra- or extracellular enzymes (Maldonado and Price, 1999; Maldonado and Price, 2000), iv) reduction of Fe in microenvironments as

e.g. the acidic food vacuoles of protozoan grazers (Barbeau et al., 1996), and v) the deposition of photochemically altered aerosols (Behra and Sigg, 1990; Zhuang et al., 1992; Erel et al., 1993; Zhu et al., 1993). During the Fe enrichment experiment SOIREE in the Southern Ocean photo(induced) Fe reduction was the main mechanism explaining the retaining measurement of high Fe(II) concentrations (Croot et al., 2001).

The Fe(II) concentrations in seawater are expected to be very low due to low total iron concentrations and because Fe(II), although well soluble in seawater, becomes rapidly oxidized by O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (Millero et al., 1987; Millero and Izaguirre, 1989; Millero and Sotolongo, 1989; King et al., 1991; King et al., 1995; King, 1998). Yet, significant and remarkably stable levels of Fe(II) have been determined in the Northeast Atlantic (Boye et al., 2003), the East-equatorial Atlantic (Bowie et al., 2002) and during a Southern Ocean Fe enrichment experiment (Croot et al., 2001). The option of Fe(II) stabilization through the involvement of organic ligands has been hypothesized to explain the presence of these relative high concentrations of Fe(II) (Croot et al., 2001; Boye et al., 2003).

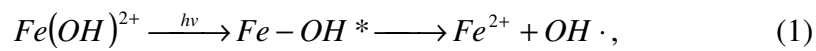
### **1.3 Fe photo(induced) redox cycle**

#### *1.3.1 Fe(III) photoreduction*

The photoreduction of dissolved and synthetic colloidal Fe(III) has been measured in seawater under laboratory and field conditions (Waite and Morel, 1984; Rich and Morel, 1990; Wells and Mayer, 1991; Waite and Szymczak, 1993; Miller and Kester, 1994). The shortest wavelength of light in the terrestrial solar spectrum is ~300 nm. Many Fe species absorb at wavelengths greater than 300 nm including Fe with ligands such as OH<sup>-</sup> (Faust and Hoigne, 1990; Faust, 1994), H<sub>2</sub>O (Langford and Carey, 1975), HO<sub>2</sub><sup>-</sup> (Evans et al., 1949), HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> (Faust and Hoffmann, 1986; Faust et al., 1989), Cl<sup>-</sup> (Langford and Carey, 1975; Nadtochenko and Kiwi, 1998), carboxylates and polycarboxylates (Parker, 1954; Parker and Hatchard, 1959; Cunningham et al., 1988; Zuo and Hoigne, 1992; Faust and Zepp, 1993), and O<sup>2-</sup> in Fe(III) (hydrated) oxides (Sherman and Waite, 1985; Faust and Hoffmann, 1986; Faust et al., 1989). Rich and Morel (1990) have shown that iron was not photoreduced at wavelengths higher than 560 nm. Correspondingly, Wells et al. (1991) observed increasing lability of colloidal iron in seawater, with a spectral dependency that generally increased with decreasing wavelength. In addition to wavelength dependency, a strong relation has been found between irradiance level and the iron photoreduction rate (Waite et al., 1995).

Diurnal variations of Fe(II) and reactive Fe(III) species have been observed in the field (Hong and Kester, 1986; O'Sullivan et al., 1991; Johnson et al., 1994). However, most information so far has been collected under artificial conditions in the laboratory. Laboratory

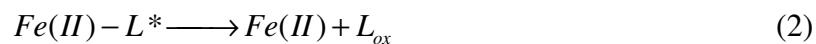
studies show that the rate of Fe(III) photoreduction is strongly dependent on the pH, decreasing rapidly with increasing pH (Waite and Morel, 1984; Sulzberger and Laubscher, 1995; Sulzberger and Laubscher, 1995) and the thermodynamic stability of the Fe(III)-(hydr)oxide phase present (Wells and Mayer, 1991; Wells et al., 1991). Direct reduction of  $Fe^{3+}$  and  $Fe(OH)^{2+}$  has been shown to be the dominant Fe(II) producing photo-reactions at low pH (David, 1976) with the more hydrolyzed species  $Fe(OH)_2^+$ , being photo-chemically less reactive (Mulay and Selwood, 1955). The photoreduction of Fe(III) hydrolysis complexes, as studied in NaCl solutions, occurs via a ligand-metal charge transfer (LMCT) reaction (Eq. 1) (King et al., 1993):



where Fe-OH\* is an excited state intermediate.

Yet, direct photo-reduction of these dissolved inorganic Fe(III) species is not a significant source of Fe(II) in natural waters with a pH above 6.5 (King et al., 1993). Increasing pH, changing solubility and hydrolyzed Fe species, decreases the solubility product of Fe and induces the formation of colloidal Fe oxides. The mineralogy of these oxides affects the photoinduced dissolution of Fe. The ability of photochemically produced Fe(II) to detach from the oxide surface decreases with increasing stability of the crystalline form (Sulzberger and Laubscher, 1995). Waite and Morel (1984) could detect photoreduced iron from amorphous Fe hydroxides at pH is 6.5 but not at pH 8. They proposed that a hydroxylated ferric surface species is the primary chromophore (light absorbing compound), analogous to the photoreduction of  $Fe(OH)^{2+}$ , and that at pH 8 the Fe(III) surface complex was more strongly hydrolyzed and less prone to photoreduction.

Knowing that most Fe in seawater is complexed or coupled to organic material it is assumed that most observed photoredox reactions in marine waters are likely to be associated with absorption of light by Fe(III)-organic chromophores. These chromophores undergo ligand to metal charge transfers (LMCT) reactions (Eq. 2) resulting in the production of Fe(II) and, as shown in most Fe-ligand model systems, in a non-reversible decomposed organic ligand (Waite and Morel, 1984). However, the absorption of light does not necessarily results in the production of Fe(II) and the decomposition of the complex. The resulting excited state situation upon light absorption can be reversed by thermal relaxation (Eq. 3).



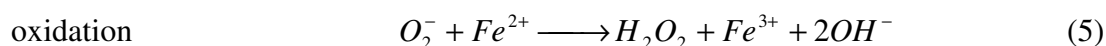
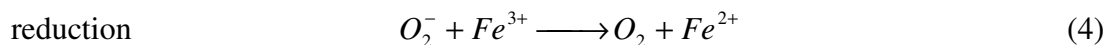


Organic matter does have the potential to increase the rate of Fe(III) photoreduction (Waite and Morel, 1984; Zuo and Hoigne, 1992) depending on the type and concentration of the reductants (e.g. oxalate, citrate, fulvic acid, sulphite) adsorbed to the Fe(III)-(hydr)oxide surface (Waite and Morel, 1984; Waite and Morel, 1984; Faust and Hoffmann, 1986; Siffert and Sulzberger, 1991; Pehkonen et al., 1993; Sulzberger and Laubscher, 1995; Sulzberger and Laubscher, 1995). Oxalate is a commonly found Fe chelator in atmospherically transported dust (Saydam and Senyuva, 2002). Complexation by oxalate extends the absorption band of Fe(III) into the visible part of the light spectrum (Zuo, 1995) and may enhance the pH range over which Fe may be photoreduced (Sulzberger and Laubscher, 1995). Kuma et al. (1992) detected high concentrations of Fe(II) during spring blooms in Funka Bay (Japan) and related this to the release of organic components from phytoplankton, thereby inducing the photoreduction of Fe. The presence of various dissolved organic substances, generally considered to be organic components released from phytoplankton such as sugar acids indeed improved the photoreduction of Fe (Kuma et al., 1995). In addition, Hudson et al. (1992) saw a similar effect when *Thalassiosira weissflogii* was added to seawater.

Marine siderophore Fe(III) complexes have shown to be photo-reactive, because they produce Fe(II) in the light (Barbeau et al., 2001; Barbeau et al., 2002; Barbeau et al., 2003). The photoreactivity of these complexes is depending on the non-reversible oxidation of the complexing functional group in the short time ( $\leq 1$  ns) that the photoinduced excited state exists. Most photo-reactive complexes are characterized by the presence of carboxylate and aminocarboxylate ligands which are oxidized irreversibly through cleavage of the carboxylate as CO<sub>2</sub>. Hydroxamate siderophores do not possess carboxyl groups involved in Fe coordination and do not undergo photoreactions, e.g. desferrioxamine B (Finden et al., 1984; Gao and Zepp, 1998). The oxidation of catechols is reversible and they are thus not photoreactive when complexed to iron (Barbeau et al., 2003). Iron-siderophore complexes using  $\alpha$ -hydroxy carboxylate functional groups to bind iron are photoreactive, whereas its free form is not photodegraded (Barbeau et al., 2003). The presence of organic photosensitisers, organically complexed Fe catalyzing Fe reduction via the photoproduction of oxygen radicals as superoxide (see below), may further increase the rate of photochemical Fe reduction (Jickells and Spokes, 2001).

The reduction of Fe(III) by photochemically produced species, called secondary photoinduced Fe redox reactions, is also possible. Superoxide (O<sub>2</sub><sup>-</sup>), reducing Fe(III) to Fe(II) has been studied by Voelker and Sedlak (1995). Superoxide and its conjugate acid, hydroperoxyl radical (HO<sub>2</sub>), are produced in sunlit waters through photochemical reactions of organic chromophores (Cooper et al., 1989). The bimolecular dismutation of superoxide has been postulated as the main source of hydrogen peroxide in the open ocean (Petasne and Zika, 1987). However, in seawater reduction or oxidation reactions with transition metals

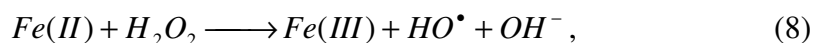
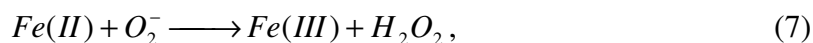
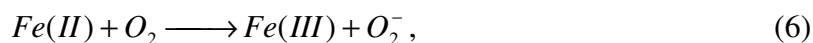
(Me), such as iron, could be the dominant mechanism of superoxide dismutation (and hydrogen peroxide formation) (Voelker and Sedlak, 1995). The reduction of iron by superoxide is faster than the oxidation (Eq. 4, 5).



Furthermore, photo-oxidation of polycarboxylates results in decarboxylation producing CO<sub>2</sub> and carbon-centered radicals. These carbon-centered radicals can also react with Fe(III) to form Fe(II) (Faust, 1994).

### 1.3.2 Fe(II) oxidation

In O<sub>2</sub> saturated seawater oxidation of Fe(II) follows immediately upon the photoinduced production of Fe(II). The Fe(II) becomes rapidly oxidized by O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (Millero et al., 1987; Millero and Izaguirre, 1989; Millero and Sotolongo, 1989; King et al., 1991; King et al., 1995; King, 1998). The oxidation of Fe(II) by O<sub>2</sub> can be described by four reactions (Weiss, 1935):



where the reactions 7 and 9 are much faster than the rate determining reactions 6 and 8.

The oxidation of Fe(II) with H<sub>2</sub>O<sub>2</sub> is the dominant oxidation pathway of Fe(II) (Moffett and Zika, 1987; Miller and Kester, 1994). The concentration of H<sub>2</sub>O<sub>2</sub>, important for the Fenton reaction (Eq. 8) (Goldstein et al., 1993; Wardman and Candeias, 1996), is dependent on spectrally determined photochemical reactions (Plane et al., 1987; Yocis et al., 2000). Primary sources of H<sub>2</sub>O<sub>2</sub> are the reaction sequence (Eq. 6-7), the iron catalyzed mechanism of superoxide dismutation resulting in hydrogen peroxide formation (Eq. 5) (Voelker and Sedlak, 1995) and the bimolecular dismutation of superoxide (Petasne and Zika, 1987).

The main source of superoxide is photochemical reactions of colored dissolved organic matter (CDOM) involving  $O_2$  (Cooper, 1983). Photobleaching of CDOM in natural waters has an inverse exponential relationship with wavelength (Osburn et al., 2001; Del Vecchio and Blough, 2002). The concentration of produced Fe(II) is not only spectrally dependent via the reduction but also via the oxidation of the Fe redox cycle.

The oxidation of Fe(II) is not only strongly dependent on the concentrations of oxygen and its radicals but also on many other factors. The pH (Singer, 1969; Millero et al., 1987), ionic strength/interactions (Millero et al., 1987; Millero, 1988; Millero and Izaguirre, 1989), temperature (Millero and Sotolongo, 1989) and the presence of surfaces (Tamura et al., 1976) play an important role in Fe(II) oxidation. These factors make the half live of Fe(II) ranging from 72 seconds (laboratory experiments by Millero et al. (1987), to several hours, as shown for the cold Antarctic waters (Croot and Laan, 2002). Furthermore, Sung and Morgan (1980) demonstrated the autocatalytic Fe(II) oxidation via oxidative precipitation of iron. Also bacteria can increase the Fe(II) oxidation rate by  $O_2$  (Sulzberger et al., 1990; Barry et al., 1994). Depending on the relative stability of the Fe(II)-organic and Fe(III)-organic complexes, organic complexation can either enhance (Sedlak and Hoigne, 1993; Voelker and Sulzberger, 1996; Emmenegger et al., 1998) or slow down the rate of Fe(II) oxidation (Theis and Singer, 1974). Extensive literature on the influence of organic complexation of Fe on the oxidation kinetics is available (Theis and Singer, 1974; Millero et al., 1987; Voelker et al., 1997; Santana-Casiano et al., 2000; Rose and Waite, 2002; Santana-Casiano et al., 2004).

#### **1.4 Biological uptake of iron**

There are several reasons to study Fe chemistry in seawater and to elucidate its biological availability for the marine biota. These include: i) the recognition that iron is a bioactive element necessary for e.g. photosynthesis (Chereskin and Castelfranco, 1982; Greene et al., 1992; Geider et al., 1993), nitrate metabolism (Timmermans et al., 1994; de Baar et al., 1997; van Leeuwe et al., 1997),  $N_2$  fixation (Mills et al., 2004) and detoxification of reactive oxygen species (Sunda and Huntsman, 1995), in concert with ii) the paradox that the biota, notably as phytoplankton needs relatively high quantities of such a scarce element in the marine environment (Boye, 2000).

At various stations in the oceans, the vertical distribution of concentrations of dissolved iron and major nutrients (N and P) are closely correlated, suggesting control by biological uptake and regeneration cycles (Martin and Gordon, 1988; Sunda and Huntsman, 1995; Johnson et al., 1997). However, at other stations such correlations have not been observed. There are still many uncertainties about the identity of the Fe species available for biological uptake by eukaryotic phytoplankton as well as their responsible uptake mechanisms.

Redox reactions and speciation are shown to be important for the bioavailability of Fe for phytoplankton. The Fe redox cycle initiated by photochemical processes is mentioned as an important mechanism by which colloidal and chelated Fe are converted into more kinetically labile inorganic species of Fe(II) and Fe(III), resulting in a higher bioavailability to phytoplankton (Finden et al., 1984; Wells and Mayer, 1991; Johnson et al., 1994; Miller and Kester, 1994). The Fe(II) is assumed to be a Fe fraction suitable for biological uptake (Anderson and Morel, 1980; Anderson and Morel, 1982; Takeda and Kamatani, 1989; Maldonado and Price, 2001).

Organic complexation increases iron solubility with respect to the formation of iron hydroxides and oxides. At the same time, it minimizes the adsorption of iron to particles, thereby maximizing the iron retention time in seawater, which benefits the biological community (Johnson et al., 1997; Sunda, 1997).

Once available for biological uptake, two common systems to transport iron over a membrane are: i) siderophore systems in which released strong Fe(III)-organic chelators are transported into the cell, and ii) ferrous or ferric ion membrane transporters binding external Fe(II) or Fe(III) upon ligand exchange with reactive iron species.

The siderophore system is well known and extensively described for marine bacteria (Hutchins et al., 1999; Yoshida et al., 2002; Martinez et al., 2003; McCormack et al., 2003; Weaver et al., 2003; Gledhill et al., 2004). Yet, there is no conclusive evidence for siderophore production in eukaryotic marine phytoplankton, although there are some studies indicating the release of siderophores or iron chelators by dinoflagellates, diatoms, *Emiliania huxleyi* and a green alga (Trick et al., 1983; Boye and van den Berg, 2000). Also, other studies have demonstrated uptake of organically complexed Fe by phytoplankton (Soriadengg and Horstmann, 1995; Hutchins et al., 1999; Maldonado and Price, 2001).

The second Fe uptake mechanism in eukaryotic marine phytoplankton is by membrane transporters that directly access dissolved monomeric inorganic iron species (Sunda, 2001). A direct relationship was found between the concentration of kinetically labile inorganic Fe species and iron uptake by the diatoms *Thalassiosira weissflogii* and *T. pseudonana* and the coccolithophore *Pleurochrysis carterae* (Anderson and Morel, 1982; Hudson and Morel, 1990; Sunda and Huntsman, 1995). According to Morel et al. (1991) the effectivity of the process is depending on the loss of water from the inner coordination sphere of the inorganic Fe species resulting in a ligand exchange between the inorganic Fe species and the receptor ligand sites on the membrane-bound iron transporters. Thus, the Fe(III) chelates and colloids are not directly available for uptake because their ligand exchange kinetics is too slow.

Equal uptake rates of dissolved inorganic Fe(III) and Fe(II) in *Thalassiosira weissflogii* (Anderson and Morel, 1982) in concert with the suggestion of Hudson and Morel (1990) that Fe(III) is the actual species transported over the membrane hint to a mechanism in

which Fe(II) is oxidized first, followed by binding to the transporter and transport over the membrane (Sunda, 2001). Supporting this idea is the similar rate constant for the loss of coordinated water, controlling ligand-association rate kinetics, for both Fe(III) and free Fe(II) in seawater (Hudson, 1998).

Not only does the chemistry of iron in seawater regulate its biological uptake and utilization by phytoplankton, conversely the activity of the phytoplankton also influences the speciation and cycling of iron (Wells et al., 1994; Price and Morel, 1998). Complexation of Fe by organic iron binding ligands not only increases Fe solubility but also influences the photochemistry and subsequently the bioavailability of Fe (Barbeau et al., 2003). Another option to examine is the role of the phytoplankton itself in generating stable Fe(II) levels or in inducing Fe(II) producing processes. Various reports describe high Fe(II) concentrations coinciding with chlorophyll-*a* maxima (O'Sullivan et al., 1991; Emmenegger et al., 2001; Shaked et al., 2002). The ability of different phytoplankton species to enzymatically reduce Fe(III) at the cell surface is known for a long time (Allnut and Bonner, 1987; Jones and Morel, 1988; Maldonado and Price, 2000), yet the underlying mechanism being poorly understood. Furthermore, Kuma et al. (1992) noticed high concentrations Fe(II) during spring blooms in Funka Bay and related this to the release of organic components from phytoplankton inducing the photoreduction of Fe. The presence of various dissolved organic substances, generally considered to be organic components released from phytoplankton, such as sugar acids, indeed improved the photoreduction of Fe (Kuma et al., 1995).

## 1.5 Rationale of the thesis

The redox-cycle of iron, initiated by photochemical processes, is mentioned as an important mechanism by which Fe is made more available for biological uptake by phytoplankton (Wells and Mayer, 1991; Johnson et al., 1994; Miller and Kester, 1994; Barbeau et al., 2001). This means that, theoretically, increased levels of UVB, related to the stratospheric ozone depletion occurring every Antarctic spring, could positively affect phytoplankton growth via the chemistry of iron.

The main scope of this thesis is to investigate the influence of irradiance and particularly UV radiation on the chemistry of Fe in seawater. The Fe chemistry is not only spectrally dependent via the reduction but also via the oxidation of the Fe redox cycle. Hydrogen peroxide is the main Fe(II) oxidant in sunlit waters. Therefore the influence of UV radiation on the photochemical production of H<sub>2</sub>O<sub>2</sub> (Chapter 2) and the photoproduction of Fe(II) was investigated first. Photoreduction was the most likely candidate mechanism to explain the retained high Fe(II) concentrations during the iron enrichment experiment SOIREE in the Southern Ocean. Here, suggested maximal photoreduction rates at 20 m depth were as high as 370 pM hr<sup>-1</sup>, despite cloudy skies (Croot et al., 2001). Therefore, the role of

UVB, UVA and VIS in driving the Fe redox cycle was investigated in deck-incubations during the *in situ* iron enrichment experiment EisenEx (Gervais et al., 2002) in the Southern Ocean (Chapter 3). To be able to accurately investigate and predict the relative impact of enhanced UVB on the photoproduction of Fe(II) in the Southern Ocean a spectral weighting function for Fe(II) photo-production from amorphous Fe hydroxides was established. A weighting function is a set of coefficients described by a mathematical expression that weighs the energy of a discrete wavelength with its biological or chemical effect, in this case Fe(II) photoproduction. This even allows prediction of the impact of natural variability of irradiance, as well as the anthropogenic effect of increased levels of UVB due to springtime stratospheric ozone depletion (Chapter 4).

Organic complexation of Fe influences the photo(induced) redox cycle. Inspired by the article of Witter et al. (2000) the influence of five model Fe-chelating ligands on the photoproduction of Fe(II) was studied including: tetrapyrrole ligands (phaeophytin and protoporphyrin IX), terrestrial hydroxamate siderophores (ferrichrome and desferrioxamine B) and the terrestrial Fe-complexing storage ligand inositol hexaphosphate (phytic acid) (Chapter 5).

It is known that phytoplankton releases organic substances to the environment. Furthermore it has been suggested that they produce siderophores (see above section 1.2). Phytoplankton could therefore actively alter the chemical environment of the Fe. This and subsequent possible photodegradation of organically bound Fe could, in this way, influence the biogeochemical cycle of iron. To study this, the influence of two Southern Ocean phytoplankton species, *Thalassiosira* sp. and *Chaetoceros brevis*, on the dissolved Fe concentration, the organic complexation of Fe and on Fe(II) photoproduction under three different optical treatments, UVB+UVA+VIS, UVA+VIS and VIS, was investigated (Chapter 6).

There is much discussion about the susceptibility of natural organic Fe binding ligands for photodegradation resulting in Fe(II). At the moment the importance of photodegradation of organic Fe binding ligands occurring in the marine environment is based on suggestions to explain datasets (Boye et al., 2001; Macrellis et al., 2001), laboratory experiments with single ligand species (Barbeau et al., 2001; Barbeau et al., 2002; Barbeau et al., 2003) and some field data showing marginal photo induced effects on the concentration of Fe binding ligands (Powell and Wilson-Finelli, 2003). On the contrary, Moffett (2001) concluded from the lack of publications describing shallow mixed layer minima and other features suggesting a surface, photochemical sink that photodegradation is not an important mechanism in marine Fe chemistry. To address the importance of the photodegradation of organic Fe binding ligands we performed experiments with estuarine Marsdiep and Scheldt water, containing high concentrations of organic Fe-binding ligands. Investigated was the presence of a weak Fe-binding ligand keeping dissolved Fe concentrations higher than the

concentrations of strong organic ligands and the solubility product of Fe (Chapter 7) and the influence of UV on this weak Fe-binding ligand and on the photodegradation of the strong organic Fe-binding ligands (Chapter 8).

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