Processes governing the supply of iron to phytoplankton in stratified seas

Alessandro Tagliabue and Kevin R. Arrigo

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The impact of iron speciation on phytoplankton dynamics in the marine environment is currently not well understood. In this study, we modified the existing CIAO model of the Ross Sea to include major aspects of iron chemistry and examined the processes governing the supply of iron to phytoplankton. We suggest that the melting of sea ice and ensuing stratification dictates the speciation and bioavailability of iron. Photo reduction is the key process governing the supply of bioavailable Fe to the resident phytoplankton of the Ross Sea. Access to organically complexed iron is of greater significance in strongly stratified waters dominated by diatoms than in weakly stratified waters dominated by Phaeocystis antarctica. Light may control phytoplankton taxonomic composition in the Ross Sea by impacting both photosynthetic performance and iron speciation. The efficiency with which iron fuels phytoplankton carbon incorporation is greater in seasonal ice zones than in permanently ice-free waters. Therefore, changes in the physical structure of the Southern Ocean could impact iron bioavailability, independent of any change in iron supply.


1. Introduction

Measurements of macronutrient distributions and phytoplankton growth made during the Discovery cruises (1924–1939) suggested that the low primary productivity of the open Southern Ocean (SO), relative to the more productive shelf regions, could be attributed to reduced iron (Fe) availability [Hart, 1934]. The utilization of trace metal clean sampling techniques developed in the 1980s confirmed that Fe concentrations on the continental shelves are much higher than in the open SO [e.g., Martin et al., 1990; Johnson et al., 1997; Sedwick and DiTullio, 1997; Coale et al., 2005]. More recently, bottle enrichment and in situ mesoscale Fe addition experiments demonstrated that the availability of Fe does indeed limit primary productivity throughout much of the modern SO [Martin et al., 1990; De Baar et al., 1995; Sedwick et al., 2000; Boyd et al., 2000; Gervais et al., 2002; Coale et al., 2004].

Consistent with these observations, substantial rates of primary productivity are often associated with the numerous coastal polynyas (areas of open water surrounded by ice) located over the Antarctic continental shelf [Arrigo and van Dijken, 2003]. Although this enhanced production is primarily the result of higher light availability in waters with reduced sea ice cover, higher Fe availability also plays an important role. The most productive polynya is located in the Ross Sea (Figure 1), where phytoplankton blooms are large [Arrigo and van Dijken, 2003; Arrigo et al., 2000; Smith et al., 2000] and net primary production (NPP) commonly exceeds 150 g C m\(^{-2}\) yr\(^{-1}\) or 40 Tg C yr\(^{-1}\) [e.g., Arrigo and van Dijken, 2004; Tagliabue and Arrigo, 2005]. The high rates of CO\(_2\) fixation associated with the Ross Sea phytoplankton blooms drive large deficits in the oceanic partial pressure of CO\(_2\) (pCO\(_2\)) [Takahashi et al., 2002; Sweeney, 2003], resulting in the uptake of 5 Tg of atmospheric CO\(_2\) each year [Tagliabue and Arrigo, 2005].

Phytoplankton blooms in the well-stratified marginal ice zones (MIZ) of the southwestern Ross Sea (such as the Terra Nova Bay Polynya, TNBP) are dominated by diatoms such as Fragilaropsis curta, F. cylindrus, and Nitzschia scuturata, while the waters of the Ross Sea polynya (RSP) are only weakly stratified and the colonial haptophyte Phaeocystis antarctica blooms profusely [e.g., Arrigo et al., 2000; Smith et al., 2000]. Despite non-limiting dissolved Fe concentrations measured in the southwestern Ross Sea during the austral spring [Fitzwater et al., 2000; Coale et al., 2005], the annual accumulation of particulate organic carbon is eventually limited by Fe, with approximately one third of macronutrients remaining at the time of ice refreeze [Sedwick et al., 2000; Tagliabue and Arrigo, 2005].

Because of its location on the continental shelf, concentrations of dissolved Fe in surface waters of the southwestern Ross Sea (0.5 nM) are greater than those measured in most other SO waters (<0.2 nM) [e.g., Martin et al., 1990; Johnson et al., 1997; Sedwick and DiTullio, 1997; Fitzwater et al., 2000; Sedwick et al., 2000; Boye et al., 2001; Grotti et al., 2001; Croot et al., 2004; Coale et al., 2005]. Concentrations are even greater in the vicinity of
melting sea-ice (>1 nM) and near the seafloor (0.6–1.0 nM) [Sedwick and DiTullio, 1997; Coale et al., 2005]. Previous field work [Edwards and Sedwick, 2001] and modeling studies [Tagliabue and Arrigo, 2005] indicate that ice-derived Fe only supports approximately 10% of regional NPP. This suggests that Ross Sea phytoplankton are reliant upon water column or sedimentary sources of Fe that persist over the winter. However, the processes governing the supply of bioavailable Fe to phytoplankton in such regions are not well understood.

Fe has a complicated cycle in seawater and the speciation of Fe is controlled by a suite of physical, chemical, and biological processes, including redox chemistry, organic complexation, precipitation, and photochemistry [Wells et al., 1995; Morel and Price, 2000]. Most Fe in the oxidizing modern ocean exists in the trivalent oxidation state (Fe(III)), and while free inorganic dissolved Fe (Fe(II) and Fe(III)) can be utilized by phytoplankton [Anderson and Morel, 1982], over 99% of dissolved Fe(III) (generally defined as <0.2 μm) is complexed by one or more organic ligands [e.g., Rue and Bruland, 1997; Witter and Luther, 1998; Nolting et al., 1998; Wu et al., 2001; Boye et al., 2001; Croot et al., 2004]. Photoreduction can convert some ligand-bound Fe(III) species to Fe(II) via ligand-to-metal charge transfer (LMCT) [Barbeau et al., 2003]. Fe is also present as particulates (typically >0.2 μm) that are unavailable to the phytoplankton and can coalesce and sink from surface waters.

Ligand concentrations in the Southern Ocean typically range from 1–2 nM (Fe equivalents) [Boye et al., 2001; Croot et al., 2004] and are consistent with concentrations measured in other oceans [e.g., Rue and Bruland, 1997; Witter and Luther, 1998; see Wu et al., 2001]. Organic ligands are produced in seawater through exudation by heterotrophic bacteria [Wilhelm and Trick, 1994; Martinez et al., 2001] and phytoplankton [Geider, 1999; Morel and Price, 2000], and are released during grazing by protozoa [Barbeau et al., 2003] and zooplankton [Hutchins et al., 1995], and during viral lysis [Poorvin et al., 2004]. Each of these distinct release mechanisms may produce ligands with unique moieties, kinetic characteristics, and functional forms. Studies utilizing competitive ligand exchange have shown that one or more ligands often are present in the SO [Nolting et al., 1998; Boye et al., 2001; Croot et al., 2004], as they are in other ocean basins. Both Rue and Bruland [1997] and Wu et al. [2001] measured low concentrations of strongly complexing ligands, whereas weakly complexing ligands were found at much higher concentrations. Wu et al. [2001] also found significant concentrations of Fe ligands within the colloidal size range (0.03–0.40 μm) in both the oligotrophic North Atlantic and North Pacific. Unfortunately, the similar conditional stability constants measured for a wide-range of ligands [Witter et al., 2000] may make it difficult to discern different species of ligands in situ.

The bioavailability of various Fe-ligand complexes for uptake by phytoplankton is currently uncertain. Experimental work using natural and model ligands suggests that at least some portion of the organically complexed Fe pool is bioavailable to phytoplankton via cell surface reduction mechanisms [Soria-Dengg and Horstmann, 1995; Hutchins et al., 1999; Maldonado and Price, 1999; Shaked et al., 2005]. The bioavailability of Fe-ligand complexes for a given phytoplankton taxon appears to depend on the specific ligand in question [Hutchins et al., 1999; Maldonado and Price, 1999].
organically complexed over the austral winter, a variety of mechanisms can supply enough Fe to phytoplankton during the spring ice melt. Phytoplankton may rely solely on photochemical processes to mobilize inorganic dissolved Fe or they may need to access a portion of the organically complexed Fe pool directly. The efficiency of Fe recycling/retention may also differ between the well-stratified MIZ regions of the Ross Sea and the weakly stratified RSP, providing analogues to processes that are likely to be prevalent throughout the SO. To investigate the importance of Fe cycling on phytoplankton dynamics, we parameterized a complex Fe supply model (including the major aspects of seawater Fe chemistry) within the existing three-dimensional Coupled Ice-Atmosphere-Ocean (CIAO) ecosystem model of the Ross Sea. Our Fe cycle model is similar in some respects to the model developed by Weber et al. [2005] to investigate the cycling of Fe at the Bermuda Atlantic Time Series (BATS). Unlike BATS, the Ross Sea is seasonally ice covered and Fe limited, and we would therefore expect ecosystem processes to exhibit a greater sensitivity to the Fe speciation and cycling represented within CIAO. Our Fe supply model is also embedded within a realistic three-dimensional ecosystem model and can therefore address questions related to spatial heterogeneity in environmental conditions or phytoplankton taxonomic composition. Specifically, our goal was to assess the role of the various physical (e.g., irradiance), chemical (e.g., organic complexation or photochemistry) and biological (e.g., Fe acquisition strategies) processes in dictating the supply of Fe to the resident phytoplankton across the diverse oceanic habitats present in the Ross Sea. In particular, we were interested in role of ligand-complexed Fe and whether an organically complexed bioavailable Fe pool was necessary to explain the observed phytoplankton dynamics.

2. Model Description

[10] Dynamics of the two major phytoplankton functional groups (P. antarctica and diatoms), zooplankton, macro-nutrients, and pCO₂ already have been successfully simulated using the CIAO model of the southwestern Ross Sea [Arrigo et al., 2003; Worthen and Arrigo, 2003; Tagliabue and Arrigo, 2005]. The physics of CIAO are based upon the Princeton Ocean Model, a primitive equation ocean circulation model [Blumberg and Mellor, 1983] with vertical mixing calculated according to the turbulence closure scheme [Mellor and Yamada, 1982]. The two phytoplankton groups in CIAO have taxon-specific nutrient utilization ratios as per Arrigo et al. [2002]. CIAO also contains state variables representing zooplankton, three detrital pools (C, P, and Fe), nitrate (NO₃), phosphate (PO₄), silicic acid, pCO₂, dissolved organic carbon, dissolved oxygen (O₂) and simulates air-sea exchange of CO₂ and O₂. A full description of the ecosystem model can be found in Arrigo et al. [2003] and Tagliabue and Arrigo [2005]. Parameter values for all rate constants detailed below are given in Table 1 and have been taken from the published literature (concentrating on Southern Ocean studies wherever possible).

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aWhere two values are separated by a backslash, the first is for P. antarctica and the second is for diatoms.
The speciation and concentration of Fe in seawater is determined in a variety of fashions that typically discriminate between dissolved (dFe, <0.2 μm) and particulate (pFe, >0.2 μm) phases (see Bruland and Rue [2001] for a discussion of the various methodologies). To more accurately simulate the complex Fe cycle in seawater, we replaced the simple Fe cycle used previously in CIAO with an Fe supply model that utilizes 4 dFe (including Fe(II), Fe(III), Fe(III)La, and Fe(III)Lb) and 4 pFe (including inorganic particles >0.4 μm and Fe associated with detritus, phytoplankton and zooplankton) pools (Figure 2). In this model, the two free inorganic Fe pools include Fe(II) and Fe(III). Fe(III) can be converted to solid inorganic Fe species (Fe(III)s) and forms ligand complexes that can be either non-bioavailable (Fe(III)La) or bioavailable (Fe(III)Lb). Total Fe (tFe) is simply the sum of the pFe and dFe pools. Bioavailable forms of Fe (bFe) in the standard simulation are taken to be Fe(II), Fe(III), and Fe(III)Lb (see Table 1 for parameter definitions).

The rate of change in the Fe(II) pool (μmol m⁻³ s⁻¹) is

\[ Q_{Fe(II)} = (1 - \alpha)Fe_{atm} + Fe_{sed} - \tau_{Fe(II)}(Fe/C_i)P_i - k_{ox}Fe(II) + k_{pr}Fe(III)La + \epsilon_z + ice_{Fe} + R_{det}Fe \]  

(1)

and is a function of oxidative loss (k_{ox}Fe(II)), photoreduction of Fe(III)La to Fe(II) (k_{pr}Fe(III)La), atmospheric deposition (Fe_{atm}), sedimentary resuspension (Fe_{sed}), sea ice melting (ice_{Fe}), remineralization of detrital Fe (R_{det}Det_{Fe}) and uptake by phytoplankton taxa i (\tau_{iFe}Fe(II)/C_iP_i), where i is either P. antarctica or diatoms). Fe(II) oxidation is modeled as a temperature-dependent (see Table 1) pseudo first order rate constant (k_{ox}) [Millero et al., 1987]. Data used to define the relationship between temperature and k_{ox} also include the low temperature Fe(II) half lives measured during the Southern Ocean Iron RElease Experiment (SOIREE) [Bowie et al., 2001]. The rate constant for photoreduction (k_{pr}) varies as a function of irradiance as per Rijkenberg et al. [2005]. The rate of atmospheric Fe deposition into open water (Fe_{atm}, 0.1 μmol Fe(II) m⁻² yr⁻¹) is taken from estimates made during SOIREE [Bowie et al., 2001] and adjusted to account for the proportion of each grid cell that is ice covered (A). Atmospheric Fe accumulating on sea ice is assumed to reach concentrations of 15 nM, 40% of which is soluble [Edwards and Sedwick, 2001]. The rate of sedimentary Fe(II) input (Fe_{sed}) is assumed to be constant (15.7 μmol Fe(II) m⁻² yr⁻¹) and is at the low end of total dissolved Fe fluxes (which include other Fe species) measured by Elrod et al. [2004] off the coast of California. While there are no sedimentary Fe(II) flux data for the SO, our Fe(II) sedimentary flux estimates result in deep dissolved Fe concentrations that are consistent with in situ measurements for the southwestern Ross Sea [Coale et al., 2005]. The Fe demand for phytoplankton taxa i per unit C fixed (P_i) is Fe/C_i (2.22 and 10 μmol Fe mol C for P. antarctica and diatoms, respectively), while the fraction of the total Fe demand by each taxa that is satisfied by Fe(II) is denoted \tau_{iFe}Fe(II) (see below). Phytoplankton demands for Fe are highly variable as a function of incident irradiance and Fe concentration, and in the absence of information describing such variability for Ross Sea phytoplankton, we use the taxon specific-ratios sensu Tagliahue and Arrigo [2005]. If the Fe/C ratio of zooplankton food is greater than their cellular Fe/C quota [Schmidt et al., 1999, Table 1], then the excess Fe consumed (\epsilon_z) is assumed to enter the Fe (II) pool.
The rate of change in Fe(III) ($\mu$mol m$^{-3}$ s$^{-1}$) is
\[
Q_{Fe(III)} = k_{as}Fe(II) - k_{pFe(III)La}Fe(III)[La] + k_{Fe(III)La}Fe(III)La
- k_{Fe(III)}LaFe(III)[La] + k_{Fe(III)La}Fe(III)La - \gamma_i Fe(III)
\cdot (Fe/C_i)P_i - k_{pcp}Fe(III) + R_{Fe(III)}Fe(III)s
\tag{2}
\]
where oxidation of Fe(II) produces Fe(III) ($k_{as}Fe(II)$). Fe(III) can be complexed by either $L_a$ or $L_b$ to form Fe(III)$La$ and Fe(III)$Lb$, respectively, at a rate that is a function of the respective ligand concentration ([La] or [Lb]) and the complex formation rate constant ($k_{Fe(III)La}$ or $k_{Fe(III)Lb}$). We include dissociation of each complex in the absence of light as a first order process ($k_{Fe(III)La}$ or $k_{Fe(III)Lb}$), while Fe(III)$La$ also can be photoreduced to Fe(II) ($k_{Fe(III)La}$, equation (1)). We do not model the two ligand pools dynamically; instead, the concentration of $L_a$ is fixed at 2 nM [Boy et al., 2001; Croot et al., 2004] and the concentration of the strong chelator ([Lb]) is set to 0.6 nM [Rue and Bruland, 1997]. Rate constants for the formation and dissociation of Fe(III)$La$ are taken from measurements of Witter and Luther [1998].

Maldonado and Price [1999] demonstrated significant phytoplankton uptake of Fe when complexed with desferrioxamine (DFO) ligands, which have been shown to be present in seawater [McCormack et al., 2003] and produced by marine bacteria [Martinez et al., 2001]. We therefore assume rate constants for the formation ($k_{Fe(III)Lb}$) and dissociation ($k_{Fe(III)Lb}$) of Fe(III)$Lb$ in accordance with the measured kinetics of DFO [Witter et al., 2000]. Calculated log conditional stability constants for $L_a$ and $L_b$ ($k_{Fe(III)La}$ and $k_{Fe(III)Lb}$, Table 1) are consistent with values reported for the SO [e.g., Boy et al., 2001; Croot et al., 2004], assuming that $\alpha_{Fe} = 10^{10}$ [Hudson et al., 1992]. The proportion of total phytoplankton uptake of Fe that is satisfied by Fe(III) is denoted as $\gamma_i Fe(III)$. Fe(III) is lost to solid inorganic forms (Fe(III)s) via scavenging/precipitation [Johnson et al., 1994] as a first order processes ($k_{pcp}Fe(III)$, $2.78 \times 10^{-5}$ s$^{-1}$) and is remineralized to Fe(III) at the same rate as detritus ($R_{Fe(III)}Fe(III)s$, $3.57 \times 10^{-8}$ s$^{-1}$).

The rate of change in the Fe(III)$La$ pool ($\mu$mol m$^{-3}$ s$^{-1}$) is
\[
Q_{Fe(III)La} = k_{Fe(III)La}Fe(III)[La] - k_{Fe(III)La}Fe(III)La
- k_{pcp}Fe(III)La + Fe/C_i(1 - \gamma_i)g/Z
\tag{3}
\]
where $L_a$ complexes inorganic Fe(III) as described above to produce Fe(III)$La$ ($k_{Fe(III)La}$) and facilitates its photoreduction to Fe(II) via LMCT ($k_{Fe(III)La}$). In order to conserve particulate Fe/C ratios, we also assume that the Fe content of unassimilated grazing (on phytoplankton taxa $i$, $Fe/C_i(1-\gamma_{pro})g/Z$) will liberate organically complexed Fe which is added to the Fe(III)$La$ pool.

The rate of change in Fe(III)$Lb$ ($\mu$mol m$^{-3}$ s$^{-1}$) is
\[
Q_{Fe(III)Lb} = k_{Fe(III)Lb}Fe(III)[Lb] - k_{Fe(III)Lb}Fe(III)Lb - \gamma_i Fe(III)Lb
\cdot (Fe/C_i)P_i + Fe/C_i(eP_i)
\tag{4}
\]
where Fe(III)$Lb$ is also produced from the organic complexation of Fe(III) ($k_{Fe(III)Lb}$, see above), but is assumed to be non-photoactive [Barbeau et al., 2003] and bioavailable to the phytoplankton. The quantity $\pi_{Fe(III)Lb}$ is the fraction of the total Fe demand for phytoplankton taxa $i$ satisfied by Fe(III)$Lb$ (see below).

To conserve planktonic Fe/C ratios, we assume that organic Fe also is lost as phytoplankton exude dissolved organic carbon ($Fe/C_i(eP_i)$) which is added to the Fe(III)$Lb$ pool. Model results are insensitive to this process.

The rate of change in solid inorganic Fe (not associated with either phytoplankton or detritus, $Q$, $\mu$mol Fe(III)s m$^{-3}$ s$^{-1}$) is
\[
Q_{Fe(III)s} = k_{pcp}Fe(III) - R_{Fe(III)s}Fe(III)s - snkFe(III)s.
\tag{5}
\]
where Fe(III)s is produced from the precipitation of Fe(III) ($k_{pcp}Fe(III)$) and is lost due to remineralization ($R_{Fe(III)s}$) and sinking ($snkFe(III)s$).

The phytoplankton light limitation term is calculated as per Arrigo et al. [2003] and the degree of Fe limitation for each taxon (dimensionless) via the Monod [1942] expression, such that (for the bioavailable Fe concentration, $bFe$)
\[
Fe_{lim} = \frac{bFe}{(bFe + K_{Fe})}
\tag{6}
\]
where $bFe$ is the sum of the concentrations of Fe(II), Fe(III), and Fe(III)$Lb$ (see above). We use $K_{Fe}$ values of Arrigo et al. [2003] and Tagliabue and Arrigo [2005], but also note the wide variability in published values for $P. antarctica$ and diatoms [Blain et al., 2002; Coale et al., 2004]. Limitation terms for all other nutrients are calculated in a similar fashion, and the phytoplankton maximum growth rate ($\mu_{max}$) is adjusted by the most limiting resource. The fraction of the total Fe demand ($\pi_i^X$) for taxa $i$ that is satisfied by Fe species $X$ (where $X$ is either Fe(II), Fe(III), or Fe(III)$Lb$) is calculated as
\[
\pi_i^X = \frac{Fe(II)|_{Fe(II)+K_{Fe}} + Fe(III)|_{Fe(III)+K_{Fe}} + Fe(III)Lb|_{Fe(III)Lb+K_{Fe}}}{Fe(II) + Fe(III) + Fe(III)Lb}
\tag{7}
\]
and $\pi_i^{Fe(II)} + \pi_i^{Fe(III)} + \pi_i^{Fe(III)Lb} = 1$. The standard run is represented by equations (1)–(7), with parameter values as described in Table 1. To assess the role of photoreduction in supplying bioavailable Fe to phytoplankton, we performed an additional run wherein the rate constant for photoreduction ($k_{pro}$) was set to zero. In order to address whether a bioavailable organically complexed Fe pool was necessary to replicate the observed phytoplankton dynamics, we also parameterized CIAO such that Fe(III)$La$ was the only ligand present (i.e. no Fe(III)$Lb$). This run also allowed us to explore if photoreduction of the Fe(III)$La$ complex can supply enough bFe to sustain the observed phytoplankton blooms. The sensitivity of phytoplankton dynamics to the values ascribed to the rate constants for photoreduction ($k_{pro}$), formation of Fe(III)$La$ ($k_{Fe(III)La}$), and dissociation of Fe(III)$Lb$ ($k_{Fe(III)Lb}$), as well as the Fe pool assigned to recycled Fe, were also explored. In order to remove the effect of taxon specific variability in phytoplankton demands for Fe, we also performed a simulation...
wherein both *P. antarctica* and diatoms were assigned the same Fe/C uptake ratio (10 μmol Fe: mol C).

### 3. Results and Discussion

#### 3.1. Comparison With Observations

[18] Dynamics of surface chlorophyll *a* (Chl *a*) using the new Fe supply model in CIAO are in excellent agreement with satellite retrievals of Chl *a* (Figures 3a and 3b). The phytoplankton bloom associated with the RSP begins at the end of November and rapidly reaches biomass levels of approximately 10 mg Chl *a* m⁻³, 90% of which is associated with *P. antarctica* (Figure 3a). Strong katabatic winds and deep mixing in the TNBP delay the onset of the phytoplankton bloom (mostly diatoms) until the beginning of January [Arrigo et al., 1998a]. Once the in situ ice melt begins and surface waters become stratified, phytoplankton in the TNBP reach a peak biomass of 6 mg Chl *a* m⁻³ by mid January (Figure 3b). By mid February, Chl *a* levels are still relatively high (~2 mg m⁻³), which is consistent with satellite data (Figure 3b). CIAO predicts that although diatoms dominate the initial bloom, *P. antarctica* makes up over half of the phytoplankton biomass during mid to late February (Figure 3b). For a more complete discussion of the significance of phytoplankton taxonomic composition, see Arrigo et al. [2003] and Tagliabue and Arrigo [2005].

[19] Annual NPP from CIAO over the whole southwestern Ross Sea is 65.1 Tg C, or 107 g C m⁻² (including the low productivity waters northeast of the continental shelf break), with rates of 186 and 91 g C m⁻² for RSP and TNBP, respectively. Model predictions of NPP are in line with the previous version of CIAO [Tagliabue and Arrigo, 2005] and both satellite-based and field estimates for the Ross Sea [e.g., Arrigo and van Dijken, 2004; Smith and Gordon, 1997].

[20] Vertical profiles of dFe from CIAO fall well within the range of in situ measurements made in the Ross Sea (Figure 4) [Johnson et al., 1997; Sedwick and DiTullio, 1997; Fitzwater et al., 2000; Sedwick et al., 2000; Grotti et al., 2001; Coale et al., 2005]. It should be noted that the highest reported in situ dFe concentrations are somewhat atypical of much of the Ross Sea as they were from studies conducted in regions of high sea ice melt where large quantities of Fe were likely released into the water column [Sedwick et al., 2000; Grotti et al., 2001]. The mean dFe concentration from CIAO is approximately 0.4 nM throughout most of the water column, increasing slightly near the sea floor. This is close to the mean in situ dFe value of 0.53 nM, which excludes the upper and lower depth quartiles that are impacted by the atmosphere and sediments, respectively. Maximum dFe concentrations produced by CIAO are found in surface waters (~1.5 nM) and result from the release of Fe as sea ice melts in spring and summer (Figure 4). Concentrations are almost as high near the sea floor due to resuspension of sedimentary dFe. Minimum concentrations of dFe are near zero in surface waters and increase with depth to approximately 0.3 nM throughout the rest of the water column, in good agreement with in situ measurements (Figure 4).

#### 3.2. Annual Cycle of Fe

[21] Processes such as Fe release from melting sea ice and photoreduction of Fe(III)La to Fe(II) can greatly impact the amount of bioavailable Fe in surface waters. Therefore, it is of interest to contrast the annual cycles of Fe in waters of the Ross Sea where the role played by sea ice processes is large (e.g., the MIZ region near the TNBP) and where it is small (e.g., the RSP). During the ice covered austral winter,
CIAO predicts dFe concentrations of approximately 0.4 nM in both the RSP and the TNBP (Figures 5a and 5b), with over 99% of the dFe pool being organically complexed (by either L\textsubscript{a} or L\textsubscript{b}). It should be noted that although these bulk dFe concentrations are high (relative to planktonic demands), the bioavailable fraction (bFe) remains low under sea ice (<0.1 nM, Figure 5a). As the system equilibrates (in the absence of light) over the long austral winter, the higher concentration of L\textsubscript{a} (relative to L\textsubscript{b}) results in Fe(III)L\textsubscript{a} dominating the dFe pool. During spring in the RSP, katabatic winds blow sea ice to the north, and as irradiance levels subsequently increase, the Fe(III)L\textsubscript{a} pool is rapidly photoreduced. This results in an increase in the concentration of the bFe pool, as the Fe(II) produced by photoreduction of Fe(III)L\textsubscript{a} is oxidized to Fe(III) and rapidly complexed by L\textsubscript{b} into Fe(III)L\textsubscript{b} (Figure 2). Fe(II) is a transient species, with a maximum concentration in CIAO of around 40 pM during periods of enhanced photoreduction, in agreement with observations from the Australian sector of the SO [Bowie et al., 2002]. In contrast, Fe(III) is rarely predicted to exceed 1 pM. The high frequency variation in bFe (Figures 5a and 5b) is caused by changes in the relative rates of photoproduction and re-oxidation of Fe(II), driven by diurnal changes in irradiance (Figure 5c). The slight increase in tFe by mid November reflects atmospheric deposition onto ice-free surface waters.

Once bFe concentrations in the RSP increase above growth limiting levels in early October, *P. antarctica* begins to bloom and concentrations of dFe and bFe are reduced to zero by early December, with pFe (mostly phytoplankton Fe) dominating the bulk Fe pool (Figure 5a). The peak in pFe lags the Chl \textsubscript{a} peak in the RSP (Figure 3a) by approximately 5 days, reflecting the increased contribution of detrital Fe and Fe(III)s to pFe. Between the end of December and mid-February, almost all pFe sinks below the thermocline, resulting in the loss of ~0.4 nM from the tFe pool in surface waters. Deepening mixed layers in early March increase tFe concentrations in surface waters as relatively Fe-rich water is mixed up from below (Figure 5a). The return of sea ice during April precludes further photochemical conversion of Fe, and therefore tFe, dFe, bFe, and pFe begin to trend towards austral winter values.

While the annual cycle of Fe within the TNBP is generally the same as in the RSP, there are some important differences (Figure 5b). As in the RSP, wintertime dFe is quite high in the TNBP, with most contained in organic complexes that are unavailable to the phytoplankton. How-
ever, high rates of ice melt in the TNBP increase tFe by 0.25 nM in January. Photoreduction of Fe(III)La also creates ample bFe in the TNBP by the beginning of December, but this remains unutilized until mid-January (Figure 5b) when the ice melt has completely stratified surface waters and phytoplankton are no longer light limited. CIAO predicts that inorganic Fe(II) concentrations are also slightly higher in the TNBP (maximum of approximately 70 pM) than the RSP (40 pM, see below for discussion). In the current version of CIAO, appreciable Fe(II) can only be produced via photoreduction of Fe(III)La (atmospheric sources are negligible). However, in nature, oxidative reactions with hydrogen peroxide and back reactions between Fe(III) and superoxide are also important in dictating Fe(II) concentrations [e.g., Crook et al., 2005]. That said, photoreduction rate constants that are derived from measuring Fe(II) evolution [e.g., Rijkenberg et al., 2005] already account for these other processes that produce Fe(II). The accumulation and sinking of pFe is predicted to occur over a much shorter timescale in the TNBP (1 month) than the RSP (2 months); this is most likely to be due to the relative delay of the TNBP phytoplankton bloom. Consistent with the higher Fe demand of diatoms, there is a greater loss of Fe from TNBP surface waters (~0.6 nM).

The annual cycle of irradiance (modulated by sea-ice cover) also drives changes in Fe speciation with respect to depth. In deep water, the ratio of Fe(II)/dFe from CIAO is 0.04, whereas during photoreduction in surface waters the Fe(II)/dFe ratio increases to 0.2 in both the RSP and the TNBP, consistent with the observations of Bowie et al. [2002]. Light attenuation by phytoplankton biomass will also affect Fe speciation. For example, CIAO shows that in waters characterized by large spring phytoplankton blooms (e.g., the RSP and TNBP), downwelling irradiance and photoreduction of Fe(III)La are retarded below the surface layers. This results in a delay in the photoreduction of Fe(III)La in subsurface waters (e.g., 25 m in the RSP, Figure 6). As the RSP spring phytoplankton bloom declines in late December, the concomitant increase in subsurface irradiance results in photoreduction of Fe(III)La at 25 m depth (Figure 6). Deepening mixed layers during the late summer will also expose subpynocline Fe(III)La to elevated light levels and subsequent photoreduction will increase bFe concentrations. Elevated bFe during the late austral summer stimulates increased phytoplankton biomass during mid March in both the RSP and the TNBP (Figures 3a and 3b).

Recycling of Fe via zooplankton grazing is of little consequence, due to the low zooplankton biomass and grazing rates within the Ross Sea [Tagliabue and Arrigo, 2003]. However, zooplankton-mediated Fe recycling will be significant in regions where large fractions of phytoplankton biomass are consumed by higher trophic levels, such as the Polar Front or near South Georgia [Atkinson et al., 2001]. Microzooplankton and bacteria could also be acting as agents of Fe recycling [Hutchins et al., 1995; Barbeau et al., 2003], but while such processes are not explicitly included in CIAO at the present time, microzooplankton grazing rates and bacterial biomass are both low in the Ross Sea [Caron et al., 2000; Ducklow et al., 2000]. CIAO predictions of export compare well with in situ data [see Arrigo et al., 2003] and it therefore appears reasonable to suggest that both the RSP and TNBP surface waters are net vertical exporters of Fe (alongside other nutrients), replenished each winter by convective mixing.

### 3.3. Significance of Photoreduction and Organic Complexation

We performed tests to examine the importance of the process of photoreduction and the presence of the Fe(III)La pool in predicting regional NPP and phytoplankton dynamics. Photoreduction of organically bound Fe is important in governing Fe speciation transitions and is posited to be responsible for the higher than expected Fe(II) concentrations measured during the later stages of SOIREE [Crook et al., 2001]. By setting the rate constant for Fe(III)La photoreduction ($k_{pr}$) to zero we were able to test the significance of photoreduction. Model results show that during the austral winter, almost all the Fe is complexed by ligands into forms unavailable to phytoplankton (Figures 5a and 5b). However, by retaining Fe within a photolabile organic complex, Fe(III)La can be rapidly mobilized into bioavailable phases once irradiance levels increase during the spring ice melt. Free Fe(II) produced by photolysis of Fe(III)La is then either consumed by phytoplankton, stabilized by L$_a$, or made available for uptake, or oxidized to Fe(III) and either taken up by phytoplankton, re-complexed by L$_a$, or lost to the refractory Fe(III) pool. In the absence of photoreduction, regional cumulative NPP over the southwestern Ross Sea is reduced by >90% to 5 Tg C yr$^{-1}$, with appreciable production limited only to regions with substantial Fe(II) input from melting sea ice (data not shown).

In the southwestern Ross Sea, the cycling of Fe is predominately governed by photochemical processes, although in other regions, recycling by zooplankton and bacteria will also be important. Herbivory rates of mesozooplankton and microzooplankton are low in the Ross Sea [Caron et al., 2000] due to the rapid rate of phytoplankton growth [Tagliabue and Arrigo, 2003]. Consequently, our findings are not sensitive to the precise Fe pool assigned to both the unassimilated grazing products and the products of detrital remineralization. In regions where secondary production plays a more important role, e.g., the Antarctic...
Peninsula region, the speciation of Fe liberated by herbivory and remineralization will likely prove to be more important.

[28] The characteristics of the ligands could prove to be of greater significance than recycling in the Ross Sea. Maldonado et al. [2005] suggest bioavailable Fe-organic complexes in the subantarctic region of the Southern Ocean could well be photoreactive. Model results suggest that assigning photolability to Fe(III)Lb would result in only a slight increase in the Fe(III) pool and little change in rates of phytoplankton primary production, especially in regions where cold surface waters retard rates of Fe(II) oxidation. Similarly, if we reduce the formation rate constant for Fe(III)La ($k_{Fe(III)La}$) by half, there is little impact on phytoplankton biomass accumulation and annual rates of photoreduction in the TNBP remain greater than those in the RSP. In the absence of photoreduction, the only scenario that results in phytoplankton biomass in accordance with observations is when the dissociation constant for Fe(III)La ($k_{Fe(III)La}$) is increased ten-fold, which approximates the role of photoreduction (i.e., breakdown of Fe(III)La complexes). However, unlike photoreduction, dissociation will also occur in dark, ice covered waters. Since there is no phytoplankton uptake during such conditions, there are increasing losses to the Fe(III) pool and biomass at the peak of the RSP bloom is reduced by around 20%. In the TNBP, we predict a reduction in phytoplankton biomass of approximately 10% at the peak of the diatom bloom, and an increase of 20% during the later $P. antarctica$ bloom. Rates of Fe(III)La dissociation in deep waters are elevated markedly during this scenario, resulting in increased deepwater bFe concentrations (by almost 0.25 nM). This extra Fe fuels additional biomass accumulation by $P. antarctica$ in the TNBP as mixed layers deepen in the late summer. Nevertheless, this suite of experiments suggest that photoreduction of Fe(III)La is the key process governing the supply of Fe to phytoplankton in regions of the SO where there is a substantial increase in irradiance resulting either from the loss of sea ice or from increased surface stratification as winds subside in spring.

[29] The ability of phytoplankton to take up ligand-bound Fe has been demonstrated in culture experiments [e.g., Soria-Dengg and Horstmann, 1995; Hutchins et al., 1999; Shaked et al., 2005] and some field studies [Maldonado and Price, 1999; Maldonado et al., 2005], but this may depend on the specific phytoplankton and ligand group in question [Hutchins et al., 1999; Blain et al., 2004]. In order to examine the potential importance of Fe(III)Lb complexes, we parameterized Ciao such that $k_{a}$ was the only ligand present in seawater and the subsequent Fe(III)La complexes were unavailable to the phytoplankton. In the absence of Fe(III)Lb, the resident phytoplankton rely on enhanced photochemical recycling of Fe(III)La to maintain bFe above growth limiting levels. This additional recycling results in a greater loss of Fe in the form of Fe(III)Js, thus reducing the total bFe pool and further highlighting the role Fe ligands play in the buffering of reactive Fe concentrations. As a result, cumulative regional NPP was reduced by 30%, from 65.1 Tg C yr$^{-1}$ during the standard run to 43.7 Tg C yr$^{-1}$.

[30] The reduction in NPP due to the absence of Fe(III)Lb was not uniform over the southwestern Ross Sea. Phytoplankton dynamics in the RSP change little, although the bloom is delayed somewhat relative to the standard run and is lower in magnitude (compare Figure 3c with Figure 3a). In line with the small changes in phytoplankton dynamics in the RSP, annual NPP is only predicted to fall by around 6%. The change in phytoplankton dynamics resulting from the loss of the Fe(III)Lb pool is much more dramatic in the TNBP, where annual NPP is reduced by 45%. Furthermore, in the absence of Fe(III)Lb, the primary (mid January) diatom bloom never develops and only when mixed layers deepen during March does an appreciable bloom form (compare Figure 3d with Figure 3b). This later bloom has never been observed in SeaWiFS satellite retrievals and is predicted to be dominated by $P. antarctica$ instead of the diatoms more commonly observed in such MIZ waters (Figure 3d).

[31] The results of these simulations suggest that the ability to access some portion of the organically complexed Fe pool is of much greater significance in MIZ waters dominated by phytoplankton with a high Fe demand (such as diatoms), than in the weakly stratified, $P. antarctica$ dominated RSP. This is consistent with culture experiments demonstrating the uptake of organically bound Fe by diatoms and other large phytoplankton via cell surface reduction mechanisms [e.g., Soria-Dengg and Horstmann, 1995; Maldonado and Price, 1999; Shaked et al., 2005] and reduced rates of uptake by smaller phytoplankton [Blain et al., 2004].

[32] Previous Ciao simulations suggested that photosynthetic characteristics control species composition in the Ross Sea during spring [Arrigo et al., 2003]. However, if the resident phytoplankton exhibit taxon-specific uptake of organically bound Fe, then regional heterogeneity in environmental conditions and the subsequent speciation of Fe also may be important in determining species composition in the Ross Sea. It appears reasonable to suggest that although dFe concentrations are high during the austral spring, most dFe will be organically complexed, with low concentrations of inorganic Fe(II) and Fe(III). The results of these simulations suggest that it is possible that $P. antarctica$ and diatoms might employ different Fe acquisition strategies to sustain their high biomass levels. In the RSP, weak stratification results in low photoreduction rates of Fe(II), but the low Fe demand of $P. antarctica$ allows this taxon to bloom profusely, despite the low bFe concentration. In the well stratified TNBP, elevated rates of sea-ice melting and photoreduction of Fe(III)La supply a much higher bFe concentration. Diatoms, with their high Fe demand, might require these high Fe recycling rates, as well as an ability to access a portion of the organically complexed Fe pool, in order to reach high biomass. Therefore, light might control species composition in the Ross Sea by impacting both phytoplankton photosynthetic performance [Arrigo et al., 2000] and Fe speciation. To address this possibility will require information about the kinetic characteristics and sources and sinks of such ligands in seawater and the subsequent bioavailability of organically bound Fe to specific phytoplankton taxa.

3.4. Efficient Fe Cycling in MIZ Waters

[33] In the MIZ, melting sea ice creates a shallow (10–20 m) stratified surface layer that is well illuminated and often augmented with exogenous Fe and sea ice algae. As a
As a result of the high light and high Fe conditions, there are often significant levels of both biological productivity [e.g., Smith and Nelson, 1986; Arrigo et al., 1998b] and trophic transfer [e.g., Hopkins et al., 1993] associated with the MIZ. Annual cumulative rates of photoreduction across the southwestern Ross Sea calculated from CIAO show there is significantly more recycling of Fe within regions characterized by significant sea ice melt and shallow mixed layers (such as the TNBP) than in the weakly stratified RSP (Figures 7a and 7b). Elevated annual photoreduction rates in the RSP are due to the greater number of ice free days in this region, compared to the surrounding MIZ (Figure 8a). The highest annual rates of photoreduction occur where the minimum annual mixed layer depth is <10 m (Figure 9). Over the course of the year, the greater flux of Fe from sea ice melting and relatively shallow mixed layers close to Edward VII Land result in the highest cumulative rates of Fe photoreduction, even though the proportional sea-ice coverage does not fall below 0.4 (Figure 7a). CIAO produces rates of Fe(III)La photoreduction that average (December through January) 0.58 and 1.13 × 10^-5 s^-1 for the RSP and TNBP, respectively, both slightly lower than previously published estimates [e.g., Miller et al., 1995;...
Barbeau et al., 2003; Emmenegger et al., 2001]. Even if the calculated rate constant for Fe(III)La photoreduction is halved, annual photoreduction is only reduced by approximately 20% across the southwestern Ross Sea and the relationship between rates of Fe(III)La photoreduction and mixed layer depth is retained (data not shown).

Typically, MIZ waters are significantly colder than non-MIZ regions such as the RSP [Arrigo et al., 2000], which will impact Fe(II) oxidation rates in CIAO by reducing the rate constant for Fe(II) oxidation ($k_{ox}$, Table 1). This is important because any decline in Fe(II) oxidation rate as temperature decreases [Millero et al., 1987] will consequently increase the residence time of Fe(II) in the euphotic zone. Sea ice melting in the MIZ of the TNBP (and other MIZ regions) reduces surface water temperatures, whereas the upwelling of circumpolar deep water in the RSP raises temperatures by over 3°C [e.g., Jacobs and Raven, 1999]. Given the average rate constant for Fe(II) oxidation ($k_{ox}$) for the growing season (between early December and early February), rates of Fe(II) oxidation are calculated to be much lower in the MIZ waters west of 170°E than within the RSP (Figure 7c). This is because the 3°C temperature difference between the TNBP and RSP yields a value for $k_{ox}$ that is 55% greater in the RSP. Higher Fe(II) production rates (photoreduction) and lower loss rates (oxidation) likely explain why the maximal predicted Fe(II) concentration in the TNBP is higher than within the RSP.

Not only does melting sea ice usually provide an exogenous supply of Fe to surface waters, it also creates an environment that is highly favorable for efficient Fe recycling. Low vertical diffusivity in ice-melt stratified waters will retard the mixing losses of bFe to deeper waters that might be expected in a weakly stratified region such as the RSP. Furthermore, water column dFe, augmented by any Fe released from sea ice, will experience an environment that is both cold (low oxidation rates) and well illuminated (high photoreduction rates) during spring, resulting in effective Fe recycling and retention. In fact, even in the absence of an ice melt source of Fe, MIZ regions exhibit high rates of Fe recycling due to their shallow mixed layers. Daily rates of photoreduction within the MIZ only decrease by ~10% and remain approximately twice those of the RSP if the Fe concentration in melting sea ice is set to zero within CIAO (considering spatial heterogeneity in open water duration, Figures 8a and 8b). The unusually large reduction in cumulative photoreduction predicted in waters near Edward VII Land was due to the large amount of ice melt and associated Fe release that typifies this region. Our results suggest, however, that high Fe photoreduction rates in the MIZ are mostly a consequence of the physical environment (e.g., high light, low temperature) and not simply due to additional Fe input from sea ice melting. This implies that interannual changes in sea ice dynamics, such as those observed in the Ross Sea during recent years [Arrigo and van Dijken, 2004], could drive significant variability in Fe cycling and hence phytoplankton productivity in polar regions.

### 3.5. Utilization of Fe

In order to understand how changes in the supply of Fe (via natural or anthropogenic means) might impact the cycling of carbon, one must understand how efficiently dFe is converted into phytoplankton carbon via photosynthesis. The iron use efficiency (IUE, sensu Raven [1988]) for a given habitat (referred to here as the apparent IUE) is a function of both biotic (Fe requirements of phytoplankton, remineralization) and abiotic (oxidation and photoreduction of Fe modulated by temperature and stratification, respectively) factors. For instance, waters conducive to Fe photoreduction and with phytoplankton having a low Fe requirement will exhibit a higher apparent IUE than waters with the opposite characteristics. In order to isolate the effect of abiotic factors on the apparent IUE, we assigned $P. antarctica$ and diatoms the same cellular Fe/C requirement (10 μmol: mol) and examined differences in the ratio of depth integrated dFe depletion to depth integrated NPP between the RSP and the TNBP. Since the physical conditions of the RSP and TNBP change throughout the year, we evaluated the apparent IUE (NPP/ΔdFe) on a monthly basis during the growing season.

The apparent IUE is always highest when mixed layers are shallow and temperatures are low (see Table 2). During November, strong katabatic winds in the TNBP result in a significantly deeper mixed layer depth (MLD, >100 m) than in the RSP (33 m), whereas the average sea surface temperature (SST) is similar in both locations (~2°C). Increased photoreduction of Fe(III)La in the RSP results in a much higher apparent IUE than within the TNBP (by >90%). Once the katabatic winds begin to slacken in mid December, the average MLD in the TNBP becomes slightly less than in the RSP, while the RSP SST is almost 1°C warmer than in the TNBP. Decreased bioavailability of Fe due to increased oxidation of Fe(II) in the RSP results in a lower apparent IUE than in the TNBP. By January, the TNBP becomes much more stratified (22 m and 5 m for the RSP and TNBP, respectively) and upwelling of

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**Table 2. General Trends in Monthly Integrated Apparent IUE and Monthly Averaged Mixed Layer Depth (MLD, m) and Sea Surface Temperature (SST, °C) for the RSP and the TNBP**

<table>
<thead>
<tr>
<th>Month</th>
<th>MLD</th>
<th>SST</th>
<th>Monthly Integral</th>
<th>Apparent IUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov</td>
<td>RSP &lt;&lt; TNBP</td>
<td>RSP ≈ TNBP</td>
<td>RSP &gt;&gt; TNBP</td>
<td>TNBP (+5%)</td>
</tr>
<tr>
<td>Dec</td>
<td>RSP &gt; TNBP</td>
<td>RSP &gt; TNBP</td>
<td>RSP &gt; TNBP</td>
<td>TNBP (+5%)</td>
</tr>
<tr>
<td>Jan</td>
<td>RSP &gt;&gt; TNBP</td>
<td>RSP &gt;&gt; TNBP</td>
<td>RSP &gt;&gt; TNBP</td>
<td>TNBP (+5%)</td>
</tr>
<tr>
<td>Feb</td>
<td>RSP &lt; TNBP</td>
<td>RSP &gt; TNBP</td>
<td>RSP &gt; TNBP</td>
<td>TNBP (+5%)</td>
</tr>
</tbody>
</table>

*When both P. antarctica and diatoms are endowed with an Fe/C ratio of 10 μmol : mol. Percentage values in parentheses are the percent change relative to the RSP apparent IUE.*
warm CDW in the RSP raises SST by almost 3°C above that of the TNBP. The combined effect of shallow mixed layers (high rates of photoreduction) and low temperatures (low oxidation rates) in the TNBP result in a much greater apparent IUE for this region in January, relative to the RSP. By February, MLD in the TNBP is again greater than in the RSP (31 m and 20 m, respectively), while average SSTs remain warmer in the RSP (by >2°C). These two conditions offset, resulting in similar apparent IUEs for both the RSP and the TNBP during this month. The role of MLD and SST upon the apparent IUE for the RSP and the TNBP is summarized in Table 2.

[38] Non-biogenic losses of Fe will be more significant in the permanently open ocean zone (POOZ) than the seasonally ice covered zone (SIZ) of the SO. As for the RSP, surface waters of the POOZ are warmer and less stratified than in the SIZ (i.e. elevated rates of oxidation, but low photoreduction rates) which result in less efficient Fe use (in terms of fueling NPP). We have shown that temporal changes in the physical environment greatly impact the rate of NPP per unit Fe removed (via the apparent IUE) in the Ross Sea. Moreover, we propose that regions of the SO that are characterized by relatively unstratified and warm surface waters (such as the POOZ) will exhibit less efficient dFe use (as a function of NPP) than those regions typified by well stratified, cold surface waters (such as the SIZ). Our analysis shows that while apparent ratios of Fe/NPP measured in the field will be robust estimators of the ratio of depletion/accumulation of various elements in a given physical region (the apparent IUE), they are not likely to be accurate reflections of the actual planktonic demands for Fe (the planktonic IUE, moles carbon fixed per mole Fe taken up, Raven [1988]) that would be measured in a laboratory or parameterized in an ecosystem model. This will be especially true if the nutrient in question (e.g., Fe) undergoes cycling that is strongly affected by variability in environmental conditions (e.g., temperature).

4. Conclusions

[39] The speciation of Fe in waters south of the Antarctic Circle (such as the Ross Sea) is controlled primarily by photochemical processes, which are, in turn, driven by the annual cycle of solar irradiance, stratification, and sea-ice melt/refreeze. We have shown that the speciation of Fe can have profound impacts upon phytoplankton, particularly within MIZ waters dominated by phytoplankton with a high Fe demand. Therefore, the nature of the spring ice-melt, and the degree of surface water stratification, will be crucial in dictating the speciation and the ensuing supply of Fe to phytoplankton. Although our Fe supply model was developed for the Ross Sea, it includes sufficient flexibility in its parameterizations for our major conclusions to be applicable to the SO as a whole.

[40] If distinct phytoplankton taxa such as *P. antarctica* and diatoms are reliant on different Fe acquisition strategies, then there may be a role for Fe in controlling species composition in the Ross Sea (and in other regions). Although dFe is above growth limiting levels at the time of the spring ice-melt, it is the chemical speciation, and in particular the nature of any organic complexation and subsequent bioavailability and/or photolability, that may be of importance in understanding its impact upon phytoplankton. The Ross Sea is a region of net Fe export and depends on convective overturn to replenish surface waters with photo-labile, organically complexed Fe during the austral winter. Further information on both the speciation of dissolved Fe and the bioavailability of such Fe species to phytoplankton is necessary to understand how changes in Fe supply might impact Antarctic phytoplankton and the regional carbon cycle. A better understanding of the plasticity in planktonic Fe demands, the bioavailability of in situ Fe-ligand complexes and the variability in sea ice Fe concentrations/speciation will aid future model improvement.

[41] We propose that MIZ waters are regions of efficient Fe recycling and, moreover, that this is primarily due to the physical environment created by the ice melt (stratification and temperature), rather than enhanced Fe supply. The ratio of dFe depletion to NPP in a given area (the apparent IUE) will depend upon the planktonic demand as well as the physical nature of the mixed layer and the extent of Fe recycling allowed therein. This could prove to be important in comparing the efficiency of Fe fertilization experiments conducted in locations characterized by different physical properties [De Baar et al., 2005]. We have shown that the cycling of Fe (in terms of NPP) is more efficient in the SIZ regions of the SO, relative to the POOZ. If, as a consequence of future [e.g., Sarmiento et al., 1998] or past [e.g., Anderson et al., 2002] climatic change, a large proportion of the SO POOZ became more stratified during the austral spring/summer, then the enhanced recycling and retention of Fe (via an increased apparent IUE) should result in enhanced primary productivity, independent of any increase in Fe supply.

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References


Arrigo, K. R., R. B. Dunbar, M. P. Lizotte, and D. H. Robinson (2002), Taxon-specific differences in C/P and N/P drawdown for phytoplankton


K. R. Arrigo and A. Tagliabue, Department of Geophysics, Stanford University, Stanford, CA 94305–2215, USA. (atag@ocean.stanford.edu)