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Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth

S.E. Fitzwater[a,*], K.S. Johnson[a,1], R.M. Gordon[a], K.H. Coale[a], W.O. Smith, Jr.[b]

[a]*Moss Landing Marine Laboratories, P.O. Box 450, Moss Landing, CA 95039, USA*
[b]*Virginia Institute of Marine Science, P.O. Box 1346, Gloucester Point, VA 23062-1346, USA*

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Abstract

Dissolved and particulate trace metal concentrations (dissolved Fe, Zn, Cd, Co, Cu and Ni; particulate Fe, Mn and Al) were measured along two transects in the Ross Sea during austral summer of 1990. Total Fe concentrations in southern Ross Sea and inshore waters were elevated > 3.5 times that of northern waters. Dissolved Zn, Cd and Co concentrations were lower by factors of 4.5, 3.5 and 1.6 in southern surface waters relative to northern waters. Dissolved Cu and Ni concentrations were similar in both areas. Elevated Fe concentrations coincided with areas of increased productivity, phytoplankton biomass and nutrient drawdown, indicating that Fe is an important factor controlling the location of phytoplankton blooms in the Ross Sea. Particulate concentrations of Fe, Mn and Al indicate two possible sources of iron to the Ross Sea, resuspension of continental shelf sediments and iron incorporated in annual sea ice and released with meltwaters.

1. Introduction

With average surface water nitrate concentrations of approximately 25 μM, the Southern Ocean constitutes the largest area of high nutrient, low chlorophyll (HNLC) waters in the world's ocean. This area of excess NO_3 extends equatorward, across the

* Correspondence address. Monterey Bay Aquarium Research Institute, P.O. Box 628, Moss Landing, CA 95039, USA. Fax: +1-831-775-1620.
E-mail address: sfitz@mbari.org (S.E. Fitzwater).
[1] Monterey Bay Aquarium Research Institute, P.O. Box 628, Moss Landing, CA 95039, USA.

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Antarctic Polar Front Zone (APFZ) to about 45°S. If the daily input of N in this region were fully utilized by phytoplankton, numerical simulations suggest that atmospheric CO_2 could be reduced by 50–90 μatm (Sarmiento and Orr, 1991; Peng and Broeker, 1990). This would account for nearly all of the glacial to interglacial CO_2 change seen over the last four glacial cycles (Petit et al., 1999). Gran (1931) and later, Martin (1990), theorized that the abundance of iron might be a key factor in regulating NO_3 utilization in these waters. Some paleo records would support this theory with high iron, high production and low atmospheric CO_2 occurring in high latitudes during Glacial epochs (Barnola et al., 1987; DeAngelis et al., 1987; Kumar et al., 1995; Petit et al., 1999).

Regions of intense blooms ($> 3\,g\,C\,m^{-3}d^{-1}$, 5–10 μg chl l^{-1}) do occur in modern Antarctic waters, but they are generally confined to shallow shelf areas, waters along receding ice margins and upwelling regions along the APFZ (Smith and Nelson, 1985, 1986; de Baar et al., 1995; Arrigo et al., 1999; Coale et al., 1999). Productivity rates and biomass are usually low (e.g., $0.1\,g\,C\,m^{-3}\,d^{-1}$, 0.1–0.2 μg chl l^{-1}) in offshore regions with high nitrate concentrations, which comprise the majority of the Southern Ocean (Holm-Hansen et al., 1977; El-Sayed, 1988; de Baar et al., 1995; Banse, 1996). It was long thought that, given the abundance of major plant nutrients, this pattern was controlled by the combined effects of solar irradiance, water column stability and grazing (Booth et al., 1982; Smith and Nelson, 1985, 1986; Nelson and Smith, 1991; Frost, 1991). Recent research suggests that micronutrients, more specifically iron, also exert a "bottom up" control on nitrate utilization in the Southern Ocean (Martin et al., 1990a, b; Lancelot et al., 1993; de Baar et al., 1995; Sedwick and Di Tullio, 1997; Timmermans et al., 1998; Coale et al., 1999; Sedwick et al., 2000).

Several studies conducted in Southern Ocean waters indicate that offshore HNLC areas may persist due to the lack of iron (Martin et al., 1990b; de Baar et al., 1990; de Baar et al., 1995; Sedwick and DiTullio, 1997; Timmermans et al., 1998; Sedwick et al., 2000; de Baar et al., 1999) or co-limitation by silica (de Baar et al., 1999; Franck et al., 1999). Martin et al. (1990b) found concentrations of dissolved Fe in neritic Gerlache Strait waters 40 to 50 times higher than those measured in the open-ocean waters of the Drake Passage. This increase in Fe was coincident with a three-fold increase in surface chlorophyll levels. Other evidence suggests that the increased productivity along the Polar front, down current from the Drake Passage, may be due to upwelling of continentally derived iron (de Baar et al., 1995). Sullivan et al. (1993) and Banse (1996) surmised that the pattern of high biomass distributions around Antarctic land masses was consistent with the prevailing currents, indicating that iron derived from continental sources may account for increased production downstream of peninsular or island projections. Direct evidence for Fe limitation was obtained from bottle enrichment experiments in the Ross Sea (Martin et al., 1990a; Sedwick and DiTullio, 1997; Coale et al., 1999; Sedwick et al., 2000), the Weddel–Scotia Seas (de Baar et al., 1990; Buma et al., 1991) and offshore Drake Passage waters (Helbling et al., 1991). These experiments showed that the addition of Fe increased phytoplankton biomass significantly in HNLC waters.

The Ross Sea provides all of the above environments in close proximity; receding ice edges and shallow coastal shelf areas, where significant blooms occur during the

summer season, and offshore HNLC regions. A field study measuring trace metal concentrations, nutrient concentrations and phytoplankton parameters in the Ross Sea during austral summer 1990 was conducted in an attempt to clarify these relationships. Two east/west transects along the same latitudes later occupied by the US-JGOFS program, were conducted over a 22-day period. These transects encompassed a variety of environments from high productive nearshore waters to offshore HNLC waters. Iron, as well as several other bioactive trace metals (Zn, Cu, Ni, Cd and Co), were measured. The trace metal concentrations as well as their relationship with nutrient distributions and phytoplankton biomass are discussed.

2. Methods

In January of 1990 the R/V *Polar Duke* occupied two east–west transects; one located along 76° 30′S and the other along 72° 30′S (Fig. 1). A total of 181 hydrographic stations were occupied during the study. All stations were sampled by CTD, and approximately half were sampled for chlorophyll, nutrients, organic C and N, biogenic silica and primary production (for details see DeMaster et al., 1992; Nelson and Treguer, 1992; Smith et al., 1996). Eight stations (four per transect) consisting of

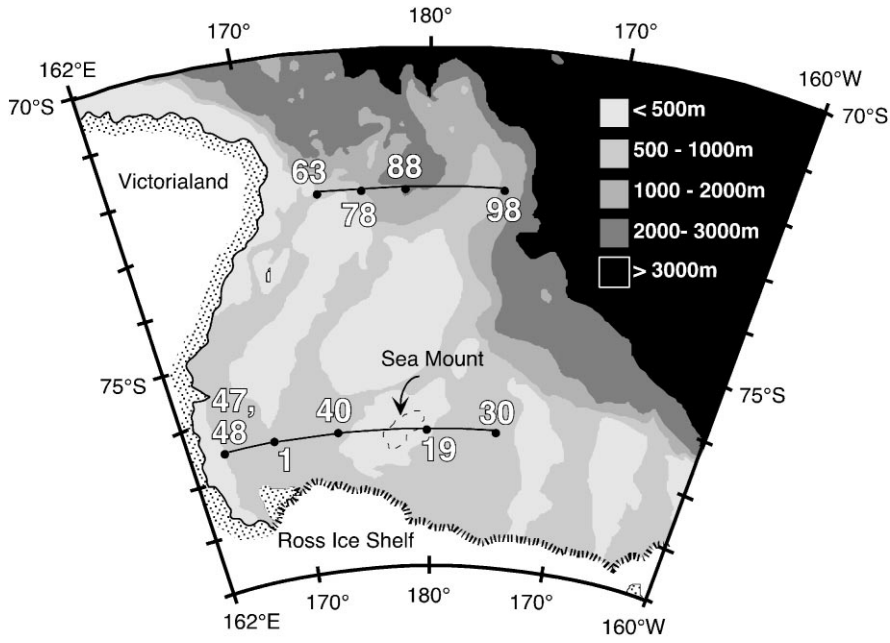

Fig. 1. Map of study area and station locations. Bathymetry contours are also shown. Note the seamount in the vicinity of 76° 30′S and 180°.

Table 1
Procedural blanks and detection limits for the APDC/DDDC extraction method (dissolved) and total bomb digestion method (particulate). See text for calculation definitions

Trace metal	*n*	Blank S.D. (total nmol)	Detection limit (nmol kg^{-1})
Dissolved			
Cd	6	0.0008 ± 0.0003	0.004
Co[a]	6	0.5 ± 0.4	5
Cu	6	0.009 ± 0.003	0.04
Fe	6	0.027 ± 0.004	0.05
Ni	6	0.005 ± 0.003	0.04
Zn	6	0.023 ± 0.012	0.14
Particulate			
Al	6	3.1 ± 0.8	0.04
Fe	6	4.6 ± 0.9	0.05
Mn	6	0.06 ± 0.02	0.001

[a]Co units are in total pmol and pmol kg^{-1}.

4–6 depths (10–375 m) were sampled for trace metals, as well as limited sampling among the broken inshore ice field west of the southern transect (Stn. 48). In addition, a surface raft sample was taken close inshore among broken ice floes (Stn. 47).

Water-column trace-metal samples were collected using acid-cleaned, Teflon-coated, 30 l Go-Flo bottles suspended on non-metallic Kevlar line and tripped with all-Teflon messengers. Following each cast, the Go-Flos were attached to the outside of a portable, filtered-air, clean laboratory and connected to filter manifolds inside the lab with polyethylene tubing. Sample water was filtered through tared, acid-washed, 142 mm, 0.4 μm Nucleopore polycarbonate filters, mounted on all-Teflon sandwiches under N_2 pressure. Filters were digested in Teflon bombs by the sequential treatment with HCl, HNO_3 and HF for the analysis of particulate Fe, Mn and Al (Eggimann and Betzer, 1976). An aliquot of the filtrate was collected in a polyethylene bottle and acidified with quadruple quartz-distilled, 6M HCl (4 ml l^{-1}, pH < 1.6). APDC/DDDC-chloroform double extraction (after Bruland et al., 1979) was used to concentrate Cd, Co, Cu, Fe, Ni and Zn. The concentrates were analyzed using platform, graphite furnace, atomic adsorption spectrophotometry with Zeeman background correction. Procedural blanks for both dissolved and particulate methods are presented in Table 1. Blanks for the dissolved fraction are total nmol found in the 1.6 ml extract following MQ water extraction. Dissolved detection limits are three times the standard deviation of the blank based on a 250 ml sample. Total bomb digestions are total nmol found in the digestion of blank filters. Particulate detection limits are three times the standard deviation of the blank based on 5 l of filtered sample. No samples were rejected.

3. Results

3.1. Hydrography

The Ross Sea is a relatively shallow basin with a strong cyclonic (clockwise) surface water circulation during austral summer. Flow in the southern portion is generally to the west, which intensifies in a northward flow along the western margin of the Ross Sea (Pillsbury and Jacobs, 1985). Total winter-ice coverage usually begins to clear along the southern portion in the early summer (November and December) resulting in one or more polynyas. As austral summer continues, ice clearing progresses in the southern polynya as well as retreat of the northern ice edge to the south (Comiso et al., 1993). This pattern was evident for the 1989 and 1990 season: the southern transect encompassed waters that had been ice-free since December, whereas the northern transect only became ice-free in mid-January (DeMaster et al., 1992; Smith et al., 1996).

The ice melt resulted in a well-stratified water column along the southern transect particularly at the western end where the mixed layer was only ~ 25 m deep. A shallow (~ 20 m), low-salinity meltwater lens (< 31.0 salinity) along the ice edge was also evident at the inshore southern station. Waters along the northern transect also were stratified, with the mixed layer slightly deeper, averaging 30–40 m in depth (Smith et al., 1996).

3.2. Biology

The Ross Sea, particularly the western shelf area, has the largest, most predictable phytoplankton blooms in the Southern Ocean (Comiso et al., 1993; Sullivan et al., 1993; Smith and Nelson, 1985; Arrigo et al., 1999). The 1990 field season was not atypical in this respect. The western end of the southern transect was dominated by an intense diatom bloom along the receding ice edge. This developed most intensely in the lens of melt water and was composed primarily of three species of *Pseudonitzschia* and occasional large concentrations of *Chaetoceros* species (DeMaster et al., 1992; Smith et al., 1996). A less intensive bloom was observed eastward (Stn. 19) that was composed of a mixed assemblage of phytoplankton. *Pseudonitzschia* spp., centric diatoms and *Phaeocystis antarctica* were all approximately equally numerically abundant (DeMaster et al., 1992). Maximal chlorophyll levels of 8.19 $\mu g l^{-1}$ were found in the meltwater lens and averaged 3.31 $\mu g l^{-1}$ along the southern transect (Fig. 2c). The only significant area of phytoplankton growth observed along the northern transect was found in inshore waters where maximal chlorophyll levels reached 2.42 $\mu g l^{-1}$ (Fig. 2d). Average chlorophyll values along the northern transect were less than 1/3 that of the south (0.89 $\mu g l^{-1}$). Although much lower in numbers, the same diatoms as found in the south numerically dominated the northern transect. All other biological parameters, primary production, POC, PON, biogenic silica and nutrient concentrations reflected these differences (see DeMaster et al., 1992; Nelson et al., 1991; Nelson and Treguer, 1992; Smith et al., 1996).

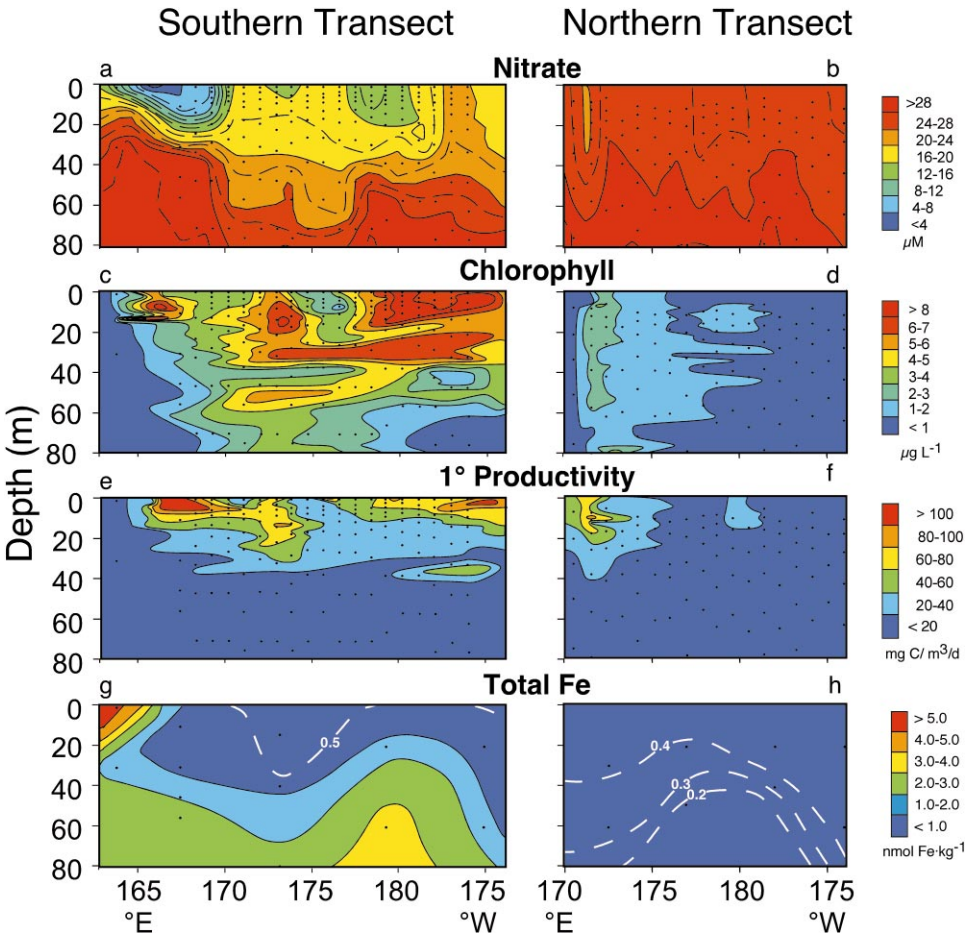

Fig. 2. Nitrate, chlorophyll, primary productivity and total Fe vertical sections along the northern and southern transects.

3.3. Chemistry

The results of the dissolved trace metal analyses along with station locations, nutrients and hydrographic data for the trace-metal stations are presented in Table 2. Particulate Fe, Mn and Al values are presented in Table 3. Details of the other hydrographic stations are discussed elsewhere (DeMaster et al., 1992; Smith et al., 1996).

Nitrate, phosphate and to a lesser extent, silica were depleted in southern transect surface waters. Nitrate reached a minimum (2.3 μM) in the meltwater lens along the ice edge (Stn. 47). Nitrate depletion elsewhere in southern transect surface waters was $\sim$ 10–12 μM, phosphate depletion $\sim$ 1.5 μM, and silica $\sim$ 15 μM when compared to

Table 2
Station location, depth, temperature, salinity, nutrient concentrations and dissolved trace metal concentration from stations along the southern (76° 30′S) and northern (72° 31′S) transects in the Ross Sea[a]

Station	Lat.	Long.	Depth	°C	Salinity	PO_4	NO_3	Si	Cd	Cu	Fe	Ni	Zn	Co
Southern transect														
47	76° 30′S	163° 53′E	0.5	−0.94	30.25	0.44	2.3	49.6	0.08	1.64	0.25	4.88	0.24	18
48	76° 30′S	163° 52′E	30	−1.27	34.61	1.93	27.1	70.3	0.62	1.99	0.22	6.46	3.95	23
1	76° 34′S	167° 29′E	10	1.18	33.92	0.38	8.3	32.0	0.04	1.23	0.07	4.78	0.35	13
			30	−1.57	34.46	1.85	24.5	70.7	0.38	1.89	0.09	5.79	1.74	18
			45	−1.54	34.52	2.04	28.3	75.4	0.68	2.08	0.12	6.18	4.29	38
			55	−1.70	34.56	2.08	29.7	76.7	0.73	2.10	0.26	6.74	4.99	36
			100	−1.80	34.61	2.06	30.2	76.4	0.69	2.15	0.21	6.53	4.90	29
			150	−1.83	34.64	2.08	30.6	76.5	0.68	2.07	0.41	6.66	5.23	41
40	76° 30′S	173° 20′E	15	0.72	34.36	1.27	16.3	62.1	0.23	1.35	0.05	5.35	0.79	< 5
			40	−0.63	34.33	1.50	18.5	66.9	0.32	1.43	0.23	5.28	0.89	< 5
			80	−1.41	34.43	2.10	29.1	76.7	0.72	2.16	0.25	6.25	4.75	27
			150	−1.56	34.51	2.12	30.9	75.0	0.68	2.17	0.31	6.08	5.33	28
			250	−1.83	34.61	2.17	31.2	78.0	0.72	2.18	0.31	6.50	5.72	31
19	76° 30′S	179° 39′E	20	−0.17	34.13	1.20	14.6	58.6	0.18	1.26	0.09	5.42	0.71	12
			60	−1.29	34.41	2.05	30.1	77.0	0.70	2.15	0.16	6.75	4.92	28
			100	−1.51	34.47	2.12	31.0	76.6	0.69	2.16	0.39	6.56	5.17	29
			150	−1.71	34.48	2.14	31.2	74.8	0.69	2.08	0.22	6.66	5.01	26
			250	−1.81	34.56	2.12	30.6	76.2	0.70	2.16	1.13	6.78	5.10	38
30	76° 30′S	175° 02′W	20	−0.78	34.03	1.49	19.2	52.2	0.18	1.54	0.08	5.84	0.78	18
			60	−1.46	34.21	2.10	27.3	62.9	0.70	1.76	0.06	6.29	2.78	26
			100	−1.33	34.30	2.20	29.6	68.4	0.68	2.03	0.09	5.80	4.42	30
			150	−1.26	34.37	2.06	32.6	74.7	0.69	2.14	0.12	6.35	4.98	26
			250	−1.45	34.43	2.10	32.9	77.4	0.72	2.22	0.23	6.26	4.88	26
Northern transect														
63	72° 31′S	172° 31′E	30	−0.30	34.26	1.86	28.4	53.3	0.55	1.92	< 0.05	6.23	2.95	26
			60	−0.42	34.28	1.99	29.5	67.1	0.61	1.91	0.12	6.30	4.00	26
			120	−0.58	34.34	2.15	31.6	79.6	0.73	2.10	< 0.05	6.08	5.20	25
			180	−0.85	34.48	2.21	32.8	90.4	0.76	2.31	0.46	6.16	6.33	28
			250	−0.98	34.59	2.16	32.0	85.7	0.73	2.21	0.43	6.08	5.26	22
78	72° 30′S	177° 00′E	20	−0.22	34.17	1.82	27.1	59.4	0.58	1.74	0.05	6.10	2.74	23
			50	−0.42	34.17	1.87	27.6	60.4	0.59	1.77	0.10	6.32	3.93	24
			100	−1.43	34.30	2.09	30.3	67.9	0.68	1.89	0.10	6.35	4.42	23
			200	0.15	34.50	2.28	33.1	93.7	0.79	2.31	0.18	6.54	7.11	27
88	72° 30′S	178° 28′W	20	−0.89	34.09	1.79	26.1	56.6	0.49	1.64	0.06	6.11	2.81	18
			40	−1.02	34.20	1.85	27.5	58.9	0.50	1.74	< 0.05	6.40	2.63	24
			100	−0.67	34.36	2.15	31.3	75.0	0.71	2.14	0.13	6.60	4.77	24
			200	0.12	34.51	2.06	32.6	87.6	0.74	2.43	0.33	6.88	6.41	29
98	72° 30′S	174° 00′W	20	−0.94	33.59	1.83	25.7	45.2	0.44	1.55	0.10	5.94	2.14	18
			60	−1.43	34.08	1.94	27.9	50.7	0.55	1.61	0.14	6.44	3.04	25
			100	−0.83	34.22	2.17	30.7	62.2	0.67	1.79	0.09	6.40	4.22	26
			175	0.84	34.50	2.35	33.6	80.5	0.80	2.16	0.23	6.46	6.16	31
			275	1.43	34.64	2.33	33.6	91.3	0.80	2.19	0.17	6.62	6.37	27
			375	1.52	34.68	2.29	33.2	95.2	0.78	2.33	0.23	6.70	6.38	30

[a]Concentrations of PO_4, NO_3, Si in μM; Cd, Cu, Fe in nmol kg^{-1}; and Ni, Zn, Co in pmol kg^{-1}.

Table 3
Particulate Al, Fe and Mn concentrations from stations along the southern (76° 30′S) and northern (72° 31′S) transects in the Ross Sea. Total particulate load, Fe : Al and Mn : Al are also included

Station	Depth	Particulates (mg l^{-1})	Al	Fe	Mn	Fe : Al	Mn : Al
Southern transect							
47	0.5	0.79	13.7	5.01	0.10	0.37	0.007
48	30	0.32	3.63	1.77	0.16	0.49	0.044
1	10	3.02	1.11	0.61	0.17	0.55	0.153
	30	1.36	2.06	0.84	0.12	0.41	0.058
	45	1.18	2.66	1.58	0.10	0.59	0.038
	55	0.71	4.30	2.60	0.10	0.60	0.023
	100	0.35	5.19	2.70	0.13	0.52	0.025
	150	0.11	5.34	2.84	0.17	0.53	0.032
40	15	1.60	2.51	0.39	0.03	0.16	0.012
	40	1.06	0.68	0.30	0.05	0.44	0.074
	80	1.11	4.20	1.97	0.09	0.47	0.021
	150	0.24	12.4	4.36	0.23	0.35	0.019
	250	0.09	11.6	3.79	0.20	0.33	0.017
19	20	3.78	1.75	0.96	0.11	0.55	0.063
	60	0.40	6.67	3.02	0.14	0.45	0.021
	100	0.16	13.7	5.17	0.30	0.38	0.022
	150	0.13	17.4	6.39	0.35	0.37	0.020
	250	0.13	12.4	4.03	0.19	0.33	0.015
30	20	1.81	1.68	0.61	0.10	0.36	0.060
	60	1.61	1.12	0.44	0.10	0.39	0.089
	100	0.19	2.43	1.03	0.04	0.42	0.016
	150	0.16	3.87	1.59	0.07	0.41	0.018
	250	0.07	14.8	4.92	0.29	0.33	0.020
Northern transect							
63	30	0.76	0.31	0.35	0.06	1.13	0.194
	60	0.41	0.25	0.20	0.04	0.80	0.160
	120	0.19	2.90	1.52	0.07	0.52	0.024
	180	0.06	10.7	3.41	0.15	0.32	0.014
	250	0.16	18.2	6.46	0.24	0.35	0.013
78	20	0.58	0.14	0.33	0.05	2.36	0.357
	50	0.40	0.18	0.12	0.03	0.67	0.167
	100	0.21	0.24	0.18	0.01	0.75	0.042
	200	0.05	0.51	0.27	0.01	0.53	0.020
88	20	0.35	0.48	0.39	0.03	0.81	0.063
	40	0.37	0.32	0.19	0.05	0.59	0.156
	100	0.18	1.35	0.93	0.03	0.69	0.022
	200	0.04	2.17	1.16	0.05	0.53	0.023
98	20	0.35	0.38	0.33	0.02	0.87	0.053
	60	0.20	0.27	0.32	0.02	1.19	0.074
	100	0.20	0.25	0.21	0.01	0.84	0.040
	175	0.04	0.46	0.22	0.01	0.48	0.022
	275	0.10	0.36	0.22	0.01	0.61	0.028
	375	0.03	0.43	0.17	0.01	0.40	0.023

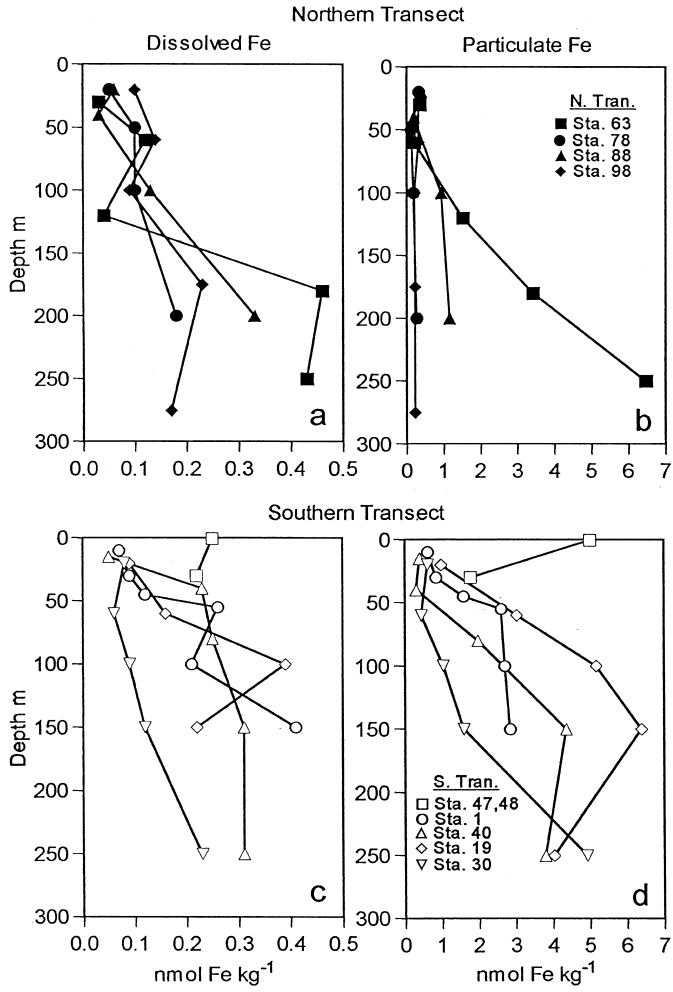

Fig. 3. Profiles of dissolved (a, c) and particulate Fe (b, d) along both transects.

northern surface waters or deep waters. These reductions were concurrent with the bloom conditions described above.

Elevated levels of both dissolved (Fe_{diss}) and particulate iron (Fe_{part}) were found along the southern transect (Fig. 3). The meltwater lens along the receding ice edge in the west and the upwelling plume found at Stn. 19 were significantly elevated in Fe_{part}. Elevated Fe_{part} concentrations also were found below 100 m at the inshore Stn. 63 on the northern transect where concentrations equaled the highest found in the core of the upwelling plume at Stn. 19 ($\sim 6.5\,nmol\,kg^{-1}$). Surface (0–30 m) concentrations of Fe_{diss} and Fe_{part} were approximately 2 and 5 times higher along the southern transect relative to the northern transect.

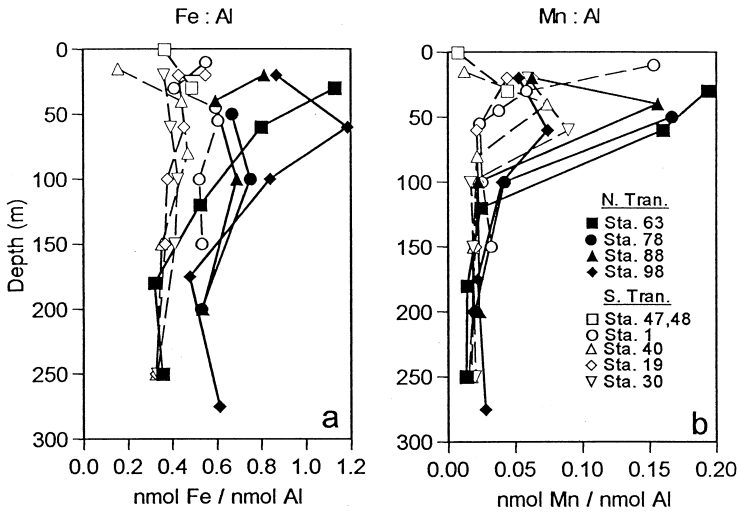

Fig. 4. Particulate iron, aluminum and manganese ratios. (a) Fe : Al ratios and, (b) Mn : Al ratios for the northern transect (closed symbols) and southern transect (open symbols).

Particulate aluminum and manganese concentrations were also elevated along the southern transect and in the deeper waters of the inshore northern Sta. 63 (Table 3). Particulate Al has been extensively used as an indicator of continental derived material. Below ~ 125 m, the $Fe_{part} : Al_{part}$ ratios for both northern and southern stations are about 0.40 (Fig. 4a). This is elevated from recent estimates of average upper crustal ratios of 0.19–0.21 (Taylor and McLennan, 1985; Wedepohl, 1995). Particulate Mn : Al ratios were ~ 0.020 below 125 m, again elevated from estimates of the average ratio for upper crustal material of 0.0034 (Fig. 4b). This is probably due to the resuspension of shelf sediments enriched with Mn and Fe oxides as has been found in other oxygenated shelf areas (Burdige, 1993; Canfield et al., 1993; Thamdrup et al., 1994).

Of the other metals analyzed, dissolved Zn, Cd and to a lesser extent Co, were lower in the surface waters of the southern transect relative to the north. These differences are apparent when comparing the offshore northern Sta. 98 with the inshore southern Sta. 1 (Fig. 5). Average Zn concentrations were approximately 4.5 times lower along the southern transect in the 0–30 m depth interval than along the northern transect (0.57 versus 2.56 nmol kg^{-1}). Cadmium was lower by a factor of ~ 3.5 (142 versus 503 pmol kg^{-1}) and Co was lower by a factor of ~ 1.6 (13.2 versus 21.4 pmol kg^{-1}) along the same depth interval. These reductions were presumably the result of biological uptake due to the increased productivity and biomass observed in surface waters along the southern transect (Price and Morel, 1990; Bruland et al., 1991; Morel et al., 1994; Sunda and Huntsman, 1995; Loscher et al., 1998).

Neither dissolved Cu nor Ni was appreciably lower in the southern transect surface waters. Average values for Cu were 1.40 versus 1.64 nmol kg^{-1}, and Ni values were 5.25 versus 6.05 nmol kg^{-1} when comparing the southern versus the northern tran-

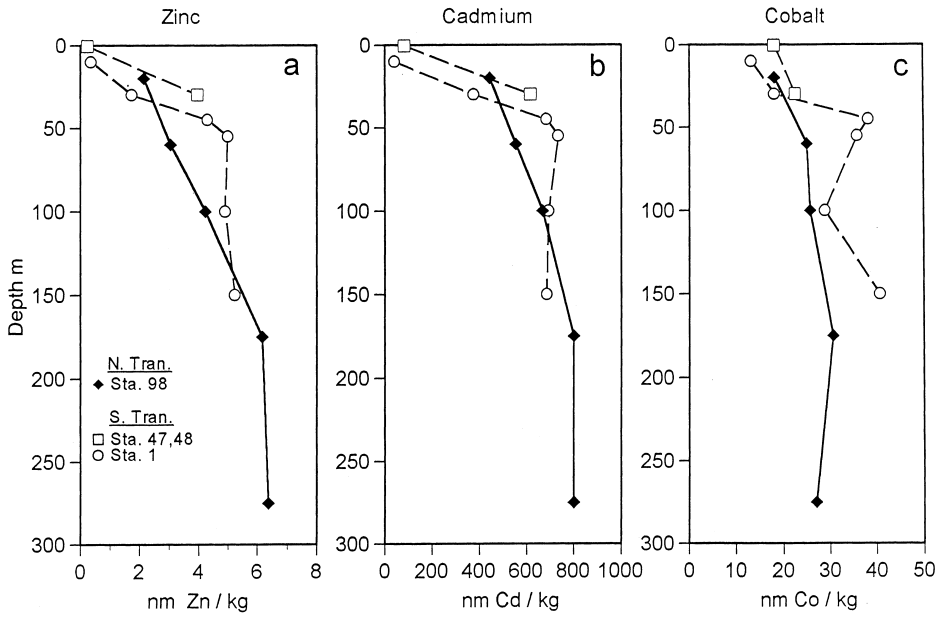

Fig. 5. Dissolved Zn, Cd and Co profiles showing the depletion at the inshore southern transect stations (47, 48 and 1) versus the northern offshore Sta. 98.

sect. Neither element showed significant depletion near the surface. Both elements however, were more than double their typical surface ocean values of ~ 0.5 and $2\,\mathrm{nmol\,kg^{-1}}$, respectively (Bruland, 1980; Bruland et al., 1991). These concentrations are reasonable given the high nutrient concentrations and strong, positive dissolved metal : nutrient correlations. Nolting and de Baar (1994) found similar concentration ranges in the Weddell–Scotia Seas area, with Cu ranging from 1.8 to 5 nM and Ni from 4 to 8 nM.

4. Discussion

4.1. Iron sources

Contour plots of total iron, nitrate, chlorophyll and primary production (Fig. 2) illustrate the following differences between surface waters of the southern and northern transects: 3.5 times more total iron, an average nitrate reduction of ~ 10–$12\,\mu M$, a doubling of productivity rates (1.41 versus $0.70\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$), and a ~ 2.5-fold increase in biomass as indicated by chlorophyll (168 versus $64\,\mathrm{mg\,Chl\,m^{-2}\,d^{-1}}$). We attribute these differences to the availability of iron. The source of iron in the Ross Sea, however, is not well known.

Resuspended particulate Fe appears to be a major source of iron along the southern transect. It is interesting to note the differences between the particulate Fe and Mn to

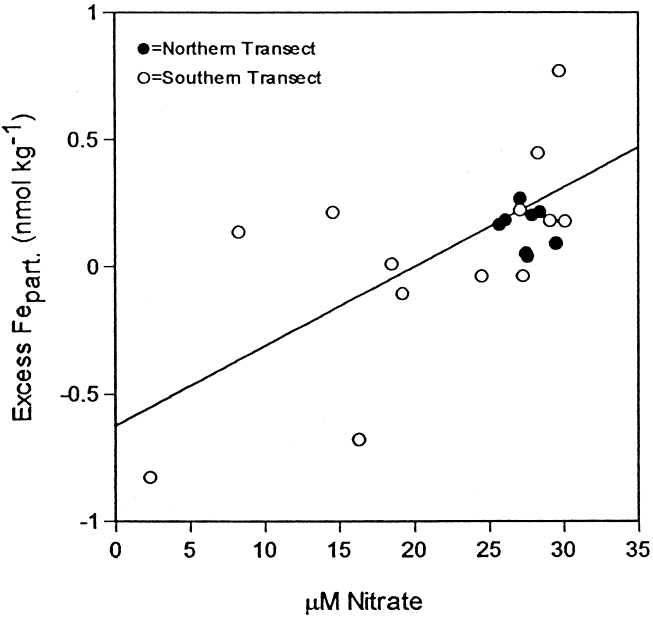

Fig. 6. Excess Fe_{part} versus nitrate for surface waters above 100 m.

Al ratios observed between the southern and northern surface waters. The ratios along the southern transect for Fe_{part} and Mn_{part} versus Al_{part} are similar to that of the deeper waters, or they show depletions in Fe_{part} (Stn. 40) and Mn_{part} (Stns. 47 and 40) relative to Al_{part}. Similar depletions in particulate Fe have been seen along the California coast (Johnson et al., 1997). Northern surface ratios for both Fe_{part} and Mn_{part} versus Al_{part} are much higher than the deep values. The excess particulate Fe can be defined with the equation:

$$Fe_{excess} = Fe_{part} - (Al_{part}(Fe_{part}/Al_{part})_{deep}),$$

where $(Fe_{part}/Al_{part})_{deep}$ is the average ratio of particulate Fe to Al in deep waters. Fe_{excess} has positive values throughout the northern surface waters (Fig. 6). Approximately 50% of the Fe_{part} in the north is in excess of that supported by the particulate Al. This Fe_{excess} must be incorporated in the biota. Although evidence suggests that this pool of particulate iron can be recycled on a time scale of days (Hutchins et al., 1993), the phytoplankton must be preferentially trapping and retaining Fe in the surface waters of this region. The absolute concentrations of dissolved and particulate iron are low along the northern transect, which limits the nutrient consumption and biomass production, and this must lead to retention of iron within the euphotic zone.

In contrast to the northern transect, many of the Fe_{excess} values are zero or negative along the southern transect. A modest correlation exists between surface nitrate concentrations and Fe_{excess} (Fig. 6). This suggests that Fe has been mobilized from the resuspended sediment, incorporated into biomass, and then exported from the system.

As a result, the large supply of resuspended shelf sediment containing particulate iron along the southern transect may enable "bloom" conditions to occur.

Sedwick et al. (2000) suggest that glacial ice melt from sources such as the Ross and Sulzberger Ice Shelves could also be another possible source of iron to the Ross Sea. Glacial ice from these sources could incorporate dust as well as material scoured from the bottom. The Ross Sea Ice Shelf bordering the southern portion of the Ross Sea is the largest floating ice sheet in the world, covering $\sim 54{,}000\,km^2$. Cold, saline water ($-1.8-2.0^{\circ}C$, 34.4–34.7 salinity, $\sigma_t \sim 28$) flows out from under the ice shelf into the Ross Sea basin. These waters have been characterized by Jacobs et al. (1970) as Ice Shelf Water (ISW) and found to flow out most strongly in the vicinity of 180°. Based on salinity and temperature (Table 2), the subsurface waters ($>100\,m$) along the southern transect in the vicinity of Stn. 19 could be from this source. Elevated concentrations of Fe_{part} observed in these waters may be coming from either meltwaters entrained in the ISW, or from possible resuspension of material from a seamount in the vicinity of 180°. This seamount is the shallowest feature of the central Ross Sea, rising to a depth of 178 m (Fig. 1). Either source or possibly a combination of the two, with ISW flow resuspending seamount sediment material, might be responsible for the elevated levels of Fe_{part} observed at Stn. 19.

Several mechanisms allowing phytoplankton to utilize colloidal or particulate iron have been identified (Wells and Mayer, 1991; Barbeau et al., 1996; Maranger et al., 1998), and the importance of resuspended sediments as a significant iron source for phytoplankton in the coastal zone has recently been recognized (Croot and Hunter, 1998; Schoemann et al., 1998; Johnson et al., 1999). Johnson et al. (1999) found elevated levels of Fe derived from resuspended material to extend as far as 200 km seaward from the California coast and to co-occur with elevated levels of chlorophyll. de Baar et al. (1995) attribute the higher chlorophyll levels found in the Polar Front Zone downcurrent from the Drake Passage to elevated Fe levels originating from resuspension of shelf material hundreds of kilometers upcurrent, although the aeolian term could not be ruled out either (Loscher et al., 1997).

Resuspended shelf sediments also may contribute to the elevated Fe_{part} concentrations found in the meltwater lens. Sedwick et al. (2000) postulate that annual sea ice may incorporate resuspended shelf sediments during formation over winter when there is deep vertical mixing occurring in the Ross Sea. Unfortunately, we do not have any estimates of the iron concentration in Ross Sea annual sea ice. However, Martin et al. (1990b) reported values for acid–soluble Fe of $\sim 25.9\,nmol\,kg^{-1}$ in ice of unknown age collected in the Gerlache Straits. de Baar et al. (1995) found glacial ice collected from the wake of an iceberg had an acid-soluble Fe concentration of 20.4 nM. The observed elevated total Fe values found in the inshore meltwater lens may be from the accumulated resuspended iron entrained in seasonal sea ice and subsequently released as the ice melts. Particulate Fe concentrations generally increase with depth along both transects. However, within the meltwater area, the total iron concentrations are highest near the surface (Fig. 2g), which is indicative of a surface source. We have calculated the estimated addition of iron from melting sea ice in the lens based on the observed salinity of 30.25 and an average mixed layer salinity of 34.6. If we assume an average concentration of 25 nM Fe added by melting

sea ice based on the above ice estimates and ~ 130 ml of fresh water per liter of seawater needed to reduce the salinity by 4.35, then an addition of 3.25 nM Fe is possible. This is in good agreement with the particulate iron concentration measured within the core of the meltwater lens of 1.77–5.01 nmol Fe kg^{-1}. One would expect that sea ice over the shallow shelf areas in the south to incorporate significantly more resuspended material during formation than in offshore waters off the shelf such as Sta. 19. This would account for the lack of significant ice edge blooms in offshore waters during the summer melt.

Sedwick and Ditullio (1997) found results indicating the significance of ice-derived Fe during two occupations of a station located in the central Ross Sea (76° 30′S, 170° 40′W) during Austral summer 1995 and 1996. The first occupation (21 and 22 December 1995) was in the presence of melting sea ice with dissolved surface iron concentrations of 2.25 nM, and nitrate concentrations of 27.1 μM. The second occupation 17 days later (7 and 8 January, 1997) found iron concentrations lowered to 0.16–0.17 nM, nitrate reduced to 17.3 μM and biomass, based on chlorophyll, to have increased almost 3-fold. They attribute the increased production to the release of iron from the melting sea ice with the subsequent reduction of dissolved iron due to biological removal.

Direct atmospheric dust deposition as a primary iron source was ruled out by Martin et al. (1990b) because of their findings of low surface-water-dissolved Fe (0.2 nmol kg^{-1}) and Mn (0.008 nmol kg^{-1}) concentrations in offshore Drake Passage waters. The atmospheric dust load in the Southern Ocean is known to be amongst the lowest in the world (Prospero, 1981; Duce and Tindale, 1991). Klinkhammer and Bender (1980) suggest that open-ocean surface Mn concentrations are strongly coupled with atmospheric dust input. Drake Passage surface Mn concentrations (Martin et al., 1990b) are lower by a factor of ~ 4 than reported values of 0.3 nM Mn for the Southern hemisphere (Klinkhammer and Bender, 1980). Aeolian dust deposition may contribute, at most, about 0.1 nM total Fe to the mixed layer when considering over-winter Fe_{part} deposition in snow found on seasonal sea ice. Sedwick et al. (2000) report values of 12.9–19.2 nM total-dissolvable Fe from snow samples collected from Ross Sea pack ice. Based on a solubility of between 10 and 90% (Sedwick et al., 2000) and an average concentration in snow of 20 nM Fe_{part}, an annual accumulation of 10 cm of snow would only contribute 0.01–0.1 nM Fe to a 20 m mixed layer.

4.2. Iron and nutrient relationships

It is now evident that iron availability may influence the uptake ratios of N, P and Si by phytoplankton and, hence, the oceanic distribution of nutrients (de Baar et al., 1997; Hutchins and Bruland, 1998; Takeda, 1998; Coale et al., 1999; Sedwick et al., 2000). We consider first the Si : N ratio and then the N : P ratio. It appears that Fe replete diatoms increase their rate of nitrate uptake, whereas the change in the uptake rate of silica is minimal resulting in lowering the Si : N ratio (Coale et al., 1999; Franck et al., 1999). This results in diatoms with less siliceous tests (Martin et al., 1989). A plot of ambient silica versus nitrate shows differences in the relationship between the

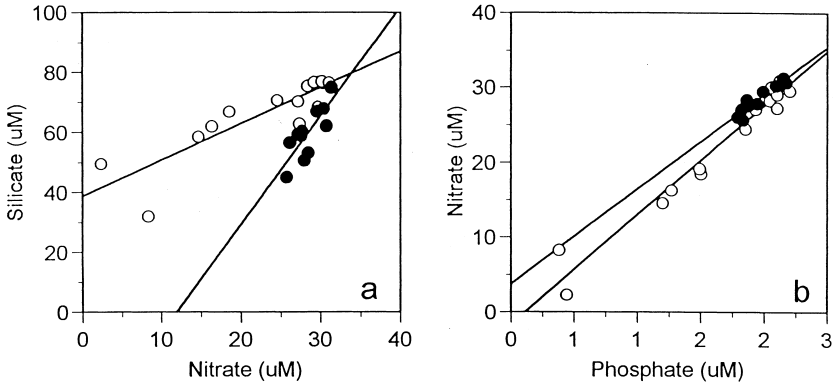

Fig. 7. Silica versus nitrate (a) and nitrate versus phosphate (b) for surface waters above 100 m along the northern (closed symbols) and southern transects (open symbols). Linear regressions, (a) $Si_{south} = 1.2NO_3 + 38.7$, $r^2 = 0.75$; $Si_{north} = 3.7NO_3 - 43.3$, $r^2 = 0.89$, (b) $NO_{3south} = 14.6PO_4 - 1.6$, $r^2 = 0.96$; $NO_{3north} = 12.7PO_4 + 3.7$, $r^2 = 0.89$.

southern and northern upper water column (Fig. 7a). Arrigo et al. (1999) used the slope of nitrate versus phosphate to determine the "disappearance ratio" of N : P in the Ross Sea. Slopes of the regressions here indicate Si : N disappearance ratios of 1.24 for the upper 100 m of the southern transect and 3.63 for the northern. This infers that phytoplankton, primarily diatoms, were consuming nitrate at a faster rate relative to silica uptake in waters supplied with Fe. These values are similar to the Si : N consumption ratios found in iron enrichment bottle experiments by Takeda (1998) in offshore Southern Ocean waters (controls = 2.3, Fe addition = 0.95) and Hutchins and Bruland (1998) in low iron California coastal waters (controls = 2.15, Fe addition = 0.95).

Nelson and Treguer (1992) investigated the possibility that perhaps silica may have become limiting in these waters, which would affect the Si : N uptake ratio. They studied the silica uptake kinetics of diatoms from three stations in the vicinity of Stn. 1, approximately 2 weeks after our trace metal sampling. The observed diatom bloom had continued, lowering silica levels from 32 μM during our sampling to 5.6–6.6 μM. The half-saturation constant for silica uptake averaged 2.69 μM. Silica uptake rates appeared to be approximately 70% of maximal values, resulting in the conclusion that silica would not become strongly limiting until concentrations below about 5 μM were reached. We can assume, therefore, that silica-limitation was not the case here and did not influence the observed Si : N ratios since the water column Si concentrations were above 30 μM. It is more likely that the differences in Si : N disappearance ratios between the northern and southern transects is a consequence of increased diatom growth along the southern transect induced by the presence of adequate iron. We cannot rule out, however, the effect of advection or possible previous blooms of non-siliceous *Phaeocystis* along the southern transect, which could influence the observed Si : N disappearance ratio.

These results, along with Takeda's (1998), also support the contention that the use of opal accumulation rates in the Southern Ocean as proxies to track past levels of productivity may be biased (Kumar et al., 1995; Hutchins and Bruland, 1998; Takeda, 1998; Boyle, 1998). Higher productivity rates, driven by higher dust rates during glacial eras, as Boyle (1998) states, "would not be reflected by higher accumulation rates of sedimentary opal and would eliminate an apparent contradiction — the lack of observed higher accumulation rates of opal had been a sticking point for the hypothesis that enhanced Southern Ocean productivity was a factor driving reduced levels of atmospheric CO_2 during glacial periods".

Phytoplankton N : P disappearance ratios also may be influenced by the presence or absence of Fe (de Baar et al., 1997; Takeda, 1999). We did not find significant differences between the southern and northern transects with a value of 15.0 for all samples (Fig. 7b). This value is similar to that found by de Baar et al. (1997) in the Atlantic sector of the Southern Ocean, where the relationship averaged 13.34 for all stations south of 52°. However, they found that the N : P ratio at stations with diatom blooms (Chl $a > 1\,\mathrm{mg\,m^{-1}}$) averaged 12.77 and were as low as 4.4 in a bloom of the diatom *Fragilariopsis kerguelensis*. de Baar et al. (1997) also found the location of the observed diatom blooms to usually coincide with elevated dissolved iron concentrations. Arrigo et al. (1999) also found a reduction in the N : P disappearance ratio in areas of the Ross Sea dominated by diatoms. Areas with diatom blooms resulted in surface water N : P disappearance ratios of 9.69 ± 0.33, whereas areas with blooms dominated by *Phaeocystis antarctica* resulted in ratios of 19.2 ± 0.61. Mixed assemblages were found to have values intermediate between the two (~ 14.5). Our findings are more indicative of a mixed assemblage, which with the exception of the diatom dominated ice edge bloom was comprised of approximately equal numbers of *Pseudonitzschia* spp., centric diatoms and *Phaeocystis antarctica* along both transects.

Thus, it appears that the presence of iron can affect the ratios of diatom Si : N uptake directly by enhancing nitrate metabolism (Coale et al., 1999). N : P uptake ratios, however, appear to be more dependent on taxonomic differences (de Baar et al., 1997; Arrigo et al., 1999) and may then be indirectly affected by the presence or absence of iron by favoring the growth of diatoms.

4.3. Zinc, cadmium and cobalt

Zinc is also an essential phytoplankton micronutrient that is a component of several enzymes systems including silica uptake and carbonic anhydrase activity (Vallee and Auld, 1990; Morel et al., 1994). Because of this bioactivity, zinc is found to be strongly correlated with silica and nitrate in the world's oceans (Bruland et al., 1991). As observed in this study, Zn can be depleted in Southern Ocean surface waters to sub-nanomolar concentrations by biological uptake (e.g., Stn.1, 10 m, $\mathrm{Zn} = 0.35\,\mathrm{nmol\,kg^{-1}}$).

Dissolved Zn and Si were found to be strongly correlated (Fig. 8a) along the northern transect and in deeper waters of the southern transect ($\mathrm{Zn} = 0.098\mathrm{Si} - 2.6$, $r^2 = 0.788$). The slope compares favorably with Zn : Si slopes found by this lab (Pacific, Atlantic and Southern Ocean, avg = 0.063) and others (Pacific Ocean =

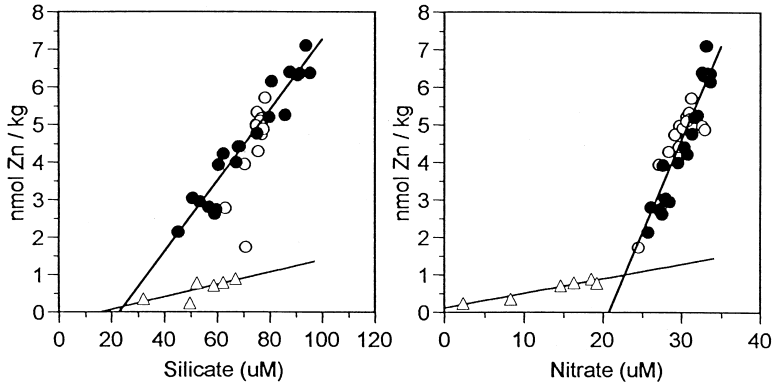

Fig. 8. Dissolved Zn versus silicate (a) and nitrate (b). Closed circles = all northern samples, open triangles = southern surface samples, open circles = all other southern samples. See text for regression analysis.

0.053, Bruland, 1980; Atlantic Ocean = 0.17, Yeats and Cambell, 1983; Scotia Sea = 0.10, Nolting and de Baar, 1994). The relationship is significantly different however in the high productive surface waters along the southern transect where the slope is substantially lower ($Zn = 0.017Si - 0.26$, $r^2 = 0.600$). Zinc was reduced to < 1 nM in these waters while Si concentrations remained above 30 μM, indicating an increase in Zn removal relative to Si.

The Zn versus NO_3 relationship are also significantly different in the southern transect surface waters (Fig. 8b). Southern surface water concentrations followed the relationship $Zn = 0.039NO_3 - 0.113$ ($r^2 = 0.9404$), which has a much smaller slope when compared to all other samples, $Zn = 0.5046NO_3 - 10.6$ ($r^2 = 0.8472$). One explanation suggested by Fig. 8 may be that, in the presence of adequate Fe, diatoms approximately double the rate of nitrate uptake relative to silica. Such added growth requires Zn for carbonic anhydrase activity and several other enzyme systems, and would result in a reduction of ambient Zn concentrations relative to silica as observed here. An alternate explanation may be that although the southern transect bloom areas were dominated by diatoms or mixed assemblages during our sampling, prior *Phaeocystis* blooms may have lowered the dissolved Zn and nitrate concentrations without affecting silica levels.

At some point it is quite possible, given the high Fe available, for this area to become Zn limited as has been found for diatoms in culture work (Price and Morel, 1990; Sunda and Huntsman, 1995). Price and Morel (1990) have found evidence that diatoms are able to replace their Zn requirement with Cd and Co under Zn limiting conditions. They found that the addition of Cd to Zn-depleted *Thalassiosira weissflogii* cells resulted in growth rates approaching 90% of maximum levels. The addition of Co also alleviated Zn deficiency although to a lesser degree (60% of maximal growth). Sunda and Huntsman (1995) also have found evidence that phytoplankton are able to replace their Zn requirement with Co in cultures. A Zn-deficient

culture of *Thalassiosira pseudonana*, a related coastal diatom to *Thalassiosira weissflogii,* yielded growth rates approximating 60% maximal levels whereas *Thalassiosira oceanica*, an oceanic species, could maintain 75–80% maximal levels by replacing Zn with Co. Open-ocean observations support these findings. Reviewing Zn and Co data from Martin and Gordon (1988) and Martin et al. (1989), Sunda and Huntsman (1995) noted a sharp reduction in Co concentrations in surface waters when Zn concentrations fell below 0.3 nM. The relative depletion of Zn, Cd and Co (4.5, 3.5 and 1.6) in surface waters along the southern transect as compared to the northern may be an indication of the onset of Zn stress or limitation. This pattern would result if Southern Ocean diatoms were able to substitute Cd and then Co in enzymatic systems as found above.

5. Conclusions

Significant phytoplankton blooms and nutrient depletion were found in the southern and western areas of the Ross Sea. These blooms corresponded to elevated levels of total Fe. Particulate iron, possibly from resuspended shelf material appears to be a significant source of these elevated levels of iron. Resuspended Fe_{part} incorporated in sea ice and subsequently released with meltwaters also may contribute to the intense ice edge blooms observed. These findings suggest that the presence or absence of adequate iron can affect the community structure by favoring diatoms. This in turn may affect the biogeochemistry of the macro-nutrient (Si, N, P) and micro-nutrient field composition. Determining the consequences of iron on regulating production, community structure and nutrient concentrations in these waters is of importance for future modeling predictions.

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