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Organic complexation of iron in the Southern Ocean

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Abstract

The chemical speciation of iron was determined in the Southern Ocean along a transect from 48 to 70°S at 20°E. Dissolved iron concentrations were low at 0.1–0.6 nM, with average concentrations of 0.25 ± 0.13 nM. Organic iron complexing ligands were found to occur in excess of the dissolved iron concentration at 0.72 ± 0.23 nM (equivalent to an excess of 0.5 nM), with a complex stability of $\log K'_{FeL} = 22.1 \pm 0.5$ (on the basis of Fe^{3+} and L′). Ligand concentrations were higher in the upper water column (top 200 m) suggesting in situ production by microorganisms, and less at the surface consistent with photochemical breakdown. Our data are consistent with the presence of stable organic iron-complexing ligands in deep global ocean waters at a background level of $\sim$0.7 nM. It has been suggested that this might help stabilise iron at levels of $\sim$0.7 nM in deep ocean waters. However, much lower iron concentrations in the waters of the Southern Ocean suggest that these ligands do not prevent the removal of iron (by scavenging or biological uptake) to well below the concentration of these ligands. Scavenging reactions are probably inhibited by such ligand competition, so it is likely that biological uptake is the chief cause for the further removal of iron to these low levels in waters that suffer from very low iron inputs.

Keywords: Iron; Biogeochemistry; Chemical speciation; Southern Ocean.

1. Introduction

The oceans play an important role in the global climate system, as they act to buffer not only heat, but also atmospheric CO_2. The biological pump is of particular interest in the atmospheric

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carbon cycle as it stimulates a net drawdown of CO_2 from the atmosphere into deep waters. The Southern Ocean is thought to play a critical role in the global ocean climate system because of its volume (20% of the earth surface is covered by the Southern Ocean). Antarctic Bottom Water (ABW) is formed by down-welling off the Filchner ice shelf. The dominant water mass in the Southern Ocean is Antarctic Circumpolar Water, in which there is massive up-welling leading to excess major nutrients, and also to excess CO_2 were it not for CO_2 draw-down by biological productivity returning it to lower CO_2 levels. A proportion of the carbon sequestered in the organic matter sinks in particulate form and may be submerged for a long period if it is remobilised in, or below, the ABW. The CO_2 draw-down to the bottom waters becomes particularly interesting if the thermohaline circulation in the N. Atlantic were to collapse due to global warming (Joos et al., 1999), thus reducing the CO_2 draw-down by the N. Atlantic, which is significant at present (Lefevre et al., 1999).

A persistence of high levels of nitrate (and phosphate) in major areas of the oceans, in particular the Southern Ocean, the sub-Arctic and the equatorial Pacific, along with lower than expected biomass, suggests that other limiting processes are at work. These areas are the so-called HNLC regions (high nutrients, low chlorophyll). It is thought that these regions are limited by low supplies of iron due to their remoteness from land (Martin and Fitzwater, 1988; Martin et al., 1991). Iron is a key element in the respiratory electron transport chains (Raven, 1988), and is essential in the synthesis route of chlorophyll (Chereskin and Castelfranco, 1982), the reduction of nitrate and nitrite and various other biological reactions requiring catalysis (Geider and Laroche, 1994). Iron limitation of oceanic phytoplankton has been confirmed by in-situ fertilisation experiments and shipboard incubations (Martin et al., 1994; Coale et al., 1996; Hutchins et al., 1998; Timmermans et al., 1998), and is also known to extend to heterotrophic bacteria in Southern Ocean waters (Pakulski et al., 1996). The biological productivity in the Southern Ocean waters is probably limited by a combination of light (Mitchell et al., 1991) and iron (Smetacek et al., 1997; Sunda and Huntsman, 1997).

The iron hypothesis has been modified by the finding that most of the dissolved iron in the oceanic water column (of the Pacific, the Atlantic, and the Mediterranean) is strongly complexed by organic matter (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; van den Berg, 1995; Witter and Luther III, 1998), suggesting that algal growth is limited not only by a general lack of iron but also by its unavailability.

The organic speciation of iron in the Southern Ocean was previously investigated in the Pacific sector in unfiltered seawater (Nolting et al., 1998). The Pacific sector of the Southern Ocean was subject to a successful fertilisation experiment ("Soiree") in which iron was added to a patch of surface seawater and confirming that the algae were iron-limited. Here we present the organic speciation of iron in the Atlantic sector of the Southern Ocean from the Polar Front (PF) zone to the ice-covered coastal region near the Antarctic peninsula.

2. Sampling and analytical procedures

2.1. Sampling

Samples were collected during a cruise (ANT XVI/3, 18 March–10 May 1999) with the German research vessel *Polarstern* in the Atlantic sector of the Southern Ocean from the PF to the edge of

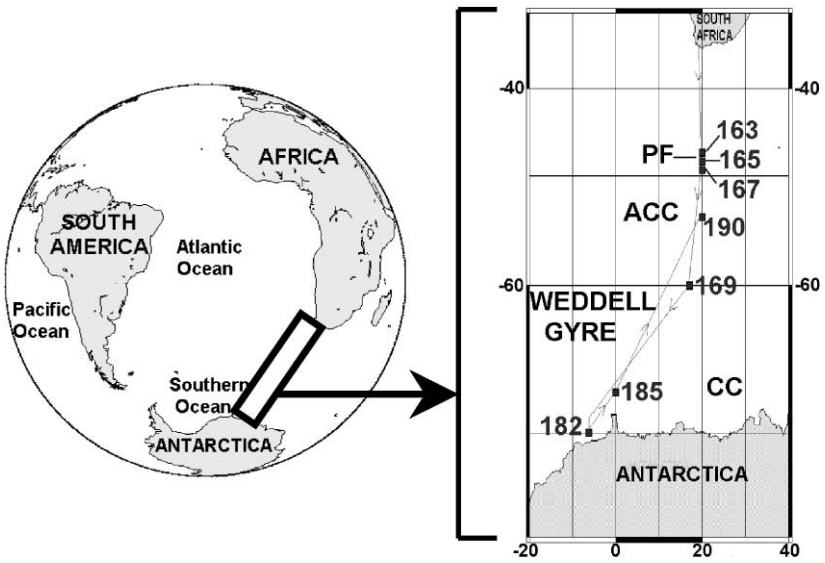

Fig. 1. Map showing station locations.

the Antarctic continent. Measurements of iron complexation by natural organic ligands were made on-board ship in samples from the water column between 48°50′S 20°E and 70°S 8°20′W, and in the pack-ice close to the Antarctic continent (Fig. 1). Temperature, salinity and chorophyll-*a* data were collected using a CTD-rosette equipped with Niskin samplers. Nutrients were determined in samples collected as for iron.

Water samples for trace metal analysis were collected, with 10 pre-cleaned 15-l Go-Flo bottles suspended from a Kevlar wire, from the upper 1000 m at 5 stations, and from the entire water column (0–4500 m) at 2 stations. Wire angle correction was made using SIS depth sensors attached to the bottom Go-Flo bottle. The Go-Flo bottles were closed by means of Teflon messengers, and were placed in a pressurised, class 100, clean container after retrieval. Samples were filtered through 0.2 μm polycarbonate filters (Sartorius "Sartobran") at a nitrogen pressure of 0.1 bar, and the filtered seawater was collected in clean, low-density polyethylene, bottles (Nalgene).

Three ice-samples were collected from an iceberg close to station 182, and one sample was collected from the ice floes surrounding the iceberg, with acid-cleaned plastic ware. The samples were melted in a laminar flow clean air bench and filtered at a mild vacuum of < 0.3 bar (to avoid damage to microorganisms) through acid-cleaned 0.2 μm membrane filters (polycarbonate, Millipore) with a polycarbonate filter apparatus (Sartorius).

Iron speciation was initiated immediately after the sample collection, in the "clean" container; analyses of a profile were usually finalised within 1–2 days, and samples were frozen at -20°C when stored longer than 1 day.

2.2. Analytical procedures

Dissolved iron was determined on-board ship by FIA with luminescence detection (de Jong et al., 1998). Samples were acidified to pH 2 with triple subboiling quartz-distilled nitric acid and

left for at least 1 h prior to analysis. Then, by in-line methods, the pH was brought to 4.5 with ammonium acetate, and the iron was concentrated on an 8-hydroxyquinoline column. After a MQ column wash the iron was eluted with an acidic carrier, mixed with the reagent (Luminol) and swept into a photon counter. The reagent blank from acid/buffer addition and MQ wash was 0.03 nM, and the limit of detection was 0.03 nM.

Organic complexation of iron was determined by cathodic stripping voltammetry (CSV) with ligand competition against 1-nitroso-2-naphtol (NN) (Yokoi and van den Berg, 1992; Gledhill and van den Berg, 1994). To minimize the reagent blank and potential changes to the original redox state, oxidant (hydrogen peroxide or bromate (Aldrich and van den Berg, 1998)) was not used. A long deposition time (300–500 s) was used instead to increase the sensitivity. A drawback was the appearance of an interfering peak, which was subtracted from the scans (see below).

Voltammetric equipment consisted of a mercury drop electrode (model VA663 from Metrohm, Switzerland) connected to a voltammeter (μAutolab from Eco Chemie, Netherlands). The mercury drop size was approximately 0.52 mm^2. The reference electrode was double-junction, Ag/AgCl, 3 M KCl, with a salt bridge filled with 3 M KCl. The counterelectrode was glassy carbon.

The seawater pH was buffered at 8.05 using borate buffer (H_3BO_3, BDH). The borate stock solution (1 M boric acid/0.3 M ammonia) was cleaned by equilibration with 50 μM MnO_2 (van den Berg, 1989) and filtration (0.2 μm polycarbonate, acid-cleaned, in-line filtration) and was used at a final concentration of 5 mM. A methanolic solution of 1-nitroso-2-naphthol (NN) ($C_{10}H_6OH.NO$, BDH) was prepared containing 0.01 M NN. A final concentration of 5 μM was used for the titrations, giving an analytical detection window (van den Berg and Donat, 1992) in the range of $10^{11.5}$–$10^{13.5}$ (based on Fe′, which is all inorganic iron). A stock solution of 10^{-6} M Fe^{III} was prepared in 0.01 M redistilled hydrochloric acid.

Seawater samples were titrated with iron, which was added in 11 increments between 0 and 8 nM, whereas ice titrations were extended to 17.5 nM due to greater initial iron concentrations. Thereto 130 ml seawater was placed in a polyethylene bottle; borate buffer (5 mM) and NN (5 μM) were added, and the sample was mixed. The Fe^{III} standard was added to 11 conditioned polystyrene vials (Sterilins), and subsequently a 10 ml aliquot of the sample/buffer/ligand mixture was pipetted into each Sterilin. Any remaining sample was pipetted into a 12th Sterilin tube, and used for the first measurement to condition the voltammetric cell. The solutions were equilibrated at least 5 h (often overnight: 12–15 h), at room temperature in a laminar-flow hood.

2.2.1. Voltammetric procedure

The equilibrated solutions were sequentially (starting from the lowest concentration) transferred to the voltammetric cell. Each solution was purged (200 s) with O_2-free nitrogen. A new mercury drop was made, and $FeNN_3$ complex species were adsorbed using an adsorption time of 300–500 s, at an adsorption potential of -0.2 V, whilst stirring with a rotating PTFE rod (2500 rpm). The stirrer was switched off for a 8 s quiescence period, thereafter the potential was scanned from -0.3 to -0.8 V either by sampled-DC (potential step 2 mV, frequency 10 Hz), or by linear-sweep (scan rate of 1.6 V/s, potential step 2.1 mV). The voltammetric cell was not rinsed during the titration to maintain the cell conditioned to the iron and NN concentrations. The Sterilin tubes were rinsed once with MQ-water between titrations, and the same order of tubes was maintained.

Preliminary measurements indicated the presence of three peaks in the voltammetric scans before the reagent (NN) was added (Fig. 2). The second peak was very close to that for iron at

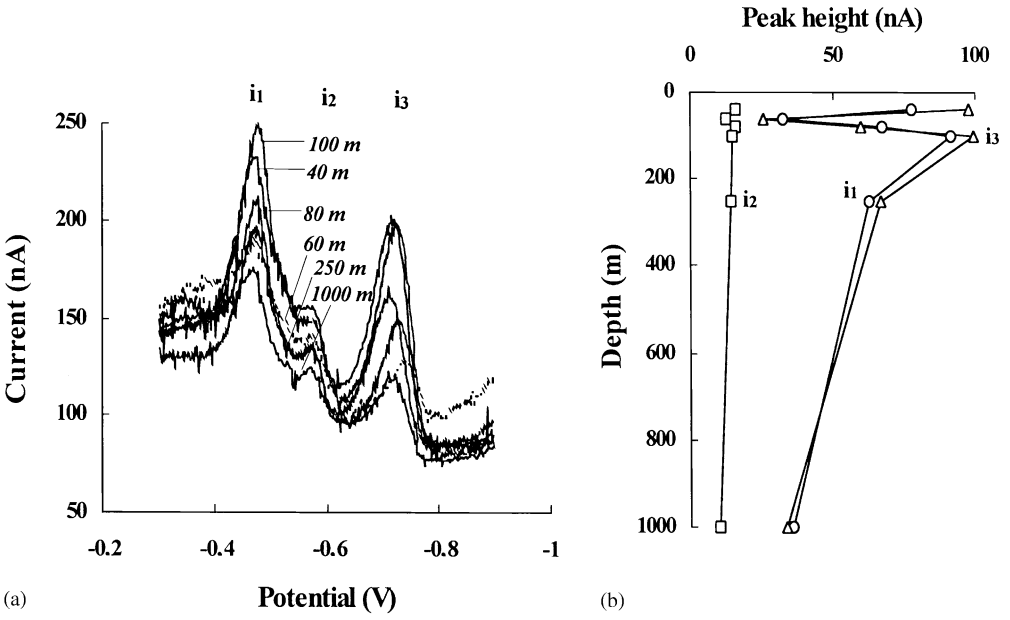

Fig. 2. Voltammetric scans and peak heights for filtered seawater (buffered at pH 8.05 using borate buffer) from various depths at station 190 showing the presence of three peaks: (a) linear sweep scans after an adsorption time of 300 s, (b) peak heights of the three peaks as a function of sample depth.

− 0.58 V. The cause of the three peaks was unknown, although the second peak resembled that of glutathione and the third peak that of thiols generally (Leal et al., 1999). In the water column the first and third peaks co-varied and had greatest values in surface waters, and the second peak was much smaller than the other two and was constant with depth (Fig. 2). Measurements of low iron concentrations indicated that the second peak interfered with the iron peak. CSV in the presence of NN, after overnight equilibration with Desferral added to the seawater to mask the iron, showed that this second peak remained present indicating that it was not due to an iron species, and confirmed that it interfered by enhancing the iron peak as the two peaks could not be separated. This peak was therefore subtracted from the scans to obtain a background-corrected peak height for iron for each sample including the standard additions.

2.3. Calculation of the organic and inorganic speciation of iron

Ligand concentrations (C_L) and conditional stability constants ($K'_{FeL} = [FeL]/([Fe^{3+}][L'])$) were calculated by linear least-squares regression of the data fitted to the following equation (van den Berg and Kramer, 1979; Ruzic, 1982; van den Berg, 1982):

$$[Fe_{labile}]/[FeL] = [Fe_{labile}]/C_L + (\alpha_{Fe} + \alpha_{FeNN3})/(C_L K_{FeL}). \quad (1)$$

Here $\log \alpha_{Fe} = 10$ (Hudson et al., 1992), and $\log \alpha_{FeNN3} = 12.5$ (from $\log \beta'_{FeNN3} = 28.39$ (Gledhill and van den Berg, 1994)).

The concentration of labile iron [Fe_{labile}] in each aliquot was calculated from the measured peak height ($Fe_{labile} = i_p/S$), where S is the sensitivity (calculated from the linear part of the titration) and i_p is the peak height obtained at the reduction potential of the $FeNN_3$ complex. The concentration of FeL in equilibrium with the added NN and iron was calculated from $[FeL] = C_{Fe} - [Fe_{labile}]$, where C_{Fe} is the total dissolved iron concentration including the iron additions. Then C_L and K_{FeL} were calculated from the slope and the Y-axis intercept of the linear least-squares regression of $[Fe_{labile}]/[FeL]$ as a function of $[Fe_{labile}]$ (Eq. (1)).

The free metal ion concentration $[Fe^{3+}]$ originally present in the seawater was calculated with the following quadratic equation:

$$[Fe^{3+}]^2\alpha_{Fe}K'_{FeL} + [Fe^{3+}](\alpha_{Fe} + K'_{FeL}C_L - K'_{FeL}C_{Fe}) - C_{Fe} = 0. \quad (2)$$

The inorganic metal concentration [Fe′] originally present in the seawater was calculated from: $[Fe'] = \alpha_{Fe}\,[Fe^{3+}]$; the concentration of organic metal complexes [FeL] was obtained by difference from the dissolved metal and inorganic metal concentrations ($[FeL] = C_{Fe} - [Fe']$). pFe is defined as $-\log[Fe^{3+}]$, and the fraction (%) of metal occurring as organic species was calculated from $([FeL]/C_{Fe}) \times 100$.

3. Results

3.1. Hydrography

The major currents within the broad eastward-flowing Antarctic circumpolar current (ACC) are associated with, from north to south, the Sub-Antarctic Front, the PF, the Southern Polar Front and the ACC-Weddell Gyre Boundary (Veth et al., 1997). The PF features a fast flowing jet ($\sim 50\,cm\,s^{-1}$) relative to the slower moving ($\sim 5\,cm\,s^{-1}$) water masses of the ACC. One criterion for identification of the PF position is given by the northern terminus of the subsurface temperature minimum layer bounded by the 2°C isotherm in the 100–300 m layer (in summer) (Belkin and Gordon, 1996). In the northern part of the area, the subsurface temperature minimum in the 100–300 m layer is above 2°C at station 163, whilst it is below 2°C at stations 165 and 167 (Fig. 3). This indicates that station 163 is located north of the PF, whereas stations 165 and 167 are south of the PF.

South of the Southern Polar Front, station 190 has higher surface salinity and lower surface temperature. Station 190 is located on the south side of the ACC. Below the relatively homogeneous layer of about 100 m, a distinct temperature minimum is found at $\sim$150 m at all these four stations (163, 165, 167 and 190). This is the Winter Water, which flows northward and subducts to form the Antarctic Intermediate Water (Whitworth, 1988). Further south at station 169 the surface salinity decreased to levels similar to those in the PF but with colder surface waters. From its geographic position, station 169 is probably located in the north-east part of the Weddell Gyre.

In the south-western part of the study area (stations 182 and 185), the surface temperature dropped below 0, and the salinity was higher than in the northern part. Both stations are within the coastal current flowing westward around the Antarctic continent. Station 182 is close to the Antarctic continent and had a deep mixed layer extending to 700 m. This station was covered by

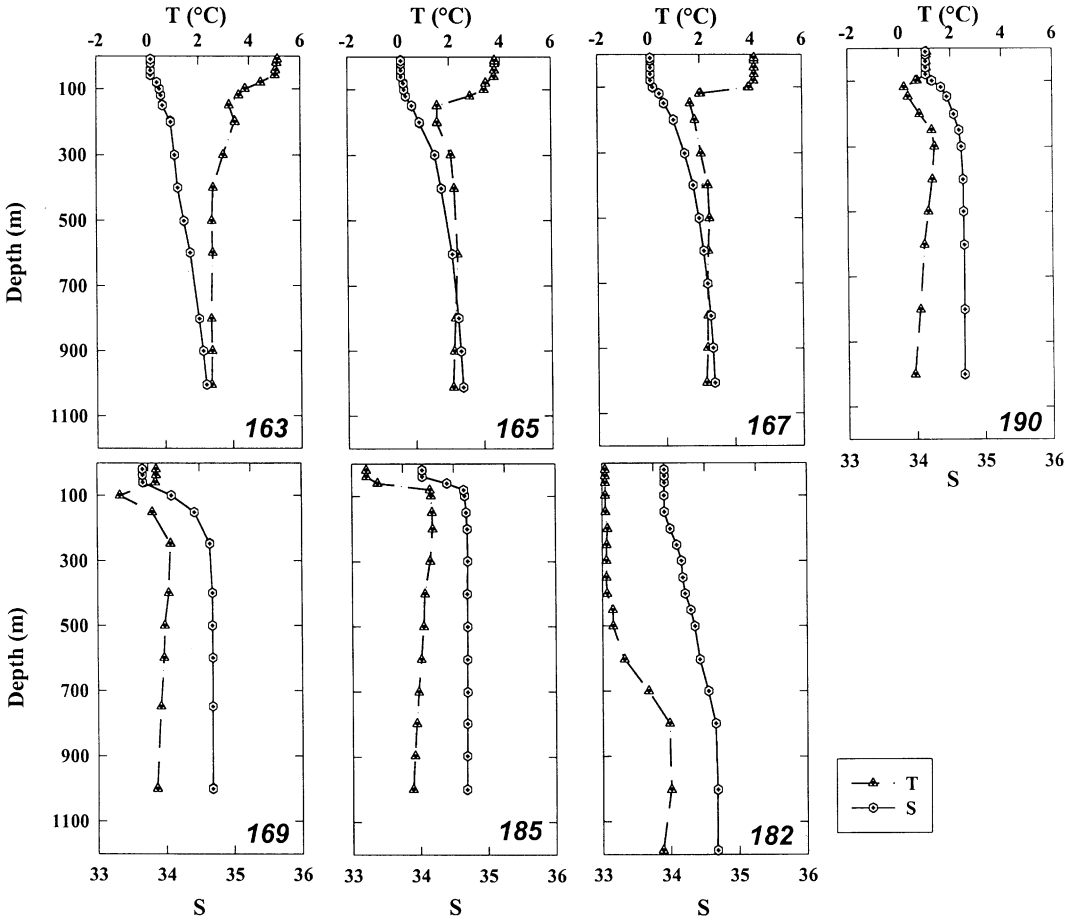

Fig. 3. Temperature (°C) and salinity at depths between 0 and 1500 m.

pack-ice. Station 185 is close to the Maud Rise. The homogeneous surface layer thickness was about 60 m, and was covered by melting ice and icebergs were surrounding the area.

The same water mass was present between 200 and 400 and 1500 m at stations 190, 169 and 185, characterised by salinities between 34.67 and 34.71, and with temperatures between 0.06 and 1.3°C. This water is the Circumpolar Deep Water which flows in a southward direction. This water mass appears also at station 185 below 800 m.

The Antarctic Bottom Water, a water mass formed in the Weddell Sea and flowing northwards, is found below 2500 m at stations 169 and 185, with lower temperature and salinity than the Circumpolar Deep Water, ranging between -0.3 and -0.7°C and between 34.65 and 34.66, respectively.

3.2. Nutrients

The nitrate concentrations (Fig. 4) were lower in the upper water column but were not depleted and had residual levels of 21–28 μM, consistent with expectation for these HNLC waters. The

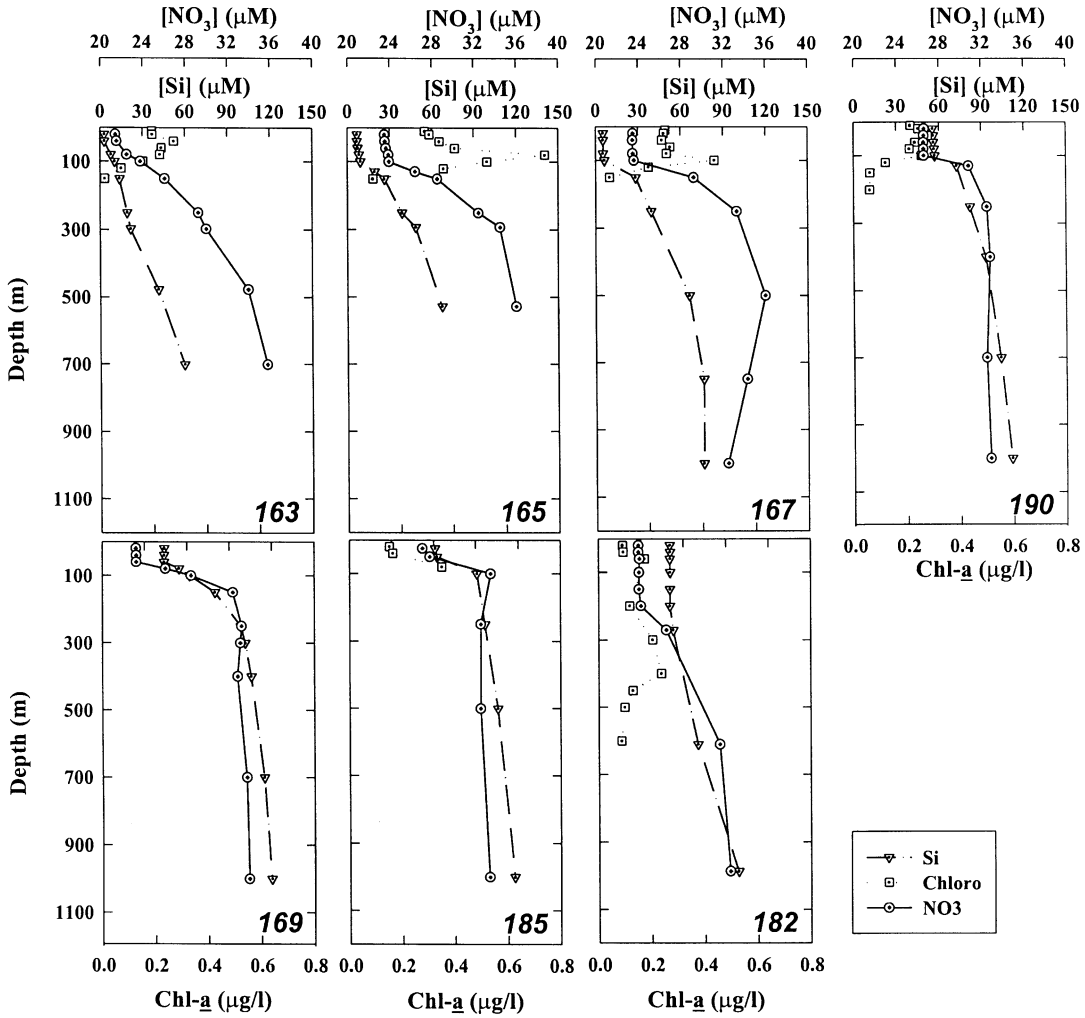

Fig. 4. Nitrate, silicate and chlorophyll-*a* concentrations.

silicate levels, on the other hand, were depleted in the upper 50–100 m and increased with depth at all stations. There was a trend in the degree of depletion of the silicate in the upper 100 m from north to south: lowest levels occurred in the edge of the PF (stations 163, 165 and 167) (3–10 μM) compared to higher levels at the stations further south (44–56 μM). Below 100 m, the silicate follows the same north–south gradient with higher levels at the southern stations (54–125 μM south of the PF and 14–76 μM for the stations in the edge of the PF). The ACC is currently the major burial site of silica in the world ocean (Treguer et al., 1995). About half the diatom ooze accumulating under the ACC is attributed to the shells of one species, *Fragilariopsis kerguelensis* (Verity and Smetacek, 1996). This species makes thick and resistant shells with 3 times as much silica as "normal" diatoms (Queguiner et al., 1997), which has been attributed to iron limitation (Hutchins and Bruland, 1998; Takeda, 1998). The simultaneous silicate depletion and nitrate excess are therefore consistent with a natural algal community controlled by a lack of iron in this region.

The chlorophyll-*a* levels tended to peak at the bottom of the silicate depleted layer, at around 100 m depth, and were generally greater when there was more silicate depletion (the more northerly stations 163, 165, and 167.

3.3. Dissolved iron

The iron data will be presented in detail elsewhere (P.L. Croot et al., in preparation). Briefly, the vertical profiles of dissolved iron from the PF region (stations 163, 165, 167) and the south side of the Antarctic Circumpolar Current (station 190) showed enrichment in the surface waters due to atmospheric inputs, and a sub-surface minimum at approximately the chlorophyll maximum due to uptake by microorganisms (Table 1, Fig. 5). The surface enrichment is clear at station 163, but the signal is weaker at the other stations potentially due to scavenging and uptake processes. Iron concentrations increased with depth below the minimum, consistent with regeneration of iron from sinking phytoplankton or faecal pellets and bacterial decomposition, reaching levels of 0.33 ± 0.18 nM ($n = 15$). The dissolved iron concentrations in the upper 150 m of these four stations ranged between 0.05 and 0.51 nM, with a mean of 0.25 ± 0.13 nM ($n = 23$). Stations 165 and 167 are very close together (30 miles) but the iron concentrations are considerably lower in the upper water column at station 165. There is no significant difference in the salinity/temperature characteristics between these two stations, but there is more chlorophyll at Station 165. The lower concentrations of dissolved iron in the upper water column of Station 165 (0.05–0.18 nM) may be consistent with greater biological uptake from these waters.

The two stations within the Coastal Current (stations 182 and 185) did not show increased iron levels at the surface, and showed a sub-surface maximum at about 50 m depth, suggesting that the sea-ice at these stations may have trapped the iron. Overall the iron concentrations were lowest in the water column of these stations, consistent with a reduced atmospheric input, and reduced upwelling, due to the sea-ice.

3.4. Iron-complexing ligands

The CSV peak height of the titrations was suppressed at low iron concentrations, indicating the presence of an excess of organic iron-binding ligands. Concentrations of the iron-complexing ligands in the upper water column (20–150 m) ranged from 0.18 (station 165) to 1.39 nM (station 167), with a mean value of 0.71 ± 0.27 nM ($n = 34$). Common features of the ligand concentrations in the water column are (Fig. 5) surface depletion, followed by an increase to a broad maximum at depths between 100 and 300 m at several stations (stations 167, 169 and 190), generally below the chlorophyll maximum and within or below the silicate-depleted layer. The ligand concentrations did not follow the pattern of chlorophyll-*a,* indicating that there was no strong correlation between the abundance of algae and the ligand concentrations. However, the broad maximum of the ligands in the upper water column suggests a link with microorganisms generally, i.e. with the bacteria as well as the phytoplankton.

The ligand concentrations were relatively constant in the deep waters (below 1000 m), with a mean concentration of 0.70 ± 0.20 nM ($n = 34$) and without major features.

The complex stability varied over two orders of magnitude, with values for the conditional stability constant ($\log K'_{\mathrm{FeL}}$) from 20.9 (station 167) to 23.0 (station 185), with an average of

Table 1
Dissolved iron speciation: concentrations of dissolved iron (C_{Fe}), the ligand (C_L), and the conditional stability constants ($\log K'_{FeL}$) were determined; the concentration of inorganic iron [Fe′], the percentage of iron organic species (FeL %), and the α-coefficient for complexation of iron by L ($\alpha_{FeL} = K'_{FeL} C_{Fe}$), were calculated

Station number	Location	Depth (m)	C_{Fe} (nM)	C_L (nM)	SD_L	$\log K'_{FeL}$	SD K'_{FeL}	[Fe′] (pM)	FeL (%)	$\log \alpha_{FeL}$
Station 163	48°50′S 20°00′E	20	0.43	0.44	0.09	22.0	0.7	16.8	96	12.6
		40	0.24	0.37	0.07	22.5	1.1	0.6	99.8	13.1
		80	0.11	0.68	0.1	22.0	0.6	0.18	99.8	12.9
		100	0.1	0.55	0.11	21.7	0.4	0.48	99.5	12.4
		150	0.51	0.72	0.11	21.9	0.6	2.0	99.6	12.8
		250	0.35	0.88	0.11	22.5	1.0	0.20	99.9	13.5
		298	0.21	0.53	0.05	21.9	0.4	0.73	99.6	12.7
		478	0.64	1.24	0.05	22.1	0.3	0.8	99.9	13.2
		701	0.38	1.29	0.09	22.0	0.4	0.41	99.9	13.1
Station 165	49°20′S 20°00′E	20	0.18	< 0.18	—	—	—	—	—	—
		40	0.13	0.49	0.07	22.3	0.8	0.20	99.8	12.9
		60	0.05	0.47	0.07	22.3	0.9	0.06	99.9	13.0
		80	0.08	0.52	0.08	22.3	0.9	0.09	99.9	13.0
		100	0.13	0.57	0.06	22.6	0.7	0.07	99.9	13.4
		129	0.15	1.01	0.03	22.4	0.4	0.06	99.9	13.4
		150	0.13	0.66	0.07	21.8	0.3	0.41	99.7	12.6
		250	0.08	0.67	0.07	22.0	0.5	0.15	99.81	12
		293	0.23	0.76	0.09	21.9	0.13	0.5	99.8	12.8
		528	0.29	0.47	0.08	22.4	1.0	0.6	99.8	13.1
Station 167	49°50′S 20°00′E	20	0.37	0.68	0.05	—	—	—	—	—
		40	0.32	0.43	0.09	22.2	0.7	1.8	99.4	12.8
		80	0.38	1.39	0.09	22.7	0.9	0.07	99.9	13.9
		100	0.48	1	0.09	22.2	0.6	0.6	99.9	13.2
		150	0.3	1.06	0.19	21.19	0.15	2.5	99.2	12.2
		250	0.28	0.62	0.1	21.8	0.5	1.2	99.6	12.6
		500	0.65	0.8	0.25	20.92	0.08	39	94	11.8
		750	0.34	0.84	0.02	22.4	0.4	0.28	99.9	13.3
		1000	0.57	0.77	0.07	21.9	0.4	3.3	99.4	12.8
Station 169	60°00′S 18°31′E	20	0.18	0.57	0.1	22.0	0.6	0.5	99.7	12.8
		60	0.15	0.7	0.1	22.3	0.9	0.1	99.9	13.2
		100	0.19	1.19	0.15	22.1	0.5	0.15	99.9	13.2
		250	0.18	0.86	0.14	21.6	0.3	0.7	99.6	12.5
		300	0.26	0.98	0.05	22.4	0.5	0.15	99.9	13.4
		400	0.28	0.65	0.09	22.3	0.8	0.4	99.8	13.1
		1000	0.26	0.77	0.12	—	—	—	—	—
		2000	0.29	0.64	0.06	21.5	0.2	2.5	99.1	12.3
		3000	0.4	0.67	0.04	22.2	0.5	0.9	99.8	13.0
		4000	0.35	0.69	0.12	23.0	1.6	0.11	99.9	13.8
		4500	0.29	0.66	0.07	21.7	0.3	1.6	99.4	12.5

Table 1 (*continued*)

Station number	Location	Depth (m)	C_{Fe} (nM)	C_L (nM)	SD_L	log K'_{FeL}	SD K'_{FeL}	[Fe′] (pM)	FeL (%)	log α_{FeL}
Station 182	70°14′S 06°08′E	20	0.17	0.43	0.06	—	—	—	—	—
		40	0.12	0.7	0.09	22.7	1.2	0.04	99.9	13.6
		60	0.32	0.66	0.09	22.2	0.7	0.65	99.8	13.0
		100	0.22	0.68	0.09	23	1.5	0.05	99.9	13.8
		150	0.15	0.65	0.2	21.4	0.3	1.3	99.2	12.2
		200	0.15	0.44	0.07	22.1	0.7	0.4	99.7	12.7
		271	0.16	0.72	0.1	22.5	1	0.08	99.9	13.4
		610	0.2	0.68	0.05	22.5	0.7	0.13	99.9	13.3
		986	0.26	0.88	0.08	21.8	0.3	0.65	99.7	12.7
Station 185	67°00′S 0°00′E	25	0.06	0.37	0.06	—	—	—	—	—
		50	0.2	1.01	0.1	21.6	0.2	0.56	99.7	12.6
		100	0.11	0.64	0.08	21.8	0.4	0.31	99.7	12.6
		250	0.14	0.63	0.05	22.2	0.6	0.17	99.9	13.0
		500	0.15	0.85	0.07	22.5	0.7	0.06	99.9	13.5
		1000	0.24	0.55	0.16	21.4	0.4	2.8	98.8	12.2
		1500	0.28	0.56	0.09	22.0	0.6	1.1	99.6	12.7
		2500	0.29	0.61	0.12	21.4	0.3	3.29	98.9	12.2
		3500	0.28	0.45	0.08	23.0	1.6	0.16	99.9	13.7
		4500	0.31	0.55	0.09	22.2	0.8	0.87	99.7	12.9
Station 190	54°00′S 20°00′E	20	0.29	0.53	0.05	22.7	1.0	0.26	99.9	13.4
		40	0.28	0.85	0.11	21.6	0.3	1.17	99.6	12.5
		60	0.11	1.05	0.08	22.1	0.5	0.09	99.9	13.1
		80	0.28	1.02	0.04	22.3	0.4	0.18	99.9	13.3
		100	0.37	0.96	0.07	22.1	0.5	0.53	99.9	13.0
		130	0.27	1.05	0.36	21.0	0.1	3.7	98.6	12.0
		250	0.11	0.58	0.08	21.6	0.3	0.56	99.5	12.4
		400	0.16	0.45	0.12	21.5	0.4	1.8	98.8	12.1
		700	0.48	0.78	0.15	21.7	0.4	3.4	99.3	12.6
		1000	0.18	0.45	0.06	22.7	1.0	0.12	99.9	13.4
Ice	Close to 70°13′S 06°07′E									
		Inflow of ice	0.22	0.93	0.09	22.0	0.5	0.28	99.9	13.0
		Ice 1	3.42	7.67	0.12	21.8	0.1	1.4	99.9	13.6
		Ice 2	2.81	5.84	0.48	21.3	0.2	4.6	99.8	13.1
		Ice 3	4.36	7.55	0.51	21.7	0.4	2.6	99.9	13.6

22.1 ± 0.5 ($n = 63$). There was little difference between the complex stability for the top 150 m and the deeper waters (log K'_{FeL} values of 22.2 ± 0.5 ($n = 23$) and 22.0 ± 0.5 ($n = 22$), respectively), the large spread in the log K'_{FeL} values masking any systematic trend if this were to exist. The spread could reflect the presence of ligand classes forming complexes of differing stabilities, but the measurements did not have the resolution to detect these. The standard deviation of the log K'_{FeL} values was large because of the low ligand concentrations (0.7 nM on average), which meant that

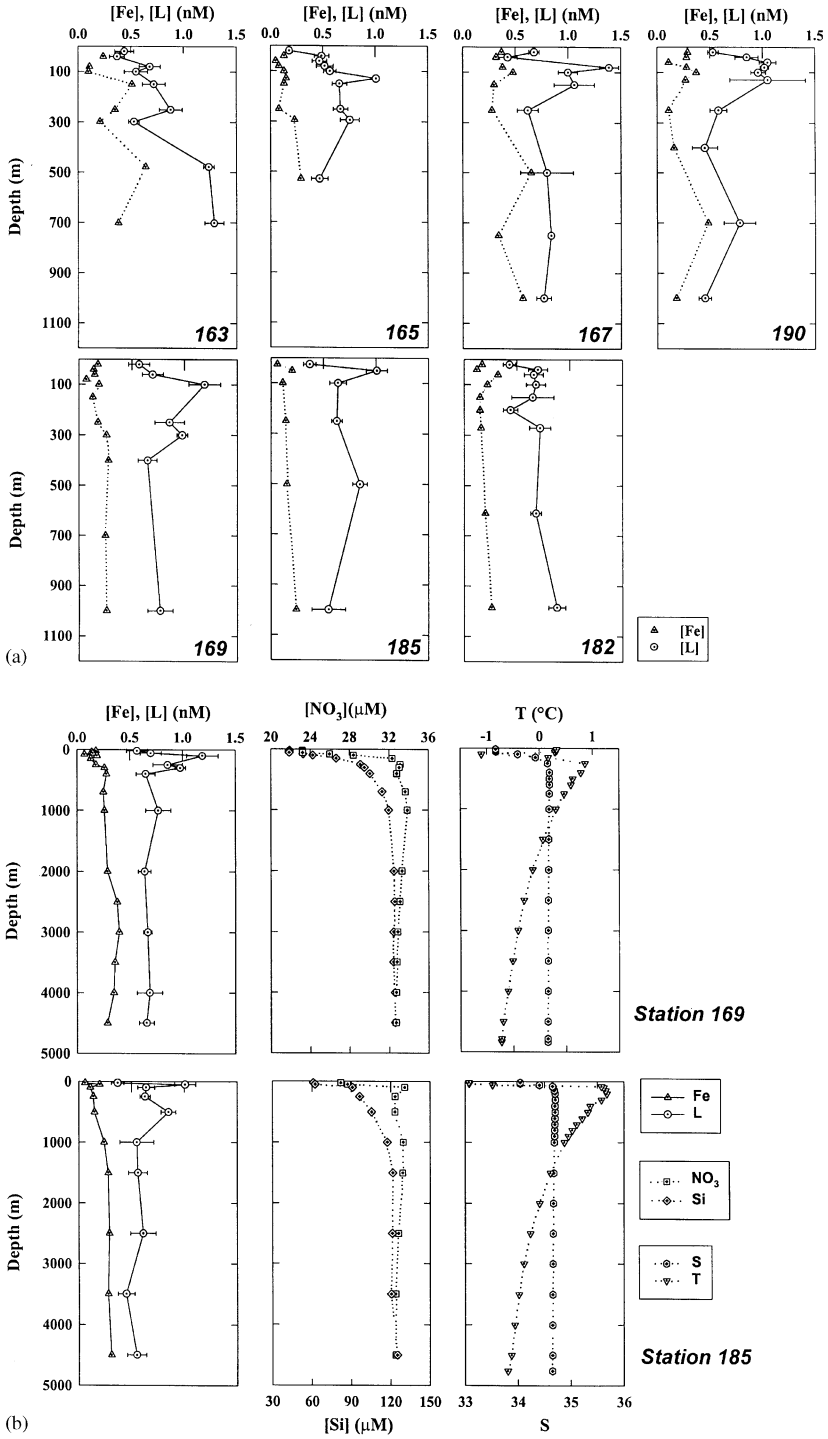

Fig. 5. Dissolved iron and complexing ligands in the water column: (a) 0 to 1000 m, and (b) deep water samples (0–4500 m), along with temperature, salinity, nutrients and chlorophyll-*a*.

the ligands were saturated with iron after the second iron addition and therefore the least-squares regression of the data had to cope with intercepts close to the origin of the graph.

The α-coefficient of iron complexation by the natural ligands (calculated from $\alpha_{FeL} = K'_{FeL}C_L$) ranged between $10^{11.8}$ (station 167) and $10^{13.8}$ (stations 169 and 182), with an average of $10^{12.9\pm0.5}$ ($n = 63$).

3.5. The iron speciation

The ligand concentrations were in excess of dissolved iron by an average 0.5 nM for all (except for two) samples (Figs. 5 and 6, Table 1): the average iron concentration was 0.25 ± 0.13 nM, compared to a ligand concentration of 0.72 ± 0.23 nM. Exceptions were two surface samples (20 m) at the most northerly stations, where the ligand and iron concentrations were similar (stations 163

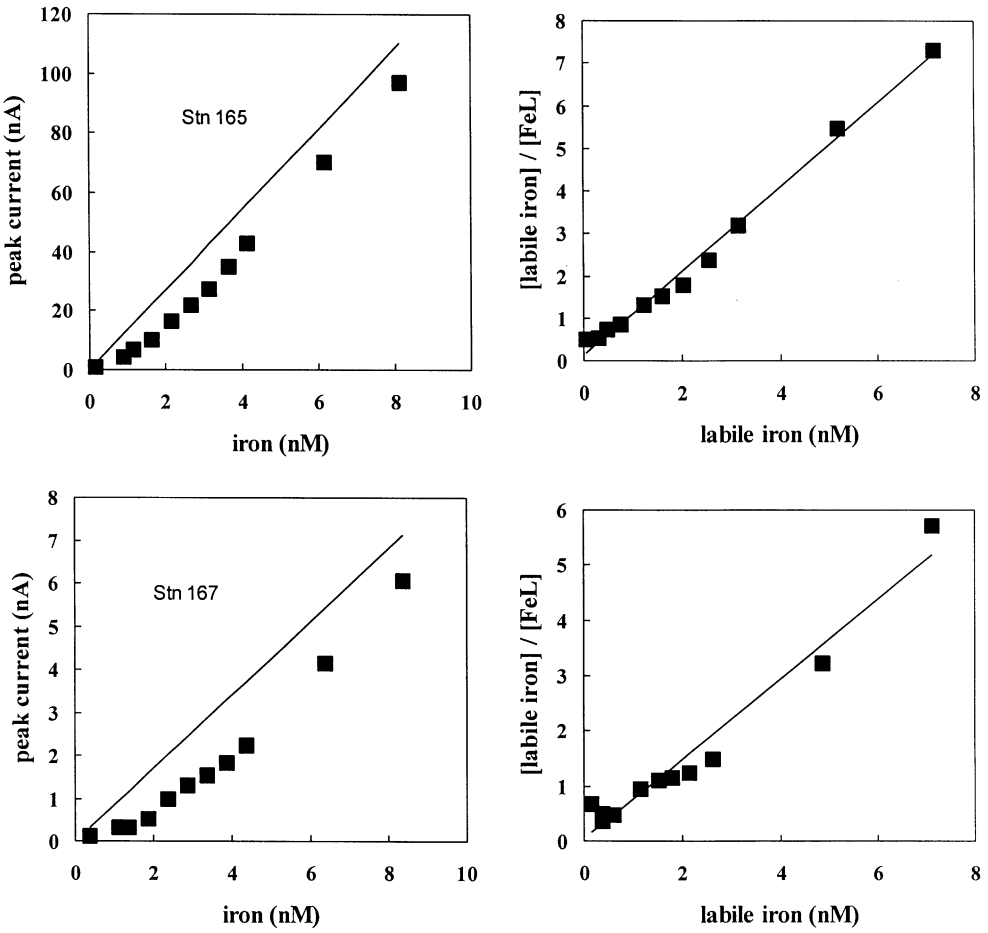

Fig. 6. Titrations of complexing ligands in Southern Ocean waters with iron. Peak heights and data linearisation are shown of a titration for two samples: one from 129 m depth at station 165, and one from 80 m depth at station 167. The ligand concentrations and stability constants are reported in Table 1.

and 165) because of a combination of enhanced iron and lowered ligand levels, possibly due to photochemical breakdown of the ligands.

Calculation of the chemical speciation of iron based on thermodynamic equilibrium shows that this is dominated by organic complexation throughout the water column, iron occurring $> 99\%$ organically bound (Table 1). This finding is comparable to the extent of organic complexation of dissolved iron in other oceanic waters, such as the North Pacific (Rue and Bruland, 1995), the Equatorial Pacific (Rue and Bruland, 1997), the North Atlantic (Gledhill and van den Berg, 1994; Witter and Luther III, 1998) and the Mediterranean (van den Berg, 1995).

The average α-coefficient for organic complexation of iron is (log value) 12.9 ± 0.5. The ratio of [FeL]/[Fe′] as calculated from α_{FeL}/α_{Fe} is $10^{2.9}$, indicating that the inorganic iron concentrations are on average almost three orders of magnitude lower than the dissolved iron concentrations. Concentrations of Fe′ calculated from the ligand and iron concentrations and the conditional stability constants, were on average 1.0 ± 1.1 pM (ranging from 0.1 to 3 pM), excluding values of 17 pM (surface seawater station 163) and 39 pM (500 m depth, station 167) (Table 1).

Analysis of ice samples showed that iron occurred there predominantly organically bound too (Table 1). The salinity of these ice samples was not determined; however, the salinity of similar samples collected at a nearby station was found to vary between 6 and 11 depending on the ice depth (T. Mock and B.M.A. Kroon, in preparation). The high salinity indicates that this is largely sea-ice (as opposed to ice from precipitation); the rather high iron concentrations suggest that there may be a significant atmospheric contribution.

4. Discussion

4.1. The distribution of the ligands

General features of the ligands are a concentration excess over iron of ~ 0.5 nM; broadly increased ligand concentrations at depths of 100–200 m, just below the photic layer; a decrease in the ligand concentration towards the surface and deeper waters; and relatively constant levels in the deep waters. These variations are likely to be a result of a balance between production and breakdown processes, including biological and abiotic (photochemical) reactions, in the upper water column.

Lowered ligand concentrations in the upper ~ 20–40 m suggest photochemical breakdown of the ligands. The possibility of this process has been suggested before (van den Berg, 1995; Rue and Bruland, 1997), but it is unexpected that it occurs at these far southern latitudes in cold waters. In association with the photochemical breakdown of the organic ligands it is possible that the iron is reduced and released as Fe(II).

A broad maximum in the ligand concentrations has been shown before to occur in the Mediterranean below the fluorescence maximum (van den Berg, 1995), pointing to activity of heterotrophic bacteria as a contributing source. However, an increase in the ligand concentration in response to iron additions to the sea surface of the iron-limited equatorial Pacific, along with increases in the chlorophyll concentration resulting primarily from an iron-induced diatom bloom (Rue and Bruland, 1997), indicates that algae as well as bacteria may be the source of ligands. Ligand production by phytoplankton has been confirmed in iron-limited cultures of the

coccolithophorid *Emiliania huxleyi* (Boye and van den Berg, 2000) in response to iron additions; siderophore production has been demonstrated in iron-limited dinoflagellate (*Prorocentrum*) and Scenedesmus cultures (Trick et al., 1983; Benderliev and Ivanova, 1994).

The absence of a simple relationship between chlorophyll and the concentration of complexing ligands in the water column is not evidence that the ligands have not been produced by the algae: ligands may be produced at low chlorophyll levels in response to iron inputs (atmospheric or from upwelling), and the primary productivity may take off in response causing an increase in the chlorophyll. The increase in chlorophyll may be associated with a reduction in the iron concentration as it is taken up. The free ligands in the photic layer may subsequently be broken down by bacterial activity, or the iron may be taken up in complexed form (both reactions would be a sink for ligands in the photic layer). The sinking cells stimulate bacterial activity with subsequent ligand releases possible to acquire iron at very low ambient free iron levels. Thus the ligand concentration may be both enhanced and reduced by microorganisms. Uptake of the iron in complexed form would be consistent with uptake of siderophore or porphyrin-bound iron; uptake of siderophore complexes has been demonstrated for cyanobacteria, whereas they are less available to eukaryotic organisms, which tend to take up inorganic or porphyrin bound iron preferentially (Hutchins et al., 1999). Growth of phytoplankton begins to become iron-limited at inorganic iron levels below 10–100 pM, and is severely limited at inorganic iron levels below 1 pM (Sunda and Huntsman, 1995). The inorganic iron levels in the Southern Ocean waters (0.1–1 pM) are severely limiting the organisms if this is the bioavailable species, consistent with the HNLC status of these waters, and it is likely that here the major route for iron uptake is via direct uptake of organic species of one form or another. The decrease in the dissolved iron concentrations in the upper water column suggests that this uptake route may be quite efficient.

4.2. Comparison with ligand concentrations in other oceans

Ranges of iron-binding ligand concentrations and their conditional stability constants in the Southern Ocean can be compared with those found in the Pacific Ocean (Rue and Bruland, 1995, 1997), the Pacific sector of the Southern Ocean (Nolting et al., 1998), the Atlantic Ocean (Gledhill and van den Berg, 1994; Witter and Luther III, 1998) and the Mediterranean (van den Berg, 1995) in Table 2. The conditional stability constants were converted to the type ($K'_{Fe3+L'}$) used here when they were different. Our titrations were fitted by a single ligand model (Eq. (1)); there was no evidence for the presence of two ligands or two classes of ligands, which would have caused the linearised plots to become curved. A previous study of iron complexation in the Pacific demonstrated the presence of two classes of iron-binding ligands in the upper water column (Rue and Bruland, 1995), whereas only the weaker class was apparent in the intermediate and deep waters (500–2000 m). The competing ligand (NN) used in our study to determine the iron speciation had a higher detection window than the ligand (salicylaldoxime) used for the Pacific study (Rue and Bruland, 1995), so it is possible that a weaker ligand would not have been detected in our titrations. The first iron addition in our titrations was between 0.5 and 1 nM (the first measurement was without added iron), which means that the strong ligand which was present at subnanomolar levels was almost saturated after one addition. These low ligand concentrations could be detected because the ambient iron concentrations were very low, but they caused a high standard deviation for the value of the conditional stability constant in our work.

The complex stability of the ligands in the Southern Ocean covers a large range ($\log K'_{FeL}$ = 21–23), encompassing the complex stability of the ligands (strong as well as weak) detected during the Pacific study (Table 2). Calculations have shown that the presence of only a few ligands can cause a spread of complex stabilities in the titration data if these ligands are covered by the titration (van den Berg and Donat, 1992) because of a lack of resolution of the data due to superimposed variability (noise). It is therefore possible that the waters studied here also contain more than one ligand; however, the actual detected ligand is the predominant one at the concentrations of Fe′ covered in the titrations.

A recent study of the Southern Ocean (Pacific sector) (Nolting et al., 1998) found much higher ligand concentrations of 2–12 nM (in *unfiltered* seawater), with lower values for the conditional stability constant, than those we found in the Atlantic sector of the Southern Ocean (Table 2). A lower concentration of NN was used in that study, and the step height in the iron titrations was 1.8 nM: the large step height would have caused a detection limit above a ligand concentration of around 1 nM, and the low NN concentration meant that weaker complexing ligands could be detected (if present at > 2 nM) whereas the low concentration of very stable complexing ligands would have been impossible to detect due to masking of the labile iron concentration by the low detection window at the lowest iron level. At least part of the iron complexing capacity detected in that study may have been derived from particulate matter because the water had not been filtered. Our data are therefore not inconsistent with those from the Pacific sector, and it is possible that the same stable complexing ligand occurs also in those waters. Our titrations were continued to 8 nM, so a second ligand would have been detected unless its complexes were 10–100 × weaker than those formed with the ligands detected in this study. It is therefore unlikely that higher concentrations of ligands, forming significant complexes with iron, were present in the Southern Ocean waters during this study.

Higher ligand concentrations were found also in the Mediterranean (van den Berg, 1995): there too the step size was > 1 nM, and the background iron concentration (2–3 nM) was much greater than that in the Southern Ocean, which meant that a low level of strong complexing ligands would have been saturated with iron and would have been undetectable. Two studies of the Atlantic (Gledhill and van den Berg, 1994; Witter and Luther III, 1998) found ligand concentrations greater than the background 0.7 nM: one of these (Gledhill and van den Berg, 1994) was in north-eastern Atlantic waters where the iron concentrations would have been sufficient to saturate a low concentration of strong complexing ligands; the other study used a method based on kinetics, which may have caused this method to focus on the higher concentration of weaker ligands. On the whole, therefore, there is no evidence available that would rule out the suggested (Rue and Bruland, 1995, 1997; Johnson et al., 1997) presence of a background level of 0.7 nM of strong complexing ligands throughout the world oceans. However, our data do not support the presence of higher concentrations of complexing ligands forming slightly weaker complexes in the water column of the Southern Ocean as found previously in the Mediterranean and Atlantic. It is likely that those ligands are produced in the upper water column by microorganisms (as demonstrated in culture (Boye and van den Berg, 2000) and during Ironex2 (Rue and Bruland, 1997)) in response to inputs of higher iron concentrations, and that these ligands are prone to relatively rapid breakdown or uptake. The presence of those ligands may therefore be of a more transient nature occurring after inputs of greater iron concentrations.

Table 2

Overview of the organic speciation of iron: concentrations of dissolved iron (C_{Fe}), inorganic iron [Fe′], and the organic ligands for iron (C_L); conditional stability constants (converted to $\log K'_{Fe3+L}$, where necessary) and α-coefficients for complexation by L ($\alpha_{FeL} = K'_{FeL} C_{Fe}$). The analytical detection window ($DW = K'_{FeNN3}[NN]^3$) is indicated. Mean values are given for calculated values for $\log \alpha_{FeL}$ and [Fe′] from the literature data. The inorganic iron was calculated using $\alpha_{Fe} = 10^{10}$

Area	Location	Filtr. (μm)	Depth (m)	C_{Fe} (nM)	DW	C_L (nM)	$\log K'_{FeI}$	$\log \alpha_{FeL}$	[Fe′] (pM)	Reference
Southern Ocean										
Atlantic sector	48°5′–70°S 20°E	0.2		0.25 ± 0.13	12.5	0.72 ± 0.23	22.1 ± 0.5	12.9 ± 0.5	0.06–3	This study
Pacific sector	58–68S 90W	Unf.	25–800	0.14–0.72	10.5	2–12	20.6–21.6	12.9	0.5	Nolting et al. (1998)
North Pacific	22°45′N 158°W	0.2	0–110	0.24 ± 0.05	11.9	$[L_1] = 0.44 \pm 0.6$	23.08	13.7	0.074	Rue and Bruland (1995)
Central Gyre			500–2000	0.72 ± 0.05		$[L_2] = 1.5 \pm 0.1$	21.48	12.6		
						$[L_2] = 2.6 \pm 0.2$	21.6	13.0	0.96	
HNLC region of the Equatorial Pacific	04°08′S 104°57′W	0.4	Surface	0.015–0.037	11.9	$[L_1] = 0.31 \pm 0.008$	22.67	13.2	0.01	Rue and Bruland (1997)
						$[L_2] = 0.19 \pm 0.09$	21.81	12.1		
Northwestern Atlantic	38°09′N 72°42′W	0.2	Surface	0.5–1.9	14.3	2–5	22.3–22.9	13.9	0.13	Witter and Luther (1998)
North Atlantic	35°3′N 19°58′W	0.4	80–100	1.6–1.8	10.4	3.5–4.8	19.0	10.6	10/pH 7	Gledhill and van den Berg
	42°17′N 20°02′W	0.4	800–1000	0.8–0.85	10.4	3.0–5.0	19.6	11.2	1.3/pH 7	(1994)
Western Mediterranean	38°7′N 4°66′W	0.4	0–165	3.1	13	4.0–12	21.3–22.5	13.6	0.8	van den Berg (1995)
	38°7′N 4°66′E		400–2500	2.6	13	6.4–7.8	19.79–20.38	12.8	4.5	
	36°41′N 12°19′E									

4.3. Possible effects of the organic complexation on iron biogeochemistry

A convergence of deep-water iron concentrations (mostly in the Pacific) to a level around 0.7 nM has been explained (Johnson et al., 1997) by a limit on iron scavenging once the iron drops below the concentration of strong iron-binding ligands (detected in the deep Pacific at a level of 0.6 nM (Rue and Bruland, 1995, 1997)): the ligand is the key as it would tend to retain iron in solution at around that level. The mean concentration of iron-binding ligands detected in the deep Southern Ocean waters in this study (0.70 ± 0.19 nM ($n = 20$)) is very similar to that in the deep Pacific, and supports the hypothesis of a strong ligand being present at around this concentration throughout the world's oceans. However, the deep water dissolved iron concentrations (0.32 ± 0.12 nM, $n = 20$) in the Southern Ocean are much lower than this ligand concentration, suggesting that lower Fe inputs compared to that in the Pacific combined with scavenging or biological uptake reactions have taken the iron to well below the level stabilised by the ligands. The inorganic iron concentration (0.1–3 pM) is well below the solubility of iron, which is estimated at 0.1–0.7 nM (Ingri et al., 1991; Kuma et al., 1996; Millero, 1998), so it is not likely that it is lowered to that level by inorganic colloid formation. It is more likely that the iron is used by bacteria (in spite of or because of the complexation) and partially converted to colloidal matter of organic nature and subsequently scavenged and taken to the sediments.

Addition of siderophores to algal cultures has demonstrated that siderophore-bound iron is less available to eukaryotic phytoplankton (Hutchins et al., 1999), although more recent work has shown that it is available to diatoms (*Thalassiosira*) previously stressed in iron-deficient conditions (Maldonado and Price, 2000); marine heterotrophic bacteria and cyanobacteria may well rely on siderophores to obtain iron (Granger and Price, 1999). Ligands similar to siderophores could therefore in some conditions tend to restrict the immediate iron availability to some eukaryotic algae, but at the same time increase it to other algae, and enhance the iron solubility and therefore its residence time, and longer-term availability, in the surface waters. The production of siderophores would be generally beneficial if it were to be confirmed that siderophore-bound iron is available to most iron-deficient phytoplankton.

It has been suggested that the strong iron-binding ligands could be siderophores (Rue and Bruland, 1997), whereas porphyrin-type ligands, released as degradation products of the cytochrome system, might be the source of the weaker ligands, which also appear to be ubiquitous and occur at greater concentration than the strong ligands, in view of their presence in the Mediterranean (van den Berg, 1995) and the NE Atlantic (Gledhill and van den Berg, 1994); these ligands may be more susceptible to breakdown or uptake in view of their absence in the Southern Ocean during this study. The strong ligands have been shown to be released by the iron-limited natural community of microorganisms (Rue and Bruland, 1997), and by iron-limited algae in culture (Boye and van den Berg, 2000), upon iron addition, and they appear to have complex stability similar to that of siderophores (Rue and Bruland, 1997), but this is not evidence for their being siderophores. The stability of the complexes detected here is similar to that of the strong ligands in the Pacific (Rue and Bruland, 1997), and also the ligand concentrations are similar: it can therefore be hypothesized that the ligands in the Southern Ocean are of the siderophore type, and that these iron species are therefore less available to some eukaryotic species, and therefore the cause for the iron limitation of the diatoms and other eukaryotic phytoplankton in these waters.

In the HNLC area of the equatorial Pacific, the concentration of strong iron-binding ligands increased upon the iron addition, probably produced by diatoms which were predominant (Rue and Bruland, 1997). Generally ligand concentrations are greater than the dissolved iron concentrations (Table 2), which suggests that their occurrence may be regulated. The production of ligands by microorganisms upon iron addition to iron-limited waters (Rue and Bruland, 1997) and by *Emiliania huxleyi* upon iron addition to an iron-limited culture (Boye and van den Berg, 2000) is consistent with such regulation.

Future work could concentrate on a more detailed analysis of the low level of strong ligands (smaller iron increments of 0.1 or 0.2 nM) to differentiate between different ligands, and on the possible role of the higher levels of more transient ligands in the biogeochemistry of iron.

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References

Aldrich, A.P., van den Berg, C.M.G., 1998. Determination of iron and its redox speciation in seawater using catalytic cathodic stripping voltammetry. Electroanalysis 10, 369–373.

Belkin, I.M., Gordon, A.L., 1996. Southern Ocean fronts from the Greenwich meridian to Tasmania. Journal of Geophysical Research-Oceans 101, 3675–3696.

Benderliev, K.M., Ivanova, N.I., 1994. High-affinity siderophore-mediated iron-transport system in the green-alga scenedesmus-incrassatulus. Planta 193, 163–166.

Boye, M., van den Berg, C.M.G., 2000. Iron availability and the release of iron complexing ligands by Emiliania huxleyi. Marine Chemistry 70, 277–287.

Chereskin, B.M., Castelfranco, P.A., 1982. Effects of iron and oxygen on chlorophyll biosynthesis. 2. Observations on the biosynthetic-pathway in isolated etiochloroplasts. Plant Physiology 69, 112–116.

Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M., Tanner, S., Chavez, F.P., Ferioli, L., Sakamoto, C., Rogers, P., Millero, F., Steinberg, P., Nightingale, P., Cooper, D., Cochlan, W.P., Landry, M.R., Constantinou, J., Rollwagen, G., Trasvina, A., Kudela, R., 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. Nature 383, 495–501.

de Jong, J.T.M., den Das, J., Bathmann, U., Stoll, M.H.C., Kattner, G., Nolting, R.F., de Baar, H.J.W., 1998. Dissolved iron at subnanomolar levels in the Southern Ocean as determined by shipboard analysis. Analytica Chimica Acta 377, 113–124.

Geider, R.J., Laroche, J., 1994. The role of iron in phytoplankton photosynthesis, and the potential for iron-limitation of primary productivity in the sea. Photosynthesis Research 39, 275–301.

Gledhill, M., van den Berg, C.M.G., 1994. Determination of complexation of iron (III) with natural organic complexing ligands in sea water using cathodic stripping voltammetry. Marine Chemistry 47, 41–54.

Granger, J., Price, N.M., 1999. The importance of siderophores in iron nutrition of heterotrophic marine bacteria. Limnology and Oceanography 44, 541–555.

Hudson, R.J.M., Covault, D.T., Morel, F.M.M., 1992. Investigations of iron coordination and redox reactions in seawater using 59Fe radiometry and ion-pair solvent extraction of amphiphilic iron complexes. Marine Chemistry 38, 209–235.

Hutchins, D.A., Bruland, K.W., 1998. Iron-limited diatom growth and Si : N uptake ratios in a coastal upwelling regime. Nature 393, 561–564.

Hutchins, D.A., DiTullio, G.R., Zhang, Y., Bruland, K.W., 1998. An iron limitation mosaic in the California upwelling regime. Limnology and Oceanography 43, 1037–1054.

Hutchins, D.A., Witter, A.E., Butler, A., Luther III, G.W., 1999. Competition among marine phytoplankton for different chelated iron species. Nature 400, 858–861.

Ingri, J., Lofvendahl, R., Bostrom, K., 1991. Chemistry of suspended particles in the Southern Baltic Sea. Marine Chemistry 32, 73–87.

Johnson, K.S., Gordon, R.M., Coale, K.H., 1997. What controls dissolved iron concentrations in the world ocean?. Marine Chemistry 57, 137–161.

Joos, F., Plattner, G.K., Stocker, T.F., Marchal, O., Schmittner, A., 1999. Global warming and marine carbon cycle feedbacks an future atmospheric CO_2. Science 284, 464–467.

Kuma, K., Nishioka, J., Matsunaga, K., 1996. Controls on iron(III) hydroxide solubility in seawater: the influence of pH and natural organic chelators. Limnology and Oceanography 41, 396–407.

Leal, M.F.C., Vasconcelos, M.T.S.D., van den Berg, C.M.G., 1999. Copper-induced release of complexing ligands similar to thiols by Emiliania huxleyi in seawater cultures. Limnology and Oceanography 44, 1750–1762.

Lefevre, N., Watson, A.J., Cooper, D.J., Weiss, R.F., Takahashi, T., Sutherland, S.C., 1999. Assessing the seasonality of the oceanic sink for CO_2 in the northern hemisphere. Global Biogeochemical Cycles 13, 273–286.

Maldonado, M.T., Price, N.M., 2000. Nitrate regulation of Fe reduction and transport by Fe-limited Thalassiosira oceanica. Limnology and Oceanography 45, 814–826.

Martin, J.H., Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M., Tanner, S.J., Hunter, C.N., Elrod, V.A., Nowicki, J.L., Coley, T.L., Barber, R.T., Lindley, S., Watson, A.J., Van Scoy, K., Law, C.S., Liddicoat, M.I., Ling, R., Stanton, T., Stockel, J., Collins, C., Anderson, A., Bidigare, R., Ondrusek, M., Latasa, M., Millero, F.J., Lee, K., Yao, W., Zhang, J.Z., Friederich, G., Sakamoto, C., Chavez, J., Buck, K., Kolber, Z., Greene, R., Falkowski, P., Chisholm, S.W., Hoge, F., Swift, R., Yungel, J., Turner, S., Nightingale, P., Hatton, A., Liss, P., Tindale, N.W., 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. Nature 371, 123–129.

Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the northeast Pacific subarctic. Nature 331, 341–343.

Martin, J.H., Fitzwater, S.E., Gordon, R.M., 1991. Iron deficiency limits phytoplankton growth in Antarctic waters. Global Biogeochemical Cycles 4, 5–12.

Millero, F.J., 1998. Solubility of Fe(III) in seawater. Earth and Planetary Science Letters 154, 323–329.

Mitchell, B.G., Brody, E.A., Holm-Hansen, O., McClain, C., Bishop, J., 1991. Light limitation of phytoplankton biomass and macrionutrient utilization in the Southern Ocean. Limnology and Oceanography 36, 1662–1677.

Nolting, R.F., Gerringa, L.J.A., Swagerman, M.J.W., Timmermans, K.R., de Baar, H.J.W., 1998. Fe (III) speciation in the high nutrient, low chlorophyll Pacific region of the Southern Ocean. Marine Chemistry 62, 335–352.

Pakulski, J.D., Coffin, R.B., Kelley, C.A., Holder, S.L., Downer, R., Aas, P., Lyons, M.M., Jeffrey, W.H., 1996. Iron stimulation of Antarctic bacteria. Nature 383, 133–134.

Queguiner, B., Treguer, P., Peeken, I., Scharek, R., 1997. Biogeochemical dynamics and the silicon cycle in the Atlantic sector of the Southern Ocean during austral spring 1992. Deep-Sea Research II 44, 69–89.

Raven, J.A., 1988. The iron and molybdenum use efficiencies of plant-growth with different energy, carbon and nitrogen-sources. New Phytologist 109, 279–287.

Rue, E.L., Bruland, K.W., 1995. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Marine Chemistry 50, 117–138.

Rue, E.L., Bruland, K.W., 1997. The role of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. Limnology and Oceanography 42, 901–910.

Ruzic, I., 1982. Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation. Analytica Chimica Acta 140, 99–113.

Smetacek, V., DeBaar, H.J.W., Bathmann, U.V., Lochte, K., VanderLoeff, M.M.R., 1997. Ecology and biogeochemistry of the Antarctic Circumpolar Current during austral spring: A summary of Southern Ocean JGOFS cruise ANT X/6 of RV *Polarstern*. Deep-Sea Research II 44, 1–21.

Sunda, W.G., Huntsman, S.A., 1995. Iron uptake and growth limitation in oceanic and coastal phytoplankton. Marine Chemistry 50, 189–206.

Sunda, W.G., Huntsman, S.A., 1997. Interrelated influence of iron, light and cell size on marine phytoplankton growth. Nature 390, 389–392.

Takeda, S., 1998. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. Nature 393, 774–777.

Timmermans, K.R., van Leeuwe, M.A., de Jong, J.T.M., McKay, R.M.L., Nolting, R.F., Witte, H.J., van Ooyen, J., Swagerman, M.J.W., Kloosterhuis, H., de Baar, H.J.W., 1998. Iron stress in the Pacific region of the Southern Ocean: evidence from enrichment bioassays. Marine Ecology-Progress Series 166, 27–41.

Treguer, P., Nelson, D.M., Vanbennekom, A.J., Demaster, D.J., Leynaert, A., Queguiner, B., 1995. The silica balance in the world ocean — a reestimate. Science 268, 375–379.

Trick, C.G., Andersen, R.J., Gillam, A., Harrison, P.J., 1983. Prorocentrin — an extracellular siderophore produced by the marine dinoflagellate prorocentrum-minimum. Science 219, 306–308.

van den Berg, C.M.G., 1982. Determination of copper complexation with natural organic ligands in seawater by equilibration with MnO_2. I. Theory. Marine Chemistry 11, 307–322.

van den Berg, C.M.G., 1989. Electroanalytical Chemistry of Sea water. In: Riley, J.P. (Ed.), Chemical Oceanography, Vol. 9. Academic Press, London, pp. 197–245.

van den Berg, C.M.G., 1995. Evidence for organic complexation of iron in seawater. Marine Chemistry 50, 139–157.

van den Berg, C.M.G., Donat, J.R., 1992. Determination and data evaluation of copper complexation by organic ligands in sea water using cathodic stripping voltammetry at varying detection windows. Analytica Chimica Acta 257, 281–291.

van den Berg, C.M.G., Kramer, J.R., 1979. Determination of complexing capacities and conditional stability constants for copper in natural waters using MnO_2. Analytica Chimica Acta 106, 113–120.

Verity, P.G., Smetacek, V., 1996. Organism life cycles, predation, and the structure of marine pelagic ecosystems. Marine Ecology-Progress Series 130, 277–293.

Veth, C., Peeken, I., Scharek, R., 1997. Physical anatomy of fronts and surface waters in the ACC near the 6 degrees W meridian during austral spring 1992. Deep-Sea Research II 44, 23–49.

Whitworth, T., 1988. The antarctic circumpolar current. Oceanus 31, 53–58.

Witter, A.E., Luther III, G.W., 1998. Variation in Fe-organic complexation with depth in the Northwestern Atlantic Ocean as determined using a kinetic approach. Marine Chemistry 62, 241–258.

Yokoi, K., van den Berg, C.M.G., 1992. The determination of iron in seawater using catalytic cathodic stripping voltammetry. Electroanalysis 4, 65–69.