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

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ABSTRACT

The speciation of dissolved zinc (Zn) was investigated by voltammetry in the Atlantic sector of the Southern Ocean along two transects across the major frontal systems: along the Zero Meridian and across the Drake Passage. In the Southern Ocean south of the APF we found detectable labile inorganic Zn throughout the surface waters in contrast to studies from lower latitudes. Using a combination of ASV titrations and pseudopolarography revealed the presence of significant concentration of electrochemically inert Zn ligands throughout the Southern Ocean. These ligands however were nearly always saturated due to the presence of excess concentrations of dissolved Zn that were associated with the high nutrient waters south of the Antarctic Polar Front (APF). Only in surface waters did the concentration of Zn complexing ligands exceed the dissolved Zn concentrations suggesting a biological source for these ligands. Our findings have clear implications for the biogeochemical cycling of Zn and for the interpretation of paleo records utilizing Zn in opal as a tracer of Zn speciation in the water column.

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1. Introduction

1.1. Zinc speciation in the ocean

Zinc (Zn) is a metal cofactor for many important enzymatic processes in both prokaryotes and eukaryotes (Vallee and Auld, 1990; Vallee and Auld, 1993) and as such is a required metal for bacteria and phytoplankton in the ocean. Of critical importance Zn is utilized in both nucleic acid transcription and repair proteins (Anton et al., 2007), and in nutrient uptake mechanisms most notably for the uptake of CO₂ via the enzyme Carbonic Anhydrase (CA) (Hu et al., 2003; Morel et al., 1994) and for the uptake of phosphate via the enzyme alkaline phosphatase (Hove et al., 1940; Shaked et al., 2006). At high concentrations Zn is toxic to phytoplankton (Florence, 1982; Stauber and Florence, 1990; Sunda and Huntsman, 1996, 1998b) and bacteria (Chen et al., 2008) but studies at near ambient seawater concentrations indicate that Zn could potentially be biolimiting for phytoplankton growth (Brand et al., 1983; Saito and Goepfert, 2008; Sunda and Huntsman, 1998a, 2000), though this has yet to be observed in the field (Coale et al., 2003; Crawford et al., 2003; Lohan et al., 2005). Through studies with organic complexing agents such as EDTA, the growth and Zn uptake rates of many phytoplankton have been shown to be related to the free Zn concentration (Brand et al., 1983; Saito and Goepfert, 2008; Sunda and Huntsman,

1995) rather than the total Zn concentration. The presence of organic complexing agents in seawater will therefore act to lower the free metal concentration of Zn reducing toxicity but also potentially limiting growth. Thus information on the speciation of Zn in seawater is clearly of importance for understanding the biogeochemical cycling of Zn in seawater.

The importance of Zn in marine biogeochemical cycles is now well established through studies in the North Pacific (Bruland, 1980, 1989; Coale, 1991; Crawford et al., 2003; Lohan et al., 2005., 2002; Martin et al., 1989), the North Atlantic (Ellwood and van den Berg, 2000; Jakuba et al., 2008a; Martin et al., 1993), subantarctic waters (Ellwood, 2004, 2008), though studies in the Southern Ocean are relatively sparse and confined to the vicinity of the Ross Sea (Coale et al., 2005, 2003; Fitzwater et al., 2000) and the Weddell Sea-Drake Passage region (Löscher, 1999; Martin et al., 1990; Nolting and De Baar, 1994; Sañudo-Wilhelmy et al., 2002; Westerlund and Öhman, 1991). All studies in the open ocean show that dissolved Zn (DZn) has a nutrient-like vertical profile with strong correlations in particular with silicate (Bruland, 1980). Concentrations of DZn in low nutrient open ocean surface waters are typically < 100 pM with concentrations increasing to 6–10 nM in deep waters (Bruland, 1980; Coale et al., 2005; Martin et al., 1993), though higher concentrations have been reported in the high silicate containing deep waters of the Bering Sea (Fujishima et al., 2001).

There have been a number of previous studies of Zn speciation in coastal waters (Kozelka and Bruland, 1998; van den Berg et al., 1986, 1987; Wells et al., 1998) and in open ocean waters

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(Bruland, 1989; Ellwood, 2004; Ellwood and van den Berg, 2000; Lohan et al., 2005). There are however no previous studies of Zn speciation from Antarctic waters that we are aware of. The main source for Zn to the oceans is believed to be riverine in origin (Shiller and Boyle, 1985), and further studies suggest that there is also apparently strong complexation of Zn in rivers (Hoffmann et al., 2007) and lakes (Ellwood et al., 2001). In estuaries, impacted by anthropogenic inputs, Zn has been found to be weakly organically complexed (Kozelka and Bruland, 1998; van den Berg et al., 1986, 1987; Wells et al., 1998) with between 50% and 99% of the Zn present as organic chelates. Estuarine marine sediments have been identified as one possible source for the Zn complexing ligands (Skrabal et al., 2006). However the long residence time of Zn in the oceans (~50,000 years) suggest this flux of organic ligands may not be important in the open ocean where most studies have found strong complexation (>98% organic Zn) in surface waters with a significant labile fraction in intermediate and deep waters, but still some organic complexation (Bruland, 1989; Ellwood and van den Berg, 2000). The identity and sources of these Zn-organic complexes is unknown at present, though they are thought to be derived from bacteria/phytoplankton (Bruland, 1989).

1.2. Determination of zinc speciation in seawater

The speciation of Zn in seawater has been predominantly determined by polarographic methods (see Section 2.1), though other methods have been employed utilizing solid phase extraction (Florence, 1982; Muller and Kester, 1990) and HPLC (Mackey, 1983). Flow injection methods utilizing fluorescence sensors also exist for zinc (Nowicki et al., 1994) but are yet to be applied to speciation schemes. Biosensors for Zn are the most recent developments (Bozym et al., 2006) however they have not yet been used in open ocean waters to our knowledge.

1.2.1. Electrochemical theory—equilibrium

There are several published voltammetric methods for Zn speciation in seawater and they fall into two categories depending on the electrochemical method employed. Anodic Stripping Voltammetric (ASV) methods utilize the solubility of Zn in Hg to concentrate Zn from seawater, for the low concentrations of Zn found in seawater a Thin Film Mercury Electrode (TFME) is required and is typically deposited onto a Rotating Disk Electrode (RDE) (Bruland, 1989). Alternatively Cathodic Stripping Voltammetry (CSV) methods employ an added ligand, which forms an electroactive complex with Zn which is adsorbed onto the surface of a Hanging Mercury Drop Electrode (HMDE) and can be reduced. For Zn a CSV method using the ligand APDC is well established (van den Berg, 1984b, 1985).

For speciation measurements the most direct approach for determining the extent and strength of zinc-organic ligand complexation by voltammetry (ASV/CSV) involves titrating the ligand(s) in a sample with added Zn and measuring the oxidation/reduction current of zinc deposited in/on the Hg electrode (TFME or HMDE). Comparisons for seawater speciation between the CSV method and the ASV TFME-RDE method have been made and in general good agreement has been found (Donat and Bruland, 1990; Ellwood, 2004). More recently the ASV TFME-RDE method has been applied utilizing a fresh mercury film for each sample (FF-ASV) and compared to the CSV method with good results (Jakuba et al., 2008b).

The theory behind the voltammetric titrations is well described (Bruland, 1989; Ellwood, 2004; van den Berg, 1985) and is presented briefly here.

In the present work we employed the ASV TFME-RDE technique (Bruland, 1989). This approach is based on the assumption that an electro-inactive complex, ZnL, is formed when a dissolved ligand (or class of ligands), L, complexes with (electroactive) Zn. From the resulting equilibrium the following conditional stability constant is formed:

$$K'_{\text{ZnL}} = \frac{[\text{ZnL}]}{[\text{Zn}'][\text{L}]} \quad (1)$$

with mass balance for L:

$$[\text{L}]_{\text{T}} = [\text{L}'] + [\text{ZnL}] \quad (2)$$

where $[\text{Zn}']$ is the total concentration of dissolved inorganic zinc species present, $[\text{L}]_{\text{T}}$ is the total concentration of all organic ligands that could bind zinc, $[\text{L}']$ is the concentration of free ligands, and $[\text{ZnL}]$ is the concentration of the zinc-organic complex with conditional stability constant, K'_{ZnL} (with respect to inorganic zinc, measured under the specific experimental conditions (e.g. pH, salinity, and temperature)). $[\text{Zn}']$ is related to the concentration of the free solvated zinc ion, $[\text{Zn}^{2+}]$, by an inorganic side reaction coefficient, α_{Zn} ($[\text{Zn}'] = [\text{Zn}^{2+}] \alpha_{\text{Zn}}$; Ringbom and Still, 1972).

The observed peak current i_p is related to the concentration of Zn in solution by the equation:

$$i_p = S[\text{Zn}'] = S[\text{Zn}^{2+}] \alpha_{\text{Zn}} \quad (3)$$

where S is the sensitivity and is readily determined in UV-oxidized samples by standard additions of Zn' . However in natural samples, S must be determined from the linear portion of the titration curve when all complexing ligands are saturated to distinguish the effects of ligand competition, which does not affect S , from surfactant interferences, which do (van den Berg, 1984a). Data in this study were analyzed with a ligand model that was a nonlinear fit to a Langmuir adsorption isotherm (Gerringa et al., 1995). The single ligand model is derived from the rearrangement of Eqs. (1) and (2) to yield a reciprocal Langmuir isotherm:

$$\frac{[\text{ZnL}]}{[\text{Zn}^{2+}]} = \frac{K[\text{L}]_{\text{T}}}{1 + K[\text{Zn}^{2+}]} \quad (4)$$

Eq. (4) was solved for K and $[\text{L}]_{\text{T}}$ by nonlinear regression analysis using existing MATLABTM routines or via a purpose built LabviewTM (National Instruments) virtual instrument (utilizing the Levenberg–Marquardt algorithm) with $[\text{Zn}^{2+}]_f$ as the independent variable and $\Sigma K_i L_i / [\text{Zn}^{2+}]_f$ as the dependent variable(s). Estimates of the errors in K and $[\text{L}]_{\text{T}}$ were obtained from these procedures. For simplicity, the weaker inorganic ligands present in the media (such as hydroxide, carbonate, and chloride), are combined to form an inorganic side reaction coefficient, α_1 . Zinc is only weakly complexed in organic free seawater, resulting in a value of $\alpha_{\text{Zn}} = 2.1$ based on literature reviews of speciation data (Byrne et al., 1988; Turner et al., 1981; Zhang and Muhammed, 2001), though laboratory studies (Lewis et al., 1995b) indicate that the $\text{Zn}(\text{OH})^+$ species may exist in concentrations greater than the free Zn^{2+} ion (Stumm and Brauner, 1975; Zirino and Healy, 1970; Zirino and Yamamoto, 1972).

For a ligand concentration of 1 nM a window of stability constant values (K') between about 10^8 and 10^{12} can be determined by the DPASV approach (Bruland, 1989). For stability constants $> 10^{12}$, only the ligand concentration and a lower limit to the stability constant (dependent on the sensitivity) are obtainable. An increase of ligand concentration by an order of magnitude (10 nM) would decrease the values of the stability constants that could be determined to between 10^7 and 10^{11} .

1.2.2. Electrochemical theory—kinetics of Zn complexes

The zinc species constituting Znⁿ are either directly electroactive (such as solvated Zn²⁺) or the dissociation rates of the complexes are so rapid, relative to their residence times in the TMF-RGCD electrode diffusion layer, that they are kinetically labile and detected as electroactive (e.g. ZnCl⁺). An assessment of the importance of this concern involves determining the formation rate of metal-organic ligand complexes (Ruzic and Nikolic, 1982). Formation rate constants for metal ligand formation are related to the water loss k_{H_2O} using the mechanism proposed by Eigen (1963):

$$k_f = K_{OS}k_{H_2O} \quad (5)$$

where K_{OS} is the equilibrium constant for the formation of an outer sphere complex. The water-exchange rate for Zn²⁺ is estimated to be $4.1 \times 10^8 \text{ s}^{-1}$ (Inada et al., 2005). Formation rates for most simple Zn²⁺ octahedral complexes are very fast $\sim 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Grant, 1973; Sharps et al., 1993). For more complex biological molecules such as porphyrins, formation rates can be very slow $\sim 1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Lavallee, 1985) due to steric restrictions or proton exchange reactions being the rate limiting step.

The rotation speed of the RDE also in part determines what species are electro-labile due to the relationship between rotation speed and the size of the diffusion layer at the electrode surface (Davison, 1978; Muller and Kester, 1990) with smaller diffusion layers at faster rotation rates leading to a shorter residence time in the diffusion layer and subsequently less time for the complex to dissociate and be transported to the Hg surface. At a fixed rotation rate the faster the dissociation rate of the complexes the greater the observed current at constant metal ligand concentrations. For a rotation rate of 3000 rpm this implies that for dissociation rates $< 1 \text{ s}^{-1}$ the current would be under kinetic control (Muller and Kester, 1990).

1.3. Theory of pseudopolarography

Only a brief outline of the theory behind pseudopolarography is provided here for more detailed information the reader is referred to the work of Lewis et al. (1995b) and Croot et al. (1999). Briefly, pseudopolarography is a method by which information on the thermodynamic stability of metal-organic complexes can be obtained by making a series of ASV measurements at more negative deposition potentials to create a current versus potential curve analogous to a polarogram. The method is based on the observation that complexation of a metal by a ligand causes a shift towards more negative potentials in the polarographic-reduction wave for the 'free' metal ion (i.e., the aqua-ion complex) (Lingane, 1941). The magnitude of this shift is directly related to the thermodynamic stability of the complex and to the concentration of the complexing ligand. For a simple one-ligand system, this relationship is predicted for conventional polarography by the Lingane equation (Lingane, 1941):

$$E'_{1/2} = E_{1/2} - \frac{0.059}{n} \log K_{ML} - \frac{0.059}{n} p \log [L] \quad (6)$$

where $E'_{1/2}$ and $E_{1/2}$ are the half-wave potentials for the complexed and free metal, respectively, K_{ML} is the stability or formation constant for the complex, p is the complex stoichiometry, n is the number of electrons transferred, and $[L]$ is the concentration of the complexing ligand.

Pseudopolarography can be used to distinguish labile from inert complexes in aqueous solutions (Branica and Lovric, 1997). The pseudopolarogram approach has been extended for studies in natural waters by the generation of pseudopolarograms for natural samples and comparing them to those obtained for metal complexation with model ligands under the same conditions. The

model ligand derived 'chelate scale' has been applied to studies of several elements in natural waters; Fe (Lewis et al., 1995a; Taylor et al., 1994), Cu (Croot et al., 1999), Cd (Tsang et al., 2006), and Zn (Lewis et al., 1995b; Vega et al., 1995). The chelate scale approach allows an estimation of the thermodynamic stability of unknown metal binding ligands in natural waters.

Here we utilize the chelate scale already developed for Zn (Lewis et al., 1995b):

$$\log K_{ML} = -22.973E'_{1/2} - 20.713 \quad (7)$$

where $E'_{1/2}$ is the observed half-wave potential from the pseudopolarogram.

1.4. 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 III and Nowlin, 1987) and the reader is referred to these works and to the companion paper in this issue on Zn distribution (Croot et al., 2011) for more detailed information.

1.5. 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 10 February 2008, headed south along the Zero Meridian, through the Weddell Sea and across the Drake Passage and finally arriving 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 speciation of zinc, a potentially important bio-element for primary production. A companion paper, in this issue, examines the distribution of Zn in the Southern Ocean (Croot et al., 2011). The overall aim of this was to improve our understanding of the Southern Ocean biogeochemistry of zinc and related elements (see also other related papers in this issue). To the best of our knowledge there has been no speciation work performed in the Southern Ocean for zinc, the nearest being in the South West Pacific (Ellwood, 2004) and thus our work provides important new data on the biogeochemical speciation of Zn.

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 6 February–16 April 2008 on board the German research vessel R.V. *Polarstern*. The cruise track consisted of three main 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 belonging to the NIOZ (de Baar et al., 2008). In brief this sampling system consists of a rectangular Titanium rosette fitted with a standard Seabird CTD and 24 modified 12 L Teflon coated GO-FLO bottles (General Oceanics, Miami, FL, USA).

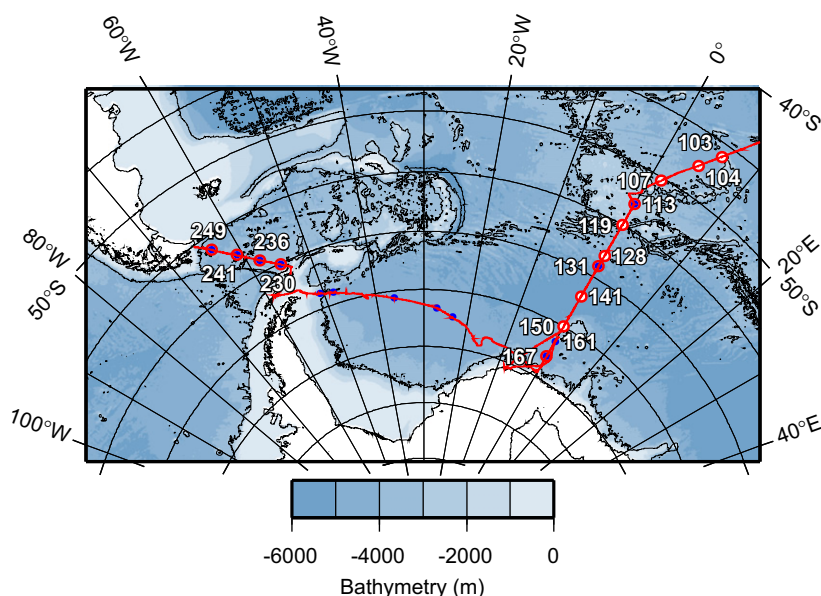


Fig. 1. Location of stations sampled during the ZERO and DRAKE expedition.

The rosette was deployed on a specially made trace metal clean Kevlar wire (17.7 mm) complete with conducting cable. 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 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 trace metal clean Teflon bottles for shipboard speciation analysis. Dissolved inorganic phosphate, silicate, nitrate, and nitrite were analyzed onboard by NIOZ using a TrAAcs 800 Auto-analyzer 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 belonging to the IFM-GEOMAR.

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. Full details of these analyses are found in this issue (Croot et al., 2011).

2.4. Zinc speciation measurements

2.4.1. Instrumentation

The voltammetric system used consisted of an Ecochemie PGSTAT30 connected to a VA663 voltammetric stand. The reference electrode was a double junction, Ag/AgCl with a saturated AgCl internal solution and a salt bridge filled with 3 M KCl. The counter electrode was a platinum rod. A rotating disk electrode (RDE) with a glassy carbon (GC) tip (2.0 mm) onto which a thin film mercury electrode deposited was used as the working electrode (TFME-GC-RDE).

2.4.2. Mercury-film formation

Before the formation of a new Hg film, the working electrode was polished by hand with 1 μm Al_2O_3 lapping film sheet (3 M) and rinsed with Ethanol and MQ water. The working electrode was then plated with a thin mercury film from a solution containing 10 mg/l of Hg^{2+} (Aldrich) and 30 mM KCl (Suprapur, Merck). After a 5-min purge period with nitrogen gas, mercury was plated from solution at an electrode potential of -1.0 V for 15 min at an electrode rotation rate of 3000 rpm. After a quiescent period of 10 s, the mercury film was stripped of metal contaminants by ramping the potential on the working electrode in a positive direction in differential pulse mode (scan rate, 20 $mV s^{-1}$; pulse modulation amplitude, 50 mV; pulse frequency, 10 s^{-1}). After stripping, the potential of the working electrode was held at -0.2 V for 5 min. If the voltammogram obtained from the mercury-film formation blanks showed low (~ 0.1 nM) levels of zinc, sample analysis would then proceed. The zinc-stripping peak occurs at -1.10 V (reference electrode: Ag/AgCl, 3 M KCl).

2.4.3. Sample titrations

After mercury-film formation blank deposition, a fresh sample was used to rinse the cell electrodes and the Teflon cell cup used for analysis. This sample rinse solution was then discarded and a fresh sample introduced. The sample was electrodeposited for 3 min at -1.2 V with a TFME-GC-RDE at a rotation rate of 3000 rpm. The TFME-GC-RDE was then stripped by scanning its potential in the differential pulse mode as described earlier. The scan was stopped and held at about -0.2 V with the TFME-GC-RDE electrode rotating for at least 2 min between depositions to completely strip the mercury film of residual metals. The 3-min deposition was repeated to obtain a second “zero addition” voltammogram, ensuring that the working electrode was conditioned for seawater analysis and that the initial scan was reproducible. Titrations were conducted by successive standard additions, with small additions initially (0.4 nM Zn) and larger additions (2 nM Zn) for the final titration steps. After each zinc addition, the sample was allowed to equilibrate for a minimum of 3 min before the next deposition stripping cycle was repeated. Titrations were carried out until a linear increase of the current was observed for at least four additions (typically this was achieved at 9–15 nM of total added Zn). Throughout the course of these titrations, pH stayed constant (± 0.1 pH units).

2.4.4. Pseudopolarography

Pseudopolarograms were recorded with the TMF-GC-RDE using an adsorption time of 3 min. The potential steps were $\Delta V=50$ mV covering a range between -0.85 and -1.40 V. In order to equilibrate the system the first measurement at -0.85 V was repeated twice. Samples were initially purged with N_2 for 5 min and then before each measurement for 10 s resulting in an analysis time of 1.5 h per sample. The voltammetric current signal was transformed to Zn concentrations using the sensitivity determined from titration data with the deposition potential held at -1.20 V.

For comparison between pseudopolarography studies using ASV it is important to have information about the operating conditions employed in the study. In the present work we used a Ag/AgCl reference electrode (Ag/AgCl in 3 M KCl), which differs from the earlier study of Lewis et al. (1995b) who employed a saturated calomel electrode (SCE) as the reference electrode. The use of different electrochemical detections schemes (Square Wave, Linear Sweep or Differential Pulse) or mercury film thickness can also lead to differences in the observed potentials of the voltammetric peaks. In general this is exhibited as faster scanning methods shifting the observed potential to more negative potentials. In the present work we observed the inorganic Zn peak at ~ -1.11 V (Ag/AgCl, 3 M KCl) which is 20 mV more negative (Zn' -1.09 V SCE) than that reported by Lewis et al. (1995b). In the present work we corrected our observed $E'_{1/2}$ by 20 mV to match the chelate scale of Lewis et al. (1995b) for calculation of $\log K$.

3. Results

For information on the distribution of nutrients, Zn (Croot et al., 2011), Fe (Klunder et al., 2011) and other trace metals

across the survey transects, the reader is referred to the related manuscripts in this issue.

3.1. Zinc speciation

Throughout both transects high concentrations of labile (Zn') were observed. Zn' and Zn^{2+} remained >0.2 nM or >0.1 nM, respectively, with the exception of one sample (S241, $Zn' < 0.1$ nM in 75 m). Strong gradients in Zn' existed in the upper 200 m of the water column (Fig. 2) along both transects. The highest Zn' values were found in deep waters, as was previously observed in the North Pacific (Bruland, 1989), with values in the Drake Passage being significantly higher than along the Zero Meridian. Depth profiles of Zn' along the Zero Meridian were characterized by distinct sub surface maxima at the edge of the euphotic zone in depths between 100 and 200 m while this feature was absent or only weakly developed in the Drake Passage. The fraction of Zn associated with strong organic ligands ranged between 50% and 90% in samples collected along the Zero Meridian section and ZnL ($ZnL=DZn-Zn'$) reached concentrations up to ~ 4 nM there. Contrary, through the Drake Passage, almost 100% of Zn was found to be labile. Only in some samples from the upper water column significant organic complexation was detected (Fig. 2).

Zn titrations of most samples showed a linear increase of Zn' with added Zn^{2+} indicating any ligands present were already saturated with Zn. Thus in most cases no estimate of $\log K'$ could be obtained from the titration data. This is consistent with earlier work where typically oceanic Zn complexing ligand concentrations are below 2 nM (Table 1), which is significantly less than the DZn

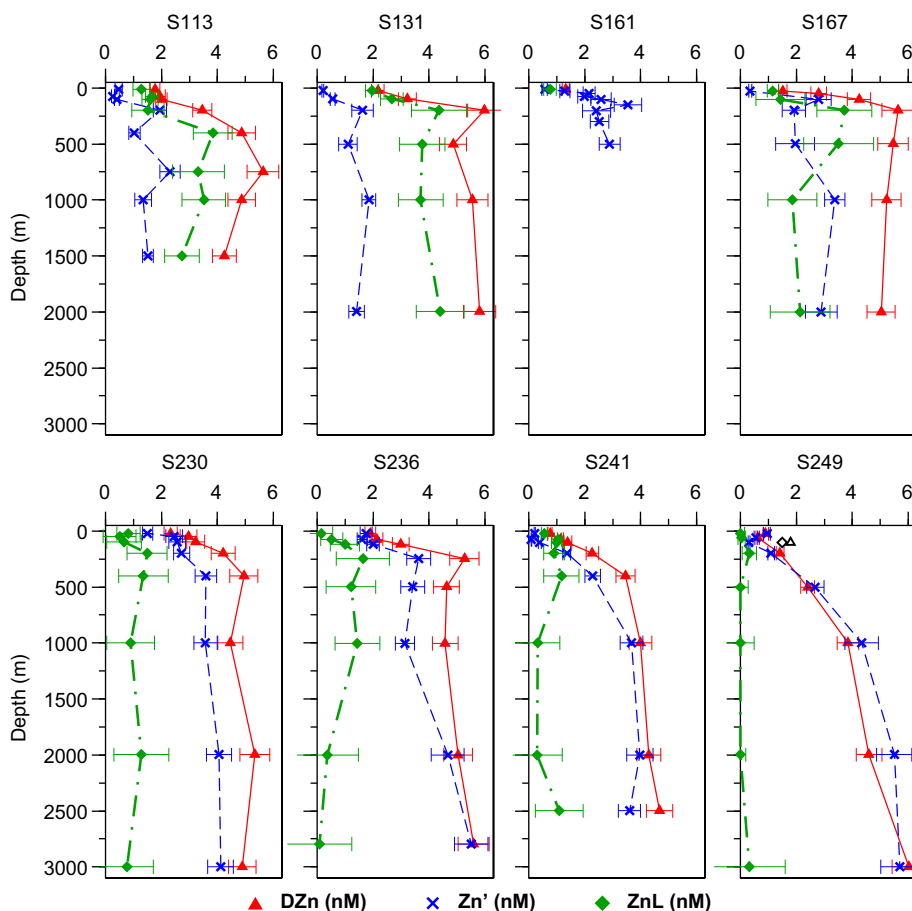


Fig. 2. Zn speciation along the ZERO Meridian (top) and across the Drake Passage (bottom).

Table 1
Zn complexation data from the present study and other relevant seawater studies.

Region	Sample	[L _T] (nmol L ⁻¹)	log K ^{znl}	References	Method
North Pacific	Profile	1.0–1.5	10.7–11.3	Bruland (1989)	ASV
North Pacific	60 and 150 m	1.7–2.3	11.0–11.5	Donat and Bruland (1990)	ASV
	60 and 150 m	1.6–2.3	10.1–10.5	Donat and Bruland (1990)	CSV
North Pacific	15 m	0.7	10.5	Lohan et al. (2005)	CSV
North Atlantic	Surface	0.4–2.5	10.0–10.5	Ellwood and van den Berg (2000)	CSV
North Atlantic	Profile	0.9–1.5	9.8–10.5	Jakuba et al. (2008b)	FF-ASV
	Profile	0.6–1.3	9.8–11.3	Jakuba et al. (2008b)	FF-ASV
South Pacific	20 m	1.3	10.6	Ellwood (2004)	ASV
	20 m	1.2	10.2	Ellwood (2004)	CSV
Southern Ocean	10–200 m	1.4–5.3	9.1–10.4	This study	ASV
Drake Passage	25–100 m	1.4–2.5	9.7–9.8	This study	ASV
Zero Meridian	10–200 m	2.5–5.3	9.1–10.4	This study	ASV

Table 2
Zn complexation data from ANTXXIV-3.

Station	Depth (m)	[Zn] (nM)	[Zn'] (pM)	[L] (nM)	log K'
S107	199.3	2.810	97 ± 12	5.34 ± 0.49	10.2 ± 0.2
S131	24.1	2.169	205 ± 15	2.67 ± 0.10	10.4 ± 0.2
S161	9.9	1.325	567 ± 69	3.18 ± 0.26	9.1 ± 0.2
S167	25.4	1.509	350 ± 39	3.72 ± 0.28	9.5 ± 0.2
S241	24.5	0.765	213 ± 19	1.37 ± 0.24	9.73 ± 0.02
S241	74.6	1.132	92 ± 7	2.55 ± 0.27	9.8 ± 0.2
S241	99.9	1.392	393 ± 32	2.51 ± 0.26	9.70 ± 0.5

Notes: Titrations were performed on a much larger data set the data above are from the small subset of data where significant excess ligand was present.

values found in these waters (Croot et al., 2011). However, in a few cases, noticeably all from the upper 200 m of the water column, curvature in the titration plots was observed indicating there was a significant ligand excess. For these samples meaningful values for *L* and log *K'* could be extracted by fitting Eq. (4) to the titration data (Table 2). Concentrations of *L* ranged between ~1 and 3.3 nM with log *K'* values between log *K'* = 9.1 and 10.2 (Table 2).

3.2. Pseudopolarography

Pseudopolarography yields further information about the chemistry of the Zn complexes present in seawater. In this context they are complementary to the metal titration protocols, which primarily provide information about excess ligands in solution. In the present study we performed a limited number of pseudopolarography experiments (Fig. 3); one sample from 10 m at S161 collected along the Zero Meridian section and three samples (25, 200, and 1000 m) from S230 in the Drake Passage.

In all samples the 1st reduction half-wave potential was observed at $E_{1/2} = -1.15$ V. This potential corresponds to a thermodynamic stability constant log *K* = 5.25 for Zn complexes (Eq. (7)). In a sample from S161 (Fig. 3) this fraction accounted for 0.58 nM (43% of Zn) while 0.31 nM (23% of Zn) was reduced at $E_{1/2} \sim -1.30$ V. The related thermodynamic stability constant was log *K* ~ 8.7. The remaining 34% of Zn was non-reducible and inert at the lowest deposition potential used in this study ($E = -1.40$ V), indicating a log *K* > 11.0 for this species. In samples from S230 only a single reduction half wave was observed at $E_{1/2} = -1.15$ V with the remaining Zn present as inert complexes. Based on the limited data set (*n* = 13) we have from the pseudopolarograms we cannot see any discernable vertical trend in the concentration of this inert complex (Fig. 3). For all pseudopolarograms there was a slight decrease in the observed currents at high negative potentials, this was possibly due to interference by organic complexes adsorbed or reduced at the electrode surface.

4. Discussion

4.1. Speciation of Zn in the Southern Ocean

4.1.1. Organic complexation of zinc—saturation of ligands and the presence of labile zinc

The major finding in the present work that differs from previous Zn speciation work in lower latitude regions (Bruland, 1989; Donat and Bruland, 1990; Ellwood, 2004, 2008; Ellwood and van den Berg, 2000) is that Zn predominated as inorganic Zn (Zn') in both surface and deep waters. Organic Zn complexes were apparently present in all samples but were mostly saturated with no free ligand existing except in some near surface waters. As a result the buffering capacity for free Zn was low leading to possible strong temporal variations in free Zn in surface waters. Additionally this finding has obvious implications for the interpretation of paleo-tracers based on Zn, which have presumed that Zn was strongly complexed in Southern Ocean waters (see Section 4.5).

On both transects a positive correlation between Zn' and DZn could be observed (Fig. 4). Along the Zero Meridian Zn' was only poorly correlated to DZn and the fraction of ZnL appeared to decrease with increasing DZn. Contrastingly in most samples from the Drake Passage Zn' was strongly correlated with DZn but no correlation between ZnL and Zn' could be observed. Our observations in the Zero Meridian are the first time depth profiles of ZnL and Zn' have been shown to vary in this manner. The few other studies investigating Zn speciation profiles in the open ocean have revealed relatively homogenous concentrations of Zn complexing ligands in depths of up to 600 m in the North Atlantic (Jakuba 2008) and North Pacific (Bruland 1989) and similar to our data from the Drake Passage.

In our study most samples were saturated with respect to Zn²⁺ so we can make the assumption that L_T = ZnL for these samples. Based on this approach deep water ligand concentrations measured from our Southern Ocean samples are significantly higher than previously reported values from the open ocean (Table 1). This was particularly the case for the Zero Meridian transect where ZnL reached up to 4.4 nM in the deep. As most of our samples were saturated we can make no general comparison between our study and earlier ones for log *K* values.

Strong apparent coupling between [Zn'] or [ZnL] and [Zn] was present at S131 ($R^2 = 0.91$), which was located at the northern extreme of where a major phytoplankton bloom had occurred earlier in the spring (Bluhm et al., 2011). Also in this region of the Weddell Gyre strong remineralization of Zn was apparently occurring just below the mixed layer (Croot et al., 2011) and this may account for the local maxima in ZnL, Zn', and DZn observed at 200 m. In the Drake Passage at S241, [L]_T increased from

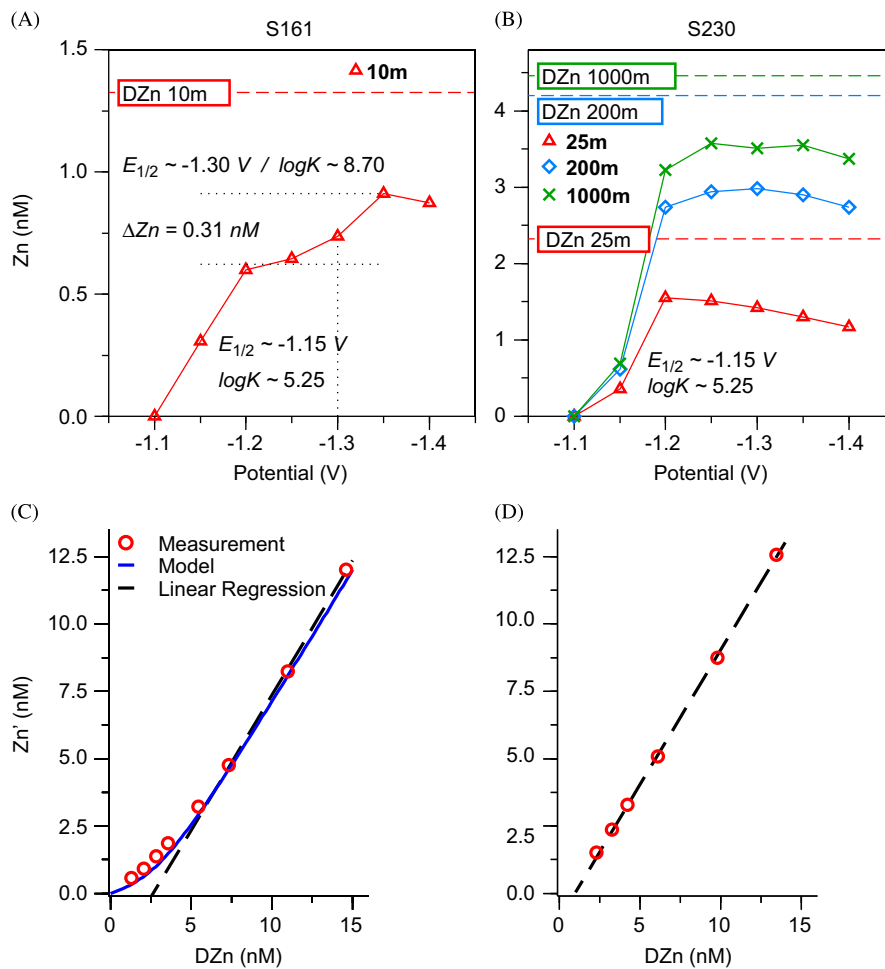


Fig. 3. Examples of speciation measurements performed during this work. Pseudopolarography examples from station 161 in the Zero Meridian (A) and station 230 in the Drake Passage (B). (C) Titration results for the same sample as in (A). (D) Titration results from the 25 m sample as in (B).

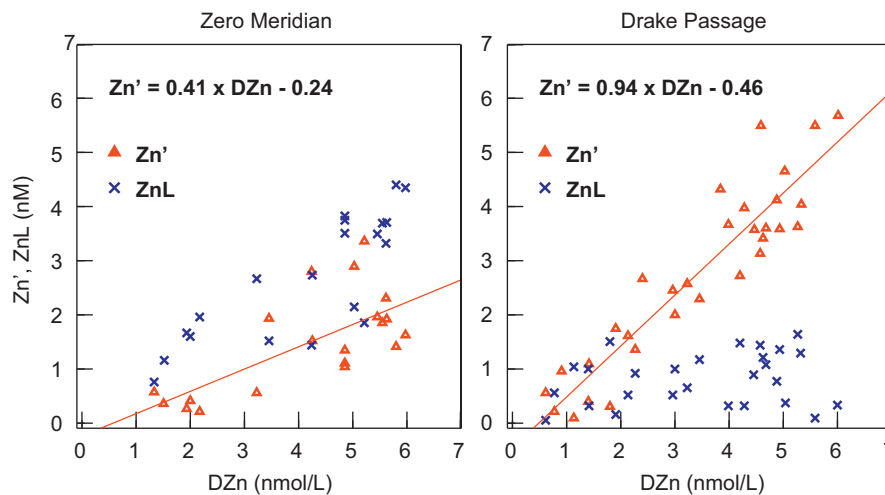


Fig. 4. Relationship between Zn' or ZnL versus dissolved Zn (DZn) for samples from the Zero Meridian (left) and the Drake Passage (right).

~ 1 nM at 25 m to ~ 2 nM at 75 and 100 m while the fluorescence maximum existed at ~ 70 m hinting towards a production of ligands by phytoplankton.

The differences observed in the ZnL concentrations between the Zero Meridian and the Drake Passage may be related to differences in productivity, physical mixing and particle export.

As van der Loeff et al. (2011) report from measurements of water column $^{234}\text{Th}/^{238}\text{U}$ ratios that particle export was elevated along the Drake Passage compared with the Zero Meridian, where shallow remineralization and low particle export lead to strong recycling in the upper water column (Croot et al., 2011; Usbeck et al., 2002).

If the vertical profiles of L are truly driven by a phytoplankton source, either directly from exudates or metabolites (Fisher and Fabris, 1982), or released via grazing (Small and Fowler, 1973), then this requires that the sink terms are also predominantly in surface waters and that the ligands in deep water are significantly long lived. Such sink terms could be uptake of L by phytoplankton or bacteria, destruction by photochemistry or removal via scavenging to particles. In the following sections we bring together other information on Zn ligands in order to assess the potential of these processes.

4.1.2. Pseudopolarography—*inert* Zn complexes

There is a fundamental difference in speciation data between pseudopolarography and metal titration experiments as the latter is based on the complexation of added metal by free ligands in the sample, while the former examines the complexes directly. In this context the two analysis techniques yield complementary data. Our pseudopolarography results indicate a significant fraction of Zn was bound to inert Zn-organic complexes as has been observed previously for some Cu complexes (Kogut and Voelker, 2003). The titration plots, on the other hand, showed no curvature with a high amount of Zn' in solution, indicating that any ligands were saturated with Zn and useful estimates of stability constants could not be inferred from these experiments. The sample from 10 m at S161 was one sample where a curvature in the titration plot was observed, pseudopolarography of the same samples showed the presence of both inorganic Zn and an organic complex. The titration data revealed the presence of a weak ligand, $L_T=3.2$ nM, $\log K'=9.12$, which was in rough agreement with the pseudopolarogram where a thermodynamic stability constant ($\log K=8.70$) for the 2nd half wave was estimated. The pseudopolarogram indicates that in the ambient sample 43% of the sample was Zn', while estimations from the titration data, by solving the quadratic equation that results from solving Eq. (4), is found to be higher at 72%. This difference for Zn' between the two techniques arises from the use of a single ligand model for the titration data when the pseudopolarogram indicates two organic species a weak labile one and a stronger inert ligand. Attempts to fit a 2nd ligand to the titration data were not successful due to this inert ligand being saturated.

The presence of electrochemically inert Zn complexes in all samples examined here and the observation that titration data from deep waters in the North Pacific (Bruiland, 1989) and the North Atlantic (Jakuba et al., 2008b), and in the Southern Ocean (this work), show the presence of a significant difference between the total zinc and labile zinc suggests that this phenomenon could be found throughout the deep ocean. The presence of a significant concentration of fully complexed Zn ligands in deep water implies that Zn speciation differs significantly from that of Fe and Cu where ligand concentrations typically exceed the dissolved metal concentration (Boye et al., 2001; Moffett and Dupont, 2007).

4.2. Kinetics of Zn complexes

The finding via pseudopolarography that a significant fraction of the Zn in the water column was inert on the time scales of measurement used here raises questions regarding the kinetics of possible Zn complexes in seawater and their relationship to bioavailability. Zinc complexes that are apparently inert are known already; with EDTA and CDTA (Lewis et al., 1995b) and indeed EDTA or CDTA has been used as a competing ligand for Zn speciation with ASV (Xue and Sigg, 1994). Measurements of the dissociation rate of ZnEDTA²⁻ are relatively slow at pH 6.35, $7.7 \times 10^{-5} \text{ s}^{-1}$ (Jervis and Krishnan, 1967), which is slightly faster

than that predicted for seawater ($\sim 3.4 \times 10^{-6} \text{ s}^{-1}$) using the titration data of Bruiland (1989) for ZnEDTA²⁻ ($\log K=7.9$) and the measured formation rate in seawater, $2.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ which is slow due to exchange reaction with CaEDTA and MgEDTA (Raspor et al., 1980). EDTA is inert for Zn dissociation on the timeframe of ASV but is also not directly reduced. Other Zn complexes may also not be reducible because of steric reasons, e.g. the Zn is contained in a ligand pocket where electron exchange cannot take place as could occur in CA (Sarhou et al., 2001). Information on the kinetics of zinc complexes is important to understand for the many paleo studies interpret Zn:Si ratios in opal as reflecting Zn speciation in seawater (Ellwood and Hunter, 2000b; Hendry and Rickaby, 2008).

The kinetics of formation for mono-glycinate complexes of Zn has been studied from 1 to 3000 bar pressure at 10 °C with $k_f=7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ indicating the rapid formation of Zn octahedral complexes (Grant, 1973). Similarly for zinc finger peptide CP-1 the formation rate was $2.8 \pm 0.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and the dissociation rate $1.6 \pm 0.6 \times 10^{-4} \text{ s}^{-1}$ at pH 7 (Buchsbaum and Berg, 2000). The formation rate of the metalloenzyme CA is significantly slower, $\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (Henkens and Sturtevant, 1968), than for the small bi- and tridentate ligands, and this is attributed to an unusually large enthalpy of activation (Romans et al., 1978). The dissociation rate of Zn from bovine CA is reported to be exceedingly slow at pH 8, $\sim 1 \times 10^{-8} \text{ s}^{-1}$ (Romans et al., 1978) resulting in a $\log K \sim 12$ (Lindskog and Malmstrom, 1962; Romans et al., 1978). Measurements of the conditional stability constant for bovine CA in seawater using CSV with APDC indicate $\log K=8.9$ (Sarhou et al., 2001), with the dissociation from the CA apparently accelerated by an associative reaction with APDC, these authors suggested the lower binding strength in seawater was due to side reactions with major cations.

There is also kinetic data for other potential Zn chelators in the ocean. Glutathione and phytochelatin are present in low nM concentrations in seawater (Ahner and Morel, 1995; Dupont et al., 2006) and can be produced/exuded in response to Zn or Cu toxicity (Dupont and Ahner, 2005; Kawakami et al., 2006; Lee et al., 1996), though its main role in cells may be as an anti-oxidant (Dupont et al., 2004; Sies, 1999). Formation rates for glutathione are fast, $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Dominey and Kustin, 1983) but the Zn-glutathione and Zn-phytochelatin complexes are thermodynamically weak and reducible by ASV (Chekmeneva et al., 2008). Polysaccharides can also be released from phytoplankton and bacteria during growth and decay (Nichols et al., 2004; Wustman et al., 1997), however they do not form strong complexes with Zn (Arino et al., 1992). Formation rates for Zn²⁺ with water soluble porphyrin complexes are very slow, $\sim 1.5 \text{ M}^{-1} \text{ s}^{-1}$, though reactions with Zn(OH)⁺ are two orders of magnitude faster at $\sim 210 \text{ M}^{-1} \text{ s}^{-1}$ (Thompson and Krishnamurthy, 1979). The formation of Zn complexes with chlorophyll derivatives and other porphyrins is also extremely slow $\sim 0.5\text{--}3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Tonucci and Von Elbe, 1992) but the complexes once formed can dissociate slowly, e.g. $2.83 \times 10^{-6} \text{ s}^{-1}$ for a water soluble Zn porphyrin (Stein and Plane, 1969), and though uncommon may persist in marine sediments for millions of years (Junium et al., 2008).

Based on the information presently available Zn porphyrin or Zn protein complexes may be the best candidates for the inert ligand found in our work with conservatively estimated dissociation rates of 10^{-6} to 10^{-8} s^{-1} , which would imply residence time (Witter and Luther, 1998) for free Zn in the water column of 16–1600 days. Longer residence times would be possible with slower dissociation rates. This may be the Zn chlorophylls found in bacterichlorophyll (Hiraishi and Shimada, 2001) or a substitution product of other porphyrins. Thus we suggest that the inert deep water ligand found in our study could be stable degradation products of bacteria and phytoplankton.

4.3. Does the reduction of organically complexed zinc contribute to labile Zn?

Previously comparisons between CSV and ASV have resulted in similar ligand concentrations for zinc but have differed significantly in the estimated $\log K_{ZnL'}$ values (Donat and Bruland, 1990; Ellwood and van den Berg, 2000). Possible reasons for these differences could be due to either to an underestimation of labile zinc by ASV, or overestimation of reactive zinc by CSV (Ellwood, 2004; Ellwood and van den Berg, 2000). In the present work we undertook no speciation measurements with CSV but can examine in detail whether ASV underestimates labile Zn (Zn'), or alternatively if there is significant reduction of organic Zn complexes at the electrode resulting in an underestimate of the effective α_{Zn} .

Previously Ellwood and van den Berg (2000) identified three hypothetical problems with ASV depending on the plating and scanning stages of the measurement as follows.

- (i) *The dissociation of the Zn-organic complex in the diffusion layer due to the depletion of inorganic zinc during the deposition step:* this would tend to lead to an overestimation of the labile metal concentration, as has been seen previously for copper (van den Berg, 1992).
- (ii) *Direct reduction of ZnL during plating:* this would lead to an overestimation of the labile metal concentration and an underestimation of α_{Zn} .
- (iii) *During the stripping step the use of differential pulse or square-wave results in the zinc undergoing repeated cycles of oxidation and reduction in the diffusion layer.* Where there may be an excess of depleted natural ligands especially at low zinc concentrations it is suggested that these ligands suppress the response of zinc at low zinc concentrations causing the very low peak heights characteristic of the ASV monitored titrations with zinc (Bruland, 1989) and results in an underestimation of the labile zinc concentration.

In case (i), the dissociation of ZnL complexes due to the removal of free Zn from the diffusion layer would only be important if the supply of labile Zn was depleted and if the dissociation rate was fast enough within the transit time in the diffusion layer. For a RDE with a rotation rate of 3000 rpm the expected diffusion layer thickness is 8.3 μm and the resulting transit time ~ 28 ms (Muller and Kester, 1990). Thus for significant ($> 10\%$) ML dissociation to occur, requires $k_d > 3.6 \text{ s}^{-1}$. Which given a typical $k_f \sim 1 \times 10^7$ for simple Zn complexes suggests a $\log K < 6.4$ and thus would require μM concentrations of the free ligand to be a significant Zn chelator under equilibrium conditions.

Pseudopolarography data suggest that case (ii) is possible as weak organic Zn complexes could be reduced at the overpotential employed under typical ASV conditions. However the data of Lewis et al. (1995b) suggest that for a potential of -1.2 V the thermodynamic $\log K$ of these complexes would only be 10^7 M^{-1} thus as for case (i) above then the ligand would need to be present at concentrations above 100 nM to influence the speciation results.

The final case (iii) is harder to examine but for the present work we frequently had significant labile concentrations of Zn, which after pre-concentration by deposition would have led to an excess of free Zn in the diffusion layer upon stripping. This high free Zn concentration would rapidly complex with free ligands in the diffusion layer and any effect on the subsequent re-oxidation current would have been small. However in the case of low Zn surface waters from other regions the situation may easily arise

where the Zn diffusing out of the Hg film is complexed and then not able to participate in the redox cycling step. This may occur even in the absence of strong Zn complexing ligands as all that is required is an excess of complexing ligands that have fast formation rates but do not dissociate within the time step of the measurement. Experimentally this could be tested by varying the deposition time of the analysis, which would vary the concentration of Zn supplied to the diffusion layer upon stripping. Indeed we have observed such an effect with a series of short deposition times with seawater collected during this work.

The overall question of whether Zn-organic complexes are reduced is evident from our pseudopolarographic data, which indicates that some of it is but there is also a significant pool of Zn which is inert on the timescales of analysis used in TMF-GC-RDE.

4.4. Implications for the biogeochemical cycling of zinc

The high labile Zn found throughout the Southern Ocean waters south of the Polar Frontal region (Fig. 5) suggests that Zn

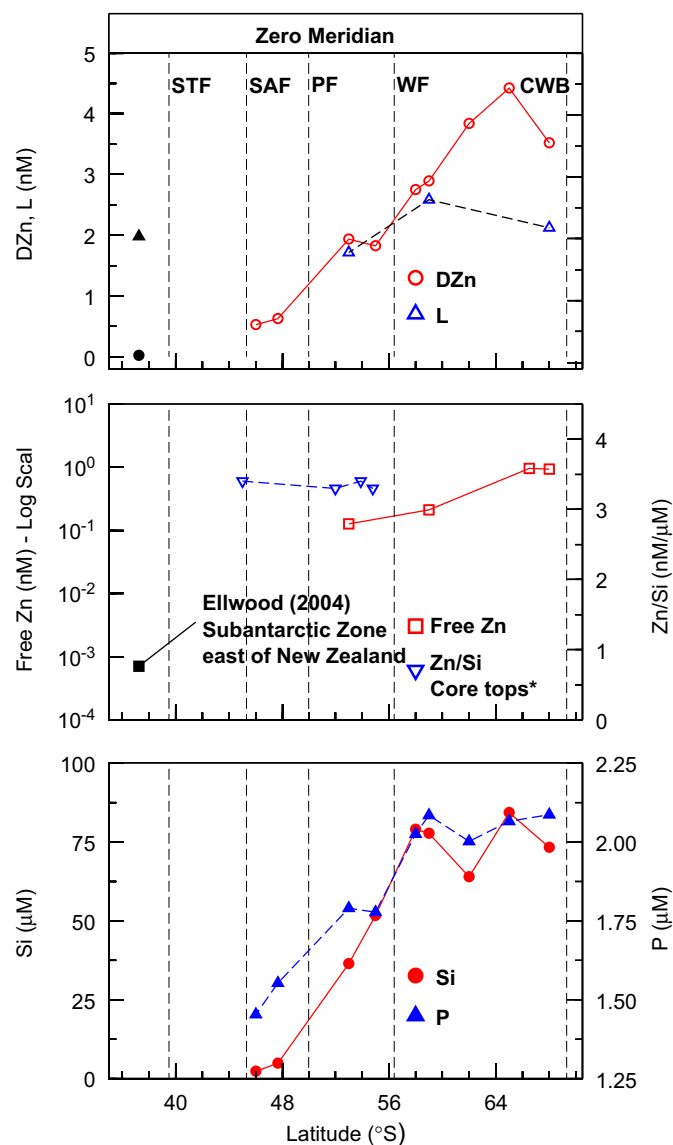


Fig. 5. Dissolved zinc and L concentrations (top), free zinc (center), and phosphate and silicate (bottom) in surface waters as a function of latitude and frontal systems along the Zero Meridian. Data from the STC region close to New Zealand are also shown (Ellwood, 2004) for comparison. The Zn:Si core top data from the same region (Ellwood and Hunter, 2000b) is shown also in the central panel.

limitation is unlikely in these waters based on existing phytoplankton Zn limitation studies (Anderson et al., 1978; Brand et al., 1983; Buitenhuis et al., 2003; Shaked et al., 2006). Culture data for Southern Ocean species is sparse but recent studies have investigated Zn limitation of growth for *Phaeocystis antarctica* (Saito and Goepfert, 2008) and the diatom *Chaetoceros calcitrans* (Timmermans et al., 2001), a species closely related to that found in the Antarctic, based on these findings it is clear that these species, and presumably other related phytoplankton, would not be Zn limited in the Southern Ocean. However, we are also missing data on the sources and sinks of the organic ligands that bind Zn in seawater and this may have important implications for Zn bioavailability in the ocean. From our work here it suggests that in the deep waters of the Southern Ocean there is a significant concentration of inert Zn-organic ligands, which are apparently long lived with implications for the transport and ultimately upwelling/ventilation of these waters to the surface.

4.5. Implications for the interpretation of Zn speciation for paleo oceanographic studies

Our work also has implications for paleo oceanographic work as in recent years the Zn:Si ratio of opal has been considered for use as a paleo tracer of past oceanic conditions for Zn speciation in the Southern Ocean (Ellwood and Hunter, 2000b; Hendry and Rickaby, 2008). The use of this proxy is based on phytoplankton culture studies using the coastal diatom *Thalassiosira pseudonana*, which showed good correlations between the free Zn concentration and the Zn:Si ratio recorded in the opal frustule (Ellwood and Hunter, 2000a). More recently this approach has been applied also to freshwater diatom species (Jaccard et al., 2009a, 2009b). Core top Zn:Si data from the Atlantic section of the Southern Ocean using this approach have been published and interpreted as a proxy for contemporary water column processes (Ellwood and Hunter, 2000b) and thus comparison with our speciation data for Zn then provides a good test of this proxy. However the dramatic change in free Zn, and macronutrients, we observed in surface waters as we transected the APF (Fig. 5) is not observed in the Zn:Si ratios of sediment opal from core tops (Ellwood and Hunter, 2000b), which remain almost constant (3.3 $\mu\text{mol}:\text{mol}$) across the frontal systems (Fig. 5). Our data is more consistent with recent reports on high Zn:Si ratios found in diatoms collected in vicinity of the Antarctic Peninsula (Diaz et al., 2010; Sherrell et al., 2010), and in sediment core data from the same region (Hendry and Rickaby, 2008), and indicates that more core top data is urgently required from the Southern Ocean to validate this proxy. Clearly further work is required on describing and identifying the Zn:Si ratio in individual diatom species if this proxy is to be fully realised as a tracer of Zn speciation in the ocean.

Our data also do not support the 'Zinc' hypothesis (Morel et al., 1994), which postulated that increased dust inputs to the Southern Ocean could have supplied Zn that stimulated phytoplankton production via increased CA utilization. As Southern Ocean Zn concentrations are clearly already sufficient in Zn for phytoplankton growth the addition of more Zn would make little difference to primary productivity.

5. Conclusions

In our study we examined the speciation of Zn in the Atlantic sector of the Southern Ocean. We observed a strong gradient in both DZn and free Zn across the APF with both parameters increasing towards higher latitudes. In the Southern Ocean south of the APF we found detectable labile inorganic Zn throughout the

surface waters, indicating a saturation of zinc-organic ligands, in contrast to studies from lower latitudes. Strong inert zinc ligands existed throughout the Southern Ocean but were nearly always saturated due to the presence of high dissolved Zn concentrations that are associated with the high nutrient waters south of the APF. Under these conditions Zn bio-limitation was unlikely south of the APF. Only in some near surface samples a ligand excess was detected suggesting a recent biological source. Using Pseudopolarography strong and inert Zn ligands were found in the surface and in deep water masses with consequences for the transport of these long-lived species and the ultimate upwelling and speciation of Zn in the surface. Based on the kinetics of known Zn complexes we suggest the liberation of natural Zn-porphyrin and -protein complexes during degradation of bacteria and phytoplankton as a possible source for these deep water Zn-organic complexes. Overall our study provided the first information on the speciation of Zn in the high latitudes of the Southern Ocean with implications for our understanding of the biogeochemical cycling of this bio-essential element.

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