Characterizing the production and retention of dissolved iron as Fe(II) across a natural gradient in chlorophyll concentrations in the Southern Drake Passage

Final Technical Report

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Introduction

Iron fertilization of high-nutrient, low-chlorophyll (HNLC) areas of the ocean has been proposed as a potential means of enhancing the sequestration and storage of carbon dioxide in the deep ocean. The macronutrient-rich waters of the Southern Ocean are of particular interest in this respect, as a region of intermediate and deep water formation. Several recent in situ Fe enrichment experiments in the Southern Ocean (SOIREE, Boyd et al. 2000; EisenEx, Smetacek 2001; and SOFeX, Coale et al. 2004) have confirmed that nanomolar increases in iron supply resulted in significant increases in phytoplankton productivity and biomass. Important questions remain, however, about the coupling of iron and carbon cycles in this region and the viability of using iron fertilization as a long-term strategy to enhance ocean carbon sequestration. Sites of natural iron fertilization in the Southern Ocean offer a unique opportunity to address such questions.

This DOE-funded study has been conducted in conjunction with an NSF-funded study of a region of the Southern Ocean with a strong natural gradient in chlorophyll concentrations which is believed to be due to natural iron fertilization. Our region of study is in the Southern Drake Passage, near the Shackleton Transverse Ridge and Elephant Island. In this area, bathymetry and hydrographic features combine to move iron-enriched shelf waters into the Antarctic Circumpolar Current, resulting in phytoplankton blooms during the austral growing season downstream of the Antarctic Penninsula. The NSF Office of Polar Programs has funded several cruises to this area to characterize the physical, chemical and biological aspects of this natural iron fertilization site, and results are currently under review for publication (Zhou et al. submitted, Measures et al. submitted, Hopkinson et al. submitted). As a component of this larger study, the DOE-funded project described in this report was focused on characterizing the distribution, lifetime and production of Fe(II) in the study area, associated with the natural supply of iron to Southern Ocean waters. Investigation of the controls on steady-state levels of Fe(II) in areas of sustained Fe fertilization in the Southern Ocean is particularly relevant to DOE's Ocean Carbon Sequestration Research Program, because retention of bioavailable Fe (eg.

as Fe(II)) in surface waters is an important factor in the development of effective iron fertilization protocols.

Objectives and approach

Given the potential significance of the Southern Ocean as an area for the development of future iron fertilization programs, it is critical that we learn more about the redox cycling of iron and the expected lifetime of Fe(II) in this regime. Previous studies of Fe(II) in the Southern Ocean have thus far been conducted in conjunction with in situ iron enrichment experiments, which have revealed that Fe(II) persists in the water over extraordinarily long timescales (days), leading to speculations that Fe(II) might be stabilized by organic complexation in this system (Croot et al. 2001; Croot and Laan 2002). More recently, evidence from the EisenEx fertilization experiment has led to the suggestion that prolonged, elevated levels of Fe(II) in Southern Ocean Fe fertilization experiments might be related to artifactually elevated levels of inorganic colloidal iron in the system (Croot et al. 2005). The DOE-funded study described herein provided a unique opportunity to characterize Fe(II) systemmatics across a *natural* gradient of iron and chlorophyll concentrations in the Southern Drake Passage. As proposed, the project was focused on the following objectives: 1) Characterize horizontal and vertical gradients of Fe(II) in the Drake Passage study area; 2) Perform incubations at sea to determine the oxidative lifetime and production rate of Fe(II) in different water masses; and 3) Conduct laboratory investigations of Fe(II) production and retention using Antarctic seawater under temperature-controlled conditions with model ligands and natural organic matter. The first phase of this project was completed on a cruise to the Drake Passage region on the R/V L.M. Gould in Feb/March 2004 (cruise # LMG0402). Subsequent laboratory studies were performed in years 2 and 3 (year 3 on no-cost extension).

Year 1 – Field Studies

Figure 1A shows the bathymetry in the region around the Shackleton Transverse Ridge (STR). This area exhibits a significant chlorophyll gradient during the austral growing season, with very oligotrophic “blue waters” to the west of the STR and significantly higher chlorophyll “green waters” to the east (Figure 1B). The focus of DOE-funded work at this site during the cruise in 2004 was to look at the distribution, lifetime, and production of Fe(II) in conjunction with the many other parameters being studied as part of the larger NSF-funded project. Instrumentation used in this study to measure Fe(II) concentrations was the FeLume system manufactured by Waterville Analytical. Chemical reagents employed followed a modified version of the protocol outlined by Croot and Laan, 2002 and the FeLume set-up for making measurements followed the method outlined by Rose and Waite, 2001 and Hopkinson and Barbeau, 2006. Using these methods and making measurements at near-zero temperatures, the system exhibited good sensitivity and reproducibility. Consistent calibration curves were obtained in the sub-nanomolar range (Figure 2). Similar calibration curves generated by standard addition were used to convert the signal from the PMT into Fe(II) concentration.

Fe(II) distributions - Studies of Fe(II) distribution in surface waters could not be as extensive as originally planned because, due to a change in the overall cruise sampling strategy, the Measures group did not deploy their towed-fish system for obtaining continuous underway trace metal data

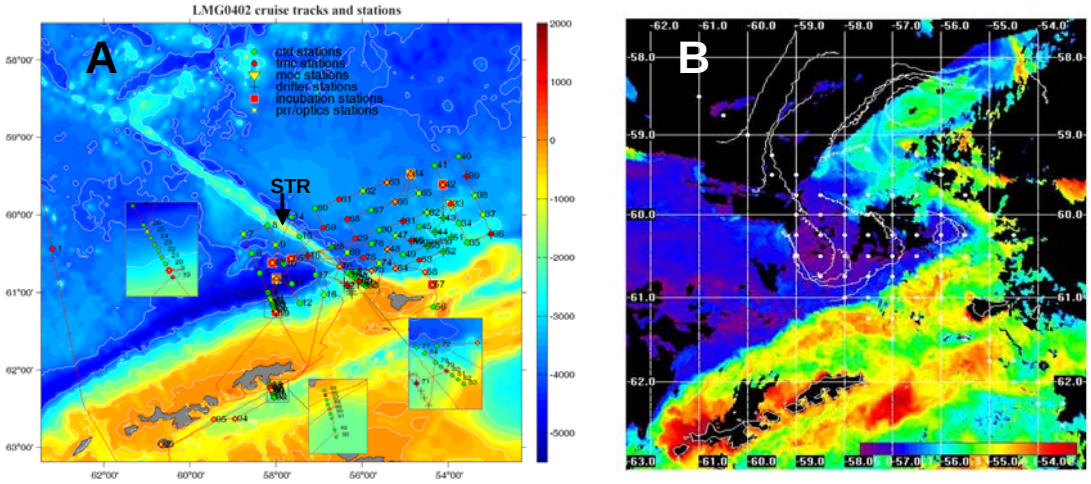


Figure 1. A. Bathymetry map of stations occupied during the cruise on the R/V LM Gould in Feb/March 2004, in the region of the Shackleton Transverse Ridge (STR). Color coding and symbols indicate activities carried out at each station. B. SeaWIFS composite image showing chlorophyll gradient in the study area during Feb/March 2004. Station locations and tracks of drifters released during the cruise are also shown.

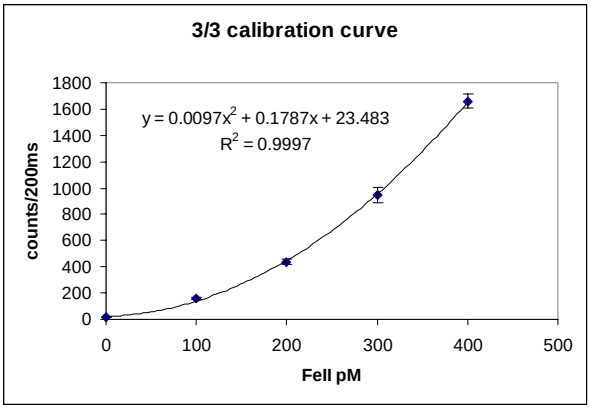


Figure 2. Typical calibration curve for FeLume sytem as employed during field work in 2004.

from surface waters. However, in conjunction with use of the trace metal rosette sampling system, at a number of stations measurements were made of Fe(II) distributions in the water column (upper 100 meters) during daylight hours. The basic protocol for these measurements was to quickly bring all GO Flos into the Measures clean van for sampling, pressurize GO Flos used for the Fe(II) profile right away, and quickly filter these samples through the Pall Supor AcroPak 200 (0.2 μm). Analysis was then conducted immediately in triplicate using the FeLume, with samples sitting in a chilled water bath until measurements were completed (about 20 minutes for a 4-5 point profile). Stations which were sampled for Fe(II) profiles included several in the "blue water zone" (Stations 27 and 55), shelf station 57, several mixed off-shelf waters (Stations 48 and 54) and one "offshore green" station, 63 (see Figure 1A for station map). Most of these profiles were taken between the hours of 11 am and 3 pm, and weather conditions, including sunlight irradiance, were variable. Measurable Fe(II) was detected at only two stations, and in bot h cases only in the sample nearest the surface (10 m): at "blue water" Station 27 Fe(II) concentrations of about 200 pM were detected at 10 m, and at shelf Station 57 Fe(II) concentrations of about 50 pM were detected at 10 m. It is possible that contamination might have contributed to the observed signal at Station 27 which was an offshore station with generally low dissolved Fe concentrations (generally 100-200 pM in surface waters, Measures et. al. submitted). The surface waters at shelf Station 57 were relatively enriched in

dissolved Fe (approximately 2nM, Measures et al. submitted), so the presence of 50 pM Fe(II) in surface waters during daylight hours may be indicative of photochemical redox cycling of iron.

While these data are preliminary and coverage is sparse, these are some of the first measurements of natural concentrations of Fe(II) in Southern Ocean waters in a region of natural iron fertilization. Our findings suggest that there might be sharp gradients of Fe(II) in surface waters in such areas, with no apparent sub-surface generation of Fe(II). In general, however, we found that Fe(II) was most often below our detection limit of about 50 pM, even in iron-enriched (~2 nM) shelf waters. During the time frame of our study, measurable Fe(II) in surface waters did not appear to be strongly correlated with chl fluorescence or total dissolved Fe concentration. These results contrast with results of several mesoscale iron addition experiments (eg. Croot et al. 2001; 2005), in which elevated levels of Fe(II) were observed for extended time periods in conjunction with Fe enrichment. Reasons for the difference are likely related to the form in which iron is added to seawater, as well as to the degree of iron saturation of organic ligands and rate of mixing/dilution processes in natural vs. synthetic iron enrichment systems.

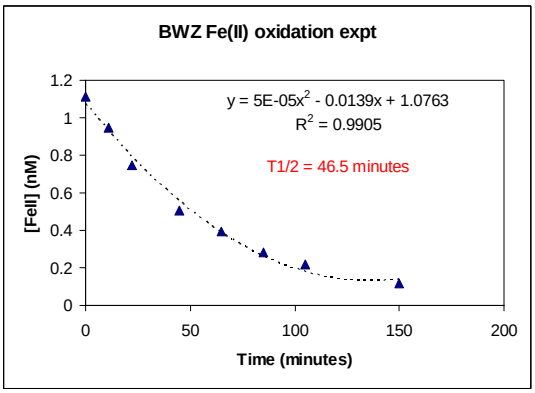


Figure 3. Fe(II) oxidation experiment with Station 27 water.

Fe(II) Lifetime - Measurements of Fe(II) lifetime in surface waters at our study site were made using water samples collected via the trace metal rosette, filtered (AcroPak 0.2 μm) and spiked with Fe(II). During lifetime experiments water samples were maintained in a temperature-controlled water bath to keep temperatures close to that of ambient surface water. The half-life of Fe(II) calculated from one experiment conducted in low chlorophyll offshore waters maintained at 2.4°C was 46 minutes (Figure 3). This compares well with what is expected for Southern Ocean waters (Croot and Laan 2002), where the half-life of Fe(II) is thought to be extended due to cold temperatures (slows oxidation kinetics) and low concentrations of peroxide (Fe(II) oxidant). During the cruise filtered surface water samples were taken at several stations across the chlorophyll gradient and frozen for Fe(II) lifetime studies on shore, with a goal of examining the influence of different water types (eg. higher chlorophyll, higher dissolved organic matter) on Fe(II) oxidation rate.

Fe(II) photoproduction - Several photochemical experiments were conducted to look at the production of Fe(II) via photoredox reactions in Southern Ocean waters. These experiments consisted of exposing filtered water samples in acid-cleaned quartz flasks to natural sunlight in the flow-through seawater incubators on the 01 deck of the Gould. Measurements of Fe(II) concentrations in the flasks were taken

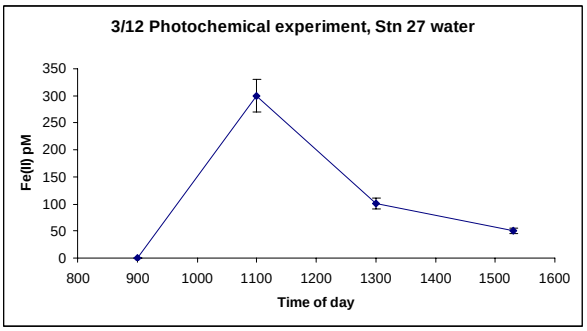


Figure 4. Shipboard study of the photo-production of Fe(II) in oligotrophic Drake passage waters.

periodically using the FeLume system. One such experiment conducted with low-chlorophyll offshore water showed a clear photoproduction cycle of Fe(II) over the course of a day, going from undetectable levels at the start of the experiment to approximately 300 pM by 11 am (Figure 4). These results may be affected by iron contamination, as 300pM is on the high side of Fe concentrations that might be expected in the oligotrophic waters of Station 27. However, our results clearly show the potential for photoredox cycling of Fe(II) in Southern Ocean surface waters on diurnal timescales.

Instrument failure - Unfortunately the PMT on the FeLume blew out about a week before the end of the cruise, so a number of further planned lifetime and photochemical experimental studies could not be carried out at sea. However, filtered samples of a number of different water types encountered on the cruise were prepared and frozen and shipped back to SIO to conduct further mechanistic studies.

Years 2 and 3 – Laboratory studies

Table 1 lists the 0.2 μm filtered, frozen water samples that were taken on cruise LMG0402 and shipped back to SIO to perform experiments. Initially, the focus of these experiments was to determine whether the chemistry of the different water types sampled in the southern Drake Passage (especially with respect to chlorophyll concentrations) had an affect on Fe(II) lifetimes and/or photoproduction. Accordingly, protocols for laboratory studies were developed.

Table 1: 0.2 μm filtered water samples from LMG0402, shipped frozen to SIO for laboratory studies

Station	Depth (m)	Liters	chl ug/L	Station characteristics
27	20	10	0.239296	blue water
57	20	6	0.12321	shelf water
71	10	2	0.1792	near STR gap
75	30	2	0.13788	near STR gap
75	500	2		"
80	20	2	1.583921	near STR gap
95	30	4	0.556071	Bransfield Strait
96	30	2	0.551894	Deception Island

Fe(II) lifetime studies - Seawater samples were thawed out in a refrigerator and then placed in trace metal clean amber bottles and stored in the refrigerator until experimental analysis. Experiments on thawed seawater were performed within 2 weeks to prevent significant pH changes to the stored seawater. Experiments were analyzed using the Waterville Analytical FeLume system (PMT repaired after the cruise). The hood used for analysis work had a black garbage bag taped to one side of it to limit the amount of light that could interfere with the experiments. The chemical reagents used to induce the chemiluminescence consisted of a luminol reagent and several Fe(II) standards used for calibrating the seawater and also used to spike the seawater and observe the subsequent decay. The luminol reagent consisted of 1.0mM luminol free acid dissolved in a solution of 0.34M Q-ammonium hydroxide. This solution was

then heated in an oven overnight at 90°C; the next day the solution was allowed to cool in the dark before a small amount of Q-HCl was added to adjust the pH. This reagent was then stored in a trace metal clean amber bottle. The luminol reagent was found to have an increased sensitivity when it was allowed to age for at least 2 days, therefore, the reagent wasn't used until it had sufficiently aged; the reagent was discarded after one week. The Fe(II) standards used for these experiments derived from a 4mM Fe(II) in 0.01M Q-HCl primary standard that was made once a month. All standards were made in trace metal clean volumetric plastic bottles and were stored in trace metal clean plastic bottles. The secondary standards, which were made daily and replaced every 3-4 hours, consisted of 0.5µM Fe(II) in 0.01M Q-HCl, 1.0µM Fe(II) in 0.01M Q-HCl, and 10µM Fe(II) in 0.01M Q-HCl. All solutions were prepared in a positive pressure clean room using a laminar flow hood. Secondary standards were used to calibrate the seawater to be analyzed using a standard addition method consisting of spikes ranging from 0.5-2.4nM. The seawater used for analysis was first placed in a Ziploc bag and allowed to sit in a waterbath at 1°C for at least half an hour. The seawater was then placed in an ice bucket at 0°C while 10mL aliquots of the seawater were placed in a 50-mL acid-clean plastic bottle that was gently stirred as the Fe(II) spikes were being added. Once the spike was added, the peristaltic pump was immediately turned on; however, the signal was not measured until 30 seconds afterwards in order to allow the spiked water to run through the entire system first. Once the calibration curve was established, the decay experiments could be run. 50-mL aliquots of the seawater to be analyzed were measured out and placed in 125-mL trace metal clean bottles. These aliquots were then sealed in two Ziploc bags, which were then placed in a larger Ziploc bag that had black tape around it to limit the amount of light exposure. This bag containing the aliquots was then placed in the waterbath at 1°C for at least half an hour. An initial signal was taken before an Fe(II) spike was added; the aliquot was then placed back in the black bag and back into the waterbath for another 5 minutes. Before an Fe(II) spike was added, the 125-mL bottle containing the seawater was placed in a Ziploc bag and into an ice bucket at 0°C. All signal measurements were taken while the bottle was in this bucket to eliminate any fluctuations in temperature. Once the Fe(II) spike was added, the signal was measured immediately. Subsequent measurements were taken every 2-10 minutes depending on how quickly oxidation was occurring. A typical decay curve obtained with this procedure is shown in Figure 5.

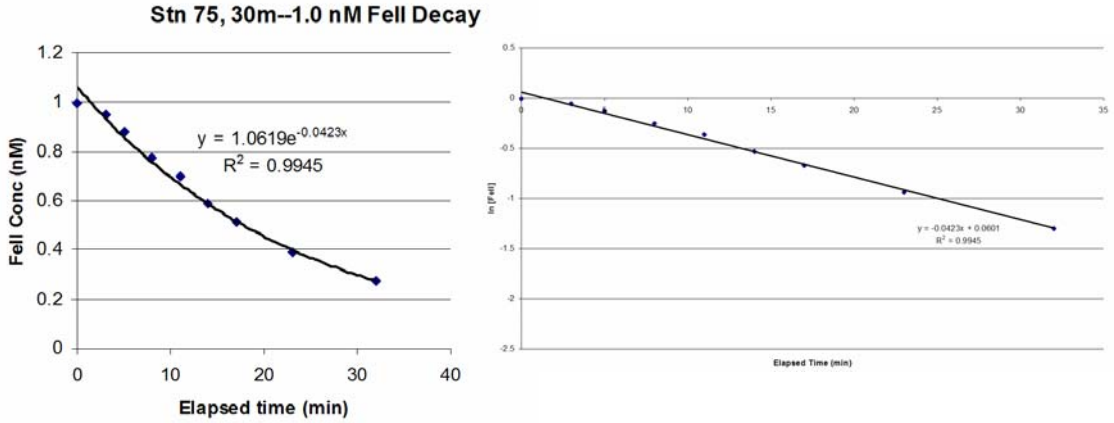


Figure 5. 1.0nM Fe(II) spike decay experiment performed with Station 75, 30 m water, at 1°C. Fe(II) half-life for this experiment was approximated at 17 minutes. Data are shown at right plotted as a funtion of the natural log of the Fe(II) concentration vs. time.

As expected, the Fe(II) decay rates determined using this procedure routinely displayed pseudo-first order decay kinetics (see Figure 5), but the rate of Fe(II) decay was consistently significantly faster than what had been determined previously at sea for these water samples (see Figure 3), with a half-life in the laboratory averaging about 12 minutes and varying significantly between experiments performed on different days. For this reason, hydrogen peroxide contamination of the water samples by laboratory air was suspected, and a measurement technique was developed to determine the extent of this problem.

Hydrogen peroxide determination - Hydrogen peroxide (H_2O_2) is an intermediate in the reduction of O_2 to H_2O and may function as an oxidant or a reductant. In addition to molecular oxygen, H_2O_2 is a major oxidant for Fe(II) under seawater conditions, via the Fenton reaction. H_2O_2 is produced in the ocean primarily by photochemical reactions involving dissolved organic matter (DOM) and O_2, which react to produce superoxide which subsequently disproportionates to form H_2O_2. Consistent with the photochemical flux, H_2O_2 distributions in the oceanic water column show a maximum at the surface. While surface H_2O_2 concentrations in the tropics and regions with high DOM can approach hundreds of nM, typical values for Antarctic surface waters are lower, in the range of 10-20 nM (Resing et al. 1993; Sarthou et al. 1997). At these low levels, contamination with H_2O_2 from laboratory air is a particular concern for experimental procedures conducted on shore. To determine the level of H_2O_2 in our collected seawater, we developed a protocol for H_2O_2 determination using the Amplex UltraRed reagent, based on personal communication with Andrew Rose (University of New South Wales, Australia) and the original work of Mohanty et al. 1997 and Zhou et al. 1997. The final reagent for H_2O_2 determination contained 200 μM Amplex UltraRed (Invitrogen A36006) dissolved in DMSO and 100 kU/L Horseradish Peroxidase (Sigma Aldrich P8125-5kU). The final reagent is diluted by a factor of 100 with the sample and analyzed spectrophotometrically at 568 nm. Sample measurements are calibrated using standard additions of H_2O_2 to the sample matrix (range 5-250 nM H_2O_2), along with a blank solution containing 10 kU/L catalase. Figure 6 shows a typical standard addition curve obtained using this method on Antarctic seawater from Station 75. In general, measurements of H_2O_2 on our thawed Antarctic seawater samples indicated the presence of 25-35 nM H_2O_2. These levels of H_2O_2, while not high by overall oceanographic standards, are on the higher end of the range observed for Antarctic seawater surface samples and therefore are likely indicative of some degree of H_2O_2 contamination. We confirmed the influence of H_2O_2 on the decay kinetics of Fe(II) in our samples by performing decay experiments with and without added catalase. Half-lives observed in the presence of even reduced amounts of catalase were over 90 minutes, in agreement with results previously reported from low-temperature Southern Ocean Fe(II) oxidation studies (Croot and Laan 2002; Croot et al. 2005). In contrast, low-temperature oxidation experiments run without catalase added had much shorter half-lives (see Figure 7). We eventually determined that even trace concentrations of catalase (0.1 kU/L, or ~6.5 μg/L) were sufficient to preserve the long half-life of Fe(II) at near-zero temperatures, a

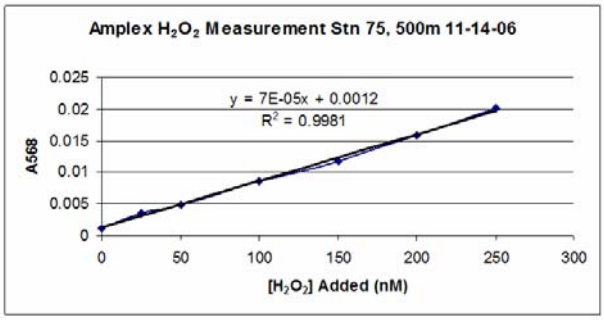
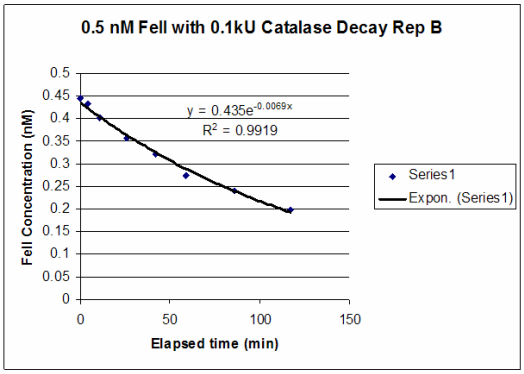
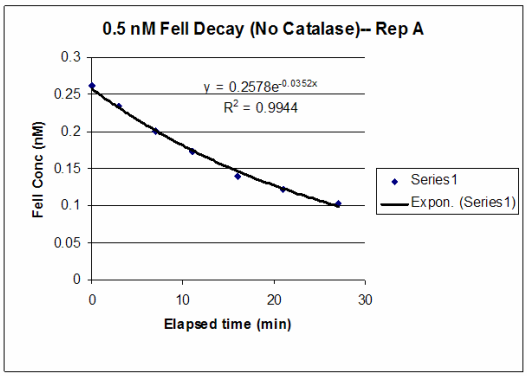


Figure 6. Typical standard addition curve for the Amplex UltraRed H_2O_2 measurement method

parameter that may be useful for future mechanistic studies. Ultimately, variability in H_2O_2 contamination from sample to sample caused us to abandon the idea of characterizing the influence of different water mass characteristics on Fe(II) lifetime. Given the difficulties associated with variable levels of H_2O_2, such a study would require detailed modeling of Fe(II) oxidation kinetics that is beyond the scope of the current project.



half-life=97.17min



half-life=19.22min

Figure 7. Fe(II) oxidation experiments carried out in the laboratory at 0-1°C, with (left) and without (right) added catalase.

Fe(II) Photoproduction – Our studies of Fe(II) photoproduction conducted on the LMG0402 cruise suggested that Fe(II) could be produced in Antarctic surface waters by photochemical reactions. Such reactions could include direct photolysis via light absorption and ligand-to-metal charge transfer (LMCT) reactions of Fe(III)-ligand complexes, or secondary reactions with photochemically produced radical species such as superoxide. The low concentrations of H_2O_2 documented for Southern Ocean waters suggests that secondary photochemical reactions may be less important here than for other oceanic regimes. Preliminary Fe speciation data from our LMG0402 cruise also suggested that Fe in our study area was bound by strong ligands with a minimum in concentration at the surface, indicating a potential photochemical sink (see Figure 8). Thus, we chose to focus on characterizing Fe(II) photoproduction via LMCT reactions.

For these laboratory experiments, we used a model photoreactive Fe(III)-siderophore complex, aerobactin (Küpper et al. 2006; Figure 9). Purified aerobactin was purchased from EMC microcollections, Tubingen, Germany. As characterized by Küpper et al. 2006, UV photolysis of the ferric aerobactin complex results in LMCT decarboxylation of the α-hydroxy carboxylic acid group of the central citrate moiety of aerobactin. The decarboxylated photoproduct forms a 3-ketoglutarate moiety and retains the ability to complex Fe(III), with a stability constant similar to that of the original ligand. Our experiments were set up to examine the influence of temperature on Fe(II) photoproduction from Fe(III)-aerobactin, reasoning that the slower oxidation rate of Fe(II) in cold Southern Ocean waters might have an effect on Fe(II) photoproduction.

The aerobactin-Fe(III) complex was synthesized by equilibrating a 1.1μM aerobactin:1 μM Fe(II) mixture at room temperature in the dark under oxygenated conditions at circum-neutral pH for at least 12 hours. This stock was then added to 50mL of filtered, oligotrophic seawater which had been previously UV-irradiated to remove DOM. Final concentrations in the experimental

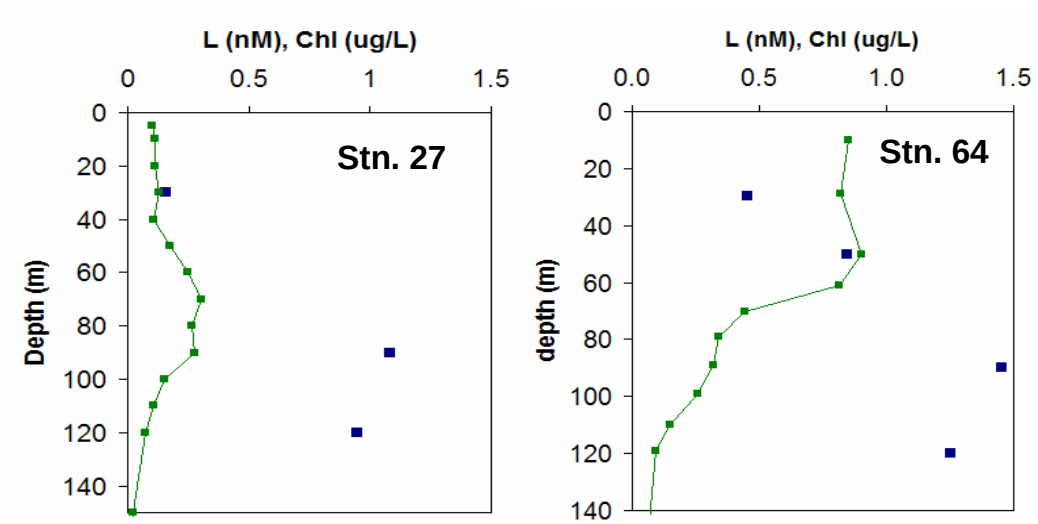


Figure 8. Fe(III) organic speciation data for Stations 27 (left, a "blue water" station west of the STR) and 64 (right, an offshore "green" station east of the STR). Chlorophyll profiles at each station are shown in green, and the concentration of strong Fe(III)-binding organic ligands at several points in the depth profile is shown by the blue squares. Ligand concentrations were determined using electrochemical methods (competitive ligand exchange/adsorptive cathodic stripping voltammetry, as in Hopkinson and Barbeau 2006). Ligand concentrations significantly exceeded the dissolved Fe concentrations at all points except the surface waters of Stn. 27, where ligand and Fe concentrations were about equal. Log K's (conditional stability constants with respect to inorganic Fe in seawater) for the ligands ranged from 11.1 to 12.5, similar to what has been observed by other investigators.

solution were 11nM aerobactin:10nM Fe(III). The UV-irradiated seawater had a pH of 7.9. The experiments were conducted in quartz glass round-bottom flasks in order to ensure optimum light penetration. For the room temperature experiment, initial time points were taken first before any complex was added, then in the dark after the complex was added. Fe(II) measurements were performed on the Waterville Analytical FeLume system as previously described. The system takes about 30 seconds to make an Fe(II) measurement. No significant change was observed after the complex was added in the dark. A sunlamp (Sperti Palm Springs sunlamp, 700 Watts) was then shined on the seawater containing the complex; Fe(II) was immediately detected by the FIA system. A maximum of 1.1 nM Fe(II) was detected. When the light was turned off, Fe(II) concentrations decreased almost instantaneously (see Figure 10). The same experiment was repeated at a temperature of 1° C, using an ice bucket to maintain temperature. When the complex was added to the 1° C UV seawater, a small amount of Fe(II) was detected. When the sunlamp was shined on the water in the ice bucket, Fe(II) was produced, but the amount produced was smaller than that produced at room temperature, the peak concentration of Fe(II) reaching about 0.3 nM. After the light was turned off, the Fe(II) did drop but not as dramatically as when the seawater was at room temperature.

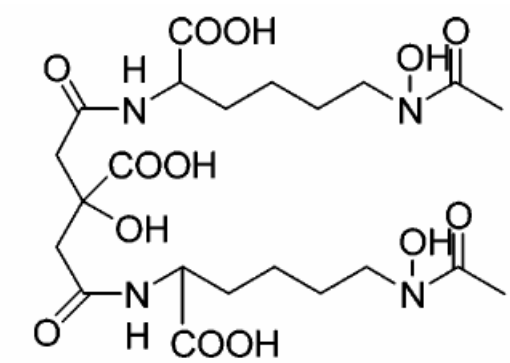


Figure 9. Aerobactin, which forms photoreactive complexes with Fe(III).

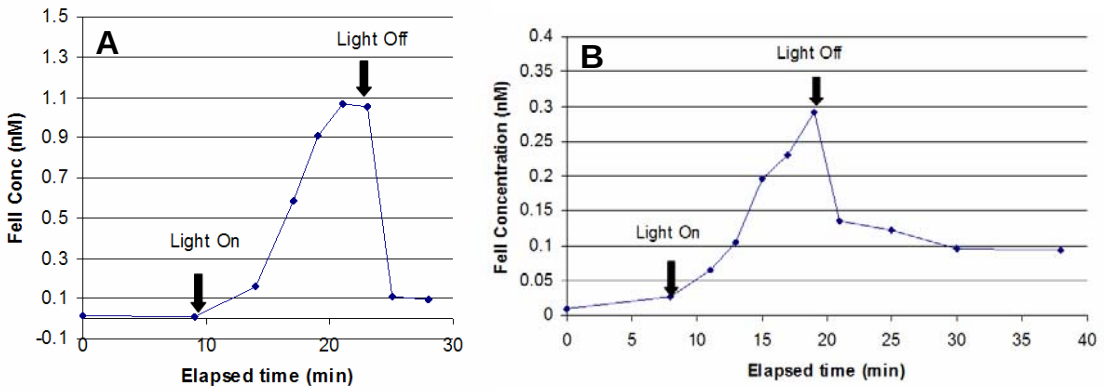


Figure 10. Fe(II) concentrations vs time for photoproduction experiments conducted with Fe(III)-aerobactin in seawater at room temperature (A) and 1°C (B). Note different scales on the y-axes.

These experiments are some of the first to employ an FeLume-type system to characterize Fe(II) photoproduction by LMCT reactions of siderophore-type Fe(III)-organic complexes in a seawater system. The results are interesting and suggestive. Perhaps most importantly, these results indicate that solution-phase LMCT reactions of strong Fe(III)-ligand complexes can be a source of "available" or "free" Fe(II), as determined by luminol chemiluminescence (most previous photochemical studies of these model compounds have employed a strong Fe(II) ligand to detect Fe(II), a technique which can be subject to potential artifacts, eg. Barbeau et al. 2001). Intriguingly, results suggest a strong dependence of Fe(II) photoproduction rate on temperature, with greater photoproduction rates at higher temperatures. Photoproduced Fe(II) also appears to be somewhat more persistent at lower temperatures, however, consistent with the longer oxidative lifetime of Fe(II) at lower temperatures. Further experimentation is needed to determine the significance of these combined effects for Fe redox cycling and bioavailability in Antarctic systems.

Conclusions

This study of Fe(II) distribution, lifetime and photoproduction is the first of its kind to be conducted in conjunction with the characterization of a site of natural Fe enrichment in the Southern Ocean. Our results suggest that, in contrast to results observed during some mesoscale iron enrichment experiments in the Southern Ocean, steady-state levels of Fe(II) are likely to remain below detection, even within a significant natural gradient in dissolved Fe concentrations. Fe(II) is, however, likely to be produced in Southern Ocean surface waters as a reactive intermediate as a consequence of photochemical reactions. This study has obtained some of the first evidence that direct LMCT reactions of strong Fe(III)-organic complexes do appear to be a viable source of available Fe(II) in Antarctic waters, and further studies are needed to characterize the temperature dependence of this phenomenon. Fe(II) lifetimes at realistic Southern Ocean environmental conditions have proven difficult to determine in a laboratory setting, due to contamination by trace levels of H_2O_2. It may be possible to overcome this difficulty, however, by targeted use of catalase and detailed kinetic modeling of Fe(II) oxidation rates.

Transitions – Related work

With current and pending NSF funding, we are continuing our interdisciplinary investigations of the Southern Drake Passage as an area of natural iron fertilization in the Southern Ocean. Iron speciation and redox cycling continues to be an area of focus in our studies, as we seek to understand processes which contribute to iron availability and promote bloom initiation and maintenance. On a more recent cruise to the area, in austral winter of 2006, our group conducted an experiment with stable iron isotope additions and both photoreactive (aerobactin) and non-photoreactive (desferrioxamine B) siderophore additions, to characterize the impact of iron speciation and dissolved/particulate partitioning on the development of early spring phytoplankton blooms. Samples from these experiments will be analyzed over the coming year and we anticipate that these results will contribute to our growing body of knowledge about the biogeochemical significance of iron redox cycling in areas of sustained iron fertilization in the Antarctic.

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Barbeau, Katherine. Photochemistry of organic iron(III) complexing ligands in oceanic systems. *Photochem. photobiol*. 2006, 82:1505-1516.

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Presentations and published abstracts acknowledging this award:

K. Barbeau, B.M. Hopkinson, R. Reynolds, H. Wang, K. Selph, C. Measures, C. Hewes, F. Malfatti, M. Manganelli, F. Azam, O. Holm-Hansen, B.G. Mitchell (2006) Phytoplankton iron stress across chlorophyll and dissolved-iron gradients in the Southern Drake Passage, *Eos Trans. AGU, 87*(36), Ocean Sci. Meet. Suppl., Abstract OS33F-06.

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