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Regulation of algal blooms in Antarctic shelf waters by the release of iron from melting sea ice

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Abstract. During summer 1995-96, we measured iron in the water column and conducted iron-enrichment bottle-incubation experiments at a station in the central Ross Sea (76°30'S, 170°40'W), first, in the presence of melting sea ice, and 17 days later, in ice-free conditions. We observed a striking temporal change in mixed-layer dissolved iron concentrations at this station, from 0.72-2.3 nM with sea ice present, to 0.16-0.17 nM in ice-free conditions. These changes were accompanied by a significant drawdown in macronutrients and an approximate doubling of algal (diatom) biomass. Our incubation experiments suggest that conditions were iron-replete in the presence of sea ice, and iron-deficient in the absence of sea ice. We surmise that bioavailable iron was released into seawater from the melting sea ice, stimulating phytoplankton production and the biological removal of dissolved iron from the mixed layer, until iron-limited conditions developed. These observations suggest that the episodic release of bioavailable iron from melting sea ice is an important factor regulating phytoplankton production, particularly ice-edge blooms, in seasonally ice-covered Antarctic waters.

Introduction

Antarctic shelf waters such as the Ross Sea are among the most biologically-productive areas of the Southern Ocean, although the mechanisms which control algal growth and biomass in these regions are poorly understood [*Tréguer and Jacques*, 1992; *Comiso, et al.*, 1993; *Sullivan et al.*, 1993; *Smith and Gordon*, 1997]. Major unresolved questions concern temporal and spatial variations in phytoplankton productivity and biomass, despite an abundance of major nutrients [*Nelson et al.*, 1987; *Smith et al.*, 1996; *DiTullio and Smith*, 1996], and the frequent association of algal blooms with receding annual sea ice [*El-Sayed and Taguchi*, 1981; *Smith and Nelson*, 1985; *Comiso, et al.*, 1993]. Variables which may be important in regulating these ice-edge algal blooms include vertical stability of the upper water column [*Smith and Nelson*, 1985], grazing by zooplankton [*Lancelot, et al.*, 1993], seeding by sea-ice algae [*Smith and Nelson*, 1985], input of ice-derived micronutrients such as iron [*Martin*, 1990], and, in some areas, depletion of macronutrients [Tréguer and Jacques, 1992].

Availability of dissolved iron may be an important factor regulating new production in high-nitrate low-chlorophyll regions of the open ocean [*Martin et al.*, 1991; *Coale et al.*, 1996a], including offshore areas of the Southern Ocean, where dissolved iron concentrations less than 0.2 nM have been measured [*Martin et al.*, 1990a; *de Baar et al.*, 1995]. Low dissolved iron concentrations (~0.1 nM) have also been measured in the shelf waters of the Ross Sea during the summer [*Fitzwater et al.*, 1996; *Sedwick et al.*, 1997a], and the results of bottle-incubation experiments suggest that iron-deficiency may limit summer algal production in this region [*Martin et al.*, 1990b]. Here we report recent observations from the central Ross Sea which provide evidence for the addition of bioavailable iron into seawater from the melting of annual sea ice, and the relatively rapid removal of this iron from the upper water column due to an algal bloom. From these observations and the results of bioassay experiments, we infer that the release of iron from melting sea ice is a key factor regulating algal blooms in Antarctic shelf waters and other seasonally ice-covered regions of the Southern Ocean.

Results and Discussion

We measured iron (Fe) and manganese (Mn) in the Ross Sea during a cruise of the RV *Nathaniel B. Palmer* in December 1995 and January 1996. Seawater samples were collected and processed using trace-metal clean techniques, and dissolved Fe and Mn and total-dissolvable Fe (TDFe, presumed to provide a measure of dissolved+particulate Fe) were determined by flow injection analysis as descibed in *Sedwick et al.* [1997b]. Dissolved nutrients were determined using standard flow-analysis techniques, and algal biomass was estimated from the sum of chlorophyll and phaeopigment concentrations -- reported here as total chlorophyll equivalents -- which were determined by shipboard fluorometer. Our ability to collect samples of open-ocean seawater and measure dissolved Fe and Mn without significant contamination is demonstrated by the vertical concentration profiles we obtained at an ice-free, deep-ocean location well away from the Antarctic continent (Station 2, 66°30'S, 178°50'E, Fig. 1). The smooth vertical profiles (Fig. 2a) and low mixed-layer concentrations of dissolved Fe (0.12-0.15 nM) and Mn (0.21-0.22 nM) are in excellent agreement with values reported by *Martin et al.* [1990a] for a deep-ocean station in the Drake Passage.

In this report we focus on results obtained from a site at approximately 76°30'S, 170°40'W in the central Ross Sea which was occupied twice during our cruise, initially as Station 4 on December 21-22, 1995, and again as Station 67 on January 7-8, 1996 (Fig. 1). Our initial occupation of this site was bordering a vast expanse of melting sea ice (brash ice), which satellite images revealed to be the western edge of the receding annual pack ice. During this first occupation,

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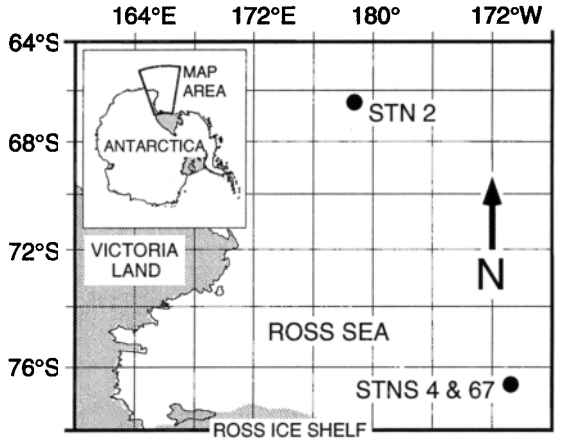

Figure 1. Map showing location of the study area.

surface-water nutrient concentrations were high (27.1 μM nitrate+nitrite, 1.90 μM phosphate, 71.3 μM silicate) and algal biomass was moderate (3.8 μg L^{-1} total chlorophyll equivalents). When this site was reoccupied 17 days later, satellite images showed that the ice edge had moved well to the east, and ice-free waters were visible in all directions. Surface-water nutrient concentrations were significantly lower than during our first visit (17.3 μM nitrate+nitrite, 1.03 μM phosphate, 52.6 μM silicate) and algal biomass had more than doubled (8.2 μg L^{-1} total chlorophyll equivalents). Integrated concentrations of total chlorophyll equivalents (to 150 m depth) at nearby stations had also doubled during this period, from 140 mg m^{-2} to 280 mg m^{-2} (W. Smith, pers. comm.). The algal community was dominated by the diatom *Nitzschia subcurvada* during both occupations. Apparently, meltwater had stimulated diatom growth, as observed in other areas of the Ross Sea [e.g., *Smith and Nelson*, 1985].

During both visits to this site we measured dissolved Fe and Mn and TDFe in seawater collected from the water column. During our first occupation of this site as Station 4, with melting sea ice present (Fig. 2b), relatively high concentrations of dissolved Fe were measured in surface seawater (2.3 nM) and near the base of the mixed layer (0.72 nM), whereas uniform dissolved Mn concentrations of 0.60-0.67 nM were observed in the upper water column. Total-dissolvable Fe concentrations were relatively high (> 2 nM) throughout the upper water column, with the highest concentration of 9.1 nM measured at the sea surface. During our second occupation of this site as Station 67, under ice-free conditions (Fig. 2c), the mixed-layer concentrations of dissolved Fe and Mn had decreased dramatically to 0.16-0.17 nM and 0.04-0.12 nM, respectively, while dissolved metal concentrations below the mixed layer were unchanged from those measured during our first visit. Total-dissolvable Fe concentrations had also decreased to < 1 nM within the mixed layer and 1.6 nM at 120 m depth. Analyses of water samples collected from other stations during the cruise suggest typical summertime "background" dissolved Fe concentrations of less than 0.5 nM in surface waters of this region, under both open-water and pack-ice-covered conditions [*Sedwick et al.*, 1997a].

Based on these observations, we surmise that the high mixed-layer concentrations of dissolved and total-dissolvable Fe observed during our initial occupation of Station 4 reflect an episodic input of dissolved and particulate Fe, most likely from the melting sea ice. Melting sea ice has been proposed as an important source of dissolved Fe for Antarctic surface waters, the Fe being derived from atmospheric dust particles which accumulate in snowfall during the winter months [*Martin et al.*, 1990a; *Martin*, 1990]. Acid-soluble Fe concentrations of 15-36 nM have been measured in snow samples collected from annual sea ice in Antarctic shelf waters [*Westerlund and Ohman*, 1991; *Edwards and Sedwick*, 1996], and could thus explain the high dissolved and total-dissolvable Fe concentrations observed in surface seawater at Station 4. However, significantly less Mn is expected to be released from melting sea ice based on the Fe/Mn mass ratio of ~60-80 reported in Antarctic snow [*Boutron and Martin*, 1980] and aerosol [*Zoller et al.*, 1974], consistent with the observed enrichment in dissolved Fe relative to Mn in Station 4 surface waters.

We assume that the area of Fe-enriched surface waters around Station 4 was similar to that of the melting sea ice we observed in this region, that is, at least on the order of tens of square kilometres. The marked decrease in mixed-layer dissolved Fe concentrations in the 17-day interval between occupations of Stations 4 and 67 must then reflect either (1) horizontal advection, (2) vertical mixing of the upper water column, or (3) uptake and removal of dissolved Fe from the water column due to biogeochemical processes, which would include both active uptake by microbes and scavenging by particulate material. From the distribution of mass observed along the cruise transects, we estimate geostrophic velocities of around 1 cm s^{-1} (500 m reference depth) during our expedition, suggesting a weak advective component and arguing against significant lateral transport. Therefore we

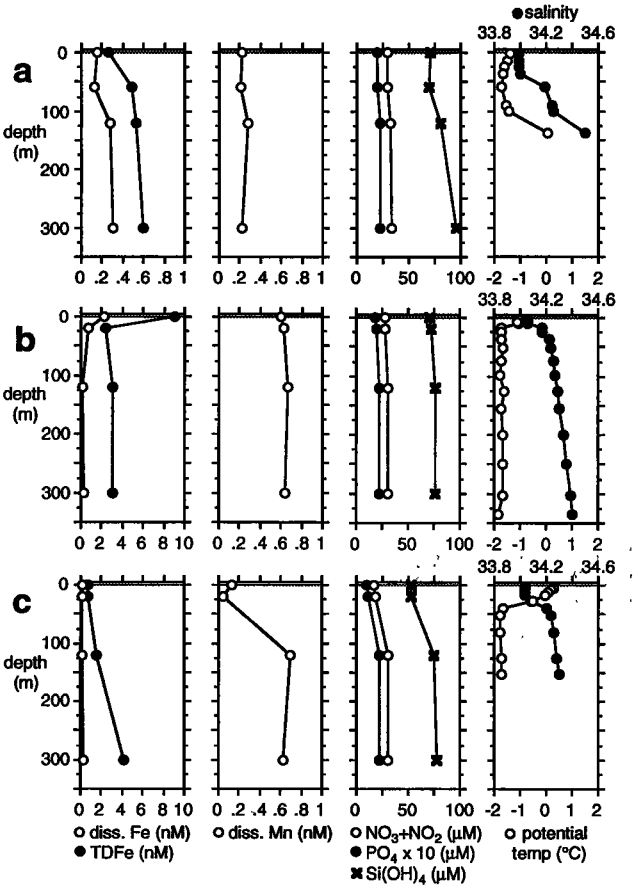

Figure 2. Vertical profiles of Fe, Mn and major nutrients from (a) Station 2, (b) Station 4, and (c) Station 67. Potential temperature and salinity profiles are from nearby stations.

suggest that a combination of vertical mixing and biogeochemical removal was responsible for the dramatic decrease in mixed-layer dissolved Fe concentrations. Some turbulent mixing of the upper water column during the several days of stormy weather between visits is consistent with the observed deepening of the thermocline (Figs. 2b, 2c), and would be expected to dilute the Fe-rich surface waters with Fe-poor deeper water. However, given the initial dissolved Fe concentrations at Station 4 of 0.72-2.3 nM in the mixed layer and 0.19-0.32 nM below the thermocline, it is unlikely that vertical mixing alone could have resulted in the dissolved Fe concentrations less than 0.2 nM which were observed in the upper water column at Station 67.

Dissolved Fe and Mn are known to taken up by biological activity within the photic zone; they are also efficiently scavenged by particulate material, and will be rapidly removed from the photic zone where vertical export flux is high [*Landing and Bruland*, 1987; *Hutchins et al.*, 1993]. Based on the observed drawdown in nutrients and trace metals, increase in algal biomass, and high vertical export fluxes measured during our expedition (~1 g m^{-2} d^{-1}; V. Asper, pers. comm.), we believe that most of the ice-derived dissolved Fe measured at Station 4 was taken up by phytoplankton and/or scavenged by sinking particles prior to reoccupation of this site as Station 67. If Stations 4 and 67 occupied a single "patch" of water, then from observed nutrient concentration profiles (Figs. 2b, 2c) we estimate the integrated drawdown in major nutrient concentrations over 17 days between stations in a 20 m-thick photic zone to be 200 mmol m^{-2} nitrate, 17 mmol m^{-2} phosphate and 380 mmol m^{-2} silicate. The rate of primary production required to consume this amount of nitrate over 17 days is around 0.94 g C m^{-2} d^{-1} (using a Redfield C/N), which compares well with the integrated primary production rate of 1.4 g C m^{-2} d^{-1} measured near Station 4 (W. Smith, pers. comm.).

Coale et al. (1996b) have recently used results from an in-situ Fe-fertilization experiment to argue that bottle-incubation experiments provide a robust indicator of algal community nutritional status in the open ocean. In an effort to evaluate the nutritional status of phytoplankton at Stations 4 and 67 with respect to Fe and Mn, we conducted Fe- and Mn-addition bottle-incubation experiments with seawater collected during both occupations of this site. In these experiments, surface seawater was collected from a Zodiac and immediately transferred into a trace-metal clean 50-L polyethylene carboy. The untreated seawater was gently mixed and transferred into trace-metal clean 1-L polycarbonate bottles under Class-100 clean-air conditions within 12 hours of collection. To one set of bottles was added an EDTA-chelated Fe solution to achieve total dissolved Fe concentrations of 4.7 nM. Another set of bottles was spiked with equivalent volumes of an EDTA-chelated Mn solution. The Fe- and Mn-treated samples, together with untreated control samples, were sealed in polyethylene bags and set in circulating surface seawater in a deck incubator shaded to 50% light intensity with neutral density screening and blue filters. Duplicate bottles for each treatment were harvested over a 7-day period and sampled for dissolved nutrients and photosynthetic pigments (our rationale for reporting total chlorophyll equivalents here is to facilitate comparison between in-situ conditions and the bottle experiments; in the latter, the results of grazing, producing phaeopigments, could lead to significant underestimates in chlorophyll-based biomass yields).

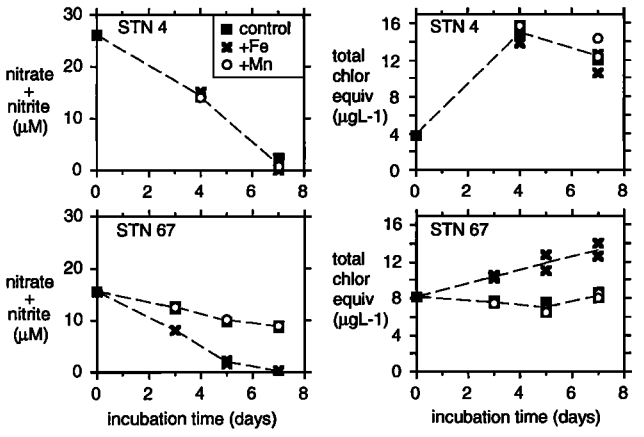

Figure 3. Concentrations of nitrate+nitrite and total chlorophyll equivalents vs incubation time in the bottle experiments from Station 4 (top) and Station 67 (bottom).

Additions of Fe and Mn to the Fe-rich surface seawater collected from Station 4 affected no significant change ($P > 0.05$; paired t-test) in net nitrate+nitrite removal rates (3.7 µM d^{-1}) relative to control samples. An average of 94% of the nitrate+nitrite initially present was removed from solution in each treatment after 7 days incubation (Fig. 3), presumably incorporated into algal biomass. No significant differences were observed in the concentrations of total chlorophyll equivalents among treatments, suggesting that Fe and Mn additions affected no change in algal biomass relative to the controls (Fig. 3). In contrast, for experiments using Fe-poor surface seawater collected during our second occupation of this site, net nitrate+nitrite removal rates were significantly higher ($P = 0.004$) in the Fe-amended bottles (2.7 µM d^{-1}) relative to both the control and Mn treatments (1.1 µM d^{-1}). In the Fe-treated incubations, an average of 98% of the nitrate+nitrite initially present was removed from solution after 7-days incubation, compared with 44% removal in control and Mn-treated samples (Fig. 3). Addition of Fe also produced an ~60% increase in the concentration of total chlorophyll equivalents over the 7 days incubation, relative to the control and Mn treatments in which total chlorophyll equivalents remained roughly constant (Fig. 3). Diatoms were the dominant algal species in both experiments. From these results we infer that the high dissolved Fe levels observed in surface waters during our first occupation of this site were sufficient for diatom growth requirements, whereas the much lower dissolved Fe concentrations observed during our second visit were limiting the drawdown of nitrate and accumulation of diatom biomass.

We conclude from our observations at Stations 4 and 67 that the algal community (predominantly diatoms) bloomed in response to the addition of dissolved Fe from the melting sea ice, and that this algal bloom affected the rapid removal (in < 17 days) of dissolved Fe from the photic zone, resulting in Fe-limited conditions. These observations implicate the episodic release of Fe from melting sea ice as an important mechanism regulating algal growth in Fe-deficient Antarctic waters, and as a primary cause of ice-edge algal blooms where there is sufficient stability of the upper water column. Further, our data support *Martin's* [1990] suggestion that Fe derived from melting sea ice stimulates short periods of enhanced new production in the Southern Ocean. At present it is difficult to assess the overall contribution of ice-derived Fe to new production in the Southern Ocean, although it may be

considerable. Major uncertainties include the concentration of "bioavailable" Fe in Antarctic snow, which likely varies from place to place, the total mass of snow on the seasonal sea ice, and the stability of the upper water column during the melting process. *Martin* [1990] estimated an annual new production of 2.3 x 10^{12} mole C due to ice-derived Fe in the Southern Ocean, which is around 30% of the estimated total new production in the region, although this calculation is likely an overestimate because it uses the entire mass of annual sea ice rather than snow cover. A more recent calculation using an estimate of the total mass of snow in the seasonal ice zone yields the much lower value of ~4 x 10^{10} mole C yr^{-1} new production [*Edwards and Sedwick*, 1996]. However, such estimates may be significantly offset by intense algal blooms in areas of Fe-rich snow, as may be the case in the Ross Sea. For example, extrapolating our observations of "Fe-driven" nitrate drawdown in the central Ross Sea (200 mmol m^{-2}, assuming a Redfield C/N ratio) over the 1.5 x 10^{13} m^2 area of annual sea ice [*Cooke and Hayes*, 1982] yields 3 x 10^{14} mole C yr^{-1} new production, a value far exceeding the estimated total new production in the Southern Ocean [*Martin*, 1990].

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