Dynamics of dissolved iron and other bioactive trace metals (Mn, Ni, Cu, Zn) in the Amundsen Sea Polynya, Antarctica

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Abstract

The Amundsen Sea Polynya is experiencing large increases in glacial meltwater input and hosts an extremely productive and long-lasting summer phytoplankton bloom, suggesting a crucial role for natural Fe fertilization. Early summer distributions and dynamics of the dissolved bioactive metals Fe, Mn, Zn, Cu and Ni were investigated during a three week period in 2010–2011, using GEOTRACES-compliant methods. Dissolved Fe was very low (0.06–0.12 nmol kg$^{-1}$) in the upper 20 m of the central polynya, suggesting that the sub-maximal rates of in situ primary productivity reported previously for this growth phase of the bloom are attributable to insufficient Fe availability. Weeks after the sampling period, phytoplankton biomass accumulated to peak bloom conditions, implying a continuous supply of bioavailable Fe to the euphotic zone. The dominant biologically-relevant Fe source was meltwater-enriched seawater flowing from the Dotson Ice Shelf cavity and delivering Fe at 0.7 nmol kg$^{-1}$ to the broader polynya. The modest Fe content of Circumpolar Deep Water (CDW; 0.3 nmol kg$^{-1}$), invading through cross-shelf troughs, was strongly augmented by benthic Fe inputs, which may combine with glacial meltwater dFe in the Dotson outflow. Sea ice melting provided a modest local Fe flux, insufficient to drive large annual blooms. Dissolved Mn was strongly reduced in surface waters, but displayed a subsurface maximum likely advected through the region from shallow coastal sediments. Nutrient-type elements Zn, Cu and Ni had large to small dynamic ranges, respectively, and increasing concentrations with depth, indicating uptake and remineralization within the polynya system. Surface water drawdown ratios of metals and nutrients provided novel estimates of metal quotas (metal/P) for the dominant bloom phytoplankton, *Phaeocystis antarctica*. At one unique mature bloom station, Zn and Cu were scavenged to low concentrations throughout the 350 m water column, a possible result of intense removal onto sinking *Phaeocystis* biodetritus. The Amundsen Sea appears to be a model region for studying the biogeochemical consequences of increased glacial meltwater inputs.

Introduction

High-latitude regions of the ocean, relative to their area, are disproportionately important in both controlling and responding to changes in global climate, in driving biogeochemical cycling of elements in the ocean and atmosphere (Caldiera and Duffy, 2000; Tagliabue et al., 2012; Jaccard et al., 2013), and in regulating nutrient supplies to the low-latitude ocean (Sarmiento et al., 2004). Polynyas, recurring areas of seasonally open water often adjacent to the continent and generally surrounded by sea ice, are focal points of productivity, heat exchange and CO$_2$ flux. In the Southern Ocean, peak productivity in polynyas can exceed 1.0 g C m$^{-2}$ d$^{-1}$, which is much greater than in the open Southern Ocean (0.2–0.4 g C m$^{-2}$ d$^{-1}$; Arrigo and van Dijken, 2003; Arrigo et al., 2008, 2015). The Amundsen Sea Polynya (ASP), located west of the smaller Pine Island Polynya (PIP), both within the Amundsen Sea (Figure 1A, B), is the most productive polynya in Antarctica per area.
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...peak rates can exceed 2.5 g C m\(^{-2}\) y\(^{-1}\); Arrigo et al., 2012), as well as the most variable interannually (Arrigo and van Dijken, 2003). The present work investigates the mechanisms by which bioactive trace metals in the water column, and iron in particular, both control and are controlled by the long-lasting and intense annual phytoplankton bloom in the ASP.

Because macronutrients are abundant and low Fe concentrations limit productivity throughout much of the Southern Ocean (Tagliabue et al., 2014 and references therein), it is reasonable to hypothesize that the highly productive ASP behaves as a natural Fe fertilization region and that the magnitude of the bloom is influenced by the flux of bioavailable Fe into the polynya euphotic zone. However, very few investigations of trace metal distributions have been conducted in the Amundsen Sea. Gerringa et al. (2012) carried out a sampling program in February of 2009, focused on the Pine Island area in the eastern Amundsen Sea, and argued that the Fe delivery associated with warm Circumpolar Deep Water (CDW)-driven melting of the Pine Island Glacier was a dominant source of Fe to the euphotic zone of the adjacent PIP. A few stations sampled in the central Amundsen Sea also suggested enhanced Fe concentrations in proximity to ice shelves (Gerringa et al., 2012). Planquette et al. (2013) examined suspended particle composition during an earlier 2007–2008 Amundsen Sea expedition and found generally high particulate Fe concentrations, especially proximal to ice shelves, and evidence in elevated Fe/Al ratios for a substantial non-crustal particulate Fe phase, presumed to be dominated by potentially bioavailable Fe oxihydroxides. Most of the 2007–2008 stations, however, were in the eastern Amundsen Sea and PIP, as logistical constraints limited the number of stations in the ASP itself. Here we present results from a much more extensive sampling effort, part of the Amundsen Sea Polynya International Research Expedition (ASPIRE; Yager et al., 2012), that included a dense sampling of both the open waters and the margins of the ASP, during the growth phase of the polynya bloom in December 2010 to January 2011.

The Amundsen Sea, along with much of west Antarctica, is in the midst of decades-long climate change that is affecting atmosphere-ocean-ice interactions in the polynyas (Stammerjohn et al., 2015; Randall-Goodwin et al., 2015). Onshore transport of warm modified CDW (mCDW) is initiated at the shelf-slope break and allows CDW to flow at depth toward the coast along cross-shelf bathymetric troughs, of which the

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**Figure 1**
Map of the Amundsen Sea showing stations sampled for trace metals during ASPIRE.

Small maps at top show (A) the location of the Amundsen Sea in Antarctica; (B) sea ice distribution on 11 January 2011, with the relative positions of the Amundsen Sea Polynya (ASP, with rectangle surround), the Pine Island Polynya (PIP), and the Thwaites Fast ice and Iceberg Tongue (TFIT); and (C) the ASPIRE cruise track with chlorophyll \(a\) (Chl \(a\)) concentration as determined by underway flow-through \textit{in situ} fluorescence. Main panel (D) shows western portion of the Amundsen Sea with bathymetry scale on right and trace metal stations grouped as Trough stations (red circles), Shallow Bank stations (black squares), Iceberg stations (green triangles) and Ice Shelf stations (yellow diamonds). Also shown is the approximate mean position of the sea ice margin of the ASP (dashed white line) and transects T1 and T2 (yellow dashed lines). doi: 10.12952/journal.elementa.000071.f001
Dotson Trough is one (Nitsche et al., 2007; St-Laurent et al., 2013), where CDW enters the cavities under the bordering ice shelves, leading to basal melting and thinning of ice shelves as well as increased calving (Rignot and Jacobs, 2002; Rignot et al., 2013). The flow of warm mCDW into both the PIP region (Thoma et al., 2008; Walker et al., 2013; Assmann et al., 2013) and the ASP region (Arneborg et al., 2012; Wåhlin et al., 2012) has increased basal melting, as most extensively studied for the Pine Island Glacier in the east (Jenkins et al., 2010; Jacobs et al 2011; Dutrieux et al., 2014) but also occurring under the Dotson (Jacobs et al., 2012; Rignot et al., 2013, 2014; Randall-Goodwin et al., 2015) and Getz (Jacobs et al., 2013) Ice Shelves bordering the ASP (Figure 1). If the glacial ice melting caused by mCDW circulation under ice shelf cavities constitutes an important Fe source to the euphotic zone of the adjacent polynya, then ASP productivity may increase in the future, on interannual to decadal time scales (Alderkamp et al., 2015).

Simultaneous with changes in ocean–ice shelf interactions, sea ice coverage in west Antarctica waters in general and in the Amundsen Sea polynyas in particular, has decreased drastically over the last few decades (Stammerjohn et al., 2008, 2015; Randall-Goodwin et al., 2015). Melting sea ice is a potentially important source of bioavailable Fe (Lannuzel et al., 2010; van der Merwe et al., 2011) and leads to salinity-driven vertical stratification in the polynya water column, both of which may affect polynya productivity. In the ASP, sea ice distribution is a function of seasonal wind velocity and the blocking effect of the Thwaites Fast ice and Iceberg Tongue (TFIT), a mélange of grounded icebergs and fast ice which forms the eastern boundary of the ASP and prevents wholesale migration of sea ice from the eastern Amundsen Sea. A recent analysis of remote sensing data has shown that sea ice coverage in the eastern portion of the ASP, just west of the TFIT (Figure 1), has shortened by about 80 days since 1979, largely a result of earlier sea ice retreat in the austral Spring (Stammerjohn et al., 2015). Thus an evaluation of the importance of melting sea ice for the overall supply of Fe and other bioactive metals to the ASP is important to consider, simultaneously with the timing of spring–summer sea ice melting relative to key physical parameters such as irradiance and stratification that are important to primary production.

Here we present dissolved trace metal distributions for stations within the ASP and in the surrounding sea ice, occupied in late December 2010 to early January 2011. Full water column profiles for the bioactive metals iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) and nickel (Ni) are discussed in the context of the sources of these micronutrients to the polynya and the biological and abiological processes that affect their distributions as the intense seasonal bloom ramps up during this period. We argue in the following that melting of glacial ice by warm seawater intrusion within ice shelf cavities, and related buoyancy gain by mCDW that has received Fe inputs from the shelf sediments, constitutes a major source of Fe to the sub-euphotic zone of the ASP; that melting sea ice is a relatively minor Fe source over the course of the bloom; and that dissolved Fe concentrations are maintained at very low levels in polynya surface waters, even as phytoplankton biomass increases during the growth phase of the bloom. We show that, while variable drawdown of metals is evident in surface waters, no other metal shows evidence of becoming limiting, and that metal to phosphate drawdown ratios can be used to estimate the trace metal composition of the dominant bloom-forming phytoplankton, Phaeocystis antarctica. The following is the first investigation of this suite of bioactive trace metals in the Amundsen Sea.

Materials and methods

Sampling

Samples were collected during the ASPIRE program aboard RVIB Nathaniel B. Palmer over the period 13 December 2010–5 January 2011 (NBP10-05) in the ASP. A custom-fabricated trace metal clean (TMC) CTD/rosette system (Seabird, Inc.) was deployed using a custom-built winch and polymer-coated aramid conducting cable turning over a dedicated anodized aluminum sheave. The Seabird 911+ CTD comprised dual temperature and conductivity sensors, oxygen and PAR sensors, and a fluorometer and transmissometer. Mounted on the polyurethane-coated aluminum rosette frame were twelve 12 L Teflon-coated externally closing Niskin bottles on which all external metal parts were aluminum, polyurethane-coated steel, or titanium (Ocean Test Equipment, Inc.). Conventional Niskin sampling valves were replaced with Teflon stopcocks and the air vents were replaced with custom plastic fittings to allow bottles to be pressurized with filtered air. The system is very similar in design to that developed for the GEOTRACES program (Cutter and Bruland, 2012). Samples were collected with the rosette moving slowly (0.1 m s⁻¹) up through the water column to avoid any possible contamination of the seawater from the frame and electronic components. In total, 20 trace metal profiles, most surface-to-bottom, were sampled during the cruise (Figure 1). Samples for dissolved trace metal analysis were collected in acid-cleaned and sample-rinsed low density polyethylene bottles (Nalgene®) by filtration at 0.2 µm using Acropak 200 capsule filters (Pall #12941) that were cleaned and conditioned before use by passing 20 L of cleanly collected seawater through each, prior to use. Seawater samples were acidified on board with hydrochloric acid (HCl, Fisher Optima) to 0.012 mol L⁻¹ HCl (approx. pH 2.0). Conventional CTD casts were also carried out at all but one of the trace metal stations as well as at additional stations, matching sampling depths to the TMC CTD casts.
Dissolved trace metal analysis

Seawater samples were analyzed for dissolved Fe, Mn, Zn, Cu and Ni over the period of January to August 2012, using an automated flow injection ICP-MS method developed at Rutgers University (Lagerström et al., 2013). Briefly, the automated device loaded a 9 mL aliquot of seawater, buffered online to pH 7.0 with 3 mL of acetic acid/ammonium hydroxide buffer, onto a column packed with Nobias PA1 chelating resin (Hitachi High-Technologies). The column was eluted with 1.5 M nitric acid directly into the nebulizer of an Element-1 sector field ICP-MS (Thermo-Finnigan, Bremen, Germany). The eluate, a 200-fold concentrate of the sample, was analyzed in medium resolution and temporal peak integration was performed in Matlab using a script written in-house. Quantification was carried out using isotope dilution (Fe, Ni, Cu and Zn) or a matrix-matched external standard curve (Mn).

Analytical duplicates were measured every sixth sample and typically displayed 1–3% deviation from the mean. The long-term precision over many analytical runs over a period of months, as demonstrated by repeated analysis of a large volume in-house seawater standard from the Ross Sea (analyzed 5–6 times during each analytical session), was 1% for Ni and Cu, 2% for Zn and 3% for Fe and Mn (Randall-Goodwin et al., Table 3 in Lagerström et al., 2013). Accuracy was verified by repeated analysis of reference seawater materials (SAFe S and D, GEOTRACES S and D), which showed agreement within one standard deviation of the consensus values for almost all elements in all reference seawaters (see Table 5 in Lagerström et al., 2013).

Nutrient analysis

Concentrations of nitrate (NO$_3^-$), phosphate (PO$_4^{3-}$) and silicate (HSiO$_4^-$) were determined by flow injection analysis onboard ship using a Lachat Instruments Quickchem FIA+ 8000s autoanalyzer according to standard protocols employed by US Antarctic Program research staff. Additional details of the nutrient sampling and analysis can be found in Alderkamp et al. (2015). Detection limits (NO$_3^-$ + NO$_2^-$ = 0.075 µmol L$^{-1}$; NO$_2^-$ = 0.009 µmol L$^{-1}$; NH$_4^+$ = 0.040 µmol L$^{-1}$; HPO$_4^{2-}$ = 0.022 µmol L$^{-1}$; and Si(OH)$_4$ = 1.90 µmol L$^{-1}$) and precision (NO$_3^-$ + NO$_2^-$ = 0.0076 µmol L$^{-1}$; NO$_2^-$ = 0.0009 µmol L$^{-1}$; NH$_4^+$ = 0.0041 µmol L$^{-1}$; HPO$_4^{2-}$ = 0.0023 µmol L$^{-1}$; and Si(OH)$_4$ = 0.193 µmol L$^{-1}$) were determined using multiple runs of standards prepared in low nutrient seawater (Yager et al., 2015).

Results

The Amundsen Sea comprises three endmember water types, with mixing among them evident in the temperature and salinity structure (T-S) of the water column (Yager et al., 2012; Randall-Goodwin et al., 2015). This mixing is well illustrated by a temperature section along Transect 1 (T1 in Figure 1D), which passed from the shelf break at Station 4 to the western end of the Dotson Ice Shelf (DIS) at Station 60 (Figures 1D and 2A). At depths below about 400 m, warm salty modified Circumpolar Deep Water (mCDW) is observed from the shelf slope break to the coastal region but is least modified (warmest and saltiest) along the deep Dotson Trough. At the DIS, mCDW is vertically mixed, especially at its western end by upwelling and increased buoyancy resulting from a <2% addition of glacial meltwater (Randall-Goodwin et al., 2015). A large portion of the glacial meltwater input to the ASP is added to mCDW from basal ice shelf melt, both from the DIS as well as from ice shelves upstream or east of the DIS. At the DIS, this meltwater-laden mixture emerges in a strong flow centered at 200–300 m at the western extreme of the DIS (Randall-Goodwin et al., 2015) where it was sampled at Station 60 (Figure 1D). Above the mCDW layer lies the Winter Water (WW), formed as a uniform deep mixed layer in fall/winter through cooling of surface waters and convective mixing driven by brine rejection during sea ice formation. This thick layer of cold, less saline water is characterized by temperatures <−1.5°C (purple color in Figure 2A; WW in Figure 2B). Finally, a thin layer of warmer Antarctic Surface Water (AASW) is formed in summer through heating by solar irradiation; it is less saline than WW because of sea ice melting and meteoric water inputs at the surface. The mixing of these water masses, and the addition of fresh glacial meltwater, is evident in a diagram of potential temperature versus salinity for stations sampled in this study (Figure 2B). Most of the water column for all of these ASP stations fell between the lower CDW-WW mixing line and the upper CDW-glacial meltwater mixing line (Figure 2B; Randall-Goodwin et al., 2015). The AASW is variably warmer and fresher than the WW, reflecting the variable stratification of the summer mixed layer resulting from varying exposure to surface melt, solar insolation and wind mixing.

The 20 trace metal stations have been divided into four groups by sub-region as follows: Dotson Trough stations, Shallow Bank stations, Iceberg stations and Ice Shelf stations (Figure 1D). The Dotson Trough stations follow the forking trough along transects T1 and T2 (Figure 1D), the main conduits in the ASP for cross-shelf transport and mixing of mCDW to the coastal region and ice shelves. At the edge of the continental shelf, Station 4 represents a local endmember for the composition of water derived from the open Antarctic Circumpolar Current (ACC), which then accesses the continental shelf via the Dotson Trough (Figure 1D). The Shallow Bank stations in the central/eastern ASP are all relatively productive stations located on the 400 m deep bank that dominates the eastern region of the ASP. Along the eastern side of the bank, Station
Figure 2
Potential temperature and salinity at stations sampled in this study.

Shown are (A) a section of potential temperature along transect T1, as per location in Figure 1D, with station numbers shown along top, and (B) a plot of potential temperature vs. salinity for all stations sampled for trace metals during ASPIRE. Highlighted are Station 4 (blue) just north of the shelf-slope break (see Figure 1) and Station 60 (red) at the western end of the Dotson Ice Shelf, characterized by outflow of meltwater-laden mCDW from the cavity under the ice shelf. Dotted black lines show mixing between CDW and glacial meltwater (upper) and CDW and WW (lower). Regional endmember values for CDW and WW are highlighted by red squares; AASW is Antarctic Surface Water. Dotted blue line is seawater freezing point at atmospheric pressure. Dotted gray lines are lines of constant density, $\sigma_\theta$.

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15 was sampled in open water amongst numerous grounded icebergs that are otherwise largely surrounded by fast ice, the TFIT (Figure 1). The Iceberg stations were occupied in relatively rapid succession (55 h total) and in varying proximity to a large (1 km $\times$ 3 km $\times$ 400 m) drifting tabular iceberg, encountered late in the expedition (Randall-Goodwin et al., 2015). Most of the Ice Shelf stations are located within 300 m of the Dotson Ice Shelf, with a single additional station located several km off the face of the eastern Getz Ice Shelf, near the center of the ice shelf face, and not near any known inflow or outflow area (Jacobs et al., 2013; Figure 1D). Station numbers indicate chronological, not spatial, order; the cruise track was complicated, a necessity of the varying geographic and logistical needs of the interdisciplinary cruise participants (Yager et al., 2012). All stations were sampled from the surface (2–20 m depth) down to within 10 m of the sea floor except Station 57.30, which was sampled over the 100 m to 500 m depth interval.

In the following subsections the vertical distributions of each of the five metals are presented for each sub-region of the polynya (Figures 3–7). To emphasize the horizontal variations in trace metal concentrations in surface waters, we then show surface maps (Figure 8) summarizing metal concentrations at each station, alongside chlorophyll $a$ (Chl $a$) concentrations so that metal distributions can be considered in the context of phytoplankton biomass. Trace metal concentrations overlain on T-S plots are shown in Figure 9. Vertical sections (Figures 10 and 11) along Transects 1 and 2 (see Figure 1D) illustrate concentrations along the core of the two branches of the trough structure. Figure 12 shows near-bottom dFe and dMn in the context of optically-determined particle concentration, while regressions of surface water concentrations of dissolved metals against the macronutrient phosphate are displayed in Figure 13.

**Dissolved Fe**

Dissolved Fe (dFe) concentrations varied strongly with depth and location throughout the ASP water column (Figure 3). With some exceptions at specific stations, concentrations were low in surface waters (mean = 0.15 nmol kg$^{-1}$), increased slightly through the upper 100–200 m, were relatively constant in the mid-water
Figure 3
Depth profiles of dissolved iron.

Concentrations of dissolved iron (dFe; nmol kg^{-1}) are shown for each station grouped as (A) Trough stations, (B) Shallow Bank stations, (C) Iceberg stations and (D) Ice Shelf stations. The analytical run-to-run precision (± 1 S.D.) of an in-house standard for Ross Sea water is shown as an inset error bar (encircled by dotted line) and is adjusted to the scale of the x-axis of each plot. Vertical dashed line is a visual reference for the approximate concentration of dFe in Winter Water. Enlarged profiles of the upper 100 m (E) are shown to provide details and visual comparison of upper water column profile shapes.

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column and then increased, sometimes dramatically, with approach to the sediment–water interface. Concentrations of dFe in the upper few hundred meters of the Dotson Trough stations (Figure 3A) differed only modestly from the profile at Station 4 located just north of the shelf–slope break, which constitutes the northerly mixing endmember for the sample set. The WW at the Dotson Trough stations (depths of approximately 100–300 m; Figures 2A and 11F) had dFe of 0.3 ± 0.05 nmol kg⁻¹, similar to the 100–300 m mean dFe at the shelf edge at Station 4 (Figure 3A). The local endmember of mCDW was represented by the deepest samples of Station 4, with dFe = 0.37 nmol kg⁻¹. This station included the least modified of our samples relative to pure CDW, but was still modified by mixing with shelf WW such that maximum temperature was approximately 1.0°C (Figure 2B), not > 2.0°C as found in pure CDW well north of the shelf break region in the open ACC (Martinson, 2012). Samples representing mCDW along the deeper sections of the Dotson Trough (deepest few samples of stations in Figure 3A and 3C, as well Station 11 in Figure 3D; with temperatures of 0.7°C) were all enriched in dFe relative to the Station 4 mCDW endmember, apparently by inputs from the shelf sediments to the near-bottom waters of the deep trough. Benthic inputs were also implied by modest near-bottom dFe increases at the Shallow Bank stations (Figure 3B) and higher dFe concentrations the near-bottom samples of Ice Shelf stations 9, 10 and 11 (Figure 3D). Near-bottom dFe exceeded 3.0 nmol kg⁻¹ in some locations, although at Stations 29 and 48 the maximum dFe was found at slightly shallower depths than the bottom-most sample.

Most of the stations in the central ASP had quite low near-surface dFe (approximately 0.1 nmol kg⁻¹; Figure 3A, B, C) and the minimum dFe concentrations for each profile typically occurred at a sub-surface depth in the upper 40 m (Figure 3E, showing detail of upper 100 m). However, interestingly, Stations 25 and 35 had some of the lowest density values (driven by low salinity; see Figure 3A in Alderkamp et al., 2015) and the highest dFe concentrations (> 0.2 nmol kg⁻¹) in the upper 15 m. Below the upper 40 m, dFe at most stations generally increased to a modest maximum at 100–200 m (e.g., Figure 3B). Stations 4 and 6 also showed sharp single-point sub-surface maxima within the upper 60 m (Figure 3E). Surface dFe was high only at Stations 9 and 10 which were ~ 200 m from the Dotson Ice Shelf near its east and west extremities, at 0.5 and 1.3 nmol kg⁻¹, respectively, suggesting a surface dFe input at these locations and sampling times (Figure 3D). The other Ice Shelf stations (5, 11 and 60) and the Iceberg stations (57.04 and 57.26; Figure 3C) had low to very low surface dFe, between 0.1 and 0.25 nmol kg⁻¹. The stations along Transect 2 (Stations 6, 50 and 48) also had generally very low dFe of approximately 0.1 nmol kg⁻¹ in the upper 100 m, increasing to 0.2–0.3 nmol kg⁻¹ by 300 m, and matching very well the dFe profiles at Stations 113 and 114 in Gerringa et al. (2012), which are roughly at the same coordinates as our Stations 6 and 48, although sampled in February 2009.

In deeper water at the Iceberg stations (Figure 3C), which are located just north of the western end of the DIS (Figure 1D), dFe varied non-monotonically with depth, reflecting the complicated mixing environment left behind by a drifting iceberg. Stations 57.26 and 57.30 showed coherent maxima, with dFe ≥ 0.5 nmol kg⁻¹ at about 200 m, a minimum at about 300 m and increasing concentrations below that. The 300 m minimum showed dFe concentrations similar to the 0.4 nmol kg⁻¹ seen in the 100–400 m depth interval at Ice Shelf stations 9, 10 and 11 (Figure 3D). Station 60, at the far western end of the face of the Dotson Ice Shelf, was unique in having unusually high dFe throughout 80–600 m, at 0.60–0.75 nmol kg⁻¹ all the way to the bottom (650 m).

**Dissolved Mn**

Dissolved Mn, like dissolved Fe, had a very large range of concentrations within the ASP sample set, spanning 0.1 to 6.5 nmol kg⁻¹ (Figure 4). Near-surface concentrations were generally low, between 0.1 and 3.0 nmol kg⁻¹, at all stations except for three of the four DIS stations, which show strong enrichments in the upper 100 m (Figure 4D). Station 9 was especially Mn-rich in near-surface waters, with the highest dMn (> 6 nmol kg⁻¹) measured anywhere in the ASP. In contrast, at the high Chl a Shallow Bank stations, near-surface dMn was always ≤ 0.6 nmol kg⁻¹ (Figure 4B and 8B), suggesting active surface Mn removal. With some exceptions, dMn showed sharp concentration increases within the upper 100 m to reach a subsurface maximum of varying intensity, centered at approximately 100 m. This subsurface maximum was especially evident in the Dotson Trough and Iceberg stations (Figures 4A, C and 10B), but was less distinct and of lower concentration in the high productivity Shallow Bank stations (Figure 4B). Concentrations generally decreased below the 100 m maximum to reach relatively low and constant values of about 1.5 nmol kg⁻¹ at 200–400 m where WW dominated, with the Shallow Bank stations (Figure 4B) having slightly lower concentrations in this interval. In contrast to Fe, all of the Trough and Shallow Bank stations (Figure 4A, B) had higher dMn concentrations throughout the water column than were found at shelf break Station 4, suggesting that shelf processes constitute a net source for dMn, except in surface waters. Station 4 had nearly uniform dMn of about 1.0 nmol kg⁻¹ from the surface to 250 m, with gradually decreasing concentrations to about 0.3 nmol kg⁻¹ near 600 m.

All stations except 4, 5, 10 and 60 had moderate to sharp increases in dMn near the bottom sediments. Of these exceptional stations, only Station 5 is located in the deeper portion of the trough. This benthic increase seemed to start somewhat deeper in the water column than for dFe, and in some cases (Stations 34, 18, 25, 35,
and 57.04) the increase was seen only in the single bottom-most sample. The concentrations of near-bottom samples varied from < 1.0 to > 5.0 nmol kg$^{-1}$, but were generally the highest dMn of each profile, except at the Ice Shelf stations (Figure 4D).

At the Ice Shelf stations, unlike at the central ASP stations, dMn increased towards the surface such that near-surface dMn concentrations were the highest in the water column (except Station 10). As noted above, concentrations in the upper 100 m at Station 9 were the highest dMn values we observed. At Station 10, surface concentrations were also relatively high, but increased further with depth from the surface value of 2.5 nmol kg$^{-1}$ to a maximum of 3.6 nmol kg$^{-1}$ at 160 m. A surface maximum was also observed at Station 5, just off the Getz Ice Shelf, and yet another near-surface maximum was evident at Station 57.04, the open polynya station most proximal to the Dotson Ice Shelf. Concentrations at Stations 9, 10 and 11 then decreased with depth to relatively constant values of 1.5 ± 0.5 nmol kg$^{-1}$ at 300–1000 m. Station 60 again showed a unique profile shape, relative to the other Ice Shelf stations (Figure 4D), but with different characteristics than the dFe profile. First, the high surface concentrations decreased to moderate values of about 2.5 nmol kg$^{-1}$ within the upper 100 m. There was then a very clear but moderate dMn maximum centered at 250 m in the core of the DIS outflow (Randall-Goodwin et al., 2015). This 250 m maximum falls within the depth range of the decreasing dMn gradient from the high surface values at Stations 9 and 10, and thus did not exceed the values found at these other stations, in contrast to dFe. Below 250 m, dMn gradually decreased to about 2.0 nmol kg$^{-1}$ near the bottom. Thus dMn was somewhat higher at Station 60 within this 300–500 m depth range, compared to dMn at the other Ice Shelf stations. Interestingly, at 600 m, dMn at Station 60 was nearly identical to that at Stations 9 and 10, though it appeared to exceed dMn at Station 11 and Station 5 in this depth range.
Dissolved Zn

Dissolved zinc distribution differed from that of dFe and dMn in that it showed strong surface depletion at productive stations (Figures 5B and 8C), only modest subsurface maxima, and concentrations that increased moderately in the deeper water column yet showed only isolated signs of strong increase near the bottom at some stations (Figure 5). The Trough stations (Figure 5A) were quite coherent and not drastically different from endmember Station 4. Marked near-surface minima were evident at all stations except Station 4, below which were found sharp concentration increases within the upper 100 m to values generally 5.0 ± 0.5 nmol kg$^{-1}$ in the WW-dominated 400–500 m interval (Figure 5). Concentrations at Station 4 were lower than those of the other Trough stations from 50 m to 300 m; below 300 m dZn at Station 4 varied within a range similar to that found in the Trough stations, 5.0–6.5 nmol kg$^{-1}$ (Figure 5A).

The Shallow Bank stations (Figure 5B) had similar shaped dZn profiles to the Trough stations, with WW values of about 5 nmol kg$^{-1}$ and deep mCDW values of 6.0–7.5 nmol kg$^{-1}$. While these characteristic profile shapes were compressed into the upper 400 m at the Shallow Bank stations, in the deep Trough stations a very similar concentration range stretched over nearly 1200 m, reaching 7 nmol kg$^{-1}$ only at bottom depths of Stations 29 and 34, near 700 m. The high Chl $a$ stations (Stations 18, 25, 35 and 50) had the lowest near-surface dZn (Figure 5A, B and 8C). The Iceberg (Figure 5C) and Ice Shelf stations (Figure 5D) had moderate or no surface minima and varying concentrations from 100 m to the bottom, with strong divergences among the three iceberg stations and concentrations generally falling between 4.5 and 7.0 nmol kg$^{-1}$. The DIS outflow station (Station 60) did not stand out from the other Ice Shelf stations as distinctly for dZn as it did...
for dFe; concentrations were nearly constant at 6 nmol kg\(^{-1}\) from 60 m to the bottom, and were only slightly higher than the other Ice Shelf stations in the 200–300 m core of the DIS outflow (Figure 5D). Station 11 had a subsurface one-point maximum at 112 m, also seen in the dFe profile. Station 5 off the Getz Ice Shelf had some of the highest Zn concentrations in the polynya during this sampling period, about 7.0 nmol kg\(^{-1}\) in the mCDW below 600 m.

The most unusual dZn profile was seen at Station 35 (Figure 5B). Here, the low dZn in the surface water decreased further to a minimum of 1.3 nmol kg\(^{-1}\) at 60 m, then increased to a small sub-surface maximum at 120 m, then decreased again and stayed low (<1.8 nmol kg\(^{-1}\)) to 335 m, increasing sharply only in the very bottom-most sample at 425 m, a sample in which dFe and dMn also showed moderate to large increases. This profile behavior differed strongly from all other profiles in the ASP, even from Station 25, just 17 km to the north (Figure 1D).

**Dissolved Cu**

Dissolved Cu profiles were broadly similar in form to those of dZn, but the relative dynamic range for dCu in the ASP was much smaller (Figure 6). While dZn varied by a factor of >5 in the ASP, dCu varied only 2-fold among all samples, with concentrations between 1.4 and 2.9 nmol kg\(^{-1}\). The profile for endmember Station 4 falls amongst those for the rest of the Trough stations (Figure 6A), suggesting that additional dCu sources on the shelf were small. Patterns of surface water dCu depletion were qualitatively similar to those for dZn, but the relative magnitude of the phenomenon was much smaller than for Zn (Figure 8D). Depth intervals dominated by WW (100–300 m) had dCu concentrations of 2.2 ± 0.1 nmol kg\(^{-1}\), although Stations 6 and 34 were slightly more elevated at about 2.4 nmol kg\(^{-1}\), and Shallow Bank stations (Figure 6B) showed lower concentrations of 2.1 nmol kg\(^{-1}\) at WW-dominated depths. Generally, deepest waters had somewhat elevated

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**Figure 6**

Depth profiles of dissolved copper.

Concentrations of dissolved copper (dCu; nmol kg\(^{-1}\)) are shown for each station grouped as (A) Trough stations, (B) Shallow Bank stations, (C) Iceberg stations and (D) Ice Shelf stations. The analytical run-to-run precision and vertical mean Winter Water concentration are depicted as per Figure 3.

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concentrations of 2.4–2.6 nmol kg\(^{-1}\), though Iceberg Station 57.30 (Figure 6C) increased to 2.9 nmol kg\(^{-1}\) at 400–500 m, the highest dCu concentrations measured in the ASP. The Ice Shelf stations showed only small dCu variations with depth, and clustered mostly in the 2.2–2.6 nmol kg\(^{-1}\) range (Figure 6D). Station 60, however, had clearly elevated though variable dCu in the core of the DIS outflow at 200–300 m, with concentrations up to 2.8 nmol kg\(^{-1}\). Evidence for benthic dCu increases was limited, though some Trough stations showed slight increases in the bottom 200 m.

As with dZn, Station 35 had a unique profile for dCu, showing both near-surface and deep water column depletion, with a minimum concentration of < 1.5 nmol kg\(^{-1}\) at 60 m, and remaining low at < 1.7 nmol kg\(^{-1}\) down to 335 m (Figure 6B). Thus the profile stands out as markedly diminished in dCu compared to the other productive Shallow Bank stations (Figure 6B). Only in the very bottom-most sample did dCu increase to match the higher concentrations at the other stations.

**Dissolved Ni**

Dissolved Ni was the least variable of the five metals in the ASP; concentrations ranged from 5.4 to 7.3 nmol kg\(^{-1}\) (Figure 7). The long-term measurement precision of ± 1.3%, however, allows even small gradients and concentration differences to be interpreted with confidence. Endmember Station 4 showed slightly low concentrations at 100–250 m and increased to a local maximum of 7.0 nmol kg\(^{-1}\) at 360 m, then decreased again to 6.6 nmol kg\(^{-1}\) (Figure 7A). The Trough stations generally showed more muted patterns, with WW-dominated depths at about 6.5 nmol kg\(^{-1}\), higher than at comparable depths at Station 4, and small increases with depth. The Shallow Bank stations (Figure 7B) showed variable behavior, with no consistent surface depletion, although Station 25 had the lowest dNi measured in the ASP, 5.4 nmol kg\(^{-1}\) at 28 m.
Concentrations generally increased with depth to the bottom. Station 35 had slightly lower concentration at 335 m compared to other Shallow Bank stations, but did not stand out as anomalous, as did the concentrations for dZn and dCu. Other stations showed very modest variability with depth and among stations, with no consistent relationships to the variations in either dZn or dCu. The Iceberg and Ice Shelf stations (Figure 7C, D) were generally slightly higher in dNi than the other ASP stations, but the DIS outflow Station 60 was only slightly higher in dNi than the other stations and did not show particularly anomalous behavior in the 200–300 m core of the outflow.

Surface water metal distributions

To compare the relative surface water distributions of these five metals, it is instructive to examine the surface concentrations in map view (Figure 8). It is clear that dFe was low, about 0.1 nmol kg\(^{-1}\), nearly everywhere in the polynya away from the ice shelves (Figure 8A), except Stations 25 and 29 with 0.20–0.25 nmol kg\(^{-1}\) (Figure 3E). Similarly, dMn was low (< 1 nmol kg\(^{-1}\)) nearly everywhere (Figure 8B), but was considerably higher in the iceberg and ice shelf stations. These dFe and dMn distributions were quite different from those of dZn and dCu, which had low values (e.g., dZn < 1.7 nmol kg\(^{-1}\)) only in the central polynya stations (18, 25, 35 and 50; Figure 8C, D), where Chl \(\alpha\) concentrations were highest (Figure 8F). Other stations showed variably higher concentrations, with the highest values found at the Ice Shelf stations, for both dZn and dCu. Surface dNi seemed generally lower in the western ASP stations, moderate in the eastern ASP and highest closest to the ice shelves (Figure 8E).

Dissolved metal distributions in the context of water mass mixing

The overall distributions of these dissolved metals in the ASP can be understood in the context of water mass mixing as illustrated in T–S diagrams (Figure 9). The distribution of oxygen sets the context for interpretation of the metal distributions (Figure 9A). During ASPIRE, much of the ASP water column was occupied by a mixture of mCDW (as expressed at Station 4), the warm salty oxygen-poor endmember, and the more oxygen-
rich cold and fresher WW, with an additional component of glacial meltwater which pulls the T-S properties in the direction of the mixing line between mCDW and glacial meltwater (Randall-Goodwin et al., 2015). Antarctic Surface Waters (AASW), the final endmember, are very fresh, variably warm, high oxygen waters. It is evident from the dFe concentrations plotted in section along Transect 1 (Figure 10A) and in T-S space (Figure 9B) that the highest concentrations lay in the central portion of the T-S field where the modest Fe content of endmember mCDW (at Station 4) was enriched by addition of glacial meltwater and inputs from shelf sediments. The WW was relatively low in Fe (0.3 nmol kg$^{-1}$) and Fe concentrations generally increased for data points closer to the mCDW-glacial meltwater mixing line, although highest concentrations were found in mCDW that had been enriched by benthic sources. The lowest dFe is evident in AASW. The dMn distribution looks somewhat similar, but unlike the situation for Fe, the mCDW endmember was very Mn-poor at the shelf break and became rapidly enriched upon mixing with shelf water masses (Figures 9C and 10B). Points near the mCDW-glacial meltwater mixing line had dMn only moderately enriched relative to WW and the highest few values were in AASW at some of the DIS stations. Overall, however, AASW was quite variable in dMn and may have been depleted or enriched relative to WW. The distributions of Zn, Cu and Ni (Figure 9D, E, F) all look similar in that shelf waters in the main mixing triangle of mCDW-WW-glacial meltwater were only modestly enriched relative to the mCDW endmember, while WW was markedly lower; AASW, while variable, generally showed the lowest concentrations for these elements.

Dissolved metal distributions in the benthic nepheloid layer

In the deepest parts of the ASP, dFe and dMn concentrations increased strongly toward the sediment-water interface and had clear though non-linear relationships to total particle concentration as measured by beam attenuation (not shown). Almost all of the stations in the ASP showed an increase in dFe (Figure 3) and dMn (Figure 4) near the sediments with only a few exceptions, e.g., Stations 4 and 5 that correspondingly displayed very low beam attenuation signals ($\leq 0.026$ m$^{-1}$) at their bottom sampling depth (Figure 12A). The other dissolved trace metals showed no distinct increase in concentration in the near-bottom samples. The stations with enhanced dFe and dMn in the bottom waters had elevated beam attenuation signals ($\geq 0.04$ m$^{-1}$), though not all bottom waters with high beam attenuation had high dFe and dMn.

Three of the stations in the Dotson Trough (Stations 6, 48 and 50), all located in the southern, deeper region, displayed especially high dFe and dMn bottom concentrations (Figures 3A, 4A, 11A and 11B). The dFe concentrations observed here were the highest we found in the ASP, with values of 2.0–3.5 nmol kg$^{-1}$ (Figure 12B). At these same stations, the highest near-bottom dMn concentrations were found, exceeding 4 nmol kg$^{-1}$ (Figure 12C). The exceptionally high dFe and dMn concentrations attained in the deep trough may result from benthic inputs not only from the bottom but additionally from the trough walls (the “bathtub effect”).
Discussion

Trace metal sources to the ASP

Sources of dissolved iron to the Amundsen Sea Polynya

The high productivity of the Amundsen Sea relative to the open Southern Ocean (Arrigo et al., 2008; Yager et al., 2012) suggests that the polynya acts as a natural iron fertilization region (Blain et al., 2007), receiving Fe inputs that are not present in the open Southern Ocean. A qualitative assessment of potential inputs can be gleaned from dFe gradients along the Dotson Trough Section (T1; Figures 1 and 10) and from the

Figure 10

Vertical sections showing 2-D distributions of dissolved trace metals along Transect 1.

Color gradient shows concentrations (nmol kg⁻¹) for (A) dFe, (B) dMn, (C) dZn, (D) dCu and (E) dNi along Transect 1 (T1; Figure 1D). Station numbers shown on upper x-axes.

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horizontal dFe distribution in surface waters (Figure 8A). In our discussion below, we argue that the melting of the Dotson Ice Shelf is the mechanism most likely responsible for delivery of dFe to the region and thus for the exceptional productivity of the ASP.

**Modified Circumpolar Deep Water as a potential Fe source to the polynya.** Because CDW in the off-shelf, open ACC is relatively enriched in dFe (0.3–0.4 nmol kg$^{-1}$; Sedwick et al., 2008; Tagliabue et al., 2012), it is reasonable to ask whether the invasion of CDW onto the shelf constitutes an important Fe source for the ASP phytoplankton bloom. To answer this question in the context of the current data set, we must use Station 4, situated over the shelf break, as the local endmember that most closely approximates the distal ACC endmember. The T-S properties (blue line in Figure 2B) of this “endmember”, Station 4, show that the warmest water at this station, found at 550–650 m, was about 1.0°C (blue line in Figure 2B), indicating that water invading Dotson Trough at the shelf break was not pure CDW as would be found well off the shelf break (> 2.0°C; Walker et al., 2013), but was already substantially modified by turbulent mixing at the shelf break, and thus is termed mCDW. Nevertheless, at these near-bottom depths of Station 4, dFe was 0.37 nmol kg$^{-1}$, in good agreement with dFe concentrations in CDW of the open ACC south of the Polar Front, measured north of the Ross Sea (Sedwick et al., 2008), in the Bellingshausen Sea just to the east of the Amundsen Sea (de Baar et al., 1999), and near the Drake Passage (Klunder et al., 2014). There was a small local maximum of 0.475 nmol kg$^{-1}$ in the dFe profile at 360 m at Station 4 (Figure 3A), suggesting a modest local input, and possibly reflecting a sedimentary contribution advected laterally from the bathymetric highs that border the trough at the shelf edge. Thus it is possible that the deeper mCDW samples at Station 4 may reflect a small Fe input that was compensated by the admixture of WW (with dFe = 0.3 nmol kg$^{-1}$; see Results above). The net effect was no discernible difference in dFe concentration between mCDW at Station 4 and reported dFe in off-shelf “pure” CDW.

The upper water column of Station 4 very much resembles the dFe properties of the open ACC as well. With the exception of an apparent single point maximum at 10 m (Figure 3A, E), dFe was very close to 0.1 nmol kg$^{-1}$ throughout the upper 50 m, similar to or lower than concentrations found in ACC surface waters south of the polar front, in regions where Fe supply limits primary productivity (de Baar et al., 1999; Sedwick et al., 2008; Klunder et al., 2014). A recent global compilation of dissolved Fe data reported a mean of 0.15 ± 0.08 nmol kg$^{-1}$ in the upper 100 m of Pacific Antarctic waters (Tagliabue et al., 2012). Thus surface dFe at Station 4 does not appear to have been affected by any Fe supplies sourced from the shelf system, consistent with the low surface dFe at the nearest on-shelf station (Station 66) and with the generally low surface dFe throughout the polynya (Figure 8A). The overall dFe profile at Station 4 is therefore very similar to what would be expected for an open ACC station further north, away from the shelf influence.

As the mCDW mixed with glacial meltwater and additional WW during transport onto the shelf, it occupied the water column at depths greater than 400 m (below the WW), and by mid-shelf (near Station 6) gained substantial sedimentary-sourced dFe (Figures 3A and 10). At all Trough stations, the dFe in WW (core in low-T waters at 200–400 m) remained quite constant at 0.30 ± 0.05 nmol kg$^{-1}$ (Figures 3A and 10). That this is lower than the dFe content of mCDW reflects the contribution of low-Fe surface water to the formation of WW on the shelf. However, starting at 400–500 m, dFe at all Trough stations increased with depth, to varying degrees, suggesting sedimentary inputs of dFe. The near-bottom dFe enrichments were also found at all Shallow Bank stations (Figure 3B) and at two of the Iceberg stations (Figure 3C). The dFe concentrations in the near-bottom samples appear to increase with station depth, such that deeper trough stations (Stations 6, 29, 48 and 50, as well as 57.26) all had bottom water dFe in excess of 1.0 nmol kg$^{-1}$, with maxima as high as 3.3 nmol kg$^{-1}$ (Figure 3A, C).

Despite these strong dFe additions to the near-bottom mCDW on the shelf, there is little evidence in the hydrographic distributions that the elevated dFe observed at > 400 m of any of the ASP stations was directly relevant as an Fe source to the euphotic zone where it could affect productivity of the ASP (Randall-Goodwin et al., 2015). The salinity-dominated vertical density gradient is too large to have allowed significant vertical mixing of the mCDW and AASW (Figures 2B and 11B). In this sense it is fair to say that mCDW by itself is not the major Fe source fueling high productivity in ASP surface waters.

**Melting sea ice not a major Fe source in the Amundsen Sea Polynya.** At many of the ASP stations, reduced salinity was observed in the upper few tens of meters (Randall-Goodwin et al., 2015; Figure 3A in Alderkamp et al., 2015). This freshening was most evident at the northern Stations 66 and 34, which had the lowest salinity and density at the surface (Figure 3A in Alderkamp et al., 2015) and were located in proximity to floating sea ice, near or within the marginal ice zone (Figure 1D). Hence it is very likely that the freshening resulted from the admixture of sea ice meltwater. None of the Iceberg nor Ice Shelf stations showed surface water salinities as low as observed at Stations 34 and 66. Sea ice and glacial ice (meteoric) water fractions were distinguished using a combination of salinity and δ$^{18}$O$_{\text{water}}$ (Randall-Goodwin et al., 2015). Using a locally-defined deep-trough CDW endmember, all water column samples collected in the ASP showed positive meteoric melt fractions and most showed negative sea ice melt fractions, indicating net sea ice formation, not melting, on yearly time scales (Randall-Goodwin et al., 2015). However, there are a few stations bordering the polynya (e.g., Station 66 and 34) that showed positive surface sea ice melt fractions, indicating the net advection and melting of sea ice into these bordering areas of the ASP (on yearly time scales; Randall-Goodwin et al., 2015). If, however, a
Bioactive trace metal dynamics in the Amundsen Sea Polynya, Antarctica

...local WW or T\textsubscript{min} endmember is used to estimate meltwater additions since the spring melt, then the majority of stations in the northern half of the ASP showed small but positive sea ice melt fractions (0.1 to 2%).

Sea ice contains elevated though highly variable concentrations of dissolved Fe (Lannuzel et al., 2010; de Jong et al., 2013), largely bound with organic ligands (Lannuzel et al., 2015), and constitutes an input of Fe to surface waters upon melting (Sedwick et al., 1997). However, none of the low salinity surface waters sampled during ASPIRE was enriched in dFe. For example, surface waters at Station 66 had the lowest salinity of samples collected for trace metals in the ASP (approximately 33.7 or 1% sea ice meltwater), but had a low dFe of about 0.1 nmol kg\textsuperscript{-1} in the upper 25 m (Figures 3A, 3E and 8A). Surface waters of other central polynya stations were generally ≤ 0.2 nmol kg\textsuperscript{-1} dFe, regardless of salinity (Figure 8A). All other dissolved metals decreased toward the surface, arguing for either very rapid uptake by plankton, or a general lack of metal inputs associated with sea ice melting. Macronutrients were somewhat depleted at Station 66, and there was modest primary production and phytoplankton biomass at 10 m (Yager et al., 2015). Bacterial production there was also high (Williams et al., 2015), suggesting a DOM contribution from sea ice melt that may have also triggered dFe uptake by heterotrophic bacteria (Delmont et al., 2014). The relatively low salinity (approximately 33.8 or 0.8% sea ice meltwater) in surface waters of Stations 25 and 35, however, was associated with both high phytoplankton biomass and relatively enriched surface dFe of 0.25–0.30 nmol kg\textsuperscript{-1}, yet surface maxima were not observed for any other measured metal, suggesting that the dFe maxima may not result from sea ice melting (which would likely have enriched other metals; Lannuzel et al., 2011). While the organic complexation of dFe in sea ice may increase its residence time in surface waters following melting (Lannuzel et al., 2015), Stations 25 and 35 seem to have been ice-free for a relatively long time (15 and 35 days, respectively; Yager et al., 2015), compared for example to Station 66 (0 ice-free days), and have developed dense phytoplankton assemblages that would be expected to drive rapid dFe uptake (Figures 1 and 8). Thus we speculate that the relatively high dFe at these stations resulted from shallow Fe recycling or possibly photochemically driven release from the particulate Fe pool. We conclude that sea ice melting may periodically constitute a local and/or ephemeral input of dFe to the ASP, but any dFe inputs from this source were largely taken up and/or removed by the early-bloom stage of the ASPIRE cruise. For the ASP as a whole, sea ice meltwater may play a more important role in stratifying the near-surface water column, allowing the light regime for bloom development (consistent with findings from ASPIRE glider surveys; Yager et al., 2012; Schofield et al., 2015), than in serving as a substantial or long-term source of bioavailable Fe to the weeks-long ASP bloom.

Atmospheric dust, iceberg and shallow sediments as potential Fe sources. There are few subaerially exposed unconsolidated sediments in the ASP region (Drewry et al., 1983; Claus-Dieter Hillenbrand, personal communication), so atmospheric dust very likely provides negligible direct inputs to the surface waters of the ASP. The evidence supporting very small atmospheric dust Fe inputs has been well discussed elsewhere; atmospheric deposition is very likely to be insignificant relative to other fluxes to the euphotic zone (Sedwick et al., 2011; Gerringa et al., 2012; Gao et al., 2013; Planquette et al., 2013), although aerosol concentrations have yet to be quantified in the ASP region. In other Antarctic regions with substantial exposed unconsolidated sediments on the proximal continent, dust sources may be somewhat more important (Winton et al., 2014). Similarly, significant near-surface inputs of dFe derived directly from glacial ice are not supported by the data presented here. Station 15, located amongst grounded icebergs at the far eastern margin of the ASP (Figure 1), showed no obvious dFe enrichments from iceberg sources relative to other shallow bank stations (Figure 3B). That said, ambient waters on this shallow bank never exceeded ice melting temperatures, ensuring relatively long residence times for the many grounded icebergs bordering the ASP to the east, and perhaps limiting dFe inputs derived from them. Iceberg Stations 57.04 and 57.26 showed very low near-surface dFe of 0.06–0.14 nmol kg\textsuperscript{-1} and no notable salinity minima in surface waters. Of the Ice Shelf stations, Stations 9 and 10 showed modest to large surface dFe maxima, but these were not associated with notable salinity minima.

The Iceberg Stations 57.26 and 57.30, influenced by a large (1 km x 3 km) drifting tabular iceberg (Randall-Goodwin et al., 2015), fell broadly in line (Figure 3C) with expectations for mixing of regional dFe endmember values for mCDW and WW as defined by other non-iceberg influenced ASP stations. These stations showed variably high dFe from 100 m to the bottom, reflecting the interleaving of mCDW (already enriched with DIS meltwater or by benthic dFe inputs) and WW and consistent with dynamic mixing processes induced by the approximately 2400 km keel of the passing iceberg. These stations showed a dFe maximum of 0.5–0.6 nmol kg\textsuperscript{-1} near 200 m where T-S properties were close to that of the DIS outflow (dFe = 0.7 nmol kg\textsuperscript{-1}) but slightly less warm and salty, reflecting a small admixture of the dFe = 0.3 nmol kg\textsuperscript{-1} WW (hydrographic properties shown in Figure 5 of Randall-Goodwin et al., 2015). Just below this maximum, at 275–300 m, Stations 57.26 and 57.30 had relative minima in Fe (0.3–0.4 nmol kg\textsuperscript{-1}) reflecting the presence of a water mass that is mostly (Station 57.30) or completely (Station 57.26) composed of WW. Given this restricted range of dFe at the Iceberg stations, consistent with conservative mixing of mCDW (influenced by nearby DIS outflow water) and WW, we could discern no additional dFe inputs from the drifting iceberg itself, although we cannot rule out incremental inputs during iceberg drift that amount to a sizeable flux in total. These results suggest that the chief influence of drifting icebergs on primary productivity may derive from the vertical mixing of dFe-rich mCDW to shallower depths, rather than the introduction of substantial...
additional meltwater-derived dFe to the ASP during the relatively short period of transit through the polynya. The importance of drifting icebergs for mixing and chemical distributions in the ASP is explored in greater detail elsewhere in this Special Feature (Randall-Goodwin et al., 2015).

Some otherwise unexplained dFe maxima may be related to shallow sedimentary dFe sources associated with the trough system (Figure 1). The first example is the small dFe maximum mentioned above, of possibly sedimentary origin and appearing at 197 m at Station 4 (Figure 3A). A second example is the modest to large enrichments of dFe seen in near-surface waters of Stations 9 and 10, which were similar in character to the concentrations of about 0.5 nmol kg$^{-1}$ in the upper 100 m at Station 126 of Gerringa et al. (2012), which was located similarly close to the northwestern side of the DIS but on the opposite (eastern) side from our Station 9, near where the ice edge intersected the coast during ASPIRE (Figure 1D) and isolated from any glacial inputs from the DIS by the westward flowing coastal current. A sedimentary source for this shallow dFe input is also partially supported by the dMn distributions (Figure 4D). We speculate that the magnitude of observed dissolved metal concentrations influenced by interaction with sediments is a function of the degree of re-scavenging intensity at high particle concentrations, the composition of resuspended particles, or the time interval since the most recent resuspension event. Interestingly, all Shallow Bank dissolved metal profiles seem to converge at the deepest samples (400 m), suggesting either very similar regional benthic inputs on the bank or rapid homogenization by near-bottom currents.

**Major Fe source associated with outflow from the Dotson Ice shelf cavity.** The major input of dFe to the upper 400 m of the ASP water column appears to be associated with basal ice shelf melt combined with mCDW emanating from the DIS cavity (and likely from other ice shelf cavities upstream of the DIS as well; Randall-Goodwin et al., 2015). Measurements of (ADCP) current velocity at Station 60, at the far western extreme of the DIS, demonstrated strong outflow to the north (0.17 Sv; maximum average velocity for 15 ADCP profiles was 0.38 m s$^{-1}$), centered on the depth range 200–300 m, just below the bottom draft of the ice shelf (Randall-Goodwin et al., 2015), consistent with predictions based on geostrophic principles as well as with observations at the Pine Island Ice Shelf (Gerringa et al., 2012, Jacobs et al., 2011). The water flowing out from the DIS cavity at Station 60 had a high fraction of glacial meltwater (about 1.5%) and may constitute a flux of new freshwater as high as 81 Gigatons per year (Randall-Goodwin et al., 2015). This outflow water was enriched in dFe to 0.7 nmol kg$^{-1}$ (Figure 3D), as well as in dCu (Figure 6D) and suspended particulate matter (R. Sherrell, unpublished data), relative to shallower and deeper water at Station 60 and relative to the other stations (9, 10 and 11) along the face of the DIS. The upper portion of the dFe profile at Station 60 is very similar to that determined in February 2009 for the upper 300 m only (Station 119 in Gerringa et al., 2012, located <0.5 km from our Station 60, with dFe about 0.1 nmol kg$^{-1}$ lower than at Station 60 at all depths), providing evidence that high dFe in the DIS outflow water is a persistent feature. In contrast, the core of the outflow at 200–300 m was only slightly enriched in dMn (Figure 3D) and showed little sign of dZn (Figure 5D) or dNi (Figure 7D) enrichment.

The transport and mixing of the DIS-sourced dFe northward along Transect 1 can be seen in Figure 10A as a progression from dark green to light blue to dark blue within the depth interval of 100–400 m, from Station 60 north across the polynya. This subsurface, northward flowing dFe source was likely made available to surface waters in the central ASP, including the productive Shallow Bank region to the east of Transect 1, by a combination of advective eddy transport (e.g., Ærthun et al, 2013; St-Laurent et al., 2014), mixing along the Dotson Trough (e.g., St-Laurent et al., 2013), fall/winter vertical mixing driven by sea ice formation and brine rejection, and wind- and iceberg-induced mixing (Randall-Goodwin et al., 2015). This northward transport of the Fe-rich DIS outflow is evident in the dFe distributions along Transect 1 (Figure 1D) as relatively high dFe concentrations of 0.3 nmol kg$^{-1}$ were found within the upper 100 m (though not in surface waters) as far north as Station 66 (Figure 3A, E and medium blue color in Figure 10A). We propose on the basis of this distribution that DIS-sourced dFe is advected and mixed out to the central polynya over a depth interval that introduces the dFe to the upper 100 m, where we expect that wind mixing dominates the flux of the meltwater-associated dFe (as well as macronutrients) up to the euphotic zone.

In contrast to the situation for the DIS outflow, Station 5, located adjacent to the central Getz Ice Shelf, was dominated by WW in the upper 500 m, with no apparent influence of glacial meltwater, and accordingly had substantially lower dFe in the upper water column, compared to the DIS stations (Figure 3D). Thus from this limited sampling, the Getz Ice Shelf does not appear to be a substantial source of Fe to the ASP, though we cannot rule out an outflow source to the west of Station 5 (Jacobs et al., 2013). A more thorough sampling of this region is an important goal for future studies.

In summary, meltwater-laden mCDW flowing out from under the Dotson ice shelf constituted a major dFe source to the upper 400 m of the water column, encompassing near-surface waters of the ASP. This flux may vary seasonally and interannually (Jacobs et al., 2012; Randall-Goodwin et al., 2015), but it is always present. Through a combination of advection and mixing processes, we suggest that the DIS outflow provides a quasi-continuous flux of the key micronutrient, dFe, that supports the highly productive seasonal phytoplankton bloom of the ASP (Alderkamp et al., 2012; Arrigo et al., 2012; Alderkamp et al., 2015; Schofield et al., 2015).
Sources of dissolved manganese to the Amundsen Sea Polynya

Dissolved Mn had strong sources in the AS shelf region, including the bottom sediments throughout the polynya, the DIS outflow and shallow coastal sediments. Dissolved Mn, like dFe, showed enriched concentrations in near-bottom waters indicative of inputs from the sediments (Figure 4). Unlike dFe, however, dMn was relatively enriched at all DIS stations, not just Station 60 (Figure 4D) and was more consistently and abundantly enriched in surface waters at those stations. This result suggests that while the DIS outflow is a source of dMn to the ASP, other sources associated with coastal sedimentary or ice shelf inputs may be of equal or greater magnitude, particularly the implied shallow sedimentary source for dMn, derived from the peninsulas bounding the DIS and likely affecting surface dFe at Stations 9 and 60. Interestingly, Station 10, just to the east of Station 60 (Figure 1D), had low near-surface dMn compared to all other DIS stations, indicating strong lateral gradients in this region (or possibly reflecting temporal variation, since Station 60 was sampled 16 days after Station 10 for logistical reasons). Station 11, in the middle of the DIS, also showed elevated dMn, which may have been mixed in from the eastern end of the DIS, following the geostrophically-predicted westward coastal current (Assmann et al., 2005; Moffat et al., 2008; Randall-Goodwin et al., 2015), or may possibly reflect inputs from glacial ice via shallow calving events on the face of the DIS.

The broader dMn distribution along the Dotson Trough Transect 1 (Figures 1D and 10B) and along Transect 2 (Figure 11B) suggests that the surface and upper water column inputs associated with the DIS and surrounding shallow landforms affect dMn distributions throughout the polynya. Surface waters (upper 40 m) were generally depleted in dMn. The Transect 1 dMn section showed generally high concentrations at 50–200 m, with local concentrations at some stations that were higher than observed in the DIS outflow (Figure 10B). Below this maximum, but above the near-bottom enrichments, was a relatively uniform WW interval with concentrations converging on 1.5 nmol kg\(^{-1}\) (Figures 10B and 11B). The end result was a substantial dMn maximum within the upper 200 m throughout the polynya, that, unlike the case for dFe, rivaled in magnitude the near-bottom enrichments (Figure 4A). This distribution suggests that dMn introduced to surface waters near the DIS may be advected and mixed out into the broader polynya to the north, but then scavenged by the strong surface biological activity of the developing bloom. The biologically removed dMn may be remineralized within the upper 200 m, contributing to the maxima, centered at approximately 100 m, that were observed at concentrations up to 5 nmol kg\(^{-1}\) at all Dotson Trough stations (Figures 4A and 10B). Similar maxima were observed in dMn profiles in the southern Drake Passage, off the northern tip of the...
Antarctic Peninsula, extending 200 km off the shelf break (Middag et al., 2012). That subsurface tongue of high dMn water, while at lower concentration than the ASP maxima, was attributed as well to advected sedimentary sources. In contrast to the situation for dFe, the overall picture for dMn suggests broadly distributed and abundant coastal sedimentary sources of Mn to the upper water column and a longer residence time for dMn than for dFe, allowing the upper water column inputs to propagate throughout the polynya.

The near-bottom enrichment of both Mn and Fe is most likely a result of desorption from resuspended sedimentary particulate matter in the nepheloid layer or mixing of reducing porewaters with high Fe$^{2+}$ and Mn$^{2+}$ into the lower water column, although the residence times of particles following resuspension events and the kinetics of dissolved-particulate exchange may result in a complicated and possibly non-linear relationship between suspended matter concentrations and dissolved metal distributions. In addition the residence time of the water at near-bottom depths may play a role. The deepest basins may have restricted flushing rates, leading to accumulation of these elements to a greater degree than observed elsewhere (Figures 10–12). For the ASP as a whole, the relationship between dMn and dFe concentrations and resuspended particle concentrations was geographically variable. For example, the highest near-bottom particle concentration (beam attenuation) was seen at Stations 15 and 35, on the shallow bank (Figure 12A), but bottom water dFe and dMn were among the lowest here (Figure 12B, C), suggesting a mechanistic or temporal disconnect between resuspended sediment concentration and sediment-derived dissolved metal concentrations. It is important to note as well that although there was a general correspondence in the locations of dFe and dMn enrichments in near-bottom samples, the dFe/ dMn ratio in the nepheloid layer was by no means constant, indicating that the sedimentary source should not be understood or modeled as a fixed-composition input. Further understanding of nepheloid layer effects on Antarctic shelf system metal distributions would be enhanced by detailed knowledge of suspended particulate and colloidal metal distributions.

Finally, it is evident that dMn was enriched by at least 2-fold throughout the water column at all polynya stations, relative to the regional endmember waters at Station 4 (Figure 4A). This concentration gradient stands in contrast to the behavior of dFe, which showed much smaller on-off shelf concentration differences. Note in particular that the northernmost polynya Station 66 had dMn of about 1.5 nmol kg$^{-1}$ in mCDW at 500–600 m, while Station 4 had dMn of only about 0.5 nmol kg$^{-1}$ in mCDW at similar depths. This three-fold lateral gradient and the high dMn found in general at polynya stations suggest strong continental and glacial Mn inputs on the shelf, relative to mCDW entering the shelf trough system from the open ACC. In turn, the upper 400 m of Station 4 appeared to be influenced by the shelf Mn sources, since the well-mixed (Figure 2B, blue line) upper 250 m showed a nearly uniform dMn of

Figure 12
Maps of near-bottom concentrations of particles, dFe and dMn.

Color gradient shows (A) near-bottom particle concentration displayed as transmissometer signal or beam attenuation (Beam att.) for the bottom sample of each station, and (B) dFe and (C) dMn concentrations in bottom-most sample of each station. Station numbers indicated in (A); Station 57.30 excluded because it was not sampled near the bottom.

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1.0 nmol kg
-1, 7-fold greater than observed in the upper water column in the open ACC, as sampled near the Polar Front in the Drake Passage (Middag et al., 2012). The mid-shelf to shelf-break gradient in upper water column dMn therefore likely continued well out into the open ACC to the north of the ASPIRE study area. It is reasonable to suggest that other trace elements with a strong source on the shelf and sufficiently long scavenging residence times (e.g., dNi) are also exported from the AS shelf waters to the open ACC.

Sources of dissolved zinc, copper and nickel to the Amundsen Sea Polynya
Dissolved Zn and Cu, like dFe and dMn, showed some evidence of enhanced near-bottom concentrations in the polynya (Figures 5 and 6), but the gradients were small and largely subsumed within a general increase in concentration with depth (Figures 10 and 11), suggesting smaller relative benthic inputs, compared to those of dFe and dMn. Instead, dZn and dCu gradients largely followed the temperature distribution (Figure 2A), with higher concentrations of 5–7 nmol kg
-1 and 2.2–2.6 nmol kg
-1, respectively, in warmer mCDW waters (Figures 5, 6, 9). Compared to the Trough stations, the upper 300 m of Station 4 was considerably lower in dZn (except for surface waters) than WW at the Trough Stations (Figure 5A), but this difference was negligible for dCu. At Station 4, both dZn and dCu reached relative maxima at 460 m, about 100 m deeper than the local maximum for dFe, suggesting sedimentary inputs from the trough walls at the shelf break, but occurring at a different depth than for Fe; alternatively, these maxima may reflect the effects of deep scavenging removal on the resultant profile shape. Overall, dZn and dCu demonstrated only small if any increases in shelf stations relative to Station 4 (Figures 5A and 6A), suggesting that a large fraction of the shelf inventory of these elements was delivered with mCDW from the open waters of the ACC. Local enrichments, however, were evident at some shelf stations, e.g., Station 34 (Figures 5A, 6A, 9D, 9E), suggesting that small scale physical dynamics may have introduced dZn and dCu from other sources that were not identified by the ASPIRE sampling scheme. The DIS outflow provided a modest input of dZn manifested as a modest concentration maximum at 100–300 m, with the near-vertical dZn profile broadly resembling that of dFe (Figures 3D and 5D). In contrast, dCu showed a relatively strong but ragged maximum in the 200–300 m core of the outflow (Figure 6D), suggesting that outflow from the Dotson cavity is a unique source of dCu to the polynya. Interestingly, the Getz Ice Shelf region may be a modest source of Zn for the ASP, as Station 5 showed high and uniform dZn of 6.5 nmol kg
-1 throughout the water column (Figure 5D); dCu at Station 5, in contrast, was slightly depleted relative to the other ice shelf profiles (Figure 6D).

Dissolved Ni was the least variable of the metals measured, with the factors driving its small variability not easily discernible. Much of the polynya water column had concentrations of 6.0–6.8 nmol kg
-1, with a general though not always monotonic increase with depth. Only a few profiles showed evidence of small benthic inputs. The shelf break Station 4 had a profile shape quite reminiscent of dFe (Figures 7A and 3A), with relatively low concentrations at 100–300 m and a local maximum at 360 m. The relative variations of dNi, however, were much smaller than those for dFe, barely exceeding the 10% range. The DIS outflow was not enriched in dNi, although two DIS stations (11 and 60) showed local maxima near 400 m. Along Transect 2, Station 50 appeared to be generally rich in dNi, while Stations 6 and 48 to the north and south were generally low relative to other trough stations (Figure 11E). The reasons for enrichment at Station 50 are not clear, but the concentration gradients are very small. Overall, it appears that much of the dNi entered the shelf region from offshore, and concentrations in the polynya rarely strayed far from the WW value of 6.5 nmol kg
-1, suggesting very small Ni inputs on the shelf itself.

Trace metal sinks in the ASP
Low dissolved Fe in polynya surface waters
Despite the intense phytoplankton bloom, high Chl a concentrations, and nutrient drawdown from WW endmembers, nitrate concentrations in surface waters were never observed to be lower than 7 μmol kg
-1 during the late December to early January field season of ASPIRE (Yager et al., 2015). At the same time, euphotic zone dFe at many polynya stations was 0.06–0.12 nmol kg
-1 (Figure 3E), similar to dFe concentrations found in the Fe-limited regions of the Pacific sector of Southern Ocean (de Baar et al., 1999; Sedwick et al., 2008; Klunder et al. 2014). Many ASP stations had a small dFe minimum near 20 m depth (Figure 3E), corresponding at most central ASP stations to the mid- to lower euphotic zone (Schofield et al., 2015). It is therefore likely that phytoplankton cells in much of the ASP euphotic zone experienced at least short-term Fe stress during the bloom development period sampled during ASPIRE, even if Fe flux to cellular uptake sites, not dFe inventory, is what ultimately controls growth rate. This conclusion is consistent with results from a series of Fe-addition incubation experiments carried out during ASPIRE, which at most stations showed that Fe addition increased photosynthesis rate and the efficiency of electron transport in photosystem II (Alderkamp et al., 2015). In the ASP, it appears that bloom development and biomass accumulation can occur under conditions of moderate Fe stress and reduced photosynthetic rate. The mechanisms that maintain Fe flux to the bioavailable pool in the euphotic zone are the subject of ongoing research; a future paper will explore the overall distribution of particulate Fe pools and the role of wind mixing, subjects beyond the scope of the research reported here.
Biological removal ratios of trace metals and macronutrients from the upper water column

To estimate the relative removal of macronutrients and micronutrient metals from the euphotic zone, resulting from primary production and associated processes, we considered the near-surface concentrations of metals and nutrients in the surface waters at various stations in the polynya (Figures 8 and 13). In this analysis, we treated the surface-most sample of each profile as a representative of the temporal progression of bloom development unique to that station, manifested as the phosphate concentration relative to the WW value (1.95 µmol L$^{-1}$ = 1.90 µmol kg$^{-1}$; Yager et al., 2015) assumed to be distributed uniformly throughout the polynya before initiation of the bloom. In this way, the inhomogeneous spatial distribution of nutrients could be taken as a proxy for the patchy temporal development of the bloom at each station, during the overall bloom growth in the ASP. This horizontal/temporal treatment of the data is similar to the more common procedure of determining vertical gradient ratios for metals and nutrients for the entire upper water column nutricline, typically extending as deep as 800 m in the lower latitude ocean (Twining and Baines, 2013, and references therein). In the vertical application, the relative remineralization of metal and phosphate is taken as a reflection of the metal:P ratio of the phytoplankton cells living in the local euphotic zone that drive the dissolved metal and nutrient profiles. However, differential remineralization, water column metal scavenging, or lateral advection and preformed nutrients within the upper water column can bias vertical gradient ratios away from initial cell quota ratios in the overlying euphotic zone, leading to erroneous inferred cellular metal quotas. In contrast, the only caveats to our horizontal/temporal approach are the effects of remineralization and abiological scavenging occurring within the euphotic zone, as we did not consider any deeper portions of the water column. Even if these effects were minimal, such that drawdown ratios largely reflect phytoplankton uptake, it is important to point out that the drawdown ratios we measure do not necessarily reflect the metal quotas of the concomitantly observed phytoplankton assemblage, because of the likelihood that cumulative metal and nutrient removal since the onset of spring stratification was driven by a taxonomic subset not necessarily represented by the assemblage present at the time of sampling. However, given that the various stations reflected different stages in the bloom development and nutrient drawdown, and most were dominated by *Phaeocystis antarctica* (Alderkamp et al., 2015), the metal to nutrient drawdown ratios determined here likely approximate metal:P intracellular ratios for this species.

Relative biological removal of trace metals and macronutrients from the upper water column

The concentration of dFe correlated poorly with PO$_4$ in polynya surface waters overall (Figure 13A). For all points in the 0–11 m depth range, dFe vs. PO$_4$ (Figure 13A) showed that dFe was apparently drawn down to low values of 0.1–0.2 nmol kg$^{-1}$ even when PO$_4$ was only moderately drawn down from the WW concentration. This effect was even more extreme if one considers that the minimum upper water column dFe concentration was often slightly deeper, at 20–30 m (Figure 3E). The dMn vs. PO$_4$ regression (Figure 13B) yielded a somewhat better correlation coefficient than for Fe, but suggests that dMn was drawn down to minimum values by the time PO$_4$ reached about 1.0 µmol kg$^{-1}$. Similar regressions of dZn and dCu to PO$_4$ (Figure 13C, D) revealed stronger correlations ($R^2$ = 0.86 and 0.74, respectively). The Ni vs. PO$_4$ regression had a non-significant correlation coefficient driven by two outlier data points, but nevertheless a linear regression seems evident. It is curious that phosphate was drawn down to levels that are below those predicted by dissolved trace metal availability in hypothesized pre-bloom euphotic zone concentrations (WW). At most of the ASP stations, surface water PO$_4$ was drawn down below 1.70 µmol kg$^{-1}$, and at most of these stations dFe was found in the low 0.1–0.2 nmol kg$^{-1}$ range (Figure 13A). If we apply the maximum Fe quota observed for *P. antarctica* growing under Fe-replete conditions (Fe:C = 8 µmol mol$^{-1}$; equivalent to Fe:P = 0.8 mmol mol$^{-1}$; Strynecki et al., 2011), then the initial WW Fe concentration of 0.3 nmol kg$^{-1}$ would be drawn down to the observed 0.1 nmol kg$^{-1}$ with a concomitant PO$_4$ removal of only 0.25 µmol kg$^{-1}$ to 1.70 µmol kg$^{-1}$. If the early season assemblage were diatom-dominated, dFe would be drawn down to the observed concentrations with even less PO$_4$ drawdown, as Fe:P in Southern Ocean diatoms, even under Fe-limitation, have a higher Fe:P of 0.6–3.1 mmol mol$^{-1}$ (Hopkinson et al., 2013; Twining and Baines, 2013). This observation suggests either conversion of the co-existing particulate Fe pool to maintain relatively steady but low dFe concentrations as PO$_4$ continues to be removed, consistent with our interpretation of the shipboard incubation results (Alderkamp et al., 2015), or a higher euphotic zone recycling efficiency for Fe than for PO$_4$. Alternatively, it is possible that early season Fe inputs, e.g., from melting sea ice, effectively boosted the dFe availability above that of the WW endmember, allowing generally greater PO$_4$ drawdown as observed during ASPIRE, even if such inputs cannot sustain the bloom throughout the season.

The Mn:P drawdown ratio of approximately 3.2 mmol mol$^{-1}$ is about 7.5–10 times higher than the vertical gradient regression of the upper water column observed in the open ACC and the Weddell Sea (Middag et al., 2012, 2013), 5 times higher than cellular Mn:P measured by Synchrotron X-ray Fluorescence (SXRF) in Southern Ocean diatoms (Twining and Baines, 2013) and 2 times higher than bulk particulate Mn:P in diatom-dominated waters just north of the Ross Sea (Cullen et al., 2003). Schoemann et al. (2001) provided evidence that Mn may be oxidized and precipitated with the mucus of *Phaeocystis* colonies, but even accounting
for this fraction, their measured total Mn:C is equivalent to a Mn:P ratio several times lower than our drawdown ratio. Thus, while the metal uptake characteristics of *Phaeocystis* remain poorly quantified in general, this analysis suggests that dMn in the ASP was removed from the euphotic zone by non-biological scavenging or bacterially-mediated oxidation to MnO$_2$ (Tebo et al., 2004), as well as by phytoplankton uptake. Thus, unlike most of the subtropical ocean, where photoreduction of particulate Mn and atmospheric Mn inputs lead to dMn maxima at the surface, scavenging removal of Mn in addition to cellular uptake, combined with lateral mixing of a coastal dMn supply to the upper water column, lead to surface minima and subsurface maxima in dMn throughout most of the ASP.

The regressions of dZn and dCu to PO$_4$ (Figure 13C, D) revealed stronger correlations ($R = 0.93$ and 0.86, respectively; $n = 20$, $p < 0.05$) than for dFe or dMn. Our Zn:P drawdown ratio of 3.4 mmol mol$^{-1}$ is about half the mean observed vertical gradient ratio for the Southern Ocean overall (Table 3 in Twining and Baines, 2013), and only about 30% of the Zn:P observed in Fe-limited diatom-dominated particulate matter north of the Ross Sea, despite somewhat lower dZn in that study (Cullen et al., 2003). Interestingly, the negative intercept of the Zn to PO$_4$ regression suggests that Zn could be depleted entirely before PO$_4$ is drawn down to very low concentrations. Vertical mixing may prevent Zn depletion, but the Zn/P ratio at high PO$_4$ in Figure 13C and the WW concentrations of dZn and PO$_4$ suggest that vertical mixing would supply Zn at a lower ratio to PO$_4$ (approximately 2.5 mmol mol$^{-1}$) than the 3.4 mmol mol$^{-1}$ at which it was

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**Figure 13**

Regressions of dissolved trace metals against phosphate, and dCu against dZn, for near-surface polynya samples.

Concentrations of dissolved trace metals (nmol kg$^{-1}$) are shown regressed against phosphate (µmol kg$^{-1}$) for near-surface (upper 11 m) polynya samples for (A) dFe, (B) dMn, (C) dZn, (D) dCu and (E) dNi. In (F) dCu is plotted against dZn for two different depth intervals: 0–11 m (red symbols and red regression equation) and > 11 m (black symbols and black regression equation). Symbol shapes represent sub-regions of the polynya as indicated by corresponding symbols in Figure 1D. Regression equation not shown in (A) because a linear fit was not significant.

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removed from the euphotic zone. We speculate that the Zn/P uptake ratio of *P. antarctica*, already apparently low compared to that of most other Southern Ocean phytoplankton, may get even lower if PO$_4$ is drawn down further, later in the bloom period. Indeed, the data hint that dZn may plateau at about 1.5 nmol kg$^{-1}$ at the lowest PO$_4$ concentrations (Figure 13C).

In contrast to Zn, our Cu:P drawdown ratio of 0.7 mmol mol$^{-1}$ is very similar to the mean vertical gradient ratio for diatom-dominated assemblages in the Southern Ocean (0.53 ± 0.13; Twining and Baines, 2013), though about half the ratio observed in a study of eurytopic zone particles north of the Ross Sea (Cullen et al., 2003). Laboratory culture studies of *Phaeocystis spp.*, under different combinations of Cu and Fe availability yielded the equivalent of Cu:P = 0.15–0.30 mmol mol$^{-1}$ under optimal Fe and Cu availability (assuming Redfield C:P = 106), with no effect of Fe limitation on Cu quotas (Guo et al., 2012), suggesting that a role for Cu in the high-affinity Fe uptake mechanism, demonstrated for some phytoplankton groups, is not present in *Phaeocystis*. Thus the mean Cu:P drawdown ratio for the ASP, which is 2–4 times higher than in the culturing study, probably does not reflect the Fe status of cells in the ASP, but more likely reflects a higher Cu availability in the ASP euphotic zone compared to the range explored by Guo et al. (2012). However, the similarity of our Cu:P drawdown ratio to ratios observed at lower total dCu concentrations farther north in the Southern Ocean (Twining and Baines, 2013) suggests strong complexation of dCu in the ASP, as recently observed in shelf waters of the Antarctic Peninsula (Bundy et al., 2013). Still, Cu utilization is sufficiently low to relative to supply that, in contrast to Zn, approximately 1.0 nmol kg$^{-1}$ dCu would remain in surface waters if PO$_4$ were completely exhausted (Figure 13D). The drawdown ratios for this *Phaeocystis*-dominated system suggest that *P. antarctica* has Zn:P ratios substantially lower than that of Antarctic diatoms, while Cu:P ratio appears similar to or somewhat lower than that of diatoms. A more detailed analysis of phytoplankton metal uptake, with comparisons to bulk particulate composition will be presented elsewhere.

Our Ni vs. PO$_4$ regression had a slope of 0.29 mmol mol$^{-1}$, which is at the lower extreme of a 5-fold range of values found in previous studies that measured the composition of cultured phytoplankton and of phytoplankton-dominated bulk particulate matter from field samples, or measured intracellular concentrations by SXRF (Twining and Baines, 2013). Compared to water column vertical Ni:PO$_4$ gradients (Twining and Baines, 2013), our slope is 3–6 times lower. Apparently Ni is not required in large quantities at all by the *Phaeocystis*-dominated ASP bloom.

As a final observation on metal drawdown, we note that the uptake of Zn was highly correlated with the uptake of Cu (Figure 13F); the upper 11 m samples showed an R for dCu vs. dZn of 0.94 (better than either dZn or dCu vs. PO$_4$; Figure 13C, D), which suggests that ASP phytoplankton consistently took up 5 times more Zn than Cu. The gradient for the remaining sub-surface data appeared to fall on a slightly lower slope (Figure 13F), suggesting either that less Cu is required, relative to Zn, in the deep euphotic zone, or that Zn is preferentially remineralized below the euphotic zone (Twining et al., 2014), although the difference in slopes was not statistically significant. These inter-element relationships provide novel quantitative clues as to the cellular composition of *Phaeocystis antarctica*.

**Evidence for zinc and copper scavenging in the deep water column of the polynya**

Among all ASP sampling stations, Station 35 had a unique trace metal signature. The low concentrations of dZn and dCu, which remained markedly low from the surface to 350 m, suggest that deep water scavenging was especially active for these metals at this location (Figures 5B and 6B). This location had the highest surface Chl $a$ fluorescence measured among all sampling stations (Figure 8F), the lowest surface water nitrate concentration, the greatest depletion of dissolved inorganic carbon, the lowest $p$CO$_2$ and the highest integrated buildup of organic matter in the upper 100 m, all suggesting that Station 35 was one of, if not the most mature bloom conditions we sampled. The apparent removal of dZn and dCu suggests that biogenic particles have a unique capacity to remove these metals throughout the water column (but not Fe, surprisingly, which showed a minimum near 300 m but maxima above and below; Figure 3B), given sufficient POC flux over time. This station may represent a region of the ASP that had experienced a stationary bloom for some period (weeks) and had not undergone extensive vertical mixing or lateral mixing with neighboring sub-regions. The lack of a comparable scavenging feature at Station 25, just 17 km to the north, speaks to the surprisingly limited horizontal scale of this subsurface Zn and Cu deficit and to the importance of a long-lived stationary bloom in driving extreme metal distributions. The mature bloom state at Station 35, however, suggests that such deep scavenging of Zn and Cu may become more widespread later in the season. While the uniform removal through the water column was not seen for any of the other metals, dFe, dMn and dNi all showed evidence of deep minima below 200 m at most of the Shallow Bank stations, suggestive of scavenging removal in a depth zone lying below a layer of apparent maxima resulting from remineralization of sinking particles (Figures 3B, 4B and 7B).

These results suggest that sinking biogenic particles have a strong affinity for dZn and dCu in particular, (relative magnitude of the effect is much larger for dZn than for dCu) through the entire upper 350 m, despite a small apparent remineralization peak at 100–150 m. Indeed, we are not aware of any reports of similar vertical profiles for these metals at any station in the ocean. Macronutrients and dissolved inorganic carbon all increased strongly with depth in the upper water column, for all Shallow Bank Stations (Yager et al., 2015), suggesting
that the low dZn and dCu concentrations at Station 35 did not represent a lack of remineralization of bulk organic matter. Recent modeling of Zn concentrations and isotopic composition at locations in the North Atlantic supports an important role for deep water scavenging in maintaining the deeper concentration increase for Zn relative to other nutrient-type elements including Cu (John and Conway, 2014); Station 35 may be an extreme example of Zn scavenging by particulate phytoplankton detritus in a uniquely productive system.

That said, Cu has long been characterized by “hybrid” behavior in the open ocean, qualitatively displaying the combined effects of biological remineralization and deep scavenging (Bruland et al., 2014), and a more dominant role of reversible scavenging has recently been argued via modeling efforts to explain Cu distributions in the temperate ocean (Little et al., 2013). The essentially constant dCu concentration from the surface to 350 m is striking, especially when considered in comparison to increasing concentrations likely dominated by remineralization at nearby stations (Figure 6B).

These findings suggest that strong sustained particle flux and possibly a unique particle composition dominated by Phaeocystis biodetritus may be responsible for the unusual scavenging effect at this location. If the above mentioned biogeochemical characteristics of Station 35 mark it as the most mature bloom station sampled, it is reasonable to suggest that other sub-regions of the ASP might show similar scavenging effects as nitrate drawdown continued until the peak of the overall polynya bloom, some 2–3 weeks after the ASPIRE sampling ended (Ducklow et al., 2015). In principle, the dZn and dCu profile shapes are a function of the relative rate of scavenging removal in the local region, the extent of deep scavenging in nearby sub-regions and the rate of lateral mixing/homogenization at depth. We speculate that Station 35 showed the scavenging effect so strongly because (1) bloom growth and export of POC had been especially rapid in the weeks preceding our sampling and (2) lateral mixing was limited at this station, suggesting it may represent a semi-isolated water column defined by an eddy (St-Laurent et al., 2014). This unique biogeochemical behavior serves as an example of how very productive shelf waters may display elemental behavior that reveals fundamental processes that are important in these locations, but are greatly diminished in the open ocean, and thus generally not inferred from open ocean metal distributions.

Summary and conclusions

This first major study of the distributions of several bioactive dissolved metals in the Amundsen Sea Polynya, carried out with GEOTRACES-compliant methods, has provided key insights into the mechanisms supporting the very productive summer phytoplankton bloom, and has revealed the extent to which concentrations of Fe, Mn, Zn, Cu and Ni are modified by processes within this shelf sea, relative to distributions in the open Antarctic waters off the shelf. While Circumpolar Deep Water (CDW) brought moderate dissolved Fe concentrations onto the shelf as it flowed from the open ACC through cross-shelf troughs to the coast, strong additional Fe sources were added within the shelf system. Gradients of Fe observed during this early summer period, when the bloom was in mid-development, suggest that while benthic Fe inputs enriched CDW in the deepest regions of the polynya, it was the circulation of CDW under the fringing ice shelves, in particular the Dotson Ice Shelf, that led to an injection of dissolved Fe into the upper water column via a strong meltwater-laden outflow from under the ice shelf cavity. Sea ice melting appeared to be a locally important source of Fe but could not provide the continuous input of Fe required to fuel the weeks-long bloom observed in the central polynya. Inputs of Fe directly to the upper water column may have also occurred during surface calving of ice shelves and from shallow coastal sediments, but the sampling strategy employed during ASPIRE was not able to quantify the impact of these sources. Simple regressions of dissolved Fe to phosphate in polynya surface waters suggest that phosphate was removed by phytoplankton to a greater extent than can be explained by the drawdown of dissolved Fe; Fe may have been recycled efficiently in the euphotic zone, or suspended particulate Fe may be a critical source of bioavailable Fe for the bloom. We found that Mn distribution differed from that of Fe, suggesting that shallow sediments may act as a polynya-wide source of Mn to the upper water column while deep benthic sources provide near-bottom inputs; mid-water column Mn concentrations were lower and near-surface waters showed strong depletion at stations away from the coastal differ-

from Fe and Mn, the biactive metals Zn, Cu and Ni had small to negligible sources on the shelf; profiles were dominated by surface removal and remineralization at depth. Of these three micronutrients, the largest dynamic range by far was exhibited by Zn, which was drawn down to low, but not limiting concentrations in productive polynya surface waters. Benthic inputs of these metals were generally small, and the Dotson outflow provided only very modestly enriched concentrations Zn, Cu and Ni. At one mid-polyyna station with biogeochemical characteristics that suggested a locally mature bloom state, Zn and Cu were strikingly removed to low concentrations throughout the water column, evidence that biogenic particles sinking under late bloom conditions may drive strong scavenging removal of these metals. Overall, the distributions of these bioactive metals, and iron in particular, suggest a critical and unique role for the bordering ice shelves and the circulation of warm CDW within the underlying cavities, driving accelerated basal melting and providing the flux of Fe necessary to maintain the intense bloom. Future analyses of the metal composition of suspended and sinking particles will augment the current interpretation, based on dissolved element distributions. The
current work reveals a level of complexity that the high-resolution multi-disciplinary ASPIRE program was well suited to capture. These findings set the stage for future studies combining targeted sampling strategies to further quantify metal input and removal processes with high-resolution physical and biogeochemical modeling approaches.

References


Bioactive trace metal dynamics in the Amundsen Sea Polynya, Antarctica


Bioactive trace metal dynamics in the Amundsen Sea Polynya, Antarctica


Contributions

• Contributed to conception and design: RMS, SES, PLY
• Contributed to acquisition of data: RMS, MEL, KOE, SES, PLY
• Contributed to analysis and interpretation of data: RMS, MEL, SES, PLY
• Drafted and/or revised the article: RMS, MEL, SES, PLY
• Approved the submitted version for publication: RMS, MEL, KOE, SES, PLY

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Competing interests

The communicating author (RMS) confirms that none of the authors has competing interests relating to the publication of this manuscript.

Data accessibility statement

Data are available in the BCO-DMO database: http://www.bco-dmo.org/dataset/615868.

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