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# Biogeochemical cycling of zinc and its isotopes in the Southern Ocean

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**Abstract**

We report Zn concentration and isotope data for seawater samples from the Atlantic sector of the Southern Ocean, collected during the IPY/GEOTRACES ANT-XXIV/III cruise along the Greenwich Zero Meridian. Data are reported for the full depth range of the water column at three stations, as well as a transect of surface samples, using a new analytical approach that is presented in detail here.

Zn concentrations increase with depth, though due to proximity to upwelling sites, surface concentrations are not as low as in some parts of the ocean such as further northward into the Sub-Antarctic Zone. For two depth profiles south of the Polar Front Zone, the physical stratification of the upper water column is reflected in sudden near-surface changes in Zn concentration with depth. In contrast, beneath 100–300 m Zn concentrations barely change with depth. Zn isotopic data beneath 1000 m, for the Southern Ocean data presented here as well as published data from the North Atlantic and North Pacific, are strikingly homogeneous, with an average $\delta^{66}Zn = +0.53 \pm 0.14‰$ (2SD, 2SE = 0.03, $n = 21$). The surface Southern Ocean is more variable, with $\delta^{66}Zn$ ranging from 0.07‰ to 0.80‰. Between the two is a thin horizon at 40–80 m which, in the Southern Ocean as well as the North Atlantic and North Pacific, is characterised by distinctly light isotopic signatures, with $\delta^{66}Zn$ about 0.3‰ lower than surface waters.

Strong correlations between Si and Zn concentrations seen here and elsewhere, coupled to the lack of any systematic relationship between Si and Zn isotopes in the Southern Ocean, suggest that the removal of Zn associated with diatom opal involves little or no isotopic fractionation. Regeneration of this Zn also explains the homogeneous Zn isotopic composition of the global deep ocean so far sampled. However, the low Zn content of opal requires that deep ocean Zn does not directly come from the opal phase itself, but rather from associated organic material external to the diatom frustule during growth. Experimental data are consistent with little or no fractionation during incorporation of Zn into this material. On the other hand, the light zinc at 40–80 m is most consistent with the regeneration of an intra-cellular pool that both culturing experiments and field data suggest will be isotopically light. The data thus imply two processes by which Zn is taken up in the surface ocean, that these pools have very different regeneration lengthscales, and that physical mixing of the oceans cannot eradicate their isotopic signatures. Finally, the deep $\delta^{66}Zn$ ocean value is significantly higher than the current best estimate of the input to the oceans. The most obvious candidate for the required light sink is the survival of some of the cellular Zn to be buried in sediment.


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## 1. INTRODUCTION

Zinc (Zn) is involved in a number of biological processes in marine micro-organisms (see recent review by Sinoir et al., 2012), such as the important role as a cofactor in the enzyme carbonic anhydrase (Lippard and Berg, 1994) that promotes $CO_2$ uptake in marine algae (Morel et al., 1994). Moreover, Zn displays nutrient-like depth profiles in the oceans (Bruland, 1980; Martin et al., 1989). For example, in the open Pacific, surface water concentrations of Zn are up to a factor of 250 times lower than those of deep waters, reflecting intense removal of Zn into phytoplankton at the surface and regeneration at depth (e.g., Lohan et al., 2002). In the surface ocean ~98% of total dissolved Zn is chelated with strong Zn-binding organic ligands (Bruland, 1989; Donat and Bruland, 1990; Ellwood and van den Berg, 2000; Lohan et al., 2002; Bruland and Lohan, 2003), so that the concentration of bio-available $Zn^{2+}$ (Sunda and Huntsman, 1992) is typically only 2–14 pM in the photic zone of the open Pacific Ocean (Donat and Bruland, 1990). It has been suggested based on laboratory studies that, at this level, Zn could limit phytoplankton growth (Brand et al., 1983; Sunda and Huntsman, 1992, 1995, 2005; Buitenhuis et al., 2003; Shaked et al., 2006), though other evidence for such limitation is equivocal (e.g., Crawford et al., 2003; see recent review by Sinoir et al., 2012).

It is well known that photosynthetic uptake of carbon and the major nutrients (e.g., Kroopnick, 1985; Altabet and Francois, 1994; De La Rocha et al., 1998) involves a kinetic isotope fractionation such that, for example, phytoplankton preferentially take up $^{12}C$ over $^{13}C$, leading to enrichment in $^{13}C$ in surface waters. If the depletion of Zn in ocean waters is associated with a similar isotopic fractionation, then Zn isotopes could potentially be used to probe the mechanisms for Zn uptake and export from the surface ocean and, moreover, be used as a paleoceaonographic tracer in similar ways to foraminiferal $\delta^{13}C$ (e.g., Andersen et al., 2011). Precise isotopic analysis of Zn (Maréchal et al., 1999) has only become possible since the development of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS). Significant isotopic fractionation of Zn in marine and environmental systems (roughly 2.5‰ total variation in $\delta^{66}Zn$, see data compiled in Cloquet et al., 2006), resulting from equilibrium and kinetic reactions during both biological and abiotic processes, have since then been found in a number of studies, highlighting the potential of Zn stable isotopes as tracers (e.g., Maréchal et al., 1999; 2000; Weiss et al., 2005; Bermin et al., 2006).

In this paper we present, for the first time, depth profiles of Zn concentrations and isotopic compositions covering the entire water column, specifically from the Atlantic Sector of the Southern Ocean. The Southern Ocean is a key region for many global oceanic processes (Marinov et al., 2006), with water from all three oceans coalescing and mixing at depth. It is also an extensive High Nutrient–Low Chlorophyll (HNLC) region (Minas et al., 1986), where trace metals (e.g., Fe) are often cited as the limiting factor for primary productivity (e.g., Boyd and Elwood, 2010). The aim of this contribution is therefore to assess the extent to which Zn isotope data can clarify the cycling of Zn in a region of the ocean where trace metals are biogeochemically important.

## 2. OCEANOGRAPHIC SETTING

The study region, at or near the Greenwich or Zero Meridian (Fig. 1), encompasses the eastward flowing Antarctic Circumpolar Current (ACC), which extends to its southern boundary (SB-ACC) from the Sub-Tropical Front (STF), and the Weddell Gyre, which extends from the SB-ACC to near the Antarctic continent. Within the ACC there are two more distinct fronts, the Sub-Antarctic Front (SAF) and the Antarctic Polar Front (APF). Within these latter frontal zones, which are narrow at any one time but meander through time, the ACC flows eastwards about

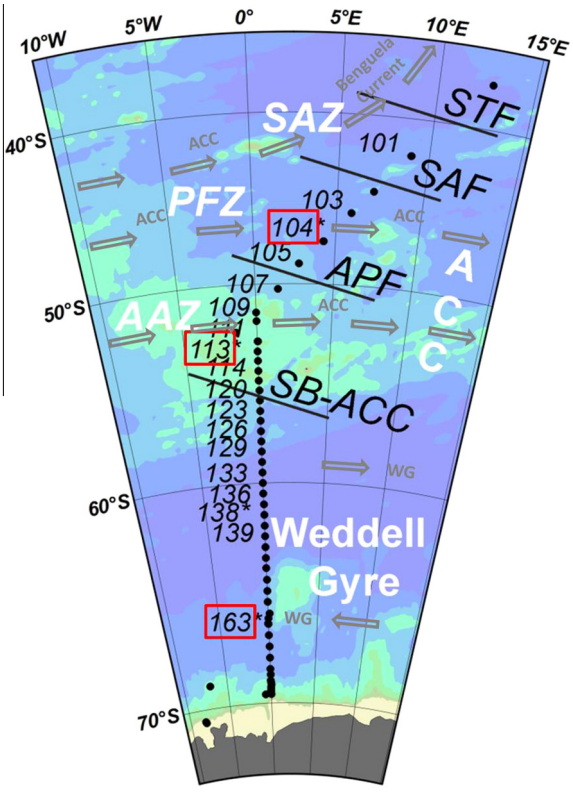


Fig. 1. A portion of the IPY ANT-XXIV/3 cruise track with sampling stations, positions of the Antarctic fronts and oceanographic regimes (see Orsi et al., 1995). AAZ = Antarctic Zone, PFZ = Polar Frontal Zone, SAZ = Sub-Antarctic Zone, WG = Weddell Gyre, ACC = Antarctic Circumpolar Current, STF = Sub-Tropical Front, SAF = Sub-Antarctic Front, APF = Antarctic Polar Front, SB-ACC = Southern Boundary of ACC. Grey arrows and associated labels show schematic surface flow directions. The Bristol lab received 3 depth profiles (see red boxes) and a subset of large surface samples (all surface samples collected are indicated by filled black circles). Asterisks mark stations sampled with ultraclean Titan frame (de Baar et al., 2008), which includes all three depth profiles analysed here for Zn. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3–4 times more rapidly than outside them (Orsi et al. 1995). The positions of the fronts during the cruise is shown in Fig. 1. Between the fronts are three wide zones of slower eastward flow (Orsi et al. 1995), the Sub-Antarctic Zone (SAZ) between the STF and SAF, the Polar Frontal Zone (PFZ) between the SAF and APF, and the Antarctic Zone between the APF and SB-ACC. The Weddell Gyre comprises an eastward branch in the ~58°S to 65°S region, and a westward return flow in the ~65°S to 69°S region, the latter separated from the Antarctic continent by the narrow, eastward flowing, Antarctic Coastal Current.

The Southern Ocean comprises all waters south of the STF. The APF is a boundary that is very significant for this study, as follows. Briefly the hydrography of the Southern Ocean is dominated by upwelling along the important frontal regions (Orsi et al., 1995, Fig. 1). Upwelling of Circumpolar Deep Water (CDW) brings waters rich in major nutrients (nitrate, phosphate and silicate) to the surface (Fig. 2). Part of these waters flows northwards where at the APF two processes take place. Firstly some portion of the northward flowing water is subducted at and beyond the APF to become Antarctic Intermediate Water (AAIW), relatively rich in N, P and Si, flowing northwards at typically ~1000 m depths far into the Atlantic, Pacific and Indian Ocean basins. Another portion of the northward-flowing water remains at the surface so that, at the APF, very intense summer blooms of large size classes of highly silicified diatoms ($Si/N_{diatom} > 3$) utilize all available silicate (Queguiner et al., 1997). As a result, north of the APF, dissolved silicate is depleted in surface waters, while nitrate and phosphate decrease more gradually until final depletion at the Sub-Antarctic Front (SAF). Another portion of the upwelled nutrient-rich waters flows southwards where eventually, due to intense winter cooling and sea-ice formation in austral winter in the Weddell Sea, the water sinks to form Weddell Sea Bottom Water (WSBW), which eventually flows northward as nutrient-rich (N, P and Si) Antarctic Bottom Water (AABW).

The general summer depletion of all three major nutrients in surface waters north of the SAF implies that the northernmost Sub-Antarctic Zone (the SAZ, between the SAF and STF) of the Southern Ocean can actually become macronutrient-depleted. In other words traveling from north to south the surface waters of the Southern Ocean have three distinct regimes of major nutrients: (i) the SAZ that in summer can become depleted in all three major nutrients N, P and Si; (ii) the PFZ that is HNLC for two major nutrients N and P, but depleted in Si; (iii) the Antarctic Ocean south of the APF, comprising the AAZ and Weddell Gyre, that is truly HNLC. In other words, the SAZ is in fact non-HNLC and limiting for all phytoplankton species, the PFZ is Si-limited for diatoms but has ample N and P for other phytoplankton species, and only the Antarctic Ocean is fully HNLC for all three major nutrients i.e., there is an adequate supply for growth of diatoms and all other phytoplankton such that, here, other limitation(s) must exist. These distinctions are important here because in the other major oceans the vertical distribution of dissolved Zn has been shown to correlate strongly with dissolved silicate (e.g., Bruland, 1980). Therefore in this study of Zn and its isotopic composition, the APF is the distinct boundary between true HNLC conditions south of the APF, as opposed to Si-limitation north of the APF. Accordingly, in terms of the major nutrients and potential relationships with Zn and its isotopes, we focus here on Si rather than N and P.

Possible limiting factors for productivity in the HNLC zone include iron (Martin et al., 1990; de Baar et al., 1990; Buma et al., 1991; de Baar et al., 1995), light (Mitchell et al., 1991; Sunda and Huntsman, 1997; de Baar et al., 2005), and zooplankton grazing (Cullen, 1991). Initial Fe fertilization experiments generally showed a much stronger response than those with addition of other bio-essential trace metals, such as Mn, Co, Cu, Zn, or combinations thereof (Buma et al., 1991; Scharek et al., 1997). Since then most studies of the role of trace metals in the Southern Ocean (Boyd et al., 2000) have focused on iron (see recent review in Boyd and Elwood 2010). More recently the covariance of dissolved Mn and phosphate in upper waters of the same Greenwich meridian suggests some co-limita-

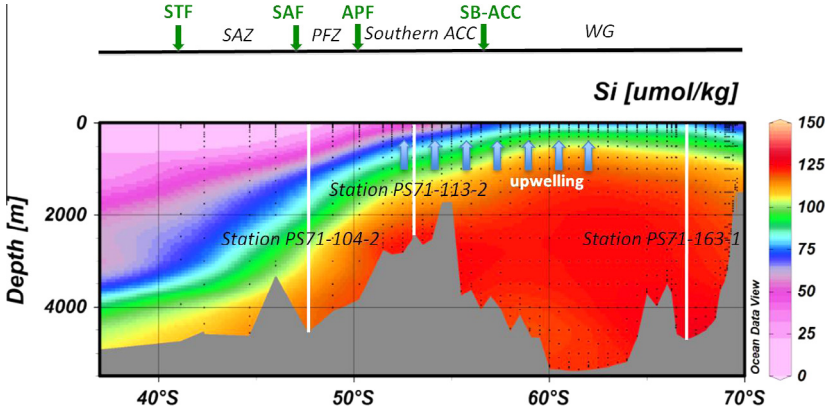


Fig. 2. N–S vertical section for dissolved silicate (μmol/kg) along the Greenwich Zero Meridian. The line at the top shows the major fronts (green) and oceanic regimes (black) discussed in the text. Abbreviations are as in Fig. 1. The depth profiles studied for Zn isotopes and concentrations are marked in white. Silicate data plotted using the ODV software (Schlitzer, 2002). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tion of Mn and Fe at some times and places in the Antarctic Ocean (Middag et al., 2011a). Also it has been suggested that sub-optimal Zn concentrations in the Southern Ocean may influence Si and N uptake rates by phytoplankton (Hassler et al., 2012). Previous water column work (Coale et al., 2005) has revealed that Zn concentrations, like the major nutrients, are high near the upwelling zone in the Antarctic Ocean and decline sharply northwards.

Andersen et al. (2011) have measured Southern Ocean core-top diatom$_{opal}$ samples extracted from marine sediments and reported systematic changes in $\delta^{66}$Zn associated with surface water Zn concentrations. These systematic changes were found to be coupled to changes in Zn/Si ratios of the diatom$_{opal}$, which had been suggested previously (e.g., Ellwood and Hunter, 2000; Andersen et al., 2011) to reflect the concentrations of bio-available Zn in the ambient surface seawater where the diatom$_{opal}$ was formed. The $\delta^{66}$Zn and Zn/Si of diatom opal, therefore, have the potential to be used for investigating Zn cycling and primary productivity in the past Southern Ocean.

## 3. SAMPLES

The seawater samples used in this study, were collected during cruise ANT-XXIV/3 (Feb–April 2008) in the Atlantic sector of the Southern Ocean as part of the International GEOTRACES program and a contribution to the International Polar Year (IPY). Seven vertical profiles were taken, of which 3 were available for study here (Figs. 1 and 2). These are at station 104 in the Si-depleted PFZ of the ACC, station 113 in the Si–N–P-rich HNLC AAZ region of the ACC, and station 163 in the Si–N–P-rich HNLC southernmost westward flowing branch of the Weddell Gyre. In addition, large (20 L) surface water samples (2–5 m) were obtained along the Greenwich Zero Meridian from 47°S to 68°S (Fig. 1), some of which were also available for study here. These are at station 105 in Si-depleted waters of the PFZ, stations 109, 111, 114, 117, 120 in the Si–N–P-rich HNLC AAZ region of the ACC, and stations 123, 126, 129, 133, 136, 139 in the Si–N–P-rich HNLC of the northernmost eastward flowing branch of the Weddell Gyre. Unfortunately, the surface samples that are likely to be the most Zn-depleted, around and northward of the Sub-Antarctic Front, were exhausted by other analyses and not available to us for study.

The TITAN trace metal clean rosette system from the Royal Netherlands Institute for Sea Research (NIOZ) was used for seawater sampling (de Baar et al., 2008). The system consisted of a titanium frame fitted with a standard Seabird CTD in a titanium housing, and 24 modified 12 L Teflon coated GO-FLO bottles deployed with a kevlar wire with internal signal cables (de Baar et al., 2008). Sample bottles were tripped on the upcast using standard Seabird CTD software. Upon recovery, the complete rosette was carefully moved into its dedicated NIOZ Class-100 clean room container specially built for sub-sampling, where filtration and sub-sampling were performed on the seawater samples using established protocols (Middag et al., 2011b). All seawater samples collected were acidified for storage to pH of around 2 using Seastar HCl. Bottles for sample collection were pre-cleaned with hot acid in the clean labs at MPI. High density polyethylene (HDPE) containers of variable sizes for samples from different water depths (20 L for surface, 10 L for intermediate, 5 L and 1 L for deep) were subjected to a hot cleaning procedure consisting of successive treatment in alkaline detergent and 6 M HCl, followed by several ultra-pure MQ water rinses to remove trace metal impurities. Sub-sampling for Zn isotopic analysis was done in the clean lab of MPI. Bottles for sub-sampling were supplied by Bristol and pre-cleaned in 20% HCl for 2 weeks, then rinsed 4 times with MQ before packing.

Major nutrients were analysed onboard by NIOZ using a Bran & Luebbe Traacs 800 Auto-analyser by standard methods described in Grasshoff et al. (1999). Samples for nutrient measurement were obtained from a CTD rosette sampler (an ultraclean CTD) in a polyethylene vial, stored in the dark at 4 °C and analysed within 12 h of sampling (Fahrbach & de Baar, 2010). A vertical section of measured silicate is plotted along the Greenwich Zero Meridian in Fig. 2. As discussed above, the low Si concentration in SAZ and PFZ in Fig. 2 is the result of the northward transport of upwelled Si-rich CDW water (south of 49°S), with the strong removal of silicate at the APF.

## 4. METHODS

In order to extract Zn, present at nanomolar (nM) levels or lower, from up to several litres of seawater, an initial pre-concentration is required before purification for isotopic analysis. Preliminary data from this laboratory (Bermin et al., 2006) used both Chelex-100 (Kingston et al., 1978) and co-precipitation with $Mg(OH)_2$ (Wu and Boyle, 1998). Extraction with Chelex-100 is adequate for high Zn concentration deep ocean samples, but for Zn-poor surface samples the blank contribution from the Chelex column is unacceptably high (Bermin et al., 2006). Co-precipitation with Mg is achieved by adding ammonia to acidified samples until the seawater's own inventory of dissolved Mg precipitates at pH$\sim$10 as $Mg(OH)_2$, bringing virtually all of the Zn with it. Again, this procedure performs adequately for Zn-rich deep ocean samples where relatively small volumes ($<$500 ml) of seawater can be used. However, for the large samples required to obtain enough Zn from depleted surface samples (in some case $>$2 L in this study), the Mg precipitate is so large that it causes difficulties during the subsequent separation and purification of Zn.

Here, a new pre-concentration approach has been used, involving the addition of a Zn-free aluminium solution to the seawater sample. The pH is then raised with ammonia, but in this case only to about 8.5–9.0 so that $Al(OH)_3$ precipitate is produced but no $Mg(OH)_2$. Since the amount of aluminium added can be controlled, subsequent handling of the precipitate during the chromatographic purification of Zn is much easier. Since these are the first data we report using this approach, we describe it in some detail in this section, including the tests we have undertaken to establish its success. We also take the opportunity to compare the Zn concentrations obtained here with those published previously for the same or similar locations (Löscher, 1999; Croot et al., 2011).

All lab work was carried out under clean laboratory conditions in Class-100 laminar flow clean hoods, using only Savillex (Minnetonka, MN, USA) PFA labware. All labware was cleaned on the hotplate, firstly with 6 M HCl, subsequently with 50% $HNO_3$ for two days, then with 1% once distilled $HNO_3$ for another day, rinsing thoroughly between each step and at the end. 18.2 MΩ MQ water was obtained from a Millipore Q-Gard® B1 system. All acids used were distilled twice.

### 4.1. Pre-concentration by co-precipitation

The initial step of co-precipitation was either done in large pre-cleaned Teflon beakers (up to 1 L), or in a clean 4 L LDPE bottle (for samples >1 L). Samples were weighed, and Zn double spike and 1.2 ml 10000 ppm Al standard solution were added. The commercial Al solution was pre-cleaned of Zn on an anion column and subsequently re-dissolved in 1 M HCl. The ratio between sample and double spike Zn is ideally 1 (Bermin et al., 2006), but there is a lot of leeway in this (see below). Beakers were left to equilibrate overnight, whereupon an ultra-clean ~11 M Romil ammonia solution was added to reach a desired pH. White precipitate began to form and the beakers were left for a few more days for the precipitate to develop. After this, as much supernatant as possible was poured off. Then the precipitate and remaining water was transferred to a smaller pre-cleaned Teflon beaker to settle again. The precipitate was then separated from the remaining supernatant by centrifugation. The centrifuged precipitate was washed with pH = 10 MQ (MQ to which a small amount of ammonia was added) and centrifuged again. The final "clean" precipitate was dissolved in 2 ml 7 M HCl, dried down, taken up in 1 ml 7 M HCl and dried down twice. The sample was finally dissolved in 1 ml (or more, depending on the amount of precipitate obtained) 1 M HCl, before passing through the anion exchange column for further purification.

The aluminium solution, despite being pre-cleaned on a column, was a significant contributor to the total blank. In addition, co-precipitation at too high a pH causes precipitation of un-wanted Mg hydroxide from seawater in addition to aluminium hydroxide. Tests were therefore conducted to ascertain the smallest amount of Al solution that could be used, as well as the minimum pH for co-precipitation, while maintaining high Zn yields. Because of the double spike approach, high Zn yields are not essential for accuracy, but they are desirable to maximize the final analyte signal during mass spectrometry. Based upon the results of these tests (see Electronic Supplementary Material (ESM), Fig. 1), it was decided to add 1.2 ml of Al solution (12 mg) and to raise the pH to 8.5–8.8 during co-precipitation. In both cases this procedure produced yields in excess of 90% (Tables 1–3) for sample sizes ⩽1 L, and greater than 70% for sample sizes >1 L, where quantitative recovery of the precipitate from 4 L bottles was difficult.

### 4.2. Column chemistry

The column procedure described by Maréchal et al. (1999), modified by Archer and Vance (2004), has been adopted, with some further minor modifications. Primarily, 1 M HCl has been used instead of 7 M HCl to dissolve precipitate and eliminate seawater matrix. There were two reasons for this: (1) 1 M HCl would contribute less blank than 7 M HCl; (2) it was easier to dissolve $Al(OH)_3$ in 1 M HCl than in 7 M HCl. Samples were loaded to the column in 1 ml (or 2 ml, depending on the amount of precipitate to be dissolved) 1 M HCl. Most metals were washed off in 12 ml 1 M HCl before Zn was collected in 4 ml 2% $HNO_3$. A column calibration was performed with Zn JMC standard and the result suggested that no Zn was eluted until 2% $HNO_3$ was put through the column. The measured column blank of this procedure was 0.2 ng for Zn.

Table 1
Zn isotopic and concentration analyses of intercalibration samples obtained from the Bruland laboratory at Santa Cruz.

| Sample ID | Depth (m) | [Zn] (nmol/kg) | $\delta^{66}$Zn (‰) | 2 sigma | Total Zn from ID (ng) | Yield (%) |
|---|---|---|---|---|---|---|
| SAFe D2[a] | 1000 | 7.66 | 0.52 | 0.03 | 103 | 91 |
| SAFe D1 | 1000 | 7.68 | 0.56 | 0.03 | 85 | 91 |
| SAFe D2 | 1000 | 7.40 | 0.52 | 0.03 | 76 | 96 |
| SAFe D2 | 1000 | 7.38 | 0.50 | 0.04 | 74 | 95 |
| SAFe S[b] | Surface | 0.051 | | | 17 | 85 |
| SAFe S | Surface | 0.052 | | | 17 | 91 |
| SAFe S | Surface | 0.050 | | | 17 | 59 |
| SAFe S | Surface | 0.049 | | | 16 | 60 |
| GSC32[c] | Surface | 1.35 | 0.08 | 0.04 | 48 | 99 |
| GSC303[c] | Surface | 1.37 | 0.18 | 0.06 | 47 | 97 |

[a] SAFe deep samples (central North Pacific) obtained from Geoffrey Smith (University of California, Santa Cruz). Each line on the table is for a separate analysis from two different bottles (D1 or D2).

[b] SAFe surface samples (central North Pacific) obtained from Geoffrey Smith (University of California, Santa Cruz). Each line is for a separate analysis from four different 4 L bottles. These analyses were done at a stage when we had not developed the methodology fully for small samples and isotopic data were not obtained.

[c] Samples from the Santa Barbara Basin (eastern North Pacific) obtained from Geoffrey Smith (University of California, Santa Cruz). Each line is a separate analysis of different 1 L bottles.

Table 2
Zn concentration (nmol/kg) and $\delta^{66}$Zn for three vertical profiles in the Atlantic sector of the Southern Ocean.

| IPY ID | Depth (m) | [Zn] (nmol/kg) | $\delta^{66}$Zn (‰) | 2 sigma[a] | Total Zn[b] in analysis (ng) | Yield (%) | [Si][c] (μmol/kg) |
|---|---|---|---|---|---|---|---|
| *Station PS71-104-2 (47°39.36′S, 4°15.7′E)* | | | | | | | |
| PS71-104-2-24 | 15 | 0.32 | 0.47 | 0.07 | 51 | 72 | 1.86 |
| PS71-104-2-22 | 50 | 0.62 | 0.25 | 0.05 | 86 | 80 | 1.86 |
| PS71-104-2-20 | 101 | 0.71 | 0.43 | 0.05 | 103 | 77 | 5.66 |
| PS71-104-2-18 | 202 | 1.03 | 0.41 | 0.04 | 129 | 74 | 10.2 |
| PS71-104-2-16 | 301 | 2.10 | 0.47 | 0.04 | 68 | 95 | 20.4 |
| PS71-104-2-14 | 399 | 2.45 | 0.44 | 0.05 | 79 | 99 | 28.1 |
| PS71-104-2-11 | 998 | 5.35 | 0.44 | 0.06 | 79 | 99 | 65.1 |
| PS71-104-2-9 | 1500 | 5.33 | 0.43 | 0.05 | 78 | 105 | 68.7 |
| PS71-104-2-8 | 1748 | 4.88 | 0.48 | 0.05 | 53 | 98 | 70.7 |
| PS71-104-2-7 | 1997 | 4.88 | 0.50 | 0.07 | 49 | 101 | 72.0 |
| PS71-104-2-6 | 2499 | 5.83 | 0.51 | 0.05 | 54 | 97 | 89.1 |
| PS71-104-2-5 | 3002 | 6.16 | 0.60 | 0.06 | 56 | 96 | 101 |
| PS71-104-2-3 | 4006 | 8.04 | 0.61 | 0.05 | 83 | 99 | 118 |
| PS71-104-2-2 | 4202 | 7.03 | 0.54 | 0.06 | 70 | 92 | 119 |
| *Station PS71-113-2 (52°59.828′S, 0.2°0.05′W)* | | | | | | | |
| PS71-113-2-24 | 10 | 3.06 | 0.80 | 0.06 | 83 | 92 | 35.4 |
| PS71-113-2-22 | 74 | 2.59 | 0.47 | 0.03 | 72 | 111 | 35.6 |
| PS71-113-2-19 | 101 | 2.69 | 0.54 | 0.04 | 76 | 108 | 35.8 |
| PS71-113-2-14 | 298 | 6.25 | 0.39 | 0.03 | 68 | 95 | 83.5 |
| PS71-113-2-12 | 401 | 6.56 | 0.48 | 0.04 | 51 | 93 | 87.8 |
| PS71-113-2-10 | 500 | 6.27 | 0.40 | 0.04 | 51 | 95 | 90.8 |
| PS71-113-2-7 | 1000 | 6.30 | 0.70 | 0.05 | 49 | 95 | 103 |
| PS71-113-2-5 | 1501 | 7.07 | 0.58 | 0.04 | 55 | 92 | 115 |
| PS71-113-2-3 | 1997 | 6.82 | 0.50 | 0.03 | 52 | 93 | 123 |
| PS71-113-2-1 | 2351 | 6.84 | 0.43 | 0.06 | 49 | 93 | 128 |
| *Station PS71-163-1 (67°S, 0°E)* | | | | | | | |
| PS71-163-1-24 | 9 | 2.57 | 0.67 | 0.04 | 34 | 94 | 62.6 |
| PS71-163-1-22 | 45 | 4.42 | 0.27 | 0.05 | 203 | 86 | 64.8 |
| PS71-163-1-20 | 74 | 7.03 | 0.53 | 0.03 | 99 | 89 | 89.8 |
| PS71-163-1-18 | 171 | 7.08 | 0.49 | 0.03 | 98 | 85 | 95.6 |
| PS71-163-1-16 | 250 | 7.18 | 0.44 | 0.03 | 99 | 86 | 98.6 |
| PS71-163-1-14 | 401 | 7.14 | 0.57 | 0.03 | 98 | 92 | 104 |
| PS71-163-1-13 | 748 | 7.56 | 0.53 | 0.03 | 99 | 91 | 113 |
| PS71-163-1-11 | 1001 | 7.73 | 0.64 | 0.03 | 91 | 88 | 118 |
| PS71-163-1-9 | 1501 | 7.79 | 0.55 | 0.03 | 90 | 90 | 123 |
| PS71-163-1-7 | 2000 | 7.62 | 0.59 | 0.03 | 104 | 78 | 124 |
| PS71-163-1-5 | 3000 | 7.60 | 0.55 | 0.02 | 104 | 86 | 123 |
| PS71-163-1-3 | 4002 | 7.30 | 0.53 | 0.02 | 98 | 86 | 124 |
| PS71-163-1-1 | 4601 | 7.35 | 0.96 | 0.04 | 78 | 92 | 129 |

[a] Internal uncertainty, with all measurement uncertainties propagated through the double spike reduction procedure. Long-term standard reproducibility is greater at 0.08‰ (see text).
[b] Total Zn analyses as obtained from the isotope dilution analysis. Total procedural blanks were 2–3 ng and the reported concentrations (in nmol/kg) are corrected for this blank.
[c] Si data here and in Table 3 from Middag et al. (2011a).

### 4.3. Procedural blanks

Quantifying the blank for a co-precipitation procedure is difficult because in order to re-produce the entire procedure a seawater sample that contains a finite amount of Zn must be used, so that all measured blanks will be maxima. Ultrapure water can be used as the "seawater" sample but, again, the large quantities of this that must be used to simulate the measured seawater sample will contain finite amounts of Zn. Here we quantified the maximum blank by extracting Zn from different volumes of MQ water, adding the same amount of Al solution as for samples to each, as well as an amount of ammonia appropriate for an acidified 1 L seawater sample (the ammonia blank was insignificant relative to other sources at 7 pg/ml). Duplicate sets of results for these MQ "samples" (Fig. 2 in the ESM), suggest a procedural blank for real samples of ~2 ng. A further constraint derives from analyses performed on extremely Zn-depleted surface samples from the Equatorial Atlantic, samples that turned out to contain as little as 0.01 nM Zn, as determined by isotope dilution. For these 4 L samples this implies a total amount of Zn found of about 2.5 ng.

All of the above suggests a blank contribution of 2–3 ng, though better quantification could reveal it to be substan-

Table 3
Zn concentration (nmol/kg) and $\delta^{66}Zn$ for 11 surface (2–5 m depth) transect stations in the Atlantic sector of the Southern Ocean.

| IPY ID | Longitude (°E) | Latitude (°S) | [Zn] (nmol/kg) | $\delta^{66}Zn$ (‰) | 2 sigma[a] | Total Zn[b] (ng) | Yield (%) | [Si] (μmol/kg) |
|---|---|---|---|---|---|---|---|---|
| PS71-105 | 3.82 | 48.04 | 0.63 | 0.14 | 0.06 | 88 | 75 | 1.89 |
| PS71-105 | 3.82 | 48.04 | 0.65 | 0.07 | 0.04 | 42 | 99 | |
| PS71-105 | 3.82 | 48.04 | 0.65 | 0.11 | 0.03 | 41 | 98 | |
| PS71-109 | 0.00 | 51.67 | 1.27 | 0.60 | 0.04 | 85 | 90 | 15.7 |
| PS71-111[c] | −0.54 | 52.17 | 6.44 | 0.48 | 0.05 | 219 | 93 | 23.3 |
| PS71-111 | −0.54 | 52.17 | 6.55 | 0.46 | 0.04 | 86 | 101 | |
| PS71-111 | −0.54 | 52.17 | 6.53 | 0.42 | 0.03 | 106 | 97 | |
| PS71-111 | −0.54 | 52.17 | 6.32 | 0.49 | 0.03 | 82 | 90 | |
| PS71-111 | −0.54 | 52.17 | 6.55 | 0.45 | 0.04 | 88 | 89 | |
| PS71-114 | 0.00 | 53.18 | 2.69 | 0.45 | 0.04 | 90 | 95 | 34.3 |
| PS71-117 | 0.02 | 54.32 | 2.76 | 0.58 | 0.04 | 96 | 92 | 44.3 |
| PS71-120 | 0.00 | 55.24 | 2.81 | 0.58 | 0.03 | 95 | 98 | 50.3 |
| PS71-123 | 0.00 | 56.30 | 3.25 | 0.50 | 0.03 | 88 | 106 | 63.8 |
| PS71-126 | 0.00 | 57.21 | 3.47 | 0.51 | 0.04 | 96 | 93 | 64.8 |
| PS71-129 | 0.00 | 58.20 | 3.69 | 0.50 | 0.04 | 102 | 96 | 67.1 |
| PS71-133 | 0.00 | 59.00 | 3.02 | 0.45 | 0.03 | 84 | 102 | 62.7 |
| PS71-136 | 0.00 | 60.24 | 2.72 | 0.52 | 0.04 | 76 | 105 | 62.1 |
| PS71-139 | 0.00 | 61.15 | 2.26 | 0.50 | 0.04 | 62 | 101 | 57.6 |

[a] Internal uncertainty, with all measurement uncertainties propagated through the double spike reduction procedure. Long-term standard reproducibility is greater at 0.08‰ (see text).
[b] Total Zn analyses as obtained from the isotope dilution analysis. Total procedural blanks were 2–3 ng and the reported concentrations (in nmol/kg) are corrected for this blank.
[c] Zn concentrations for sample PS111 reproduce across duplicate analyses of separate aliquots from the same 20 L MPI container, but the data are highly anomalous. We suspect that the original 20 L MPI bottle must have been contaminated before or during original sampling, and these data are not considered further.

tially lower. Sample volumes analysed here ranged from 0.1 to 2.2 L, yielding total amounts of Zn analysed of 34–219 ng. With the above absolute maximum procedural blank of 3 ng, the Zn blank contribution to the smallest sample analysed was less than 9%. Previous measurements of the isotopic composition of (larger) blanks in this laboratory gave $\delta^{66}Zn = 0.17 \pm 0.18‰$ (Bermin et al., 2006; $\delta^{66}Zn_{JMC\text{-}Lyons} = [(^{66}Zn/^{64}Zn_{sample}/^{66}Zn/^{64}Zn_{JMC\text{-}Lyons}) - 1] \times 1000$, where JMC-Lyons refers to the Johnson Matthey Zinc standard JMC batch 3–0749, obtained from the lab of Francis Albarède; Maréchal et al., 1999). All samples measured here were corrected for the contribution of a 3 ng blank with an isotopic composition of +0.2‰, but the size of these corrections is insignificant for all measured isotopic compositions compared to other sources of analytical uncertainty. In other words, if the blank contribution was really close to zero, the data reported in the paper would not change by more than about 0.03‰.

### 4.4. Mass spectrometry

Isotopic analysis of Zn was performed on a Thermo Finnigan Neptune MC-ICPMS at Bristol at low mass resolution. Samples were introduced into the mass spectrometer in 2% (v/v) nitric acid via an Aridus desolvating nebuliser system (Cetac, Omaha, NE, USA) and desolvating spray chamber. The spray chamber was held at 105 °C and the desolvator at 160 °C. Typical Ar sweep gas settings were 4.25–4.75 L/min with little day-to-day variation in the sweep gas required to obtain the optimum Zn signal. No $N_2$ was used as $ArN_2$ would result in interference on $^{68}Zn$. All stable isotopes of Zn, as well as $^{62}Ni$, $^{63}Cu$, $^{65}Cu$ were collected simultaneously in static mode using a multiple Faraday collector array. Data collection consisted of 30 × 4 s integrations and each measurement was preceded by a blank measurement (15 × 4 s integrations) of the 2% $HNO_3$ used to make the analyte solutions and followed by a wash or two in clean 2% $HNO_3$. The blank signal was subtracted from the sample signal and normally amounted to no more than 0.02% of total analyte 64 ion beam.

All Zn isotopic data are reported relative to the Johnson Matthey Zinc standard JMC 3-0749, obtained from the lab of Francis Albarède (Maréchal et al., 1999). The standard delta per mil notation is used and is defined as:

$$\delta^{66}Zn = \left[\frac{(^{66}Zn/^{64}Zn)_{sample}}{(^{66}Zn/^{64}Zn)_{JMC}} - 1\right] \times 1000$$

Mass discrimination artefacts, that may be introduced at any stage in the chemical and mass spectrometric procedure, were corrected using the double spike method as detailed in Bermin et al. (2006). All uncertainties cited are 2SE of 30 4 s integrations propagated through the full double spike reduction procedure unless specified. To test the robustness of the double spike approach, JMC standard and double spike were mixed at various ratios and analysed during every analytical session (see Fig. 3 in ESM for data).

### 4.5. Tests on real seawater samples

Zn isotopic data for samples from the GEOTRACES IC1 intercalibration project (BATS station, 31°40′N

64°10′W) have already been reported by this laboratory (Boyle et al. 2012). No other Zn data were reported for these samples so that we cannot demonstrate inter-laboratory consistency at this stage. However, the duplicates analysed by us and reported in Boyle et al. (2012) are all consistent with each other. Furthermore, analyses of deep ocean samples by S. John and T. Conway (pers. comm. September 2012) are yielding the same results as we obtain here and in Boyle et al. (2012). There are a number of other laboratories now pursuing Zn isotopic measurement of seawater so that we hope that this situation improves soon. With this in mind Table 1 reports data obtained here for other samples from recent intercalibration efforts.

Though no isotopic data have been reported yet for these samples from other laboratories, the concentrations obtained here are consistent with those measured elsewhere with completely independent approaches. Thus the consensus values for Zn in SAFe D1 and D2 are $7.1 \pm 0.6$ and $7.2 \pm 0.5$ nmol kg$^{-1}$ while that for the SAFe surface sample is also identical to those obtained here at $0.064 \pm 0.019$ nmol kg$^{-1}$ (http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html). The Bruland laboratory at Santa Cruz has measured 1.42 nmol kg$^{-1}$ for Zn in the Santa Barbara sample, whereas we obtain 1.35 and 1.37 nmol kg$^{-1}$ for two duplicate aliquots from two different bottles.

### 4.6. Standard-addition tests

Another test of our procedure involves the addition of standard to seawater samples from which Zn has been removed, to seawater samples with very small natural Zn concentrations, and to MQ water, all followed by preconcentration, column purification and mass spectrometric analysis. Fig. 3 shows results obtained for addition of variable amounts of JMC standard to seawater samples from which Zn had been removed (supernatant poured off from a previous Al co-precipitation, retained and treated as a new "sample") and MQ. The result for the seawater samples was $\delta^{66}Zn = +0.08 \pm 0.03‰$ ($n = 12$), and for MQ $\delta^{66}Zn = -0.01 \pm 0.02‰$ ($n = 8$). Although the value for the seawater supernatant samples was close to zero, the data indicate that a small amount of seawater Zn was left in the supernatant after co-precipitation, resulting in the slightly elevated $\delta^{66}Zn$. Evidence for this came from the comparison of seawater supernatant samples with different amounts of JMC standard added. For those with only 30 ng of standard Zn added, the $\delta^{66}Zn$ was more elevated from the expected 0‰ (and also closer to the seawater $\delta^{66}Zn$) than those to which 200 ng of standard Zn was added, due to a larger relative contribution of the residual seawater Zn. A sample calculation illustrates how this is possible. For example, for 30 ng of standard Zn added, the typical shift away from 0‰ at the limits of uncertainty is about 0.1‰ towards the original seawater sample value of +0.46‰. Thus the shift is of the order of 20% of the total difference between the predicted 0‰ and the original seawater sample. This would require an amount of residual seawater Zn of 8 ng. If the yield from the original co-precipitation is 90–95%, and given an original amount of Zn in the seawater sample of around 100 ng for these samples, then a residual amount of seawater Zn of around 5–10 ng is plausible. Data for the MQ samples, which had negligible amounts of Zn originally, all fell within the error of the expected 0‰ (Fig. 3).

Another test was performed by adding different amounts of standard JMC Zn to a set of 4 L samples obtained from the surface Equatorial Atlantic, which through previous analysis by isotope dilution had been found to contain only 0.01–0.03 nmol kg$^{-1}$ sample Zn. The data are illustrated in

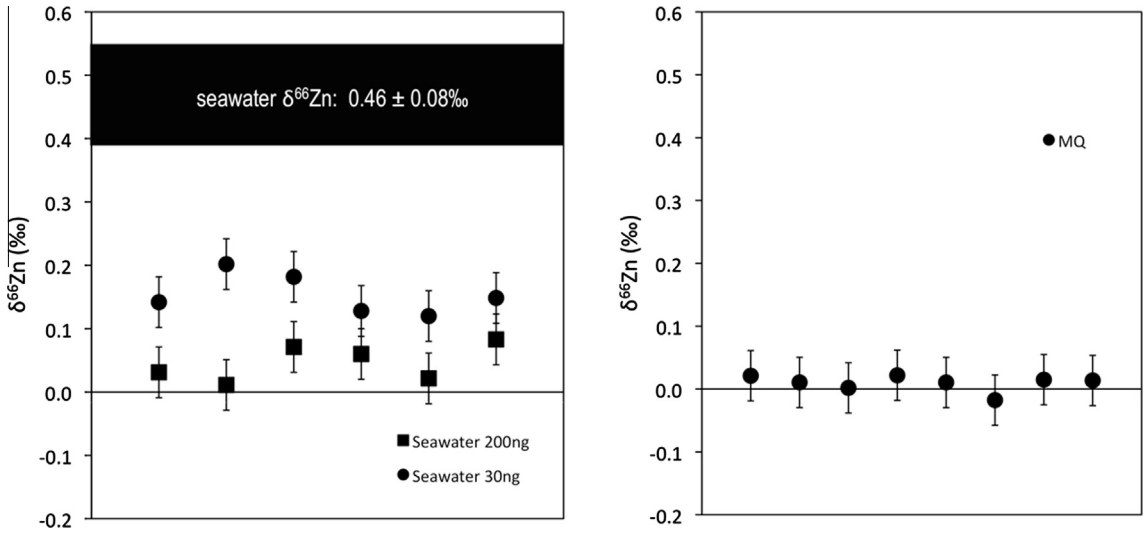


Fig. 3. Isotopic data for pre-co-precipitated seawater supernatant samples and MQ samples to which Zn JMC standard has been added. "Seawater 30 ng", "Seawater 200 ng" represent the supernatant samples to which 30 and 200 ng standard Zn were added, respectively. The result obtained for the supernatant samples was $\delta^{66}Zn = +0.08 \pm 0.03‰$ ($n = 12$). The slightly elevated $\delta^{66}Zn$ suggests that a small amount of Zn was left in these samples after co-precipitation. The result for MQ samples was $\delta^{66}Zn = -0.01 \pm 0.02‰$ ($n = 8$), all falling within the error of the expected 0‰, demonstrating the robustness of the double spike approach.

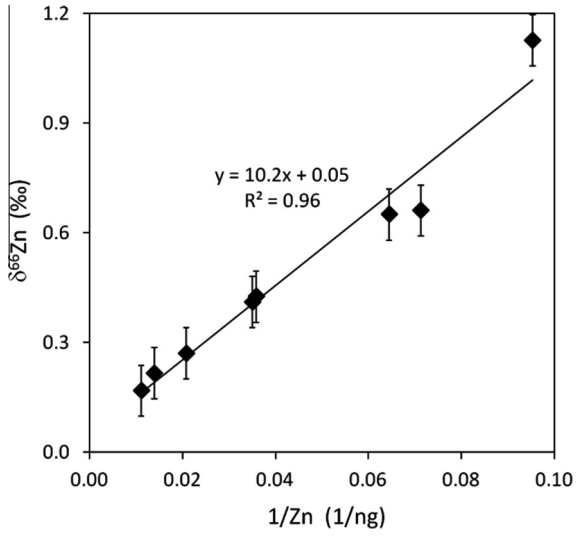


Fig. 4. Plot of measured Zn isotopic data for 4 L surface Equatorial Atlantic samples to which various amounts of JMC standard and double spike have been added, versus the reciprocal Zn amounts. In this case the original sample Zn was not removed, previous isotope dilution analysis having indicated that sample Zn concentrations were very small, at 0.01–0.04 nmol $kg^{-1}$.

Fig. 4. The good fit of the data to a straight line might be taken to indicate simple mixing between standard Zn ($\delta^{66}Zn = 0$, low 1/Zn) and sample Zn.

### 4.7. Intercomparison of Zn concentrations with previous data from the Southern Ocean

Seawater samples from locations close to those analysed in this paper have been the subject of two other studies for Zn concentrations (Löscher, 1999; Croot et al., 2011). Direct intercomparison between these studies and ours is made difficult by the fact that the previous studies are not often from precisely the same location, depths etc. Fig. 5 shows a depth profile from our Station PS71-113-2 along with data from exactly the same location for samples collected on the same cruise with the same sampling equipment and filtration (Croot et al., 2011), and data from a composite depth profile made up of samples from other nearby sites in the Southern ACC collected in 1992 (Löscher, 1999). The latter dataset is from a time when contamination control during sample collection was a lot more difficult than now, and has some outliers, but it is also clear that the agreement between these data and ours at depths $\geqslant$ 1000 m is essentially perfect. The data from Croot et al. (2011), on the other hand, are about 25–50% lower than both our data, and the Löscher (1999) data beneath 1000 m where a meaningful comparison can be made. The Croot et al. (2011) data were obtained using simultaneous dithiocarbamate–freon extraction followed by graphite furnace atomic absorption spectroscopy. Since the publication of the Croot et al. (2011) data, it has become apparent that this approach, when performed on samples that have been acidified with HCl, yields Cd concentrations that are up to about 50% lower than by isotope dilution (O. Baars and

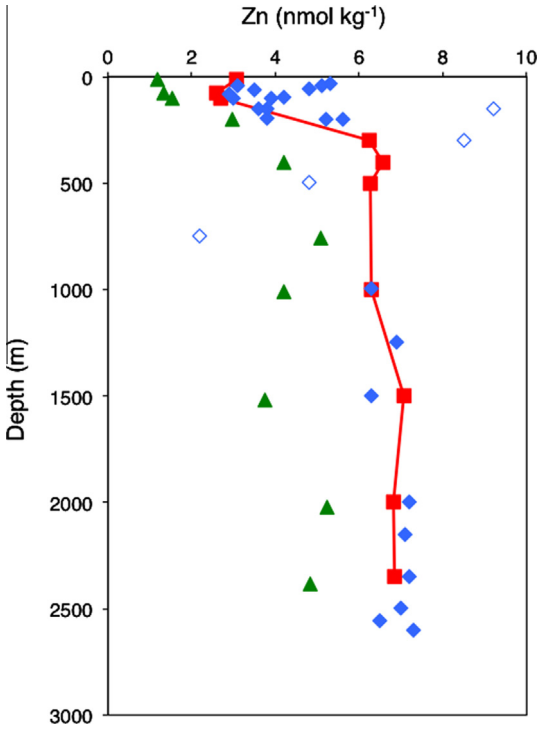


Fig. 5. Plot of measured Zn concentration data for Station PS71-113-2 (red squares) compared with data for the same location in Croot et al. (2011) (green triangles) and with data for a composite of nearby stations (895, 897, 947, 949) published in Löscher (1999). The latter data are plotted as blue diamonds, with obvious outliers in this older dataset highlighted by the open symbols. Beneath 1000 m the data obtained here are in very good agreement with Löscher (1999) while the data of Croot et al. (2011) are displaced towards lower values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

W. Abouchami, unpublished data). It seems likely that this problem applies also to the Croot et al. (2011) Zn data. It may be related to incomplete stripping of the metals from organic complexes during the pre-concentration step. The problem is particularly apparent in samples that had been acidified with HCl and analysed shortly after acidification, while it can be eliminated for samples that are acidified using oxidizing acids like $HNO_3$ (P.L. Croot, pers. comm.).

## 5. RESULTS

### 5.1. Three vertical profiles along Greenwich Zero Meridian

Data for the three vertical profiles PS71-104-2, PS71-113-2, PS71-163-1 (Fig. 1) analysed in this study for dissolved Zn concentrations and isotopic compositions are presented in Table 2. The data are shown as depth profiles, with other key oceanographic parameters, in Figs. 6–8.

The water column at the most southerly station, PS71-163-1 (Fig. 6), in the Weddell Gyre, is extremely stratified at the surface, with temperature and salinity increasing quickly from surface minima of −0.8 °C and 34, to about 0.9 °C and 34.7 at the AASW (Antarctic surface water)–

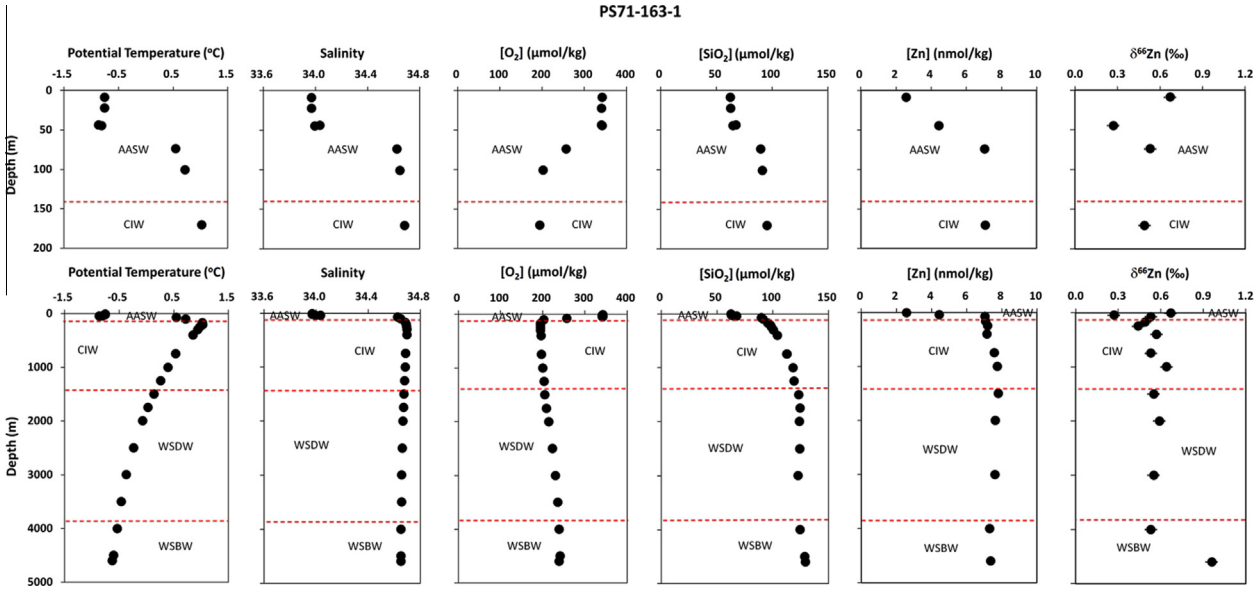


Fig. 6. Depth profiles of potential temperature (°C), salinity, oxygen concentration (μmol/kg), silicon (μmol/kg), dissolved Zn concentration (nmol/kg), Zn isotopic composition (‰) of samples collected at station PS71-163-1 (67°S, 0°E). Salinities are reported on the Practical Salinity Scale (PSS78). Water mass abbreviations: AASW, Antarctic Surface Water; CIW, Central Intermediate Water; WSDW, Weddell Sea Deep Water; WSBW, Weddell Sea Bottom Water.

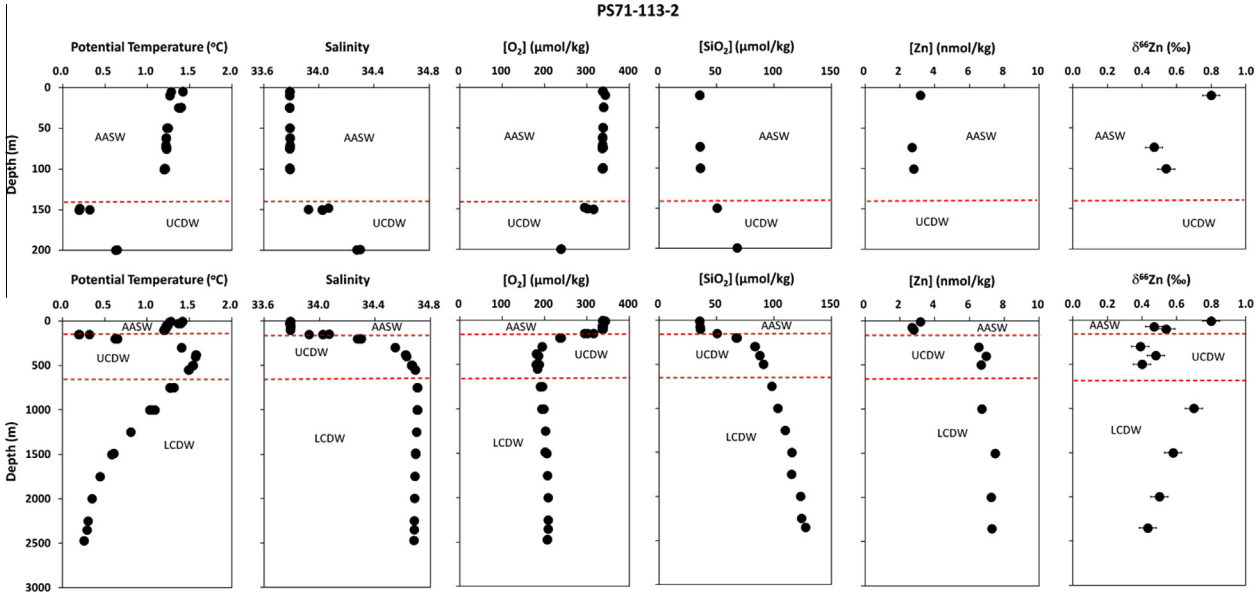


Fig. 7. Depth profiles of potential temperature (°C), salinity, oxygen concentration (μmol/kg), silicon (μmol/kg), dissolved Zn concentration (nmol/kg), Zn isotopic composition (‰) of samples collected at station PS71-113-2 (52°59.828′S, 0.2°0.05′W). Water mass abbreviations as in Fig. 6 plus: AAIW, Antarctic Intermediate Water; UCDW, Upper Circumpolar Deep Water; LCDW, Lower Circumpolar Deep Water; WSBW, Weddell Sea Bottom Water.

CIW (Central Intermediate Water) boundary at 200 m. This stratification must be driven by the low surface salinity, given the sharp 1.7 °C decrease in temperature in the surface layer. The AASW–CIW boundary also corresponds to an $O_2$ minimum. Si is relatively high at the surface (60 μmol/kg) and also increases sharply with depth, but the AASW–CIW boundary is not as sharp as for the physical parameters or $O_2$. Though there is an inflexion in the Si depth profile at this depth, concentrations continue to increase relatively smoothly through it.

The Zn concentration profile looks more like salinity than Si. Zn concentrations are not particularly low at the surface (2.5 nM), and increase quickly to about 7 nM at 74 m. Beneath this boundary, salinity, oxygen and Zn are

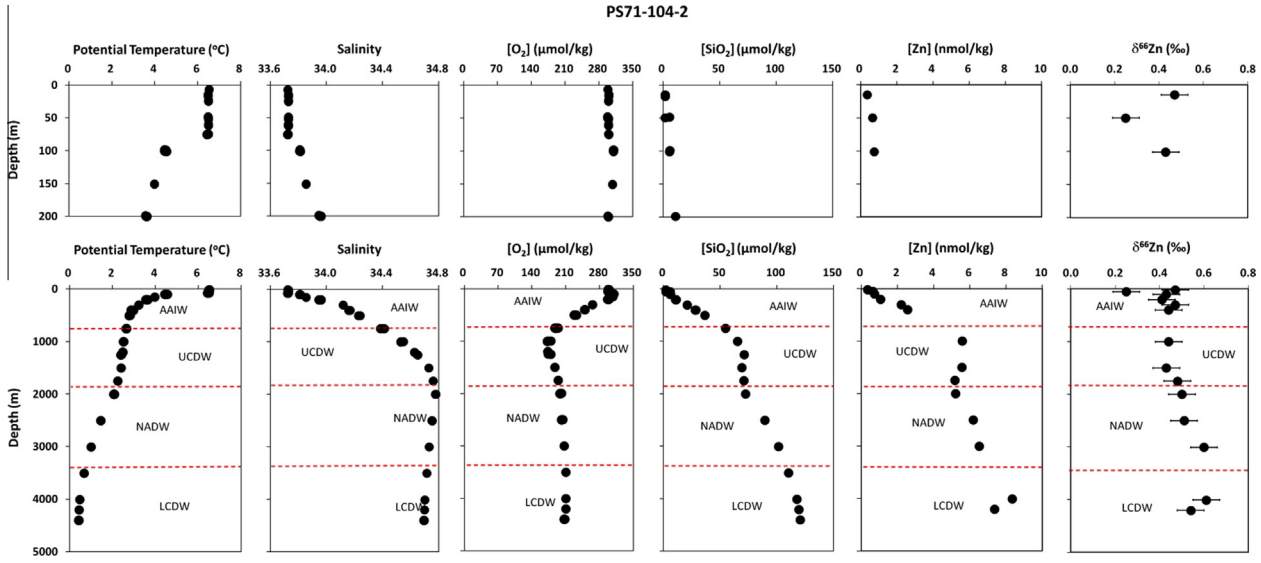


Fig. 8. Depth profiles of potential temperature (°C), salinity, oxygen concentration (μmol/kg), silicon (μmol/kg), dissolved Zn concentration (nmol/kg), Zn isotopic composition (‰) of samples collected at station PS71-104-2 (47°39.36′S, 4°15.7′E). Water mass abbreviations as in Figs. 6 and 7 plus: NADW = North Atlantic Deep Water.

very homogeneous with depth, with Zn concentrations between 7.1 and 7.8 nM. There is a slight maximum (7.8 nM) at 1000–1500 m, close to the CIW–WSDW (Weddell Sea Deep Water) boundary. Si concentrations, by contrast, continue to increase beneath the AASW–CIW boundary and only reach their maximum in the bottom-most sample measured. The $\delta^{66}$Zn profile shows a maximum of +0.67‰ at the surface, in contrast to quite an extreme minimum of +0.27‰ within AASW at 45 m. Beneath this, from 170 to 4000 m, $\delta^{66}$Zn is extremely homogeneous at $+0.53 \pm 0.10$‰ (2sd). There is a very slight minimum (+0.44‰ to +0.49‰) at the AASW–CIW boundary, and a very slight, broad, maximum (+0.64‰ at 1000–2000 m, decreasing to +0.53‰ at 4000 m), but these features are barely analytically significant. The bottom-most sample shows very anomalous $\delta^{66}$Zn at +0.97‰.

Station PS71-113-2 (Fig. 7) is within the ACC, in the Antarctic Zone to the south of the Polar Front. The major physical oceanographic difference between this station and PS71-163-1 is slightly less extreme stratification, though it is still significant. The upper 100 m of the water column has the low salinity that is characteristic of AASW, and is also characterised by homogeneously high dissolved $O_2$ and moderately low, Si (at 35 μmol $kg^{-1}$). Potential temperature is more variable at 1.2–1.4 °C. The core of UCDW (Upper Circumpolar Deep Water) beneath AASW is characterised by a temperature maximum (~1.6 °C at 400 m) and a slight $O_2$ minimum (185 μmol $kg^{-1}$ at 400 m). Salinity shows a very slight maximum in UCDW. Beneath the core of UCDW, salinity and $O_2$ remain relatively constant to the bottom. Si in contrast increases sharply at first in UCDW, down to the core of UCDW, and then more slowly but monotonically to the bottom.

The pattern of the Zn concentration profile, as with Station PS71-163-1, looks more like salinity and inverse $O_2$ than Si. AASW at 0–100 m is characterised by the lowest Zn concentrations, but still relatively high for surface water, at 2.6–3.1 nM. There is then a step change into UCDW, resembling the sharp increase in salinity and drop in $O_2$. UCDW Zn concentrations are homogeneously high at around 6.3–6.6 nM. In LCDW (Lower Circumpolar Deep Water), Zn concentrations increase slightly to 6.8–7.1 nM, but relative to Si, for example, are relatively homogeneous from 100 m to the bottom of the water column.

The $\delta^{66}$Zn profile at PS71-113-2 exhibits a clearer structure than that at PS71-163-1. As with PS71-163-1, the $\delta^{66}$Zn profile at PS71-113-2 has a pronounced surface maximum (+0.8‰), and again there is a sharp drop in the sub-surface, to +0.47 to +0.54‰ at 74–101 m, still within AASW. Note that no sample has been measured at 40–50 m in this profile (c.f., more pronounced minima at 40–50 m at both stations 163-1 and 104-2; Table 2). Uppermost LCDW has a $\delta^{66}$Zn value of +0.70‰ at 1000 m. Between AASW and uppermost LCDW, UCDW appears to have a lower $\delta^{66}$Zn, at +0.39‰ to +0.48‰, a minimum that is just about analytically significant relative to the values immediately above and below. Below 1000 m, and for the remainder of LCDW down to the bottom at 2351 m, the $\delta^{66}$Zn value decreases gradually and monotonically, from the high of +0.70‰ at 1000 m to +0.43‰ at the bottom. As noted above, Zn concentrations change very little through this isotopic structure in the lower water column beneath AASW.

Station PS71-104-2 (Fig. 8) is also within the ACC, in the low-Si PFZ, between the APF and the SAF. The upper water column at this station is significantly less stratified than the other two. This station is in the Polar Frontal Zone formation region of AAIW, and surface salinity is marked by the minimum (33.73) that is characteristic of that water mass. Salinity then increases to a slight maximum (34.78) at 2000 m, in the upper levels of NADW (North Atlantic Deep Water, see Fig. 3 of Middag et al., 2011a). The core of UCDW is characterised by the same

minimum in dissolved oxygen seen at Station PS71-113-2. Temperature decreases monotonically downward from a surface maximum of 6.5 °C, though with inflection points near the boundaries of the main water masses. Surface Si concentrations are much lower than the other two stations – at ~1.9 μM here in contrast to 63 and 35 μM at the other two stations. Si increases monotonically downward, though again with inflection points at the boundaries of the water masses, notably at the UCDW–NADW boundary, above which Si is relatively constant with depth but below which there is a renewed increase.

The Zn concentration profile, in contrast to those at the other two stations studied, looks much more like Si than salinity. Surface Zn concentration is much lower at this station, at 0.32 nM – a feature that mirrors the Si contrast between the three stations. Zn concentrations then increase steeply through AAIW to reach a maximum of ~5.35 nM at 1000–1500 m in the core of UCDW. This maximum occurs at the same depth as the homogeneous Si concentrations above the UCDW–NADW boundary. Zn concentrations then undergo a renewed increase through NADW and into LCDW, reaching 8.04 nM at 4006 m. The bottom-most point has distinctly lower Zn concentration at 7.03 nM.

As with the other two profiles $\delta^{66}$Zn shows a clear change from a higher value right at the surface (+0.47‰) to a minimum at 50 m (+0.25‰). Through the remainder of AAIW and UCDW, $\delta^{66}$Zn returns to homogeneously heavier values (at +0.44 ±0.06‰ at 100–2000 m), consistent with the values for UCDW seen at Station PS71-113-2 (+0.39‰ to +0.48‰). NADW and LCDW appear to be characterised by slightly heavier values, with two measurements at +0.60‰ and 0.61‰. Again, this is consistent with the heavier values seen in LCDW – up to +0.70‰ – relative to UCDW at Station PS71-113-2. A slightly lower $\delta^{66}$Zn is found in the bottom-most sample than directly above, paired with the distinctly lower Zn concentration in this sample relative to the measurement directly above.

### 5.2. Surface transect along Greenwich Zero Meridian

In addition to the above depth profiles, samples from 11 surface transect stations PS105, PS109, PS114, PS117, PS120, PS123, PS126, PS129, PS133, PS136, PS139 were also analysed for dissolved Zn concentrations and isotopic compositions. Data are presented in Table 3. The Zn data, with other key oceanographic parameters, are plotted against latitude in Fig. 9.

Note that though the Zn concentration reproduces across duplicate analyses of two separate aliquots from the same 20 L MPI container, the data for Station PS111 (52.17°S) are highly anomalous. We suspect that the original 20 L MPI bottle must have been contaminated before or during original sampling, and these data are not plotted, nor considered further in the results and discussion sections below. Relatively smooth transitions between the other samples across the latitudinal transect suggest no such problems.

The surface transect sampling stations covered, from north to south, the PFZ, the Antarctic Zone (AAZ) of

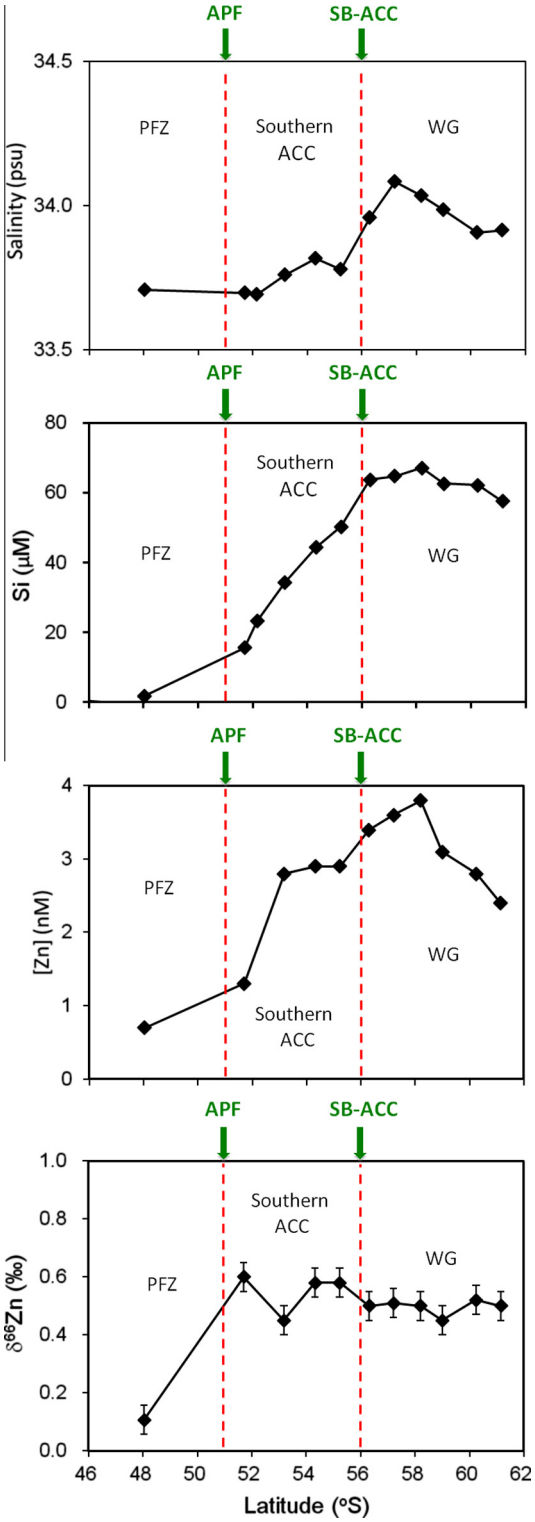


Fig. 9. Plots of measured salinity, Si concentration (μmol/kg), dissolved Zn concentration (nmol/kg), Zn isotopic composition $\delta^{66}$Zn (‰) of surface transect samples (filled diamonds) and near surface samples (open diamonds) collected at vertical profiles PS71-104-2, PS71-113-2, PS71-163-1 against latitude. Abbreviations for surface oceanographic regimes as in Fig. 1.

the ACC and the northern end of the Weddell Gyre. The highest Si values are in the Weddell Gyre and the region of strong upwelling in the AAZ of the Southern ACC (c.f., Fig. 2). The peak in surface Zn concentrations also occurs here, but is sharper and centered on 58°S, near the boundary between the Weddell Gyre and the Antarctic Circumpolar Current. In fact, as with the depth profiles, the pattern of Zn concentrations in the southern regions of the surface transect most closely matches salinity. Both salinity and Zn have a sharp peak near the boundary between the Weddell Gyre and the Antarctic Circumpolar Current, and more rapidly declining values north of this as far as about 53°S. Thereafter, further north, the pattern in Zn concentrations begin to look more like that of Si.

$\delta^{66}Zn$ is relatively constant at +0.45‰ to +0.6‰ across the Weddell Gyre and into the southern ACC as far as about 53°S (Fig. 9). The only datum that is significantly different along the entire transect is at 48°S (+0.10‰).

## 6. DISCUSSION

### 6.1. Controls on Zn isotope systematics in surface waters

Overall, the Zn isotope data reported here display a total variation in $\delta^{66}Zn$ of about 0.9‰, representing about 40% of the total variation yet reported for Zn isotopes on Earth (see compilation in Cloquet et al., 2006). However, perhaps the most striking aspect of the Southern Ocean depth profiles is their relative homogeneity. Thus, apart from one outlier, the datum for the deepest sample at location PS-71-163-1 (at +0.96‰), the variation in the entire dataset beneath 50 m is only at about the 4 sigma level (mean and $2SD = 0.51 \pm 0.15$‰). There is more variation above 50 m, with $\delta^{66}Zn$ values as high as +0.8‰ and as low as 0.07‰.

Zn depletion in the surface ocean is generally attributed to biological uptake, and enrichments at depth as due to return of Zn to the dissolved pool from particulate material that is biologically-packaged in the photic zone (e.g., Bruland and Lohan, 2003 and Sinoir et al., 2012). If biological uptake of Zn in the surface ocean is associated with even a small isotope fractionation there should be a clear impact on the isotopic composition of the small residual surface pool. Though upwelling of nutrient-rich waters means that surface Zn concentrations are not nearly as low in our study area as in many parts of the ocean (e.g., Bruland, 1980; Lohan et al., 2002; Boyle et al., 2012), it is still the case that Zn concentrations at 5–15 m are up to 20 times lower than those of the deep Southern Ocean. Even if the kinetic fractionation associated with cellular uptake of Zn is as small as +0.2‰ ($\delta^{66}Zn_{dissolved}$ - $\delta^{66}Zn_{cell}$), a residual dissolved pool of 5% should be 0.6‰ heavier than the Zn upwelled from the deep ocean, assuming Rayleigh fractionation in a closed system. The implied heavy dissolved phase $\delta^{66}Zn$ are not seen in the surface waters analysed here.

One obvious potential reason for the lack of an imprint on isotopic compositions of strong apparent vertical Zn cycling is that biological uptake is associated with negligible isotopic fractionation of Zn isotopes. Experimental data that quantifies fractionation of Zn isotopes upon biological uptake are scarce. The single relevant culturing experiment performed thus far (John et al., 2007) suggests that the cellular quota of Zn in an oceanic diatom is 0.2–0.8‰ lighter, depending on ambient free $Zn^{2+}$ concentrations that are thought to drive different uptake mechanisms, than the culture medium. This finding is consistent with a single study in a Swiss lake (Peel et al., 2009), where organic-carbon-rich particulates produced during the spring bloom are preferentially enriched in the light isotopes of Zn, by an amount close to the upper end of the isotopic separation implied by the culture experiments.

It is also theoretically possible that the intense vertical cycling of Zn in the oceans is dominated by an abiotic process, such as scavenging onto particulate material in surface waters and release back to the dissolved phase in the deep. Such a process has been invoked to explain the vertical distributions of many other trace metals (for example aluminium, thorium, see Bruland and Lohan, 2003 for a review). However, none of these metals show the extreme surface to depth fractionation (up to 200 times lower concentrations in the photic zone than the deep) that Zn does. Moreover, adsorption onto particulate surfaces is also associated with isotopic fractionations that should also lead to deviations in the residual dissolved pool (e.g., Pokrovsky et al., 2005; Gélabert et al., 2006; Balistrieri et al., 2008; Juillot et al., 2008).

Perhaps the strongest evidence for the biological cycling of Zn in the oceans is the well-established close correlation between its depth distribution in the oceans and that of silica (Bruland, 1980). The generally close association of Si and Zn has led to the suggestion that both are regenerated together through the dissolution of diatom opal in the deep ocean. However, culture experiments have shown that Zn contents of the opal phase of diatom cells are very small, and that 97–99% of the Zn in diatoms is in organic material (Ellwood and Hunter, 2000). Moreover, the Zn/Si ratio of diatom opal is 1–2 orders of magnitude smaller than in the deep Pacific (Bruland, 1980; Ellwood and Hunter, 2000; Lohan et al., 2002), also arguing against the importance of the opal phase as the source of deep ocean Zn. One way to explain the close correspondence of the deep regeneration profiles of Si and Zn, that is also consistent with the lack of Zn in the opal phase, is to invoke a Zn-rich organic phase that is intimately associated with the diatom frustule (c.f., Lohan et al., 2002). Thus, regenerated Zn does not derive from the opal phase itself, but it is only exposed to oxidation in the deep ocean when the opal dissolves. It is well established that polysaccharides and proteins coat the silica frustule of diatoms, and that these bear functional groups (e.g., amino, carboxyl) that have a strong affinity for metal ions, including Zn (e.g., Gélabert et al., 2006).

These considerations have two obvious implications for the interpretation of the dissolved phase Zn concentration and isotope data presented here. Firstly, they imply that there is more than one biologically-controlled pathway by which Zn is removed from the surface ocean – into proteins and enzymes within phytoplankton cells in all phytoplankton groups, and into an organic phase that is, physically, intimately associated with the opal frustule of diatoms. These two uptake mechanisms may be associated with different isotopic fractionations and their relative importance

will depend on local phytoplankton ecology, thus complicating oceanic Zn isotopic data. Secondly, the regeneration of these two different pools, one at shallower depths in association with intra-cellular organic matter, and one at greater depths coupled to opal dissolution, could lead to a partial decoupling, both between depth profiles of Zn isotopes and those of Zn (and Si) concentrations, and between the upper and deep ocean.

In the ensuing sections we discuss each of these implications, first for surface data and then for the sub-surface and deep ocean.

### 6.2. Controls on Zn in surface waters: relationships between Zn isotopes and Si and Zn concentrations

The association between Zn and Si concentrations discussed in the previous section is seen in the Southern Ocean data (Fig. 10a), but there is systematic structure in this relationship. Moreover, Zn isotopes show no relationship at all with either Si (Fig. 10b) or Zn concentrations. We suggest that the structure apparent in the surface water Zn–Si relationship in Fig. 10a, as well as the lack of any coherent relationship with Zn isotopes (Fig. 10b), may both be a consequence of the multiple controls discussed in the previous section. For example, on the Zn–Si plot (Fig. 10a) the upper ocean data (the surface (2–5 m) samples with the filled symbols, all profile data from depths above 100 m, but down about 300 m at 104–2) clearly separate into two arrays with different slopes, corresponding geographically to the Weddell Gyre and the ACC (c.f., a similar geographic split for Cd isotope data for these samples; Abouchami et al., 2011). In most of the ACC zone, Zn–Si data for the upper water column follow a tight linear correlation that comes close to going through the origin. In contrast, surface data to the south of about 56°S, within the Weddell Gyre, fall on a much steeper trend. There is a transition zone in the southernmost ACC (53–55°S), where Zn concentrations flatten out at 2.7–2.8 nmol $kg^{-1}$ while Si is variable (Fig. 10a, see also Fig. 9). Data for the deeper levels (all data beneath about 300 m) at all stations are at the high concentration end of both trends. Geographically the top ends of both the surface trends, those closest in chemistry to deep waters, are for surface waters in the upwelling zone centered on 58°S.

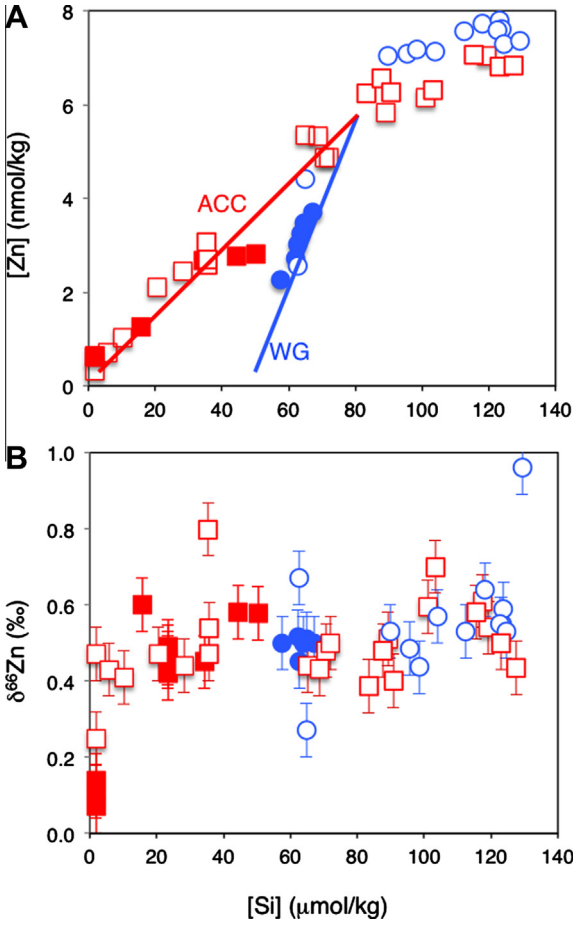


Fig. 10. Cross-plots of Si concentrations versus (A) the new Zn concentration and (B) isotopic data. Data from the ACC (north of 56°S) are plotted as red squares and data from the Weddell Gyre (WG, south of 56°S) as blue circles. Solid symbols are for surface samples (collected at 2–5 m and presented in Table 3), and open symbols for sub-surface (from depths ⩾ 10 m, as presented in Table 2) and deep samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In terms of the ideas discussed in Section 6.1, it is noteworthy that diatoms peak in abundance at 52–56°S, just north of the upwelling zone (Alderkamp et al., 2010). Their proportion of the phytoplankton assemblage then decreases steadily and monotonically northward as the Si supply via horizontal advection from the upwelling zone decreases. The concomitant decrease in Zn along the ACC trend might suggest that Zn concentrations are subject to the same control. In the portion of the Weddell Gyre for which we present surface data, diatoms also decrease in relative importance southwards to be replaced by a peak in haptophytes (60% of total phytoplankton at 62°S; Alderkamp et al., 2010). Though the requirement of haptophytes for Zn is not clear, the lesser importance of diatoms in this region, as well as lower productivity overall, could explain both the high surface Si concentrations in the WG (Fig. 9) and the steep slope of the Zn/Si relationship in Fig. 10a.

The impact of these changes in microbial ecology are hard to pinpoint at this early stage in the development of oceanic Zn isotopes. But, for example, it may be that the relative lack of correlation between Zn isotopes and Si concentrations (Fig. 10b) is a result of the dominance of Zn removal into an organic phase, such as external polysaccharides that are ultimately associated with the opal frustule, and that does not involve a strong isotopic fractionation. Alternatively, any associated isotope fractionation would need to be more or less balanced by uptake of Zn into the actual cell, with the preference for light isotopes that is expected for this process, that has been observed in culture, and that has been inferred in lakes. It is noteworthy that Zn attached to the external surfaces of diatoms in culture experiments (John et al., 2007) is either unfractionated with respect to Zn in the medium (low free $Zn^{2+}$ concentra-

tions) or slightly enriched in heavy isotopes (high free $Zn^{2+}$ concentrations). Note that we do not suggest that uptake of Zn into cells does not occur – rather that it may not be the dominant mode of Zn removal from these Southern Ocean surface waters. Indeed, the next section will argue for the regeneration of such an intra-cellular pool to explain the shallow sub-surface data.

### 6.3. Sub-surface Zn isotopic minima: the signature of regenerated intra-cellular Zn

The clearest and most consistent feature of the Zn isotopic data in the three depth profiles (Figs. 6–8) is seen at the near surface, where data at around 50–70 m are distinctly lighter than the datum for the uppermost samples from the same depth profiles. Thus at PS71-163-1, the 9 m analysis gives $\delta^{66}Zn = +0.63‰$, while the analysis at 40 m gives $+0.27‰$. At PS71-113-2 $\delta^{66}Zn$ at 10 m is $+0.80‰$ while at 74 m it is $+0.46‰$. At PS71-104-2 $\delta^{66}Zn = +0.46‰$ at 15 m and is $+0.25‰$ at 50 m. Thus there is a fairly consistent $0.31 \pm 0.09‰$ shift to lighter values in the immediate sub-surface from the uppermost level measured. A similar shift is seen at the only other relatively complete depth profile yet published. At the BATS station in the tropical North Atlantic (Boyle et al. 2012), the surface datum is 0.28‰ heavier than that at 75 m. Zn isotope data for the upper water column in the NE Pacific (Bermin et al., 2006) show a similar pattern: the datum at 75 m is 0.2 per mil lighter than at the surface. At both BATS and the NE Pacific there is then a more gradual move towards a heavier deep ocean value with depth. In the depth profiles presented here this sub-surface minimum in $\delta^{66}Zn$ is often quite abrupt, which appears consistent with similarly abrupt changes in physical oceanographic parameters to values that then characterise much of the deeper water column (e.g., Fig. 6).

Thus, at this early stage, the shift from heavy Zn at the surface to lighter Zn in the immediate sub-surface is developing into a consistent feature of oceanic Zn isotopes. In four out of the five cases outlined above (BATS, NE Pacific, three Southern Ocean profiles), the horizon with the isotopically-light Zn also has higher Zn concentrations than the surface datum. Scavenging of Zn via adsorption onto particulate surfaces preferentially removes the heavy isotope from solution (Maréchal et al., 2000; Pokrovsky et al., 2005; Gélabert et al., 2006; Balistrieri et al., 2008; Juillot et al., 2008) and would thus leave an isotopically-light residual dissolved pool. Though the situation is complicated by the fact that upwelling advects Zn into the upper ocean, the increasing Zn concentrations with depth do not appear to be consistent with scavenging. Moreover, a scavenging origin for the light isotopes at around 50 m leaves open the cause, in two of the three depth profiles investigated in the Southern Ocean (PS71-113-2 at $+0.8‰$ and PS71-163-1 at $+0.67‰$), of the distinctly heavy isotopic composition of dissolved Zn right at the surface, heavier, for example, than any likely continental source (Little et al., 2013), with nothing to date suggesting that such an input would be heavier than about $+0.4‰$. Thus, it seems probable that the enrichment of the light isotopes at 50–75 m are coupled to a corresponding depletion at the surface. It is most likely then that this isotopic fractionation is driven by a kinetic fractionation (John et al., 2007; Peel et al., 2009) associated with uptake into a cellular pool (surface) and regeneration of that same pool in the very shallow sub-surface.

Following the discussion in the Sections 6.1 and 6.2, we stress again that uptake of Zn into the cells of phytoplankton for metabolic use is likely to be only one of the processes by which Zn is removed from the surface ocean. In the view presented here, a second process by which Zn is associated with organic material within diatom frustules may often drive the bulk of the Zn depletion in surface water, and we suggest that the lack of correlation between Zn isotopes and Si concentrations (Fig. 10b) implies that this must occur with minimal isotopic fractionation. Thus surface waters in the Southern Ocean do not develop the extremely heavy residual Zn isotopic compositions that would be expected if the observed Zn depletion arose purely from uptake into the interiors of cells with a kinetic isotopic fractionation. The crucial point, however, is that the pool of Zn associated with the opal is regenerated only in the deep ocean, when the opal itself dissolves. Thus, the much shallower regeneration of the light intra-cellular pool shows up as a distinctive feature of the water column at 50–75 m, even though the impact of it in the surface ocean is obscured by another process.

We acknowledge that this interpretation of the Zn isotopic data is speculative at present, that these qualitative ideas need to be tested experimentally and with further field data, and particularly with at least a one-dimensional numerical model that parameterizes the key processes. Such a model would also have to take account of vertical transport of Zn by advection and diffusion, which would dampen the signature of the biological processes we invoke. Such a one-dimensional model is beyond the scope of the present contribution, but is something that is being actively pursued. As we show in the next section, however, the idea of two broad mechanisms behind the depletion of Zn in surface waters, and different lengthscales for the regeneration of the two resultant pools of Zn in the near surface and deep ocean, also explain some otherwise puzzling features of deep Southern Ocean zinc distributions, and the emerging pattern of Zn isotopes in the deep ocean more generally.

### 6.4. The Zn isotopic composition of the deep ocean: regeneration of a distinct pool of Zn

As already stated, a striking feature of the Southern Ocean Zn isotope dataset is the homogeneity of the deep ocean. Thus, apart from one outlying datum for the bottom sample at PS71-163 (which may be affected by a sedimentary source), the 17 samples from $\geqslant 1000$ m yield $\delta^{66}Zn = 0.54 \pm 0.04$ (2 SE). Fig. 11 presents a summary of Zn isotopic composition data from different parts of the world's deep oceans, from this study and from Boyle et al. (2012). The datum plotted on Fig. 11 for the deep Pacific is for the SAFE deep sample, one of the intercalibration samples tabulated here (Table 1). Though data are admittedly still scarce, the striking feature of Fig. 11 is the *overall* homogeneity of Zn isotopes in the deep ocean. Beneath 1000 m, the $\delta^{66}Zn$ in three geographically wide-

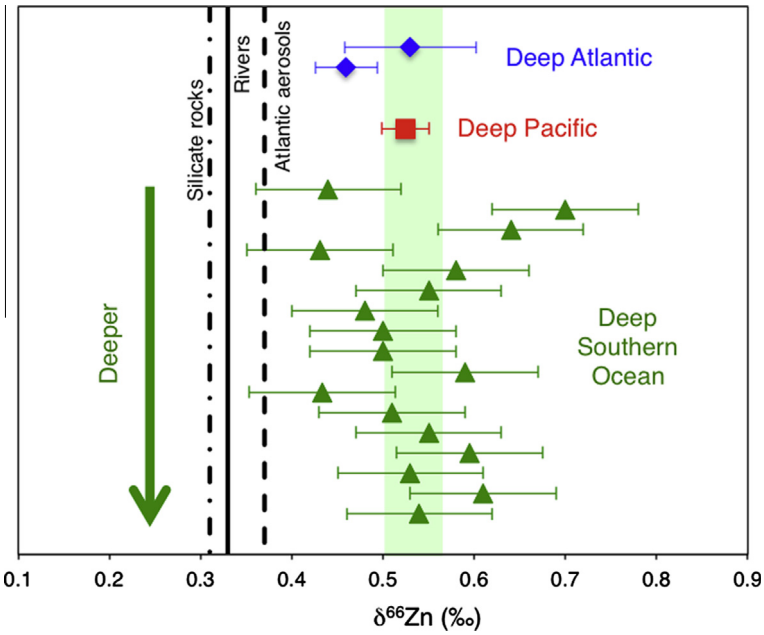


Fig. 11. A summary of Zn isotopic data thus far available for different parts of the world's deep oceans (⩽1000 m), compared to estimates of the likely inputs to the ocean (Little et al., 2013). The solid vertical line shows the $\delta^{66}$Zn of rivers, the dashed line that for Atlantic aerosols, and the dot–dash line that for silicate rocks and sediments of the continental crust (all compiled in Little et al., 2013). Blue filled diamonds represent the deep North Atlantic (BATS; Boyle et al. 2012), red filled squares the deep North Pacific (SAFe; this study), and green filled triangles the deep Southern Ocean (Atlantic sector, this study, arranged by depth (green arrow), and omitting the bottom-most sample from Station PS71-163). Data plotted for Southern Ocean samples are single analyses and their associated analytical uncertainties (±0.08‰). Data for the Atlantic and Pacific are averages and 2SEs of multiple analyses of the same sample. The shaded green band shows 2SE either side of the mean for all the deep ocean data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spread locations is essentially identical, with an average and 2sd of $+0.53 \pm 0.14‰$ (2SE = 0.03, $n = 21$).

In common with many oceanographic parameters, it is expected that the greatest variation in Zn isotopic compositions will be found in the upper ocean – it is here that the biogeochemical processes that impart the largest isotopic fractionations are expected to occur. The deep ocean, on the other hand, is where Zn that is cycled between different phases (dissolved, biological and inorganic particulates) in the upper ocean is largely returned to the dissolved phase (e.g., Bruland, 1980). Thus it is perhaps no surprise that the deep ocean is relatively homogeneous. It is more surprising that the deep North Atlantic and the deep North Pacific exhibit no difference in $\delta^{66}$Zn (c.f., $\delta^{13}$C, for example; Kroopnick, 1985) despite the rough factor of 4–5 difference in total Zn concentrations between these two water masses.

It is very difficult to see how the drawdown of Zn in the surface ocean via cellular uptake with a kinetic isotope fractionation similar to that implied by published culturing and field studies (John et al., 2007; Peel et al., 2009) would not result in a significant isotopic difference between the deep Atlantic and deep Pacific. On the other hand, the homogeneity of deep ocean Zn isotope compositions is perfectly explicable if: (a) intra-cellular Zn is regenerated in the shallow sub-surface as suggested in the previous section; (b) the dominant process by which Zn is removed from the surface ocean is not via such intra-cellular uptake but rather via a process that leads to its ultimate association with the opal frustules of diatoms, one which is not associated with a significant isotopic fractionation; (c) these processes are fast enough that mixing cannot eliminate the isotopic gradients. Such an explanation is, as noted earlier, completely consistent with the similar patterns of Si and Zn regeneration in the deep ocean, while accommodating the two additional observations deriving from culturing studies and the water column data presented here: that Zn in diatoms is predominantly in an organic phase (Ellwood and Hunter, 2000), and that intra-cellular uptake involves a significant isotopic fractionation (John et al., 2007), one that is not consistent with the lack of heavy Zn isotope signatures in the very Zn-depleted surface ocean.

### 6.5. Zn isotopic composition of the oceans and its relationship to input and output fluxes

In terms of the Zn isotopic cycle of the ocean as a whole, the relationship of oceanic dissolved Zn isotope compositions to those of the inputs is clearly important. Thus the second feature illustrated in Fig. 11 is the fact that the average deep ocean dissolved Zn isotopic composition appears to be slightly heavier than the likely continental input (Little et al., 2013). Given the higher Zn concentrations in the deep ocean relative to the surface, and the fact that 75% of the volume of the oceans is also beneath 1000 m, the deep ocean value must be very close to the whole ocean average. For example, for the depth profiles in Table 2, as

well as for that from the North Atlantic in Boyle et al. (2012), the average of all the data, weighted by concentration, is only 0.04 per mil less than the average of the data beneath 1000 m, given earlier as $0.53 \pm 0.03$ (2SE, $n = 21$).

The input flux to the oceans appears to be dominated by the dissolved riverine flux, with a small but significant source from atmospheric aerosols (Little et al., 2013). A significant hydrothermal input to the oceans has never been identified for Zn in depth profiles measured close to ocean ridges (e.g., Bermin, 2006) in contrast to some other elements (e.g., German et al., 1991 and Middag et al., 2011a for Mn; Klunder et al., 2011 for Fe). It appears that all the (considerable) Zn emanating from hydrothermal systems is very quickly precipitated in sulphides (German et al., 1991) near the source. The hydrothermal fluids that have been measured (John et al., 2008) have a $\delta^{66}$Zn at +0.24‰, slightly lighter than other inputs.

Thus an isotopically light sink from the dissolved pool appears to be required by the fact that the dissolved pool is slightly heavier than the inputs. Light sinks from the ocean are well-known for some other transition metals, such as Mo and Cu (e.g., Siebert et al., 2003; Barling and Anbar, 2004; Little et al., 2013) but none of these help with the Zn issue. For example, Zn isotopes in Fe-Mn crusts and nodules are universally heavier than deep seawater (Maréchal et al., 2000; Little et al. 2013), implying not only that this output does not represent the required light sink, but also that if this is a significant output the requirement for a light sink is increased. The single study available of oceanic carbonate (Pichat et al., 2003) suggests that this small sink is also isotopically heavy. The ideas presented in earlier sections suggest that the diatom opal sink of Zn probably closely reflects surface seawater itself and will also be heavier than the inputs (c.f., Andersen et al., 2011), while Zn sorption to organic material should also be either the same as seawater or slightly isotopically heavy (Gélabert et al. 2006; John et al., 2007).

The only important removal pathway from the dissolved pool in the oceans that is likely to be isotopically light is the pool of Zn that is taken up intra-cellularly by phytoplankton. As noted in previous sections, a single culturing study (John et al., 2007) has demonstrated that diatoms take up the light isotopes of Zn such that $\Delta_{\text{seawater–diatom cell}} = +0.2$ to +0.8, with the fractionation varying systematically with the free $Zn^{2+}$ concentration of the medium. A study of a Swiss lake (Peel et al. 2009) has demonstrated that sinking particulates associated with the summer algal bloom have a $\delta^{66}$Zn 0.8‰ lighter than the water column. Moreover, Andersen et al. (2011) invoked the same uptake of light Zn isotopes into phytoplankton organic material to explain the progressively heavier isotopic signature of diatom opal, which these authors interpreted to be recording surface seawater, as upwelled Zn is progressively depleted in the surface waters of the Pacific Sub-Antarctic Zone of the Southern Ocean. We have suggested earlier that it is regeneration of this pool that yields the light Zn isotopic composition of the shallow sub-surface in the Southern Ocean and elsewhere.

It thus seems likely that the portion of the isotopically light cellular Zn that survives regeneration and is buried in sediments could represent the sink that seems to be required by the oceanic Zn cycle as we understand it thus far. Zn isotopic analysis of organic-rich sediments may provide a means of testing this suggestion. Though fraught with uncertainty, a simple calculation can provide a preliminary assessment of its feasibility. Little et al. (2013) suggest that the magnitude of a missing light sink must be around $3 \pm 2 \times 10^8$ mol yr$^{-1}$, depending on its isotopic composition. Data on the Zn/C ratio of marine phytoplankton are scarce but those in Ho et al. (2003) for a variety of cultured organisms suggest that it is of the order of $0.6 \times 10^{-6}$ mol/mol. Field data for plankton tows in the same paper show Zn/P ratios up to 5 times greater than the cultured organisms. These data would imply a carbon burial rate to achieve the required Zn sink of 0.3–8 $\times 10^{13}$ mol yr$^{-1}$. Unfortunately large uncertainties on this estimate derive from the input parameters, but the range does span published estimates of carbon burial rates at 1–2 $\times 10^{13}$ mol yr$^{-1}$ (e.g., Hedges and Keil, 1995).

## 7. CONCLUDING REMARKS

We have reported the first full depth profiles for dissolved Zn isotopes in the ocean, as well as data for a surface transect along the zero meridian in the Atlantic sector of the Southern Ocean. The new isotopic data, taken together with data for the deep North Pacific and published data for the North Atlantic, exhibit three principal features. The first is the homogeneity of the deep ocean, such that the data presented here for beneath 1000 m, in combination with more limited data from the North Pacific and North Atlantic, have a $\delta^{66}\text{Zn} = +0.53 \pm 0.14$‰ (2SE = 0.03, $n = 21$). Secondly, and though there are both heavy and light isotopic values in the surface Southern Ocean, there is no systematic shift towards heavy isotopic compositions as would be expected (John et al., 2007; Peel et al., 2009) if the well-established Zn drawdown in the surface ocean is achieved dominantly through intra-cellular uptake of Zn. Thirdly, surface values *are* always heavier than data for the shallow sub-surface (40–80 m), both in the dataset presented here and in two published partial depth profiles from the North Atlantic and North Pacific (Bermin et al., 2006; Boyle et al., 2012).

These new Zn isotope data are consistent with a scenario whereby Zn removal from the surface ocean occurs via two processes, a dominant one that does not involve an isotopic fractionation and a lesser one that preferentially removes the light isotope. We suggest that the dominant process is the incorporation of Zn into organic matter associated with diatom frustules, while the second is the metabolic uptake of Zn into the cells of all phytoplankton. Such a hypothesis is consistent with the data presented here, as well as some key observations that have been made about the oceanic Zn cycle in previous work. Firstly, dissolved Zn concentrations in this study and elsewhere are closely tied to Si, but structure in the correlations for surface water (Fig. 10a) suggests a dependence on microbial ecology, in particular the dominance or not of opal-building organisms in the phytoplankton assemblage. The well-established observation of strong Si–Zn concentration correlations is coupled

to the fact that there is no systematic relationship at all between Si and Zn isotopes (Fig. 10b), implying that the removal of Zn coupled to Si removal involves little or no isotopic fractionation. On the other hand, increases in Zn concentration with depth down to 80 m are associated with distinctly lighter isotopic compositions than the rest of the water column, including the overlying photic zone. We suggest that this is the signature of the regeneration of intracellular zinc, while the main increase in Zn concentrations in the deep ocean, closely tied to Si, is the result of the regeneration of organic material intimately associated with diatom frustules, that is only re-mobilised when the opal itself dissolves (c.f., Lohan et al., 2002).

The scenario outlined above is consistent with what we know about the interactions between Zn and its isotopes, Si and biology from experiments and field studies. For example, culture studies have demonstrated that the Zn content in the opal phase of frustules is very small (Ellwood and Hunter, 2000), about 1–3% of the total Zn in diatoms with the rest associated with one or more organic phases. In addition, the Zn/Si ratio of the deep ocean is 1–2 orders of magnitude greater than in diatom opal (e.g., Bruland, 1980; Lohan et al., 2002). Both of these constraints have rendered the close association between Si and Zn concentrations in the deep ocean a real conundrum. A solution to this puzzle is provided by the fact that polysaccharides and proteins coat the silica frustule of diatoms, and that these bear functional groups (e.g., amino, carboxyl) that have a strong affinity for metal ions, including Zn (e.g., Gélabert et al., 2006). Culture experiments have also shown that the Zn associated with these organic substances (Gélabert et al., 2006) is isotopically identical to Zn in the culture medium at free $Zn^{2+}$ concentrations equivalent to those found in the surface ocean (John et al., 2007). In our proposed scenario, it is this Zn that is regenerated with Si, but only when the opal frustule itself dissolves, in the deep ocean. The fact that the uptake of this pool of Zn involves little isotope fractionation explains the lack of a relationship between Si concentrations and Zn isotopes in the portion of the Southern Ocean studied here, where diatoms are an important part of the phytoplankton population. The relative dominance of this process would also explain the fact that the deep Atlantic, the deep Southern Ocean and the deep Pacific are isotopically identical for Zn (Boyle et al., 2012; this study). On the other hand, both culture experiments and field data demonstrate that uptake of Zn into the interiors of cells for metabolic purposes shows the expected preference for the light isotopes (John et al., 2007; Peel et al., 2009). We further suggest, therefore, that this represents a different process, a pool that is regenerated at much shallower levels, and one that explains the light isotopic signature seen at 40–80 m in the Southern Ocean, the North Atlantic and the NE Pacific.

Clearly these qualitative ideas, though for the first time yielding a wholly consistent picture of the oceanic Zn cycle, need to be tested. They imply, in particular, a decoupling of the shallow and deep ocean for Zn, with the isotopic characteristics of the two being determined by different processes. A quantitative 1D model is required to ascertain, for example, whether the light signal in the shallow sub-surface can be maintained against upward advection of deep waters in the Southern Ocean. A prediction of these ideas would be that the vertical component of the oceanic cycle of Zn and its isotopes would differ in regions where diatoms dominate, as opposed to where non-silica-building organisms are the main contributors to the phytoplankton assemblage.

In addition, we have addressed the mass balance of the whole ocean, using the data in this paper, published data for Zn isotopes in other parts of the ocean, and data on the inputs and outputs (Little et al., 2013). The large and homogeneous deep ocean Zn reservoir is about 0.2‰ heavier than our current best estimate of the inputs of Zn to the ocean, so that an isotopically light sink is required for the whole ocean isotopic mass balance. The sinks that have been characterised, in contrast, are all heavier than the inputs. We advance the working hypothesis that it is the burial of isotopically light Zn in cellular organic matter that represents the light sink from the oceanic dissolved pool. This idea can also be tested through the isotopic analysis of organic-rich sediments.

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## APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.07.045.

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