Organic iron(III) speciation in surface transects across a frontal zone: the Chatham Rise, New Zealand

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Abstract. Iron (Fe) is a critical nutrient in marine systems and the organic complexation of Fe is a central factor of the marine biogeochemistry of Fe. In the present study, total dissolved Fe and its organic speciation were measured in filtered seawater samples ($<0.2\ \mu\text{m}$) collected along three surface transects across the subtropical (ST) front, east of New Zealand, in austral spring (October 2000). Total dissolved Fe concentrations were low ($\sim 0.1\ \text{nM}$) in the subantarctic (SA) waters. The highest Fe concentration ($\sim 0.8\ \text{nM}$) was observed at the mixing boundary north of the Subtropical Convergence (STC) and then decreased relatively quickly both southward and northward. Cathodic stripping voltammetry was used to determine Fe speciation. The dissolved Fe(III) was fully complexed ($>99.9\%$) by natural organic ligands, which were found to occur in excess of the dissolved Fe concentration at $1.29 \pm 0.33\ \text{nM}$ (equivalent to an excess over Fe of $\sim 1.0\ \text{nM}$), and with a complex stability of $\log K'_{\text{FeL},\text{Fe}^{3+}} = 22.67 \pm 0.22$. The total ligand concentrations were consistently higher ($\sim 0.5\ \text{nM}$) in the ST and STC waters than in the SA waters. Our Fe data imply that the regional currents may be an important vehicle for transporting the elevated Fe across the front.

Extra keywords: organic speciation, subtropical front.

Introduction

Iron (Fe) is an essential micronutrient for phytoplankton and plays an important role in regulating their growth in some regions of the ocean. It is an important constituent of such biochemical processes as photosynthesis, nitrate and nitrite reduction, and many other biosynthetic reactions (Sunda 1989; Hutchins 1995). *In situ* Fe fertilisation experiments and shipboard enrichment incubations have proven that Fe limits primary production in high-nutrient, low-chlorophyll (HNLC) regions, including the Subarctic Pacific, the Equatorial Pacific, and the Southern Ocean (Martin and Fitzwater 1988; Martin *et al.* 1994; Coale *et al.* 1996; Boyd *et al.* 2000, 2004a).

Fe is predicted to be present primarily in the form of Fe(III) oxy-hydroxides in oxic seawater (Turner *et al.* 1981; Hudson *et al.* 1990). It occurs at extremely low concentrations in the open ocean owing to the hydrolysis of thermodynamically stable Fe(III) compounds, and the resulting formation of sparingly soluble hydroxides and oxides. Voltammetric speciation methods have been developed to gain insight into the degree of complexation of Fe(III) with natural organic ligands in seawater. Electrochemical measurements (Gledhill and van den Berg 1994; Rue and Bruland 1995; Wu and Luther 1995) have shown that most of the dissolved Fe in the oceanic waters is strongly complexed by organic matter, which enhances the otherwise very low ($0.1\ \text{nM}$) Fe solubility (Wu *et al.* 2001).

The hypothesis that an inadequate Fe supply is the major factor that controls phytoplankton production in HNLC areas of the open ocean (Martin *et al.* 1991) has been modified by this finding, and suggests that algal growth is limited not only by a general lack of Fe but also by its restricted availability. Therefore, Fe speciation is important for understanding the cycle of Fe among biotic and abiotic forms in marine systems.

During the recent Southern Ocean Iron Release Experiment (SOIREE), a marked increase in ligand concentrations towards the end of the experiment was observed and the dissolved Fe concentration remained high ($> 1\ \text{nM}$) (Crook *et al.* 2001). Moreover, the SOIREE bloom flourished for at least 55 days suggesting that a sufficient proportion of the added Fe was retained within the mixed layer (Abraham *et al.* 2000). Crook *et al.* (2001) speculate that the observed ligands provide the mechanism to maintain Fe in the surface ocean. The source of the ligands and their affinity for Fe is unknown, and how the Fe retention system is primed and then maintained raises fundamental questions about Fe cycling in HNLC polar waters.

In the present paper, we present the distribution and organic speciation of Fe along three surface seawater transects across a frontal zone, near the Chatham Rise, east of New Zealand. The location of New Zealand at the edge of the Southern Ocean provides a natural laboratory for studying ocean processes in a variety of oceanic conditions. The subtropical front (STF) is a dynamic region of enhanced

Table 1. Hydrographic, nutrient and dissolved iron data

Station ID ^A	Latitude	Longitude	Temperature (°C)	Salinity	PO ₄ ³⁻ (μmol L ⁻¹)	Si (μmol L ⁻¹)	Nitrate + nitrite (μmol L ⁻¹)	Fe – Otago – GFAAS (nM)	Fe – NIWA – GFAAS (nM)	Fe – NIWA – FI-CL (nM)
11F	45°50.6'S	171°33.4'E	8.2	34.3	1.02	4.54	20.01	0.29	–	–
12F	45°55.4'S	172°27.8'E	8.4	34.3	1.11	3.96	16.93	0.09	–	–
13F	46°02.1'S	173°32.7'E	8.6	34.3	0.96	3.13	13.76	0.11	–	–
14F	46°14.4'S	175°48.9'E	8.8	34.3	0.95	1.11	13.51	0.07	–	–
16F	45°21.0'S	178°29.8'E	9.6	34.4	0.95	1.18	12.15	0.27	0.28	0.30
17F	44°33.5'S	178°36.0'E	9.0	34.3	2.22	1.56	14.34	0.15	0.17	0.30
18F	44°00.0'S	178°29.4'E	10.1	34.7	2.01	0.35	6.69	0.10	0.24	0.27
19F	43°41.2'S	178°30.1'E	10.4	34.6	1.99	<0.07	5.72	0.20	0.24	0.35
20F	43°15.7'S	178°29.3'E	11.2	34.8	1.92	<0.07	4.97	0.44	0.30	0.38
21F	43°03.7'S	179°29.5'E	11.1	34.8	0.41	<0.07	5.08	0.53	0.31	0.31
22F	42°52.1'S	178°29.8'E	12.6	35.0	0.45	0.86	5.44	0.84	0.31	0.46
23F	42°44.9'S	178°29.8'E	12.1	34.9	0.38	<0.07	6.77	0.65	0.35	0.41
24F	42°16.9'S	178°31.2'E	14.1	35.3	0.30	0.77	3.92	0.41	0.42	0.50
25F	41°38.8'S	178°30.7'E	14.1	35.4	0.27	0.79	2.55	0.27	0.42	0.41
26F	41°11.1'S	178°28.9'E	14.0	35.3	0.31	0.94	4.56	0.10	0.30	0.31
27F	40°26.7'S	178°09.5'E	14.5	35.3	0.30	0.51	2.56	0.26	–	–
28F	40°12.3'S	177°50.4'E	14.1	35.2	0.32	0.55	2.60	0.22	–	–
30F	39°49.7'S	177°20.0'E	12.9	34.9	0.33	1.72	2.96	0.61	–	–

GFAAS, Graphite furnace atomic absorption spectrometry. FI-CL, Flow injection chemiluminescence.

^AIn the present study, the Otago transect covers sampling stations 11F to 14F, the Hawkes Bay transect covers sampling stations 27F to 30F, and the Chatham Rise transect covers sampling stations 16F to 26F.

primary production (Bradford-Grieve *et al.* 1997; Boyd *et al.* 1999), where subtropical (ST) water mixes with subantarctic (SA) water forming the subtropical convergence (STC). The speciation measurements are compared with chlorophyll *a* concentrations and the hydrography of the area.

Materials and methods

Study area

The study area is located east of the New Zealand landmass. Eighteen stations (Table 1) were sampled in austral spring (5–19 October 2000) on board the New Zealand Research Vessel *Tangaroa* (TAN0010 cruise). The voyage consisted of a section from Otago Peninsula east to 178°30'E (the Otago transect), then due north to 41°S (the Chatham Rise transect), then north-west to Cape Kidnappers (the Hawkes Bay transect) (Fig. 1).

Oceanic circulation south and east of New Zealand is strongly controlled by bathymetry (Heath 1985). The STC weaves northward along the shelf-break of the eastern South Island of New Zealand, where it is referred to as the Southland Current, before heading further east across the Chatham Rise. The STC appears to be topographically locked to this region where the seafloor rises sharply from a depth of ~2300 m to ~350 m (Heath 1985; Belkin and Gordon 1996). This dynamic region separates the southward-moving warm, saline, nutrient-depleted ST waters from the northward-moving cold, less saline, nutrient-replete SA waters. The macronutrient signatures of these two water masses are quite different. Subtropical waters are characteristically low in nitrate (NO₃⁻, 0.7 μM), silicate (Si, 1.3 μM) and phosphate (PO₄³⁻, 0.3 μM), whereas the opposite is true of SA waters (NO₃⁻, 18 μM; Si, 4 μM and PO₄³⁻, 1.4 μM). The SA waters are HNLC in character (Bradford-Grieve *et al.* 1997; Boyd *et al.* 1999).

The major currents north of the STC are the East Cape Current (ECC) and the Wairarapa Eddy (WE) (Chiswell and Roemmich 1998). The ECC is a persistent southward flow, attached to the east coast of

the North Island, and then joined by flow from the Southland Current. Part of the total flow is recirculated in the cyclonic eddy (WE), which is centred near 41°S 178°30'E and part flows away to the north-east (Chiswell 2000). The ECC itself retroflects near 42°S and then flows into and along the STC providing the northern source of subtropical water to the front.

Sample collection and handling

Surface seawater was collected by means of a modified towed steel torpedo-shaped 'fish' covered with metal-free, epoxy coating (Braungardt *et al.* 1998). The fish was deployed ~6 m away from the hull to avoid contamination. The design of the 40 kg fish ensured that the sampling hose pointed forward and maintained a ~1–2 m depth at speeds of 1–12 knots. Seawater samples were pumped continuously into a Class-100 clean air laboratory container using a peristaltic pump and polyethylene (PE) tubing. All sample tubing was thoroughly acid-washed before use (10% HCl). Sub-samples were taken by filling acid-cleaned 500-mL PE bottles (Nalgene, Rochester, NY) following on-line filtration through acid-cleaned Sartobran-P capsules (0.45 μm prefilter, 0.2 μm final filter; Sartorius, Göttingen, Germany). Samples for speciation measurements were then double bagged and quickly frozen at –20°C. They were transported frozen to the laboratory and only thawed immediately before analysis.

Macronutrients and conductivity–temperature–depth

Temperature and salinity were measured with a Sea-Bird conductivity–temperature–depth meter (CTD; Sea-Bird Electronics, Bellevue, WA). Macronutrients were determined immediately after collection on single aliquots of filtered samples using an Astoria Analyzer 300 series autoanalyzer (Astoria-Pacific International, Clackamas, OR). Dissolved reactive phosphorus was determined by the autoanalytical method of Downes (1978) modified by eliminating the reductant. Silicic acid was determined using the method of Smith and Milne (1981), and nitrite

Fig. 1. Location map showing the sampling stations, surface water masses and surface circulation patterns, relative to the Chatham Rise.

plus nitrate were determined using the method developed by Nydahl (1976).

Duplicate chlorophyll *a* (chl *a*) samples were collected on GF/F filters and folded into aluminum foil and immediately frozen. Ashore, chl *a* was extracted into 90% acetone and determined by fluorometry (Strickland and Parsons 1972).

Total dissolved iron determinations

Total dissolved Fe was concentrated from the acidified samples in the Otago laboratory using an ammonium–pyrrolidine–dithiocarbamate (APDC)/diethyl–ammonium–diethyldithio–carbamate (DDDC) chelation/solvent extraction technique, adapted from that of Danielsson *et al.* (1982) by substituting chloroform for Freon–11 as the extracting solvent as described in detail by Frew and Hunter (1995) and Frew *et al.* (2001). The sample aliquot to be extracted was generally 150 g and duplicate aliquots were analysed from each sample. Fe in the extracts was determined by graphite furnace atomic absorption spectrometry (GFAAS, PE 4100 ZL; Perkin-Elmer, Wellesley, MA). Recovery efficiencies were determined by standard addition analysis of previously extracted seawater and blanks were determined by analysing Milli-Q water (Millipore, Billerica, MA) or previously extracted seawater. Extraction efficiencies were $90 \pm 4\%$, blanks were <0.03 nM, and the detection limit was 0.05 nM (2σ). Standard operating conditions, including Zeeman background correction, were used.

In addition, duplicate samples from the Chatham Rise transect were analysed by a similar solvent extraction/GFAAS method at NIWA, Hamilton. The NIWA samples were also analysed by chemiluminescence using the Obata method (Obata *et al.* 1993). A comparison of Otago and NIWA results is presented in Table 1.

Cathodic stripping voltammetry iron speciation determinations

Organic complexation of Fe was determined by competitive ligand exchange–adsorptive cathodic stripping voltammetry (CSV) with ligand competition against 2-(2-thiazolylazo)-*p*-cresol (TAC) (Croft and Johansson 2000).

The voltammetry equipment consisted of a Metrohm VA 663 stand (Herisau, Switzerland), with a multi-mode electrode and a μ autolab type II potentiostat (Eco Chemie, Utrecht, The Netherlands). The working electrode was a hanging mercury drop electrode (HMDE) with a 'medium' mercury drop ($0.4 \text{ mm}^2 \pm 10\%$), the reference electrode was double-junction Ag/saturated AgCl electrode with a salt bridge filled with 3 M KCl and the counter electrode was glassy carbon. During the CSV analyses, all samples were contained in Teflon sample cups (Metrohm), and stirred with the inbuilt PTFE Teflon stirring tip (1500 rpm) of the VA 663.

Subsamples (10 mL) of seawater were pipetted into a series of 12 Teflon bottles and buffered at pH 8.0 with 1.0 M stock buffer of EPPS (*N*-(2-hydroxyethyl)-piperazine-*N'*-2-propanesulfonic acid;

Sigma-Aldrich, St Louis, MO). Iron spikes were added to all but two of the bottles, yielding concentrations from 0 to 4 nM. The added Fe was allowed to equilibrate with the natural ligands for 1 h at room temperature. After this equilibration period, 10 μ L of 10 mM methanolic TAC solution was added and the sample left to equilibrate for at least 5 h (often overnight, 15–18 h). The equilibrated solutions were then sequentially (starting from the lowest concentration) transferred to the Teflon cell cup. Each solution was de-aerated for 4 min with oxygen-free nitrogen gas. A fresh Hg drop was made, and $\text{Fe}(\text{TAC})_2$ complex species were adsorbed at an applied potential of -0.4 V for 120 s, while stirring at 1500 rpm. The stirrer was switched off for a 5-s quiescence period; thereafter the potential was scanned in the differential pulse mode from -0.38 to -0.65 V at 2.55 mV s^{-1} (pulse amplitude 49.95 mV) and the cathodic stripping current from adsorbed $\text{Fe}(\text{TAC})_2$ recorded. Cell cups were rinsed with Milli-Q water between analyses. Each Teflon bottle was consistently used for a particular Fe addition.

Calculation of the iron speciation

Measurements of Fe organic speciation using electrochemical methods focus primarily on determining the strength of Fe-binding ligands in seawater (the conditional stability constant, K'_{FeL}), and the concentration of total naturally occurring organic Fe-binding ligands (L_T). The theoretical basis of the calculation of ligand concentration from titration data for labile metal concentration was introduced by Ruzic (1982), van den Berg (1982) and in the specific case for Fe by Gledhill and van den Berg (1994), and Rue and Bruland (1995). In the present study, the total ligand concentrations [L_T] and the conditional stability constants K'_{FeL} for the formation of the Fe-ligand were calculated by performing a non-linear least-squares fitting algorithm of the data fitted to the following equation (Gerringa *et al.* 1995):

$$[\text{FeL}] = \frac{[L_T]K'_{\text{FeL}}[\text{Fe}']}{1 + K'_{\text{FeL}}[\text{Fe}']} \quad (1)$$

where $[\text{FeL}]$ represents the organically-bound fraction of the Fe-binding ligands and $[\text{Fe}']$ is the sum of all the inorganic species. K'_{FeL} is the conditional stability constant with respect to Fe' under these conditions (in this case pH 8.0 seawater). To convert K'_{FeL} to $K'_{\text{FeL,Fe}^{3+}}$, the conditional stability constant for FeL with respect to free Fe^{3+} , the relationship between Fe' and Fe^{3+} , $\alpha'_{\text{Fe}} = [\text{Fe}']/[\text{Fe}^{3+}]$, can be used:

$$K'_{\text{FeL,Fe}^{3+}} = \alpha'_{\text{Fe}} K'_{\text{FeL}} \quad (2)$$

Here α'_{Fe} of $10^{10.0}$ from the work of Hudson *et al.* (1992) is used. $[\text{Fe}']$ is related to the Fe reduction peak current (I_p) by the following relationship:

$$[\text{Fe}'] = \frac{I_p}{S\alpha_{\text{Fe}(\text{TAC})_2}} \quad (3)$$

where S is the analytical sensitivity. Previously S was determined from the linear region at the high Fe end of the titration, a method that is somewhat prone to errors of judgment and leads to an underestimation of S and L_T . Correction of S by modelling has been made before (Turoczy and Sherwood 1997; Hudson *et al.* 2003; van den Berg 2006) and a similar iterative procedure is used in the present study. The side reaction coefficient for $\text{Fe}(\text{TAC})_2$ is denoted by $\alpha_{\text{Fe}(\text{TAC})_2}$ with a value of 250 (Croot and Johansson 2000).

Speciation data was calculated for K'_{FeL} and L_T using the Gerringa non-linear regression fitted for a single ligand model. The standard deviations of K'_{FeL} and L_T were calculated from non-linear least-squares regression of the titration curves using the computer program NLREG (www.nlreg.com/, verified June 2006). Errors were reported

for 95% confidence intervals. The ambient $[\text{Fe}']$ was estimated by solving Eqn (1), using the calculated values of K'_{FeL} and L_T at the ambient dissolved Fe concentration. The concentration of FeL can thus be calculated from:

$$[\text{FeL}] = [\text{Fe}] - [\text{Fe}'] \quad (4)$$

where $[\text{Fe}]$ is the total dissolved Fe concentration. So the percentage of Fe occurring as organic species is calculated from:

$$[\text{FeL}]\% = \frac{[\text{FeL}]}{[\text{Fe}]} \times 100\% \quad (5)$$

Results

Nutrient, chlorophyll *a* and hydrographic data

Nutrient and hydrographic data associated with each sampling station are presented in Table 1. The Chatham Rise transect crossed two main water masses separated by a frontal boundary (Fig. 1), which are described by the temperature–salinity (T–S) properties of warm, salty ST waters ($T = 14^\circ\text{C}$, $S = 35.4$), intermediate salinity STC waters, and cold, less saline SA waters ($T = 8.5^\circ\text{C}$, $S = 34.3$) (Fig. 2). Macronutrient concentrations were generally higher in SA waters (NO_3^- , 14–20 μM ; Si, 1.5–4.5 μM and PO_4^{3-} , 1–2.2 μM) than in STC or ST waters (NO_3^- , 2–6 μM ; Si, $\sim 0.7 \mu\text{M}$ and PO_4^{3-} , $\sim 0.35 \mu\text{M}$) (Figs 2, 3; Table 1).

Chlorophyll *a* concentrations remained relatively constant, with values ranging between 0.08 and 0.24 mg m^{-3} along the Otago transect. Chlorophyll *a* increased sharply to $\sim 0.75 \text{ mg m}^{-3}$ on the Chatham Rise and then decreased to $\sim 0.4 \text{ mg m}^{-3}$ at 41°S . Along the Hawkes Bay transect, chl *a* concentrations ranged between 0.72 and 0.89 mg m^{-3} (Fig. 3).

On the Chatham Rise, Si concentrations dropped below the detection limit (0.07 μM) accompanied by the high chl *a* concentrations, suggesting significant Si utilisation by the phytoplankton community.

Dissolved iron and iron-binding ligands in three surface transects

The results of the organic speciation work along the three surface transects are shown in Fig. 3, collated in Table 2. Low dissolved Fe concentrations were observed in the SA waters and remained relatively constant at $\sim 0.1 \text{ nM}$. Along Hawkes Bay, the dissolved Fe concentration was high ($\sim 0.6 \text{ nM}$) in the surface water above the continental shelf, then decreased to $\sim 0.3 \text{ nM}$ in a south-easterly direction (offshore).

For the Chatham Rise transect, the dissolved Fe concentrations showed a different pattern, in which elevated dissolved Fe concentrations were up to 0.8 nM at the north flank of the Chatham Rise, then decreased to $\sim 0.1 \text{ nM}$ both northward and southward.

Along with the dissolved Fe concentrations, the average concentration of total organic-complexing ligands was

Fig. 2. Transects showing salinity, temperature and PO_4^{3-} concentrations.

Fig. 3. Concentrations of silicon, chlorophyll *a*, dissolved iron and ligands along the three transects.

$1.29 \pm 0.33 \text{ nM}$ ($n = 18$). There was a difference between the concentration for the SA waters and the ST waters (L_T values of $0.95 \pm 0.19 \text{ nM}$ and $1.43 \pm 0.15 \text{ nM}$ respectively). 'Excess' ligand concentration is defined as the concentration of total Fe-binding ligand minus the concentration of total dissolved

Fe at each measured station. The average 'excess' ligand concentration was $0.98 \pm 0.30 \text{ nM}$ ($n = 18$, Table 2).

Estimated values of Fe' ranged from ~ 0.01 to 0.2 pM with slightly elevated Fe' over the Chatham Rise transect. There was no systematic change in the conditional stability constant

Table 2. Iron speciation data along the three surface transects

Station ID ^A	Total dissolved Fe-binding ligand L_T (nM)	Log $K'_{FeL, Fe^{3+}}$	'Excess' Fe-binding ligand ($L_T - Fe$, nM)	Fe' (pM)	FeL (%)
11F	1.00 ± 0.06	22.82 ± 0.18	0.71	0.06	99.98
12F	0.85 ± 0.09	22.85 ± 0.24	0.76	0.02	99.98
13F	0.90 ± 0.08	22.54 ± 0.20	0.79	0.04	99.96
14F	1.16 ± 0.15	22.92 ± 0.32	1.09	0.01	99.98
16F	0.66 ± 0.08	22.69 ± 0.28	0.39	0.14	99.95
17F	1.12 ± 0.08	22.35 ± 0.20	0.97	0.07	99.95
18F	1.36 ± 0.09	22.47 ± 0.14	1.26	0.03	99.97
19F	1.24 ± 0.05	22.44 ± 0.08	1.04	0.07	99.97
20F	2.00 ± 0.16	22.57 ± 0.24	1.56	0.08	99.98
21F	1.34 ± 0.09	22.61 ± 0.18	0.81	0.16	99.97
22F	1.40 ± 0.20	23.02 ± 0.56	0.56	0.14	99.98
23F	1.72 ± 0.16	22.68 ± 0.18	1.07	0.13	99.98
24F	1.17 ± 0.18	22.75 ± 0.40	0.76	0.10	99.98
25F	1.53 ± 0.16	22.78 ± 0.18	1.26	0.04	99.99
26F	1.50 ± 0.26	22.23 ± 0.30	1.40	0.04	99.96
27F	1.39 ± 0.14	22.74 ± 0.22	1.13	0.04	99.98
28F	1.38 ± 0.16	22.56 ± 0.34	1.16	0.05	99.98
30F	1.58 ± 0.20	23.05 ± 0.30	0.97	0.06	99.99

^AIn our calculation, the subtropical waters include stations 24F to 30F, the SA waters include stations 11F to 17F, and the subtropical convergence waters include stations 18F to 23F.

($K'_{FeL, Fe^{3+}}$, with respect to Fe^{3+}). The values varied from $10^{22.23}$ to $10^{23.05}$ (mean ± s.d. = $10^{22.67 \pm 0.22}$).

Discussion

Dissolved iron

There are very few attempts at analytical intercomparison for trace metals reported to date. Although a tremendous amount has been learnt about the distribution and biogeochemistry of Fe in recent years, the ability to relate one study to another remains problematic. The most recent international analytical intercomparison study (Bowie *et al.* 2006) showed that different analytical methods give significantly different dissolved Fe concentrations. Moreover, Bowie *et al.* (2006) highlighted the variability in reported Fe concentrations even when the same analytical methods were used. The coefficient of variation for the GFAAS methodology was close to 50%.

The Otago and NIWA results from the present study generally agree well with no systematic trend in differences. The Otago results show a maximum at station 22F (Fig. 4) that is not apparent in the NIWA data and the possibility of contamination cannot be excluded. However, this point coincides with local maxima in nutrient concentrations (PO_4^{3-} and Si, Table 1) and the variation between Fe results is still only 50%, similar to the expected level of variability for this technique (Bowie *et al.* 2006). We used the Otago dataset for interpretation of CSV titration results because it is the only full Fe dataset available in the present study.

The dissolved Fe concentrations found in the SA and ST surface waters (from ~0.1 nM along the Otago transect to ~0.3 nM along the Hawkes Bay transect) are comparable with

Fig. 4. Comparison of three different dissolved Fe datasets for surface waters along the Chatham Rise transect.

those in surface waters in the Southern Ocean (~0.1 nM (Sedwick *et al.* 1997; Bowie *et al.* 2001) to ~0.6 nM (de Jong *et al.* 1999)). The highest concentration was found just north of the Chatham Rise (0.8 nM, Station 22F).

The higher Fe concentration (~0.6 nM) found in the Hawkes Bay transect is probably related to the proximity of landmasses to the ST water – maxima in T, S and macronutrient concentrations are also observed at station 22F, suggesting the importance of physical transport mechanisms. The T-S properties of this water (Fig. 5) indicate it has a subtropical source and is likely from the East Cape Current. This indicates the ECC is a significant source of dissolved Fe for the STC.

River run-off from the New Zealand landmass tends to increase Fe concentration in ST water rather than SA water because the Subtropical Front and Southland Front always lie south of the South Island, which prevents a classical 'island

Fig. 5. Temperature–salinity (T–S) diagram for surface waters along the three transects.

wake effect' (Boyd *et al.* 1999; Signorini *et al.* 1999). A previous study showed the surface concentrations of Fe decreased dramatically across the Otago shelf (Croot and Hunter 1998). It appears that the Southern Current acts to control the flux of Fe across the shelf by transporting materials rapidly along the shelf further north. Furthermore, the role of atmospheric deposition in the supply of Fe to the study area is at present uncertain (Boyd *et al.* 2004b). A recent atmospheric Fe deposition flux study in the eastern Atlantic Ocean suggested that wet deposition dominated in the intertropical convergence zone, whereas dry deposition dominated in the other regions of the transect, where rainfall rates were much lower (Sarthou *et al.* 2003).

The sampling station with the highest dissolved Fe concentration is located at 42°52'S, coincident with the location where the ECC is mixing with the STC. It has been suggested (Garner 1959) that the transport of subtropical water by the ECC into the STC is important in maintaining the convergence over the Chatham Rise. Thus, our Fe data may imply that the regional currents (e.g. ECC) could be an important vehicle for carrying the elevated Fe from the coastal waters to the north flank of the Chatham Rise, which may then trigger phytoplankton growth. The relatively high primary productivity within the STF over the Chatham Rise likely arises because the front provides a regime with both sufficient macronutrient and micronutrient (Fe) to drive primary production. The possibility that mesoscale eddies could play a role in nutrient supply to the upper ocean has been suggested by several researchers (Franks *et al.* 1986; Falkowski *et al.* 1991).

The organic iron-binding ligands

A representative titration of the ligands is shown in Fig. 6, which shows the peak height (representing labile Fe) versus the total Fe added. The CSV titration with Fe showed clear Fe-binding at low Fe additions to all samples, indicating the presence of excess organic Fe-binding ligands. All data presented in the present work have been calculated assuming only one class of Fe-binding ligand.

Results from the surface transects show that the total Fe-binding ligand concentrations are consistently higher (~ 0.5 nM) in the ST and STC waters (1.47 ± 0.22 nM, $n = 12$)

than in the SA waters (0.95 ± 0.19 nM, $n = 6$). 'Excess' ligands represent the portion of ligands in excess of the total dissolved Fe and available to complex any new Fe that enters the system. Again, a similar trend is observed that the mean 'excess' ligand concentration in the ST and STC waters is ~ 0.3 nM higher than the mean concentration in the SA waters. We also performed the speciation calculation using both Otago and NIWA dissolved Fe data from the Chatham Rise transect. Because the total ligand is in excess of total Fe, using the NIWA Fe data alters the total ligand concentration by 0.1–0.2 nM. Only at station 22F is a higher difference observed (0.4 nM). Despite the discrepancies between different Fe datasets, differences in calculated ligand concentrations using either one are small.

Organic Fe speciation measurements (Table 3) have been reported from different oceanic regimes. Despite differences in the choice of CSV approaches used by various research groups, one common finding is the presence of the excess Fe-binding ligands in the world's oceans, ranging from ~ 1 to ~ 10 nM. Their conditional stability constants range in magnitude between 18 and 23. The ligand concentrations and their conditional stability constants in the present study are comparable with those found in the Atlantic sector of the Southern Ocean (Boye *et al.* 2001), the central gyre of the North Pacific (Rue and Bruland 1995) and the Arabian Sea (Witter *et al.* 2000a).

Rue and Bruland (1995) observed the presence of two classes of ligands in the Central North Pacific. The absence of curvature in the linearised titration data of our study suggests that Fe complexation in our water samples is consistent with the single ligand model. There is no evidence for the presence of two classes of ligands. However, the linearity of the titration curves does not exclude the existence of weak ligands in excess of Fe(III) in the samples. The detection window of a CSV method is determined by the balance of the relative stabilities of the natural complex and the complexes formed with the added ligand. According to van den Berg and Donat (1992), no Fe is detected if the natural complex is much more stable than the complex with the added ligand, whereas no complexation is detected if the natural organic complex is much weaker than the complex with added ligand and is outcompeted by the added ligand. The competing ligand (TAC) used in our study has a detection window (centred by $\alpha_{\text{Fe(TAC)}_2}$ and within one order of magnitude on either side) between $10^{11.4}$ and $10^{13.4}$, which is higher than the ligand (Salicylaldoxime) used for the Pacific studies (Rue and Bruland 1995, 1997). It is therefore possible that excess weak ligands with a $\alpha_{\text{FeL}} < 10^{11.4}$ would not have been detected in our titrations. Thus, the choice of analytical competition strength employed can bias the estimates of both ligand concentrations and conditional stability constants.

The conditional stability constant with respect to Fe^{3+} depends on the assumption of the inorganic side reaction coefficient. There is still some debate regarding the existence

Fig. 6. Representative titration curve for surface seawater sample from station 25F: (a) current (nA) is plotted versus total amount of Fe; and (b) non-linear least-squares fit using Gerringa method.

of various inorganic Fe(III) species, especially $Fe(OH)_3^0$. Likewise, the value of the α'_{Fe} used by different researchers varies from $10^{8.5}$ to $10^{11.9}$. It is therefore better to use the organic α coefficient (α_{FeL} , product of conditional stability constant $K'_{FeL,Fe^{3+}}$ and the ligand concentration L_T , the binding potential of the organic ligands) when comparing results with work by others (Table 3).

The relative constancy of the conditional stability constants ($\log K'_{FeL,Fe^{3+}} = 22.67 \pm 0.22$) determined in the present study is still not able to rule out the presence of different types of ligands across the water masses. Witter *et al.* (2000a) argue that the CSV method cannot distinguish between different organic moieties that may be present in seawater, because the measured conditional stability constants do not vary in a systematic manner with Fe-binding ligand structure. Moreover, results from the surface transects show that the total Fe-binding ligand concentrations are consistently higher (~ 0.5 nM) in the ST and STC waters than in the SA waters.

The biological purpose of the organic ligands in the oceans is not yet fully understood. Possibilities are that the ligands may serve to buffer trace metal activities within the physiological tolerance range for microorganisms, or limit the scavenging loss of bioactive metals to sinking particles. It is perhaps interesting to ask why the excess ligand concentrations are slightly higher in the ST and STC waters. Is this phenomenon linked to the local planktonic community structure, the biological sources of the ligands, or the biological and abiotic reactions in the water? There was no clear evidence available from the present study. However, the parallel increase in the ligand and Fe concentrations, along with increases in the chlorophyll *a* concentration, may suggest that the ligand concentrations were increased by microorganisms in response to the increased overall Fe concentration or that there was simply more cells and hence more ligands.

Previous research in this study area showed that in spring, SA phytoplankton populations were dominated by eukaryotic picophytoplankton and diatoms had a relatively low biomass (Chang and Gall 1998). Bacterial production was strongly

correlated with chlorophyll *a* and primary production (Smith and Hall 1997). Heterotrophic bacteria made a large contribution to total community biomass and the bacterial biomass was almost double in the ST waters than in the SA waters. The results from Smith and Hall's study suggest that in New Zealand oceanic water masses bacteria are of significant biogeochemical importance. It is therefore likely that the bacteria may contribute positively to the discrepancy in the ligand concentrations between the ST and SA waters found in the present study.

Iron availability

It has not yet been possible to define which forms of Fe (organic complex Fe(III), inorganic Fe(III), Fe(III) or particulate Fe) are more bioavailable. At the end of the SOIREX experiment, Fe(II) appeared to comprise the major portion of dissolved Fe species (Croot *et al.* 2001), implying a previously unheralded importance for Fe(II) and organic complexation in the Southern Ocean. However, the CSV method used in the present study is not able to measure the redox speciation (Fe(II)/Fe(III)).

A previous study in the same frontal zone (Boyd *et al.* 1999) showed that primary production was dominated by cells $< 2 \mu\text{m}$ (cyanobacteria) in SA waters. In contrast, STC and ST waters had higher algal biomass/production levels. *In vitro* Fe enrichment incubations in SA waters indicated the alleviation of Fe stress, also the iron-mediated increases in chlorophyll *a* (in particular, increases in large diatoms). In spring, irradiance and Fe may both control diatom growth, whereas during summer, as mean irradiance increases and silicate concentrations decrease, Fe limitation, Fe/Si colimitation, or silicate limitation may constrain diatom growth.

Calculation of the chemical speciation based on the thermodynamic equilibrium shows that Fe is fully ($> 99.9\%$) complexed by organic ligands throughout the waters studied. The ratio of organic/combined inorganic Fe ($[FeL]/[Fe'] = \alpha_{FeL}/\alpha_{Fe'}$) is $10^{3.8}$, which means the inorganic dissolved Fe concentrations are on average over three orders

Table 3. Overview of the organic speciation of iron: concentrations of dissolved iron, the ligands- L_T , conditional stability constants (with respect to Fe^{3+}) and α -coefficients for complexation by L (α_{FeL}) compiled from the literature
The analytical detection (DW) is indicated

Area	Location	Filter (μm)	Depth (m)	DW	$\log \alpha'_{Fe}$	Fe (nM)	L_T (nM)	$\log K'_{FeL, Fe^{3+}}$	$\log \alpha_{FeL}$	Reference
South Ocean	40°–46°S, 178°30'E	0.2	Surface	12	10	0.1–0.84	1.20 ± 0.33	22.75 ± 0.18	13.8	This study
Southern Ocean	50°–60°S, 6°E	0.4	25–1500	12	10	0.1–0.6	0.9–3.0	21.4–23.5	13.8	Croot <i>et al.</i> (2004)
Atlantic sector										
Eastern north Atlantic	42°–51°N, 2°–23°W	0.2	Surface	13	10	0.6–1.9	2.43 ± 0.85	20.8 ± 0.25	12.2	Boye <i>et al.</i> (2003)
Southern Ocean	48°5'–70°S, 20°E	0.2	20–4500	13	10	0.25 ± 0.13	0.72 ± 0.23	22.1 ± 0.5	12.9	Boye <i>et al.</i> (2001)
Atlantic sector										
Arabian Sea	14°–18°N, 59°–65°W	0.4	25–600	13	8.9	1.51 ± 0.37	1.7 ± 0.22	21.9 ± 0.1	13.1	Witter <i>et al.</i> (2000b)
Southern Ocean	58°–68°S, 90°W	Unf.	25–800	11	11.9	1.71 ± 0.31	6.33 ± 1.16	22.5 ± 0.9	14.3	Nolting <i>et al.</i> (1998)
Pacific sector						0.14–0.72	2–12	20.6–21.6	12.4–13.2	
Northwestern Atlantic	38°09'N, 72°42'W	0.2	Surface	13	10	0.5–1.9	2–5	22.2–22.9	14.0	Witter and Luther (1998)
North Sea	56°30'–61°30'N, 59°–65°W	0.4	0–70	11	8.5	0.6–5	2.3 ± 0.4	20.3 ± 0.6	11.7	Gledhill <i>et al.</i> (1998)
							39.2 ± 0.5	21.4 ± 0.3	14.0	
North Pacific	22°45'N, 158°W	0.2	0–110	12	10	0.24 ± 0.05	[L_1] = 0.44	23.08	13.7	Rue and Bruland (1995)
			500–2000			0.72 ± 0.05	[L_2] = 1.0	21.48	12.5	
Central Gyre HNLC	04°08'S, 104°57'W	0.4	Surface	12	11	0.015–0.037	[L_1] = 0.31	22.67	13.2	Rue and Bruland (1997)
region of the							[L_2] = 0.19	21.81	12.1	
Equatorial Pacific										
Western	38°7'N, 4°66'W	0.4	0–165	13	11.5	3.1	4.0–12	21.3–22.5	13.7	van den Berg (1995)
Mediterranean	36°41'N, 12°19'E		400–2500			2.6	6.4–7.8	19.79–20.38	11.9	
North Atlantic	35°3'N, 19°58'W	0.4	80–100	10	8.5	1.6–1.8	3.5–4.8	19.0	10.6	Gledhill and van den Berg (1994)
	42°17'N, 20°02'W	0.4	800–1000			0.8–0.85	3.0–5.0	19.6	11.2	

Unf., Unfiltered. L_1 and L_2 represent two different types of ligands.

of magnitude lower than the dissolved Fe concentrations. In spite of the higher dissolved Fe concentration, the free inorganic Fe concentration Fe' is only $\sim 0.2 \mu M$, well below the value ($2\sim 10 \mu M$) required to meet the metabolic demands for growth of oceanic phytoplankton (Sunda and Huntsman 1995; Trick and Wilhelm 1995). Although the estimation of Fe' provides an indication of the size of the most labile Fe pool available to bacteria and phytoplankton, evidence exists for the ability of phytoplankton and bacteria to access Fe from some Fe organic complexes (Hutchins *et al.* 1999; Maldonado and Price 2001; Barbeau *et al.* 2003). Recently, Maldonado *et al.* (2005) demonstrated that Fe within their model ligands is available for uptake and growth by indigenous plankton, but that photolability of those complexes does not determine Fe bioavailability. In contrast, light significantly enhances Fe acquisition from the *in situ* ligands. Comparison of the Fe' concentrations in the different water masses shows high Fe' at the Chatham Rise transect, which could partly explain the high primary production over that area. In general there was only a weak relationship between Fe' and the chlorophyll *a* data.

The sources and chemical structures of the Fe-complexing ligands are presently unknown, although it is clear that they must be of biogenic origin. Although early work suggested that phytoplankton access only inorganic forms of Fe, it is now understood that diatoms are able to utilise Fe bound to several organic chelators like siderophores via thermal, photochemical and cell surface reductase mechanisms (Kuma *et al.* 2000; Maldonado and Price 2001; Barbeau *et al.* 2003). Evidence of Fe–siderophore use by marine heterotrophic bacteria and cyanobacteria has also been obtained (Granger and Price 1999; Hutchins *et al.* 1999). If, indeed, the organic Fe chelators in the Southern Ocean are predominantly of bacterial origin, prokaryotic microbes may play a significant role in controlling the availability of dissolved Fe, thus regulating production of eukaryotic phytoplankton. Future work is required on Fe uptake by a variety of bacteria and phytoplankton in the laboratory and in the field as well as characterisation of the Fe-binding ligands to provide better understanding of the biogeochemistry of Fe in seawater.

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