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The distribution of dissolved zinc in the Atlantic sector of the Southern Ocean

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ABSTRACT

The distribution of dissolved zinc (Zn) was investigated in the Atlantic sector of the Southern Ocean in the austral autumn of 2008 as part of the IPY GEOTRACES expedition ZERO & DRAKE. Research focused on transects across the major frontal systems along the Zero Meridian and across the Drake Passage. There was a strong gradient in surface zinc concentrations observed across the Antarctic Polar Front along both transects and high zinc levels were found in surface waters throughout the Southern Ocean. Vertical profiles for dissolved Zinc showed the presence of local minima and maxima in the upper 200 m consistent with significant uptake by phytoplankton and release by zooplankton grazing, respectively. Highest deep water zinc concentrations were found in the centre of the Weddell Gyre associated with Central Intermediate Water (CIW), a water mass which is depleted in O_2, elevated in CO_2 and is regionally a CFC minimum. Our data suggests that the remineralization of sinking particles is a key control on the distribution of Zn in the Southern Ocean. Disappearance ratios of zinc to phosphate (Zn:P) in the upper water column increased southwards along both transects and based on laboratory studies they suggest slower growth rates of phytoplankton due to iron or light limitation. Zinc and silicate were strongly correlated throughout the study region but the disappearance ratio (Zn:Si) was relatively uniform overall except for the region close to the ice edge on the Zero Meridian.

1. Introduction

1.1. Dissolved zinc in the ocean

Zinc (Zn) is a required metal for bacteria and phytoplankton in the ocean as it serves as a metal cofactor for many important processes (Vallee and Auld, 1990, 1993). Most notably Zn is utilized for both nucleic acid transcription and repair proteins (Anton et al., 2007), in the enzyme alkaline phosphatase (Hove et al., 1940; Shaked et al., 2006) and for the uptake of CO_2 via the enzyme carbonic anhydrase (CA) (Hu et al., 2003; Morel et al., 1994). Zn is however a minor component ($\sim$70 ppm) of continental crust (Rudnick and Gao, 2003; Taylor and McLennan, 1985) but can be enriched in aerosols and rainwater due to anthropogenic processes (Nriagu and Pacyna, 1988). Measurement of Zn in the ocean is complicated by contamination issues (Fitzwater et al., 1982) as Zn is ubiquitous in the laboratory and is typically used as sacrificial anodes on equipment deployed in seawater. The first reliable trace metal data for Zn were collected by Bruland and co-workers (Bruland, 1980; Bruland et al., 1979) and showed two important features: (1) that Zn was present in surface waters in the North Pacific at extremely low concentrations (<1 nM) and (2) that the vertical profile of Zn was strongly correlated to the macronutrients (Si, NO_3^- and PO_4^{3-}), suggesting a role for Zn in oceanic biogeochemical cycles.

Initial laboratory studies examining the influence of Zn on phytoplankton growth showed that coastal species could be Zn limited (Anderson et al., 1978; Brand et al., 1983; Sunda and Huntsman, 1992 and that Zn was important for silicate uptake in diatoms (Rueter and Morel, 1981). These results led Morel and co-workers to suggest the 'Zn hypothesis' (Morel et al., 1994), analogous to the iron hypothesis of Martin and Fitzwater (1988), by which low Zn concentrations could limit CO_2 uptake and ultimately growth rate in some cells via the absence of the enzyme CA. Limitation by Zn has also been linked to low rates of phosphate uptake from dissolved organic phosphorus in oligotrophic waters via its central role in the enzyme alkaline phosphatase (Shaked et al., 2006). Overall the laboratory studies have strongly suggested that Zn limitation in the ocean could be a strong control on phytoplankton productivity and nutrient cycles.

In contrast to iron limitation there have been few studies examining Zn limitation with natural phytoplankton communities and in general there have only been minimal effects on the bulk community observed (Coale, 1991; Coale et al., 2003; Cochlan et al., 2002; Crawford et al., 2003; Ellwood, 2004; Franck et al., 2003, 2000; Gall et al., 2001; Leblanc et al., 2005; Scharek et al., 1997). In the HNLC North Pacific (Coale, 1991; Crawford et al., 2003; Leblanc et al., 2005) incubations of ambient seawater with additional Zn have seen small to no chlorophyll increases, but induced subtle changes in the composition of the phytoplankton community. Studies in the low silicate HNLC subAntarctic zone (Leblanc et al.,

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2005) indicated that Zn additions saw changes in the silicate limited diatom community with a shift from a large colonial pennate (*Pseudonitzschia sp.*) to a smaller less silicified pennate (*Cylindrotheca closterium*). In a study encompassing 3 HNLC regions (Franck et al., 2003), Zn additions were found to only influence Si and NO_3^- uptake kinetics at Big Sur, off the Californian coast, while for the Southern Ocean and the Eastern Tropical Pacific it was suggested that no effect was seen due to the lack of Zn limitation in those waters. Evidence for Zn limitation in the open ocean is apparently complicated by the more widespread phenomena of iron limitation.

The Zn taken up into diatom cells is mostly found in the soft parts with only 1–3% being found in the diatom frustules (Ellwood and Hunter, 2000a). It is suggested that the Zn incorporated into the diatom frustule records the Zn speciation in the seawater at the time of growth (Ellwood and Hunter, 1999, 2000a) and the resulting Zn:Si ratio of the diatom opal can be used for paleo interpretations of Zn speciation in the ocean (Ellwood and Hunter, 2000b). Using this approach it has recently been suggested (Hendry and Rickaby, 2008) that changes in Zn:Si in the Antarctic peninsula over the last 100 years is related to recent ice melt that influences the Zn speciation in surface waters.

1.2. The Zero Meridian and Drake Passage study region—water masses

The physical oceanography of the Atlantic sector of the Southern Ocean has been extensively reviewed (Orsi et al., 1995; Veth et al., 1997; Whitworth and Nowlin, 1987) and the reader is referred to these works for more detailed information. Here we provide a short description of the relevant water masses and processes. Earlier investigations have found that biological activity in the Southern Ocean is strongly linked to frontal systems (Bathmann et al., 1997; Lutjeharms and Valentine, 1984; Pakhomov et al., 2000; Read et al., 2002; Turner et al., 2004) where the Subtropical Front and the Polar Front are shown to be the areas of the most intense activity.

1.2.1. Frontal systems in the Southern Ocean

For an overview of the location of the various frontal systems throughout the entire Southern Ocean the reader is referred to a recent study (Sokolov and Rintoul, 2009) where the location of the frontal systems was identified from sea surface height data. In the following description of the Southern Ocean physical oceanography we concentrate on the previous studies in the Atlantic sector.

The Subtropical Front (STF) defines the northern boundary of the Southern Ocean and separates the warm, salty temperate surface waters from cold subAntarctic waters (Orsi et al., 1995; Whitworth and Nowlin, 1987). Along the Zero Meridian the STF is commonly observed between 41°S and 42°S, as evidenced by its large salinity and temperature gradients and often elevated chlorophyll a concentrations (Lutjeharms and Valentine, 1984; Read et al., 2002). South of the STF is the eastward flowing Antarctic Circumpolar Current (ACC), which is dominated by two major fronts, the SubAntarctic Front (SAF) and the Antarctic Polar Front (APF) (Orsi et al., 1995; Whitworth and Nowlin, 1987). The SAF is an important biogeographical boundary separating Antarctic and subAntarctic/subtropical groups of zooplankton (Pakhomov et al., 2000). The position of the SAF ($S<34.2\theta>4-5$ °C) has been reported between 45°S and 48°S in this region (61°W–61°E) (Lutjeharms and Valentine, 1984; Pakhomov et al., 2000; Read et al., 2002) and the spatial variability of this front is apparently related to a number of standing meanders as the SAF passes through a complex topography (Sokolov and Rintoul, 2009). The SAF also indicates the location of the rapid northward sinking of the salinity minimum associated with Antarctic Intermediate Water (AAIW), from near the surface in the Polar Front ($S<34$) to depths greater than 400 m in the SAZ ($S<34.30$) (Orsi et al., 1995). The zone between the STF and the SAF is referred to as the SubAntarctic zone (SAZ), and surface water (SubAntarctic surface water—SASW) stratification in this region is controlled mainly by temperature. Biological production has been suggested to be limited by silicate in the SAZ, but also across the ACC (Pollard et al., 2002).

The APF is defined from either the sub-surface or surface expression for $\theta<2$ °C and the location of the APF varies between 49°S and 51.5°S in the region of the Zero Meridian (Lutjeharms, 1985; Lutjeharms and Valentine, 1984; Orsi et al., 1995; Read et al., 2002; Turner et al., 2004; Veth et al., 1997; Whitworth and Nowlin, 1987). The cold surface water in the APF, termed the Antarctic Surface Water (AASW), reaches all the way to the Antarctic Continental Shelf (Orsi et al., 1995) Below the AASW is a saltier and more nutrient-rich water mass called the Circumpolar Deep Water (CDW) (Orsi et al., 1995). The CDW is derived from North Atlantic Deep Water (NADW) and covers most of the area from the APF to the Weddell Gyre (Veth et al., 1997). In this region biological production is not limited by the macronutrients, nitrate and phosphate but instead is iron limited (Croot et al., 2004; de Baar et al., 1995) as has been clearly shown in meso-scale iron enrichment experiments in this region (Croot et al., 2005; Gervais et al., 2002; Hoffmann et al., 2006). The area between the SAF and the APF is referred to as the Polar Frontal Zone (PFZ) (Pollard et al., 2002; Whitworth and Nowlin, 1987) where salinity is equally as important as temperature in regulating surface water density and stratification, and primary production has been shown to be also limited by silicate availability (Pollard et al., 2002).

Along the Zero Meridian a further front, the Southern Polar Front (SPF), is found south of the APF at 56°S. Veth et al. (1997) found at 6°W that the main current is flowing parallel to the America–Antarctica Ridge and that the SPF coincides with the average northern slope of the ridge and the ACC–Weddell Gyre Boundary Front (see below) with the average southern slope. The southern boundary of the ACC, also called the continental water boundary (CWB), is defined where the upper part of the CDW (UCDW) signal enters the surface mixed layer at around 62°S, where it mixes with the fresher and colder AASW ($S<34.40$, $\theta<0.5$ °C) (Orsi et al., 1995; Pollard et al., 2002; Whitworth and Nowlin, 1987). In the vicinity of the Zero Meridian this coincides with a frontal feature separating the ACC and the Weddell Gyre (Veth et al., 1997) and here it is specifically called the Weddell Gyre Boundary. The UCDW is characterized by low oxygen and high nutrient concentrations and is found above the much saltier ($S>34.70$) Lower Circumpolar Deep Water (LCDW) (Orsi et al., 1995). When UCDW water mixes with SASW it brings macronutrients and iron to the surface, which can fuel phytoplankton blooms. South of this boundary, between 62°S and the continent, is the Weddell Gyre (WG) (Veth et al., 1997), also referred to as the zone south of the ACC (SACCZ) by Pollard et al. (2002).

The Antarctic bottom water (AABW) is the coldest and the most dense water mass in the world ocean with over 60% of it formed in the Weddell Sea (Orsi et al., 1999). The AABW is formed in the southern and western margins of the Weddell Basin from Weddell Sea Deep (WSDW; -0.7 °C $<\theta<0$ °C) and Bottom Water (WSBW; $\theta<-0.7$ °C), which are produced via interactions of warmer mid-depth and surface water masses with different shelf waters (Huhn et al., 2008). Warm deep water (WDW; $\theta>0$ °C) is LCDW advected into the Weddell Basin after splitting from the ACC and entering the Weddell Gyre at 20–30°E (Hoppema et al., 1997; Klatt et al., 2002; Orsi et al., 1995).

The water masses in the Drake Passage are similar to those outlined above (Barre et al., 2008; Sprintall, 2003; Thompson et al., 2007) though a further deep water mass has been identified by ^{3}He anomalies (Well et al., 2003) that exist between UCDW and LCDW

and is of South Pacific origin. Meso-scale eddy activity can be important in the Drake Passage and throughout the ACC (Kahru et al., 2007). The Drake Passage has also been identified as a 'hot spot' for diapycnal mixing (Garabato et al., 2004) due to the influence of rough bottom topography on the strong current flows in this region.

1.3. Aim and scope of this work

As part of the International GEOTRACES program and as a contribution to the International Polar Year (IPY), a major international research expedition was undertaken in the Southern Ocean using the icebreaker *Polarstern*. The vessel departed Cape Town, South Africa, on the 10th of February 2008, headed south along the Zero Meridian, through the Weddell Sea and across the Drake Passage and finally arrived in Punta Arenas, Chile, on April 16, 2008. The major focus of this cruise was to examine the distribution and speciation of key trace elements and their isotopes (TEIs) in the Southern Ocean. The work reported here focuses on the distribution of zinc, a potentially important bio-element for primary production. A companion paper focuses on simultaneous measurements of zinc speciation (Baars and Croot, 2011). The overall aim of this work was to improve our understanding of the Southern Ocean biogeochemistry of zinc and related elements (see other papers this issue).

2. Materials and methods

2.1. Hydrographic setting

Samples were collected during the IPY GEOTRACES cruise, ANTXXIV-3 (Cape Town, South Africa, to Punta Arenas, Chile), from 10 February to 16 April 2008 onboard the German research vessel *R.V. Polarstern*. The cruise track consisted of 3 transects: (i) along the Zero Meridian, (ii) across the Weddell Sea and (iii) across the Drake Passage (shown in Fig. 1).

2.2. Water sampling

Seawater samples were obtained using the TITAN trace metal clean rosette system of the NIOZ (de Baar et al., 2008). In brief this sampling system consists of a rectangular titanium rosette fitted with a standard Seabird CTD in a titanium housing and 24 modified 12 L Teflon coated GO-FLO bottles (General Oceanics, Miami, FL, USA). The rosette was deployed on a specially made trace metal clean Kevlar wire (17.7 mm) complete with internal conducting cables. Sample bottles were tripped on the upcast using standard Seabird CTD software. Upon recovery of the rosette the complete rosette was carefully moved into a Class 100 clean room container specially built for sub-sampling from this system. Care and maintenance of the GO-FLO bottles was performed by NIOZ technicians using established protocols (Bruland et al., 1979). In the sampling clean room, filtered water samples were collected using slight N_2 overpressure and filtration through 0.2 μm filter cartridges (Sartorius) from the relevant GO-FLO into 1 L acid-cleaned low density polyethylene bottles for later analysis (acidified onboard with Q-HCl, 2 mL per L) in the laboratory in Kiel. Dissolved inorganic phosphate, silicate, nitrate and nitrite were analysed onboard by NIOZ using a TrAAcs 800 Auto-analyser from Bran & Luebbe (Norderstedt) by standard methods described in Grasshoff et al. (1999). Analytical work at sea for zinc was carried out in an over-pressurized class 5 clean air container (IFM-GEOMAR).

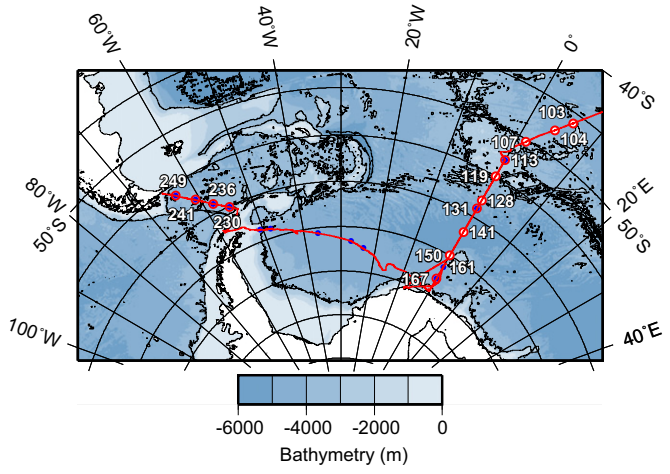

Fig. 1. Location of stations sampled for zinc during the research expedition ZERO & DRAKE (ANTXXIV-3).

Table 1
Zn analysis performance parameters.

Sample	[Zn] (nmol L^{-1})	Blank (nmol L^{-1})	Reference
NASS-5	2.00	0.07 ± 0.04	This study
	1.56 ± 0.60		CRM NRCC
SAFE S	< 0.03	0.07 ± 0.04	This study ($n=2$)
	0.09 ± 0.04	0.09 ± 0.04	Ellwood (2008)
	n.d.	0.07 ± 0.04	Sohrin et al. (2008)
	0.068 ± 0.014		GEOTRACES consensus value
SAFE D2	7.29 ± 0.52	0.07 ± 0.04	This study ($n=4$)
	6.84 ± 0.26	0.09 ± 0.04	Ellwood (2008)
	7.45 ± 0.28	0.07 ± 0.04	Sohrin et al. (2008)
	7.19 ± 0.70		GEOTRACES consensus value

Notes: 95% confidence intervals are presented (2σ). The GEOTRACES consensus values are found at http://www.ldeo.columbia.edu/res/pi/geotraces/documents/SAFeReferenceSample-Zn.pdf, and consensus values for the SAFe reference samples are indicated above.

2.3. Total dissolved zinc determination

Samples were analyzed in the laboratory by graphite furnace atomic absorption (ETAAS, Perkin-Elmer Model 4100ZL) after pre-concentration by simultaneous dithiocarbamate-freon extraction, from seawater (100–250 g) (Danielsson et al., 1978). The accuracy of the analytical procedure was evaluated by measurement of the certified seawater standard NASS-5 (National Research Council of Canada), and the SAFe intercalibration samples S and D2; details of these analyses are found in Table 1.

3. Results

3.1. Distribution of dissolved zinc in the Atlantic sector of the Southern Ocean

3.1.1. Zero (Greenwich) Meridian

The hydrographic conditions encountered during ANTXXIV-3 along the Zero Meridian are shown in Fig. 2. Vertical profiles of dissolved Zn (TDZn) concentrations are shown for the Zero Meridian section in Fig. 3. At all stations Zn was at a minimum in the upper water column and increased with depth. There was a marked Zn increase from north to south with peak concentrations at S141. Two strong Zn gradients were observed along this transect. The first pronounced Zn change was detected when the APF was crossed at ~50°S between S104 and S107 in the upper 1000 m.

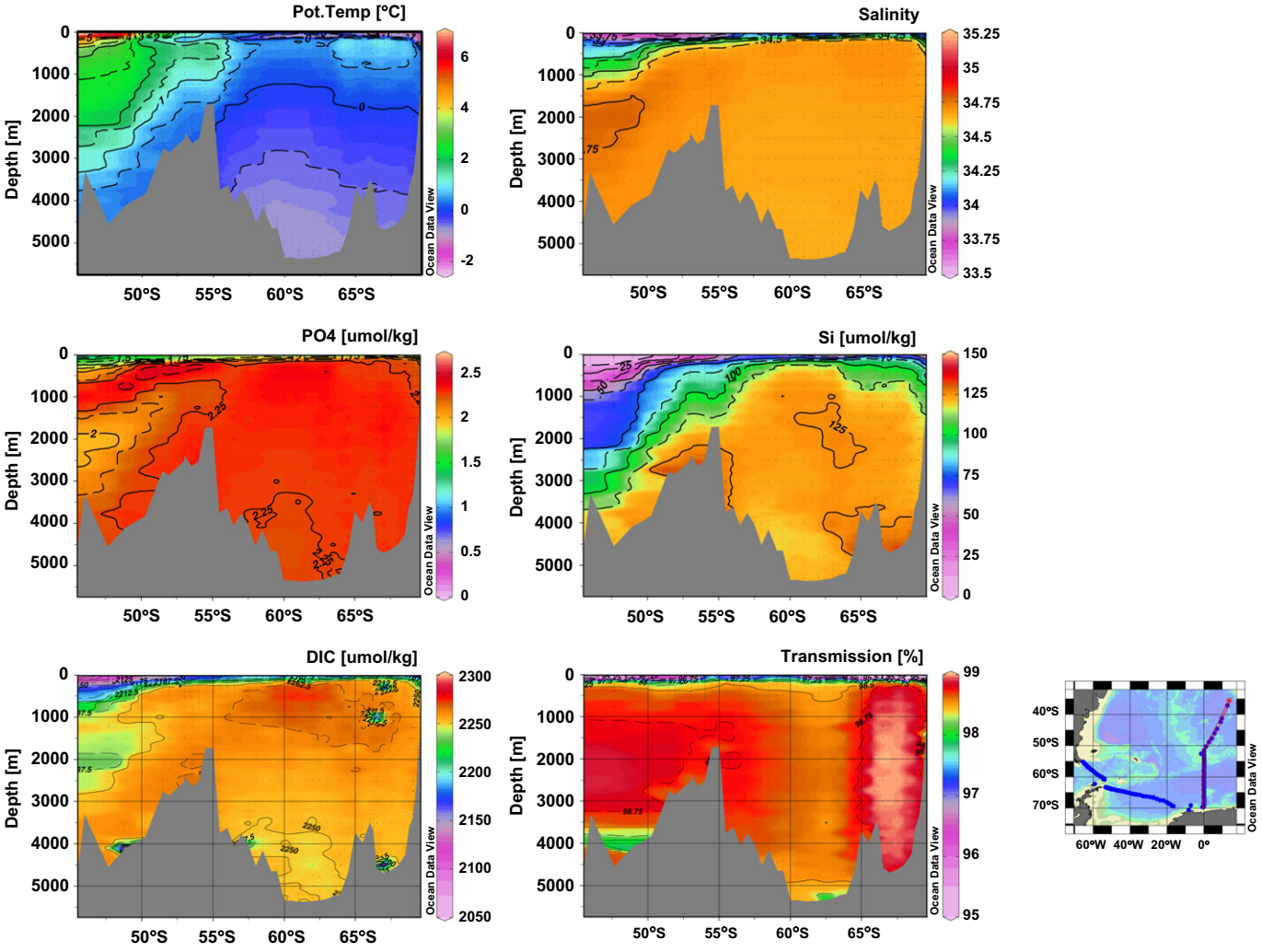

Fig. 2. Distribution of (top left) potential temperature, (top right) salinity, (bottom left) phosphate and (bottom right) silicate along the Zero Meridian during ANTXXIV-3.

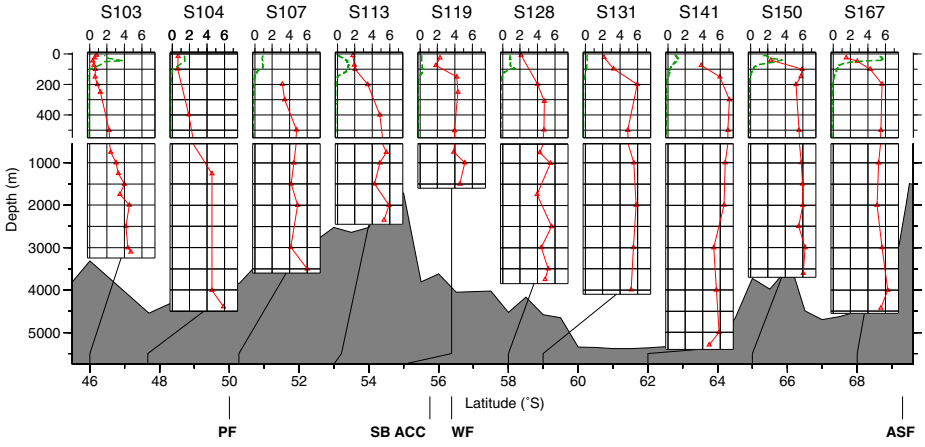

Fig. 3. Distribution of Zn along the Zero Meridian during ANTXXIV-3.

Secondly there was a steep gradient between S128 and S141 stretching over the whole water column. Further south than S141 near surface Zn values decreased again slightly at intermediate depths. The lowest Zn concentrations within the upper 200 m were found north of the APF at S103 (0.21 nM in 45 m) while surface waters south of the APF Zn was always >1 nM. A major plankton bloom had been present along the Zero Meridian in January 2008 from 60°S to 65°S (Bluhm et al., 2011), though by the time of our transit (February–March 2008) the bloom was greatly reduced in its surface coverage and shifted closer to the Antarctic continent (see below). In the region covered by this high phytoplankton activity we occupied three stations: S141, S150

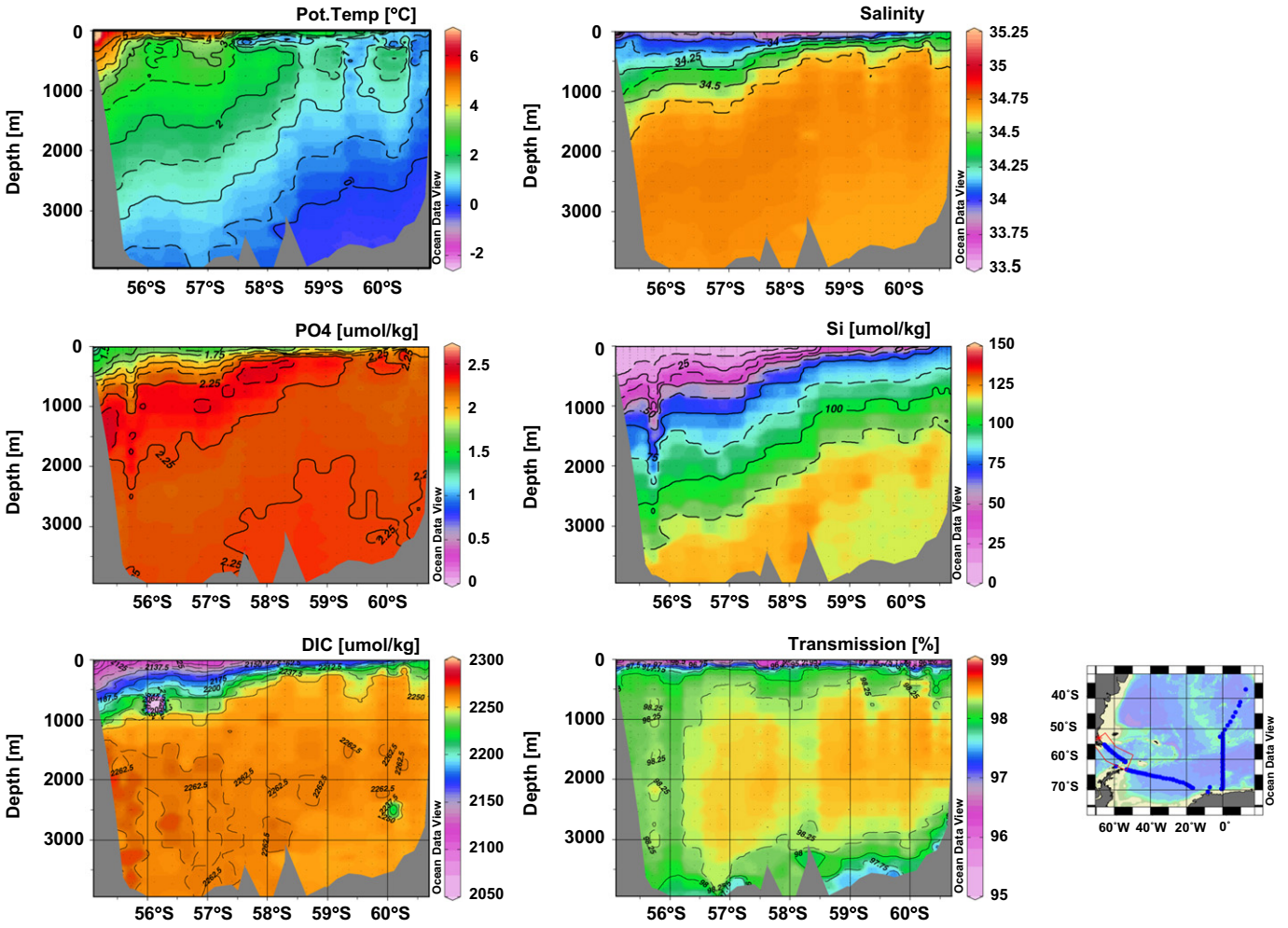

Fig. 4. Distribution of (top left) potential temperature, (top right) salinity, (bottom left) phosphate and (bottom right) silicate across the Drake Passage during ANTXXIV-3.

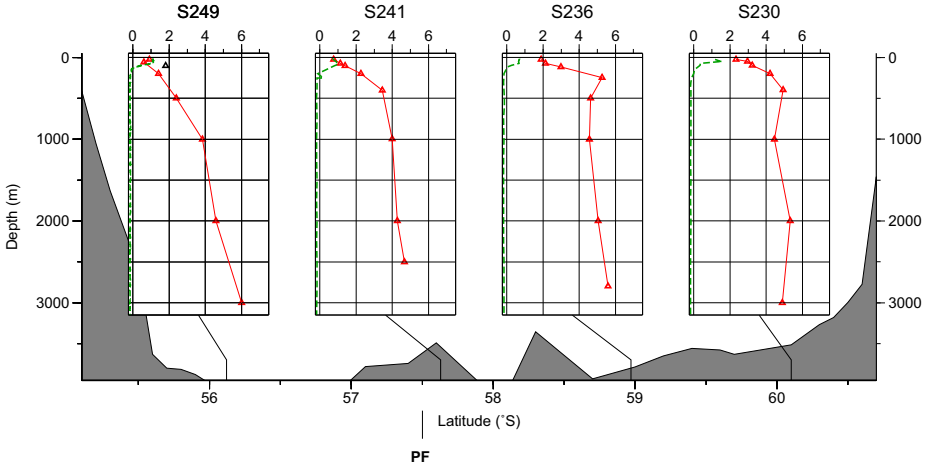

Fig. 5. Distribution of Zn across the Drake Passage during ANTXXIV-3.

and S167. For all of these stations Zn in the upper water column did not fall below 1 nM, though strong vertical gradients for Zn existed (Fig. 3). At the more northerly stations, S103, S104 and S119 sub-surface minima were observed at depths between 50 and 100 m with a concentration decrease of about 0.4 nM compared to the top sample in the water column. In contrast, between S131 and S167 sub-surface maxima could be found at depths from 100 to 300 m.

Deep water Zn concentrations increased with latitude with the highest concentrations in WDW in the Weddell Gyre and in the LCDW/AABW that flowed out of the Weddell Bain into the South East Atlantic (Fig. 3).

Table 2
Zn:P (nmol:μmol) ratios in other studies including locations.

Location	*Slope*	*Intercept*	R^2	*n*	Reference
North Pacific					
< 500 m	1.575 ±	−0.56 ±	0.900	15	Bruland (1980)
North Atlantic					
< 500 m	2.557 ±	1.257 ±	0.200	19	Yeats and Campbell (1983)
Southern Ocean					
Ross Sea					
Southern stations < 500 m	5.314 ±	−6.454 ±	0.825	23	Fitzwater et al. (2000)
Northern stations < 500 m	7.525 ±	−10.948 ±	0.811	19	Fitzwater et al. (2000)
Weddell Sea					
< 500 m	8.195 ±	−9.377 ±	0.365	51	Nolting et al. (1991)
< 500 m	4.008 ±	−4.67 ±	0.146	111	Westerlund and Öhman (1991)
Atlantic 6°W					
South of polar front 49° 59′ S	2.243	−1.114	0.420	37	Löscher (1999)
North of PF	3.730	−2.722	0.211	55	Löscher (1999)
Drake Passage					
< 500 m (south of PF)	5.977 ±	−10.354 ±	0.965	8	Martin et al. (1990a)
Overall < 500 m	4.857 ±	−6.625 ±	0.728	65	This study
Zero Meridian < 500 m	4.820 ±	−6.32 ±	0.766	46	This study
Drake Passage < 500 m	5.271 ±	−8.018 ±	0.731	19	This study
Zero north of PF	1.667 ±	−1.688 ±	0.753	12	This study
Zero south of PF; north of WG	3.800 ±	−4.810 ±	0.863	12	This study
Zero south of WG	6.888 ±	−10.221 ±	0.811	22	This study
Drake north of PF	3.533 ±	−5.254 ±	0.974	9	This study
Drake south of PF	5.892 ±	−8.762 ±	0.872	10	This study

3.1.2. Drake Passage

The hydrographic conditions we observed during ANTXXIV-3 across the Drake Passage are shown in Fig. 4. The Zn concentrations in the Drake Passage (Fig. 5) were similar to the Zero Meridian section, with significant increases in the upper 1000 m south of S241, which was approximately the location of the APF (~57.5°S). From S249 to S241, Zn decreased within the upper 100 m leading to the lowest concentrations at S241 (0.21 nM in 25 m). The northernmost station (S249) was characterised by a shallow sub-surface minimum with a Zn decrease of ~0.30 nM from 25 to 50 m. At three stations (S249, S236, S230) sub-surface maxima were visible in the profiles at depths of 100, 250 and 400 m.

3.2. Zn to nutrient ratios in the water column

In the following sections, we compare vertical profiles of Zn with the corresponding macronutrient data. We use the term disappearance ratio (Arrigo et al., 1999) to describe the slope of the correlation between zinc and macronutrients. This term is equivalent to other terms commonly used such as uptake ratio or extended Redfield ratio.

3.2.1. Zn:P

Dissolved Zn was not strongly correlated with phosphate over the whole water column, either on a station by station basis or for the full dataset as phosphate concentrations varied little in the deep waters (Figs. 2 and 4), while Zn concentrations increased towards the south along both transects. However strong correlations ($R^2 > 0.9$) were found between dissolved Zn and phosphate in the biologically active upper ocean (0–400 m) along both transects. On a station by station basis, the Zn:P ratio (nmol:μmol) in the upper water column (0–400 m) increased with latitude from ~2 north of the PF to ~7 in the Weddell Gyre for both the Zero Meridian and the Drake Passage transects.

3.2.2. Zn:Si

For the complete dataset in this work, we found a significant Zn versus Si correlation for in the Southern Ocean (Table 3 and Fig. 7). Separate linear regressions of data from the Zero Meridian and the Drake Passage resulted in almost identical slopes and intercepts (Table 2). The overall Zn:Si relation was Zn (nM) = 0.039 Si (μM) + 0.437 ($R^2 = 0.821$, $n = 121$). Both parameters were in the broad range of values reported previously from the Southern Ocean. For separate stations the slopes remained relatively constant (0.023–0.056) while intercepts varied on a larger scale (–1.84 to 2.15). Negative intercepts were found at S128, S131 and S167. The highest Zn:Si slopes were observed at S150 and S167 in the upper 200 m where a phytoplankton bloom had been present over the last 3 months (Bluhm et al., submitted for publication). The relationship between Zn and Si was non-linear in more southerly deep waters (> 500 m) of the Weddell Gyre where Si reached almost constant concentrations of ~125 μM while Zn varied slightly.

4. Discussion

4.1. Controls on the distribution of dissolved zinc in the Southern Ocean

4.1.1. Zero Meridian

Previous work in this region concentrated on the APF region (Löscher, 1999) where a strong surface gradient in dissolved Zn was observed. Our data for this region compare favourably with the earlier work though we did not find Zn concentrations above 7 nM anywhere along our transects, while Löscher reports such values in LCDW at several stations. These differences may be related to local enrichment or analytical differences. Löscher also reported local sub-surface maxima for Zn at the pycnocline in the vicinity of the ACC at 52° and 53°S, which were attributed to the release of sea ice diatoms from melting sea ice and subsequent remineralization releasing Zn. Such seasonal differences in the near surface distribution may be important as the Löscher work was performed in spring while ours was in autumn.

Distinct local minima in the vertical profiles of Zn were seen in several profiles (S103, 104, S119) associated with the chlorophyll maximum and indicate uptake of Zn by phytoplankton in the

euphotic zone but below the active mixed layer (Brainerd and Gregg, 1995). Interestingly it also strongly suggests slow physical mixing in the water column at these depths in order to maintain this gradient (Croot et al., 2007). As these stations were either north of the APF (S103 and S104) or in the centre of the ACC zone it suggests that this is more likely to occur in zones of low current shear.

Local maxima in dissolved Zn were also found at a southerly station along the transect (S150). At S150 the maximum is clearly seen in the water depth range 100–200 m. This corresponds to a shallow zone of strong remineralization that has been seen in this region with ^{234}Th (Usbeck et al., 2002) and previously was identified as a layer with elevated TCO_2/reduced oxygen found in the central part of the Weddell Gyre and termed as Central Intermediate Water (CIW) (Whitworth and Nowlin, 1987). The intense Si recycling in the surface layer is due to the strong remineralization of sinking material (Beucher et al., 2004) due to a combination of small iron limited phytoplankton and a zooplankton grazing community dominated by copepods or salps, which are producing rapidly dissolving fecal pellets (Usbeck et al., 2002 and references therein). A related hypothesis is that the biogenic opal has a high dissolution rate due to a lower Al:Si ratio (van Bennekom et al., 1991). Zinc is known to be assimilated directly from diatoms by grazing copepods (Wang et al., 2001) while simultaneously released by the direct action of zooplankton grazing (Hutchins and Bruland, 1994) or released later from sinking fecal pellets (Small and Fowler, 1973). Temporal and spatial changes in the abundance of salps versus copepods/krill (Atkinson et al., 2004; Pakhomov, 2004) may be important in the recycling of trace metals, as the copepod fecal pellets may sink faster (Dubischar and Bathmann, 1997) and release less material in the upper water column than those of salps. Interestingly during this expedition, measurements of ^{234}Th (Rutgers van der Loeff et al., 2011) indicated that remineralization of Th in the late summer was less intense in this region than observed previously in the autumn (Usbeck et al., 2002). Comparison with ^{234}Th (Rutgers van der Loeff et al., 2011), Mn (Middag et al., 2011) and Fe (Klunder et al., 2011) data from this cruise suggests that Zn is more easily remineralized from marine particles and/or scavenged less than these other more particle reactive elements in this region.

In the centre of the Weddell Gyre (60°–64°S), in the region of the CIW and WDW, is where the highest silicate concentrations were found (>124 μM) during this expedition. Previous expeditions along the Zero Meridian have also repeatedly identified this region as a CFC minima (Klatt et al., 2002) where a westward flow brings deep water into the interior of the Weddell Gyre (Klatt et al., 2005). It is in this CFC minimum that we find the highest deep water Zn concentrations (S141) overall and from Fig. 3 it appears that these high values are confined to the WDW as concentrations decrease in the WSDW and WSBW. Bottom water enrichments of silicate in this region can be variable with import of remotely formed WSDW (Hoppema et al., 1998; Hoppema et al., 2001) with higher dissolved Si due to input from the opal rich sediments of the Enderby Basin (Van Beusekom et al., 1997). The Zn maxima at S141 found in the WDW is therefore more consistent with the dissolution of material from the surface layers as has been seen for silicate earlier (Rutgers van der loeff and van Bennekom, 1989). Thus it appears that the process captured at S150 at shallow depths is responsible for the more widespread Zn enrichment at S141. The lack of a shallow Zn maximum at S141 may be related to the presence of a phytoplankton bloom in this location in early January 2008, which had dissipated by the time of our occupation, while a significant bloom was still maintained at S150 at the time of sampling (see also related papers in this issue (Bluhm et al., 2011; Rutgers van der Loeff et al., 2011)).

4.1.2. Drake Passage

There have been several previous studies for dissolved Zn in the vicinity of the Drake Passage, Antarctic Peninsula and Western Weddell Sea. Our data are almost identical to the earlier work of Martin et al. (1990b) in the Drake Passage, whose stations were located slightly to the east of our transect. In both our study and in the Martin et al.'s work, Zn vertical profiles are smooth and similar to the macronutrients. Other studies from the Weddell Sea region have shown similar concentrations though much more scatter in the Zn data (Westerlund and Öhman, 1991) or significantly higher concentrations indicating possible contamination (Nolting and De Baar, 1994). For our stations closest to the Antarctic Peninsula, the surface Zn concentrations are similar to that found by Sañudo-Wilhelmy et al. (2002); however those authors did not report any vertical profiles so further comparison is limited.

At S236 we again saw evidence for shallow Zn remineralization (Fig. 5), as also observed in the Weddell Sea along the Zero Meridian; however this feature was possibly associated with a meso-scale cyclonic eddy (Bluhm et al., 2011) that could have had elevated chlorophyll and zooplankton in its core. Overall the Zn distribution across the major frontal systems in the Drake Passage was similar to that in the Weddell Sea (Figs. 3 and 5). High Zn concentrations at 3000 m at S249 may indicate the presence of inflowing South East Pacific deep water, which has been found previously in this location by ^{3}He anomalies (Well et al., 2003). Samples for ^{3}He were taken during this cruise (Oliver Huhn—personal communication), but the analysis was not completed at the time of writing.

4.1.3. Zinc in surface waters of the Southern Ocean

Along both transects there was a strong polarwards gradient in surface Zn concentrations (Fig. 8), which closely followed that for silicate and phosphate. Crucially however Fig. 8 reveals information about the order of nutrient removal in this region with silicate removed slightly before Zn while elevated phosphate and nitrate (data not shown) concentrations remain. There is no significant trend for Fe in this region as concentrations are uniformly low (Croot et al., 2004; Klunder et al., 2011). This sequence of nutrient removal has obvious implications for the structure of the phytoplankton and zooplankton communities that exist here.

4.1.4. Zinc residence times in surface waters in the Southern Ocean

The major source for Zn to surface waters in the Southern Ocean is clearly through upwelling and vertical mixing of Zn-rich intermediate and bottom waters. Precipitation is a small source to the Southern Ocean region with measured fluxes typically low $\sim$0.4–1 μmol m^{-2} y^{-1} (Arimoto et al., 1990; Halstead et al., 2000); ice core records from Antarctica also support low Zn fluxes by precipitation (Hong et al., 1998). Zn may also be supplied by melting from icebergs or ice shelves but this is also believed to be a small source term (Hendry and Rickaby, 2008). The residence time for Zinc in the whole ocean is estimated to be $\sim$50,000 years (Shiller and Boyle, 1985) based on riverine inputs to the ocean. Previously an estimate of 12 ± 7 years has been made for the residence time of Zn in surface waters close to the Antarctic Peninsula using a simple advection/diffusion model (Sañudo-Wilhelmy et al., 2002). In the present work we estimated the upwelling flux, at each station occupied, by a simple vertical mixing model (Croot et al., 2007), which considers only the flux due to diffusion and does not include the vertical advection of deep waters. The Zn inventory in the upper 200 m was combined with the flux estimate to obtain residence times for Zn in the study region. Using a mean vertical diffusion rate of 3×10^{-5} m^2 s^{-1} (Cisewski et al., 2005; Law et al., 2003) for the Southern Ocean we estimate residence times of 45 ± 23 years throughout our survey region, with slightly lower

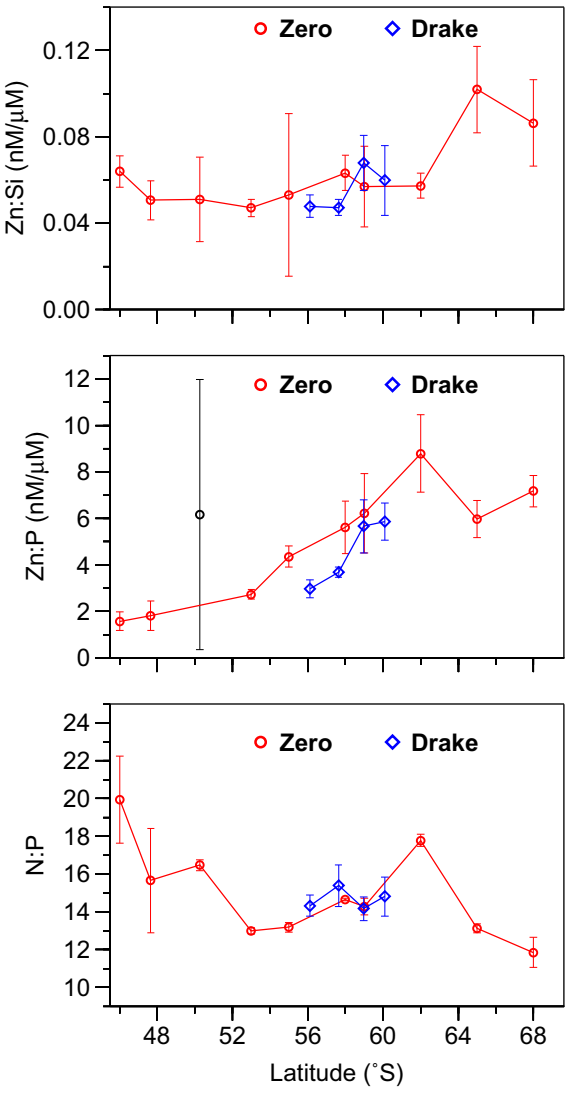

Fig. 6. Water column disappearance ratios for (top) zinc to silicate (centre), zinc to phosphate and (bottom) nitrate to phosphate for samples from ANTXXIV-3.

values in the Weddell Gyre compared to the ACC (data not shown). The lowest residence time was 15 years for S150 in the centre of the Weddell Gyre, which may reflect the intense remineralization occurring there. It should be noted that in regions with more intense vertical mixing, such as the Drake Passage (Thompson et al., 2007), the ACC (Geibert et al., 2002) or in eddies (Kahru et al., 2007), we would expect significantly lower residence time estimates.

4.2. Zn nutrient ratios in the water column

4.2.1. Zn:P ratios

Data from the Southern Ocean and other oceanic regions for the Zn:P disappearance ratio in the water column vary widely (Table 2). The Drake Passage value of Martin et al. (1990b) is slightly higher than what we found in the same region but similar to what we found in the Southern part of the Zero Meridian. This difference may be related to the location of the stations as the Martin et al. (1990b) data is located closer to the Antarctic Peninsula.

Fig. 6 indicates that the disappearance ratio for Zn:P in the water column increases with increase in latitude along the Zero Meridian and across the Drake Passage. There are several possible processes that could account for this trend and they are all related to the *in situ* growth rate of the phytoplankton. In this section we examine four key processes we have identified that may influence the growth rate and which may explain the observed Zn:P pattern in surface waters of the Southern Ocean: (I) temperature, (II) iron limitation, (III) species composition and (IV) photoperiod or irradiance.

Slow growth rates may lead to higher Zn:P ratios by a simple 'biodilution' or 'growth rate dilution' effect, in which cells constantly accumulate trace metals over time but accumulate non-metal biomass (e.g. P or N) in relation to the growth rate of the cell (Cullen et al., 2003; Kudo et al., 1996; Sunda and Huntsman, 2000), leading to high metal to P ratios at slow growth rates. Sunda and Huntsman (2005) highlighted the role of 'biodilution' when examining Zn:C ratio in CO_2 limitation of a coastal diatom. However as Sunda and Huntsman (2005) point out, Zn requirements may differ between phytoplankton species and on the parameter limiting growth rates. While CO_2 limitation is possible for diatoms and is important because of the Zn requirement for CA (Sunda and Huntsman, 2005), we do not discuss it further here as it would be unlikely that CO_2 limitation is important in the Southern Ocean at present.

Temperature is well known to have a strong influence on phytoplankton growth rates (Eppley, 1972). There are no studies we are aware of that directly examine the influence of temperature on Zn:P ratios in phytoplankton. In the present work for the Zero Meridian we find a strong correlation between the temperature in the mixed layer and the Zn:P for stations south of the APF ($Zn:P = -1.8 \pm 0.2T$ (°C)$+5.8 \pm 0.2$, $R^2 = 0.938$, $n = 7$). However this relationship can only hold in cold waters as it predicts negative Zn:P ratios above 4 °C and so must be considered as fortuitous. Additionally as all cells growing south of the APF are well adapted and indeed optimised for these conditions (Fiala and Oriol, 1990) it seems unlikely that such a small temperature range could have such an impact on Zn:P simply via biodilution.

Iron limitation is an important aspect of biogeochemical cycles in the Southern Ocean as has been amply demonstrated in the meso-scale iron enrichment experiments performed there (de Baar et al., 2005). Laboratory studies have shown that Fe influences the N:P ratio in diatom species isolated from the Southern Ocean (Timmermans et al., 2004). Sunda and Huntsman (2000) observed in their experiments with the open ocean diatom *Thalassiosira oceanica*, that Zn:P ratios were elevated when Fe was limiting diatom growth. The effect of iron limitation on Zn:P ratios in plankton has also been studied during iron enrichment experiments, most notably by Twining et al. (2004) during SOFeX, who used Synchrotron X-Ray Fluorescence on individual cells taken from both the north (low silicate) and south (high silicate) iron enriched patches to obtain Zn:P values. During SOFeX it was found that diatom samples from within the iron enriched patches had a lower mean Zn:P (6.2 nmol:μmol) than outside (8.1 nmol:μmol). Contrastingly autotrophic and heterotrophic flagellated cells had small increases in the Zn:P ratio in going from low iron to high iron waters. Twining et al. (2004) also noted that heterotrophs had higher Zn:P than autotrophs and that the Zn and P were frequently co-located in heterotrophs and that this may reflect increases in the RNA and P content of the heterotrophic cells, which results in a higher Zn stoichiometry. During SEEDS II the bulk Zn:P also apparently decreased after iron addition (Nakatsuka et al., 2009). The results of shipboard bioassay iron enrichment experiments performed in the Southern Ocean (Cullen et al., 2003) are also of relevance here. In these experiments the Zn:P ratio of the natural assemblages decrease with increase in additions of dissolved Fe (initial: 11.1 ± 0.7 nmol μmol^{-1}; control: 4.0 ± 0.1 nmol μmol^{-1}; +2.5 nM Fe: 2.1 ± 0.1 nmol μmol^{-1}). The results outlined here do suggest that Fe is a strong candidate for controlling the Zn:P disappearance ratio in Southern Ocean waters.

Previous field work has shown that the N:P ratio in Southern Ocean waters varies according to the dominant phytoplankton community with values lower than the Redfield N:P ratio (Redfield et al., 1963) associated with diatom blooms (de Baar et al., 1997) and higher than Redfield N:P with *Phaeocystis* blooms (Arrigo et al., 1999). Fig. 6 shows the N:P disappearance ratios for the upper water column along the transects surveyed in this work. South of the APF where surface silicate remains above zero the values of N:P are at or below the Redfield ratio, the only exception being at S141 in the centre of the Weddell Gyre where elevated N:P and Zn:P were found. Prior to our occupation of S141 there had been an extensive phytoplankton bloom present between 61° and 64°S in January 2008, with chlorophyll *a* at 1.9 μg L^{-1} in 40 m depth at 64°S with *Phaeocystis* in abundance (Uli Bathmann, ANTXXIV/2, Weekly Report No. 8, 17 January–25 January 2008). Thus this *Phaeocystis* bloom was most likely the cause of this anomalous N:P seen in our data and possibly the Zn:P. A recent compilation of elemental quotas in marine phytoplankton from laboratory studies (Ho et al., 2003), under Fe replete conditions, found a wide range of N:P ratios but a smaller range in Zn:P (0.07–1.7 nmol:μmol), though none of the species tested were polar in origin or *Phaeocystis* species. Overall however diatoms dominated the phytoplankton community in the waters we examined during ANTXXIV-3 and there is currently no laboratory data for Zn:P with species isolated from this region.

Irradiance has also been shown in laboratory studies to influence the Zn:P ratio of phytoplankton (Finkel et al., 2006) with the Zn:P ratio in several phytoplankton species increasing significantly with decrease in irradiance. The photoperiod is also important as a related study using the diatom *Thalassiosira pseudonana* (Sunda and Huntsman, 2005) gave an increase in the Zn:P ratio with a decrease in the photoperiod, which these authors ascribed in part to an increased cellular requirement for Zn to support enhanced CA fixation of carbon and a reduced growth rate. However in this same study a reduction in the light intensity resulted in a reduced cellular zinc requirement, which was possibly linked to a decrease in the growth rate with resulting lower demand for CA and other Zn enzymes. Interpreting the laboratory data in the context of our field data is complicated as along the Zero Meridian the signal we observed in the water column would have been integrated over the growing season until our arrival in late summer and this would include both the effects of a long photoperiod and relatively low light levels, to which Antarctic phytoplankton would be well photo-acclimated.

Considering the information currently at hand it would suggest that iron or iron/light limitation is the critical factor behind the Zn:P ratio observed in our work. Further work on this aspect of nutrient biogeochemistry is clearly then required.

4.2.2. Zn:Si ratios

The Zn:Si ratio in seawater is reported more often (see Table 3) than the Zn:P ratio and has become important for paleo studies who seek to use this parameter as a measure of past ocean conditions (Ellwood and Hunter, 2000b; Hendry and Rickaby, 2008). Previous work in the Southern Ocean showing good correlations between Zn and Si shows low values (~0.033–0.038 nmol:μmol) in the productive APF and SPF regions (Löscher, 1999), with values similar to the North Pacific (~0.054 nmol:μmol) (Bruland, 1980) in the Drake Passage (~0.059 nmol: μmol) (Martin et al., 1990b). Other data from this region show poor correlations between Zn and Si in the Weddell Sea (Nolting and De Baar, 1994; Westerlund and Öhman, 1991) or nearby the Antarctic Peninsula (Sañudo-Wilhelmy et al., 2002).

The lower values of Zn:Si found in the vicinity of the APF and SPF in the Löscher study along 6°W compared to our work may be related to the sampling period, as the Löscher study was performed in the spring (October–November 1992) compared to our autumn sampling. Similarly the elemental composition of Antarctic diatoms (mostly *Corethron* sp.) has been examined earlier (Collier and Edmond, 1984) for a sample collected in the field (66°44′S, 30°00′E, January 1976) to the east of our study region. In this sample the bulk Zn:Si ratio was found to be 0.026 μmol $mmol^{-1}$ with a Zn:P of 13.3 nmol μmol^{-1}, which is significantly higher than what we observed in the water column but taken together with the low Zn:Si ratio may indicate iron limited growth of the large *Corethron* cells (Timmermans et al., 2004). This would also be consistent with the data from the Drake Passage (Martin et al., 1990b), which was also sampled in Autumn (March–April 1989), and is similar to the values we found in the same region (Table 3). A temporal component in the Zn:Si ratio would imply a

Table 3
Zn:Si (nmol:μmol) ratios in other studies including locations.

Location	*Slope*	*Intercept*	R^2	*n*	Reference
North Pacific					
Whole water column	0.054 ± 0.001	0.02 ± 0.09	0.992	43	Bruland (1980)
North Atlantic					
Whole water column	0.17 ± 0.03	2.3 ± 0.4	0.500	41	Yeats and Campbell (1983)
South West Pacific					
Depths < 1000 m	0.077	0.201	0.914	97	Ellwood (2008)
Southern Ocean					
Ross Sea					
Deep waters	0.098	−2.60	0.788		Fitzwater et al. (2000)
High productivity waters	0.017	0.26	0.600		Fitzwater et al. (2000)
Weddell Sea					
Depths < 300 m	0.10	0.94	0.640	55	Nolting et al. (1991)
Whole water column	0.034	1.78	0.24		Westerlund and Öhman (1991)
Atlantic 6°W					
Polar Front 49° 59′ S	0.038 ± 0.006	2.21 ± 0.46	0.828	11	Löscher (1999)
sACC 53° 58′ S	0.033 ± 0.004	2.73 ± 0.40	0.846	15	Löscher (1999)
Drake Passage					
Whole water column	0.059 ± 0.005	0.20 ± 0.36	0.941	10	Martin et al. (1990a)
Overall (all data)	0.040 ± 0.002	0.67 ± 0.26	0.859	130	This study
Zero Meridian (all data)	0.040 ± 0.004	0.65 ± 0.34	0.837	99	This study
Drake Passage (all data)	0.039 ± 0.004	0.71 ± 0.17	0.918	31	This study

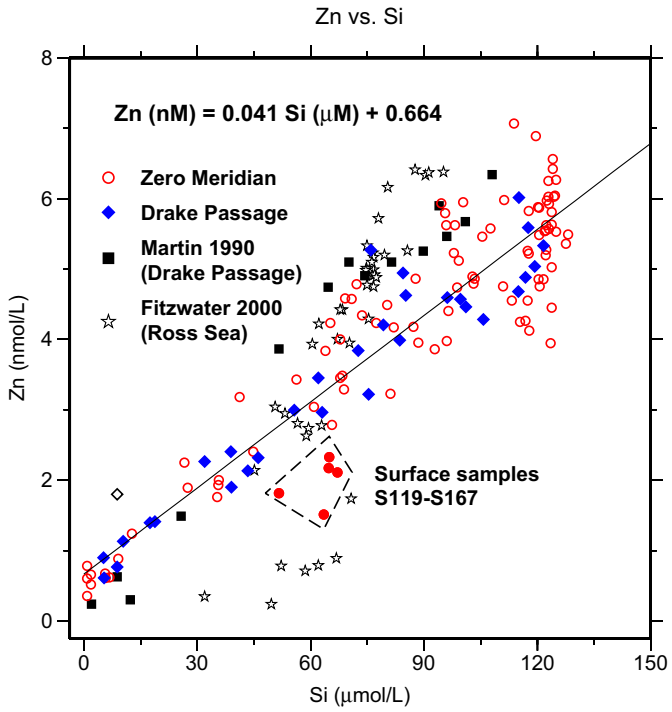

Fig. 7. Zinc versus silicate for samples from ZERO & DRAKE and other studies in the Southern Ocean.

greater utilization of Zn over the later part of the growing season and this could be considered consistent with an initial Fe rich bloom in the spring followed by slower growth of Fe depleted organisms.

Unfortunately the Zn:Si drawdown ratio has not been measured regularly during iron enrichment experiments. In SOIREE a decrease in labile Zn was observed though dissolved Zn remained constant during the course of the iron induced bloom (Frew et al., 2001). During the SEEDS experiment in the North Pacific (Kinugasa et al., 2005) the dissolved Zn did decrease during the course of the bloom consistent with an uptake ratio of 0.043 μmol mol^{-1} (Zn:Si) and 1.16 μmol mol^{-1} (Zn:P) into the cells. However for SEEDS it is not clear if these drawdown ratios changed significantly upon iron addition.

The 'biodilution' effect used for the Zn:P ratio may not hold for Zn:Si as the Si content of phytoplankton cells is known to be dependent on iron nutrition also (Hutchins and Bruland, 1998; Takeda, 1998) with faster growing diatoms being more weakly silicified than slow growing ones. Indeed Zn may be required for silicon uptake (De La Rocha et al., 2000) and this may lead to a relatively narrow range of Zn:Si values in the open ocean. Along the Zero transect Zn:Si (Fig. 7) was relatively constant with the exception of the southernmost stations that had slightly higher values.

Surprisingly given the field data regarding Zn:Si there is almost no data for Zn:Si in diatoms under laboratory conditions with the only published studies focusing on the incorporation of Zn into diatom frustules in both seawater (Ellwood and Hunter, 1999;

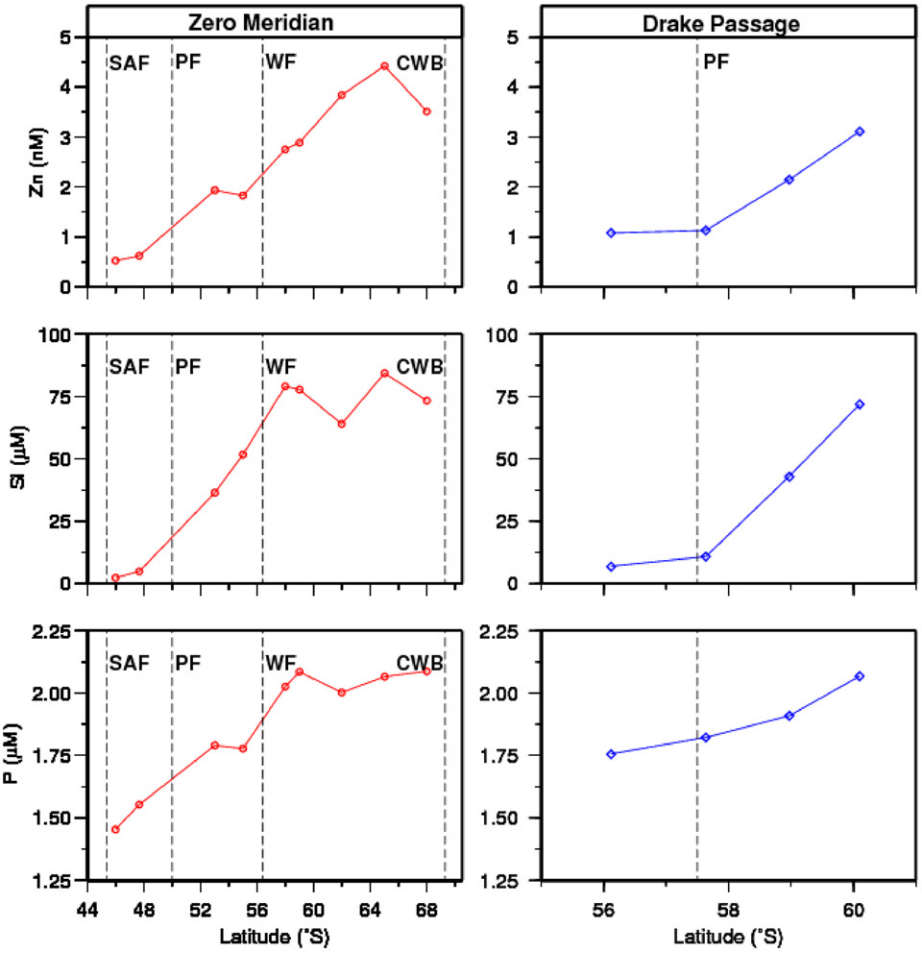

Fig. 8. Near surface concentrations of (top) zinc, (centre) silicate and (bottom) phosphate along the Zero Meridian (left) and the Drake Passage (right).

Ellwood and Hunter, 2000a) and freshwaters (Jaccard et al., 2009a; Jaccard et al., 2009b). It is thus not clear physiologically why Zn and silicate should be so highly correlated together in the ocean. Initial laboratory studies showed that Zn modulates silica uptake in a coastal diatom (Rueter and Morel, 1981). This hypothesis was further expanded upon by the analysis of silicon transporters in diatoms (Sherbakova et al., 2005), which were hypothesised to have a central cysteine rich Zn binding site that controlled Si uptake. Later studies showed that the affinity of Si transporters in a diatom was linked to Zn speciation but that the number of transporters was not affected by Zn deplete conditions (De La Rocha et al., 2000). A recent study examining Si uptake kinetics also found that the removal of Zn by chelation did not alter Si uptake (Thamatrakoln and Hildebrand, 2008) and suggested that the silicate uptake inhibition observed by Rueter and Morel was from a secondary effect of Zn on cellular metabolism. An alternative function for Zn in silicate uptake has recently been suggested with the finding that Zn–polyamine complexes can capture silica and may be important in the trans-membrane transport of $Si(OH)_4$ in silicifying organisms (Danilovtseva et al., 2009). While the evidence points to a connection between Zn and the Si uptake of diatoms it is not clear yet exactly how this link occurs physiologically.

The Zn:Si ratio in deep waters is also used in paleo oceanographic studies as a proxy for the Zn environment of benthic forams (Marchitto et al., 2000), which can be utilized as water mass tracers (Marchitto et al., 2002). Indeed due to the lack of deep water Zn data a global deep water ratio of 0.052 for Zn:Si nmol:μmol has been typically used with measured Si concentrations (Marchitto et al., 2000). Our new dataset indicates that this approach may slightly overestimate the Zn concentrations in the bottom waters of the Southern Ocean. Additionally the Zn:Si ratio in opal has been used as a proxy for Zn speciation in the water column (Ellwood and Hunter, 1999) and for changes in freshwater runoff from the Antarctic Peninsula (Hendry and Rickaby, 2008). Our data in this paper and in our companion paper (Baars and Croot, 2011), which shows that there is little Zn complexation by organic ligands in the Southern Ocean, is in good agreement with recent reports on high Zn:Si ratios in Antarctic diatoms (Diaz et al., 2010; Sherrell et al., 2010) and contrasts with the low and uniform Zn:Si ratio of opal in core tops reported in the Southern Ocean (Ellwood and Hunter, 2000b). Clearly further work is required if this proxy is to be fully realised as a tracer of Zn speciation in the ocean.

5. Conclusions

During the IPY research expeditions ZERO and DRAKE we undertook measurements of dissolved Zn throughout the water column of the Atlantic sector of the Southern Ocean. From the results we have compiled we have 5 major findings:

(1) Zinc concentrations and macronutrients were high throughout the surface waters south of the APF.
(2) Local minima and maxima were present in vertical profiles of dissolved Zn, indicating significant uptake by phytoplankton and release via grazing, respectively.
(3) Zinc concentrations in the deep waters of the Southern Ocean were the highest in CIW of the Weddell Gyre due to local remineralization of sinking particulate matter.
(4) A significant trend was observed in the water column Zn:P disappearance ratios along both the ZERO and DRAKE transects. The increase in Zn:P ratio at higher latitudes is tentatively ascribed to slow growth rates of phytoplankton due to iron limitation and/or light limitation.
(5) Zinc and silicate were strongly correlated throughout the study region but the disappearance ratio (Zn:Si) was relatively uniform overall except for the region close to the ice edge on the Zero Meridian.

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