

University of South Australia



**PROJECT REPORT:**  
**Dissolution of Hematite in Seawater and  
its Potential Impact on Phytoplankton  
Growth**

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## Executive Summary

Iron is well known to be a key limiting factor controlling primary production in the world's oceans. In many oceans, including the Southern Ocean, primary production is lower than expected based on macronutrient levels (e.g. nitrogen, phosphorus). Numerous studies have demonstrated in laboratory studies that increasing soluble iron concentrations enhance phytoplankton growth when compared to typical surface oceanic water concentrations. Furthermore, "meso-scale" *in-situ* iron fertilization experiments have similarly demonstrated that increasing dissolved iron concentrations substantially elevates the primary production in these waters. Marine environments demonstrating these characteristics are commonly referred to as High Nutrient Low Chlorophyll (HNLC) waters.

In HNLC waters, which are usually off continental shelves, although some coastal waters are genuine HNLC waters, the main source of iron is from atmospheric deposition. Iron oxides in well oxygenated high pH waters are highly stable, and under many situations, are not soluble to a significant extent. Hematite solubility is among the most stable Fe species in well mixed O<sub>2</sub>-H<sub>2</sub>O systems. However, in HNLC environments even a small increase in dissolved iron has been shown to stimulate algal growth. There are several factors which may enhance the dissolution of Fe in high pH waters. These include:

- concentration of dissolved organic matter;
- mineralogy (ferrihydrite, goethite, hematite);
- ionic substitution;
- particle-size and surface area;
- particulate deposition rate;
- redox; and
- ultra-violet radiation.

Evidence exists within the literature that phytoplankton, terrestrial plants and bacteria may enhance Fe solubility when in Fe-limited or deficient waters. The organic exudates

released by these organisms are usually low molecular weight organic acids, which are able to complex Fe and other trace elements, and also reductively dissolve Fe minerals. The presence of organic ligands in the presence of sunlight may enhance iron oxide dissolution, especially at low pH. The likelihood of photo-reductive dissolution reactions being significant decreases as the pH increases. However, limited studies have been published on the importance of photolytic-redox reactions with natural iron oxides.

Nevertheless, the literature does suggest limited Fe solubility in high pH systems such as seawater.

Large differences in dissolved Fe concentrations exist between HNLC waters and typical coastal waters. In general, Fe concentrations (particulate and dissolved) decrease with distance from the shore-line, continuing away from continental shelves. Higher chlorophyll concentrations in coastal waters may be partly attributed to greater dissolved Fe. However, numerous factors influence phytoplankton in these areas. Genuine coastal HNLC areas have been identified, especially in upwelling oceans, such as around the Great Australian Bight.

Hematite solubility in coastal waters is likely to be limited, although higher than in HNLC areas. Coastal waters possess higher dissolved organic carbon concentrations, higher sediment loads, and high phytoplankton abundance. These factors may potentially enhance solubility.

Hematite deposition overall is generally less likely to have an impact on primary productivity in coastal waters than HNLC areas. Unless data is available on the response of phytoplankton to Fe addition in coastal waters, and also the solubility of specific Fe sources, it is difficult to make conclusions about the impact of hematite ore deposition into seawater.

### **Iron solubility in seawater-Chemical analysis:**

The data on the solubility of iron in seawater is presented in Appendix B. Extraction of 0.5-2.0 mm size fraction of iron ore material did not yield any soluble iron content. Extraction of 0.1- 0.5 mm ore fraction with seawater resulted in 0.62 mg/kg (61.9 ppb) soluble iron. Although this soluble iron is only a minor amount, its impact on the phytoplankton biomass needs to be determined.

It is recommended to conduct further research into the quality of seawater (chemical analysis) collected from the port area including the upstream and downstream areas which will help to assess the impacts of iron ore dust on phytoplankton biomass in the coastal system.

Centrex has provided background data on the shipment size (80,000 tonnes) and frequency (shipment every 18 days) for their Eyre Peninsula project. Information from their environmental consultants indicates that minimal dust escape will occur during normal ship loading. The environmental consultant has also indicated that in a worst case situation up to 70kg of dust may escape the loading process onto the surrounding land or waters. Based on preliminary analysis of an Fe rich seawater sample, 931  $\mu\text{g Fe/kg ore}$  would be extracted from the 0.5 – 0.1 mm fraction. Assuming 75 kg and a volume of impacted water of 50 000  $\text{m}^3$ , it is estimated that the Fe concentration in that body of water would increase by 1.5  $\text{ng/L}$  or 0.02  $\text{nM}$ , assuming little dispersion and sedimentation.

With such a small mass of product being deposited into a large sample area the large scale effects may be minimal, especially in iron-rich waters, based on the preliminary work conducted.

Further test work is required to determine the impact of this event in the waters surrounding the loading operation, which will involve testing water samples from the ship loading area for baseline data and then repeating the solubility tests. Until these tests are completed, a definitive answer on the effects of soluble iron on phytoplankton biomass cannot be stated.

## 1. Introduction

The utilization of iron can be traced back to the early history of human civilization. Iron utilization is directly associated with development in modern society. Iron is applied worldwide for commercial purposes and is applicable in more areas than possibly any other metal. Iron alloys are eventually processed to containers, cars, laundry machines, bridges, buildings, and even small springs. Iron compounds are applied as pigments in glass and paint production, or are processed to pharmaceuticals, chemicals, iron fertilizers, or pesticides. These are also applied in wood impregnation and photography. Iron compounds are applied in precipitation reactions, to remove compounds from water in water purification processes.

The world's crude steel production in recent years is over 1.2 billion tons. Some 300 million tons are recycled. The largest crude steel producer in the world during the last decade has been China which produces over 1/3 of global crude steel. China is also the largest steel user in the world which consumed around 30% of total globe annual steel produced. The crude steel production in Australia is around 8 million tonnes annually and ranked in at 22<sup>nd</sup> in the world. Iron ore production among the top three countries are China, Brazil and Australia with just over 200 million tons each. Australia is ranked as the No 1. in iron ore exporting country in the world at present. The largest iron ore mine in the world is Mount Whaleback in the Pilbara, Western Australia.

Iron is an essential element for all organisms, however, it is only required in small quantities (McBride, 1994). Although excessive Fe intake in humans can be toxic, Fe deficiency in humans and other organisms is the most common issue worldwide. The total amount of iron in the human body is approximately 4 g, of which 70% is present in red blood colouring agents. Iron is a dietary requirement for humans, just as it is for many other organisms. Men require approximately 7 mg iron on a daily basis, whereas women require 11 mg. Iron deficiency in humans occurs in all developed countries, although, as in the case of other micronutrients, it is a greater issue in developing countries. Similarly, Fe deficiency in terrestrial and aquatic plant life plays a critical role on the productivity of an ecosystem. In calcareous, high pH soils, as well other soil types, Fe deficiency may limit the composition of plant life and agricultural crops which may be grown.

The productivity of marine ecosystems has long been known to be limited by low concentrations of dissolved Fe in seawater. Areas of the world's oceans which contain high concentrations of macronutrients such as N, P, Si, but possess low levels of phytoplankton are referred to as High-nutrient, low-chlorophyll (HNLC) regions. Approximately 40 % of the world's surface waters are HNLC waters, including much the Southern Ocean, equatorial Pacific and subarctic Pacific (Moore et al. 2002), stretching from the south of Australia and to the Antarctica southwards. As early as 1957 (Harvey, 1957) it was hypothesised that micronutrients such as iron and manganese limited the productivity of these waters. It wasn't until Martin et al. (1990) showed a clear relationship between dissolved Fe concentrations and chlorophyll (primary production) that the importance of Fe in marine productivity was widely recognised. Martin et al. (1990) further made the suggestion that addition of Fe would dramatically increase primary production (i.e. photosynthesis). The suggestion was that Fe fertilisation in the vast HNLC waters could potentially reduce global CO<sub>2</sub> emissions via massive stimulation of phytoplankton growth. The "iron hypothesis" proposed by Martin et al. (1990) resulted in a substantial research effort to understand the role that iron plays in the world oceans and the carbon cycle (Stumm and Morgan, 1996). In most HNLC areas, a substantial proportion of the iron comes from atmospheric deposition, originating from continental land masses, and therefore Fe deposition may be quite seasonal. Thus increases in Fe deposition to these regions are believed to result in increases in primary production, depending on the solubility and speciation of the iron introduced into the system.

## **2. Chemistry of Iron**

Acquisition of any element by phytoplankton is primarily governed by both the chemistry and speciation of that element in the environment. Similarly the fate and chemistry of iron introduced in the oceanic environment are influenced by a complex series of extra-cellular reactions that takes place dynamically in the sea water. Marine waters get enriched with iron in two different dominant oxidation states, namely ferrous (Fe II) and ferric (Fe III). However, Fe (III), representing the highest oxidation state of iron, is the most dominant inorganic species encountered in the seawater under oxic conditions (Waite 2001; Yoshida et al. 2006). Ferric iron is almost insoluble or very minutely

soluble. Also it is present in thermodynamically stable  $3^+$  oxidation state (Morel and Hering 1993; Stumm and Morgan 1996; Waite 2001). On the other hand, the dissolved inorganic species of Fe (III) in seawater predominantly include the hydrolysis products such as  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3^0$  and/or  $\text{Fe}(\text{OH})_4^-$  (Byrne and Kester 1976; Stumm and Morgan 1996; Hudson et al. 1992; Kuma et al.1993) (Figure 1). Precipitation of these ferric (oxyhydro-) oxides ( $\text{FeO}_x$ ) on phytoplankton cell surfaces is a common phenomenon in the surface waters of the oceans. This extracellular  $\text{FeO}_x$  also has potential affinity to adsorb other trace metal compounds (Tang and Morel, 2006).

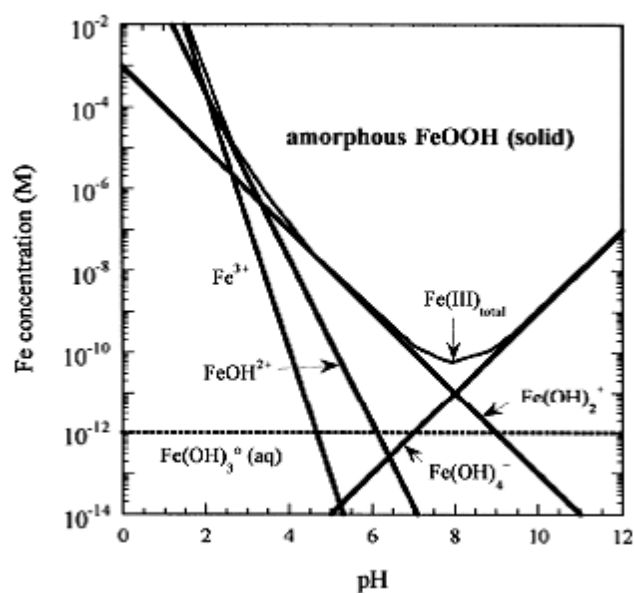


Figure 1: Solubility of iron as a function of pH in a  $\text{O}_2\text{-H}_2\text{O}$  system (Stumm and Morgan, 1996).

#### a. Sources of Iron in Seawater

There are three primary sources of iron in oceans and coastal waters: fluvial inputs, atmospheric deposition and upward transportation of Fe from hydrothermal vents, resuspension and diffusion (Ussher et al., 2004). The speciation of Fe from the different sources can vary and may include particulate iron, which may include phyllosilicate materials, iron oxides, biological, colloidal or dissolved forms, depending on the source (Stumm and Morgan, 1996). In coastal waters, one of the most important mechanisms of iron deposition into the ocean is by river borne fulvic-iron complexes. Krachler et al. (2005) reported that rivers draining sphagnum peatlands on silicate rocks contribute

dissolved Fe concentrations of more than  $8000 \text{ nmol L}^{-1}$ . They have estimated the dissolved iron input to the ocean's surface waters is around  $15 \times 10^9 \text{ mol y}^{-1}$  assuming that 5% of the global discharge of river water is true "peatland runoff"). Particulate-incorporated Fe from fluvial sources represents approximately 99% of the total inputs from riverine sources, and as such is not necessarily bioavailable of any biota. Furthermore, the residence time of Fe associated with particulates in the water column depends on the particle size fraction, and their subsequent settling rate, salinity and hydrodynamic conditions. The high concentrations of dissolved or colloidal fulvic acids is an important factor in explaining the higher concentrations of dissolved iron ( $\sim 1000 \text{ nM}$ ) in river systems, as compared to pelagic waters  $0.01\text{-}2.5 \text{ nM}$  (Ussher et al. 2004).

Particulate and dissolved Fe concentrations decrease with distance away from shorelines, and also with distance from the continental shelf (Falkowski et al. 1998). In coastal waters, due to the comparatively high inputs from rivers, resuspension, and diffusion, the role of atmospheric deposition is low. By contrast, pelagic surface water Fe concentrations are highly dependent on aerial deposition from crustal aerosols. Between  $20 - 50 \times 10^{12} \text{ g Fe y}^{-1}$  is deposited to the world's oceans, with dissolved Fe accounting for a small fraction ( $< 3\%$ ). However, wet deposited crustal or anthropogenic particulates may contribute significantly to the proportion of bioavailable iron in surface waters of HNLC. Dust particles are known to experience several wet-dry cycles in its transportation to the ocean. In addition, iron solubility in wet aerosols is likely to be much more soluble than in seawater (Siefert et al. 1994). Atmospheric dust ( $0.1 - 10 \text{ }\mu\text{m}$ , average  $2 \text{ }\mu\text{m}$ ) is believed to have aerial residence times of between days to several weeks. Results to date suggest that between 30 -95 % of Aeolian dust is removed via wet deposition processes (Jickells et al. 2005). Compared to seawater, cloud-rainwater is known to possess much higher oxalate, dimethylsulfide and formate concentrations (Erel et al. 1993; Faust and Zepp, 1993; Key et al. 2008), much lower pH values ( $\text{pH} < 5$ ) and exposed to considerable ultra-violet radiation before deposition. Photochemical reductive dissolution of Fe (III) minerals prior to deposition is favoured under these conditions (Schwertmann, 1991; Johansen and Key, 2006), and Fe (II) concentrations may reach concentrations in the range of  $1500 \text{ }\mu\text{M}$  (Ussher et al. 2005). Although aqueous Fe (II) is generally oxidised to Fe (III) rapidly in the high pH and Eh conditions of seawater, Voelker and Sedlak (1995)

suggested that in irradiated surface waters, Fe (II) may represent a 30-75 % of total dissolved Fe.

However, several coastal areas have been demonstrated to be genuine HNLC waters (Bruland et al. 2001; Hutchins and Bruland, 1998; Maldando et al.1999; Takeda et al. 1995; Hutchins et al. 2002). Hutchins and Bruland (1998) reported iron-limited diatom growth off the central California coastal upwelling regime. Initial Fe,  $\text{NO}_3^-$ ,  $\text{H}_2\text{SiO}_3$  and chlorophyll *a* concentrations were 0.1-0.5 nM, 12.3  $\mu\text{M}$ , 15.1  $\mu\text{M}$  and 0.52  $\mu\text{g L}^{-1}$ , respectively, typical of pelagic HNLC waters. Addition of 2.5 nM to HNLC waters resulted in a 3-4 fold increase in pelagic HNLC waters and importantly demonstrates that Fe-limitation is not unique to remote chlorophyll *a* concentrations over 2 days. Similar results were reported by Bruland et al. (2001), whilst Malkando et al. (1999) and Takeda et al. (1995) reported Fe limited productivity in the Pacific and Northwest Indian Oceans, respectively. The presence of non- pelagic HNLC waters importantly demonstrate that Fe-limitation is not unique to remote marine waters and that local conditions may be generated that can produce iron-limited primary productivity.

#### **b. Fe oxy(hydr)oxides**

An Iron-Oxygen system contains a variety of iron oxide and iron oxide hydroxide minerals. Iron oxides minerals include Hematite  $\alpha\text{-Fe}_2\text{O}_3$ , Magnetite,  $\text{Fe}_3\text{O}_4$ , Maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , Wüstite  $\text{Fe}_{1-x}\text{O}$ . Naturally occurring iron oxide hydroxides are also a common form of iron bearing minerals such as Goethite  $\alpha\text{-FeOOH}$ , Lepidocrocite  $\alpha\text{-FeOOH}$ , Akaganeite  $\beta\text{-FeOOH}$ , Feroxyhyte  $\delta\text{-FeOOH}$ , , Ferrihydrite, Bernalite  $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ . Hematite is the most common mineral form of iron oxide among iron oxides and oxide hydroxide, and is the main iron ore extracted from the earth. For this reason, the majority discussion in this report will mainly focused on hematite.

The crystallographic systems of iron containing minerals are varied and hematite crystallizes in the rhombohedral system. All iron bearing minerals are colored and the color of hematite varies from black to steel or silver-gray, brown to reddish brown, or red. Varieties of hematite in minerals include *kidney ore*, *martite* (pseudomorphs after magnetite), iron rose and specularite (specular hematite). While the forms of hematite

vary, they all have a rust-red streak. Hematite is harder than pure iron, but much more brittle.

Cation substitution on iron bearing minerals can take place on both naturally occurring and synthetic iron minerals. The cation substitutions of iron take place according to similarity principle in charge and size of the guest ion with host iron. This suggests that the level of substitution can be related, at least in part, to the match between the radius and valency of the guest ion and those of Fe. Common guest ions which are capable of replacing a portion of iron in the hematite lattice are Al (III), Cr (III), Mn (III) etc. Due to the isostructural substitution, the characteristics of the iron bearing minerals are also affected to a certain extent.

The formation of hematite is usually associated with volcanic activity, particularly when water is present. Grey hematite is typically found in places where there has been standing water or mineral hot springs. The mineral can precipitate out of water and collect in layers at the bottom of a lake, spring, or other standing water. Clay-sized hematite crystals can also occur as a secondary mineral formed by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite, is responsible for the red color of many tropical, ancient, or otherwise highly weathered soils

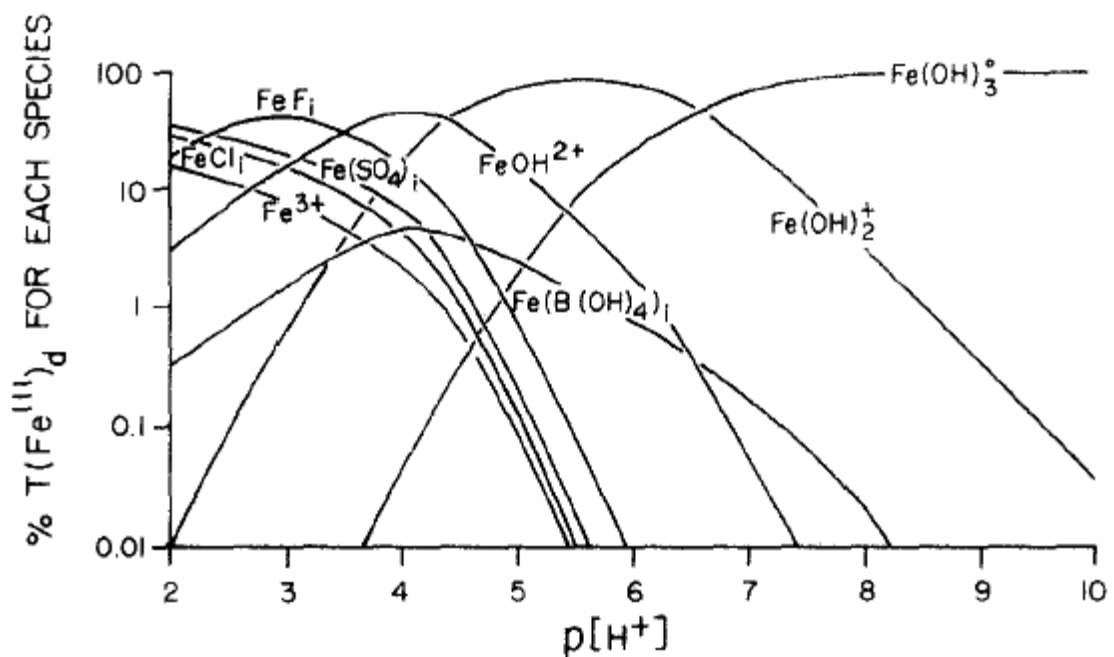
### **c. Solubility of Hematite**

#### **i. Effect of pH and Eh**

The solubility of pure iron oxide minerals at different pH and Eh conditions has been very thoroughly studied under laboratory conditions. In the euphotic zone of most coastal and oceanic waters, the pH is generally 8.2 and considered oxic. Therefore, in these environments dissolved inorganic iron exists almost exclusively as ferric iron ( $\text{Fe}^{\text{III}}$ ), and a very small proportion as ferrous iron ( $\text{Fe}^{\text{II}}$ ). The two oxidation states have unique biogeochemical behaviour, as they are known to be present in different concentration profiles in the ocean environment.  $\text{Fe}^{\text{II}}$  has a considerably higher solubility at a given pH, due to its much higher first hydrolysis constant ( $\text{pK}_{\text{a},1} = 9.4$ ).  $\text{Fe}^{\text{II}}$  becomes unstable and oxidises rapidly to  $\text{Fe}^{\text{III}}$  under aerobic conditions at  $\text{pH} > 5.0$ .  $\text{Fe}^{\text{III}}$  readily becomes hydrolysed and forms polynuclear oxyhydroxides in a step wise reaction, and

hydrolysed forms of Fe represent major dissolved species of Fe (Figure 2). As a result, the solubility of iron decreases with increase of pH greater than 4, and increases to a pH of approximately 8.0. In estuarine environments, in anoxic sediments, the iron concentrations are considerably greater due to reductive dissolution of iron oxides and the higher solubility of  $\text{Fe}^{\text{II}}$  (Langmuir, 1997). The slightly higher dissolved Fe concentrations found with increasing depth, similarly to nutrient deep-sea profiles, may be attributed to consumption by biota in the euphotic zone, rather than Eh influences.

Under the oxic conditions of upper surface waters in seawater, and in the absence of biotic-mediated dissolution or photolysis, hematite dissolution without significant aerial transportation will ultimately be controlled by seawater properties, particularly, the ambient pH. Ignoring the role of dissolved organic substances, model calculations performed with PHREEQC (Parkhurst, 1995), suggest a soluble concentration in the order of  $10^{-4}$  nM, which is lower than reported concentrations in deep-sea oceans (Bergquist et al. 2007; Takata et al. 2004; Ussher et al. 2004). Lui and Millero (2002) have attributed differences in solubility in deep-sea oceans to dissolved organic ligands.



**Figure 2.** Speciation of dissolved iron in sea water as affected by pH (Byrne and Kester, 1976)

## ii. Effect of ionic strength

Seawater contains high concentrations of cations and anions, and are generally constant away from estuarine waters (Stumm and Morgan, 1996). Table 1 provides concentrations of the major anions and cations. The ionic strength has a very limited role in influencing iron solubility in seawater. Lui and Millero (1999) found that the solubility of synthetic iron oxides was considerably lower in NaCl solutions at different ionic strengths compared to seawater at the same pH and temperature. Lui and Millero (2002) later concluded that the additional solubility of iron oxides in seawater compared to ionic solutions was principally due to dissolved natural organic matter. Complexation of Fe from  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  represents a very small percentage of total Fe. However, Surana and Warren (1969) found that the presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  accelerated the rate of dissolution of natural goethites. The proposed mechanism was the formation of surface complexation at the surface, enhancing detachment and accelerated dissolution. A source of Fe ignored in many studies on atmospheric dust deposition into seawater is from ion exchange from  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  of deposited dust. Although  $\text{Fe}^{3+}$  is preferentially exchanged at exchange sites (McBride, 1994), the high concentration of positive charge ( $\sim 0.62 M$ ) some exchangeable Fe being released from terrestrial dusts. The literature is dominated by studies on the dissolution of synthetic hematite and goethite in seawater.

Table 1. Ionic composition of seawater (Stumm and Morgan, 1996).

Constituent	Concentration $\text{g kg}^{-1}$ seawater
$\text{Na}^+$	10.800
$\text{Mg}^{2+}$	1.300
$\text{Ca}^{2+}$	0.400
$\text{K}^+$	0.400
$\text{Sr}^{2+}$	0.008
$\text{Cl}^-$	19.3
$\text{SO}_4^{2-}$	2.712
$\text{Br}^-$	0.067
F-	0.001
B	0.005

### iii. Effect of Particle Size

Solubility products of pure solid phases are always determined using highly crystalline and finely divided crystals (Stumm and Morgan, 1996). As particle size increases, the surface area available for reaction increases (Sposito, 1994). However, in nature, mineral phases are often not finely divided or pure, which is known to influence mineral solubility. Torrent et al. (1987), for example, found that in a range of hematites a significant portion was non-crystalline and readily soluble. In general, as particle size decreases the rate and magnitude of dissolution of a mineral phase increases. Empirically determined solubility constants for the different particle size (S) fractions can be approximated according to (Stumm and Morgan, 1996):

$$\log K_{s0} = \log K_{s(S=0)} + \frac{2\gamma}{2.3RT} S \quad (x)$$

Where  $S=0$ ,  $\log K_{s(S=0)}$  is estimated solubility constant,  $\log K_{s0}$  is the particle and  $\gamma$  is the free surface energy of the solid,  $R$  is the gas constant and  $T$  is temperature (K). Cornell and Giovanoli (1993) found that hematite dissolution rates were highly dependent on initial surface area, although hematite heated at  $> 600^\circ\text{C}$  showed higher dissolution rates compared to synthetic hematite, possible due to greater structural defects due to heating (Cornell and Schwertmann, 2003). The rate of particle settling is similarly highly dependent on particle size, such that the proportion of fine particulates deposited into the ocean is a critical issue, since residence in the euphotic zone and dissolution rates are both higher under the same conditions as coarse particulates.

Under the same environmental conditions (temperature, solution composition, light), dissolution of iron oxides depends on crystal size, surface area and ionic substitution. However, since many of these parameters are closely related, it is often difficult to distinguish the role of each factor (Cornell and Schwertmann, 2003). The relationship between surface area, particle size and dissolution characteristics are complicated by the role of ligand-assisted dissolution and the mechanism of dissolution (Duckworth and Martin, 2001). The surface area of hematites were found to increase with increasing Al substitution up to 14 mol%. In this study the dissolution decreased with increasing Al substitution (Torrent et al. 1987). Similarly, Larsen and Postma (2001) found that, with the exception of lepidocrocites, dissolution rates were related to surface area.

#### iv. Effect of Ionic Substitution (Solid-solutions)

Naturally occurring hematite and goethite are unlike synthetic forms. Natural iron oxides typically have significant structural defects and also significant amounts of ionic substitutions from other elements. The principal element substituting for  $\text{Fe}^{3+}$  in hematite and goethite is  $\text{Al}^{3+}$  (Cornell and Schwertmann, 2003). However, other elements are known to also substitute for Fe, including Mn (Alvarez et al. 2006; Cornell and Schwertmann, 2003), Ni, Zn, Co and Cr (Singh et al. 2002; Trolard et al. 1995; Manceau et al. 2000)). Substitution of foreign elements into mineral lattice structure are solid-solutions, and may significantly influence the solubility of the substituting element, but more importantly, the mineral itself (Stumm and Morgan, 1996; McBride, 1994; Trolard et al. 1995).

Aluminum is the most common and usually significant element in iron oxides. Despite Al often increasing the surface area, aluminum is typically associated with increasing stability of hematite (Cornell and Schwertmann, 2003). Torrent et al. (1987) showed clearly in synthetic goethite and hematite that increasing Al substitution resulted in a decreased rate of reductive dissolution by Dithionite (Fig.3). The effect of other transition element substitutions have been less well studied, however, they generally show similar trends for hematite. Xie and Dunlop (1998) found that natural maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) dissolved faster than goethite or hematite, and that Cu, Zn and Pb constituents were released at the earlier stages of dissolution in 6 M HCl. Alvarez found that increasing Mn content in synthetic goethite increased the dissolution rate, whilst it was reduced in hematite.

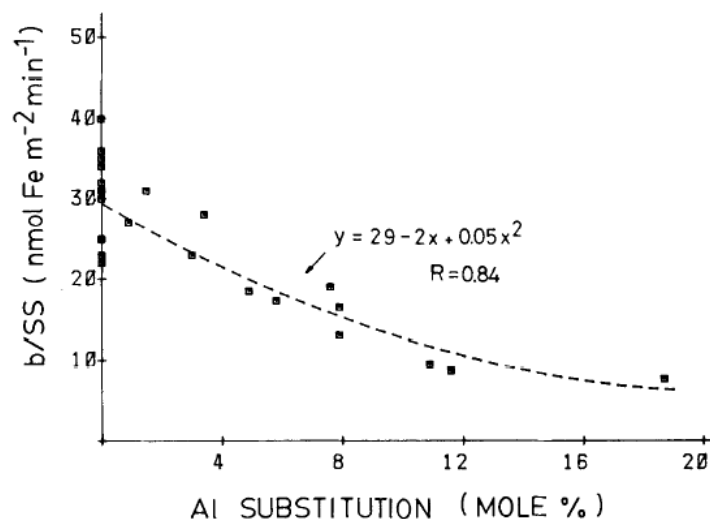


Fig 3. Effect of Al substitution on the rate of hematite reductive dissolution by dithionite (Torrent et al. (1987)).

## **Effect of temperature**

Solubility of iron in sea water is greatly controlled by temperature (Liu and Millero, 1999; 2002). Iron solubility in marine water is greater at lower temperatures. The temperature effect is much more prominent at low pH condition than at higher pH values, due to the low solubility at these conditions. Liu and Millero (2002) observed a solubility of  $0.5 \pm 0.07$  nM,  $0.35 \pm 0.06$  nM and  $0.34 \pm 0.05$  nM of iron at  $5^{\circ}$ ,  $25^{\circ}$  and  $50^{\circ}$  C temperatures, respectively at pH 8.1. The high salinity level of sea water, which occurs naturally, is also a factor responsible for enhancement of iron solubility compared to low ionic strength water.

## **v. Effect of Organic substances**

Organic chelators exist in seawater at significant levels. The concentration of such organic ligands in marine waters depends heavily on the location and distance from, depth of water, season and other among other factors (Nakabayashi et al. 2001, Kuma et al. 1996). Dissolved and particulate iron concentrations in near shore waters is generally considered to be quite high compared with the pelagic waters partly due to terrigenous natural organic matter. Coastal waters possess much greater particulate iron concentrations due to their proximity to fluvial deposition sources (Falkowski et al. 1998). Nonetheless, the Fe (III) solubility in sea water is greatly controlled by organic complexation with those chelator compounds (Kuma et al. 1996; Waite 2001; Liu and Millero 2002; Tani et al. 2003; Chen et al. 2004; Takata et al. 2004). It subsequently regulates dissolved iron concentrations in seawater (Nakabayashi et al. 2001; Rose and Waite 2004). The natural organic compounds in marine systems in general increase the overall solubility of iron. They have very high selectivity and affinity towards iron which ensures attainment of reasonably rapid equilibrium. These compounds include siderophore and many other unidentified molecules. They contain various Fe-binding functional groups such as hydroxamate or catecholate (Macrellis et al. 2001). Siderophores are excreted into the sea water by certain aquatic microorganisms. They are usually low-molecular weight (300–1000 Da) compounds. Specific functions of siderophore include binding iron with certain marine cyanobacterial species (Hutchins et al. 1999) or certain marine heterotrophic bacterial species (Reid et al. 1993) and thus helping iron uptake by those microorganisms.

The role of organic acids and dissolved organic matter is seen in Podzols. In the absence of light, Fe, Al, Mn oxides in Podzol and podzolic soils are reductively dissolved by leaching of soluble organic acids. Podzol soils are distinguishable by the clear definition of illuviated and eluviated horizons with increasing depth. Podzols are broadly defined by the removal of metal oxide minerals in one horizon (E Horizon or bleached horizon) and accumulated at another horizon with depth (eluviated). Although various hypotheses have been proposed to explain the accumulation in the eluviated horizon, it is generally accepted that the removal of Fe, Al, Mn is due to reductive dissolution from organic acids (Lundstrom, 2000; Lundstrom, 1993; Raulund-Rasmussen *et al.* 1998). The reductive dissolution of metal oxides in the E horizon during podzolization is proposed to occur via ligand substitution reactions (either inner sphere (ligand exchange) or outer-sphere (anion exchange) followed by electron transfer reactions between the reductant (organic acid) and oxidant (metal surface) (Fig. 4). Reductive dissolution in aquatic systems are proposed to occur via similar mechanisms, however, this assisted in the presence of ultra-violet radiation (See Photolysis).

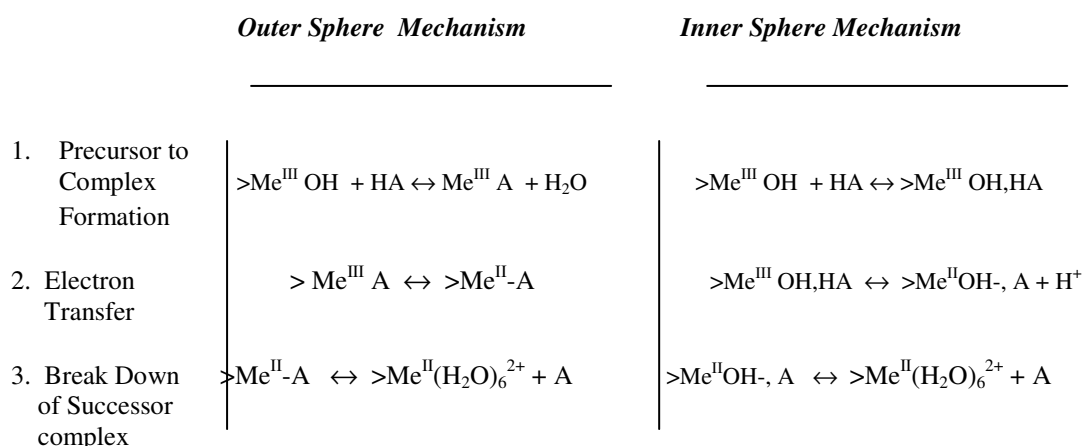


Fig. 4. Illustration of proposed mechanisms for the reduction of metal oxide surfaces by substituted phenols as proposed by in Sparks (1989).

## vi. Photolysis

It is a well established mechanism that changes in the redox chemistry of iron in sea water is primarily initiated by some photochemical processes (Rich and Morel, 1990; Johnson et al. 1994; Wells et al. 1991; Kuma et al. 1996; Rijkenberg et al. 2005). Iron is photoreduced by light with wavelengths less than 560 nm, and is typically in the UV region (Rich and Morel, 1990). Photoreduction increases the lability of colloidal fraction

of iron in the sea water. The extent of this increase depends on the spectral lines of the applied light (Wells et al. 1991) as well as light intensity (Waite et al. 1995). Generally, it increases with decreasing wavelengths (Wells et al. 1991). Although the UV range of light negatively affects the marine primary producers by impairing photosynthesis, these light spectra have a positive effect in releasing sequestered iron ( $\text{Fe}^{\text{III}}$ ). Thus, the retention time and bioavailability of iron in the euphotic zone can increase in the part of the year when UV radiation is high. However, presence of an elevated level of any oxidising agent (such as ozone) in the sea water can suppress the photoreduction process. The effect of photoreduction by UV radiation in increasing soluble iron level is more prominent in the oceanic waters compared to the coastal seas. This may be because UV radiation causes reduction in the organic matter content of the sea water by oxidative reaction and organic matter content in coastal water is much more than in the open ocean. It has been reported that iron solubility limits of fresh solid amorphous  $\text{Fe}(\text{OH})_3$  in ultraviolet (UV)-irradiated open-ocean waters (free of organic ligands) is  $\leq 0.1 \text{ nmol L}^{-1}$  (Kuma et al. 1996), whereas for inorganic  $\text{Fe}^{\text{III}}$  hydrolysis species ( $\text{Fe}^{\text{III}}$ ) it is  $\sim 0.08 \pm 0.03 \text{ nmol L}^{-1}$  (Wu et al. 2001).

In natural waters, solar radiation in the UV to near-UV range has been attributed to an increase in dissolved Fe concentrations (mostly as  $\text{Fe}^{\text{II}}$ ) (Wells et al. 1991a; 1991b; McKnight et al. 1988; Emmenegger et al. 2001). Little to no data exists on the extent to which photoreduction of hematite in seawater results in (a) significant local increases in dissolved Fe concentrations and (b) whether this is bioavailable to phytoplankton. Hematite is the most stable Fe oxyhydroxide mineral in the pH-Eh range. There is some evidence that at the pH and Eh of seawater, hematite is unlikely to be photoreduced. Sherman (2005) suggested that the photolysis of hematite is not feasible at high pH, but conceded that organic ligands may play some role. Siffert and Sulzberger (1991) found that hematite was photoreduced to a very marked extent in acidic (pH 3) deaerated (limited  $\text{O}_{2(\text{aq})}$ ) solutions in the presence of oxalate (1 mM); however, in the presence of  $\text{O}_{2(\text{aq})}$  photoreduction of hematite (pH 3, oxalate) was severely retarded. Similarly, Sulzberger and Laubscher (1995) similarly found that the more stable iron oxyhydroxides (hematite and goethite) are not readily photoreduced in oxic environments, in comparison to ferrihydrite and lepidocrocite, even in the presence of acidic (pH 3) oxalate solutions (1 mM). They suggested that the rate of  $\text{Fe}^{\text{II}}$  re-oxidation was greater than  $\text{Fe}^{\text{II}}$  removal from the solid-solution interface, limiting net dissolution of these phases. Re-

oxidation of  $\text{Fe}^{\text{II}}$  may be due to  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$  and  $\text{O}_2$ . The highly favourable conditions in these experiments do not exist in seawater, and these studies alone indicate that substantial photoreductive dissolution in seawater is unlikely.

It is necessary to be cautious about these conclusions, as they represent a very small body of research. For example, despite the high pH, Emmenegger et al. (2001) has shown the dissolved Fe concentrations to be stimulated (increased) as a result of photoreduced Fe minerals in the pH range of 6.9-9.1 in freshwater systems. Furthermore, recent literature has shown unequivocally that many members of the plant-kingdom are able to actively reductively dissolve Fe minerals for nutritional purposes. Terrestrial and aquatic species are known to release organic exudates, including oxalate, presumably as a micronutrient sequestration strategy. Organic exudates are usually only produced when under some kind of stress, such as for example, nutrient limitation or toxicity. Marine phytoplankton have been reported, for example, to release dimethyl sulphide (DMS), under iron-deficiency, high UV-radiation, high  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}_2$  (Sunda et al. 2002). Key et al. (2008) has shown that DMS and other oxidation products of dimethyl sulfoxide (DMSO) in the presence of UV radiation caused significant photoreduction of ferrihydrite. Similarly, Barbeau et al. (2001) found that microbially produced siderophores caused photoreduction, suggested to increase Fe acquisition. Unfortunately, data on hematite in seawater in this new area of research does not seem to have received much attention. Also, the role that dissolved organic carbon plays in Fe oxyhydroxide photochemistry in seawater has received little attention, but may play a significant role (Stumm and Morgan, 1995).

### **3. Iron Uptake by Phytoplankton**

The majority of iron released from the lithosphere into surface environments including soils is by weathering of primary silicate and sulphide minerals. In the presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$  and in the common pH range ( $>2$ ) of surface environments, the released  $\text{Fe}^{\text{II}}$  is oxidized to  $\text{Fe}^{\text{III}}$  and followed by rapid hydrolyzed to form  $\text{Fe}^{\text{III}}$  oxide and oxy-hydroxide. The average concentration of iron in the crust of the earth is 51g/kg, the third most abundant cationic element after Si (269 g/kg) and Al (81g/kg). All of the major iron oxides are found in living organisms except hematite. The absence of hematite suggests that biological environments do not provide suitable conditions for the formation of this

oxide. Iron is a dietary requirement for most organisms, and plays an important role in natural processes in binary and tertiary forms. Oxidized tertiary iron cannot be absorbed by organisms freely, except at very low pH values, due to ferric iron's very limited concentrations in the environment. Iron usually occurs in soils in tertiary form, but in water saturated soils it is converted to binary iron, thereby enabling plant iron uptake.

Most algae contain between 20 and 200 ppm of iron, and some brown algae may accumulate up to 4000 ppm. The bioconcentration factor of algae in seawater is approximately  $10^4 - 10^5$ . Sea fish contain approximately 10-90 ppm and oyster tissue contains approximately 195 ppm of iron (all are dry mass). Adding soluble iron may rapidly increase productivity in oceanic surface layers. It might play an important role in the carbon cycle. Iron is essential for nitrogen binding and nitrate reduction, and it may be a limiting factor for phytoplankton growth. Solubility in salt water is extremely low.

The iron cycle means reduction of tertiary iron by organic ligands (a process that is photo catalysed in surface waters), and oxidation of binary iron. Iron forms chelation complexes that often play an important role in nature, such as haemoglobin, a red colouring agent in blood that binds and releases oxygen in breathing processes. Organisms take up higher amounts of binary iron than of tertiary iron, due to higher solubility, and uptake mainly depends on the degree of saturation of physical iron reserves.

Green plants apply iron for energy transformation processes. Plants that are applied as animal feed may contain up to 1000 ppm of iron, but this amount is much lower in plants applied for human consumption. Generally plants contain between 20 and 300 ppm iron (dry mass), but lichens may consist up to 5.5% of iron. When soils contain little iron, or little water soluble iron, plants may experience deficiency problems. The Plant uptake ability varies markedly, and it does not only depend on soil iron concentrations, but also upon pH values, phosphate concentrations, Ca, K and genetic factors, even when sufficient amounts of iron are present. This is generally due to high pH values.

In oceanic waters off the continental shelf, phytoplankton growth is limited essentially by Fe. The so-called HNLC waters off the continental shelves of the world receive, as mentioned previously, Fe primarily by atmospheric dust deposition (Casar et al. 2007;

Jickells et al. 2005). Iron deposited directly into the euphotic zone of the HNLC waters is believed to be largely as Fe<sup>II</sup>, which is much more soluble, as a result of photoreductive dissolution in aerial transport (Jickells et al. 2005). The length of time that Fe remains as Fe<sup>II</sup> may be prolonged due to further oceanic photoreductive dissolution, and maintained via complexation with dissolved organic matter.

The large areas of HNLC waters and the limited primary productivity in these waters due to Fe limitations, has prompted considerable research into the ability of phytoplankton to “drawdown” CO<sub>2(g)</sub> from the atmosphere during photosynthesis (Jickells et al. 2005; Ussher et al. 2004). Stimulation of phytoplankton has potentially a much greater ability to reduce atmospheric CO<sub>2</sub> concentrations than terrestrial plant life. Numerous large scale iron fertilization studies (OIF) have been conducted to examine the role (Boyd et al. 2007). Although it is being widely criticized (e.g. Chisholm et al. 2001), OIF studies have demonstrated that Fe fertilisation in waters limited by Fe solubility and supply, even in small quantities, do stimulate primary production, which may last for several weeks (Boyd et al. 2007; Hutchins et al. 1999; Falkowski et al. 1998).

Coastal and continental waters generally have higher concentrations of dissolved concentrations of Fe, as a result of inputs from particle resuspension, fluvial inputs and diffusion from anoxic sediments (Falkowski et al. 1998; Ussher et al. 2004). Coastal waters also tend to be much more productive waters. Ward et al. (2006) found around the eastern Great Australian Bight that chlorophyll concentrations were comparatively high compared to deep-sea waters. Although, the coastal waters was far less productive in winter as compared to summer. The limiting effect of Fe on primary productivity of coastal waters depends on the location, climatic and hydrological factors (Hutchins and Bruland, 1998). HNLC waters in coastal areas have been reported to occur in several locations internationally (Bruland et al. 2001; Hutchins and Bruland, 1998; Maldando et al. 1999; Takeda et al. 1995; Hutchins et al. 2002). Primary productivity in these areas are likely to be highly variable, due to the proximity to land. Given that Fe deposition from the atmosphere does tend to control primary productivity growth in HNLC areas, it is important to understand the Fe biogeochemistry where Fe is being deposited. Coastal areas are however subject to higher sediment loads, dissolved organic carbon and proximity to Fe sources and are less likely to have Fe-limited primary productivity.

#### **4. Iron solubility in seawater study**

The data on the solubility of iron in seawater in this study is presented in Appendix B. Extraction of 0.5-2.0 mm size fraction of iron ore material did not yield any soluble iron. However, extraction of 0.1- 0.5 mm ore fraction with seawater resulted in 0.62 mg/kg soluble iron. Although this soluble iron is only a minor amount, its impact on the phytoplankton biomass needs to be determined. In addition, quantities of other soluble metals such as zinc, nickel, cobalt and manganese were found in the seawater extract of the ore material. These may have an impact on the phytoplankton biomass. Further research into the role that the hematite ore has on micronutrient chemistry and phytoplankton productivity is necessary before sound conclusions can be made.

#### **5. Conclusions and Future Work**

Iron is well known to be a key limiting factor controlling primary production in the world's oceans. In many oceans, including the Southern Ocean, primary production is lower than expected based on macronutrient levels (e.g. nitrogen, phosphorus). Numerous studies have demonstrated in laboratory studies that increasing soluble iron concentrations enhance phytoplankton growth when compared to typical surface oceanic water concentrations.

There are several factors which may enhance the dissolution of Fe in high pH waters. These include (a) concentration of dissolved organic matter; (b) mineralogy (ferrihydrite, goethite, hematite); (c) ionic substitution; (d) particle-size and surface area; (e) particulate deposition rate; (f) redox and (g) ultra-violet radiation.

Evidence exists within the literature that phytoplankton, terrestrial plants and bacteria may actively enhance Fe solubility when in Fe-limited or deficient waters. The organic exudates released by these organisms are usually low molecular weight organic acids, which are able to complex Fe and other trace elements, and also reductively dissolve Fe minerals. The presence of organic ligands in the presence of sunlight may enhance iron oxide dissolution, especially at low pH. The likelihood of photoreductive dissolution reactions being significant decreases as the pH increases. However, limited studies have been published on the importance of photolytic-redox reactions with natural iron oxides.

Nevertheless, the literature does suggest limited Fe solubility in high pH systems such as seawater.

Regarding the observed iron solubility in seawater in this study it would be prudent to carry out further work on the quality of seawater from the coastal area near the Centrex mining operations including the iron content in the upstream and downstream areas, which will help to establish more conclusive findings.

Centrex has provided background data on the shipment size (80,000 tonnes) and frequency (shipment every 18 days) for their Eyre Peninsula project. Information from their environmental consultants indicates that minimal dust escape will occur during normal ship loading. The environmental consultant has also indicated that in a worst case situation up to 70kg of dust may escape the loading process onto the surrounding land or waters. Based on preliminary analysis of an Fe rich seawater sample, 931  $\mu\text{g Fe/kg ore}$  would be extracted from the 0.5 – 0.1 mm fraction. Assuming 75 kg and an volume of impacted water of 50 000  $\text{m}^3$ , it is estimated that the Fe concentration in that body of water would increase by 1.5  $\text{ng/L}$  or 0.02  $\text{nM}$ , assuming little dispersion and sedimentation.

With such a small mass of product being deposited into a large sample area the large scale effects may be minimal, especially in iron-rich waters, based on the preliminary work conducted.

Further test work is required to determine the impact of this event in the waters surrounding the loading operation, which will involve testing water samples from the ship loading area for baseline data and then repeating the solubility tests. Until these tests are completed, a definitive answer on the effects of soluble iron on phytoplankton biomass cannot be stated.

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**Table 2. Solubility products of the iron oxides at 25 C**

Oxide	Sol. Product	K <sub>so</sub> or	Reference	
Goethite	*K <sub>so</sub>	1.4 ±	Schindler et al., 1963	
	K <sub>so</sub>	-40.7	Langmuir, 1969	
	* K <sub>so</sub>	-0.02 <sup>b)</sup>	Lindsay, 1979	
	* K <sub>so</sub>	0.82 <sup>b)</sup>	Tardy & Nahon, 1985	
	K <sub>so</sub>	-39.80)	Hsu & Marion, 1985	
	K <sub>so</sub>	-40.32 <sup>c)</sup>	“”	
	K <sub>so</sub>	-40.83 <sup>c)</sup>	“”	
	K <sub>so</sub>	1.40+0.1	Bigham et al., 1995	
	K <sub>so</sub>	-42.4 ±	Diakonov, 1998	
Lepidocrocit	* K <sub>so</sub>	2.72	Van Schuylenborgh, 1973	
	* K <sub>so</sub>	2.5	Hashimoto & Misawa, “”	
	K <sub>so</sub>	-39.5"		
	K <sub>so</sub>	-42.48 ±	Vale et al., 1974	
	* K <sub>so</sub>	1.39	Lindsay, 1979	
	K <sub>so</sub>	-41.4 <sup>b)</sup>	Diakonov, 1998	
	*K <sub>so</sub>	3.04 +	Biedermann & Chow,	
Schwertman	*K <sub>so</sub>	17.4+0.1	Bigham et al., 1995	
Schwertman	*K <sub>so</sub>	2.01 +	Yu et al., 2002	
Ferrihydrite	*K <sub>so</sub>	3.96 + 0.1	Biedermann & Schindler,	
	*K <sub>so</sub>	3.55 + 0.1	Schindler et al., 1963	
	K <sub>so</sub>	-39.5	Langmuir & Whitte- more,	
	K <sub>so</sub>	-39.02 +	Vlek et al., 1974	
	*K <sub>so</sub>	4.3 <sup>g)</sup>	Byrne & Kester, 1976	
	K <sub>so</sub>	-31.7 <sup>\$</sup>	Fox, 1988	
	K <sub>so</sub>	-37.7 <sup>b)</sup>	Diakonov, 1998	
	2-line	K <sub>so</sub>	-4.23	Yu et al., 2002
	6-line	*K <sub>so</sub>	-	" "
Fe(OH) <sub>2</sub>	*K <sub>so</sub>	12.85+0.2	Feitknecht & Schindler,	
	K <sub>so</sub>	-15.15 +	“”	
	K <sub>so</sub>	-14 <sup>f)</sup>	“”	
Hematite	*K <sub>so</sub>	-1.88 <sup>b)</sup>	Baes & Mesmer, 1976	
	K <sub>so</sub>	-42.75	“”	
	*K <sub>so</sub>	0.09	Lindsay, 1979	
	*K <sub>so</sub>	1.69	Tardy & Nahon, 1985	
Magnetite	*K <sub>so</sub>	12.02 <sup>h)</sup>	Sweeton & Baes, 1970	
Maghemite	*K <sub>so</sub>	1.59	Lindsay, 1979	
	K <sub>so</sub>	-40.41	" "	
	K <sub>so</sub>	-40.5 <sup>b)</sup>	Diakonov, 1998	
	K <sub>so</sub>	-40.06 ±	Sadiq & Lindsay,	
Soil-Fe <sup>III</sup>	K <sub>so</sub>	-39.0 ±	Bohn, 1967	
	*K <sub>so</sub>	2.7	Lindsay, 1979	

a) Background electrolyte 3 M  
NaClO<sub>4</sub>

b) calculated from  $AG_f$

c) Ionic strength  $5 \cdot 10^{-3} + 4 \cdot 10^{-2}$ ;  
0.2 M, resp.~

$[\text{Fe}^{3+}][\text{OH}^-]^{2.35}$

d)  $(\text{Fe}^{3+})(\text{H}^+)^{-2.70}$

e) in sea water

f) freshly precipitated

g) for the reaction:  $\text{Fe}_2\text{O}_3 \cdot x(\text{SO}_4)_x$   
 $+ (3+x)\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 6\text{OH}^- +$   
 $x\text{SO}_4^{2-} + 2x\text{H}^+$

h) see Text

i) Q natural sample

**Table 3. Past, present and future average surface ocean pH**

<b>Time</b>	<b>pH</b>	<b>pH change</b>	<b>Source</b>
Pre-industrial (1700s)	8.179	0.000	analysed field
Recent past (1990s)	8.104	-0.075	field
2050 (2×CO <sub>2</sub> = 560 ppm)	7.949	-0.230	model
2100 (IS92a)	7.824	-0.355	model

**Table 4. Isoelectric points and points of zero charge of various iron oxides and minerals.**

<b>Iron minerals</b>	<b>IEP</b>	<b>PZC</b>	<b>Reference</b>
Goethite	-	7.5	Yates et al., 1975
	7.4	-	Tipping and Cook, 1982
	8.5	8.9	Hsi and Langmuir, 1985
		9.2	Lumsdon and Evans, 1994
	9.4	9.5	Hiemstra and Van Riemsdijk, 1996
	8.4		Blesa et al., 1997
	9.4*	-	Boily et al., 2001
Lepidocrocite		7.45	Gupta, 1976
		6.7	Waite and Morel, 1984
		7.29	Zhang et al., 1992
Akaganeite	7.3		Matijevic and Scheiner, 1978
	6.4		Rubio and Matijevic, 1979
	7.2	7.2	Kanungo, 1994
Ferrihydrite		7.9	Davis and Leckie, 1979
		7.8	Charlet and Manceau, 1992
Hematite		8.5	Parks and De Bruyn, 1962
	-	9.48	Huang, 1971
	7.0	-	Chang et al., 1983
	7.2 (synth.)	7.5	Hsi and Langmuir, 1985
	7.0 (nat.)	7.8	Hsi and Langmuir, 1985
	9.3	9.5	Penners et al., 1986
	8.5	8.5	Liang and Morgan, 1990
	9.5	9.5	Schudel et al., 1997
Magnetite		8.5-8.8 <sup>#</sup>	Jordan and Eggleston, 1998
	6.8	-	Tewari and McClean, 1972
	-	7.1	Astumian et al., 1981
	6.2	6.4	Ardizzone et al., 1982
	6.0	-	Sun et al., 1998
	-	6.3	Marmier et al., 1999
Maghemite	6.6	6.6	Garcell et al., 1998
CoFe <sub>2</sub> O <sub>4</sub>	8.2	8.2	Ardizzone et al., 1987
		6.5	de Vincente et al., 2000

\* measured with the Acoustosizer.

# measured with the scanning force microscope

## Appendix B.

### Methods:

*Iron ore particle size fractionation:* Iron ore material was dried in the oven at 105<sup>0</sup>C for 4 h and then sieved through 2 mm, 0.5 mm and 0.1 mm pore size sieves in order to separate various particle size fractions.

*Iron solubility in seawater:* Seawater, collected from Glenelg beach, South Australia was used for the iron solubility study. Various fractions (2-0.5 mm, 0.5-0.1 mm and less than 0.1 mm) of the iron ore material (in duplicate) were shaken with seawater (1:10 ratio; 5 g ore material with 50 ml seawater) for 24 h in an end-over-end shaker and the seawater extract was passed through 0.22 µm pore size filter prior to analysis by ICP-MS. The % recovery for the elements was checked by spiking acidified water at 50 ppb of multi element mix solution. The % recoveries from spike samples (in triplicate) for various elements ranged between 98-110.

*Elemental analysis of iron ore material:* Iron ore material was dried at 105<sup>0</sup>C for 4 h and fractionated as described above (2-0.5 mm, 0.5-0.1 mm, <0.1 mm and <0.25 mm). A 0.5 g of the each fraction in duplicate was digested with concentrated nitric acid for 48 h and the extracts after appropriate dilution were filtered through 0.22 µm pore size filter and elemental analysis was done by ICP-MS.

National Institute of Standard and Technology (NIST) Standard Reference Material (SRM) 2711 (Montana soil) was analysed after utilizing the same digestion and analytical procedures as that of samples using the USEPA method 3051. The soil digests were measured by ICPMS. The percentage of recoveries of multi-elements of NIST SRM 2711 (Montana soil) were presented in Table A.

**Table A1. Elemental recoveries for NIST standard (SRM 2711).**

Element	Percentage recovery
As	102
Mg	95.3
Al	97.4
P	91.3
Fe	92.0
Cr	96.5
Mn	92.9
Ni	98.2
Cu	99.5
Zn	94.6
Cd	104
Pb	99.2

*ICP-MS Analytical method:* An Agilent 7500c (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometry (ICPMS) was used for the determination of metals/metalloids in seawater samples. USEPA method 6020A was employed to analyse the metals/metalloids in seawater. A number of internal standards such as Sc, Ru, In and Ir were used to check the instrument drift. The samples were diluted into 10-fold to reduce the interferences. Appropriate known spike samples were analysed in every 15 samples to check the variation of the instrument. The analytical results show that the check spike samples were within the range. The instrument features an octopole based collision/reaction cell with helium or hydrogen as a cell gas. The positioning of the torch was computer-controlled in all three axes. Ni sampler and skimmer cones were used with an orifice diameter of 1.0 and 0.7 mm, respectively. A Babington nebulizer with a scott spray chamber (Agilent Technologies) was used for sample introduction. The ICPMS is equipped with a Cetac ASX-510 autosampler (Cetac Technologies, Omaha, USA) for automation of the analyses. As concentrations were measured at m/z 75 using external calibration and Ru at m/z 102 was used as an internal standard to correct for instrument drift.

Table A2. pH and Dissolved organic carbon content of the seawaters.

Sampling site	pH	DOC
		mg/L
Sea water 1 (Port Lincon)	7.95	10.89
Sea water 2 (Port Lincon)	7.90	9.09
Sea water 3 (Glenelg Beach)	8.10	10.81

**Table B1. Extraction of iron ore material with seawater**

Extracting solution	Particle size	Concentration of metals in different particles of ore (mg/ kg)													
		Al	As	Cd	Cr	Co	Cu	Fe	Ni	Pb	Zn	Mg	P	K	Mn
Sea water (pH8.10)	2-0.5mm	bdl	bdl	0.009	bdl	0.24	bdl	bdl	1.34	bdl	0.90	bdl	0.03	47.5	29.6
	0.5-0.1mm	bdl	bdl	0.02	bdl	0.32	bdl	0.62	1.72	bdl	3.33	bdl	0.008	19	38.4
	<0.1mm	bdl	bdl	0.03	bdl	0.35	bdl	0.91	1.76	bdl	8.50	bdl	bdl	bdl	36.2
Detection limit (µg/L)		1	0.1	0.1	0.1	0.3	0.1	1.0	0.1	0.1	0.5	1	>10	>5	0.5
% spike (at 50ppb) recovery		109	105	107	103	105	107	103	106	98	97	109	110	110	104

Bdl; below detection level

The ore material was fractionated based on particle size and shaken with seawater (1: 10 ratio) for 24 hours, extract was filtered through 0.22 µm pore size filter prior to analysis by ICP-MS

Table B2. Elemental analysis of iron ore material in the acid digest (mg/kg), except where indicated\*.

Particle size	Al	As	Cd	Cr	Co	Cu	Fe* (%)	Ni	Pb	Zn	Mg	P	Mn
<0.25mm (total)	10629.6	34.1	0.05	10.9	8.6	37.2	54.2	17.76	5.3	28.4	741.5	3766	755.6
2-0.5mm	11063.6	28.2	0.05	8.8	8.2	36.6	52.6	13.45	4.71	25.7	763.6	4697	835.6
0.5-0.1mm	12071.6	35.4	0.07	11.4	8.9	23.7	50.7	17.89	5.52	20.1	858.7	4901	805.1
<0.1mm	12028.6	40.3	0.14	12.1	7.9	35.1	51.9	14.44	5.70	48.5	816.6	4357	580.8