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Journal Article**Author(s):**

Sieber, Matthias; Conway, Tim M.; [De Souza, Gregory](#) ; Hassler, Christel S.; Ellwood, Michael J.; Vance, Derek

Publication date:

2020-01

Permanent link:

<https://doi.org/10.3929/ethz-b-000373649>

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Originally published in:

Geochimica et Cosmochimica Acta 268, <https://doi.org/10.1016/j.gca.2019.09.039>

Cycling of zinc and its isotopes across multiple zones of the Southern Ocean: Insights from the Antarctic Circumnavigation Expedition

Sieber, M.^{1,*}, Conway, T. M.², de Souza, G. F.¹, Hassler, C. S.^{3,4}, Ellwood, M. J.⁵, and Vance, D.¹

¹Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Zürich, Switzerland

²College of Marine Science and School of Geosciences, University of South Florida, Florida, USA

³Department F.-A. Forel for Environmental and Aquatic Sciences, University of Geneva, Switzerland

⁴Swiss Polar Institut, EPF Lausanne, Lausanne, Switzerland

⁵Research School of Earth Sciences, Australian National University, Canberra, Australia

*Corresponding author: matthias.sieber@erdw.ethz.ch Phone: Tel: +41 44 632 93 83

Keywords: trace metals; biogeochemistry; zinc; antarctic circumpolar current; isotopes; nutrient cycling

Abstract

Zinc (Zn) is an essential micronutrient, playing an important role in several key processes in marine phytoplankton. Here, we present the first high-resolution depth profiles for dissolved Zn and $\delta^{66}\text{Zn}$ from all major zones of the Southern Ocean, collected during the Antarctic Circumnavigation Expedition in Austral Summer 2016/2017. The dataset reveals that Zn cycling changes between different regions of the Southern Ocean. Within the Antarctic Circumpolar Current (ACC), Zn cycling is closely linked to phosphate (PO_4), governed by uptake and regeneration, seasonal mixing, and upwelling. Here, uptake by phytoplankton is associated with a very small fractionation ($\alpha = 0.99995$), resulting in slightly elevated surface $\delta^{66}\text{Zn}$ (up to +0.67‰), overlying a shallow subsurface $\delta^{66}\text{Zn}$ minimum (+0.36‰ at ~200 m). South of the ACC, a partial coupling of Zn and silicate (Si) results in a shift of the Zn isotope systematics and a deep enrichment of Zn and Si. Two possible mechanisms could potentially cause this change: 1) reversible scavenging onto sinking particulates, or, 2) association of isotopically heavy Zn with diatom frustules. We also observe the effects of regional processes on Zn in the surface Southern Ocean: firstly, natural Fe fertilization near the Balleny Islands appears to lead to reduced Zn uptake (relative to phosphate) by phytoplankton, that is associated with a greater apparent Zn isotope fractionation than elsewhere in the Southern Ocean ($\alpha = 0.99987$); secondly, meltwater inputs from the Mertz Glacier add small amounts of isotopically light Zn to surface waters near the Antarctic shelf. Overall, we propose that the lack of distinct $\delta^{66}\text{Zn}$ signatures transported in intermediate waters of the lower latitude global oceans is due to near-complete uptake of Zn by phytoplankton in the surface Southern Ocean with only a small isotope fractionation, in contrast to elements like cadmium and silicon.

1. Introduction

Transition metals such as zinc (Zn) are vital micronutrients for marine phytoplankton, and their availability is thought to be an important control on biological productivity in the surface ocean (Morel et al., 2014). Specifically, Zn plays an important role in several crucial processes in phytoplankton, such as DNA replication, and as a cofactor in enzymes required for efficient carbon fixation and the uptake of dissolved organic phosphorus (Shaked et al., 2006; Twining and Baines, 2013; Morel et al., 2014). Water-column concentrations of dissolved Zn show a nutrient-type depth profile in the oceans, typically characterized by extreme depletion in surface waters and enrichment at depth (Bruland, 1980; Lohan et al., 2002; Conway and John, 2014; Zhao et al., 2014; Middag et al., 2019). Additionally, Zn concentrations show a remarkable global correlation with those of dissolved silicon (Si), with greatest enrichment at depths greater than those for the macronutrients phosphate (PO_4) and nitrate (NO_3), and the nutrient-like trace metal Cd (Bruland, 1980). While the co-variation of Zn and Si was observed by Bruland et al. (1978), following the first measurements of dissolved Zn profiles, the reasons for the near-linear relationship between the two elements remained unclear for several decades. For example, in phytoplankton cells Zn, like P and Cd, is mostly associated with organic matter (Collier and Edmond, 1984; Twining and Baines, 2013), while only a very small fraction of Zn is incorporated into the siliceous frustules of diatoms (Ellwood and Hunter, 2000). This suggested that Zn should be regenerated at a more shallow level, with PO_4 and NO_3 , and that there is no direct mechanism linking Zn and Si.

Recently, two hypotheses have been put forward to resolve this apparent discrepancy for Zn-Si systematics. The first relies on the idea that Zn and Si distributions are coupled through their similar biogeochemical behavior in the surface Southern Ocean, and that the Southern Ocean ‘hub’ exerts a global influence on Zn cycling (Vance et al., 2017; de Souza et al., 2018), analogous to well-known processes controlling the major nutrients (Sarmiento et al.,

2007). As such, the low-latitude coupling of Zn and Si is coincidental, not *in situ* mechanistic. Simply, the correlation comes about because of high Zn uptake rates into Southern Ocean diatoms, leaving Antarctic surface waters depleted in Zn. The physical circulation then exports the low-Zn waters into the upper ocean of the low latitudes, while trapping the majority of Zn in the deep ocean, analogous to Si (Sarmiento et al., 2007; Vance et al., 2017). Subsequent work (e.g. de Souza et al., 2018; Roshan et al., 2018; Weber et al., 2018; Middag et al., 2019) has confirmed the dominance of these Southern Ocean processes. The second hypothesis put forward by Weber et al. (2018) suggests that high deep Zn concentrations in the North Pacific require further vertical cycling and transfer of Zn from surface to deep outside the Southern Ocean, by both biological uptake and regeneration and via reversible scavenging of Zn. . In a recent detailed study of Zn, its isotopes, and their relationship to major nutrients, Vance et al. (2019) find evidence for significant vertical biological cycling, but not reversible scavenging, in the NE Pacific.

In the last decade, dissolved Zn stable isotope ratios ($\delta^{66}\text{Zn}$) have become available as an additional tool to provide insights into the oceanic distribution of Zn and its role in global marine nutrient cycles (Bermin et al., 2006), although data have remained scarce. However, even with the spatially-limited data available, a first characterization of the $\delta^{66}\text{Zn}$ distribution shows that the global deep ocean (below 500 m) is fairly homogeneous, despite relatively large variations in Zn concentrations ($\sim +0.45$ to $+0.5\text{‰}$; Conway and John, 2014, 2015; Zhao et al., 2014; Samanta et al., 2017; John et al., 2018; Wang et al., 2019). In the upper ocean, the picture is mixed. Within the surface ocean of the North Atlantic and both North and South Pacific basins, data generally show a decrease to lower $\delta^{66}\text{Zn}$ values in near-surface waters, sometimes associated with higher $\delta^{66}\text{Zn}$ at the very surface (Conway and John, 2014, 2015; John et al., 2018; Vance et al., 2019; see also Wang et al., 2019). While this pattern is largely at odds with available culturing studies on diatoms, cyanobacteria and coccolithophores, most of which would suggest preferential uptake of isotopically light Zn (John et al., 2007; John and Conway,

2014; Köbberich and Vance, 2017, 2019; Samanta et al., 2018), preferential uptake of heavy Zn may be possible under Fe-limiting conditions or by different species (Köbberich and Vance, 2017, 2019; Ellwood 2018). Preferential uptake of heavy isotopes may therefore explain a fractionation towards light values. Another explanation proposed for the observed light surface signatures is reversible scavenging of heavy Zn onto sinking particles (John and Conway, 2014). Furthermore, recent studies in the Tasman Sea have presented data consistent with the uptake and regeneration of light Zn controlling the shape of seawater $\delta^{66}\text{Zn}$ profiles (Samanta et al., 2017), illustrating the relative complexity of the Zn isotope cycle compared to those of other macro- and micronutrients like N, Si, and Cd (e.g. Sigman et al., 2000; de Souza et al., 2014; Sieber et al., 2019). Adding further complexity, organic speciation of Zn and the presence of organic ligands in seawater may play an important role in the size and direction of Zn isotope fractionation observed either in the ocean, or in culture (Köbberich and Vance, 2017, 2019; Samanta et al., 2017, 2018). In the Southern Ocean, where free Zn^{2+} is likely to be high (Baars and Croot, 2011), and thus organic ligands may play relatively less of a role in Zn isotope cycling, existing studies show near-homogenous $\delta^{66}\text{Zn}$ profiles, with surface waters exhibiting only slightly elevated $\delta^{66}\text{Zn}$ values followed by a slight minimum at very shallow depths below (100 -200 m), in contrast to other oceanic regions (Zhao et al., 2014; Wang et al., 2019). However, these existing Southern Ocean studies lack the depth-resolution in the upper ocean to fully resolve such features.

Here, we present 17 profiles of high depth-resolution dissolved Zn and $\delta^{66}\text{Zn}$ of the top 1000 m from the Pacific and Atlantic sectors of the Southern Ocean, across all the major zones of the Southern Ocean, collected during the Antarctic Circumnavigation Expedition (ACE). Each profile includes 8 to 9 samples within the uppermost 300 m, allowing us to examine the Zn cycle in the upper Southern Ocean in unprecedented detail. Our dataset highlights the strong coupling between Zn and PO_4 cycling, and allows us to unravel the Zn isotope systematics in the upper ocean of the ACC. A shift in the behavior of Zn cycling in the south of the ACC

suggests a mechanism partially coupling Zn and Si cycles, offering an explanation for the Zn enrichment of the deepest ocean water masses. On a regional scale, Fe fertilization from islands and freshwater inputs from glaciers influence Zn and $\delta^{66}\text{Zn}$ in surface waters. The Zn isotope systematics in the upper Southern Ocean, observed here and previously (Zhao et al., 2014; Wang et al., 2019) explain the lack of an elevated $\delta^{66}\text{Zn}$ signal in the intermediate and deep waters of the low latitudes, in contrast to Cd, Si and N (e.g. Sigman et al., 2000; de Souza et al., 2012; Abouchami et al., 2014).

2. Oceanographic Setting

Our study region, the Atlantic and Pacific sectors of the Southern Ocean, encompasses all of the major Southern Ocean zones (Fig. 1). The Southern Ocean circulation is dominated by the eastward flowing Antarctic Circumpolar Current (ACC) that encircles Antarctica and connects the Pacific, Atlantic and Indian Sectors (Talley, 2013). Three major fronts that are associated with transitions in water properties and biogeochemical characteristics separate the ACC into broad, dynamically homogeneous zones (Orsi et al., 1995). The Antarctic Polar Front (APF) is the central ACC front, and the Subantarctic Front (SAF) and the dynamical Southern ACC Front (SACCF) mark the northern and southern boundaries of the ACC, respectively. In the Antarctic Zone (AZ), the latitudinal belt between the Antarctic Polar Front (APF) and the Southern ACC Front (SACCF), strong wind stress curl result in Ekman upwelling that brings nutrient-rich Upper Circumpolar Deep Water (UCDW) to the surface (Talley et al., 2011). Part of these upwelled waters flows northwards, as Antarctic Surface Water (AASW), across the APF into the Polar Frontal Zone (PFZ), which extends northward to the SAF. Deep vertical convection during winter in the PFZ and further north across the SAF, in the Subantarctic Zone (SAZ), leads to subduction of AASW and the formation of intermediate water masses Sub-Antarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW; e.g. McCartney,

1982; Sloyan and Rintoul, 2001). The other part of the upwelled waters is transported southwards, into the high southern latitudes of the Southern Zone (SZ). The SZ contains the Weddell and Ross Gyres, and encompasses the entire area between the Southern Boundary (SB), which marks the southern extent of UCDW, and the Antarctic shelf in the south. In the SZ, very dense deep waters are formed due to sea ice formation and ventilate the deepest parts of the ocean.

3. Sampling and analytical methods

Seawater samples spanning the uppermost 1000 m of the water column were collected during Legs 2 and 3 of the Antarctic Circumnavigation Expedition on board the R/V Akademik Tryoshnikov during austral summer 2017 (January - March 2017). High depth-resolution profiles (six to eight samples in the uppermost 200 m) at seventeen stations (ACE station numbers 08 - 20, 21 - 25) in the Atlantic and Pacific sectors of the Southern Ocean were sampled for dissolved Zn and $\delta^{66}\text{Zn}$ (Fig. 1). These samples have been previously described for dissolved Cd and $\delta^{114}\text{Cd}$ (Sieber et al., in press). Seawater was sampled using a trace metal clean sampling rosette equipped with 12 L X-Niskin bottles, attached to a Dynema line, and filtered through AcroPak capsule filters (0.2 μm , Pall) into acid-cleaned 1 L or 4 L LDPE bottles. The filtered seawater samples were later acidified at ETH Zürich by addition of 1.2 mL 9.6 M Teflon double-distilled HCl per liter of sample, and samples were stored for at least 3 months at pH ~2 before processing.

Prior to sample processing, preliminary Zn concentrations were determined at the University of South Florida. For this, subsamples (45 mL) were amended with Zn double spike and preconcentrated using a seaFAST system (Elemental Scientific; Lagerström et al., 2013). Zn concentrations were then measured on an Element XR HR-ICP-MS using the isotope dilution technique. These preliminary Zn concentrations were used only to guide subsequent

double-spike addition for isotope analyses, and the values are not reported here. Processing of larger sample volumes (1-4 L) was carried out at ETH Zürich following slight modification of previously published methods (Conway et al., 2013; Sieber et al., 2019). Briefly, a ^{67}Zn - ^{64}Zn double spike was added to obtain a sample-to-spike ratio of 1:1. A batch extraction technique using Nobias PA-1 chelating resin was then used to extract trace metals from seawater, following Conway et al. (2013). Metals were eluted from the resin and purified by an anion-exchange chromatography technique using 20 μL PTFE micro-columns filled with AG-MP1 resin, as described in Sieber et al. (2019). The Zn fraction was eluted with 2 M HNO_3 + 0.1 M HBr , then evaporated to dryness and redissolved in 0.3 M Teflon-distilled HNO_3 for analysis by MC-ICPMS. The same procedure was used for 1 L and 4 L samples. The method has a total procedural blank of <0.2 ng per liter of seawater, and effectively purifies Zn from major cations and interfering elements (Cu, Ni).

Zn isotope analyses were performed on a Thermo Neptune Plus Multi-Collector-ICPMS at the Institute of Geochemistry and Petrology at ETH Zürich, using an Aridus II desolvating system (Cetac), normal Ni sample and skimmer cones (Archer et al., 2017). Zn stable isotope ratios are expressed in delta notation relative to the JMC-Lyon Zn standard:

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

Repeat measurements of a secondary standard, IRMM-3702, were used to evaluate the long-term instrumental precision. For this standard, we obtain a $\delta^{66}\text{Zn}$ value of $+0.30 \pm 0.06\text{‰}$ (2SD) over three years, consistent with previously-reported values (Archer et al., 2017). We use this uncertainty as a conservative estimate of 2σ uncertainty on $\delta^{66}\text{Zn}$ for all samples, except for low concentration samples where the larger internal error is considered a more conservative estimate of uncertainty. Concentrations reported herein were calculated using the isotope dilution technique based on on-peak blank, interference and mass-bias corrected $^{67}\text{Zn}/^{66}\text{Zn}$

ratios measured simultaneously with isotope analyses. We assign a 2% uncertainty to concentrations measured using this approach (Conway et al., 2013). Analysis of the reference materials SAFe D1 and D2 alongside our samples yield excellent agreement with the consensus values for both Zn concentrations and $\delta^{66}\text{Zn}$ (Table S1).

4. Results

Dissolved Zn concentrations and isotopic compositions for all ACE stations are tabulated in Supplementary Data, along with temperature, salinity, and oxygen and major nutrient concentrations. The data are also shown as depth profiles in Figs 2 and 3. Additionally, we show Zn^* profiles to highlight variability in the relationship between Zn and Si, relative to the deep Southern Ocean Zn/Si ratio (Wyatt et al., 2014). We express Zn^* following Conway and John (2014) as:

$$\text{Zn}^* = \text{Zn} - \text{Si} \times \text{Zn/Si}_{(\text{deep})}$$

The deep Southern Ocean Zn/Si ratio ($0.064 \text{ mmol mol}^{-1}$) is based on our data from samples below 500 m, and is identical to observations from the global deep ocean (Vance et al., 2017).

Dissolved Zn concentrations range from 0.02 to $7.59 \text{ nmol kg}^{-1}$, with Zn at its most depleted at the surface and exhibiting a general increase with depth (Fig. 2). Stations within a single dynamic-biogeochemical zone of the Southern Ocean display similar Zn concentration profile shapes, even across different sectors of the Southern Ocean (Fig. 3). Generally, Zn concentrations decrease from south to north, both in the surface and in the deep ocean (Figs 2, 3). The dissolved Zn concentration maximum also becomes progressively deeper northwards ($\sim 100 \text{ m}$ in the SZ to $>1000 \text{ m}$ in the SAZ; Fig. 2). The highest surface Zn concentrations (up to 3.5 nmol kg^{-1}) are seen south of the Southern Boundary of the ACC, in the SZ, accompanied by a steep increase at shallow depths to relatively constant, high Zn concentrations ($>7 \text{ nmol}$

kg⁻¹) below 200 m (Fig. 3). Only one station in this zone (16) exhibits slightly lower Zn concentrations at depth (~6 nmol kg⁻¹). To the north of the SZ, in the AZ, surface concentrations are considerably lower (0.75 to 1.2 nmol kg⁻¹) and Zn concentrations reach a relatively constant value (~6 nmol kg⁻¹) at greater depths (Fig. 3). This trend continues into the PFZ, with surface concentrations <0.5 nmol kg⁻¹, and with the subsurface increase becoming more gradual compared to the stations further south. The lowest Zn concentrations are seen in the surface waters of the SAZ (<0.02 nmol kg⁻¹), coupled with a gradual increase in concentrations in deeper water that continues throughout the profiles (Fig. 3). Stations located close to the Mertz Glacier (11, 12), present an exception to the general north-south pattern. Here, surface waters show the lowest Zn concentrations south of the APF (down to 0.19 nmol kg⁻¹; Fig. 3). While they do also show a sharp increase at shallow depths, deep Zn concentrations here are lower as well (~5 nmol kg⁻¹).

Dissolved $\delta^{66}\text{Zn}$ ranges from +0.30‰ to +0.67‰, representing a similarly-small range to that observed previously in the Southern Ocean (Zhao et al., 2014; Wang et al., 2019). Across all zones and sectors, significant variation in $\delta^{66}\text{Zn}$ is restricted to the upper 200 m, while waters below generally show very little variability ($+0.44 \pm 0.08\text{‰}$, 2SD, $n = 63$; Fig. 2). In the SZ, $\delta^{66}\text{Zn}$ profiles exhibit a relatively pronounced $\delta^{66}\text{Zn}$ minimum (down to +0.30‰) in the shallow subsurface (~100 m; Fig. 3). However, with the exception of stations located downstream of the Balleny Islands (13, 14), SZ surface waters do not show an increase in $\delta^{66}\text{Zn}$ towards the very surface, but instead lie close to the deep ocean average (Fig. 3). Further north, in the AZ, surface waters display elevated $\delta^{66}\text{Zn}$ values (+0.51‰ to 0.63‰), followed by a slight $\delta^{66}\text{Zn}$ minimum in the subsurface (+0.36‰ to +0.40‰; ~200 m; Fig. 3). Higher surface $\delta^{66}\text{Zn}$ values persist as surface waters cross the APF into the PFZ (up to +0.67‰). However, north of the APF, the corresponding subsurface $\delta^{66}\text{Zn}$ minimum is no longer present. Further north, in the SAZ, $\delta^{66}\text{Zn}$ profiles show almost no variability outside of error (Fig. 3). As with the Zn concentrations, $\delta^{66}\text{Zn}$ values in surface waters at the two stations located close to the Mertz

Glacier (11, 12) present an exception to the general pattern, showing a lighter isotopic composition in the subsurface ($\sim +0.35\text{‰}$).

5. Discussion

We first discuss Zn cycling and Zn isotope systematics within the ACC, in the AZ and the PFZ. We then examine how Zn concentration and $\delta^{66}\text{Zn}$ distributions differ further south, in the SZ, where the Southern Ocean gyres are important oceanographic features. The SZ also includes stations located in Fe fertilized waters near the Balleny Islands, allowing us to study the effects of natural Fe fertilization on Zn cycling in the Southern Ocean. Furthermore, stations close to the Mertz Glacier provide insights into the effect of ice edge processes on surface waters on the Antarctic Shelf. Finally, we consider the role of the Southern Ocean for the global $\delta^{66}\text{Zn}$ distribution, and discuss the absence of characteristic Zn isotope signatures in southern-sourced intermediate waters.

5.1 Zn and $\delta^{66}\text{Zn}$ cycling in the ACC

The linear relationship between Zn and Si has been described for most of the global ocean (Vance et al., 2017; de Souza et al., 2018; Weber et al., 2018). Fig. 4a shows that, though waters in the AZ broadly follow this pattern, there are also significant deviations. This non-linear relationship implies different uptake and/or regeneration dynamics for the two elements in the Southern Ocean that is reflected in the Zn^* profiles (Fig. 3): surface waters often exhibit slightly negative Zn^* , Winter Water a Zn^* of $\sim 0 \text{ nmol kg}^{-1}$, followed by a Zn^* maximum below and a slow return towards to a Zn^* of 0 nmol kg^{-1} with depth. In contrast, Zn and PO_4 show a steep, linear relationship in the upper ocean (Fig. 4b): the linearity suggests that Zn is regenerated over the same length scale as PO_4 , whilst the high slope reflects the fact that it is

taken up in significantly higher quantities than PO_4 , relative to their ocean-mean concentrations (Twining and Baines, 2013; Vance et al., 2017). These first order observations in the AZ are in good agreement with recent studies from the Atlantic and Indian Sectors of the Southern Ocean (Zhao et al., 2014; Wang et al., 2019), and are particularly well-resolved here. But our high-resolution data allow us to go further to examine in more detail the interactions between uptake and regeneration, seasonal mixing, and upwelling controls on Zn and $\delta^{66}\text{Zn}$.

The stoichiometry of Southern Ocean diatoms (Twining and Baines, 2013) predicts that Zn and Si should be taken up in high quantities relative to PO_4 in the surface waters of the AZ. However, AASW (top ~50 m) displays slightly negative Zn^* values (Fig. 3) indicating that Zn uptake rates are slightly higher compared to Si. Consequently, AASW plots just below the global Zn-Si trend line (Fig. 4a). In the subsurface (~100 m), samples within the deep winter mixed layers plot close to the global trend ($\text{Zn}^* \sim 0 \text{ nmol kg}^{-1}$). These deep winter mixed layers are formed during vertical convection driven by strong winds and cooling of surface waters during wintertime (Park et al., 1998). In summer, remnants of the cold winter surface waters remain in the subsurface mixed layers, also called Winter Water (WW), indicated by a temperature minimum ($<0^\circ\text{C}$; Fig. 4a). Mixing of Zn-depleted AASW with the underlying Zn-rich deep waters can partly explain the return to a Zn^* of 0 nmol kg^{-1} (i.e. a deep ocean Zn/Si ratio) in WW. However, shallow remineralization of Zn overprints this process (Zhao et al., 2014), as supported by the observation that Zn^* continues to increase below WW (100 – 200 m). Samples from these depths subsequently plot above the global Zn-Si trend (Fig. 4a). Regeneration of Zn continues down to ~250 m, where Zn concentrations reach a maximum, coinciding with the core of upwelling UCDW (characterized by an oxygen minimum). Zn concentrations remain fairly constant below 250 m, indicating that it is the continuous deep remineralization of Si that causes samples from LCDW to return to a Zn^* of 0 nmol kg^{-1} and return to the global trend line (Fig. 4a). Overall, this indicates shallower regeneration-addition

of Zn compared to Si, which remains in frustules and is remineralized at greater depths (Vance et al., 2019).

In the PFZ, the importance of the different processes affecting the Zn-Si relationship shifts away from biological cycling and towards vertical mixing. However, the same biological and physical processes occurring in the AZ continue to influence the Zn-Si relationship (Fig. 4c). Surface waters are very slightly depleted in Zn relative to Si, although to a lesser extent, indicated by the less negative Zn^* values (Fig. 3). The difference in regeneration length scales of the two elements is also most striking close to the APF (station 20), where a pronounced Zn^* maximum is observed below the mixed layer (Figs 3, 4c). Further north into the PFZ (stations 09, 24), however, more vigorous vertical mixing reaches greater depths, reducing deviations from the Zn-Si correlation. The strong depletion of Zn in surface waters here ($<0.5 \text{ nmol kg}^{-1}$) results in lower Zn concentrations in the mixed layers than observed further south, and the increasing influence of Zn-rich deep water masses during vertical mixing drives the Zn-Si relationship back towards the global trend line (Fig. 4c).

The Zn- PO_4 relationship in the AZ is defined by a very steep, linear trend (Fig. 4b), consistent with shallow cycling of both Zn and PO_4 over similar length scales (Zhao et al., 2014; Vance et al., 2017), and with observations that most of the Zn within phytoplankton cells is co-located in organic matter with PO_4 (Twining and Baines, 2013). The steepness of the slope ($6.5 \text{ mmol mol}^{-1}$; Fig. 4b) reflects the high Zn uptake by phytoplankton compared to relatively low PO_4 uptake, but it is somewhat lower than Vance et al. (2017) observed (8 mmol mol^{-1}). This difference stems from the fact that the calculation by Vance et al. (2017) included data from the deep ocean in the SZ, that is richer in Zn compared to the AZ (see Section 5.2), which likely results in overestimation of the Zn uptake. Contrary to the Zn-Si relationship, where mixing and upwelling result in visible differences throughout the water column, the same processes appear to have little effect on the Zn- PO_4 relationship (Fig 4b). Instead, both Zn and PO_4 are

dominated by concomitant uptake and regeneration in the shallow upper ocean, and vertical mixing follows the slope set by biological cycling (Fig 4b). Thus, Zn and PO₄ show similar behaviors in the deep mixed layers and the upwelling waters. Moving north across the APF, we observe a shift away from the AZ pattern described above, the most striking feature in the Zn-PO₄ relationship in the PFZ being a break in the linear relationship at low Zn values (Fig. 4d). This break reflects the increased PO₄ uptake by phytoplankton in surface waters north of the APF (Vance et al., 2017). Surface waters close to the APF (station 20) still follow the steep slope, while surface waters further north in the PFZ (stations 09, 24) constitute the shallow slope (Fig. 4d). The subsurface is dominated by deep vertical mixing and thus follows the steep slope set further south in the AZ.

The behavior of Zn isotopes in the AZ (Fig. 5a) appears to be generally consistent with the evolution of Zn* throughout the water column described above (Fig. 4a): uptake-driven Zn depletion in AASW results in slightly heavier surface values, consistent with the suggestion in Wang et al. (2019) of a very slight preference for light Zn by the phytoplankton (Fig. 5a). In the subsurface (~100 m), just as for Zn*, any isotopic signal in WW appears to have been obscured by a combination of deep winter mixing and regeneration of isotopically light Zn, resulting in $\delta^{66}\text{Zn}$ values similar to the deep ocean. Below WW (100 – 200 m), the Zn* maximum is associated with regeneration of slightly light Zn, and indeed we can identify a slight $\delta^{66}\text{Zn}$ minimum at these depths (Fig. 5a), again consistent with findings for the Indian sector of the Southern Ocean in Wang et al. (2019). Further north, in the PFZ, the same biological-physical processes continue to affect $\delta^{66}\text{Zn}$, though, as for Zn*, the relative importance shifts towards vertical mixing becoming dominant. In the Pacific Sector PFZ (stations 09, 20), surface waters retain a negative Zn*, and exhibit elevated $\delta^{66}\text{Zn}$ values (Figs 3, 5b). Surface waters in the Atlantic PFZ (station 24), however, lack an isotopically heavy surface signal. As Zn* values here are positive and Zn concentrations relatively low (<0.5 nmol kg⁻¹), we speculate that surface inputs, e.g. dust inputs from the South American continent (e.g.

Mahowald et al., 2005), could potentially be the source of this difference to the Pacific Sector, given the $\delta^{66}\text{Zn}$ composition of +0.3‰ of dust inputs (Little et al., 2014). The pronounced Zn^* maximum in the subsurface at the APF is also reflected in a slight $\delta^{66}\text{Zn}$ minimum with $\delta^{66}\text{Zn}$ values slightly below the deep ocean average (station 20; Fig. 5b). Further north (stations 09, 24), vertical mixing intensifies and reaches greater depths and, as a result, the subsurface $\delta^{66}\text{Zn}$ minimum fades and $\delta^{66}\text{Zn}$ signals become increasingly homogeneous, analogous to Zn^* .

Our high-resolution data allows us to investigate the Zn isotope systematics in more detail (Fig. 6). If we consider the surface waters in the AZ and the PFZ, and consider the Zn and $\delta^{66}\text{Zn}$ characteristics of upwelled deep water as the starting point of a Rayleigh-type isotope fractionation, we obtain a fractionation factor associated with Zn uptake of $\alpha = 0.99995 \pm 0.00001$, i.e. preferential uptake of the light isotope by 0.05 ± 0.01 per mil. This is in good agreement with recent estimates for the Indian Sector AZ in Wang et al. (2019). This finding highlights the small magnitude of isotope fractionation associated with the high Zn uptake in the Southern Ocean compared to that predicted by early culture studies (John et al., 2007; John and Conway, 2014). However, the Rayleigh framework disregards mixing and regeneration processes in the subsurface, and our discussion above has shown that in fact a series of processes determines the $\delta^{66}\text{Zn}$ distribution in the upper ocean within this region. The expected deviations from Rayleigh fraction behavior because of mixing can be derived using a simple binary mixing model with AASW and UCDW as endmembers (Fig. 6b). Indeed, Fig. 6a clearly shows that subsurface mixing strongly influences the isotope systematics, especially within the PFZ where mixing has a proportionally larger effect due to the increased concentration difference between surface and underlying waters. This becomes increasingly important north of the APF, where mixing between surface and deep waters appears to explain the upper ocean isotope distribution (Fig. 6b).

5.2 Zn and $\delta^{66}\text{Zn}$ cycling south of the ACC

5.2.1 Southern Zone

South of the ACC, in the Southern Zone, we observed significantly higher Zn concentrations than further north, both in the surface and in the deep ocean (Fig. 3). Furthermore, Zn cycling and Zn isotope systematics are significantly different within the SZ (Fig. 7) compared to within the AZ and further north (see Section 5.1).

Apart from showing higher Zn and Si concentrations, the Zn-Si relationship is largely consistent with that for the AZ (Figs 4a, 7a). In the SZ, AASW is slightly depleted in Zn relative to Si, followed by a Zn excess in the subsurface and a subsequent return to the global trend with depth (Fig. 7a). The major difference in the SZ is that positive Zn^* values in the subsurface are associated with WW, indicating that the deep water signal is less important due to the lack of active upwelling south of the SB. From the Zn- PO_4 relationship (Fig. 7b) it can be seen that concomitant cycling of Zn and PO_4 still controls the upper ocean (top 200 m), with a slope ($6.3 \text{ mmol mol}^{-1}$) similar to the AZ ($6.5 \text{ mmol mol}^{-1}$; Fig. 4b). However, at high PO_4 concentrations there is a break in the relationship, where Zn concentrations continue to increase while PO_4 remains fairly constant (Fig. 7b). In addition, over the same concentration range Zn and Si both increase, forming the upper end of the linear trend (Fig. 7a). This suggests that, in contrast to Zn cycling in the ACC, in the SZ part of the Zn ($\sim 25\%$) may be associated with Si and reaches deeper Southern Ocean waters.

Due to the lack of deep ocean data (below 1000 m), we can only speculate on possible reasons for this change in Zn cycling in the SZ. Putative continental sources would most likely be found in the freshly formed bottom waters that have cascaded down the Antarctic continental shelf into the open SZ and remain uncharacterized at present. Therefore, we propose two upper ocean mechanisms that could potentially explain the partial coupling of Zn and Si in the SZ. In the first hypothesis, a fraction of the Zn would be associated with the frustules of diatoms,

providing a direct link between the two elements (Lohan et al., 2002; Zhao et al., 2014). While initial culturing studies have demonstrated that the Zn content of diatom frustules is negligible (Ellwood and Hunter, 2000), recent findings have proposed that this value could be significantly higher during Fe-limitation (up to 30%; Ellwood et al., 2018). In this scenario, it is conceivable that a combination of biogeochemical differences in the surface ocean and varying phytoplankton species could be the cause of the different Zn cycling behavior in the AZ and the SZ. A second hypothesis is that reversible scavenging of Zn onto particles drives the Zn flux to the deep ocean (John and Conway, 2014). Weber et al. (2018) have recently hypothesized that reversible scavenging is necessary to maintain the linear correlation between Zn and Si throughout the global ocean. Therefore, it seems possible that this process could also affect Zn cycling in the SZ.

We can further investigate the cycling of Zn in the SZ using the isotope data (Fig. 7c). The Zn* maximum in WW is associated with a $\delta^{66}\text{Zn}$ minimum, but surface and deep waters show little variation from the deep ocean average. While the subsurface minimum is consistent with regeneration of light Zn, analogous to the AZ, there is a lack of a corresponding heavy surface signal. We suggest that the lack of high surface $\delta^{66}\text{Zn}$ values here is linked to the different cycling of Zn in the SZ compared to the AZ, and we consider the isotope systematics in the light of the two hypotheses proposed above. In order to explain the observed $\delta^{66}\text{Zn}$ profiles, the process transferring part of the Zn to the deep ocean would have to mask a heavy surface signal, and would therefore need to be associated with preferential uptake of isotopically heavy Zn, or Zn with a near-deep ocean signature, as previously suggested by Zhao et al. (2014). Gradual regeneration of such slightly isotopically heavy Zn at greater depths, where Zn concentrations are high, would be unlikely to have a resolvable effect on deep $\delta^{66}\text{Zn}$ values.

Recent studies have shown that preferential uptake of heavy Zn by *Chaetoceros* sp. is possible under Fe-limiting conditions (Köbberich and Vance, 2017; Ellwood et al., 2018),

depending on uptake rate, Zn speciation and Fe availability ($\Delta\delta^{66}\text{Zn}_{\text{medium-cells}}$ of -0.42 to +0.85‰ as Fe', the inorganically bound and unchelated pool, decreases; Köbberich and Vance, 2017). If heavy Zn is preferentially incorporated into the frustules while light Zn is associated with the organic-rich parts of the phytoplankton cells, this could also explain the isotope distribution. But the same can be achieved with reversible scavenging. In this case, adsorption of slightly heavier Zn onto sinking particles (John and Conway, 2014; Weber et al., 2018) could balance out any surface signals associated with preferential uptake of light Zn. Therefore, both mechanisms can explain the partial coupling of Zn and Si, as well as the $\delta^{66}\text{Zn}$ distribution in the SZ. We acknowledge that the two hypotheses are speculative at present and need to be tested with further laboratory and field experiments. Regardless of the mechanism, however, the incorporation of some of the Zn into frustules also provides a possible explanation for the high Zn concentrations found in Antarctic Bottom Water (AABW; Middag et al., 2019), that is formed along the continental margins of the SZ (Talley et al., 2011). While continental sources remain uncharacterized at present, they could provide another mechanism for the decoupling of Zn from P at depth and the enrichment of Zn in the deep ocean of the SZ.

5.2.2 Potential impacts of Fe fertilization at the Balleny Islands

Surface waters near the Balleny Islands display elevated chlorophyll-a and Fe concentrations, suggesting that these surface waters are likely affected by island Fe fertilization (Fig. 8a; Sieber et al., in press). This provides us with the opportunity to study the effects of natural Fe fertilization on Zn cycling in the Southern Ocean. A previous study on the impacts of Fe fertilization on the Kerguelen plateau (Wang et al., 2019) did not observe any significant changes in the region affected by Fe fertilization. However, in their study the Fe fertilized waters at the Kerguelen plateau lie north of the APF, while unfertilized waters lie south of the APF. Thus, the observed variations across gradients in Fe fertilization were impossible to

deconvolve from the biogeochemical changes across the front. The Balleny Islands do not suffer from this problem, with all our stations (13-15) located south of the Southern Boundary. Stations are located close to the islands (14), as well as upstream (15) and downstream (13) (Fig 8a). Hence, they provide a unique opportunity to gain further insights into the effects of Fe fertilization on Zn and its isotopes.

In order to better understand the impacts of Fe fertilization on Zn uptake and Zn isotope systematics, we consider the relative concentration difference between surface waters and mixed layers (~100 m), rather than absolute values. This allows us to gauge the drawdown of Zn by phytoplankton uptake in surface waters, relative to supply from the mixed layer. Analysis of these relative concentration differences shows lower values at stations close to and downstream of the islands (~2 nmol kg⁻¹; 13, 14), where higher Fe concentrations are available, compared to the station upstream (~3 nmol kg⁻¹; 15). This would be consistent with reduced Zn uptake by phytoplankton when relieved from Fe limitation, which has been observed in culture (Sunda and Huntsman, 2000). Furthermore, the lower concentration differences are associated with slightly elevated $\delta^{66}\text{Zn}$ values in surface waters (>+0.5‰ in the top 30 m), while waters upstream lack this feature (15). Subsurface waters at all three stations show a $\delta^{66}\text{Zn}$ minimum in the winter mixed layer (~100 m) and a return to constant values below (Fig. 3), and are likely controlled by the same processes discussed in Section 5.2.1. The Zn isotope systematics reveal a fractionation factor associated with Zn uptake that is significantly higher than that calculated for AZ surface waters ($\alpha = 0.99987 \pm 0.00003$). This would suggest that relief from Fe limitation leads to increased preferential uptake of isotopically light Zn. Mechanistically, this effect might be the direct result of increased [Fe'], a change in species composition, or a switch to a lower-affinity uptake pathway at higher Zn concentration with greater isotope fractionation (John et al., 2007; Köbberich and Vance, 2017, 2019). Again, we note that a Rayleigh approach does not consider subsurface processes that are likely to influence the Zn isotope systematics.

5.2.3 Ice edge processes

Surface waters on the Antarctic shelf, near the Mertz Glacier (stations 11, 12), exhibit significantly lower Zn concentrations ($<0.4 \text{ nmol kg}^{-1}$; Fig. 9a) than other stations south of the SB. The low surface Zn concentrations coincide with similarly anomalously low Cd concentrations, as well as lower macronutrient concentrations (Sieber et al., in press). These surface waters also have significantly reduced salinity (down to 32.5 psu, Fig. 9a), indicative of freshening by glacial meltwater (Sieber et al., in press). However, as for Cd, a salinity normalization of Zn concentrations shows that this freshening cannot explain the low Zn concentrations in the upper few tens of meters (Fig. 9a). Thus, the low Zn concentrations are likely a result of enhanced productivity near the Mertz Glacier, potentially driven by Fe supply via glacial meltwater (Sherrell et al., 2015) or some other means of continental input. Fig. 9b reveals that the low-Zn, less saline surface waters also exhibit lower $\delta^{66}\text{Zn}$ values ($\sim +0.35\text{‰}$) than the underlying water column, suggesting that an additional process is affecting the $\delta^{66}\text{Zn}$ signatures of these waters. This cannot be easily explained by biological uptake, given that our observations in all other zones of the Southern Ocean show very slight preferential uptake of light Zn by phytoplankton (Fig. 6). Instead, the light Zn in surface waters could be an indication of a continental Zn source with a $\delta^{66}\text{Zn}$ signature close to that of the continental crust ($+0.3\text{‰}$; Little et al., 2014) or isotopically lighter. The small fractionation of Zn associated with phytoplankton uptake, in combination with the low surface Zn concentrations, renders $\delta^{66}\text{Zn}$ signatures in these surface waters susceptible to inputs that can overprint the biological signal (Fig. 9c). This is analogous to the decoupling of concentrations and isotopic compositions observed for Cd (Sieber et al., in press), with the important difference that the isotope fractionation imposed by biological uptake is much stronger for Cd than for Zn: as a consequence of which any addition of an isotopically light pool has a more distinct influence

on surface $\delta^{66}\text{Zn}$ compared to $\delta^{114}\text{Cd}$ (Sieber et al., in press). We speculate that Zn could be added to surface waters from glacially-derived particles associated with meltwater input but more data would be needed to resolve the interactions of various processes in the upper few tens of meters. By contrast, the underlying Continental Shelf Water (CSW) remains largely unaffected any freshwater isotope signal, likely due to higher Zn concentrations at depths below 150 m attenuating any signal.

5.3 Implications for the global distribution of dissolved $\delta^{66}\text{Zn}$

Despite the similarities between Zn cycling and the cycling of Si and Cd in the surface Southern Ocean, there is a major difference in the large-scale $\delta^{66}\text{Zn}$ distribution: unlike Si or Cd isotopes, which carry distinct isotope signatures, southern-sourced water masses AAIW and SAMW do not carry a $\delta^{66}\text{Zn}$ signature that is resolvable from the deep ocean reservoir (Fig. 10). Instead, isotopically homogeneous profiles are seen throughout the intermediate and deep ocean for most regions north of the SAF. For both Si and Cd, isotopically heavy signatures are formed in the surface Southern Ocean and, through deep mixing, imparted to AAIW and SAMW during intermediate water mass formation north of the APF (Fripiat et al., 2011; de Souza et al., 2012; Abouchami et al., 2014; Sieber et al., 2019). In contrast, we suggest that the very small isotope fractionation seen for Zn in the surface Southern Ocean, in combination with the stark depletion south of the APF, are responsible for the lack of an elevated $\delta^{66}\text{Zn}$ signal imparted to AAIW and SAMW, as we discuss below.

In spite of the small apparent isotope fractionation associated with the uptake of Zn in the AZ, by the time surface waters reach the PFZ they exhibit considerably higher $\delta^{66}\text{Zn}$ values than the deep ocean ($\sim +0.25\text{‰}$ higher), only somewhat smaller than what has been observed for Cd ($\sim +0.7\text{‰}$ higher; Abouchami et al., 2011; Xue et al., 2013; Sieber et al., in press). In fact, the inferred overall isotope fractionation for both elements (the difference between surface

and deep waters) is very similar, on a per atomic mass unit (amu) basis ($\sim 0.13\text{‰}$ for Zn and $\sim 0.15\text{‰}$ for Cd). Despite the fact that the fractionation of Zn isotopes during uptake may be complicated by distinct uptake pathways and speciation (Köbberich and Vance, 2017), it still seems conceivable that the observed small isotope fractionation in surface waters would provide enough leverage to affect intermediate water and, on the face of just this evidence, it is surprising that it does not. However, the major difference between Zn and Cd is the more extreme depletion of Zn south of the APF, which leaves surface waters north of the APF with very low Zn concentrations (down to $0.12 \text{ nmol kg}^{-1}$), a decrease by approximately a factor of 50 relative to the upwelling deep waters ($\sim 6 \text{ nmol kg}^{-1}$). By comparison, Cd concentrations north of the APF (down to 0.2 nmol kg^{-1}) see only a fourfold decrease from upwelling deep waters ($\sim 0.8 \text{ nmol kg}^{-1}$; Sieber et al., in press). Hence, the heavy Zn left in PFZ surface waters is no longer sufficient to leverage a significant change of the $\delta^{66}\text{Zn}$ signal during deep winter mixing. Instead, any remaining $\delta^{66}\text{Zn}$ surface signatures are overprinted in the mixed layers because of the dominance of deep ocean Zn, and further lost during the seasonal addition of regenerated Zn from summertime export. While the spatial decrease seen for Si is on a similar scale to Zn, Si isotopes show a fractionation that is almost an order of magnitude greater than that seen for Zn ($\sim 1\text{‰}$ per amu; e.g. Fripiat et al., 2011). Therefore, we suggest that the more substantial Si isotope variations in Southern Ocean surface waters are able to overcome the low concentrations, giving surface water enough significance to affect the Si isotope signature of deep mixed layers and subsequently AAIW and SAMW, while surface waters cannot affect Zn isotopes in the same manner.

6. Conclusion

Here, we have presented the first high depth-resolution dissolved Zn and $\delta^{66}\text{Zn}$ data from all major zones of the Southern Ocean from the Antarctic Circumnavigation Expedition.

Our dataset reveals in detail how Zn cycling changes throughout different regions of the Southern Ocean. In the Antarctic Zone, a close interplay between uptake and regeneration, seasonal mixing, and upwelling controls the Zn and $\delta^{66}\text{Zn}$ signals in the upper Southern Ocean. Our observations show that Zn uptake in the AZ is associated with a very small fractionation ($\alpha = 0.99995$), but that the same isotope systematics do not extend to the waters south of the ACC. Instead, Zn cycling in the Southern Zone is consistent with a partial coupling of Zn and Si, leading to deep enrichment in the SZ, and subsequently to the high Zn concentrations observed in AABW (Middag et al., 2019). We propose that natural Fe fertilization near the Balleny Islands could be the cause of reduced Zn uptake as well as preferential uptake of light Zn by phytoplankton ($\alpha = 0.99987$). Furthermore, increased productivity near the Mertz Glacier results in low surface Zn concentrations, and a shift towards isotopically lighter Zn indicates Zn addition from glacial sources with a near-crustal $\delta^{66}\text{Zn}$ signature. While we only observe this process close to the Mertz Glacier, meltwater inputs could possibly have a larger scale influence on Southern Ocean surface waters. Finally, we propose that small fractionation observed in the surface Southern Ocean, in combination with the strong depletion leads to a homogenous $\delta^{66}\text{Zn}$ signal in the intermediate and deep waters of the low latitudes. In conclusion, our study shows that the distributions of Zn and $\delta^{66}\text{Zn}$ are not as consistent throughout the different zones of the Southern Ocean, as seen for other micronutrients such as Cd or macronutrients such as N and Si. While isotopic variations between different areas are small, there are systematic differences that could be identified in our high-resolution data. More high-resolution studies are necessary in order to fully understand how different processes affect Zn and its isotopes, especially given the subtlety of the isotope effects that some of these processes appear to impart.

Acknowledgements

We thank the captain, crew and water sampling team aboard R/V Akademik Tryoshnikov on the Antarctic Circumnavigation Expedition, and Corey Archer for assistance in the lab at ETH Zürich. This work forms part of project 15 of the Antarctic Circumnavigation Expedition voyage, which was supported with funds from EPFL, Swiss Polar Institute and Ferring Pharmaceuticals. The PhD studies of MS were supported by ETH Zürich.

Figures

Figure 1. Bathymetric map of the Southern Ocean showing the cruise track (orange line) and the locations of stations from which samples were collected during Legs 2 and 3 of the Antarctic Circumnavigation Expedition cruises. White lines represent the Subtropical Front (STF), the northern boundary of the Southern Ocean, and the principal fronts of the Antarctic Circumpolar Current (ACC): Subantarctic Front (SAF), Antarctic Polar Front (APF), Southern ACC Front (SACCF), and Southern Boundary (SB). Front locations from Orsi et al. (1995), map modified from Sieber et al. (in press).

Figure 2. Depth profiles of dissolved Zn, $\delta^{66}\text{Zn}$, and Zn* from all ACE stations, across the major zones of the Southern Ocean.

Figure 3. High-resolution depth profiles (top 300 m) of dissolved Zn, $\delta^{66}\text{Zn}$ and Zn^* from ACE stations located in different Southern Ocean zones.

Figure 4. Zn-Si and Zn-PO₄ relationships, colored for temperature, for all ACE stations located in the AZ (a, b), and PFZ (c, d). The dashed line in the Zn-Si plots represents the global Zn-Si correlation (Vance et al., 2017) with points above the line exhibiting positive Zn* while points below the line show negative Zn*. Arrows in the Zn-PO₄ plots represent biological cycling in the upper Southern Ocean.

Figure 5. (a) Zn-Si relationship for ACE stations located in the AZ (a) and in the PFZ (b), colored for $\delta^{66}\text{Zn}$. The dashed line represents the global Zn-Si correlation (Vance et al., 2017) with points above the line exhibiting positive Zn^* while points below the line show negative Zn^* .

Figure 6. (a) Zn isotope systematics in the Antarctic and Polar Frontal Zone. To estimate α we only consider AASW (top 50 m) that mostly remains unaffected by strong vertical mixing and regeneration, and we use the composition of upwelling waters as the starting point. The dashed lines show the expected deviations from Rayleigh behavior because of mixing derived from stations 20 at the APF and stations in the PFZ. (b) Binary mixing between AASW and UCDW at station 20, located close to the APF, and in the PFZ, represented by dashed lines, in $\delta^{66}\text{Zn}$ vs. $1/\text{Zn}$ space.

Figure 7. Zn-Si relationship (a) and Zn-PO₄ relationship (b) for all ACE stations located in the Weddell and Ross gyres within the Southern Zone, colored for temperature. The dashed line represents the global Zn-Si correlation (Vance et al., 2017). (c) Zn-Si relationship for the same stations, colored for $\delta^{66}\text{Zn}$.

Figure 8. (a) ACE stations near the Balleny Islands (13-15) plotted on a map of chlorophyll-a, based on satellite observations during time of sampling (February 2017; NASA-OBPG, 2018). (b) Zn isotope systematics for stations downstream of the Balleny Islands (13, 14).

Figure 9. Stations 11 and 12, located on the Antarctic shelf, close to the Mertz Glacier: (a) Zn, $\delta^{66}\text{Zn}$, PO₄, salinity and salinity-corrected Zn concentration depth profiles of the top 300 m; salinity-corrected Zn concentrations are normalized to the subsurface salinity of 34.5 psu; (b) plotted in Zn vs. salinity space, colored for $\delta^{66}\text{Zn}$; (c) plotted in $\delta^{66}\text{Zn}$ vs. 1/Zn space.

Figure 10. Schematic cycling of Cd (a) and Zn (b) in the upper Southern Ocean. Arrows represent the meridional circulation across the Southern Ocean fronts (dashed lines) and zones, after Talley et al. (2011). Arrow thickness represents observed dissolved Cd (range: ~0 to 1 nmol kg⁻¹) and Zn concentrations (range: ~0 to 7.5 nmol kg⁻¹), respectively. Colors indicate dissolved isotope signatures of water masses.

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