Regeneration of Fe(II) during EIFeX and SOFeX

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[1] Investigations into Fe(II) cycling during two Southern Ocean mesoscale iron enrichment experiments, SOFeX and EIFeX, clearly show the importance of Fe(II) to iron speciation during these experiments. In both cases the added Fe(II) persisted significantly longer than its expected oxidation time indicating a significant Fe reduction process at work. During EIFeX diel studies showed a strong photochemically induced cycle in Fe(II) production in sunlit surface waters. Our results suggest that the photochemical cycling of iron may also be important in unfertilized waters of the Southern Ocean. **Citation:** Croot, P. L., K. Bluhm, C. Schlosser, P. Streu, E. Breitbarth, R. Frew, and M. Van Ardelan (2008), Regeneration of Fe(II) during EIFeX and SOFeX, *Geophys. Res. Lett.*, *35*, L19606, doi:10.1029/2008GL035063.

1. Introduction

[2] Over the last few years there have been four meso-scale Southern Ocean iron enrichment experiments; beginning with SOIREE [*Boyd et al.*, 2000] in 1999, followed by EisenEx [*Croot et al.*, 2005], SOFeX [*Coale et al.*, 2004] and more recently EIFeX [*Croot et al.*, 2007a; *Hoffmann et al.*, 2006]. Each of these experiments has seen a previously iron deplete low productivity region become transformed into a highly productive system via the removal of iron limitation by the addition of Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$) [*de Baar et al.*, 2005] demonstrating on the mesoscale the same effects as in the original bottle experiments of Martin et al. in the Southern Ocean [*Martin et al.*, 1990].

[3] In seawater Fe(III) is poorly soluble and is rapidly hydrolyzed resulting in the formation of various Fe(III) oxyhydroxide phases with differing chemical reactivities. In oxygenated natural waters Fe(III) is the dominant redox species, as while Fe(II) is more soluble than Fe(III) at alkaline pH, Fe(II) is rapidly oxidized by O_2 and H_2O_2 [*Millero and Sotolongo*, 1989; *Millero et al.*, 1987]. Dissolved Fe(III) is strongly complexed by organic chelators in seawater [*Rue and Bruland*, 1995], most likely produced by bacteria or phytoplankton, which increase iron solubility [*Kuma et al.*, 1996]. The reduction of Fe(III) to Fe(II) by photochemical or other processes is a possible mechanism by which colloidal iron is made more bioavailable to phytoplankton [*Rijkenberg et al.*, 2005; *Wells et al.*, 1991]. In tropical waters, Fe(II) is viewed as a short lived intermediate in iron cycling [*Johnson et al.*, 1994], existing at low concentrations (pM or less), however during spring blooms in colder coastal waters [*Kuma et al.*, 1992] Fe(II) has been detected at elevated concentrations ($\sim$ 1 nM). More recently significant concentrations of Fe(II) have been detected at depth in the sub-oxic waters of oxygen minimum zones [*Hopkinson and Barbeau*, 2007; *Moffett et al.*, 2007].

[4] There have been several laboratory studies undertaking precise measurements of Fe(II) oxidation rates in seawater at nM levels [*King*, 1998; *King et al.*, 1995; *Millero and Sotolongo*, 1989; *Millero et al.*, 1987; *Santana-Casiano et al.*, 2006]. However the measurement of Fe(II) in ambient seawater is complicated by low concentrations (<100 pM) and possible artifacts induced by the analytical method employed [*Croot and Hunter*, 2000]. The recent development of flow injection chemiluminscence techniques [*Croot and Laan*, 2002] now permits studies into the speciation and cycling of Fe(II) in natural waters, analytical techniques with minimal sample perturbation. In this paper we present new data on the role of Fe(II) during SOFeX and EIFeX, two Southern Ocean iron enrichment experiments.

2. SOFeX and EIFeX Settings

[5] Information on the setting and major findings for the iron enrichment experiment at the SOFeX Southern Patch have previously been published [*Buesseler et al.*, 2004; *Coale et al.*, 2004]. The iron enrichment in the SOFeX Southern Patch involved 4 iron infusions (Table 1) in waters of the Northern Ross Sea sector of the Southern Ocean in the austral summer of 2002. Overviews of the physical conditions and the major findings of all of the iron enrichment experiments performed to data can be found in two recent summary papers [*Boyd et al.*, 2007; *de Baar et al.*, 2005].

[6] The EIFeX study was performed in a mesoscale cyclonic eddy, embedded in a meander of the Antarctic Polar Front. For more details on the Fe fertilization in EIFeX see the following: [*Croot et al.*, 2007a; *Hoffmann et al.*, 2006]. All sampling sites reported in this manuscript were located within the fertilized waters as identified by several criteria: iron concentration, Fv/Fm, pCO_2 and chlorophyll [*Smetacek et al.*, 2005].

3. Methodology

3.1. Sampling of Surface Seawater—SOFeX

[7] Surface sampling was performed by pumping seawater from a towed fish into a temporary trace metal clean

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Table 1. Comparative Information for SOFEX and EIFEX

Iron Experiment	Infusion Reference[a]	pH Info Reference[b]	Infusions	Date– First Infusion	Date– Last Infusion	Latitude	Longitude	T °C[c]	$t_{1/2}$[d] (mins)
SOFEX -SOUTH	Coale et al. [2004]	Hiscock and Millero [2005]	4	(I) 24/1/2002	(IV) 4/2/2002	66.45°S	171.8°W	−0.5	139/28.5
EIFEX	Croot et al. [2007a]	R. G. J. Bellerby (personal communication, 2004)	2	(I) 12/2/2004	(II) 26/2/2004	49.4°S	2.25°E	3.97	52/18.8

[a]References for information on the infusions with Fe(II) during these experiments.

[b]References for the *in situ* pH and required CO_2 parameters to calculate *in situ* pH, at the time of the initial iron infusion. In all experiments the initial $pH_T = 8.08 \pm 0.01$.

[c]Mixed Layer Water Temperature at time of first infusion. All times UTC.

[d]Predicted Fe(II) half-life in minutes based on 100% O_2 saturated seawater or 30 nM H_2O_2 extrapolated using the equations developed for $5-45°C$ by *Millero and Sotolongo* [1989] and *Millero et al.* [1987].

room constructed using HEPA filters and plastic sheeting in the rear of the USCG RIB *Polar Star*. Contamination from the ship was avoided by towing the fish (1 m long solid stainless steel, epoxy coated torpedo of 50 kg) at ∼5 m distance away from the ship at 2–3 m depth. Samples were pumped onboard using a Teflon diaphragm pump through ∼25 m of flexible reinforced PVC tubing that had been extensively cleaned with 1M HCl and rinsed with DI water previously. The incoming seawater was filtered in-line (Sartorious Sartobran: 0.4 μm prefilter and 0.2 μm final filter and connected directly to the Fe(II) analysis system. The transit time between the fish and the detector was estimated to be approximately 120 s.

3.2. Sampling of Surface Seawater in the Water Column—EIFeX

[8] For vertical sampling of seawater, modified Teflon coated PVC General Oceanics (Miami, FL, USA) GO-FLO bottles of 8 L were used. Immediately upon recovery of the bottles, samples were filtered in-line through 0.2 μm filter cartridges (Sartorious Sartobran filter capsule 5231307H5) by N_2 overpressure into acid cleaned 60 mL Teflon bottles (Nalgene). For EIFeX all sampling and analysis was performed in a Class 5 sea going clean container (Clean Modules, UK).

3.3. Fe(II) Determination During EIFeX and SOFeX

[9] Fe(II) was determined during EIFeX using the same chemiluminescence flow injection analysis system (Waterville Analytical, Maine) as described earlier [*Croot and Laan*, 2002; *Croot et al.*, 2007b]. For SOFeX an alternative system developed at the University of Otago was used with a Photo-Multiplier-Tube (PMT) instead of a photon counter, which led to a lower signal to noise ratio than for the EIFeX data. Samples from vertical profiles (EIFeX) were maintained at the ambient seawater temperature ($\sim-0.5-4°C$) to maintain oxidation of Fe(II) at *in situ* rates. The detection limit for this technique during this work (all analysis) ranged from 4 to 20 pM (EIFeX) and 20–80 pM (SOFeX), and depended mostly on the background chemiluminescence from the luminol reagent. Concentrations of Fe(II) for underway samples were based on comparison of peak area (not height) with standard solutions and fitted to a quadratic function [*Croot and Laan*, 2002; *Rose and Waite*, 2001]. Peak width and shape was used as criteria for the determination of Fe(II) at <100 pM levels as the presence of a small injection peak can bias peak height based analysis to

anomalously higher Fe(II) levels. A further criteria for the detection of Fe(II) [*Croot et al.*, 2005]) was that discrete samples should be measurable for at least one half-life ($t_{1/2}$). In practice this raises the quantifiable limit above the detection limit based on the blank with the new limit dependent on the oxidation time of Fe(II) in each sample. All pH data reported here are based on the total hydrogen ion concentration scale and data from other pH scales were converted using the appropriate algorithms [*DOE*, 1994].

3.4. H_2O_2 Measurements During EIFeX

[10] In EIFeX H_2O_2 was measured in discrete samples using a flow injection chemiluminescence (FIA-CL) reagent injection method [*Yuan and Shiller*, 1999] with a FeLume analyzer (Waterville Analytical) as described previously [*Croot et al.*, 2004].

4. Results and Discussion

4.1. Surface Fe(II) in the SOFeX South Patch

[11] Surface sampling for Fe(II) was performed on two occasions in the SOFeX South patch (Figure 1) 12 and 14 days after the last Fe infusion (Table 1). Although the Fe(II) data are highly scattered, it is clear that maximal concentrations were found in the iron enriched patch where Fe replete phytoplankton showed increased F_v/F_m values. Dissolved Fe inside the patch (0.3–0.4 nM) would suggest that the predominant Fe species in solution at this time was Fe(II). The presence of Fe(II) long after the added Fe(II) should have been oxidized to Fe(III) indicates the presence of a significant Fe(III) reductive process as suggested also for SOIREE [*Croot et al.*, 2001]. Unfortunately as we only have transect data from SOFeX we can not compare the temporal variability in Fe(II) and light to distinguish whether the Fe(II) was photochemically produced.

4.2. Water Column Fe(II) During EIFeX

[12] In EIFeX water column sampling at the patch centre, as marked by a central GPS drifter buoy, was performed repeatedly over 48 hours (Figure 2) 9–10 days after the last iron infusion. While Fe(II) concentrations were relatively low on the first day, higher concentrations were found in the near surface waters on the 2nd day coincident with an increase in surface irradiation. Mixed layer depths shallowed during this time from an initial 110 m to ∼80 m, while the 1% light level (400–700 nm light) was constant at around 45 m depth (data from R Röttgers, GKSS). The rapid increase in Fe(II) found on the 2nd day (Figure 2) with
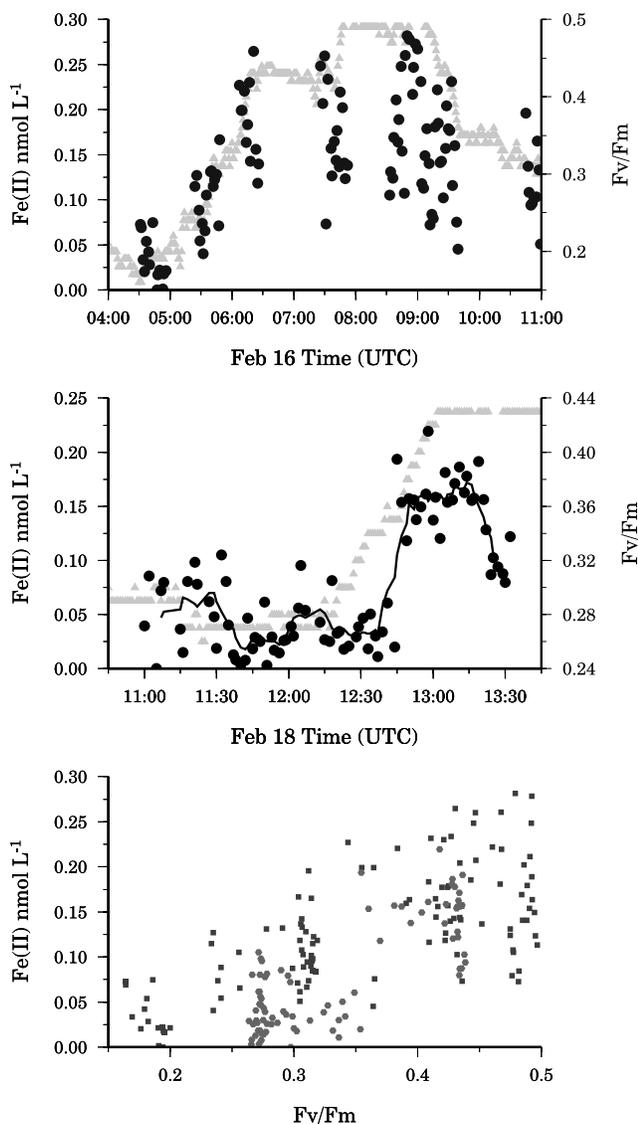
Figure 1. Real time measurements of Fe(II) (black circles) and F_v/F_m (gray triangles) from the SOFEX Southern Patch (RV Polar Star: Feb 16–18, 2002). (top) February 16, 2002 transect across the patch. (middle) February 18, 2002 transect into patch waters, the solid black line is a 5 point running mean for the Fe(II) samples. (bottom) Fe(II) plotted against F_v/F_m for all data (Feb 16–18, 2002). The water temperature in patch during this time was ~−0.03 °C. F_v/F_m data courtesy of Ed Abraham (NIWA).

increasing sunlight also indicates that the rate of Fe(II) formation was faster than the mixing time for the mixed layer allowing a vertical gradient to develop. Dissolved Fe (0.32 ± 0.06 nM, n = 9) and total Fe (0.75 ± 0.11 nM, n = 9) during this time were relatively constant throughout the mixed layer. However compared to SOFeX, Fe(II) in EIFeX was apparently a much smaller component (6–25%) of the dissolved Fe species present.

4.3. EIFeX In Situ Fe(II) Half-Lifes

[13] Measurement of the half-life of Fe(II) (see auxiliary material) during the 48 hour station in EIFeX found values ranging from 380–1700 s indicating relatively slow oxida-
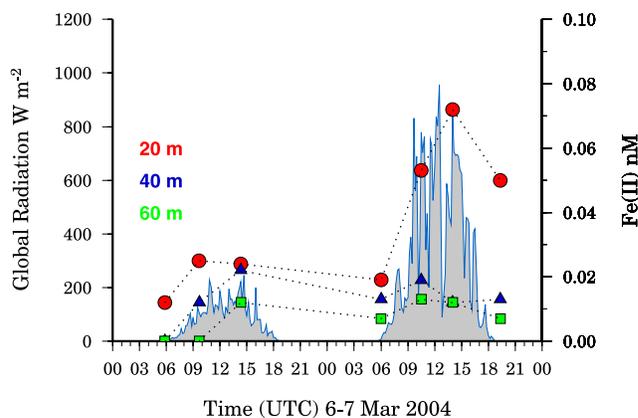

Figure 2. Observed diel cycle of Fe(II) in the water column (colored symbols) and global radiation (gray shading) at the patch centre during EIFEX (March 6−7, 2004: 9−0 days since the last infusion of Fe(II). The mixed layer depth at this time ranged from 80−110 m.

tion rates.[1] Oxidation of Fe(II) at this time was apparently dominated by the high concentrations of H_2O_2 that had formed during the phytoplankton bloom (37 − 66 nM), however Fe(II) half-lifes were often a factor of 2 slower than anticipated from extrapolation of laboratory studies [*Millero and Sotolongo*, 1989]. It is unclear whether these slow oxidation kinetics indicates organic complexation or not, as recently discussed [*Croot et al.*, 2007b], as it is currently difficult to assess the role of pM concentrations of stable Fe(II) organic complexes. Assuming pseudo steady state conditions, with the production of Fe(II) equal to the oxidation rate, we estimate production rates for Fe(II) during EIFeX (Table S1) ranging from 19−247 pM h^{-1}. These high rates of Fe(II) production are strongly suggestive of photoreduction processes [*Croot et al.*, 2007b].

4.4. Role of Light, Organic Ligands, Biology and O_2^-

[14] The diel data from EIFeX is the strongest indicator yet that the Fe(II) signal seen days after the final iron enrichment is predominantly photo-produced. Photoreduction of iron bound to marine siderophores in seawater has been shown to occur [*Barbeau et al.*, 2001] with subsequent degradation of the siderophore. Other weaker Fe complexes may also be photoreduced; *Kuma et al.* [1992] found Fe(II) in a coastal spring blooms and suggested iron hydroxycarboxylic acid complexes may be responsible [*Kuma et al.*, 1995]. Southern Ocean bottle incubations amended with iron and gluconate or glucaric acid have also shown significant Fe(II) levels for several days [*Öztürk et al.*, 2004]. Degradation pigments such as Phaeophytin have also recently been suggested to favor Fe(II) photo-production [*Rijkenberg et al.*, 2006]. At present however, unfortunately we have no information at the functional group level on the iron-organic complexes that were present during the Southern Ocean iron enrichment experiments.

[15] Biologically mediated production of Fe(II) [*Maldonado and Price*, 2000; *Shaked et al.*, 2004] is also an potential source term that may be related to light levels

via photosynthesis. In the present work we can not rule out this source but based on previous studies [*Croot et al.*, 2001; *Croot et al.*, 2007b] it would appear to be an important but minor component based on the kinetic data for production rates available at present.

[16] O_2^- also appears to be important in the Southern Ocean experiments [*Croot et al.*, 2005] and while it is predominantly photochemically produced it is also formed from O_2 oxidation of Fe(II) which is the predominant pathway for Fe(II) oxidation at low H_2O_2 concentrations. Recent laboratory work [*Fujii et al.*, 2006; *Garg et al.*, 2007] has shown that O_2^- can reduce Fe bound to colloids and weak organic complexes, both of which are abundant in an iron enrichment experiment. Currently though we are lacking data for Fe(II)/Fe(III), O_2^- reaction rates at Southern Ocean temperatures and this information is required to determine the importance of this biogeochemical pathway.

4.5. The Impact of Fe(II) on the Residence Time for Dissolved Iron

[17] The presence of significant concentrations of the more soluble redox form of iron in seawater, Fe(II), during SOFeX and EIFeX apparently helped to maintain iron in the soluble and dissolved phases thus increasing the overall residence time for iron in the mixed layer. Extensive redox cycling of iron will also contribute to the transfer of iron from colloidal Fe(III) phases (inorganic or organic) into the soluble phase where it is thought to be more bioavailable to phytoplankton.

5. Conclusions

[18] Data from EIFeX and SOFeX point towards the importance of Fe(II) in maintaining Fe in the mixed layer and for providing a highly bioavailable iron source for phytoplankton during this time. Results strongly suggest that this Fe(II) is maintained by a combination of photochemical production, slow oxidation and possibly organic complexation. Future work needs to examine these processes in greater detail to more precisely determine the role of temperature, organic complexation and O_2^- on iron biogeochemistry in Polar waters.

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