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Peter N. Sedwick
Old Dominion University, Psedwick@odu.edu

Giacomo R. DiTullio

Denis J. Mackey

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Iron and manganese in the Ross Sea, Antarctica: Seasonal iron limitation in Antarctic shelf waters

Peter N. Sedwick
Antarctic CRC, Hobart, Tasmania, Australia

Giacomo R. DiTullio
Grice Marine Laboratory, Charleston, South Carolina

Denis J. Mackey
CSIRO Division of Marine Research and Antarctic CRC, Hobart, Tasmania, Australia

Abstract. Dissolved iron and manganese and total dissolvable iron were measured in water column samples collected from the polynya region of the southern Ross Sea during cruises in November-December 1994 (spring 1994) and December 1995 to January 1996 (summer 1995). Iron and manganese addition bottle incubation experiments were also performed during these cruises in order to assess the nutritional sufficiency of ambient iron and manganese concentrations for growth of the phytoplankton community. Generally high dissolved iron concentrations (> 0.5 n*M*) and relatively complex iron and manganese vertical profiles were obtained during the spring 1994 cruise, compared with the summer 1995 data. Dissolved iron concentrations in the upper water column averaged 1.0 n*M* during spring 1994 and 0.23 n*M* in summer 1995, excluding two stations where concentrations exceeding 1 n*M* are attributed to inputs from melting sea ice. The observed differences in the distribution of iron and manganese between spring 1994 and summer 1995 are attributed to seasonal decreases in the upwelling of bottom waters and melting of sea ice, which supply these metals into the upper water column, combined with the cumulative removal of iron and manganese from the water column throughout the spring and summer, due to biological uptake, vertical export and scavenging by suspended and sinking particles. Results of the metal addition bottle incubation experiments indicate that ambient dissolved iron concentrations are adequate for phytoplankton growth requirements during the spring and early summer, when algal production is highest and *Phaeocystis antarctica* dominates the algal community, whereas low dissolved iron concentrations limit algal community growth later in the summer, except in the stratified, iron-enriched waters near melting sea ice, where diatoms are able to bloom. Our observations and the inferred seasonal distributions of *P. antarctica* and diatoms in these waters suggest that iron availability and vertical mixing (i.e., irradiance) exert the primary controls on phytoplankton growth and community structure in the southern Ross Sea during the spring and summer.

1. Introduction

The Ross Sea is one of the most productive areas in the Southern Ocean, although the processes which control algal growth, biomass, and community structure in the region are not well understood [*Sullivan et al.*, 1993; *DiTullio and Smith*, 1996; *Smith and Gordon*, 1997; *Arrigo et al.*, 1998a, b]. A large coastal polynya is frequently established in the southern Ross Sea during the spring, and by the late summer, most of the continental shelf region is free of ice [*Jacobs and Comiso*, 1989]. Elevated phytoplankton biomass is typically observed in the southern Ross Sea during the spring, reaching a maximum in December, then declining during January [*Comiso et al.*, 1993; *Smith and Gordon*, 1997; *Arrigo et al.*, 1998a, 1999]. Here the algal community is dominated by the colonial prymnesiophyte *Phaeocystis antarctica* during the spring and early summer, when algal production rates reach a maximum, whereas diatom species are abundant later in the summer, when lower production rates have been measured [*Gowing et al.*, 1996; *Leventer and Dunbar*, 1996; *Arrigo et al.*, 1998a; *Bates et al.*, 1998]. Large spatial and temporal gradients in phytoplankton growth rates, biomass, and species composition have been observed in this region, despite an abundance of major nutrients [*Smith et al.*, 1996; *DiTullio and Smith*, 1996; *Gowing et al.*, 1996; *Smith and Gordon*, 1997], and diatom blooms are often associated with retreating seasonal sea ice during the summer [*Smith and Nelson*, 1985, 1990; *Comiso et al.*, 1993; *Arrigo et al.*, 1998a, 1999]. Factors thought to be important in controlling algal production and community structure in these waters include vertical stability of the upper water column [*Smith and Nelson*, 1990; *Arrigo et al.*, 1998a, 1999], seeding by sea ice algae [*Smith and Nelson*, 1986; *Leventer and Dunbar*, 1996],

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grazing by zooplankton [*DiTullio and Smith*, 1996], light limitation due to sea ice cover and self shading [*Smith et al.*, 1996], and availability of micronutrient elements such as iron [*Martin et al.*, 1990a; *Sedwick and DiTullio*, 1997].

The availability of dissolved iron is thought to be a key factor regulating phytoplankton production in high-nitrate low-chlorophyll regions of the open ocean [*Martin et al.*, 1991; *Coale et al.*, 1996a], including much of the Southern Ocean, where dissolved iron concentrations < 0.2 n*M* have been measured [*Martin et al.*, 1990b, *de Baar et al.*, 1995; *Sedwick et al.*, 1997; *de Baar et al.*, 1999]. There is also some evidence that iron deficiency may limit algal growth rates in the high-nutrient high-chlorophyll waters of the Antarctic continental margin. Low dissolved iron concentrations of ~0.1 n*M* have been measured in surface waters of the southern Ross Sea in summer 1990 [*Fitzwater et al.*, 1996] and summer 1995-1996 [*Sedwick et al.*, 1996], and the results of bottle incubation experiments indicate that iron deficiency may limit algal production in this region during the summer [*Martin et al.*, 1990a, 1991; *Sedwick and DiTullio*, 1997]. Availability of dissolved iron may thus play an important role in regulating phytoplankton production in the southern Ross Sea. Another micronutrient element of interest in this regard is manganese, which is known to occur at low concentrations (< 0.1 n*M*) in surface waters of the southern Ross Sea [*Sedwick et al.*, 1995, 1996; *Sedwick and DiTullio*, 1997] and to be actively removed from seawater by algae of the genera *Phaeocystis* [*Davidson and Marchant*, 1987; *Lubbers et al.*, 1990]. Although bottle incubation experiments have provided no evidence of algal manganese deficiency in the Ross Sea during the summer [*Martin et al.*, 1990a, 1991], it is conceivable that massive spring blooms of *Phaeocystis antarctica* [*El-Sayed et al.*, 1983; *Palmisano et al.*, 1986; *Arrigo et al.*, 1998a] could result in water column manganese concentrations low enough to limit algal growth.

Here we present results of water column iron and manganese measurements and iron and manganese enrichment bottle incubation experiments performed in the southern Ross Sea during two cruises, the first in spring and early summer 1994 (spring 1994) and the second in midsummer 1995-1996 (summer 1995). Our trace metal data suggest that there are significant seasonal variations in the distributions of iron and manganese in these waters. During the spring 1994 cruise, when much of the region was covered by sea ice, we obtained relatively complex water column profiles, with generally high dissolved iron concentrations (> 0.5 n*M*) in the upper water column. In contrast, during summer 1995, when ice-free conditions were widespread, we observed relatively smooth vertical profiles, with low dissolved iron concentrations (< 0.5 n*M*) in the upper water column at most stations. We propose that these apparent seasonal differences in iron and manganese distributions reflect decreasing inputs of these metals into the upper water column during the spring and summer, combined with the effects of biological uptake, vertical export, and particle scavenging. The water column measurements and results of the bottle incubation experiments indicate that algal community growth is limited by iron deficiency in much of the southern Ross Sea during the summer, except where localized iron sources exist, such as melting sea ice. Thus the availability of iron is arguably as

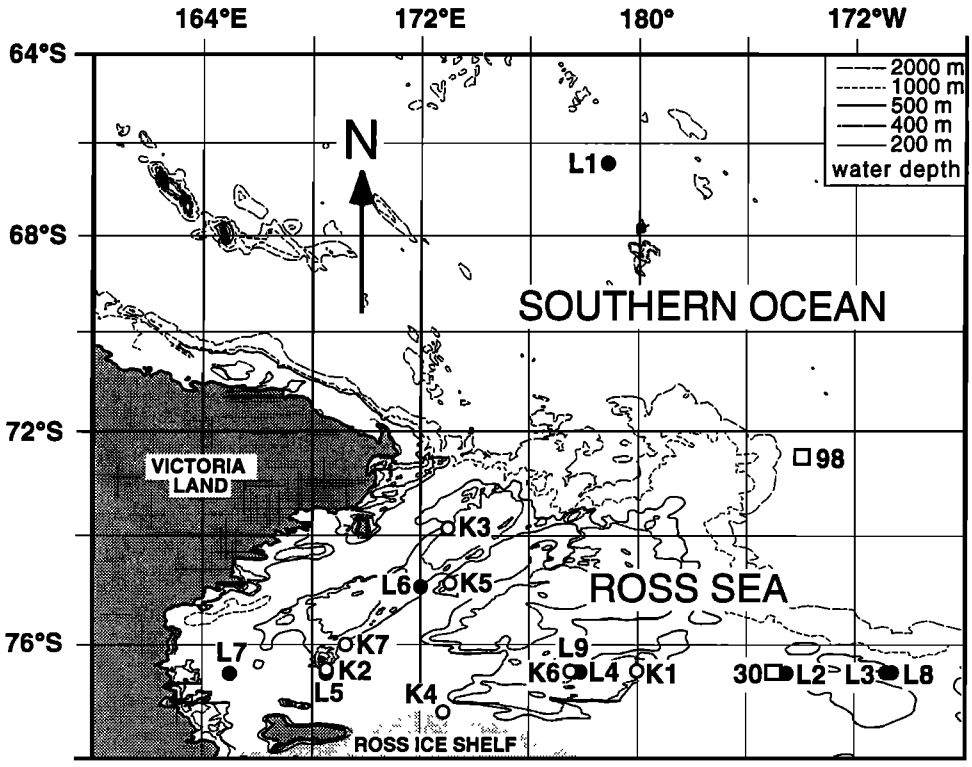

Figure 1. Study area, seafloor bathymetry, and locations of stations sampled for trace metals in November-December 1994 (spring 1994, K1-K7, open circles), December 1995 to January 1996 (summer 1995, L1-L9, solid circles), and January 1990 (squares [*Johnson et al.*, 1997]). Map and bathymetry from the General Bathymetric Chart of the Oceans Digital Atlas, published by the British Oceanographic Data Centre on behalf of the Intergovernmental Oceanographic Commission and International Hydrographic Organization, 1994.

important as physical forcing in controlling algal production and community structure in this region during the spring and summer.

2. Methods

The work described here was performed during two cruises aboard RV *Nathaniel B. Palmer* in November-December 1994 (spring 1994) and December 1995 to January 1996 (summer 1995). The primary focus of these cruises was phytoplankton production in the polynya region of the southern Ross Sea, particularly along latitude 76°30'S. On these expeditions we measured iron and manganese in water column samples and conducted iron and manganese addition bottle incubation experiments using the native plankton communities. Rigorous trace metal clean techniques were employed in an effort to avoid contamination of the water samples and incubation treatments [*Martin et al.*, 1976; *Bruland et al.*, 1979; *Sedwick et al.*, 1997]. Water column samples for trace metal determinations were collected at seven stations (K1-K7) during the spring 1994 cruise and nine stations (L1-L9) during the summer 1995 cruise, under a variety of sea ice and water column conditions (Figure 1 and Table 1). Sea ice was present at most of the stations sampled during spring 1994, whereas most of the trace metal stations occupied during summer 1995 were free of ice. A single bottle incubation experiment was performed during the spring 1994 cruise (at station K1), and three bottle incubation experiments were performed during the summer 1995 cruise (at stations L3, L6, and L8). Preliminary results of this work are presented by *Sedwick et al.* [1995, 1996] and *Sedwick and DiTullio* [1997]. An important contrast between these two cruises was in the observed phytoplankton communities, which was also reflected in the species compositions of the bottle incubation experiments. During spring 1994 the algal community was dominated by *Phaeocystis antarctica* [*Smith and Gordon*, 1997], whereas during the summer 1995 cruise, diatoms such as *Nitzschia subcurvata* were also abundant [*Gowing et al.*, 1996]. This seasonal difference in algal community structure is apparently typical of the southern Ross Sea [*Arrigo et al.*, 1998a, 1999].

2.1. Cleaning Procedures

The polycarbonate water column samplers (see section 2.2) were initially cleaned by rinsing with deionized water (DIW, > 18 MΩ cm resistivity), extended soaking in a dilute aqueous solution of Triton X-100 surfactant, then extended soaking in ~1 *M* subboiling quartz-distilled hydrochloric acid (Q-HCl) in a Class-100 clean-air laboratory, with DIW rinsing after each soaking step. After initial cleaning, the water samplers were used on the two cruises discussed here and on a cruise in the Subantarctic Southern Ocean in January 1995 [*Sedwick et al.*, 1997]. During these cruises the samplers were stored wet in clean polyethylene bags. After the final deployment of each cruise, the water samplers were flushed with DIW then stored in clean polyethylene bags. The Nalgene low-density polyethylene or Teflon FEP bottles used for storage of water samples were cleaned by 2 days soaking in ~1 *M* Q-HCl, followed by 2 days conditioning over boiling ~6 *M* HCl fumes [*Tschopel et al.*, 1980], with DIW rinsing after each treatment. Bottle caps were soaked for 2 days in ~1 *M* Q-HCl, followed by 2 days soaking in ~6 *M* Q-HCl, with DIW rinsing after each treatment. The bottles were stored filled with ~0.5 *M* Q-HCl and were rinsed with DIW followed by several volumes of sample solution immediately before use. Other laboratory equipment (polyethylene, polypropylene, polysulfone, Teflon FEP, and Teflon PTFE) used in contact with water samples or reagents were cleaned by 2 days soaking in ~1 *M* Q-HCl, followed by 2 days soaking in ~6 *M* Q-HCl, with DIW rinsing after each treatment. Bottles and carboys used in the incubation experiments were cleaned with dilute aqueous solutions of Triton X-100 or Micro detergent, rinsed with DIW, soaked for ~1 week in ~1 *M* Q-HCl or Mallinkrodt AR Select hydrochloric acid, then rinsed with DIW. All items were rinsed and dried under a Class-100 clean-air bench or in a Class-100 clean-air laboratory and then stored in sealed clean polyethylene bags

Table 1. Trace Metal Hydrocast Stations, Ross Sea, Spring 1994 and Summer 1995

Station*	Location	Sampling Date	Sea Ice Conditions	Water Depth, m
K1†	76°29'S, 179°57'E	Nov. 14, 1994	8/10 ice cover	400-450
K2	76°29'S, 168°31'E	Nov. 17, 1994	10/10 ice cover	700-750
K3	73°53'S, 172°57'E	Nov. 20, 1994	9/10 ice cover	300-350
K4	77°12'S, 172°49'E	Nov. 23, 1994	8/10 ice cover	650-700
K5	74°59'S, 173°05'E	Nov. 28, 1994	9/10 ice cover	500-550
K6	76°29'S, 177°31'E	Dec. 3, 1994	5-6/10 ice cover	350-400
K7	76°01'S, 169°13'E	Dec. 6, 1994	edge of brash ice	500-550
L1	66°30'S, 178°50'E	Dec. 19, 1995	ice-free	3000
L2††	76°31'S, 174°32'W	Dec. 21, 1995	ice-free	550-600
L3†	76°30'S, 170°44'W	Dec. 21, 1995	edge of brash ice	500-550
L4	76°30'S, 177°46'E	Dec. 24, 1995	ice-free	350-400
L5	76°30'S, 168°30'E	Dec. 28, 1995	9/10 ice cover	700-750
L6†	75°00'S, 172°00'E	Dec. 31, 1995	ice-free	550-600
L7	76°31'S, 164°58'E	Jan. 4, 1996	some bergy bits	750-800
L8†	76°30'S, 170°37'W	Jan. 8, 1996	ice-free	500-550
L9	76°30'S, 177°43'E	Jan. 10, 1996	ice-free	350-400

*Stations L1, L3, and L8 are referred to as stations 2, 4, and 67, respectively, by *Sedwick and DiTullio* [1997]. Stations L1-L9 are referred to as stations K1-K9, respectively, by *Sedwick et al.* [1996].

†Fe and Mn addition bottle incubation experiments were conducted with surface seawater from these stations.

††Only a surface water sample was collected, which contained 0.38 n*M* dissolved Fe, 1.81 n*M* TDFe, and 0.58 n*M* dissolved Mn.

or plastic containers. Poretics polycarbonate filter membranes were soaked for several days in ~6 *M* Q-HCl, followed by DIW rinsing and storage in DIW.

2.2. Sample Collection

Surface seawater samples were collected from the windward side of the ship in 1 L low-density polyethylene bottles mounted in an acrylic frame on an acrylic-coated aluminum pole while slowly underway [*Boyle et al.*, 1994], immediately before occupying each hydrocast station. Subsurface water column samples were collected by hydrocast in 6 L trace metal water samplers suspended from a Superbraid nonmetallic line, using solid teflon messengers and an epoxy-coated steel end weight. The water samplers, which were custom-built at CSIRO Division of Marine Research, are made of polycarbonate and have silicone rubber O-ring seals, Teflon PTFE spigots, an external closure mechanism made of silicone rubber and nylon, and several small external components made of high-purity titanium. In order to readily identify any contamination associated with individual water samplers [see *Martin et al.*, 1990b] only four samplers were used during these cruises. Vertical concentration profiles with samples from more than four depths were obtained from two successive hydrocasts using three water samplers, performed within a period of 12 hours. Sample depths were estimated from line out, which was read from a metering block with a stainless steel sheave. All sampling equipment was wrapped with polyethylene when not in use in an effort to avoid contamination by airborne dust.

2.3. Processing and Analysis

Upon recovery the water samplers were transferred to the shipboard laboratory and mounted in front of a Class-100 clean-air bench for processing. Seawater samples were immediately filtered through 0.4 μm pore-size Poretics polycarbonate membranes into Nalgene low-density polyethylene (LDPE) or Teflon FEP bottles for analysis of dissolved trace metals and major nutrients. Nitrogen gas passed through an in-line 0.2 μm pore Teflon membrane filter was used to pressurize the water samplers, and samples were drawn under the clean-air bench through Teflon FEP tubing and in-line Teflon PTFE filter holders. The surface-seawater sample bottles were sealed in polyethylene bags upon recovery then transferred into the clean-air bench, where they were pressure-filtered through 0.4 μm pore-size Poretics polycarbonate membranes using filtered nitrogen gas and Nalgene polysulfone filter flasks. Unfiltered subsamples were collected in 60 mL Nalgene LDPE bottles, acidified with J. T. Baker Ultrex II (spring 1994 samples) or Seastar (summer 1995 samples) double-quartz-distilled concentrated hydrochloric acid (2 mL acid per liter sample), and stored for later analysis of total dissolvable Fe in Hobart. Transfer tubes, filtering apparatus, and sample containers were rinsed with several volumes of sample solution before final collection of subsamples, and all sample manipulations were performed within the clean-air bench following stringent trace metal clean protocols. On the basis of the low and uniform dissolved Fe and Mn concentrations measured at several remote open-ocean locations using this same sampling and processing apparatus (see section 3.1) we assume that the typical level of contamination introduced by the water samplers, transfer tubes, filtering apparatus, and sample containers is negligible.

Filtered samples were acidified with J. T. Baker Ultrex II (spring 1994 samples) or Seastar (summer 1995 samples) double-quartz-distilled concentrated hydrochloric acid (0.52 mL acid per liter sample) within 48 hours of collection, and dissolved Fe was determined by flow injection analysis with in-line preconcentration following a modification of the procedure of *Measures et al.* [1995]. Standard solutions in a seawater matrix were prepared by addition of iron standard solutions (prepared in dilute hydrochloric acid) to low-Fe seawater. The low-Fe seawater was either filtered open-ocean seawater purified (i.e., Fe removed) using resin-immobilized 8-hydroxyquinoline [*Resing and Mottl*, 1992] or filtered seawater collected during the cruises. For each analysis the concentration of the low-Fe seawater was determined using the method of standard additions. All dissolved Fe analyses were performed at sea, except for samples from stations K7 and L9, which were analyzed in Hobart. Total dissolvable Fe (TDFe) was determined in Hobart by the same method after > 6 months storage of the acidified samples and is assumed to provide a measure of the concentration of dissolved plus acid-soluble particulate iron in the water samples. The iron concentration of the previously opened Seastar hydrochloric acid (70 n*M* Fe) was determined before the cruise by analysis of deionized water containing successive additions of acid, and this concentration is used as a blank correction for Fe in the acidified summer 1995 samples; the reported assay of the unopened Ultrex II hydrochloric acid (6.3 n*M* Fe) is used as a blank correction for Fe in the spring 1994 samples.

Dissolved Mn was determined at sea in the filtered, unacidified samples within 48 hours of collection by flow injection analysis with in-line preconcentration following a modification of the procedure of *Resing and Mottl* [1992]. Standard solutions in a seawater matrix were prepared by addition of manganese standard solutions (prepared in dilute hydrochloric acid) to low-Mn seawater. The low-Mn seawater was either filtered open-ocean seawater purified (i.e., Mn removed) using resin-immobilized 8-hydroxyquinoline [*Resing and Mottl*, 1992] or filtered seawater collected during the cruises. For each analysis the concentration of the low-Mn seawater was determined using the method of standard additions. Both analytical methods have an estimated relative uncertainty of < 20% based on peak area reproducibility, from which detection limits of ~0.02 n*M* are estimated based on peak area absorbance of samples containing 0.09 n*M* dissolved Fe and 0.12 n*M* dissolved Mn. The summer 1995 Fe measurements have an additional uncertainty arising from subtraction of the acid blank concentration, which results in estimated uncertainties in dissolved Fe concentrations of ~30% at 0.1 n*M*, 24% at 0.2 n*M*, and 20% at and above 0.3 n*M* and estimated uncertainties in TDFe concentrations of ~40% at 0.2 n*M*, 26% at 0.5 n*M*, and 23% at 1 n*M*. Dissolved major nutrients (nitrate+nitrite, phosphate, and silicic acid) were determined in filtered seawater samples at sea by L. Gordon and A. Ross, using standard flow analysis techniques.

2.4. Bottle Incubation Experiments

2.4.1. Spring 1994. The iron and manganese addition bottle incubation experiments we performed were similar in design to those described by *Martin et al.* [1990a]. At station K1, surface seawater was collected from the bow of a slowly moving Zodiac > 500 m upwind of the ship. The seawater was collected by submerging two 20 L polycarbonate carboys

which were rinsed with seawater several times before filling. The carboys were immediately transferred into a shipboard cold room (0-4°C). The untreated seawater was gently mixed and transferred into 1200 mL polycarbonate bottles, with several rinses, under Class-100 clean-air conditions. Bottles were amended with 3.0 n*M* Fe, added as $Fe(NO_3)_3$ in dilute hydrochloric acid, or 3.0 n*M* Mn, added as $Mn(NO_3)_2$ in dilute hydrochloric acid. The concentrations of nitrate and acid present in the added Fe and Mn solutions were low enough to have negligible effect on the nitrate concentration and pH of the seawater used in the experiments. The Fe- and Mn-amended bottles, together with untreated control samples, were tightly capped, sealed in polyethylene bags, and set in circulating surface seawater at ambient temperature in a deck incubator shaded to 50% of incident irradiance with neutral density screening and blue filters. This level of shading was intended to simulate the average light field within the upper mixed layer of the water column. Bottles for each treatment (added Fe, added Mn, and control) were sacrificed after periods of 6 and 9 days and sampled for dissolved major nutrients and photosynthetic pigments. Subsamples from selected control treatments were filtered as for surface seawater samples and surveyed for dissolved Fe and Mn to check for spurious contamination.

2.4.2. Summer 1995. In experiments conducted at stations L3, L6, and L8, surface seawater was sampled from a Zodiac as described above, except that seawater collected in a single 20 L carboy was transferred into a clean 50 L polyethylene carboy in the Zodiac, and the full 50 L carboy was immediately transferred into the shipboard cold room. The seawater was transferred into 1200 mL polycarbonate bottles as described above. In the iron treatments, bottles were amended with either 2.5 n*M* Fe (station L3; "high" ambient Fe concentration) or 4.1 n*M* Fe (stations L6 and L8; "low" ambient Fe concentration), added as $Fe(NO_3)_3$ chelated ~1:1 (molar basis) with ethylenediaminetetraacetic acid (EDTA, added as the disodium salt) in dilute hydrochloric acid. In the manganese treatments, bottles were amended with either 2.5 n*M* Mn (station L3) or 4.2 n*M* Mn (stations L6 and L8), added as $Mn(NO_3)_2$ chelated ~1:1 (molar basis) with EDTA in dilute hydrochloric acid. The EDTA was used in the added Fe and Mn solutions in order to maintain these metals in dissolved (chelated) form during addition to the seawater samples [*Coale*, 1991; *DiTullio et al.*, 1993]. Speciation calculations using the MINEQL computer code (Environmental Research Software) indicate that the final concentrations of EDTA in the seawater samples were low enough to have negligible effect on the Fe and Mn speciation. In the experiment at station L6, single bottles were also amended with 4.1 n*M* unchelated Fe and 4.2 n*M* unchelated Mn. Again, the nitrate and acid added in the Fe and Mn treatments had negligible effect on the nitrate concentration and pH of the starting seawater. The Fe- and Mn-amended bottles and untreated control samples were incubated as described for the spring 1994 experiment, and duplicate bottles for each treatment were sacrificed over periods of 7-10 days and sampled for dissolved major nutrients, photosynthetic pigments, and (in selected control treatments) dissolved Fe and Mn.

2.4.3. Photosynthetic pigments. Chlorophyll *a*, accessory pigments (chlorophyll *c*3, fucoxanthin and 19'-hexanoyloxyfucoxanthin) and total phaeopigments were determined by high-performance liquid chromatography (HPLC) in material filtered from the incubation bottles as described by *DiTullio and Smith* [1996]. In each of the summer 1995 experiments, relatively high concentrations of phaeopigments (comparable to the chlorophyll *a* concentrations) were measured in samples from the incubation bottles, indicating that significant grazing had occurred, possibly by microzooplankton such as heterotrophic dinoflagellates and ciliates (M. Gowing, personal communication, 1999). In these experiments the sum of total chlorophyll and phaeopigment concentrations, reported here as "total chlorophyll equivalents," was measured using a shipboard fluorometer, following extraction and sonification of the filtered material in 90% acetone. Our rationale for measuring and reporting fluorometric total chlorophyll equivalents in the summer 1995 experiments is to account for the effects of grazing on algal biomass produced during the incubations, which would lead to significant underestimates in biomass yield based on chlorophyll *a* concentrations. This is not the case for the spring 1994 experiment, in which phaeopigment concentrations were below our limit of detection in most of the treatments, and for which HPLC chlorophyll *a* concentrations are used to estimate algal biomass accumulation in the incubation bottles.

3. Results

3.1. Water Column Profiles

The reliability of open-ocean trace metal measurements is an important consideration, given the ease with which samples may be contaminated during collection, processing, and analysis, and the current lack of both standard reference materials and interlaboratory comparisons. Our ability to collect samples of open-ocean seawater and determine dissolved Fe and Mn without significant contamination is demonstrated by the vertical concentration profiles we have obtained for these metals at several remote open-ocean locations. Station L1, occupied during the summer 1995 cruise (Figure 1), was an ice-free, deep-ocean location well away from the Antarctic continent. Here we obtained smooth vertical concentration profiles and measured low mixed layer concentrations of dissolved Fe (0.12-0.15 n*M*) and Mn (0.21-0.22 n*M*) in excellent agreement with data reported by *Martin et al.* [1990b] for an Antarctic deep-ocean station in the southern Drake Passage (0.10-0.16 n*M* dissolved Fe and 0.08-0.21 n*M* dissolved Mn). In addition, the dissolved Fe profiles we have measured between 45° and 53°S in the open Southern Ocean to the southwest of Tasmania [*Sedwick et al.*, 1997, 1999] are in close agreement with a recent compilation of open-ocean dissolved Fe profiles presented by *Johnson et al.* [1997]. In the results presented here, dissolved Fe and Mn concentrations are considered as "high" if they exceed typical open-ocean upper water column concentrations of < 0.5 n*M* [*Johnson et al.*, 1997; *Landing and Bruland*, 1987].

3.1.1. Spring 1994. The stations sampled for trace metals during spring 1994 were generally in or near areas of significant sea ice cover (Table 1), with surface mixed layer depths ranging from ~20 to 150 m. Along 76°30'S the surface mixed layer averaged around 30 m in depth, with temperatures of less than -1.5°C and salinities in the range of 34.3-34.8 [*Smith and Gordon*, 1997; *Bates et al.*, 1998]. Water column concentrations of the major nutrients were generally high (> 18 μ*M* nitrate, > 1.4 μ*M* phosphate, and > 65 μ*M* silicic acid)

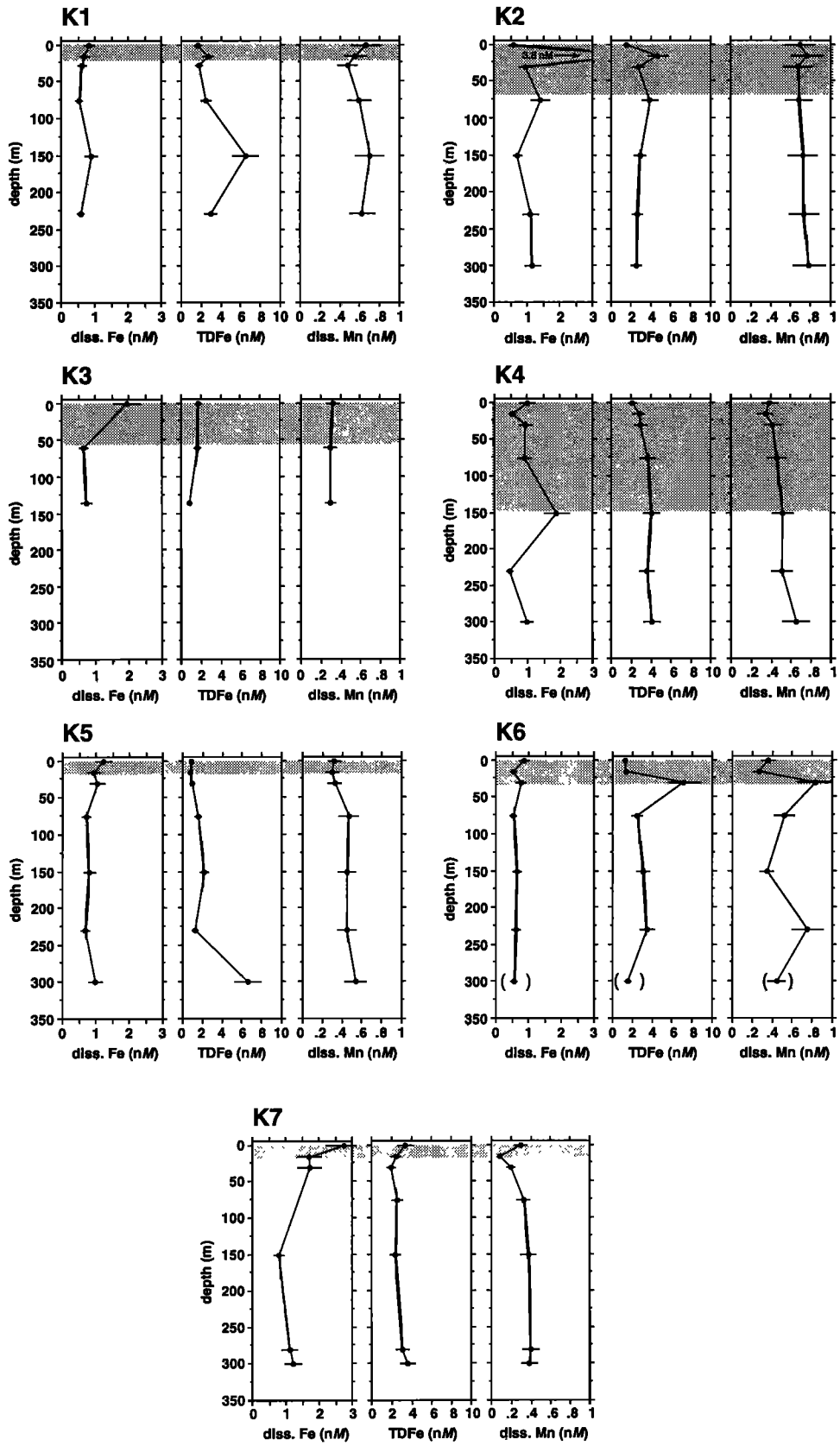

Figure 2. Vertical concentration profiles of dissolved iron (diss. Fe), total dissolvable iron (TDFe), and dissolved manganese (diss. Mn) from spring 1994 cruise. Shading indicates approximate depth of surface mixed layer, and error bars show estimated analytical uncertainties (the data points in parentheses are from a sample thought to have pretripped in the upper mixed layer, based on major nutrient concentrations).

[*Gordon et al.*, 1996]. Compared with typical open-ocean conditions, the water column concentrations of dissolved and total dissolvable Fe and dissolved Mn were generally high (Figure 2), similar to values reported for midlatitude coastal regions [e.g., *Landing and Bruland*, 1987; *Wu and Luther*, 1996; *Johnson et al.*, 1997, 1999]. The observed concentration ranges were 0.45-3.8 n*M* dissolved Fe (mean = 1.0 n*M*), 0.66-7.12 n*M* TDFe (mean = 2.7 n*M*), and 0.08-0.83 n*M* dissolved Mn (mean = 0.48 n*M*). The vertical concentration profiles display a variety of features, including mixed layer maxima in dissolved Fe (stations K2, K3, and K7), and both shallow and deep maxima in TDFe and dissolved Mn (e.g., stations K1 and K6). There are no clear relationships between these features and geographic location, hydrography, or sea ice cover, except for the mixed layer maxima which may be related to sediment inputs from nearby Franklin Island for station K2 and inputs from melting sea ice (brash ice) at station K7 (see section 4). These relatively complex vertical concentration profiles are quite different from those observed in the deep open ocean and presumably reflect a number of input and/or removal processes.

3.1.2. Summer 1995. The summer 1995 stations were ice-free or nearly ice-free, except for stations L3 and L5 (Table 1). Surface mixed layer depths at the trace metal stations were generally shallower than for the spring 1994 stations, ranging from ~5 to 50 m, although along 76°30'S, mixed layer depths were similar to or, later in the cruise, greater than those observed during spring 1994 [*Bates et al.*, 1998]. Mixed layer temperatures along 76°30'S varied from approximately -1.5°C to +1.5°C, with salinities ranging from 33.2 to 34.5 [*Bates et al.*, 1998]; here the upper water column was generally warmer and fresher than in spring 1994, presumably owing to the addition of meltwater from sea ice which had melted during the spring and early summer. Water column major nutrient concentrations were significantly lower than in spring 1994 (> 12 μ*M* nitrate, > 0.6 μ*M* phosphate, and > 40 μ*M* silicic acid) [*Gordon et al.*, 1996] but not so low as to limit phytoplankton growth. The observed concentration ranges of TDFe (0.27-9.17 n*M*, mean = 2.31 n*M*, excluding the high concentration of 35.2 n*M* measured in one near-bottom sample) and dissolved Mn (range = 0.03-0.79 n*M*, mean = 0.39 n*M*) were generally similar to those measured during spring 1994, although at a number of stations (e.g., L5, L6, L7, and L8) these species and dissolved Fe were depleted in the upper water column relative to concentrations below 100 m depth (Figure 3). In contrast to spring 1994, dissolved Fe concentrations were relatively low throughout the water column (range = 0.09-0.57 n*M*, mean = 0.23 ± 0.11 n*M*), except at stations L3 and L9, where higher concentrations of 0.70-2.25 n*M* were observed in the upper mixed layer. We have argued that the high concentrations of dissolved and total dissolvable Fe measured in the upper water column at station L3 were due to iron released from melting sea ice observed at this site [*Sedwick and DiTullio*, 1997]. There was no direct evidence for this process at station L9, although relatively warm surface waters (-0.2°C) near this station were not inconsistent with recent meltwater inputs. Given the shallow water depth at station L4 (350-400 m), the high TDFe concentration of 35.2 n*M* measured at 300 m depth at this station probably reflects elevated particulate Fe concentrations in near-bottom waters, so this value has not been included in the average of water column TDFe concentrations for the summer 1995 cruise.

3.1.3. Comparison with other data. The only published water column trace metal data from the Ross Sea are those collected by the Moss Landing Marine Laboratories (MLML) group, who measured dissolved and particulate Fe in water samples collected along 76°30' and 72°30'S in January 1990 [*Martin et al.*, 1991; *Fitzwater et al.*, 1996; *Johnson et al.*, 1997]. The MLML group report average concentrations in the upper water column (< 60 m depth) of 0.12 ± 0.07 n*M* dissolved Fe and 1.1 ± 0.9 n*M* particulate Fe along 76°30'S and 0.08 ± 0.04 n*M* dissolved Fe and 0.28 ± 0.09 n*M* particulate Fe along 72°30'S [*Fitzwater et al.*, 1996]. These mean values for 76°30'S compare well with our mean summer 1995 concentrations of 0.18 ± 0.08 n*M* dissolved Fe and 1.08 ± 0.81 n*M* total dissolvable Fe for water depths ≤ 60 m, excluding stations L3 and L9, where we believe high iron concentrations may reflect meltwater inputs. Complete MLML data for two stations from the January 1990 cruise are presented as an appendix to *Johnson et al.* [1997] (see http://www.mlml.calstate.edu/data/irondata.htm) and are plotted in Figure 4 as vertical concentration profiles for dissolved Fe and total dissolvable Fe (calculated as the sum of dissolved and particulate Fe), together with data from our stations L8 and L1. Our stations L3 and L8 are the closest stations to MLML station 30, for which we have water column Fe profiles (Figure 1); however, station L3 is excluded from this comparison because of the high Fe concentrations which we attribute to meltwater input. Our dissolved Fe concentrations for station L8 are ~0.05-0.1 n*M* higher than, although nearly within error of, those for MLML station 30, whereas the TDFe data from these two stations are in excellent agreement. MLML station 98 was located in deep water (> 3200 m) well to the north of our Ross Sea stations, and the iron profiles from this station are very similar to those we obtained at our deep-ocean station L1 (Figure 4).

3.2. Incubation Experiments

On the basis of results from bottle iron enrichment experiments and an in situ iron fertilization experiment in the equatorial Pacific, *Coale et al.* [1996b] have argued that bottle incubation experiments provide robust diagnostic information regarding the nutritional status of the oceanic algal community, at least with respect to iron. The objectives of the Fe and Mn enrichment bottle incubation experiments which we performed in the Ross Sea were to evaluate the nutritional sufficiency of ambient Fe and Mn concentrations for the native phytoplankton community. These experiments were purely diagnostic in nature and not intended to mimic the biogeochemical and ecological processes of the natural ecosystem. In the manner of *Martin et al.* [1990a], we assume that observed decreases in nitrate+nitrite and increases in chlorophyll *a* or total chlorophyll equivalents in the incubation bottles provide relative measures of net accumulation of algal biomass as a function of time, thus relative algal growth rates for the different treatments. The xanthophyll pigments fucoxanthin and 19'-hexanoyloxyfucoxanthin are thought to be indicative of diatoms and *P. antarctica*, respectively, in waters of the Ross Sea [*DiTullio and Smith*, 1996], and laboratory studies suggest that 19'-hexanoyloxyfucoxanthin is the main carotenoid in *P. antarctica* cells grown under the "low-iron" (< 2-10 n*M* Fe) conditions [*van Leeuwe and Stefels*, 1998] used in our field

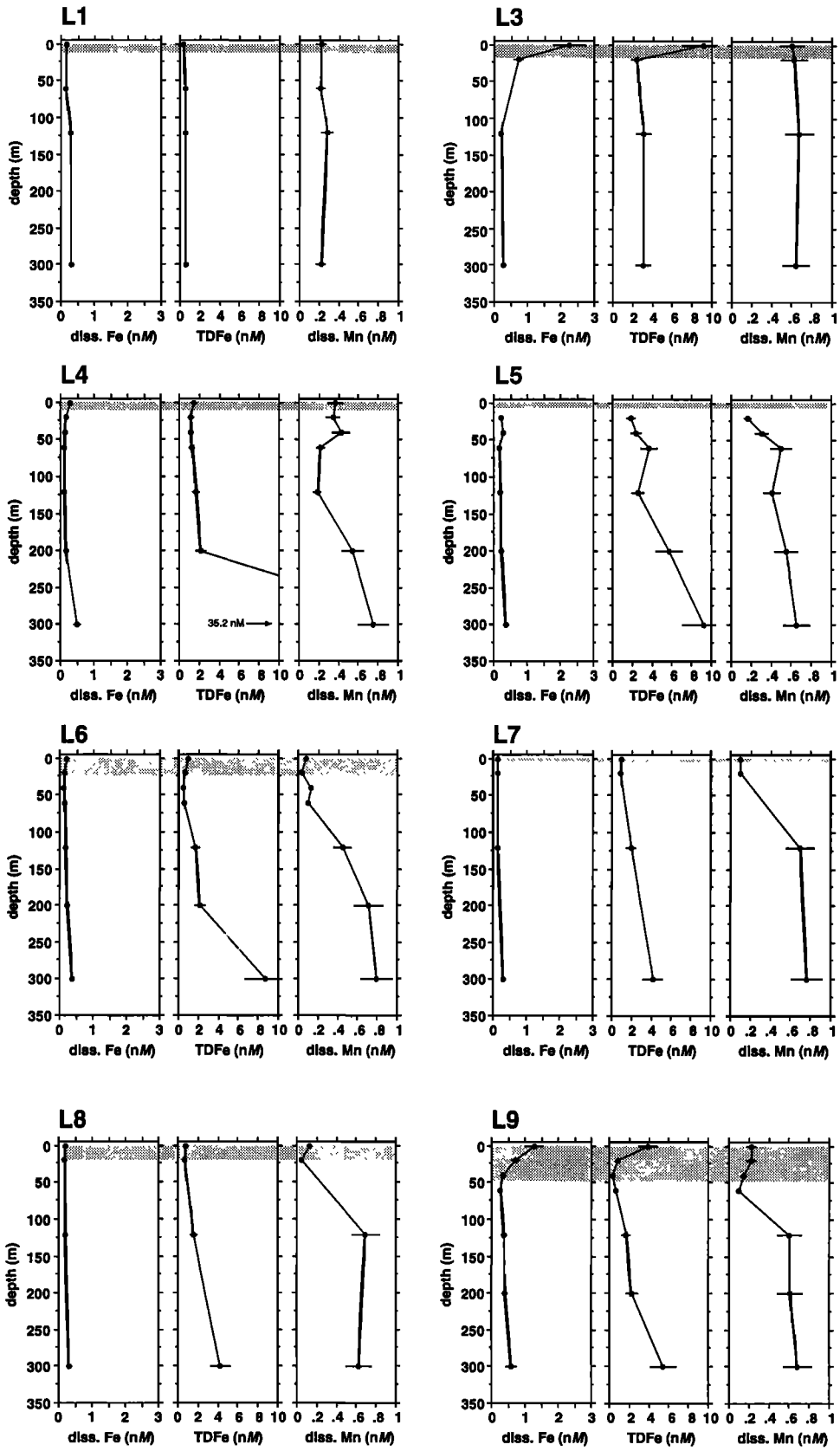

Figure 3. Vertical concentration profiles of dissolved iron (diss. Fe), total dissolvable iron (TDFe), and dissolved manganese (diss. Mn) from summer 1995 cruise. Shading indicates approximate depth of surface mixed layer, and error bars show estimated analytical uncertainties.

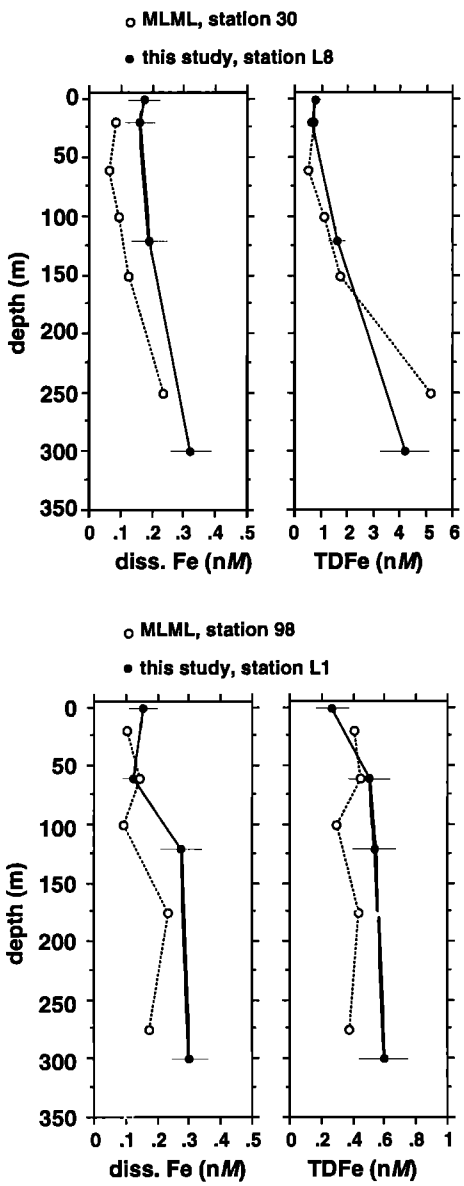

Figure 4. Vertical concentration profiles of dissolved iron (diss. Fe) and total dissolvable iron (TDFe, calculated from dissolved Fe+particulate Fe) from Moss Landing Marine Laboratories group Ross Sea stations [*Johnson et al.*, 1997], together with data from this work.

experiments. Therefore we assume that 19'-hexanoyloxyfucoxanthin and fucoxanthin were the main carotenoids produced by *P. antarctica* and diatoms, respectively, in our experiments, and we interpret observed increases in the ratio of fucoxanthin:19'-hexanoyloxyfucoxanthin (fuco:hex) to indicate increases in the abundance of diatoms relative to *P. antarctica* in the incubation bottles. This interpretation is supported by our measurements of chlorophyll *c*3, a pigment thought to be produced by *Phaeocystis antarctica* but not by diatoms [*Jeffrey et al.*, 1997].

3.2.1. Spring 1994. Microscopic observations (D. Garrison, personal communication, 1996) and algal pigment composition (fuco:hex = 0.04, chlorophyll *c*3 = 1.2 μg L^{-1}) indicate that the algal community was dominated by colonial *Phaeocystis antarctica* at station K1, where seawater was collected for the single incubation experiment performed during the spring 1994 cruise. The nitrate+nitrite versus time data from this experiment provide no clear evidence for algal Fe or Mn deficiency, with nitrate being completely consumed in all treatments after 9 days incubation (Figure 5). The chlorophyll *a* versus time data (Figure 5) also provide no indication of algal Fe or Mn deficiency; the Fe-amended bottles actually produced less chlorophyll *a* relative to the manganese and control treatments after 6 days (p = 0.01, unpaired student's t test), and there was no significant difference between chlorophyll *a* concentrations in the Fe, Mn, and control treatments after 9 days ($p > 0.3$). Microscopic observations (Carol Kosman, personal communication, 1995) and the generally low fuco:hex ratios (Figure 6) and high concentrations of chlorophyll *c*3 (0.3-6.4 μg L^{-1}; data not shown) measured in the incubation bottles indicate that *Phaeocystis antarctica* remained the dominant algal species during the course of the experiment. This is consistent with the silicic acid:nitrate+nitrite (Si:N) drawdown ratios observed in the incubation bottles (0.15-0.17, molar basis, after 9 days), which are low compared with the diatom-dominated summer 1995 experiments. However, the higher fuco:hex ratios measured in the Fe-treated bottles (fuco:hex > 1.3) relative to the Mn and control treatments (fuco:hex < 0.25) after 6 and 9 days (Figure 6), as well as lower chlorophyll *c3* concentrations measured in the Fe-treated bottles (< 0.31-1.54 μg L^{-1} in Fe treatments and 2.01-6.39 μg L^{-1} in Mn and control treatments; data not shown), suggest that addition of iron stimulated the growth of diatoms relative to *P. antarctica*. Thus our experimental results indicate that the ambient concentrations of dissolved Fe (~0.8 n*M*) and Mn (~0.7 n*M*) in the upper mixed layer were high enough to meet the growth requirements of the algal community, which was dominated by *Phaeocystis antarctica*, although iron addition apparently favored the growth of diatoms relative to that of *P. antarctica*.

3.2.2. Summer 1995. Microscopic analyses (D. Garrison, personal communication, 1996) and the relatively high fuco:hex ratios (> 1.7; Figure 6) and low chlorophyll *c*3 concentrations (< 0.16 μg L^{-1}; data not shown) measured in starting seawater and incubation bottle samples indicate that pennate diatoms were the dominant algal species in each of three experiments conducted during summer 1995. The experiment at station L3 was conducted near the edge of a large area of melting sea ice, which satellite images revealed to be the western edge of the receding annual ice pack, and we have argued that the unusually high trace metal concentrations measured in surface waters at this station (2.3 n*M* dissolved Fe, 9.1 n*M* TDFe, and 0.60 n*M* dissolved Mn) were derived from the melting sea ice [*Sedwick and DiTullio*, 1997]. The nitrate+nitrite versus time data from this experiment (Figure 5) show that nitrate was almost completely consumed after 7 days, with no significant difference in nitrate drawdown between treatments ($p > 0.1$, unpaired student's t test). There were also no significant differences ($p > 0.3$) between the increases in total chlorophyll equivalents in the three treatments (Figure 5). These results indicate that the relatively high ambient Fe and Mn concentrations in surface waters at station L3 were sufficient for the growth requirements of the algal community. However, we note that significantly higher

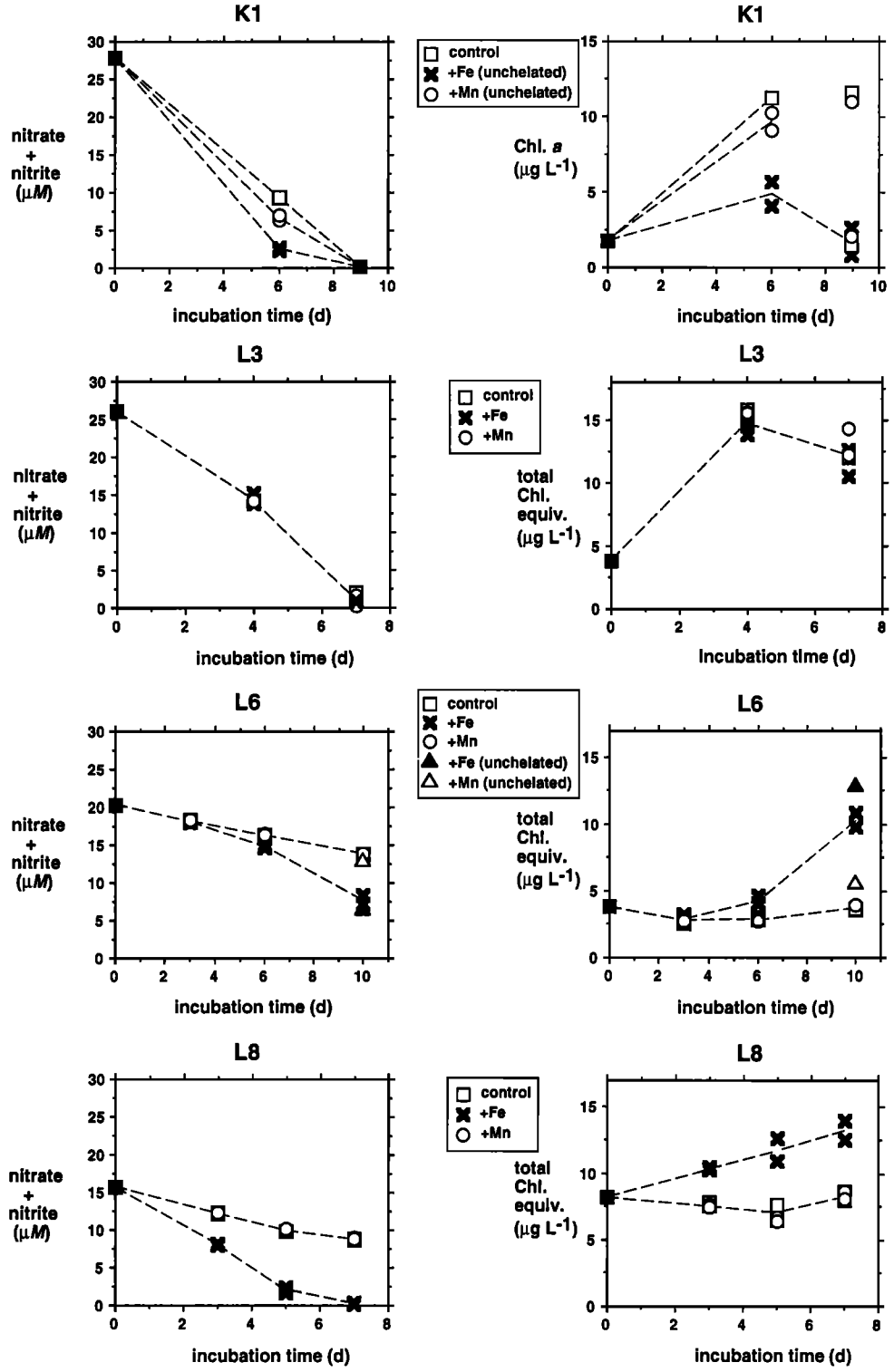

Figure 5. Results of bottle incubation experiments from stations K1, L3, L6, and L8. (left) Concentration of dissolved nitrate+nitrite versus incubation time. (right) Concentration of chlorophyll *a* or total chlorophyll equivalents versus incubation time.

fuco:hex ratios were measured in the Fe-treated bottles relative to the control and Mn treatments after 4 and 7 days ($p < 0.005$), suggesting that addition of iron favored the growth of diatoms relative to *Phaeocystis*, as observed in the spring 1994 experiment.

Much lower trace metal concentrations were measured in surface waters at the two ice-free stations where experiments were conducted, station L6 (0.17 n*M* dissolved Fe, 0.95 n*M* TDFe, and 0.07 n*M* dissolved Mn) and station L8 (0.17 n*M* dissolved Fe, 0.75 n*M* TDFe, and 0.12 n*M* dissolved Mn). In

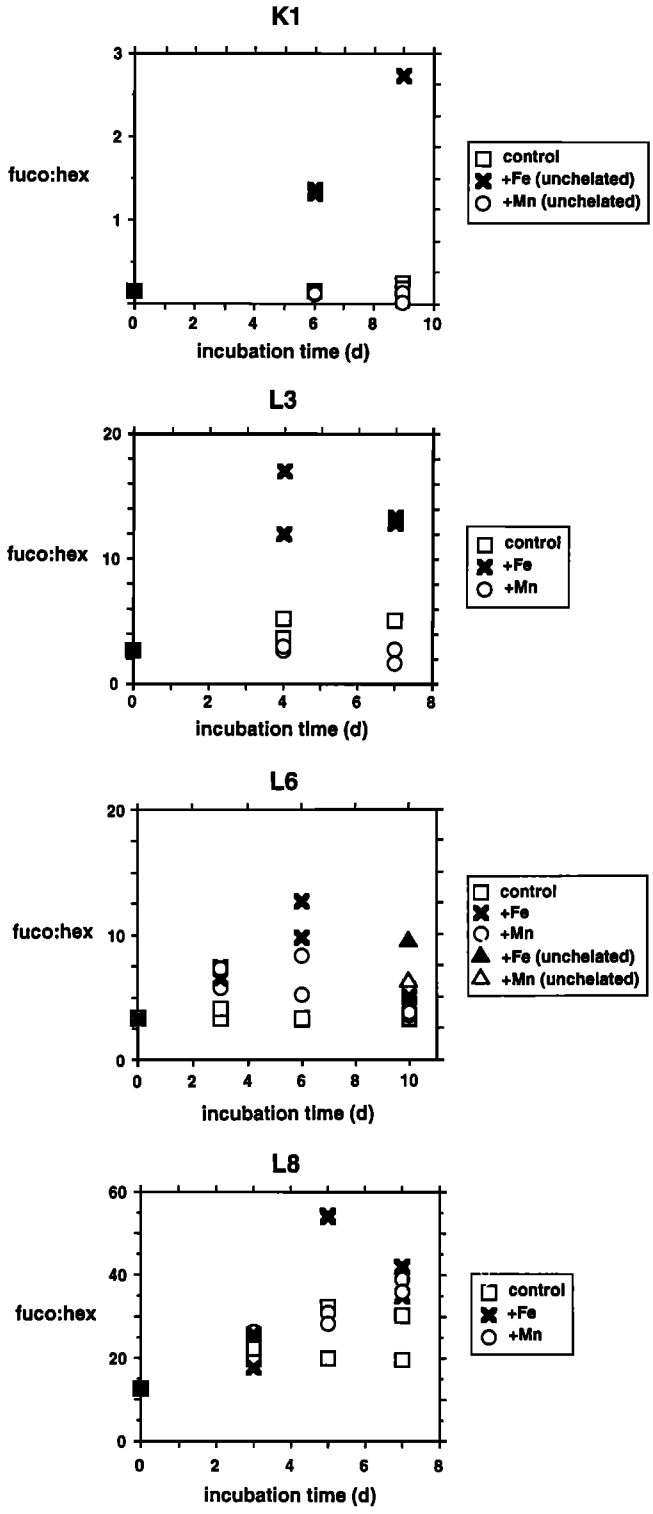

Figure 6. Ratio of fucoxanthin to 19'-hexanoyloxyfucoxanthin (fuco:hex) in particulate material versus incubation time in incubation experiments at stations K1, L3, L6, and L8.

both experiments the nitrate+nitrite and total chlorophyll equivalents versus time data (Figure 5) suggest that addition of iron mediated a significant increase in both nitrate drawdown ($p < 0.01$) and concentration of total chlorophyll equivalents ($p < 0.01$) relative to the control and manganese treatments after 7-10 days. These results indicate that the dissolved Fe concentrations of 0.17 n*M* were limiting phytoplankton community growth rates in surface waters at stations L6 and L8 but provide no evidence of algal Mn deficiency at these stations. In both of the experiments, fuco:hex ratios either remained roughly constant or increased with time (Figure 6), suggesting that diatoms dominated the algal community in the incubation bottles. There was some evidence that iron addition favored the growth of diatoms relative to *Phaeocystis*, in the higher fuco:hex ratios measured in the Fe-treated bottles relative to the control and Mn treatments ($p < 0.01$) at day 10 in the station L6 experiment and at day 5 in the station L8 experiment. Although the unchelated Fe and Mn treatments were not replicated, there appears to be little difference between results for the chelated and unchelated Fe and Mn treatments used in the station L6 experiment (Figures 5 and 6), suggesting that the use of EDTA in these type of experiments may be unnecessary.

3.2.3. Comparison with other data. Our experimental results from summer 1995 are generally consistent with results reported by *Martin et al.* [1990a, 1991] for Fe and Mn addition experiments performed at four stations in the Ross Sea in January and February 1990. The results of these experiments indicated that the growth of diatoms was limited by iron deficiency at three of these stations, including two stations near MLML stations 30 and 98 [*Martin et al.*, 1990a], where low dissolved Fe concentrations (< 0.2 n*M*) in the upper water column are reported (Figure 4). For the station where experimental results indicated iron-replete conditions, *Martin et al.* [1990a, p. 6] remark that "in view of the proximity to the coast and the abundance of ice, adequate amounts of iron were expected," implying that mixed layer iron concentrations were relatively high due to iron supplied by coastal sediments or sea ice. We note that this station at 76°33'S, 167°37'E [*Martin et al.*, 1991] was located between our stations L5 and L7 (Figure 1), where we measured relatively low dissolved Fe concentrations (< 0.3 n*M*) in the upper water column (Figure 3), which suggests that the high Fe concentrations inferred by *Martin et al.* [1990a] were episodic, perhaps supplied from melting sea ice (see section 4).

4. Discussion

4.1. Distribution of Iron and Manganese in the Water Column

The iron and manganese profiles we obtained in the southern Ross Sea are quite different from the smooth vertical concentration profiles of these metals at our offshore station L1 and other offshore locations in the Indian-Pacific sector of the Southern Ocean, where dissolved Fe and Mn concentrations are typically ~0.2 n*M* or less in the upper 300 m of the water column [e.g., *Martin et al.*, 1990b; *Johnson et al.*, 1997; *Sedwick et al.*, 1997; *de Baar et al.*, 1999]. To explain the concentration profiles we observed in the Ross Sea, it is necessary to consider the likely input and removal processes for these metals in this Antarctic continental shelf setting and changes in the relative importance of these processes during the spring and summer. *Martin et al.* [1991] suggest that shallow, nearshore waters are important sources of iron in coastal regions of the Ross Sea. These waters would presumably derive dissolved and particulate iron and manganese from bottom sediments. In this regard, bottom waters in general must be considered as potentially important sources of these trace metals to the upper water column in shelf

areas like the Ross Sea, much of which is < 500 m in depth (Figure 1). Recent work by *Johnson et al.* [1999] in the California Current System indicates that upwelling of particles from the benthic boundary layer provides a significant source of particulate and dissolved iron into coastal surface waters. This same process would also be expected to deliver manganese into the upper water column. In the southern Ross Sea, deep vertical mixing of the water column and the upwelling of subsurface waters near the slope front [*Jacobs and Comiso*, 1989] are both likely to bring metal-rich bottom waters into the euphotic zone. Such deep mixing is likely to be most important during the winter months and should diminish during the spring as sea ice melts and the water column becomes stratified.

A second likely source of iron and manganese in the upper water column in this region is melting sea ice [*Martin et al.*, 1990a, 1991; *de Baar et al.*, 1995]. Sea ice that is formed in offshore Antarctic waters would be expected to contain only low concentrations of Fe and Mn, given that this ice forms from the freezing of surface seawater, which generally contains low concentrations of these metals. However, there are two processes whereby the melting of sea ice could contribute significant concentrations of iron and manganese into the upper water column of the Ross Sea: (1) the release of sediment-derived metals contained in sea ice that formed in coastal waters and (2) the release of mineral-aerosol dust contained in snow on the sea ice. In the coastal region of the southern Ross Sea, intense sea ice formation is thought to occur during the winter months, when the water column is least stratified [*Jacobs and Comiso*, 1989]. This sea ice would be expected to incorporate particulate iron and manganese that is upwelled from bottom sediments, as described above, or contained in bottom sediments that are picked up by grounded ice. Much of this sea ice will be advected away from the coast by offshore katabatic winds [*Markus et al.*, 1998] and could provide an important source of particulate iron and manganese into surface waters of our study region when the sea ice melts. As yet there are no reported measurements of the concentrations and solubilities of iron and manganese in sea ice from Antarctic shelf waters such as the Ross Sea; however, *Löscher et al.* [1997] report total dissolvable Fe concentrations of 10.8-99.3 n*M* for sea ice samples collected from the Atlantic sector of the Southern Ocean, values which are 1-2 orders of magnitude higher than TDFe concentrations in the upper water column at our offshore station L1.

In the Southern Ocean the flux of mineral-aerosol Fe and Mn into the sea is probably lower than anywhere on Earth [*Duce and Tindale*, 1991; *Martin et al.*, 1990b; *Edwards et al.*, 1998], so atmospheric deposition is unlikely to be a significant source of dissolved iron in open-ocean surface waters [*de Baar et al.*, 1995]. However, in seasonally ice-covered Antarctic waters such as the Ross Sea, mineral aerosol accumulates in snow on sea ice during the winter months and is released into the surface ocean when the pack ice melts [*Martin*, 1990]. The volume of snow involved is considerable: In the Ross Sea a mean snow depth of 13.6 cm is reported for pack ice in May-June 1995 [*Sturm et al.*, 1998], and higher values would be expected in the late winter. Snow samples collected from pack ice using trace metal clean techniques during our spring 1994 cruise contained 12.9-19.2 n*M* total dissolvable Fe, of which 10-90% is readily soluble, based on the solubility of aerosol iron in east Antarctic snow [*Edwards*, 1999]. Thus snow on sea ice in our study region is likely to contain soluble aerosol iron in concentrations between 10 and 140 times higher than surface water dissolved Fe concentrations at our offshore station L1, although the aerosol Mn concentrations in this snow are expected to be much lower, given the Fe:Mn mass ratios of 60-80 measured in Antarctic snow [*Boutron and Martin*, 1980] and aerosol [*Zoller et al.*, 1974]. Clearly, there is potential for the Fe and Mn contained in sea ice and the Fe contained in overlying snow to significantly increase the concentration of these metals in surface waters of the Ross Sea when the sea ice melts and the upper water column is highly stratified. Most of the pack ice in our study region typically melts in late November and early December [*Jacobs and Comiso*, 1989]; therefore the maximum input of sea ice-derived Fe and Mn into surface waters of the southern Ross Sea is likely during late spring and early summer. However, this process would be expected to continue during the summer at the edge of the retreating ice pack, as we have suggested for our ice edge station L3 [*Sedwick and DiTullio*, 1997].

A final possible source of iron and manganese which must be considered in our study region is from the melting of glacial ice from sources such as the Ross and Sulzberger Ice Shelves. Such glacial ice would derive these metals from mineral aerosol contained in the glacial ice [*Edwards et al.*, 1998; *Edwards*, 1999] and also from lithogenic material and marine sediments scoured by the basal glacial ice as it is transported across the continent and shallow coastal regions. The iron and manganese in this glacial ice could be delivered into the upper water column of the southern Ross Sea as a result of meltwater emanating from beneath the Ross Ice Shelf [*Jacobs et al.*, 1985] and from the melting of icebergs calved from the ice shelves. However, we have no evidence to argue that either of these processes constitute major inputs of Fe and Mn in waters of our study region. The water column trace metal profiles we obtained next to the Ross Ice Shelf at station K4 (Figure 2) do show a maximum in dissolved Fe concentration (~2 n*M*) at 150 m water depth, although corresponding hydrographic profiles do not suggest meltwater inputs at this water depth. Although icebergs may provide significant iron and manganese inputs into surrounding seawater [*de Baar et al.*, 1995], they were not commonly observed during our cruises, and we assume that meltwater inputs in the southern Ross Sea are dominated by annual sea ice rather than glacial ice.

The processes which remove iron and manganese from the water column in the Ross Sea are likely to be dominated, either directly or indirectly, by biological production in the euphotic zone. Iron exhibits nutrient-like behavior in the ocean, with dissolved iron being transformed into particulate form by phytoplankton production in the upper water column [*Martin and Gordon*, 1988]. A portion of this particulate iron is exported to deeper waters with sinking organic material, some of which is remineralized, releasing dissolved iron at depth [*Johnson et al.*, 1997]. In addition, dissolved iron is known to be scavenged by sinking particles throughout the water column, at least where dissolved Fe concentrations exceed ~0.6 n*M* [*Johnson et al.*, 1997]. Likewise, the removal of dissolved Mn from the oceanic water column is thought to occur primarily via biological uptake and scavenging by suspended and sinking particles, with dissolved Mn maxima being observed in the water column where oxygen concentrations are low [*Bruland et al.*, 1994; *Johnson et al.*, 1996; *Statham et al.*, 1998]. Generally high algal production rates and vertical export fluxes were measured on both of our

cruises [*Smith and Gordon*, 1997; *Bates et al.*, 1998; *Asper and Smith*, 1999]. Thus we propose that dissolved and particulate iron and manganese are continually removed from the upper water column of the Ross Sea during the spring and summer owing to biological uptake by phytoplankton and vertical export of organic matter and scavenging by suspended and sinking particles. As the water column becomes stratified during the summer months, removal of these species from the water column would be most pronounced within the euphotic zone owing to uptake by phytoplankton.

Given that vertical overturn of the water column is dramatically reduced during the spring and that most of the annual pack ice in the southern Ross Sea melts during November and December [*Jacobs and Comiso*, 1989], the greatest inputs of Fe and Mn into the upper water column would be expected during the winter, spring, and early summer rather than later in the summer. In contrast, the removal of these metals from the upper water column due to biological uptake, vertical export, and scavenging would be likely to continue throughout the phytoplankton growing season, from spring through late summer. Taken together, these considerations provide a plausible explanation for the generally higher Fe and Mn concentrations in the upper water column and more complex vertical concentration profiles we obtained during spring 1994 (mid-November-early December) compared with summer 1995 (late December-mid-January). We propose that the water column Fe and Mn distributions observed in spring and early summer (Figure 2) are the result of significant inputs of these metals into the upper water column from upwelled deep waters (in winter and early spring) and sea ice meltwater (in spring and early summer), combined with the rapid removal of these metals from the water column due to algal uptake, vertical export, and scavenging. During the summer season, we suggest that inputs of Fe and Mn into the euphotic zone are much reduced owing to the absence of upwelling and sea ice, whereas algal uptake, vertical export, and particle scavenging continue to remove these metals from the upper water column. As a result, the upper water column becomes depleted in dissolved Fe and Mn and total dissolvable Fe relative to deeper waters (> 100 m depth), as observed in the trace metal profiles from stations L6, L7, and L8 (Figure 3).

During the summer, away from shallow coastal areas, we propose that relatively high concentrations of Fe and Mn are only observed in surface waters at or near the edge of the retreating pack ice, such as at station L3 and perhaps station L9 (Figure 3). It is important to note that we do not suggest the presence of pack ice in itself to constitute a source of iron and manganese but rather the melting of the pack ice, which provides an episodic input of these metals in the meltwater. Enrichments in iron and manganese will not necessarily be associated with low-salinity surface waters, given the nonconservative behavior of Fe and Mn in seawater and the potentially rapid uptake of these species by phytoplankton during ice edge blooms. For example, the ice-free station L8 was occupied very close to the location of station L3 (within 10 km), although 17 days later. At this time, satellite images showed the edge of the receding pack ice, the presumed source of the high mixed layer Fe concentrations measured at station L3, to be well to the east of station L8. Dissolved Fe and Mn concentrations in the surface mixed layer at station L8 (0.16-0.17 n*M* Fe and 0.04-0.12 n*M* Mn) were much lower than at station L3 (0.72-2.3 n*M* Fe and 0.60-0.62 n*M* Mn), although mixed layer salinities were similar at the two stations (34.0-34.1). From this and the results of the iron addition experiments performed at these stations, which indicate that the algal community was iron-replete at station L3 and iron-limited at station L8, we have argued that ice-derived Fe resulted in a diatom bloom in the area of station L3, resulting in the biological removal of Fe and Mn from the mixed layer, prior to our reoccupation of this area at station L8 [*Sedwick and DiTullio*, 1997].

4.2. Implications for Algal Production

The concentration of dissolved iron in seawater is known to regulate phytoplankton growth rates and community composition in open-ocean waters, including at least part of the Southern Ocean [*Coale et al.*, 1996a; *Johnson et al.*, 1997; *Boyd et al.*, 1999]. In equatorial Pacific waters, *Coale et al.* [1996b] have shown that algal iron uptake follows a Michaelis-Menten relationship, with a community half saturation constant for growth of 0.12 n*M* dissolved Fe, where "dissolved" is operationally defined using a 0.4 μm membrane filter. However, algal iron requirements and the concentration at which dissolved iron limits phytoplankton growth are likely to vary with algal community composition and with physical characteristics of the environment. Larger phytoplankton species generally have higher cellular iron requirements, and algal iron requirements are generally higher under conditions of low light [*Sunda*, 1994; *Sunda and Huntsman*, 1997]. Manganese is also known to be an essential micronutrient for phytoplankton growth [*Bruland et al.*, 1991], and limitation of algal growth by Mn deficiency has been demonstrated in laboratory experiments [e.g., *Brand et al.*, 1983; *Sunda and Huntsman*, 1986]. However, convincing evidence of algal growth limitation due to Mn deficiency in ocean waters has so far not been demonstrated [e.g., see *Martin et al.*, 1990a; *Coale*, 1991]. Given that the results of our bottle incubation experiments and earlier work by *Martin et al.* [1990a] indicate that addition of dissolved Fe but not Mn increases phytoplankton growth rates in the Ross Sea, we will restrict our discussion to the role of iron as a limiting nutrient in these waters.

If the data collected during our two cruises are typical of spring and summer conditions in the southern Ross Sea, then our water column trace metal measurements demonstrate a significant seasonal change in the dissolved Fe concentration of surface waters in this region. The mean dissolved Fe concentration in the upper water column (< 60 m depth) decreased from 1.2 ± 0.8 n*M* in spring 1994 (all stations) to 0.18 ± 0.08 n*M* in summer 1995 (excluding stations L3 and L9, where meltwater inputs are likely). The results of our bottle incubation experiments suggest that this decrease in dissolved Fe concentration within the euphotic zone exerts an important control on phytoplankton growth in these waters. The experiment conducted in spring 1994 at station K1 indicates that surface waters at this location were replete with iron. The surface water trace metal concentrations (0.82 n*M* dissolved Fe, 1.6 n*M* TDFe, and 0.66 n*M* dissolved Mn), sea ice conditions, and algal community composition observed at this station were typical of those encountered during the spring 1994 cruise, so our results from this experiment may be applicable to much of our study region during the spring and early summer, when *Phaeocystis antarctica* dominates the algal community. In contrast, the experiments conducted at stations L6 and L8 during the summer 1995 cruise indicate that

the low ambient concentrations of dissolved Fe (< 0.2 n*M*) were limiting the growth of the diatom-dominated algal community. The one experiment from the summer 1995 cruise which indicated iron-replete conditions was that conducted at station L3, where we propose that melting sea ice was responsible for transient high concentrations of dissolved Fe in the surface mixed layer. On the basis of these observations we infer that phytoplankton growth rates are limited by low dissolved Fe concentrations in much of the southern Ross Sea during the summer.

During both of our cruises the dissolved major nutrients nitrate, phosphate, and silicic acid were present in relatively high concentrations at all stations [*Bates et al.*, 1998] and thus cannot explain variations in algal production and community composition. *Arrigo et al.* [1998a, 1999] propose that water column stability plays a major role in controlling phytoplankton biomass and community structure in the southern Ross Sea. These authors argue that the typical early season *Phaeocystis antarctica* bloom develops because this species is better adapted than diatoms to the highly modulated light environment (i.e., vertical mixing) during spring and early summer, whereas diatom-dominated blooms are favored by the highly stratified ice edge waters later in the summer season. In this model the demise of the *Phaeocystis* bloom and the absence of diatom blooms in open-water regions during the summer are presumably a result of increased vertical mixing and horizontal advection of surface waters in the absence of sea ice. We suggest that availability of dissolved iron may be of equal importance as water column stability in regulating algal production in the southern Ross Sea, given that the highest rates of primary production have been observed during the spring and early summer, when on the basis of our observations, these waters are replete with iron. Later in the summer, the growth of both *P. antarctica* and diatoms is likely to be limited by the low concentrations of dissolved iron, except near the retreating ice edge, where the elevated iron concentrations in shallow meltwater lenses allow diatom blooms to occur.

However, it is noteworthy that *Phaeocystis antarctica* should dominate the spring bloom under iron-replete conditions, given that shipboard and in situ iron addition experiments suggest that iron-replete conditions generally favor the growth of diatoms relative to smaller algal species, where major nutrients are abundant [*Martin et al.*, 1991; *Coale et al.*, 1996a; *Sedwick et al.*, 1999]. The spring dominance of *P. antarctica* is thought to reflect the neutral buoyancy of colonial *P. antarctica* and the ability of *P. antarctica* to maintain near-maximal photosynthetic rates under low levels of irradiance [*Arrigo et al.*, 1998a, 1999]. This latter observation may be interpreted in terms of the dependence of algal iron requirements on irradiance and cell size, in that the cellular iron requirements of phytoplankton are thought to increase as irradiance decreases and cell size increases [*Raven*, 1990; *Sunda*, 1994; *Sunda and Huntsman*, 1997]. Thus, even with relatively high dissolved iron concentrations in the southern Ross Sea during spring and early summer, the irradiance/mixing regime may be such that the growth rate of diatoms is limited by iron deficiency (i.e., diatom growth is colimited by iron and light availability), whereas the growth rate of the smaller *P. antarctica* cells is not. This is consistent with the results of our spring 1994 experiment, in which elevated fuco:hex ratios and lower chlorophyll *c*3 levels in the Fe-treated bottles indicate that iron addition favored the growth of diatoms relative to *P. antarctica*, despite relatively high ambient dissolved Fe concentrations of 0.82 n*M*, suggesting that the native diatom population (as distinct from the algal community) was iron limited. Finally, we note that recent field observations indicate that ammonium satisfies ~30% of diatom N requirements in the southern Ross Sea [*Arrigo et al.*, 1999]. This is consistent with widespread iron limitation of diatom growth in these waters, given that phytoplankton require iron to reduce nitrate [*Price et al.*, 1991].

In addition to regulating the production and export of organic carbon in the Ross Sea, the availability of iron may exert an important control on the production and export of biogenic silica in this region. The Ross Sea is an area of large-scale accumulation of biogenic silica, and diatom production in these waters may play a significant role in the oceanic silicon cycle [*DeMaster et al.*, 1996; *Nelson et al.*, 1996]. Recently, *Hutchins and Bruland* [1998] and *Takeda* [1998] have reported results of field experiments which suggest that diatoms incorporate more silicon relative to nitrogen and carbon when growing under iron-limited conditions. These observations are consistent our experimental results from stations L6 and L8 (summer 1995), where we suggest that iron deficiency was limiting the growth of the diatom-dominated algal community. In these experiments, there was little increase in the net silicic acid drawdown in the Fe-treated bottles relative to the Mn and control treatments (data not shown), despite roughly twofold increases in net nitrate+nitrite drawdown in the Fe-treated bottles (Figure 5). Our results indicate that iron addition mediated significant decreases ($p < 0.01$) in the Si:N drawdown ratio relative to the Mn and control treatments after 7-10 days: from 0.73 ± 0.02 to 0.49 ± 0.04 at station L6 and from 1.40 ± 0.01 to 0.57 ± 0.02 at station L8. If we assume that these changes primarily reflect changes in the uptake of silicic acid with respect to nitrate by diatoms, then these results suggest that diatoms grown in our experiments were more heavily silicified under iron-limited conditions. This implies that the ratio of Si:N (and presumably Si:C) assimilated by diatoms may change during the course of ice edge blooms, as dissolved Fe concentrations decrease, possibly resulting in enhanced export of heavily silicified diatom biomass as the blooms terminate.

4.3. Concluding Remarks

Our observations, together with the results of earlier trace metal measurements and iron addition experiments [*Martin et al.*, 1990a; *Fitzwater et al.*, 1996], suggest that phytoplankton growth in the southern Ross Sea is commonly limited by low concentrations of dissolved iron (< 0.2 n*M*) during the summer, except in the highly stratified, iron-rich waters of the ice edge region, where diatom blooms occur. In contrast, iron-replete conditions (~1 n*M* dissolved Fe) exist during the bloom period of spring and early summer, as a result of iron supplied from upwelled bottom waters and melting sea ice. At this time *Phaeocystis antarctica* dominates the algal community, apparently because the small *P. antarctica* cells are better adapted to the poorly stratified water column, in which diatom growth may be colimited by the availability of light and iron. We conclude that iron availability and irradiance (controlled by vertical mixing) exert primary controls on phytoplankton growth rates, community composition, and algal nutrient assimilation in the southern Ross Sea during the spring and summer, thus controlling the biological drawdown of nutrients

and CO_2 [*Arrigo et al.*, 1999] and the vertical export of organic carbon and opal [*Hutchins and Bruland*, 1998] in these waters.

However, it is important to realize that our data represent observations from only one spring season and one summer season, one year apart. Significant interannual variations in physical parameters such as sea ice cover [*Arrigo et al.*, 1998a; *Parkinson*, 1998] may strongly affect the geochemical processes in the water column, and it is conceivable that what we have interpreted as seasonal variations in the distribution of trace metals may to some extent represent interannual variations. Further field observations are required to verify that this region is a seasonally iron-limited ecosystem and to better understand the relative importance of physical and chemical forcing on algal growth and community structure. Some of this information will likely be provided by data collected during the recent U.S.-JGOFS cruises in the Ross Sea. In addition, it is of interest to investigate the distribution and nutritional sufficiency of iron in other highly productive areas of the Antarctic continental shelf, such as Prydz Bay and the Amundsen, Bellingshausen, and Weddell Seas.

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G. R. DiTullio, Grice Marine Laboratory, University of Charleston, 205 Fort Johnson, Charleston, South Carolina 29412.

D. J. Mackey, CSIRO Division of Marine Research, GPO Box 1538, Hobart, Tasmania 7001, Australia.

P. N. Sedwick, Antarctic CRC, GPO Box 252-80, Hobart, Tasmania 7001, Australia. (e-mail: P.Sedwick@utas.edu.au)

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