# THE TRACE ELEMENT COMPOSITION OF SUSPENDED PARTICULATE MATTER IN THE AMUNDSEN SEA POLYNYA, WEST ANTARCTICA

By

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#### ABSTRACT OF THE THESIS

The trace element composition of suspended particulate matter in the Amundsen Sea Polynya, West Antarctica By KATHLEEN MARIE HARAZIN

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The Amundsen Sea Polynya is one of the most productive regions in the Southern Ocean. Since macronutrients are abundant, natural iron (Fe) fertilization is likely responsible for large seasonal phytoplankton blooms; however, little is known about the mechanism of Fe supply to this polynya, in particular with respect to various forms of particulate Fe. During December 2010 and January 2011, water samples were filtered by contamination-free methods to collect suspended particulate matter; subsamples of these filters were digested or chemically leached, and analyzed for Fe and a suite of other metals. High crustal particle concentrations were measured throughout the polynya, with highest values observed where strong northward flow emanates from under the melting Dotson Ice Shelf, propelling particulate and dissolved Fe to sub-euphotic zone depths in the central polynya. Potentially bioavailable fractions were investigated by comparing chemically leachable fractions to "excess" (non-crustal) fractions, calculated from average crustal element/aluminum ratios. The Dotson Outflow Station has high concentrations of both total and labile particulate Fe fractions, suggesting substantial inputs of potentially bioavailable particulate Fe to the polynya, fueling phytoplankton blooms.

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In the euphotic zone, suspended matter analyses can reveal cellular metal concentrations of the phytoplankton assemblage. Non-crustal Zn/P is exceptionally high throughout the polynya compared to most literature values for marine phytoplankton, but is consistent with previous determinations in Antarctic waters near the Ross Sea. Both Zn/P and Cd/P show lower ratios in higher primary productivity polynya regions, suggesting a biodilution effect, competitive uptake antagonism with Fe, or reduced availability of dissolved Zn and Cd resulting from prior biological activity. In contrast, Cu/P is relatively high at the high productivity stations where Zn/P and Cd/P are low, and dissolved Cu is at minimum for the polynya. These high Cu/P ratios may reflect high quotas unique to bloom-dominating *Phaeocystis antartica*, suggestive of a Cu-requiring reductive Fe uptake pathway.

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#### **1 INTRODUCTION**

The Southern Ocean plays a major role in modulating global climate through formation of deep water masses and exchange of heat and gases at the air-sea interface. Additionally, the Southern Ocean has a large potential for biological uptake and storage of atmospheric CO<sub>2</sub> (e.g. Sarmiento and Toggweiler, 1984; Sarmiento et al., 2004; Caldeira and Duffy, 2000, Park et al., 2010). As a High Nutrient Low Chlorophyll (HNLC) region, it is characterized by relatively high nutrient concentrations, but low rates of annual net primary production (NPP). The low rates of productivity are attributed to a number of potential factors, including light limitation (e.g. Sedwick et al., 2000, 2011; Boyd et al., 2007, 2010), silicic acid limitation, and grazing by zooplankton (Banse et al., 1994, 2002). Iron limitation also controls NPP, as Fe is a required micronutrient, and Fe concentrations in the Southern Ocean euphotic zone are generally extremely low. The efficiency of the biological pump in the Southern Ocean influences glacialinterglacial atmospheric CO<sub>2</sub> (e.g. Sigman and Boyle, 2000; Sigman et al., 2010), and changes in aeolian Fe deposition in surface waters may contribute to changes in pump efficiency on geologic timescales (Martin et al., 1990; Petit et al., 1999).

Off the coasts of Antarctica, highly productive polynyas have some of the highest rates of NPP in the world, in contrast to the open waters of the Southern Ocean (Arrigo et al., 2003). A polynya is an open body of water surrounded by sea ice; these regions can be seasonal or year round, and are formed by strong winds continually pushing sea ice away from the continent, relatively warm deep waters upwelling and melting ice, or both. The high productivity can attributed, at least in part, to the relatively shallow, stratified waters; polynyas sit over the shallower continental shelf, and the melting of sea ice can create a stable layer of fresh surface water. Coastal Antarctic waters contribute up  $\sim 30\%$  of total productivity in the entire Southern Ocean (Arrigo et al., 2008).

The Amundsen Sea Polynya has the highest annual productivity (per unit area) of 37 Antarctic polynyas, as observed using remote sensing (Arrigo et al., 2003). The Amundsen Sea Polynya International Research Expedition (ASPIRE) was carried out on the RV/IB Nathaniel B Palmer from December 2010 to January 2011. The ASPIRE team seeks to explore the physical, chemical, and biological dynamics of the Amundsen Sea Polynya, and to investigate the mechanisms leading to the long-lasting very productive summer bloom in the polynya.

#### 1.1 The Amundsen Sea

#### 1.1.1 Physical setting

The Amundsen Sea is situated between the Bellingshausen and Ross Seas in the Pacific Sector of the Southern Ocean (Figure 1.1). The Amundsen Sea Polynya is bounded by the Thwaites Ice Tongue to the east, Marie Byrd Land and the Western Antarctic Ice Sheet to the south, and by sea ice to the west and the north. It overlies deep continental shelf (>300 m) and extends over the deep Dotson trough (> 1200 m at maximum depth) (Randall-Goodwin, 2012; Yager et al., 2012).



Duration Trend (days yr <sup>-1</sup> )									
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**Figure 1.1.** Location of the Amundsen Sea and the Amundsen Sea Polynya. Figure taken from Yager et al. 2012. (a) The Amundsen Sea is located in the eastern Pacific sector of the Southern Ocean. WAP = Western Antarctic Peninsula; BS = Bellingshausen Sea; PIP = Pine Island Polynya; RSP = Ross Sea Polynya. Grey represents wintertime sea ice cover, while black represents polynyas. White areas bordering the continent represent the continental shelf. (b) The 1979-80 to 2010-11 trends (days yr<sup>-1</sup>) in sea ice season duration for the West Antarctic region of the Southern Ocean, showing strong seasonal decreases in the Amundsen Sea Polynya. The red box outlines the region of the Amundsen Sea Polynya. The solid contour is the continental shelf break, and the dotted contour outlines sea ice trends significant at the p < 0.01 level (after Yager et al., 2012).

The upper 300 to 500 m of the water column within the polynya is relatively cold and fresh due to melting of proximal glacial ice and vertical wintertime mixing, forming the Winter Water mass. Below these depths, water is relatively warm and salty. Circumpolar deep water (CDW, ~2° C) enters through three troughs at the shelf break, two that lead to Pine Island Bay (Walker et al., 2007), and one that leads to the Dotson and Getz ice shelves (Wåhlin et al., 2010). While the bottom inflow through the Dotson trough is slightly colder than the bottom inflow leading to Pine Island Bay, the two inflows have similar heat fluxes (Wåhlin et al., 2010), since CDW preferentially enters the eastern Amundsen Sea at depth (Walker et al., 2007; Thoma et al., 2008) with little temperature/salinity modification (Jacobs et al., 2011). Towards the coast, CDW is modified (to mCDW) (Arneborg et al., 2012) by mixing with subsurface Winter Water and glacial meltwater, and flows under regional ice shelf cavities, and is eventually upwelled along the coast (Walker et al., 2007). The strength of upwelling of mCDW in the Amundsen is attributed to the southerly position of CDW (due to the continental slope-proximal position of the Antarctic Circumpolar Current, relative to other regions in the Southern Ocean) as well as a persistent clockwise-directed wind field (Jacobs et al.,1996; Jacobs and Comiso,1997; Hellmer, 2004).

The inflow of relatively warm CDW has major implications for melting of glaciers on the Antarctic continent. Melting below ice shelves in Amundsen is highly sensitive to bottom water temperatures; therefore, melting is primarily controlled by intrusion of CDW and by vertical mixing (Holland et. al, 2008, Pritchard et al., 2012). Presently, the Amundsen Sea is the primary site for accelerated melting of a portion of the West Antarctic Ice Sheet, a situation having implications for global sea level rise; furthermore, a climatically-driven increase in CDW flow onto the shelf is thought to be responsible for this accelerated melting (e.g., Rignot, 1998; Rignot and Jacobs, 2002; Shepherd et al., 2004; Jenkins et al., 2010; Jacobs et al., 2011).

The flow of CDW onto the shelf may be affected by the southward shift of the Polar Westerlies (Bracegirdle, 2013). In particular, seasonal trends in the Southern Annular Mode (SAM) (i.e. significant positive phase trends in the summer and autumn of recent decades) may affect the Westerlies. Although models predict a strong seasonal variability in the inflows, recent mooring results indicate that warm water is continuously supplied to the Amundsen Shelf year-round (Arneborg et al., 2012). However, recent studies have observed a long-term shift in the SAM towards more persistent positive trends, leading to a southward shift in the Westerlies (e.g. Sallée et al., 2010); this may have important implications for CDW flow onto the continental shelf in future decades and a multitude of other climatic feedbacks. The Amundsen polynya appears from November to March as a result of latent heat transfer and the seasonality of katabatic winds (Randall-Goodwin, 2010). Over the past decade, the size of the polynya has varied, as has its timing and duration (Arrigo et al., 2012). While katabatic winds maintain some open space year round, polynya areas are much larger from October to March due to higher ambient temperatures. In early December the polynya area is around 10,000 km<sup>2</sup>, and during the austral summer peak, it can reach 60,000 km<sup>2</sup>. Between 1997 and 2010, the average peak size was 27,333 ± 8749 km<sup>2</sup>, and the polynya was open 132 ± 17.5 days (Arrigo et al., 2012). The polynya closes much faster than it opens, and the opening and closing is more related to smaller scale winds than it is to climatic states (such as the SAM or the El Niño Southern Oscillation).

While the timing of the opening and closing of the polynya has varied greatly over the past decade, the timing and duration of the phytoplankton bloom has been much more predictable. Arrigo et al. (2003) found that the bloom length within the ASP has averaged  $73 \pm 10.5$  days. Peak productivity in the Amundsen Sea Polynya is in January, when Chl *a* reaches as high as 35 mg m<sup>-3</sup> (A. Alderkamp, per. comm.), and mean Chl *a* reaches up to 7 mg m<sup>-3</sup>; the January mean Chl *a* is two to three times greater than that of other Antarctic polynyas. The adjacent Pine Island Polynya reaches 4 mg m<sup>-3</sup>. In the ASP, peak net primary productivity (NPP) reaches 0.76 g C m<sup>-2</sup> d<sup>-1</sup> (or 277 g C m<sup>-2</sup> yr<sup>-1</sup>); this is four to six times greater than the sea ice zone, and three to five times greater than the marginal ice zone (the boundary between open ocean and the sea ice zone) (Arrigo and van Dijken, 2003). In contrast, average NPP for the whole Southern Ocean, south of  $50^{\circ}$ S, falls below 57 g C m<sup>-2</sup> yr<sup>-1</sup> (Arrigo et al., 2008).

#### 1.1.2 The chemical environment of the coastal water column

In the Amundsen Sea, mixing of distinct water masses on the continental shelf (Arneborg et al., 2012; Assmann et al., 2005; Jacobs and Comiso, 1997; Jenkins et al., 2010; Thoma et al., 2008; Wåhlin et al., 2012; Walker et al., 2007) affects the chemical environment within the polynya. Macronutrients are abundant in Antarctic waters generally, due to vigorous deep vertical mixing and underutilization by phytoplankton. Productivity, as well as community composition, are controlled by Fe and light, the two main growth limiting factors in Antarctic waters (Alderkamp et al., 2012; Coale et al., 1996; De Baar et al., 1990; 2005; Sunda and Huntsman, 1997). While nutrient rich CDW may deliver some Fe to coastal regions, water column Fe on the continental shelf does not originate primarily from the open ACC. Therefore, understanding the source and delivery mechanisms of Fe (and other bioactive trace metals) is crucial to understanding productivity within the polynya. The goal of this thesis is to understand metal uptake by phytoplankton and recycling of bioactive trace metals within the polynya. In addition to the upwelling of Fe-rich mCDW (Gerringa et al., 2012; Sedwick et al., 2000), trace metals can potentially be sourced from atmospheric inputs (Cassar et al., 2007; Jickells et al. 2005), release from surface sediments into the water column, melting sea ice (Lannuzel et al., 2007, 2011), melting (or potentially calving) of ice shelves (Pritchard et al., 2009; Wåhlin et al., 2010), and the related mechanism of Fe release from drifting icebergs (Lin et al., 2011; Helly et al., 2011) (Figure 1.2).



**Figure 1.2.** A schematic of potential sources of Fe (and other bioactive trace metals) in the Amundsen Sea Polynya. Iron may be found within crustal particles (black triangles), sedimentary Fe minerals (orange diamonds), and biogenic material (green ovals). From Yager et al., 2012.

The Southern Ocean has the lowest atmospheric depositional fluxes of Fe in the world (e.g. Duce and Tindale, 1991, Jickells et al., 2005, Wagener, 2008). However, much of this atmospheric input is soluble and therefore biologically accessible (Cassar et al., 2007). Despite relatively high bioavailability, aerosols likely do not contribute significantly to the trace metal load in the Amundsen Sea (Gerringa et al., 2012, Planquette et al., 2013). Sea ice in the East Antarctic contains trace metal loads derived from water column Fe scavenged during ice formation, as opposed to dust deposition, and seasonal ice melt can contribute significantly to the supply of Fe (but not other bioactive metals, such as Zn, Cd, Cu, and Mo; Lannuzel et al., 2011). Icebergs, having

broken off from continental ice shelves, may deliver trace metals to coastal Antarctic waters. Studies have shown that icebergs originating from the Ross Ice Shelf play a large role in micronutrient delivery to phytoplankton within the Weddell Sea (Lin et al., 2011, Helly et al., 2011). In the Amundsen Sea, a 100-150 m thick water mass consisting of mCDW that has been modified by subsurface melting of ice shelves appears at intermediate depths; this water mass may be enriched in Fe due to continental ice shelf meltwater contributions (Wåhlin et al., 2010).

#### 1.1.3 Evidence for long, intense, Fe-fertilized blooms in Antarctic polynyas

Studies within the Amundsen Polynya have been limited by the difficulty in accessing the polynya, due to the sheer isolation by the surrounding sea ice. Recently, Fe dynamics within the adjacent Pine Island Polynya (PIP; located in the Amundsen Sea, located west of the Thwaites Ice Tongue) have been studied as part of the DynaLIFE cruise in 2009 (Arrigo and Alderkamp, 2012). In the Amundsen Sea, deep waters intrude through three deep troughs, two of which lead to Pine Island Bay. There, mCDW becomes enriched in Fe due to interaction with sediments and basal melting of the Pine Island Glacier (Gerringa et al., 2012). The Fe-enriched mCDW upwells and delivers Fe to the central PIP phytoplankton bloom. As phytoplankton remove the dissolved Fe, organic matter production creates ligands that help bind additional Fe, and making Fe more bioavailable (Thuroczy et al., 2012). Consequently, high concentrations of bioavailable Fe are sustained, and this persistent Fe pool fuels the phytoplankton bloom, resulting in high rates of productivity (Alderkamp et al., 2012). Furthermore, nutrient addition

As a result, phytoplankton draw down  $NO_3^-$  to growth limiting levels, a phenomenon rarely seen in the open Southern Ocean (Mills et al., 2012). These results highlight the role of iron from melting glaciers in fueling phytoplankton blooms in the PIP.

The Oden Southern Ocean 2007-08 Expedition sought to investigate the physical, biological, and chemical characteristics of the Amundsen Sea more broadly. The expedition performed a transect from the open Southern Ocean to the continental shelf towards the southern Pine Island Bay, and then from the Crosson Ice Shelf to the Dotson and Getz Ice Shelves. Only a few stations overlapped geographically with ASPIRE stations (in particular, the Ice Shelf Stations; see Methods 2.1). Planguette et al. (2013) analyzed the size fraction as well as trace metal composition (P, Fe, Mn, Al) of particulates (>0.45  $\mu$ m; see Introduction 1.2.2) in order to determine the provenance of particulates, with implications for the sources of Fe. Similarly to the Pine Island Polynya (Gerringa et al., 2012), atmospheric deposition does not contribute significantly to the soluble Fe fluxes in the Amundsen Sea Polynya. Iron derived from sea ice may have been present at stations more proximal to the shelf break, where sea ice still covered 50-80% of surface waters. The dominant contributions of particulate Fe likely come from ice shelf melting/calving and sediment resuspension. Planquette et al. (2013) found that particulate Fe is dominated by a mixture of unweathered crustal particles and sedimentary authigenic Fe, based on Fe/Al ratios (Further discussed in Discussion 4.1). Additionally, particulate Fe has a very small biogenic fraction, rarely exceeding 10% of total particulate Fe, even in the euphotic zone at high phytoplankton biomass (see Introduction section 1.2.2). The results suggest that mCDW is enriched by sediment interactions and basal melting of the ice shelves in the Amundsen Sea Polynya, similar to the PIP. The ASPIRE cruise sought

to further investigate Fe enrichment in upwelled mCDW; furthermore, Planquette et al. (2013) did not present data for the biogenic fraction of other biologically important metals, and this addressed in this thesis using samples from ASPIRE.

#### **1.2 Bioactive trace metals**

#### 1.2.1 Role in physiology and limitation

Many trace metals are required for cellular functions, resulting in active uptake by phytoplankton. While some metals (e.g., Fe and Zn) have several functions within cells, others have highly specific functions, often unique to specific taxonomic groups. Iron is required for many important cellular processes, including respiration, photosynthesis, C and N fixation, nitrate and nitrite reduction, and chlorophyll synthesis. Similarly, Zn also plays many roles within the cell. Zinc is widely used as a cofactor in carbonic anhydrase (Zn-CA), which catalyzes the interconversion of  $CO_2$  and  $HCO_3$ . Zinc is also critical in DNA replication (Zn fingers) and may also be used in low  $PO_4$  environments as a cofactor of alkaline phosphatase, to cleave phosphate groups from dissolved organic phosphorus compounds (Jakuba et al., 2008). Furthermore, both Fe and Zn play important roles in macronutrient acquisition.

Some metals with more specific cellular functions include Cu, Ni, and Co. Copper plays an important role in the uptake of Fe through a Cu-based high electron affinity Fe transport (HAFeT) system which allows Fe-limited diatoms to more readily access ligand-bound Fe; phytoplankton can also lower their Fe requirement by using Cu-based enzymes instead of Fe-based enzymes (e.g. Peers and Price, 2006, Maldonaldo et al., 2006, Annett et al., 2008). Copper can also be present in the copper superoxide dismutase (SOD) (La Fontaine et al., 2002). Nickel is required for both urease (Oliveira and Antia 1986; Frausto da Silva and Williams, 2001) and superoxide dismutase (Frausto da Silva and Williams, 2001; Dupont et al., 2010). Cobalt is a cofactor in vitamin B12 and may substitute for Zn as a co-factor in some enzymes, when Zn availability is low (Sunda and Huntsman, 1995).

Cadmium also appears to play a role in biology based on its distribution in the oceans and its correlation with phosphate, although Cd is not known to be required for any cellular process. However, Cd, as well as Co, can substitute for Zn in Zn-CA, especially when Zn concentrations are low (Price and Morel 1990; Morel et al., 1994; Lee and Morel, 1995; Xu and Morel, in press). While a unique Cd-CA exists in some organisms (Lane and Morel, 2000), it is not common, and available evidence suggests that most biological Cd is associated with Zn-CA substitution, or with co-transport by a non-specific transport system, even in the absence of a strong cellular requirement (Cullen et al., 1999).

The availability of metals can limit phytoplankton growth and productivity, and may do so in high nutrient low chlorophyll (HNLC) regions, where macronutrients (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-</sup>) are underutilized by phytoplankton. The Southern Ocean has been shown to be light limited, silica limited, and also limited by zooplankton grazing (Banse et al., 1994, 2000). The first order control on productivity is light, as Antarctic waters experience large seasonal variability in sea ice and solar irradiance. Iron limitation exerts a strong additional control on productivity in the Southern Ocean (de Baar et al., 1990; Buma et al., 1991; Martin, 1990; Coale et al., 1996; Sunda and Huntsman, 1997), as dissolved Fe concentrations in the open Southern Ocean rarely exceed 0.1 nM in surface waters (e.g. Bowie et al., 2011). Because of the diversity of functions Fe serves, and its potential for limiting productivity in large regions of the ocean, Fe has been the focus of many trace element studies (e.g. Boyd, 2010, and references within). A large number of iron-enrichment experiments performed in HNLC waters shows that Fe amendments promote phytoplankton growth (Boyd et al., 2007). Although these experiments have clearly demonstrated an increase in productivity and biomass as a result of Fe amendments, the effect of these amendments on intracellular trace metal contents has not been as widely studied. This thesis provides valuable, direct observations on trace metal contents in natural assemblages of phytoplankton in an environment experiencing potential natural Fe fertilization.

#### 1.2.2 Trace metals in particulates

Dissolved metals are traditionally considered the most biologically accessible phase to phytoplankton. However, particulate forms of trace metals may be a quantitatively significant and potentially bioavailable reservoir of trace metals. Suspended particles (operationally defined as material that is filtered out of seawater by a 0.45 µm nominal pore size filter) have a shorter residence time relative to dissolved trace metals, and may quickly be solubilized and made available to marine biota. Furthermore, particulate concentrations may be equal to or may exceed dissolved concentrations in the euphotic zone. For example, in areas proximal to sources of iron (coastal regions, sediment-water interface or nepheloid layer), particulate Fe, Al, and other crustallysourced metal concentrations can greatly exceed concentrations in the dissolved phase (Berger et al., 2008). Furthermore, within phytoplankton blooms, particulate Fe and Zn concentrations can rival the dissolved concentrations, suggesting efficient biological uptake of metals (Sherrell et al. 1992).

The distribution of particles depends on metal sources as well as interaction with the dissolved phase. A vertical profile for particulate Fe, Mn, or Al may have high concentrations in the surface waters due to aeolian or fluvial inputs. Alternatively, a profile for particulate P, Cd, or Zn may also have high surface concentrations, but in this case due to high productivity and biomass production. For example, particulate Fe (pFe) in surface waters in the Atlantic increases significantly toward the equator, where waters are heavily impacted by atmospheric deposition of dust from the African continent (Mahowald et al., 1999; Barrett et al., 2012). In the subsurface, minima may occur due to rapid sinking of large particles following biological uptake and/or aggregation. Consequently, concentrations are enhanced at depth due to disaggregation of these particles; passive scavenging and sediment resuspension may also increase concentrations at depth. While these are typical features, profile type is highly dependent on magnitude of inputs and processes, as well as characteristics of the metal in question.

The composition of suspended particulate matter is variable depending on oceanic regime, but typically consists of varying fractions of the major phases, particulate organic matter (POM), biogenic calcium carbonate, biogenic silica, lithogenic material (clays), and authigenic Fe + Mn oxyhydroxides. The trace metal concentrations of each component contribute to the total particulate concentration. These individual components can be lumped into two main categories: refractory (lithogenic, crustal) or labile (biogenic+authigenic).

In this thesis, the trace element composition of particles from the Amundsen Sea Polynya is determined. The total particulate composition is analyzed using a HF+HNO<sub>3</sub> acid digestion method that completely dissolves the sample material. In order to quantify the total "labile" (i.e. bioavailable) fraction, two different methods are employed: (1) Calculation of the refractory fraction using upper crustal Metal/Al ratios (McLennan, 2001) and subtraction the derived metal value from the total (Martin et al., 1989); and (2) exposing sample particles to a weak chemical leach (25% HAc; Berger et al., 2008). Because the labile fraction largely represents biogenic material (i.e. biomass), we can use these values to estimate the trace metal quotas of natural phytoplankton assemblages (expressed as Metal/P or Me/P).

#### 1.2.3 Trace metal quotas in natural phytoplankton assemblages

The trace metal quotas in phytoplankton reflect the biochemical demands of the cell. The activity of various enzymes and metabolic processes of the cell dictate the need for metals, depending on what essential metals are used in processes. However, a number of factors may control trace metal uptake beyond simple physiological demand. These factors include trace metal availability, aqueous pCO<sub>2</sub>, irradiance and light levels, antagonisms or synergisms (metal-metal interactions), luxury uptake and metal storage, and species composition.

Trace metal availability, particularly the availability of Fe, can influence the uptake of Zn, Cd, Cu, and other metals for a suite of reasons. Cullen et al. (2003) showed a general decrease in Zn/P and Cd/P in phytoplankton from the Ross Sea as a result of Fe additions to bottle incubations. The authors attribute these decreasing Me/P ratios to

"biodilution," where growth rates increase, leading to larger increases in biomass (P) relative to Zn or Cd. Similarly, Semeniuk et al. (2009) found that increasing dissolved Fe (dFe) decreases Cu/P in phytoplankton; however, the lower Cu/P in this case was likely a result of lower Cu demand due to lifting of Fe stress. Dissolved CO<sub>2</sub> also influences metal uptake, specifically for Zn and Cd. Under low CO<sub>2</sub> conditions, phytoplankton increase CA activity. As CA activity increases, so does demand for Zn and Cd (Cullen et al., 2001). Dissolved metals may antagonistically inhibit uptake of other metals through competition during uptake. In culture studies, cellular Cd/P decreases in response to increasing dZn and dMn, potentially due to competitive inhibition at cellular uptake sites (Sunda and Huntsman, 1996, 1998, 2000). Furthermore, culture studies of T. weissfolgii show that dCd and dFe may compete for cell surface transport sites (Foster and Morel 1982; Harrison and Morel, 1983). One of the most important factors that control metal contents of natural assemblages is taxonomic composition. Because of unique biochemical demands by various taxa, taxonomic differences in metal uptake can be significant. For example, Ho et al. (2003) analyzed the Metal/P ratios of incubated phytoplankton, and found that chlorophytes generally have higher Zn but lower Mn, Cd, and Co relative to prymnesiophytes (coccolithophorids) and bacillariophytes (diatoms). A more expansive and detailed discussion of factors affecting trace metal uptake by phytoplankton can be found below in the Discussion.

#### **2 MATERIALS AND METHODS**

#### 2.1 Sample collection

All samples were acquired throughout December 2010 to January 2011 as part of the ASPIRE cruise on the Nathaniel B. Palmer (Yager et al., 2012). In total, casts were taken at 68 stations, 21 of which included trace-metal clean profile casts (Figure 2.1). Station locations range from regions of high productivity in the central polynya to more northerly stations close to or within the sea ice to southerly samples near the Dotson and Getz ice shelves.



**Figure 2.1.** The shiptrack of the ASPIRE cruise. Circles denote stations sampled for this thesis; red circles represent total digests, and yellow circles represent digest and leach. Track colors correspond to fluorescence-based estimates of Chl *a* concentrations (legend).

To collect water samples, externally-closing Niskin bottles were mounted on a trace metal clean CTD-rosette deployed on Kevlar cable from a dedicated epoxy- and plastic-coated winch. To ensure a trace metal-clean setup, hardware surfaces were coated with either polyurethane or epoxy so that no metal was exposed. New Teflon-coated Niskin bottles were cleaned using the method of Cutter and Bruland (2012).

After rosette recovery, Niskin bottles were taken immediately to the Class 100 clean deck-mounted van. Acid-cleaned 0.45 µm pore size polysulfone filters (Supor, Pall/Gelman, 47 mm and 25 mm) mounted in polypropylene filter holders (Advantex-MFS for 47 mm, Millipore Swinnex for 25 mm) were used for filtration of samples. Most samples were filtered using the smaller 25 mm filters; however, 47 mm filters were commonly used for upper water column samples, since the smaller filters would clog more quickly than the larger filters (~4 times the effective filter area) during the filtration of particle-rich samples.

Particles in the water samples will have likely settled by the time filtration commences, so the Niskin bottles were slowly inverted to resuspend and homogenize the particulate matter immediately before the start of filtration (Planquette and Sherrell, 2012). The filter holders were attached to the Niskin-mounted stopcocks via polyethylene tubing and polypropylene fittings. The rotating Teflon stopcocks replaced the typical push-type valve in the Niskin bottles (Cutter and Bruland, 2012). Once the initial unfiltered salinity and nutrient samples were drawn from the Niskins, the Niskins were air-pressurized (8 psi) from the Niskin vent, which is positioned in the headspace. To initiate filtration, the stopcocks were opened, and the filter holder was inverted to allow air to escape. A small fraction of seawater is lost through this process, but the amount is insignificant compared to the total filtered volume.

Air bubbles in the inverted filter holder were allowed to rise to the top of the headspace to help provide an even distribution of particles on the filter. This step of inversion is only for a few seconds, with water flowing, before tightening the filter holder. Then the filter holder is turned right side up for the remainder of the filtration period. A prefilter screen was not used. The seawater remaining on the filter holder after filtering was removed using gentle suction with a plastic syringe. Filtrate was collected in 11 L plastic buckets, and transferred in aliquots to a 2.0 L graduated cylinder to determine volume filtered. The total volume filtered varied from 0.6 to 10.3 L, but most were ~10 L.

#### 2.2 Materials and cleaning procedures

Preparation and cleaning of materials follow procedures previously established by Planquette and Sherrell (2012) and Cullen et al. (1999, 2001). All containers used were either low density polyethylene, polypropylene, and were acid-leached with 10% (vol/vol) HCl (Fisher Scientific Trace Metal Grade) at 60 C° overnight. Filters (batch of 100) were acid-cleaned in a 1 L low density polyethylene bottle filled with 10% HCl. As with sample bottles, the bottle holding the acid and filter membranes was then bagged and placed in an oven at 60 °C overnight. After cooling and gentle resuspension of the filters, the acid was carefully decanted; the bottle was then refilled and rinsed with MilliQ® H<sub>2</sub>O five times with gentle inversion in order to prevent creasing, bunching, or folding of filters. After the first three rinses, the bottle sat full of  $H_2O$  for one day to allow acid to diffuse from filter pores, and then rinsed again.

Teflon digestion vials (15 mL and 3 mL Savillex, Minnetonka, MN) were initially cleaned in boiling aqua regia for 4 hours and then rinsed with MilliQ® H<sub>2</sub>O (18.2 MΩcm, <5 ppb TOC). After the initial cleaning and between subsequent digestions, 1.0 mL of OPTIMA grade 10% HF/90% HNO<sub>3</sub> (vol/vol) was added to each vial which was then tightly capped and set on a hotplate at 135 °C for 4 hours.

Titer plates used as autosampler sample containers during ICP-MS runs were cleaned using nitric acid. Between analytical sessions, remaining analyte was rinsed from the titer plate, and 5% HNO<sub>3</sub> was added to the plate's wells and left to sit overnight; the following day, the plate was rinsed at least five times with MilliQ® water and dried.

All work was carried out in Class-100 laminar flow hoods and benches. Electronic pipets used in the digestions, leaches, and analyses, were calibrated gravimetrically, and nominal volumes are given in the following.

#### 2.3 Subsampling and splitting of filters

#### 2.3.1 Filter Homogeneity

One of the biggest challenges for particulate sampling rests in unavoidable filterto-filter variability in the degree of sample homogeneity across the face of the filter. Ideally, the particulates should be deposited evenly and homogenously in a perfect circle centered on the filter, with the sides equidistant from the filter edges. However, the 0.45  $\mu$ m nominal pore size filters typically catch a great diversity of particulate sizes, the largest few of which can be visibly distributed in an uneven manner. Additionally, smaller particles can aggregate on the surface of filters "clogged" by a heavy influx of particulate matter. Filter homogeneity matters to the accuracy of the analyses since there are not multiple filters per depth. Instead, the filters are cut in half, reserving one half of the filter for digestion, and the other for leaching.

Prior to any subsampling, halving, leaching, or digestion, all filters were photographed and categorized based on the homogeneity or heterogeneity (e.g., presence of air bubbles, large particles, uneven particle distribution, etc.) (Figure 2.3). Samples were given labels A-E based on commonly occurring features that distinguish the filters from one another (Figure 2.2). Given the diversity of sample distribution characteristics, many had multiple labels (Figure 2.4). Additionally, notes were taken on particularly anomalous filters (for example, if they had very large particle or air bubble).

In general, the upper depths of each cast tended to produce more heterogeneous filters, simply due to the large influx of matter being filtered and perhaps the larger, more adherent, organic-rich nature of the particles. Because of the high concentration of organic-rich particles, filters would easily clog and slow the filtering process; clogging may increase homogeneity as well in some cases, since less well-loaded portions of the filter will filter more water as the filter starts to clog. To minimize filtration times and maximize total particulate mass per sample, larger filters (47 mm) were used on these depths. Therefore, the larger filters tend to be more heterogeneous and darker in color than the smaller filters taken at intermediate and deeper depths (Figure 2.5). Filters also showed a wide assortment of hues, usually correlating to sample depth. Shallower filters tended to be a dark moss green, and tended to have more visibly large particles. In contrast, deeper filters tended to be beige and more homogenous. Additionally, deeper

particles had a larger tendency to shift on the face of the filter post-filtration, suggesting a less adherent, more inorganic composition.



**Figure 2.2**. Simplified depictions of filter-to-filter variability. This is not an extensive list of all the "defects" possible, but rather the most common characteristics of filters. Many filters fell into multiple categories. The vertical black lines represent the ideal axis for halving filters. The "hole punch" in B is the result of subsampling for SEM imaging (discussed in 3.2).



**Figure 2.3.** Filters with characteristics illustrated in Figure 2.2. Filter color varies greatly among filters, although these differences are exaggerated due the due to the automatic white balance settings on the camera. Figure 2.5 shows color variation more realistically.

A. A homogenous and centered filter.

B. Filter with a hole punch as a result of subsampling with a 6 mm biopsy punch. The half of the filter with the hole was used in the complete digestions. The loss in sample area is accounted for when calculating concentration of metals.

C. Filter with air bubble. In most cases, bubbles were small, circular, and <5% of the area of the filter. In this extreme case, the bubble is elongate and asymmetrical. The filter was cut so that the bubble was bisected as evenly as possible.

D. Filter with particles. Even though this filter has a relatively even spread of large particles, many filters were patchier and/or had a greater assortment of particle sizes.

E. This sample is homogenous yet the sample area is eccentric; not centered on the filter. In this case, the filter was cut along the x-axis as pictured, so that both halves had the same ratio of sample:filter and the sample area would be bisected as perfectly as possible.

F. Accumulation/aggregation at edge. In this filter, a darker green band appears at the top and continues clockwise to the lower left. This label applied to any accumulation (complete band around the edge vs. segment(s)) but the type of accumulation was noted.



**Figure 2.4.** Example of a filter that would have multiple labels (C, E). These filters are more of a challenge when it comes to halving the sample. On one hand, the filter could be cut so that the bubble is bisected (green line). Alternatively, it could be cut so that the eccentricity of the filter area is bisected. Additionally, the filter could be cut somewhere between the two lines based on a visual estimation of empty space. Ultimately the bubble was bisected for this filter; other filters may have been judged differently.



**Figure 2.5.** Filters from all depths at Station TM08. In the upper left is the filter for the most shallow depth, and depth increases moving right; the row below follows the previous row. The darkest colors correlate with the upper 100 m. Although this station only has 25 mm filters, most other stations had 47 mm for the shallowest three or four depths. Top row depths (from left to right): 20 m, 86 m, 111 m, 202 m Middle row depths: 271 m, 339 m, 366 m, 437 m Bottom row depths: 693 m, 739 m, 1028, 1069 m
## 2.3.2 Sampling for SEM

In order to assess qualitatively the composition of particulate matter collected, subsamples of filters were examined using a scanning electron microscope (SEM). Filters from six depths at Station TM08 (Event 183), as well as a filter blank, were imaged. Only one station was subsampled, with the goal of visually examining particle composition at a typical polynya station, ancillary to the primary geochemical data. Six of the twelve total depths from TM08 were sampled to see how particle composition varies as a function of depth. Because Station TM08 was located within the central polynya (i.e., not on the shelf break, and not directly adjacent to potential particulate sources), matter collected should be fairly representative of typical particles in the polynya. Furthermore, particulate trace metal concentrations were predicted to be relatively high due to high concentrations of biomass, and this station was chosen in the hopes that the primary elemental signals would overwhelm any possible contamination resulting from hole punching.

Five filters (depths 16 m, 41 m, 86 m, 321 m) were subsampled using a sterile 6 mm stainless steel biopsy punch, a plastic mallet, and an acrylic cutting board. Filters were subsampled one at a time immediately after removal from the freezer, and all other filters remained in the freezer to prevent thawing. Each filter was transferred from its plastic bag to a large, acid-clean polystyrene Petri dish placed upon the cutting board. The punch was held slightly above the filter and was given one firm hit with the mallet, and the punch was quickly removed. The filter was replaced to its original dish, and the 6mm subsample was place in its own separate dish. The subsamples were imaged at the SEM facilities of the Materials Science and Engineering Department at Rutgers

University. Prior to imaging, subsamples were mounted on studs and carbon-coated, then left in a desiccator overnight. Both low-magnification and high-magnification images of different particle types were taken. For general images (magnification = 1000x), the view represents ~12% of total 6mm punch area (Figure 2.7).

The filters revealed a wide variety of organic and inorganic material. Filters from all depths were covered with a fine-grained amorphous substance, likely organic biodetritus (Figure 2.6). The coverage of this film seems to be at a maximum in the shallowest sample and to decrease with depth. Generally, the most common particle types observed were (1) diatom frustule fragments, (2) terrigenous/inorganic mineral grains, and (3) sea salt crystals. While not perfect representations, as filters were less homogenous than predicted based on appearance to the naked eye, these images highlight prevalent characteristics of particulate material collected. Diatom frustules, for the most part, are fragmented so that species cannot be identified. However, some frustules (<20%) remained mostly intact. Fragments of *Corethron criophilum*, *Fragilariopsis sp.*, and other common Southern Ocean diatoms were seen throughout the filters at all depths. The relative abundance ratio of diatom to non-biogenic inorganic fragments decreases with depth, although large grains of inorganic material appeared in shallower filters as well. The appearance of cubic salt crystals had no depth dependence, and abundance varied greatly throughout the filters; Figure 2.7E shows the crystals' typical geometric shapes and textures.



**Figure 2.6.** Left: Suspended particles on filter from Station TM08, Event 183, 16 m depth, at 5000x magnification. Right: Supor 0.45µm blank filter for comparison, same magnification. The 16m filter has a film of organic material; all other depths also had this film. Lower left and center right: salt crystals. Center: unidentified dinoflagellate.







**Figure 2.7.** SEM images of a blank filter and filters from four depths at TM08. All images are at the same magnification (1000x), and represent  $\sim$ 12% of the sample area on the filter. The scale bar in 5D is different from the others (20 µm rather than 10 µm), but is proportional and comparable. A. Unused blank filter. Almost perfectly homogenous.

B. 16 m. In the center of this view is an unidentified chain-forming diatom. Fragilariopsis can be seen in the upper right corner. Smaller centric and spherical diatoms can be seen throughout. Filter pores are mostly covered by and filled with the organic film.

C. 41 m. Amorphous organic material and a diatom fragment.

D. 86 m. Salt crystals dominate this view, which is not typical for most of this filter or the filters in general. This filter did not have high Ca relative to other filters, suggesting that this view represents an unusual aggregation of salt crystals.

E. 321 m. Mostly unidentified material, with some salt crystal, Fragilariopsis, and other fragments.

### 2.3.3 Subsampling filters for digestion and leaches

Because the particulate samples were subjected to two independent chemical digestion and leaching treatments, the sampled filters needed to be subsampled in a quantitatively representative fashion. In order to calculate the concentration of pMe in seawater, we assume that cutting the filter in half yields a perfect 50/50 split by mass. Samples are not weighed before and after cutting, as the mass is dominated by the filter itself, with additional contributions from dried sea salt. Given typically non-concentric sample areas, a perfect split of the sampled area would therefore not be expected to yield a 50-50 mass split. Hence, the sample areas were cut in half by visual area, not by mass. To assess the accuracy and precision of the cutting, however, unused blank filters of both sizes (25 mm and 47 mm) were cut using a template and light table, and weighed. The average inaccuracy in subsampling is equivalent to  $\pm 2.15\%$  (1SD, n=4 for each filter size) of the whole filter mass, assumed to be a comparable uncertainty for area, since blank filters can be assumed to be uniform in density (Table 2.1).

All filters were cut in half under Class 100 clean conditions using a pre-made template (multiple filter-sized circles, printed on an 8x11.5" transparency, which was then plastic-laminated and stored in 0.1% HCl overnight), a portable fluorescent light table, and a fabric cutter (disc-style "pizza cutter") with a ceramic blade cleaned in 10% HCl overnight. The light table was covered with a layer of translucent styrofoam to insulate the lightbulb-produced heat from the frozen filter (Phoebe Lam, WHOI, and Marie Séguret, Rutgers Univ., pers. comm.). Again, only one filter remained outside of the freezer at any given time, to prevent thawing, which could lead to particle loss and/or excessive adhesion of particles to the cutting blade. The filter was transferred from its

dish to the clean template using clean Tefzel® forceps, carefully gripping the edge outside of the collected material. The filter was then carefully rotated to the position that yielded the most symmetric halves, based on appearance and position of the sampled area (Figure 2.3). The blade was run vertically down the filter in a smooth and quick motion; one half went back to the original dish and was refrozen immediately, while the other was placed in a 15 mL Savillex Teflon digestion vial. Between each cut, the blade was rinsed with MilliQ H<sub>2</sub>O and patted dry with polyester clean room wipes. Blank filters, including process blanks, were cut after the blade was initially cleaned for a subsampling session, and before cutting samples (refer to Methods 2.6 for definitions of blanks). Each blank or sample filter was cut using a new area of the template, to avoid sample carry-over even though only the backs of the filters contacted the template sheet. The filters were placed against the inside wall of the vials, round edge down and at least 3 mm above the bottom, so that the filter does not contact the acid in the bottom of the vial. An aliquot of MilliQ H<sub>2</sub>O (0.4 mL) was added to each vial so that the filter would more easily "stick" to the wall of the vial. This volume also acted as a diluent for the digestion acids added at a later stage (Section 4.2 below). The Teflon vials were kept capped and in the clean bench as the default state.

**Table 2.1.** Filter halving results, using blank Supor 0.45µm 25mm and 47mm filters. The % error column gives the % by which the whole filter area is misestimated by the subsample in each cutting trial. Although accuracy and precision was slightly better for 47 mm filters, the mean including both filter sizes was used for simplicity.

Filter size (mm)	Half A (mg)	Half B (mg)	Total (mg)	% A	% B	% error
25	10.948	11.824	22.772	48.08	51.92	3.85
25	11.478	11.272	22.750	50.45	49.55	0.91
25	12.088	10.638	22.726	53.19	46.81	6.38
25	11.668	11.080	22.748	51.29	48.71	2.58
47	34.820	34.914	69.734	49.93	50.07	0.13
47	35.420	34.186	69.606	50.89	49.11	1.77
47	34.342	35.214	69.556	49.37	50.63	1.25
47	37.126	37.350	74.476	49.85	50.15	0.30
Average				50.38	49.62	2.15

### 2.4 Digestion and leaching of filters

### 2.4.1 Digestion

The complete digestion procedure consists of (1) closed vial digestion with refluxing in HF/HNO<sub>3</sub> mixture, followed by a dry down, (2) adding concentrated HNO<sub>3</sub> and a performing a second dry down, and (3) redissolution with refluxing in dilute HNO<sub>3</sub>. This reflects a slightly modified version of published protocols used in this lab (i.e. Planquette and Sherrell, 2012).

After the filter half has been properly positioned in the vial, 0.6 mL of ultrapure grade (Fisher OPTIMA®) 16.67% HF/83.3% HNO<sub>3</sub> (vol/vol) spiked with 5 ppb Thullium (Tm) as a recovery monitor. The electronic pipet was set at the slowest

dispensing speed (to ensure no backsplash of the HF solution), and aimed directly at the filter (to ensure that the filter was saturated with solution, and that the filter was adhered tightly to the vial wall, with no underlying air gaps). This volume of acid solution did not typically cover the entire bottom of the vial, and did not contact the filter piece itself. The vials were capped tightly, and placed on a Teflon-coated hotplate (commercial griddle) within a Class-100 clean exhaust hood. To ensure proper refluxing, the vials were arranged equidistant from the heating element (same temperature) and at least 1 inch apart from each other (for airflow and cooling of vapors in top of vials, enhancing refluxing action). The samples were refluxed for 4 hours and left to cool. Throughout all steps, heavy duty Nitrile gloves and full protective gear was worn to minimize chances of contact with HF acid.

After refluxing, caps were checked for tightness and each vial was slowly "rolled" in order to collect HF/HNO3 droplets from the cap and walls of the vial, for safety and to minimize sample loss when vials were opened. Once this had been done to all samples, the vials are lined up and uncapped; the vials themselves were put back on the hotplate, while the caps (in the same order as the vials) were adjacent to the hotplate. The plate was then set at 135 °C for 15-20 minutes. Once remaining solution volume began to visibly decrease, the temperature was lowered to 88 °C. The samples were watched carefully with a clean inspection "dental" mirror to avoid "burning", as heating after dryness causes charring, discoloration, and the possibility of incomplete redissolution; they were removed from the hotplate with under ~5 uL remaining in the vial. This concluded the first dry down. For the second dry down, 100 uL of concentrated ultrapure HNO<sub>3</sub> (Fisher OPTIMA®) was added to each vial to redissolve the sample and drive off most remaining HF (higher volatility for HF compared to HNO<sub>3</sub>). The pipet was aimed at the filter remains on the wall, in order to ensure complete saturation and redissolution of sample adhered to the filter. The dry down process was repeated while maintaining the hotplate at 88 °C.

In the final step, dried-down residue ( $<5\mu$ L) was redissolved/diluted in 3.0 mL 5% HNO<sub>3</sub> (Fisher OPTIMA®) spiked with 10 ppb Sc and 1 ppb In (ICP-MS internal standard drift monitors) and vials were then refluxed again (cap on) at 135 °C for one hour to ensure complete redissolution. After refluxing was complete, but before the vials cooled down, the vials were rolled once again to collect droplets from the walls and caps, saturate the remaining filter piece, and fully homogenize the solution. Finally, the samples were transferred by decanting into acid cleaned 15 mL polypropylene centrifuge tubes, resulting in working solutions of slightly less than 3 mL.

#### 2.4.2 Leaching

For a subset of samples, the remaining filter half was subjected to a chemical leaching procedure to solubilize an operationally defined "labile particulate" fraction of the elemental composition of the suspended particulates. The leach procedure was adapted from Berger et al. (2008) and Hurst and Bruland (2007). The remaining filter halves were placed in 15 mL clean centrifuge tubes using Tefzel® forceps. To minimize the amount of reagent used, filters were placed at the tapered bottom, and often the corners of the filters overlapped, though all efforts were made to optimize the exposure of the sampled filter face to the leaching reagents. While 25 mm filters could be positioned with very little overlap, the larger 47 mm filters often curled, and a filter would end up

folded over itself (i.e. it did not lie flush against the tube wall). Prior to beginning the leach, a hot water bath was set up, and a steady 90 °C temperature was reached before initiating the sample leaching.

Hydroxylamine hydrochloride (0.02 M, reagent grade) in 25% (vol/vol) acetic acid (glacial, Fisher OPTIMA®) was added to each vial in order to ensure that the filter half was completely submerged. For 25mm filters, this required 1.0 mL, and for 47 mm filters, this required 3.0 mL. The tubes were placed in a rack which was placed in the hot water bath, making sure to completely submerge the tips of the tubes so that the bath level was higher than the leach solution in the tubes. The bath was maintained at 90 °C for 10 minutes and then left to cool to room temperature over the course of about 2 hours. After cooling, the samples were centrifuged for 20 minutes at 5000 rpm in a swinging bucket rotor. The supernatant was transferred by pipet to clean vials. For the 25 mm filters, 0.8 mL was transferred to 3 mL Teflon vials, and for the 47 mm filters, 2.6 mL was transferred to 15 mL Teflon vials.

The samples were then spiked with 300 uL of 10 ppb Tm solution to yield a concentration of 1 ppb Tm in the final solution after dry down and dissolution. The leachate was then acidified with 100 uL concentrated HNO<sub>3</sub> (Fisher OPTIMA®) and set uncapped on a hot plate at 135 °C. Similar to the digestions, the temperature was lowered to 88 °C after 15-20 minutes, and the samples dried down to <5 uL. The addition of 100 uL HNO<sub>3</sub> and subsequent dry down was repeated. Finally, as with the digestions, samples were dissolved in 3.0 mL 5% HNO<sub>3</sub> spiked with 10 ppb Sc and 1 ppb In as drift monitors. This procedure is expected to have removed the organic acid from the solution and switched the sample matrix to dilute HNO<sub>3</sub>.

#### 2.5 HR-ICP-MS analysis

Samples were analyzed on a Thermo Finnigan Element 1 Sector Field Inductively Coupled Plasma Mass Spectrometer using using low (300) and medium (4300) resolution (m/ $\Delta$ m) settings. Immediately before the analysis, 600 µL of digest or leach solution was deposited into each well of an acid-cleaned polypropylene titer plate with 1.5 mL wells. Digest vial, filter, and process blanks were run at the beginning of analysis to avoid carry over after analysis of samples (Refer to Methods 2.6 for definition and discussion of blanks). After every ten samples, a replicate sample, a sample spiked with 50 uL of multielemental standard, and a titer well blank were run.

A flow injection system was used for sample introduction, rather than free aspiration. Samples were injected through a PFA-ST (perfluoroalkoxy, HF resistant) nebulizer connected to a modified SC- FAST system (ESI, Omaha, NE). The SC-FAST system consists of an autosampler, a six-port valve, a syringe pump for sample uptake, a vacuum rinsing pimp, and a micro-peripump. This system allows for the processing of small volumes, minimizing the need for dilution and large initial sample volumes, and thus making it ideal for analysis of small marine particulate samples.

A multi-element mixed stock standard solution (containing Ba, Al, P, Ca, Fe, Sr, Cd, Th, Ti, V, Mn, Co, Ni, Cu, Zn, and Mo) was prepared gravimetrically from primary standards, in 0.8 M HNO<sub>3</sub> (SPEX CertiPrep, NJ, U.S.A.; High Purity Standards, SC, USA; primary standards certified to  $\pm 0.3\%$ ). Two 10-point standard curves were prepared through serial dilutions and run at the beginning and end of each run. All samples, standards, and blanks were spiked with and normalized to In in order to correct for

variable signal suppression caused by variations in sample, standard, and blank matrix and to correct for sample-independent sensitivity variations during the run. The Sc internal standard was evaluated but was found less precise than In-normalization; Sc was thus not used.

### 2.6 Blanks

For our analyses, we have four types of blanks: analytical blanks, vial blanks, unused filter blanks, and process blanks (Figure 2.6). Analytical blanks represent signal added by the instrument and/or titer plate; vial blanks were empty vials carried through the digestion, and thus represent digestion procedure + analytical blank; unused filter blanks, which represent the contribution from acid-clean filters + digestion + analytical; and process blanks, which had 2.0 L of 0.2  $\mu$ m pre-filtered seawater filtered through them, and therefore represent on-board filtering + filter + digestion +analytical. In general, metal concentrations are in the order analytical < vial < filter < process, as would be predicted based on potential sources of blank, and the fact that blanks are represented as cumulative values (Figure 2.7). Not every element follows this pattern, however. For example, for Zn, Cd, Ca, Ni, and P, vial blank values exceeded unused filter blank values. Cd and Th also had relatively high analytical blanks, likely resulting from slightly contaminated titer plate wells. Most of these discrepancies are due to a small number of individual blanks with relatively high concentrations; the values in Figure 2.6 represent averages. Process blank concentrations were consistently the highest for all elements.



**Figure 2.8.** Average digest concentrations for analytical (titer) blanks, vial blanks (VB), filter blanks (FB), and process blanks (PB). Note that the y-axis is in log scale. The process blank average has not yet been sea salt corrected, resulting in high Ca and Sr concentrations.



**Figure 2.9**. Average concentrations for analytical (titer) blanks, vial blanks (VB), filter blanks (FB) compared to process blanks. All values have been normalized to process blank average (PB AVG) for each element. The process blank average has not yet been sea salt corrected, resulting in high relative Ca and Sr concentration.

The process blank was chosen for blank subtraction for the digests for two reasons. First, process blanks have the most "handling," and have gone through the same steps as the samples, and are thus the most conservative estimate of relevant blank. Secondly, process blanks generally had the highest elemental concentrations relative to other blank types, but were still substantially lower than virtually all sample elemental concentrations.

The average Ca concentration of process blanks exceeded sample Ca concentrations in most cases. This is due to relatively large mass of sea salt dried on the process blanks after the preparation of these blanks. In order to circumvent this issue, the blank associated with filtration was isolated by taking the difference between the average process blank and average filter blank. A sea salt correction method (outlined in section 2.8 of the Methods) was applied to this value, and the new value was added back to the average filter blank, yielding a "sea salt corrected" process blank. For most elements, PB values remained essentially unchanged, but Ca, Sr, and Mo were notable exceptions. This method eliminates Ca over-subtraction and allows for a proper blank subtraction following sea salt correction of the samples (necessary since the quantity of residual sea salt on filters is highly variable).

Figure 2.10 shows elemental concentrations for each type of blank associated with the chemical leaching procedure. In all cases, vial blank concentrations and unused filter blank concentrations are very similar, and oftentimes vial blank values exceed unused filter blank values. Since no leach data were produced for the process blanks, the average leach filter blank value had to be used for the leach blank subtraction. Table 2.2 summarizes the percent blank corrections using the average sea salt corrected relative process blank, as percent of sample concentrations, for the digests, and similarly the average relative filter blank for the leach. In general, the % blank corrections for the leaches were higher than those of the digests, except for Th, V, Co, Ni, and Cu. All mean % blank corrections are < 25%, and most fall at < 5%. Sr has a negative blank correction (blank addition) due to the sea salt correction of the process blank (see Section 9 for more details).



**Figure 2.10.** Average concentrations for analytical (titer) blanks, leach vial blanks (LVB), and leach filter blanks (LFB). Note that the y-axis is in log scale.

**Table 2.2.** The mean percent blank corrections for all elements. These values represent the percentage of sea salt corrected process blank relative to the total sea-salt corrected particulate concentrations.

DIGESTS				LEACHES				
Cd	2.0	Mn	0.58	Cd	3.2	Mn	0.70	
Ва	1.3	Fe	1.1	Ва	2.5	Fe	2.0	
Th	2.1	Со	3.3	Th	0.86	Со	1.9	
AI	0.89	Ni	24	AI	5.7	Ni	9.0	
Р	3.4	Cu	19	Р	19	Cu	3.8	
Ca	0.21	Zn	14	Ca	0.72	Zn	25	
Ti	3.8	Sr	(-12)	Ti	17	Sr	6.7	
v	1.0	Мо	7.6	v	0.86	Мо	20	

### 2.7 Uncertainty analysis

Four sources of uncertainty in the overall determination of oceanographic particulate elemental concentrations can be quantified, as summarized by Table 2.3. First is the uncertainty associated with the volume filtered. For most samples, filtered volume ranges from 5-10 L; for upper water column sample filters that tended to clog more, some samples represented <3 L filtered. Following filtration, the filtrate volume is measured in 2.0 L increments, with an error of approximately  $\pm 20$  mL. This uncertainty is difficult to quantify exactly, but an estimate of 1% can be used realistically. The second source involves the filter halving procedure (as covered previously in Methods 2.3.3). The third source of error is the uncertainty associated with the dispensed volume from gravimetrically calibrated electronic pipettes. Finally, analytical uncertainty represents the error contribution from the ICP-MS instrument and is determined by replicated analyses, and tabulated individually for each element. There is also uncertainty associated with blank subtraction and the variability in the determination of multiple blank filters; this contribution to uncertainty is not considered in this section.

These errors are propagated to yield the mean total uncertainties for each total elemental concentration (pre-blank subtraction), both for the digests and for the leaches (Table 2.4). The largest source of uncertainty is that associated with filter halving. Values for every element average around 2.5%, but all values remain under 5%.

**Table 2.3.** Estimated uncertainties associated with each step ofdetermining particulate elemental concentrations. Each uncertainty isgiven as decimal fraction relative error.

Volume filtered	0.01							
Filter halving	0.0215							
Pipetting	0.002							
Replicates	DIGESTS LEACHES							
	Cd	0.008	Th	0.021	Cd	0.009	Th	0.015
	Cs	0.008	Al	0.014	Cs	0.015	Al	0.003
	Ва	0.007	Р	0.011	Ва	0.004	Р	0.005
	La	0.010	Са	0.010	La	0.004	Са	0.004
	Ce	0.009	Ті	0.008	Се	0.004	Ti	0.010
	Pr	0.009	V	0.010	Pr	0.006	V	0.011
	Nd	0.012	Cr	0.014	Nd	0.003	Cr	0.005
	Sm	0.015	Mn	0.016	Sm	0.010	Mn	0.009
	Tb	0.011	Fe	0.009	Tb	0.002	Fe	0.008
	Gd	0.012	Со	0.011	Gd	0.005	Со	0.005
	Dy	0.011	Ni	0.014	Dy	0.008	Ni	0.008
	Но	0.030	Cu	0.037	Но	0.065	Cu	0.003
	Er	0.011	Zn	0.026	Er	0.006	Zn	0.021
	Tm	0.017	Rb	0.013	Tm	0.005	Rb	0.005
	Yb	0.016	Sr	0.016	Yb	0.008	Sr	0.013
	Lu	0.017	Y	0.016	Lu	0.031	Y	0.018
	Pb	0.024	Мо	0.035	Pb	0.023	Мо	0.028

TOTAL % ERROR									
	DIG	GESTS		LEACHES					
Cd	2.50	Th	3.18	Cd	2.55	Th	2.83		
Cs	2.51	AI	2.78	Cs	2.80	AI	2.39		
Ва	2.47	Р	2.63	Ва	2.42	Р	2.42		
La	2.60	Са	2.57	La	2.42	Са	2.42		
Се	2.55	Ti	2.49	Ce	2.41	Ti	2.56		
Pr	2.56	V	2.57	Pr	2.45	V	2.61		
Nd	2.66	Cr	2.77	Nd	2.40	Cr	2.44		
Sm	2.83	Mn	2.89	Sm	2.59	Mn	2.55		
Tb	2.62	Fe	2.55	Tb	2.38	Fe	2.51		
Gd	2.67	Со	2.62	Gd	2.44	Со	2.43		
Dy	2.63	Ni	2.75	Dy	2.51	Ni	2.50		
Но	3.82	Cu	4.43	Но	6.94	Cu	2.39		
Er	2.63	Zn	3.55	Er	2.46	Zn	3.15		
Tm	2.94	Rb	2.72	Tm	2.42	Rb	2.42		
Yb	2.89	Sr	2.88	Yb	2.51	Sr	2.70		
Lu	2.94	Y	2.85	Lu	3.87	Y	3.00		
Pb	3.41	Мо	4.23	Pb	3.32	Мо	3.64		

**Table 2.4.** The total propagated error (%) for each determined particulate

 elemental concentration in seawater.

#### 2.8 Sea salt correction

Although excess seawater is removed from the filter on shipboard, immediately following filtration, sea salt crystals do remain, as evidenced by SEM images and high concentrations of Ca and Sr for process blanks. In order to properly assess the composition of particulates, the sea salt fraction must be excluded from total concentrations. Calcium largely originates from either seawater or calcium carbonate, the latter of which, in the oceanic water column, is dominated by biogenic calcite, which has a Sr/Ca ratio nearly 10-fold lower than that of seawater. The Sr/Ca of our samples was calculated at slightly greater than the mean seawater Sr/Ca, suggesting an overwhelming dominance by seawater, with a small potential crustal component or Sr-rich mineral (e.g.  $SrSO_4$ ) component. We can simplify this finding to assert with little error that all particulate Ca in this Antarctic data set originates from seawater. Taking the average concentration of elements in the ocean and assuming sea salt has elemental ratios comparable to mean seawater (http://www.mbari.org/chemsensor/pteo.htm), and using particulate Ca concentrations, we can estimate what fraction of the total measured particulate concentrations derive from sea salt on the filter (i.e. originally dissolved, not particulate). This value is subtracted from the total measured particulate concentrations.

This correction is done on both the digest filters and leach filters (Table 2.5). While most elements have a very small and negligible contribution from sea salt, Cs, Sr, and Mo have a more substantial sea salt fraction. Notably, the sea salt correction for Ba is also relatively high, but still well below 5%. All other elements have < or <<1% sea salt correction. Additionally, Sr has a negative process blank correction (blank addition) due to the sea salt correction of the process blank (see Methods 2.6). This over-subtraction implies that the sea salt correction method is not perfect; this may be attributed to the escape of water (and thus salts) during thawing. For example, although great care was placed on keeping samples frozen, a large power outage during the Hurricane Sandy of November 2012 resulted in prolonged thawing of samples. Regardless, this method for sea salt subtraction does not significantly affect most elements, and the magnitude of sea salt contribution to total particulate elemental contributions is smaller than most blank contributions. No attempt was made in this study to quantify particulate Ca or Sr in any case.

**Table 2.5.** Mean percent sea salt correction for the sample set. These numbers represent the fraction that has been subtracted from the total blank-corrected concentrations. Since all Ca was assumed to be from salt, the percent subtracted is necessarily 100% for this element.

DIGESTS				LEACHES				
Cd	0.17	Th	0.00030	Cd	0.77	Th	0.0014	
Cs	6.7	Al	0.00013	Cs	18	Al	0.0018	
Ва	2.5	Ρ	0.39	Ва	4.1	Ρ	0.56	
La	0.035	Са	100.00	La	0.0080	Са	100.00	
Ce	0.0019	Ti	0.00048	Се	0.0041	Ті	0.024	
Pr	0.020	V	3.1	Pr	0.056	V	5.1	
Nd	0.025	Cr	0.39	Nd	0.068	Cr	(-0.0055)	
Sm	0.019	Mn	0.0028	Sm	0.038	Mn	0.0031	
Tb	0.050	Fe	0.00026	Tb	0.17	Fe	0.014	
Gd	0.036	Со	0.011	Gd	0.12	Со	0.0140	
Dy	0.056	Ni	0.83	Dy	0.1823	Ni	0.71	
Но	0.056	Cu	0.11	Но	0.074	Cu	0.15	
Er	0.10	Zn	0.065	Er	0.30	Zn	0.063	
Tm	0.038	Rb	0.066	Tm	0.00024	Rb	0.080	
Yb	0.11	Sr	78	Yb	0.29	Sr	93	
Lu	0.13	Y	0.19	Lu	0.41	Υ	0.41	
Pb	0.012	Мо	47	Pb	0.0.14	Мо	63	

# **3 RESULTS**

### 3.1 Total particulate concentrations

Stations are grouped according to region (Figure 3.1). Element concentrations show a wide range of geographic variability. Three distinct elemental groups emerge: (1) elements whose profile shapes and concentration ranges vary greatly between stations, and strongly correlate with pAl, (2) elements whose profiles do not vary greatly from station to station, and correlate with pP, and (3) elements whose profiles vary substantially between stations, but do not necessarily correlate with other elements. All values represent concentrations that have been corrected for contributions from dried sea salt, as described in the Methods 2.8.



**Figure 3.1.** Map of the polynya with all stations plotted. Black boxes group stations into geographic regions. (TM = Trace Metal) Northeastern Stations: TM14, TM15, TM17, TM21 Western Stations: TM05, TM07, TM08, TM24, TM34 Iceberg Stations: TM26, TM30, TM31 Iron Curtain Stations: TM09, TM10, TM11, TM29

# 3.1.1 Crustal-type elements: Al, Fe, Co, Th, Ti, V

Particulate Al concentrations span a wide range of values throughout the polynya. Profile behavior is highly region-dependent (Figure 3.2). The lowest concentrations (~5 nM pAl) are observed at Western Station TM05 and in the surface depths of the Northeastern Stations. The highest concentrations are observed at the mid-depth of the Iceberg Stations and at Iron Curtain Station TM29, with values exceeding 300 nM pAl at TM29. All Northeastern Stations show similar concentrations as well as concentration gradients, with the exception of TM14, which shows a relatively large increase starting at ~200 m depth.

Particulate Al and Fe concentrations strongly correlate with each other ( $r^2 = 0.97$ ). As such, particulate Fe concentrations also span a wide range of values throughout the polynya, from <1 nM up to 90 nM pFe (Figure 3.3). In Northeastern Stations, surface minima of <10 nM extend to ~100 m, then increase varyingly with depth. The Western Stations, in contrast, show higher variability with depth. Some trends are reflected in multiple profiles, but no consistent trends emerge. In general, the Western Stations have lower overall pFe concentrations; TM05, located close to the shelf break, has the lowest pFe values of all the stations, never exceeding 10 nM. The Iceberg Stations show even higher variability with depth, and have pFe concentrations as high as 60 to 80 nM below 175 m. The Iron Curtain stations have the highest surface values at 40 nM, with these values extending to depth, and strong similarity among Stations TM09, TM10 and TM11 in the upper 400m. Station TM29 stands out, however, as the surface values double with depth to >80 nM at 150 m; these are the highest pFe values observed in the polynya.

Other elements that correlate well with Al ( $r^2 > 0.90$ ) include Ti, Co, Th, and V (Figures 3.4 to 3.7). These elements exhibit very similar spatial trends to those of pFe, with highest concentrations at TM29, and lowest at TM05. Titanium and Co have ranges of 500 to 14,000 pM and 3 to 30 pM, respectively (Figures 3.4 & 3.6). Thorium exhibits the lowest concentrations of the five, with a maximum pTh of 8 pM (Figure 3.5). A large, anomalous spike in concentration appears in all crustal-typle elemental concentrations at 70 m depth at Western Station TM07.



Figure 3.2. The distribution of pAl grouped by region within the polynya.



Figure 3.3. The distribution of pFe grouped by region within the polynya.



Figure 3.4. The distribution of pTi grouped by region within the polynya.



Figure 3.5. The distribution of pTh grouped by region within the polynya.



Figure 3.6. The distribution of pCo grouped by region within the polynya.



Figure 3.7. The distribution of pV grouped by region within the polynya.

# 3.1.2 Biogenic-type elements: P, Zn, Cd, Ni, Cu

Particulate P concentrations are highest in the Northeastern Stations; surface concentrations at TM17 exceed 200 nM (Figure 3.8), and all stations show a strong decrease in pP with depth to low and relatively invariant concentrations below 200m. The Iron Curtain Stations have the lowest pP concentrations, with surface maxima at TM11 and TM29 barely exceeding 50 nM. Additionally, TM09 and TM10 have no surface maxima. The gradient between surface maximum and subsurface minimum is deepest (30 to 100 m) at the central stations located nearest the center of the ice shelf face.

The elements that correlate with pP ( $r^2 > 0.70$ ) include Zn, Cd, Ni, and Cu (Figures 3.9 to 3.12). At all stations, these elements show surface maxima that decrease to subsurface minima or values equal to low deepwater concentrations, within the first 100 m. The concentration profiles of particulate Zn, Cu, and Ni broadly reflect these patterns. Maximum values reach 1000 pM, 100 pM, 200 pM, and 150 pM at the surface of TM17 for pZn, pCd, pCu, and pNi, respectively. Surface maxima for each element are less pronounced at the Iron Curtain stations, especially for pCu and pNi.

While pNi concentrations generally correlate with pP, the strength of correlation varies with region (Figure 3.11). The highest Ni values are observed at Western Station TM24 and the Northeastern Stations. At the Iceberg Stations, pNi reaches a less pronounced surface maximum, with more variable deep concentrations than pP, pZn, or pCd. At the Iron Curtain Stations, the strong correlation between pNi and pP breaks down, and profile variations in pNi resemble variations in pAl ( $r^2 \sim 0.8$  for the Iron Curtain Stations only). That is, no surface maximum in pNi are observed, with

concentrations  $\sim$  20-30 pM throughout the water column; higher pNi concentrations are seen at depth in TM29.



**Figure 3.8.** The distribution of pP grouped by region within the polynya. Northeastern Station TM17 10 m data point is off scale (561 nM).



Figure 3.9. The distribution of pZn grouped by region within the polynya.



**Figure 3.10.** The distribution of pCd grouped by region within the polynya.



**Figure 3.11.** The distribution of pNi grouped by region within the polynya. Western Station TM24 10 m data point is off scale (208 pM).


**Figure 3.12.** The distribution of pCu grouped by region within the polynya.

### 3.1.3 Other elements: Mn, Ba

The elements that do not strongly correlate with either the biomass associated pP or the crustal particle associated pAl include Mn and Ba. Furthermore, these elements only weakly correlate with each other ( $r^2 = 0.59$ ), and thus show essentially independent distributions. Total pMn shows a range of 250 to 3500 pM. In general, values fall at the lower end of the range (< 1000 pM) in the upper 100 m of the water column. For most stations, the range increases to 1500 pM to 2750 pM by 200 m depth. The notable exception is Western Station TM07, which remains in this lower range even at 1200 m depth. In the Western Stations, surface values do not exceed 1 nM, and concentration then vary with depth. All stations show two subsurface maxima, and then increase with depth, although these features do not occur at the same depths. Profiles at Western Stations TM07 and TM05 converge to similar low concentrations at around 600 m. Additionally, Western Station TM07 has a very high pMn concentration at 70 m, similar to the single point maxima in this sample for the crustal-type elements. All Northeastern Stations have similar concentrations that increase with depth, reaching a near-bottom maximum. Iceberg Stations also have similar concentrations and an increase with depth, although concentrations remain relatively constant below 200m. Iron Curtain Stations show more inter-regional variability, with TM29 resembling Iceberg Station profiles more than other Iron Curtains Stations.

Particulate barium shows a dynamic range of 50 to 1000 pM; similar to pMn, surface values (< 100 m) tend to be low (<300 pM). While these concentrations also increase with depth, the gradient is much smaller than that seen for pMn. The lowest pBa concentrations are also seen at TM07.



**Figure 3.13.** The distribution of pMn grouped by region within the polynya. Western Station TM07 70m (7250 pM Mn) has been omitted.



**Figure 3.14.** The distribution of pBa grouped by region within the polynya.

#### **3.2 Labile concentrations**

Selected samples from Stations TM05, TM08, TM09, TM21, and TM29 were subjected to the chemical leaching procedures in an effort to determine an operationallydefined labile fraction of the particulate trace metals. We expect this leaching procedure to release metals associated with biogenic material and abiotic particulate material such as Fe, Mn, and Al oxyhydroxide phases, or metals bound to the surface of aluminosilicate clay minerals (Berger et al., 2008). The absolute concentrations of leachable pAl (pM), determined by the acetic acid leaching procedure are described in Methods section 2.4.2 and shown in Appendix Table A2. The concentrations relative to the total particulate concentration, expressed as "% labile" (%LMe), are shown below (Figure 3.15). Station TM21 depths 60 and 120 m have been omitted due to large outlier concentrations for all elements, likely due to contamination during the leaching procedure.

Aluminum, Fe, Ti, and Ba have consistent labile fractions throughout the water column. Only a few points deviate from the largely flat %LPMe profiles, and most of these points exceed 100% due to procedural issues. The proportion of labile to total elemental abundance remains relatively constant for each of these four elements across all stations. On average (and excluding outliers),  $9 \pm 5\%$  of total pAl is labile independent of the absolute pAl concentration;  $23 \pm 11\%$  of total pFe is labile; <5% of total pTi is labile; and  $28 \pm 12\%$  of total pBa is labile. These fractions tend to be lower in the surface and subsurface depths of TM29 and TM09, the Iron Curtain stations. A significant anomaly is seen in %LAl, %LFe, and %LBa at station TM05, 50m depth, where values increase to 40%, 98%, and 50%, respectively (Figure 3.15).

Although total Th concentrations correlate with total Al concentrations, %LTh shows a larger range of variability, from ~0 to 30%. Stations further from the coastline tend to have higher %LTh. Similarly, crustal-type Co shows even larger variability, with % labile ranging from 10 to 80%.

The remaining elements (P, Zn, Cd, Cu, Ni, Mn) have widely variable labile fractions. In general, % labile is well over 40% for these elements, with many points exceeding 100% due to apparent procedural artifacts. In particular, %LZn and %LCd often exceed 100%. Calculated non-crustal Zn and Cd (dicussed below in Results 3.3) indicate that Zn and Cd are mostly labile (78% and 99%, respectively, on average), and refractory particles may ave been siphoned up during the leaching procedure, adding to the apparent labile fraction.; however, leach data should still not exceed total concentrations. No spatial trends can be discerned from these data.

# 3.3 Calculated "non-crustal" concentrations

The labile and refractory fractions of particulate element concentrations can be estimated based on assumptions about terrestrial source material. The average composition of the upper crust is well-constrained (e.g., McLennan, 2001, Wedepohl, 1995). Furthermore, some elements have little or no biological function, and thus have negligible concentrations in biogenic marine particulate matter, hence are primarily sourced from continental landmasses. The upper crust has high concentrations of aluminum, largely due to the high abundance of aluminosilicate minerals. Assuming that Al has a completely terrestrial provenance, and associated particles have similar Me/Al ratios as the upper crust, the "crustal" fraction of the total particulate concentration can be calculated and subtracted from the total to yield a "non-crustal" particulate concentration. This "non-crustal" fraction represents the potentially bioavailable fraction of the total concentration, although it may in theory exceed the leached concentration as weak acid leaching may not solubilize some more refractory yet non-crustal solid phases.

Elements that strongly correlate with Al could also potentially be used for this correction, in place of Al. Ti would likely be the next best option as it has no known biological function and has a primarily terrestrial origin. Furthermore, the % labile results indicate that >95% of the total pTi concentration is refractory. However, the abundance of Ti in the upper crust is much lower than Al, and Ti-bearing minerals (such as rutile) are not ubiquitous, hence use of mean crustal Ti concentrations are more likely to lead to inaccuracies in the crustal particle fraction for any given regional lithology. Although Fe has a strong correlation with Al and is widely abundant in the crust. Fe also has a large biological function and is actively taken up by organisms, and also occurs in authigenic minerals in the marine environment, e.g. Fe(oxy)hydroxides. Thorium-232 also exhibits a strong correlation, but displays a spatially variable %LTh in the Amundsen Sea, as well as a less well-constrained mean crustal abundance compared to Al. Therefore, Al and Element/Al ratios are used in this calculation of the % crustal contributions to each particulate element. These estimates can then be compared to the chemical leaching treatment from which the empirical "labile element" concentrations are derived (Figure 3.16). In general, our leach data compare well with the calculated non-crustal values, particularly for rare earth elements and crustal-type elements.



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**Figure 3.15.** Percent labile (leachable) particulate concentrations for each element.



**Figure 3.16**. Comparison of the mean calculated "crustal" fraction and the mean measured "non-leachable" fraction of total particulate elemental concentrations for the Amundsen Sea. The mean non-leachable Cd, P and Zn appear <0 due to apparent uncorrected procedural blanks that increased the leached concentrations for these elements, in artifact, in some samples.

#### **4 DISCUSSION**

#### **4.1 Particulate Phases**

### 4.1.1 Crustal-type Elements

Based on the leach results presented above, most, but not all, of particulate Al is in a refractory phase. Although particulate Fe is also mostly in a refractory phase, the labile phase is more variable compared to that of Al and constitutes about 25% of total particulate Fe. Particulate Mn is largely in a labile phase, although there is a great deal of variability within the polynya. This trend of %LAl < %LFe < %LMn agrees with results of similar leaches from coastal North Pacific waters (Berger et al., 2007) as well as calculated LpMe (labile particulate metal concentrations) from a Western Equatorial Pacific shelf environment (calculated from Total Dissolvable – Dissolved metals; Slemons et al., 2012).

For the crustal-type elements, leach results compare well with the calculated noncrustal values. Particulate Fe leach concentrations correlate well with calculated noncrustal Fe concentrations for the Western and Northeastern Stations. However, leachable Fe tends to be lower than calculated non-crustal Fe at the Iron Curtain Stations (e.g., Figure 4.1a). Two possible scenarios may explain this offset. In the first scenario, the crustal Fe/Al ratio used in the crustal correction is lower than that of the local lithology provided by mechanical weathering, leading to overestimates of non-crustal Fe at these stations. Alternatively, most of the labile Fe at TM29 and TM09 may be in chemically "harder to access" phases, such as less soluble, more crystalline Fe oxyhydroxides, leading to incomplete dissolution by the leaching process. These authigenic Fe particles can form in environments like surface sediments as labile Fe minerals such as ferrrihydrite age and are transformed into more refractory forms such as goethite and hematite (Raiswell, 2011).

While total Fe, Ti, and Th correlate with total particulate Al, scatter around the predicted crustal ratios may reveal information regarding the sources of the particulate material to the polynya system. Comparing the % crustal Fe, Ti, and Th with total particulate Al may show the relative contributions of crustal particles and Meoxyhydroxide particles. Generally, % crustal Ti remains constant regardless of total particulate Al concentrations (Figure 4.2a). In contrast, % crustal Fe decreases with increasing pAl (Figure 4.2b), and % crustal Th increases with increasing pAl (Figure 4.2c). In general, this trend suggests that non-crustal particulate Ti somehow scales with pAl, generating a constant %crustal Ti, or alternatively the mean crustal Ti/Al ratio used in this work is too low for the lithology of the study region, and crustal Ti is in fact near 100%, like Al, and thus invariant with pAl. This second interpretation is supported by low % leachable Ti (See Results Figure 3.15). In contrast, Fe and Th show varying % crustal fractions with varying pAl. The highest concentrations of pAl are associated with increased fraction of soluble Fe and decreased soluble Th. This further suggests that fluxes of crustal particles co-occur with proportionally greater inputs of non-crustal particles, such as Fe-rich oxyhydroxides. Specifically, the depths above the ice shelf draft (surface to 200 m) of Dotson Outflow Station TM29 are almost entirely dominated by crustal influences at moderate pAl concentrations. However, the high pAl subsurface samples (>200m) at TM29 consist of both crustal and non-crustal particles; these noncrustal particles may include authigenic pFe originating from subglacial particulate reservoirs and/or resuspended sediments from under the ice shelf. Similarly, while

calculated crustal Fe below 200 m depth is higher than crustal Fe above 200 m depth, the relative proportion of non-crustal Fe is greater below 200 m (LpFe > 30%) than above 200m (LpFe > 10%). This scenario is corroborated by leach data, which show low LpFe in the upper 200 m, and higher LpFe below 200 m, a pattern shown by %LpFe as well (Figure 4.1b).



**Figure 4.1.** Particulate Fe at Iron Curtain Station TM29, the Dotson Outflow Station. (a) Total particulate Fe, leachable Fe, and calculated non-crustal Fe, and (b) % leachable Fe, calculated as LpFe/pFe\*100%.



**Figure 4.2.** A comparison of % crustal Ti, Fe and Th versus total particulate Al concentrations. Values are calculated using mean crustal ratios to Al (see text). Three points exceeding 100% have been excluded for each element. The high pAl values generally come from the Iceberg Stations and Iron Curtain Stations, while Western and Northeastern Stations have much lower pAl on average. Black lines indicate linear regressions of the data.

### 4.1.2 Biogenic-Type Elements

For crustal-type elements, leach concentrations are comparable to calculated noncrustal values. In contrast, for biogenic-type elements, leach concentrations are nearly equal to total particulate concentrations, generally exceeding calculated non-crustal concentrations. While some elements have small but nontrivial mean lithogenic fractions according to calculated values (Cu: 27% crustal, Zn: 23% crustal), leach values suggest that these elements primarily exist in a labile phase (%leachable >95%), and that calculated crustal fractions are over-estimated. However, in the near-surface depths, leach results for biogenic-type elements tend to be significantly lower than both calculated noncrustal values and total particulate concentrations, except for station TM21. Because these depths exhibit maxima in living biomass (i.e. particulate P), this offset may be the result of high concentrations of intracellular, protein-bound phases not fully solubilized by the leach method, a conclusion that contradicts the assumptions of Berger et al. (2008) this this leach technique results in complete dissolution of the biogenic fraction.

Nickel, unlike other biogenic-type elements, has a large crustal correction, resulting in negative calculated non-crustal values (Results, Figure 3.16). Similar to the other biogenic-type elements, leach results were comparable to total particulate results. Outflow Station TM29 is an exception to this general trend. Here, calculated non-crustal Ni is negative, potentially due to a large overestimation of the crustal Ni component. However, leachable Ni is not equal to either the calculated non-crustal Ni or the total particulate values; instead, %leachable Ni ranges from 50 to 75% total particulate concentrations. This suggests that the regional Ni/Al ratio of refractory particles is greatly overestimated by mean crustal ratios, while leachable results give a reasonable estimate of bioavailable Ni.

## 4.1.3 Sources of Particulate and Bioavailable Fe

The total particulate Fe concentrations, and more specifically the labile component, can be used to identify sources of potentially bioavailable pFe to the polynya. Sources may include atmospheric aerosols, glacial runoff, sediments, sea ice melt, and other water masses originating outside the polynya (e.g. CDW). Our particulate data show trends that support previous hypotheses regarding glacial runoff and modified, sediment-enriched CDW contributing to particulate Fe within the polynya (i.e. Planquette et al., 2013, Gerringa et al., 2012). The outflow from the western end of the Dotson Ice Shelf cavity delivers high concentrations of pFe into the polynya (Station TM29; Figure 3.3). However, temperature and salinity properties of the water masses associated with the edge of the ice shelf imply complicated hydrography with many small-scale features. This complexity of mixing features helps to explain the relatively large variations in pFe distributions among the Iron Curtain Stations. Additionally, hydrographic data and beam attenuation-derived particle distributions suggest that the main outflow from the Dotson Ice Shelf seems restricted to ~200-300 m at TM29, just under the ice shelf draft. This is supported by the maximum in pFe at TM29 at those depths, a feature not found at adjacent station TM10 (Results Figure 3.3).

The higher % leachable pFe below 200 m (~20% LpFe) relative to surface layers (<10%) at TM29 implies a shift in particle composition. While the surface layers are mostly dominated by crustal particles, potentially sourced from ice broken off the face of the ice shelf during small near-surface calving events, the subsurface maximum has a large leachable component. This leachable pFe potentially reflects Fe oxhydroxides picked up from bottom sediments by mCDW, which then transports them into and out of the glacial cavity. However, since the concentration of pFe in the outflow at TM29 exceeds by almost 2-fold the pFe concentrations seen in deep waters at the other Fe Curtain stations (Results Figure 3.3), it seems likely that pFe is added within the cavity, likely from a combination of glacial particulates released during melting and local sediment resuspension driven by the strong outflow current.

Sediment resuspension generally does not play a large role in the pFe distribution through most of the polynya water column. While higher pFe concentrations are seen in the deepest samples (which are typically 5-10m above bottom) at many stations, these enrichments are not seen above 50 m from the deepest sample, indicating a relatively thin bottom nepheloid layer well isolated from subsurface and surface depths. However, sediments appear to play a larger role in the pFe distributions at the Iron Curtain Stations, as mentioned above.

Particulate loads originating from icebergs may also contribute to the total pFe load in the polynya. The subsurface depths of the Drifting Iceberg Stations have some of the highest particulate Fe in the polynya, following the Dotson Ice Shelf Stations. No enrichment in particulate Fe concentrations is seen in surface layers, but subsurface melt from the bottom of the iceberg may contribute to the particulate load. However, icebergs drifting through the polynya may play a more important role in water column mixing than in pFe supply. The high magnitude of the concentrations, as well as the high variability, suggests a Dotson Ice Shelf source that is being mixed vertically, vigorously and in a manner that results in interleaving with other water masses. This strongly contrasts to other studies that propose substantial Fe additions from icebergs in the Southern Ocean (e.g. Raiswell et al., 2008; Lin et al., 2011; Helly et al., 2011; Vernet et al., 2012). The iceberg may be contributing to the total Fe load, but the Dotson outflow likely contributes most of the pFe load to these stations. In contrast, the Grounded Iceberg Station (TM14) shows no evidence of input from or mixing due to the adjacent grounded icebergs, as values compare closely to those of adjacent Northeastern Stations, providing further evidence of limited Fe input fluxes directly from melting icebergs. A more complete analysis of mixing processes, detection of melting, and potential influences on dissolved

and particulate Fe is currently being carried out by ASPIRE co-PI Sharon Stammerjohn (S. Stammerjohn, U. Colorado, pers. comm.)

Two remaining potential sources of pFe are atmospheric aerosol deposition and sea ice melt. No station shows any high surface pFe relative to subsurface pFe, indicating a negligible role for atmospheric inputs, in agreement with previous estimates (Planquette et al., 2013, and references therein). Sea ice processes, however, present a slightly more complicated story. Hendry et al. (2010) proposes enrichment in deep Al, and potentially other elements, due to sediment resuspension induced by vertical mixing associated with brine rejection during sea ice formation during the austral winter. During the austral summer, upwelling may bring this micronutrient rich water to the surface. In our study, generally high pAl and pFe in the Iron Curtain Stations may partially result from similar winter sea ice formation processes, with mCDW transporting high dissolved and particulate metals into and out of the Dotson glacial cavity. However, this is speculative, since we have no data during the austral winter.

Sea ice melt may be directly providing particulate loads to the upper water column at a few stations. At Shelf Break Station TM05 and Getz Ice Shelf Stations TM07 (both Western Stations), high pFe and high leachable pFe are seen at a subsurface depth (50 m and 70m, respectively). While Fe contamination cannot be ruled out, no other samples from the polynya were obviously contaminated, and preliminary  $\delta^{18}$ O of seawater data show a distinct water mass containing sea ice melt at this depth in the Western Polynya (pers. comm., Sharon Stammerjohn). This may indicate a particulate contribution from sea ice melt; furthermore, the high leachable fraction for pFe (>98%; Results Figure 3.15) and other elements suggest Fe-rich sediments and/or organic matter being trapped during sea ice freezing and released upon melting (Lannuzel et al., 2011; van der Merwe et al., 2011). However, since this lens of sea ice melt is spatially restricted and peripheral to the central polynya, it likely does not contribute substantially to the central phytoplankton blooms. Although sea ice melt has the potential to add Fe to the system (Planquette et al., 2013), the general lack of pFe maxima in surface layers suggests no substantial presence of Fe associated with buoyant meltwaters at most polynya stations, although it is possible that Fe additions with meltwater have since been removed by biologically-mediated aggregation and sinking.

#### 4.2 Me/P in Biogenic Fraction

#### 4.2.1 Southern Ocean Analogues

As a HNLC region, the Southern Ocean offers a unique setting for studying the effect of Fe limitation and natural Fe fertilization on metal quotas in phytoplankton. Experiments conducted in the Southern Ocean find increases in phytoplankton biomass as a result of purposeful mesoscale Fe additions. However, changes in phytoplankton Zn/P, Cd/P, and other Me/P as a result of iron additions appear to be unique to each study or study region, implying a variety of mechanisms controlling phytoplankton metal quotas. For example, bottle incubation experiments from the diatom-dominated northern Ross Sea found decreasing Zn/P and Cd/P with increasing Fe additions (Cullen et al., 2003), while mesoscale Fe additions in the open Southern Ocean north and south of the Polar Front had a smaller and more variable effect on Zn/P and Cd/P (Twining et al., 2004).

In the Ross Sea study, various concentrations of dissolved iron were added to whole surface water samples, which were then incubated on deck for 10 days (Cullen et al., 2003). Samples were given treatments of 0 (control), 0.2, 0.5, 1, and 2.5 nM Fe additions; particulate (phytoplankton) Zn/P and Cd/P decreased with increasing Fe treatments after 10 days of growth. Additionally, initial Me/P was measured in the starting water (time=0), and two separate treatments of 10 nM Zn and 10 nM Zn + 2.5nM Fe were carried out. While the Zn addition alone yielded Zn/P similar to the initial euphotic zone particles (starting water) and Cd/P about 30% lower than initial, the Zn+Fe addition yielded lower Zn/P and Cd/P, indicating a suppressive effect of Fe fertilization on Zn/P and Cd/P (Figure 4.3, 4.4). The lower Zn/P and Cd/P with higher Fe additions may be a result of inhibition of the uptake of other bioactive metals by the added bioavailable Fe (Foster and Morel 1982; Sunda and Huntsman 1998; Sunda and Huntsman 2000), or alternatively a result of increasing growth rate (a larger increase in cellular P relative to cellular metals; the "biodilution" effect) (Kudo et al. 1996; Sunda and Huntsman 1998; Payne and Price 1999; Cullen et al. 2003).

Conversely, measurements during the SOIREE (Boyd et al, 2000) and SOFeX (Coale et al., 2004) mesoscale Fe addition experiments observed increased Cd/P (Frew et al., 2001), Zn/P, Ni/P, and Mn/P in phytoplankton (Twining et al., 2004). Frew et al. (2001) noted an increase in phytoplankton Cd/P in response to Fe additions south of the Polar Fontal Zone in the Australian Sector (SOIREE); dissolved Cd:PO<sub>4</sub> ratio also decreased in the upper 5 m of the water column as both nutrients were utilized, suggesting preferential utilization of Cd in an iron-replete setting. It should be noted, however, that the particulate or cellular Cd/P was not measured directly in this study, but was calculated using the difference between dissolved concentrations in filtered and unfiltered acidified seawater. Twining et al. (2004) analyzed intracellular trace metals in phytoplankton from the Pacific Sector of the Southern Ocean (directly north and south of the Antarctic Polar Frontal Zone) after large additions of iron sulfate during the SOFeX experiment. Individual cell Me/P ratios, rather than bulk particulate Me/P, were analyzed using synchrotron X-ray Fluorescence. In contrast to the Cullen et al. (2003) study, the authors observe smaller and more variable changes in Me/P which depend mostly on cell taxonomic group. However, the authors generally attribute increases in Me/P to higher demands for micronutrients; since Zn, Mn, and Ni are essential to cell growth processes, such as nutrient acquisition and cellular biomass production, higher growth rates would increase metal demands. Essentially, the authors hypothesize that cellular demands for metals would increase when fertilization no longer constrains productivity and cell growth. Furthermore, the authors observe no systematic increase in cellular metals after Fe additions. More importantly, most the sense of the Me/P change upon Fe addition seems to depend more on taxanomic group than on the specific bioactive metal. In contrast to our results, diatom Me/P ratios decrease by 31% (SD = 7%) as a result of mesoscale Fe amendments, while autotrophic flagellate Me/P ratios increase by 32% (SD = 5%), and Mn/P and Zn/P increase 23% in heterotrophic flagellates (Twining et al., 2004).

For comparison, the Cullen et al. (2003) Me/P values will be referred to in the following subsections. These values are more comparable to our ASPIRE measurements for several reasons. First and foremost, the chemical digestion method for bulk euphotic zone and incubation bottle particles used in Cullen et al. (2003) is the same method used

in this study. Furthermore, our data and the Cullen et al. (2003) data come from similar oceanic regimes, i.e. Antarctic waters south of the Polar Front. The Me/P ratios resulting from the Zn and Zn+Fe additions (Cullen et al., 2003) are compared here to our determined ratios, since the Amundsen Sea Polynya is generally Zn replete, with dissolved Zn concentrations near maximum levels found in any oceanic euphotic zone outside of some polluted coastal regions (R. Sherrell, pers. comm. 2013). Our surface dissolved Zn concentrations exceed 3-4 nM for most stations (except for TM21, where surface dZn does not exceed 1.8 nM; R. Sherrell, unpubl. data), while the initial dissolved Zn for the Cullen et al., (2003) experiment region, south of the Antarctic Polar Front just north of the western Ross Sea, was  $\sim 1$  nM at the time of sample collection for incubation. While the additions (10 nM Zn each) are high relative to our Zn concentrations, our Zn concentrations do not represent initial concentrations, but rather concentrations after partial drawdown. Full water column profiles suggest that Winter Water dissolved Zn concentrations in the Amundsen Sea, before seasonal biological drawdown, are ~6 nM (R. Sherrell, unpubl. data). This value is consistent with maximum CDW Zn concentrations observed recently in the Atlantic sector of the Southern Ocean and in the Drake Passage (Croot et al., 2011).

### 4.2.2 Zn/P and Cd/P

The biomass-normalized concentrations of biologically important metals can be investigated by calculating metal to phosphorus ratios in biogenic particulate matter. The Zn/P ratios of non-crustal particulate concentrations in the Amundsen Polynya range from 2.5 to 57 mmol/mol (Figure 4.3). Values generally increase with depth (Figure 4.3). These trends are likely the result of preferential remineralization of P and/or Zn adsorption on deeper suspended particles. The non-crustal Zn may largely exist in intracellular, protein-bound phases, leading to lower solubility and accessibility to heterotrophic bacteria, relative to cellular P. Therefore, as organic matter is resolubilized, P is remineralized faster than Zn, leading to higher Zn/P values in residual particulate matter at depth. However, the literature contains no findings that can distinguish with certainty this mechanism from water column adsorption of remineralized Zn<sup>2+</sup> onto residual suspended matter, a process far less likely for the anionic phosphate species. Because the non-crustal concentrations include metals associated with authigenic particles, the calculated Me/P ratio includes elements adsorbed to or co-precipitated with Fe and Mn oxyhydroxides. The highest Zn/P values are seen at depth at the Iron Curtain Outflow Station (TM29), potentially due to low growth rates (producing high surface particulate Zn/P), and strong subsequent adsorption of Zn to particles at depth.

The Cd/P ratios in the polynya range from below process blank levels to 3.1 mmol/mol, and also show low surface values and an increase with depth at the shallower depths, similar to that of Zn/P (Figure 4.4). However, an inflection is seen around 300 to 400 m depth, where Cd/P ratios again decrease, such that near-bottom particles have Cd/P ratios similar to euphotic zone values. This inflection is seen at all stations (Figure 4.4). Similar to Zn/P, the increase in Cd/P with depth may be the result of preferential remineralization of P as suspended matter sinks and is transported through the water column. However, unlike with Zn/P, the inflection in Cd/P profiles suggest a shift in remineralization efficiency. For example, Cd may be remineralized more efficiently below the inflection point. An alternative explanation involves sediment resuspension

and scavenging. Surface sediments may have a lower Cd/P due to a preferential loss in Cd from decaying organic matter at the sediment surface, relative to readsorption of released P onto Fe oxyhydroxides precipitated when Fe<sup>2+</sup> in sediment pore water is reoxidized. It may be that Zn is more efficiently adsorbed onto the same authigenic particles, so that surface sediments have similar Zn/P to raining deep particulate organic matter. If the sediment is resuspended, it can contribute a substantial fraction of Zn, Cd and P, influencing Zn/P and Cd/P in the water column at depth; this low-Cd/P and high Zn-/P would explain the continuous increase in Zn/P with depth, and the decrease in Cd/P below 400 m.

In the euphotic zone (upper 50 m), distinct regional trends appear in both Zn/P and Cd/P. The Northeastern Stations have consistently lower Zn/P compared to other regions (Figure 4.3b). The Iron Curtain and Iceberg Stations have only a few euphotic zone samples, but Zn/P is generally high, potentially due to higher crustal Zn concentrations not accounted for by the crustal correction. These high Zn/P values may also be associated with slow-growing cells that have accumulated Zn relative to slowly assimilated P; these cells may be light-limited due to strong vertical mixing associated with local upwelling, maintaining cells at a low average irradiance.

Euphotic zone Zn/P has distinct regional trends that can be compared to Zn/P values observed in published iron addition experiments. In the Amundsen Sea, euphotic zone Zn/P is lowest at the Northeastern Stations (5.62 mmol/mol); this average value falls close to the Cullen et al. (2003) Zn/P value recorded after additions of dissolved Zn+Fe (6.06 mmol/mol, Figure 4.5). Euphotic zone non-crustal Zn/P ratios are higher in the

Western Stations, ranging between the Zn and Zn+Fe addition values (6.06-11.96 mmol/mol). The Iceberg and Iron Curtain Stations exhibit similar values.

Euphotic zone particulate Cd/P shows similar regional differences and can also be compared to published literature. As with Zn/P, Northeastern Station Cd/P (0.46 mmol/mol) falls very close to the Cullen et al. (2003) Cd/P in the incubation with Zn+Fe addition (0.47 mmol/mol, Figure 4.6). The Western Stations have a slightly higher average Cd/P (0.56 mmol/mol); however, the shelf break station (TM05) has a high average euphotic zone Cd/P (0.93 mmol/mol), very similar to the Cd/P in the Cullen et al. (2003) Zn-only addition (0.93 mmol/mol). The average of the Western Stations (excluding TM05) is 0.44 mmol/mol, which is closer to the Zn+Fe addition value of 0.47 mmol/mol. The Iceberg and Iron Curtain Station Cd/P values fall within these ranges, with a few values greatly exceeding 0.93 mmol/mol.

To summarize the trends within the context of the polynya, both Zn/P and Cd/P are lowest at the high productivity (Chl  $a \sim 45 \text{ mg m}^{-3}$ , CO<sub>2</sub> ~ 100 ppm) stations where natural iron fertilization fuels the phytoplankton bloom (Alderkamp et al., in prep.). In contrast, higher Me/P ratios are seen in the more remote stations (i.e., Shelf Break Station TM05), where both dissolved and particulate Fe concentrations are low, as is primary productivity.

A number of factors may be controlling euphotic Zn/P and Cd/P. Our regional trends suggest that growth effects and biodilution exert a primary control. Cells from high productivity stations may have taken up Cd and Zn slower than P, since growth rates were high. Conversely, phytoplankton at the low productivity stations may have taken up Cd and Zn at relatively faster rates than P assimilation, leading to high Me/P.

Consequently, our Cd/P and Zn/P may be controlled ultimately by iron availability (which controls growth rate). Our data support Cullen's (2003) observation that quotas decrease with Fe additions and related increases in growth rate. Phytoplankton in the Northeastern Stations are not iron-limited, and likely have not felt Fe-stress in preceding weeks (though they may have started to experience Fe stress at the time of sampling; A. Alderkamp, in prep.). The Western Stations, especially TM05, are more distal to the central bloom; they are surrounded by a high percent cover of sea ice and phytoplankton in this region may have been Fe-stressed throughout the season, despite the presence of Fe-bearing sea ice, in addition to being light-limited.

Freedom from iron limitation alone cannot explain the magnitude of our data at the productive stations, as our Cd/P and Zn/P ratios at those stations are higher than those measured after the iron-only additions to the incubations of Cullen et al. (2003). In these incubations, dZn was likely drawn down (not measured), reducing Zn availability and resulting in lower Zn/P values. In the Amundsen polynya, Zn is replete and widely available, similar to the Zn and Zn+Fe addition incubations in the Ross Sea experiment. However, differences in regional Zn/P and Cd/P within the polynya may have been influenced by Zn availability, in addition to Fe availability. Although Zn is generally replete in the polynya, the high productivity Northeastern Stations may have generated higher concentrations of organic Zn ligands that limits Zn availability, further acting to reduce Zn/P in the phytoplankton assemblage in this region.

Stratification also increases growth rates, by shoaling the mixed layer and keeping phytoplankton closer to the surface and at higher mean irradiance. A lack of stratification would lead to slower growth rates and explain the very high Zn/P and Cd/P outside of

stratified, high productivity regions. Strong vertical mixing has been observed at the Iceberg and Iron Curtain Stations. This strong upwelling deepens the mixed layer and keeps phytoplankton perpetually out of light. Under low-light conditions, growth rates are slowed; consequently, Zn/P and Cd/P can be expected to increase, the opposite of biodilution. Although euphotic zone Zn/P and Cd/P data are limited for the Iron Curtain and Iceberg Stations, the data are highly variable, with very high outliers. Regardless, stratification could also be affecting growth rates at the Western and Northeastern Stations, in addition to Fe availability.

While growth rates (controlled by Fe availability and potentially stratification) exert a primary influence Zn/P and Cd/P, other controls undoubtedly influence our metal ratios. Secondary controls, such as phytoplankton assemblage taxonomic composition, dissolved  $CO_2$  and pH, and metal antagonisms, which are discussed in 4.2.5 in the context of trends in Me/P for other bioactive metals.



**Figure 4.3.** The Zn/P (mmol/mol) of non-crustal particulate concentrations. The Zn/P (> 0.1) of 140 m at TM09 is not displayed. The black, orange and green lines correspond to Zn/P measured following treatments of incubation samples in Cullen et al. (2003).



**Figure 4.4.** The Cd/P (mol/mol) of non-crustal particulate concentrations. Legend as per Figure 4.3.



**Figure 4.5.** Regional profiles of Zn/P (mmol/mol) of the non-crustal portion of suspended particles. Legend refers to TM station number.



**Figure 4.6.** Regional profiles of Cd/P (mmol/mol) of the non-crustal portion of suspended particles.



**Figure 4.7.** Euphotic zone (< 50 m) Zn/P (mmol/mol) sorted by region. Black lines represent Zn/P values from Cullen et al., (2003), after additions of dissolved Zn (solid) and dissolved Zn and Fe to 10.7-day bottle incubations (dashed). Note that Western Station TM34 10 m (36.46 mmol/mol) is not shown. Also note the different x-axis scale for the Northeastern Stations.



**Figure 4.8.** Euphotic zone (< 50 m) Cd/P sorted by region. Black lines represent Cd/P values taken from Cullen et al., 2003, after additions of dissolved Zn (solid) and dissolved Zn and Fe (dashed).

The Cu/P ratios of non-crustal particulate concentrations range from 0.73 to 18 mmol/mol (Figure 4.9). Like Zn/P (and to an extent, Cd/P), values increase with depth (Figure 4.9). The mechanism(s) controlling the trends of Zn/P and Cd/P with depth likely control Cu/P with depth. Specifically, preferential remineralization of P and/or preferential deep re-adsorption of Cu could drive Cu/P up with depth; additionally, resuspension of sediments with high concentrations of scavenged copper can explain the highest values, seen below 600 m.

Some regional trends are apparent in our Cu/P profiles (Figure 4.10). Most Iceberg, Iron Curtain, and Northeastern Stations show a steady increase in Cu/P with depth, and a surface-deep difference in Cd/P of ~10 mmol/mol, regardless of depth. Western Stations TM24 and TM34 exhibit similar patterns. Iron Curtain Station TM11 shows increasing Cu/P until 400 m, where values remain high but variable. This may be indicative of complex patterns of interleaving water masses (Wåhlin et al., 2010), variably influenced by lateral advection and resuspension of sediments at different depth intervals.

Regional trends are apparent in euphotic zone Cu/P as well, as with Zn/P and Cd/P (Figure 4.11). However, these patterns do not mimic those of Zn/P and Cd/P. Furthermore, Cu/P differences are more unique to individual stations rather than to groups of stations. While the Northeastern Stations consistently have the lowest Zn/P and Cd/P, this is not necessarily the case for Cu/P (Figure 4.10b). In the euphotic zone, TM05 consistently has the lowest Cu/P (average 0.69 mmol/mol), omitting one flier (13.25 mmol/mol) (Figure 4.10a). Western Station TM08 consistently has the highest euphotic

Cu/P (1.81 mmol/mol, Figure 4.11). Other stations fall between these two values. Additionally, vertical gradients within the euphotic zone are seen at some Western and Northeastern Stations. Specifically, at Western Stations TM24, TM08, and Northeastern Stations TM17 and TM15, Cu/P increases with depth within the upper 50 m.

Our Cu/P values exceed the Cu/P values in Fe addition incubations, measured by Cullen et al. (2003). Unlike Zn/P and Cd/P, which compare well with the +Zn and Zn+Fe additions, our Cu/P compare best with the Initial (1.44 mmol/mol) and Zn addition (0.7 mmol/mol) Cu/P values (Figure 4.11). Western Station TM05 Cu/P ratios, the lowest in our dataset, fall close to the Cullen et al. (2003) Cu/P of 0.7 mmol/mol in the Zn addition treatment. Most of our Cu/P values fall within the range defined by the Initial and +Zn values, with Western Station TM08 being the primary exception and markedly higher.

While TM05 has the highest Zn/P and Cd/P, the low Cu/P at this station indicates that factors other than iron availability and growth rate exert a strong control on Cu uptake. Indeed, Cullen et al. (2003) found little to no change in Cu/P with Fe additions and Zn additions, compared to control bottles. However, copper uptake might be expected to increase under iron limitation due to one of copper's biological functions. In regions where iron concentrations are low, diatoms can reduce their Fe requirements by a number of mechanisms, including using electron transfer proteins with alternative trace metals (in particular, using Cu-containing plastocyanin instead of Fe-containing cytochrome c6; Peers and Price, 2006). Additionally, a high electron affinity Fe transport (HAFeT) system can allow iron-limited phytoplankton to access organically bound Fe (Maldonado et al., 2006); this HAFeT system requires Cu. Therefore, Cu requirements

may be higher under Fe stress, although there is a lack of published cellular metal data to support this supposition.

A recent study has used Cu radioisotope tracers to track Cu uptake in natural phytoplankton assemblages from the subarctic Northeast Pacific, and observes its dependence on dFe and dCu (Semeniuk et al. 2009). The authors found that dissolved Cu exerts a stronger control on Cu/P than dissolved Fe does, although dFe still influences ratios, in that lowering dFe may increase biochemical Cu demand and thus uptake of Cu. Additionally, the authors assert that the redox state of dissolved Cu and the ratio of ligands to total dCu may be even more important than total dissolved Cu. A potential mechanism for this control is the reductive release of organically complexed Cu(II) by membrane-bound cupric reductase.

These results may explain trends observed in the Amundsen polynya euphotic zone. However, a comparison of dissolved Cu and particulate Cu/P yields mixed results. For example, surface dCu at low-Cu/P station TM05 ranges from 1.9 to 2.1 nM (R. Sherrell, pers. comm. 2013), while surface dCu at high-Cu/P TM08 reaches 2.2 nM. This would support the hypothesis that higher dCu yields higher Cu/P, but the differences in dCu are very small. As well, no clear correlation is seen for other stations. The Northeastern Stations have surface dCu ranging from 1.5 to 1.7 nM, while surface dCu at TM05 exceeds 1.9 nM. The Cu/P of the Northeastern Stations generally fall between the average Cu/P ratios of TM05 and TM08. Furthermore, the variations of dCu within the upper 50 m do not correlate with the euphotic zone vertical gradients seen at TM24, TM08, TM17, and TM18. These results suggest that dCu and dFe are not the primary controls on Cu/P in this system.
The concentration of organically complexed Cu may be the primary control on our Cu/P values and distributions. Specifically, *Phaeocystis* may rely on a reductive mechanism for Cu acquisition; in that case, *Phaeocystis* would thrive more under high ligand concentrations rather than high concentrations of either total dissolved Cu or free Cu<sup>2+</sup>. While only total dissolved Cu has been measured for the ASPIRE stations, organically complexed Cu concentrations may be high at TM08 (due to biological production of ligands) and low at TM05 (due to low ligand production at low primary production). The gradients seen at some stations may be explained by the breakdown of ligands closer to the surface, either through biological mechanisms or photo-reduction. However, our data are limited to total dissolved, total particulate, and leachable Cu, and a clear answer is not available without Cu speciation information. Alternatively, *Phaeocystis* may have elevated Cu requirements for a currently unknown reason (the issue of taxonomic differences is discussed in further detail in 4.2.5).



**Figure 4.9.** The Cu/P (mmol/mol) of non-crustal particulate concentrations.



Figure 4.10. Regional profiles of non-crustal Cu/P (mmol/mol).



**Figure 4.11.** Non-crustal Cu/P from euphotic zone depths (< 50 m) compared to values taken from Cullen et al. (2003). Note that Western Station TM34 10 m (11.75 mmol/mol), TM05 50 m (12.05 mmol/mol), and Iceberg Station TM30 20 m (10.36 mmol/mol) are not shown on the graphs. Also note the differences in x-axis scales.

## 4.2.4 Ni/P

While previous elements have used calculated non-crustal values to determine Me/P, Ni/P cannot be determined using non-crustal values due to the large crustal correction, which often yields negative values. However, leach results for Ni may effectively represent biogenic particle values because leach results are positive and in all cases represent a <100% fraction of total Ni concentrations. Therefore, we can use the leach data to calculate Ni/P as an estimate of phytoplankton assemblage composition. For the calculation, leachable P was used for consistency.

The Ni/P values for leached particulate concentrations range from 0.46 to 8.98 mmol/mol (Figure 4.12). Similar to Cd/P and Zn/P, Ni/P increases with depth. Euphotic zone values exhibit a tight range of Ni/P, from 0.63 to 1.8 mmol/mol (although 50m depth at TM05 has a Ni/P of 3.93 mmol/mol). Interestingly, these values are quite comparable to the range (0.73 to 1.15 mmol/mol) reported by Twining et al. (2004) for the initial south patch of the SOFeX experiment (Figure 4.13). Excluding the lowest values (0.63 mmol/mol, TM29, 40m), the mean of euphotic zone value (n = 4) is  $1.52 \pm 0.24$  mmol/mol.

Despite the limited leachable Ni/P data from the euphotic zone, an interpretable geographic trend appears. The lowest points originate from Iron Curtain Stations. The next highest Ni/P comes from Western Station TM08 and Northeastern Station TM21. The highest comes from Shelf Break station TM05. While spatially very separate, TM08 has moderate to high productivity, although it is not as productive as TM21. The high Ni/P from TM05 coincides with the depth where high total particulate concentrations, as

well as high leach concentrations (with %leachable approaching 100%), are observed for several elements, including Al and Fe. These high values may be associated with a unique water mass bearing distinct particle types (briefly described in 4.3) and may not represent true intracellular concentrations. The  $\delta^{18}O_{sw}$  of this sample is unusually high, consistent with a significant fraction of sea ice melt, despite its sub-surface location. We speculate that the unique chemical composition of the particles may reflect their recent origin within sea ice (Sharon Stammerjohn, U. Colorado, pers. comm. 2013).

The biological mechanisms dictating Ni requirements might give insight into our high (relative to previously recorded values) and potentially regionally variable euphotic zone Ni/P. Nickel is required for both urease (Oliveira and Antia, 1986; Frausto da Silva and Williams, 2001) and superoxide dismutase (Frausto da Silva and Williams, 2001; Dupont et al., 2010). The former converts urea to CO<sub>2</sub> and NH<sub>3</sub>, while the latter acts as an antioxidant defense for cells by catalyzing the dismutation of superoxide. Interestingly, phytoplankton have been shown to produce urease regardless of N source being utilized (Fan et al., 2003). Previous work has shown that cellular Ni/P of diatoms is relatively high compared to non-diatoms (Twining et al., 2004, 2011); these high Ni-requirements suggest a critical role of urease and/or superoxide dismutase in diatom biochemistry (Twining et al., 2012). Indeed, diatoms increase urease activity when grown on nitrate in nutrient-replete conditions (Peers et al., 2000); urease activity also appears increase with growth rate (Fan et al., 2003). In the ASP, *Phaeocystis* may function similarly to Southern Ocean diatoms with respect to N uptake, and our relatively elevated Ni/P may be a result of heightened activity of urease. Our Ni/P values do not seem to correlate with growth rate (as measured using rates of primary productivity), but nitrate is replete

throughout the ASP (generally >25  $\mu$ M); if *Phaeocystis* increases urease activity in highnitrate conditions, then demand for Ni would also be increased.



**Figure 4.12.** Ni/P ratio in several stations using chemical leach results rather than calculated non-crustal values. The Ni/P of TM05 at 10 m is negative due to blank subtraction for leachable Ni.



▶ 5 📕 8 🔺 9 ● 21 ● 29 — Twining et al. (2004) South Patch Initial

**Figure 4.13.** Euphotic zone Ni/P (<50 m depth), calculated using leachable Ni/P as opposed to non-crustal values. For comparison, South Patch Initial Ni/P is shown in grey line (Twining et al., 2004).

# 4.2.5 Co/P, Mo/P, Fe/P

Although biologically relevant and interesting, Co/P, Mo/P, and Fe/P cannot be interpreted for a number of reasons. The Co/P of non-crustal particulates is difficult to interpret given the high crustal correction; no more than 30% of total particulate concentrations is non-crustal. Similarly, molybdenum has a high sea salt correction which indicates that sea salt accounts for 47% of total Mo concentrations on average, making Mo/P also difficult to interpret.

Non-crustal euphotic zone Fe/P values (excluding two points) are at least 5 times greater than intracellular Fe/P values from the literature (Twining et al., 2004), and subsurface values exceed 10,000 times intracellular Fe/P (Twining et al., 2004). However, up to twelve euphotic zone samples at various stations do not exceed 10 mmol/mol, and fall close to the mean Fe/P across major phytoplankton taxonomic groups (7.5 mmol/mol; Ho et al., 2003). Our generally high Fe/P values are likely a result of cofiltration of Fe oxyhydroxide particles co-existing with phytoplankton and biodetritus in the euphotic zone. For these reasons, unfortunately, cellular Fe/P cannot be estimated with accuracy from this data set.

#### 4.2.6 Other controls on Me/P

## 4.2.6.1 Taxa

The biogenic particulate matter collected from the euphotic zone represents a natural mixed phytoplankton assemblage rather than a single genus. Therefore, the Me/P ratios reflect metal contributions from multiple taxa. The Amundsen Sea is largely dominated by *Phaeocystis antarctica* within the AS and PI polynyas; beyond the shelf break, diatoms dominate (Mills et al., 2012), although moderate silicate drawdown in the ASP relative to well-mixed winter water implies some activity of diatoms within the polynya. High abundances of prasinophytes and cryptophytes are also observed in the eastern section of the polynya (Mills et al., 2012).

Within the Amundsen Sea Polynya, *P. antarctica* dominates, making up >60% (based on fucoxanthin concentrations, a marker pigment for diatoms, and 19'hexanoyloxyfucoxanthin concentrations, a marker pigment for haptophytes) of the phytoplankton community during the summer 2009 DynaLife cruise. It should be noted that the ASPIRE cruise occurred the year prior to the DynaLife cruise; furthermore, the DynaLife cruise occurred later in the bloom period (February), while ASPIRE took place earlier (December to January). However, the relative assemblage in the polynya likely was similar, although it should be noted that assemblage composition varies somewhat throughout the polynya (Mills et al., 2012). Within the south central polynya (Iceberg Stations), diatoms compose only ~10% of the total phytoplankton. In contrast, up to one-fourth of the community located on the easternmost edge of the ASP (Northeastern Station TM21) consists of diatoms, at least as found during DynaLife; a small, but significant, abundance of prasinophytes is seen here. At the shelf break (comparable to Western Station TM05), almost all phytoplankton are *P. antarctica*.

The variations in Me/P could reflect differences in community composition, given that higher abundances of prasinophytes and diatoms appear in the DynaLife dataset at stations near the location of the Northeastern ASPIRE stations. Ho et al. (2003) found that when cultured in identical conditions, chlorophytes (including prasinophytes) exhibited relatively high Zn and Cu quotas, as well as relatively low Mn, Cd, and Co quotas, compared to prymnesiophytes and bacillariophytes (coccolithophorids and diatoms, respectively). It should be noted that *Phaeocystis* is also a prymnesiophyte, and shares similar evolutionary lineage with coccolithophorids. However, the contribution from prasinophytes to bulk Me/P likely does not explain Me/P variability, due to the small variability and small absolute percentage in %prasinophyte. Pigment data from the ASPIRE program are not yet available as of this writing.

Regional Me/P may be controlled, at least in part, by the relative abundances of *Phaeocystis* and diatoms. While no studies have previously measured *Phaeocystis* Me/P, diatom Me/P has been well documented. Cullen et al. (2003) noted that diatoms made up most particulate material from his study site north of the Ross Sea, with *Fragillariopsis*, *Pseudonitzschia*, and *Nitzschia* dominating the sample matter. Our SEM images show that the frustules of these genera, in addition to other diatom genera such as *Corethron*,

appear throughout the water column. At the Northeastern Stations, where diatom abundance may be higher than at other stations, in agreement with the surface distribution of silicate (Maria Lagerström and Robert Sherrell, pers. comm. 2013), Zn/P and Cd/P fall tightly in the Zn+Fe addition range of diatom-dominated particulate matter from Cullen et al. (2003). This inference is very speculative considering the quantitative limitations and the lack of data (i.e., the exact community composition and Me/P for each community component).

The phytoplankton assemblage would certainly influence regional Cu/P variability. While no Cu/P for *Phaeocystis* has been measured, other prymnesiophyte Cu/P has been measured: *E. huxleyi*, 0.07 mmol/mol, and *G. oceanica*, 0.11 mmol/mol (Ho et al., 2003). The same study found Cu/P ranging between 0.17 mmol/mol and 0.28 mmol/mol. This suggests that diatoms tend to have higher Cu/P than prymnesiophytes. However, the Cu/P of prasinophytes, dinoflagellates, and chlorophytes have even higher Cu/P than do diatoms and prymnesiophytes. Interestingly, our average euphotic zone Cu/P is 2.10 mmol/mol, at least twice as high as the highest Cu/P in Ho et al. (2003). In contrast, our Cu/P compare well with other published Southern Ocean mixed assemblages (1.44 mmol/mol, Cullen et al. 2003; 2.0 mmol/mol, Collier and Edmond, 1984). These assemblages are dominated by large diatoms, however. This suggests that while our Cu/P may be somewhat influenced by diatoms with relatively high Cu requirements, other factors (such as total dCu and/or organically complexed Cu, as mentioned previously) may be more important.

# $4.2.6.2 \text{ pCO}_2$ and metal-metal interactions

The concentration of dissolved  $pCO_2$  has been shown to affect metal quotas (e.g. Cullen et al. 1999; Sunda and Huntsman 2005; Cullen and Sherrell, 2005; King et al., 2011). Cullen et al. (1999) showed that dissolved CO<sub>2</sub>, as well as Zn, exerts a strong influence on cadmium uptake in phytoplankton. Cadmium plays a role in inorganic carbon acquisition, by substituting for Zn in Zn-carbonic anhydrase (Zn-CA), or being used in a separate Cd-carbonic anhydrase found in some diatoms (Cd-CA; however, this likely makes up a negligible fraction of cellular Cd; Cullen et al., 2005). At low pCO<sub>2</sub>, CA activity is enhanced, leading to a higher demand for Zn and Cd. Consequently, low pCO<sub>2</sub> may result in higher Cd/P and Zn/P. However, if Zn is available at high concentrations, Cd uptake may not necessarily be higher under low pCO<sub>2</sub> as the Zn-Cd antagonism would hold under these circumstances, suppressing Cd uptake and counterign the CO<sub>2</sub> effect.

The regional trends in dissolved  $pCO_2$  do not correlate with either Zn/P or Cd/P, despite the potential control of  $pCO_2$  on cellular Zn and Cd through CA activity. The Northeastern Stations have the lowest  $pCO_2$  in the region, with values around ~100 ppm; these stations also have the lowest Zn/P and Cd/P of the polynya. The Western stations have higher  $pCO_2$  at 200 to 250 ppm, and have higher Zn/P and Cd/P than the Northeastern Stations. Finally, the Iceberg and Iron Curtain Stations have the highest  $pCO_2$  exceeding 350 ppm; Zn/P and Cd/P are highly variable in these regions.

If  $CO_2$  influenced CA activity, and thus Zn and/or Cd uptake, we might expect the low pCO<sub>2</sub> Northeastern Stations to have the highest Zn/P and Cd/P. Conversely, the ages of particles may explain the discrepancy. During the early stages of the bloom, CO<sub>2</sub> must have been higher, and was subsequently drawn down to ~100 ppm by primary production. If these cells or detrital particles produced by them remain from earlier in the season, the Zn/P and Cd/P may represent an environment with relatively higher CO<sub>2</sub>. However, considering the generally short residence time of particles and that ASPIRE sampling took place well after the phytoplankton bloom had started, such an explanation is highly speculative. Regardless, CO<sub>2</sub> does not seem to correlate with either Cd/P or Zn/P, suggesting that regional variability is dominated by other factors, such as metal bioavailability, biodilution, and taxonomic effects.

While CO<sub>2</sub> may not be the dominant control in regional Cd/P or Zn/P variability, CO<sub>2</sub> may influence smaller-scale variations within regions. The near-surface Cd/P and Zn/P in the Northeastern Stations generally follows TM21 > TM15 > TM17 > TM14 (these shallower data points are representative of the euphotic zone in this generally highbiomass region). The most highly productive among these stations, TM21, would not have the highest surface Cd/P or Zn/P if growth rate were the main control. Measurements of local CO<sub>2</sub> show TM21 having the lowest dissolved CO<sub>2</sub> at 100 ppm, and TM14 having the highest at 250 ppm; pCO<sub>2</sub> at TM15 and TM17 fall between these two values. Variability in Cd/P and Zn/P amongst the Northeastern Stations is very small, but these small variations may reflect local CO<sub>2</sub> concentrations and the CA activity of the phytoplankton assemblage.

Other dissolved trace metal concentrations can control Me/P ratios through uptake antagonism. That is, dissolved metals inhibit uptake of other metals through competition during uptake. In culture studies, cellular Cd/P decreases in response to increasing dZn and dMn, hypothesized to be a result of competitive inhibition at cellular uptake sites (Sunda and Huntsman 1996, 1998, 2000). Furthermore, culture studies of T. weissfolgii show that dCd and dFe may compete for cell surface transport sites (Foster and Morel 1982; Harrison and Morel 1983). If Zn is antagonistic towards Cd, then an inverse relationship is seen between Zn/P and Cd/P (Cullen et al., 1999). However, our Cd/P and Zn/P show no relationship with one another in the ASP (at best, a very weak positive correlation). The lack of antagonism may reflect dynamics of the relative availability of dZn and dCd in the polynya. Hutchins and Bruland (1998) found that Zn is drawn down first, and Cd is drawn down only after Zn is drawn down to the point where the availability ratio of dZn/dCd became very low. If this were happening in the ASP, then Cd/P would increase as dZn decreases (and dZn/dCd increases). In this case, Zn/P may decrease since dZn decreases. However, if the two metals are taken up in roughly the initial available ratio, dZn/dCd would not change. The latter scenario seems to be the case in the ASP, as Cd/P and Zn/P generally increase and decrease in tandem. Alternatively, the lack of antagonism may again be a taxa-specific phenomenon, and *Phaeocystis* may differ from diatoms in that respect. This is again speculation, since the metal uptake mechanisms of *Phaeocystis* have not yet been thoroughly studied.

# **5 CONCLUSION**

The Amundsen Sea Polynya, West Antartica, is a region of intense productivity that may, in combination with other Antarctic polynyas, play a significant role in influencing local and global climate. While primary productivity in most of the Southern Ocean is iron limited, coastal polynyas, including the Amundsen Sea Polynya, experience natural iron fertilization. High concentrations of particulate Fe are propelled from beneath the Dotson Ice Shelf and into the central Amundsen Sea Polynya, fueling long productive summertime phytoplankton blooms in this region. Our data show that this Fe is likely sourced from a combination of glacial particles released by ice shelf melting, resuspended sediments within the ice shelf cavity, and particles suspended in basal melt water from under the grounded glacier. The particulate Fe from this source contains a substantial fraction in chemically labile forms, and thus potentially bioavailable within the polynya. The provenance and flux of this labile particulate Fe is especially important when considering the effect of future Antarctic ice mass loss and melt water inputs to the coastal ocean of West Antarctica on future regional productivity.

The composition of the biogenic fraction of suspended particulate matter in the surface waters of the polynya also reveal new insights on metal uptake by phytoplankton under natural iron fertilization conditions. The results of this study represent novel quantification of the metal contents of phytoplankton assemblages dominated by *Phaeocystis antarctica*. Similar to previous findings with Antarctic diatoms, the Zn and Cd contents of the Amundsen blooms are generally high, but decrease in areas of highest productivity, likely a result of biodilution and/or reduced availability of dissolved Zn and Cd, driven by biological ligand production. Relatively high values and within-polynya

spatial variations in Cu/P may reflect a high demand for Cu by *Phaeocystis*, potentially due to a Cu-requiring Fe uptake mechanism under Fe limitation. As labile particulate Fe availability may be altered by climate change and ocean-ice interactions within future decades, these findings may have large implications for the cycling of trace metals in the Southern Ocean, and potentially in other oceanic basins.

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# 7 APPENDIX

**Table A1.** The total particulate (> $0.45\mu$ m) element concentrations (pM) for depth profile stations in the Amundsen Sea Polynya. Values have been corrected for residual sea salt contributions to each element. Blue shaded cells represent data that was not generated, while yellow shaded cells represent erroneously high values that have been omitted. Station locations and sampling times are given in Table A3.

тм	Depth (m)	Cd	Ва	Th	Al	Р	Ti	V	Mn	Fe	Со	Ni	Cu	Zn
	2	33.6	128.3	0.17	9471	29294	101.5	8.0	159.1	903	2.0	11.1	22.4	369.5
	10	39.1	140.7	0.15	5587	48834	114.0	8.7	177.5	1049	2.2	11.3	29.7	279.1
	25	44.6	154.3	0.17	4460	47957	144.5	10.0	184.9	1342	2.4	15.2	35.6	387.5
	50	1.8	375.0	1.86	64591	2508	3139.9	55.2	955.7	18416	9.0	12.1	35.1	65.8
	70	26.7	141.7	0.15	5042	19620	158.0	9.0	216.7	1176	1.9	8.2	23.4	168.4
5	100	9.4	175.3	0.18	5250	6500	173.6	12.9	356.1	1338	2.3	4.4	24.7	54.6
	150	9.6	167.7	0.39	12402	5592	476.4	20.3	618.2	3350	3.6	5.4	21.9	59.7
	250	4.1	183.5	1.06	41509	3396	1517.2	44.1	1379.3	11371	7.3	9.0	27.4	64.9
	360	4.0	217.7	0.77	33812	3085	1159.1	48.0	1658.4	9791	7.5	7.1	35.2	58.6
	559	0.9	257.8	0.47	21048	2143	879.0	17.1	263.8	5655	3.5	6.4	28.5	52.3
	636	6.9	440.8	0.86	35135	7225	1479.5	33.6	600.8	10053	6.2	12.1	39.2	78.7
	10	54.6	338.0	2.72	81208	146044	3499.0	77.3	914.4	18879	13.0	129.6	323.4	1330.4
	25	11.3	221.0	2.39	75318	31268	3348.7	71.3	783.2	20598	9.7	10.7	42.7	203.9
	50	4.4	136.0	1.08	41955	10005	1960.8	38.8	662.0	12539	6.5	9.9	26.3	185.8
	70	12.8	766.1	6.35	240832	14154	8658.7	269.4	7249.8	63928	34.3	39.5	120.2	290.2
	100	11.4	158.8	1.69	57066	29638	2453.5	56.7	533.7	14693	7.1	11.9	47.0	231.6
7	150	8.2	95.5	1.00	34056	25527	1454.4	36.0	374.7	8914	4.5	8.2	34.8	110.7
	260	9.9	173.9	1.53	57235	24787	2355.9	56.6	595.2	14772	6.8	12.4	38.3	198.1
	420	1.5	285.4	1.62	52293	1960	2535.5	40.6	804.0	14288	7.3	12.5	26.8	40.3
	640	1.9	26.3	0.26	11239	7719	477.2	9.5	97.1	2735	1.4	0.9	5.8	136.9
	750	2.8	91.1	0.54	20220	3834	804.2	27.5	404.7	5481	3.0	5.3	14.5	40.4
	1000	1.5	339.7	1.56	66859	2720	3174.3	45.5	834.4	17143	9.1	13.3	36.8	67.5
	1227	5.7	160.3	1.18	40529	3264	1780.5	45.5	1071.3	12157	6.7	11.0	20.4	56.1
	9	34.7	117.8	1.94	43927	115187	1904.7	45.2	482.2	8373	7.3	63.7	124.1	615.7
8	15	19.8	126.9	1.89	56332	55610	2312.1	49.3	451.5	13252	7.0	66.3	109.6	558.2
	25	12.4	77.4	1.00	33608	38053	1305.4	30.4	290.3	8648	4.2	41.6	76.5	220.6

	40	14.3	251.4	3.08	94964	38007	3570.1	78.1	979.4	24013	11.5	119.4	102.7	234.6
	85	15.3	142.9	1.91	48665	39662	1864.7	43.5	462.7	12206	6.0	47.3	95.3	231.2
	140	5.7	181.2	2.11	66875	6367	2440.3	57.7	1154.9	17132	7.3	14.2	33.3	90.2
	200	5.5	166.9	1.43	69715	3371	2323.9	45.9	1166.4	16018	7.8	9.5	24.8	62.7
	320	10.7	241.8	2.11	80213	6730	2896.2	74.1	2113.3	20792	10.7	17.8	35.5	99.9
	420	3.4	183.6	1.70	61509	3258	2226.9	55.3	1439.8	16027	8.2	10.5	26.7	64.7
	525	3.3	324.0	2.54	99716	4246	3654.4	92.6	2041.5	29966	12.6	17.3	41.2	93.8
	640	2.4	318.6	1.86	66897	2774	2441.0	58.4	1685.0	18474	8.1	19.7	49.7	79.0
	760	2.0	879.6	4.06	162706	4189	6049.1	123.8	2154.3	51171	18.3	34.2	54.2	157.1
	10	6.1	293.5	6.37	194160	15162	6432.4	128.1	1191.9	49807	16.6	30.5	54.6	625.5
	67	5.8	280.9	6.25	189048	11033	6077.6	114.8	1142.6	46783	15.5	28.2	43.4	177.6
	100	7.0	241.9	4.89	160118	9108	4885.8	94.7	1039.7	39203	13.3	22.8	36.0	153.9
	140	2.7	222.9	4.63	149116	4286	4779.0	93.8	1144.2	38069	12.8	20.1	31.5	404.9
	240	6.4	273.1	3.62	122639	4217	4406.6	91.1	1596.8	32786	12.5	16.7	34.8	107.2
9	280	2.0	432.2	2.70	102144	2963	3752.7	83.0	1941.7	31474	12.0	19.8	35.0	89.3
	320	9.9	383.6	5.02	180457	4469	7009.3	143.0	1960.7	54191	19.8	25.7	46.3	154.4
	350	5.6	305.2	3.38	116651	3819	4573.9	100.3	1686.6	36853	13.7	17.2	36.2	98.7
	440	3.2	357.3	3.71	138749	3757	6362.7	127.2	1653.0	43823	18.3	23.0	46.5	126.1
	600	5.0	226.8	3.58	120462	5331	3934.4	80.3	1388.4	30758	10.8	15.4	30.8	97.6
	740	3.7	354.1	4.17	147691	5986	5188.1	104.1	1704.9	42749	14.6	23.9	36.1	129.2
	10	5.1	328.2	4.31	148666	7381	5671.9	118.2	1594.7	44380	15.5	19.5	44.1	132.6
	90	4.7	269.4	3.16	124882	10117	5025.1	106.0	1326.5	40742	13.9	19.7	52.6	132.0
	160	5.1	209.8	3.07	114706	9285	4091.7	79.0	1029.9	28411	11.3	16.7	36.6	153.1
	240	3.3	273.6	2.91	113611	4666	4365.0	100.4	1707.4	37030	13.4	18.7	39.2	102.5
10	275	5.3	279.3	2.95	123236	4845	4873.2	96.8	1560.6	38571	13.2	18.5	35.8	114.0
	350	3.2	355.2	3.36	130025	4008	5798.3	121.8	1693.0	46505	17.0	18.6	42.0	108.5
	470	2.8	340.8	3.13	141387	3890	5974.2	117.3	1711.3	47080	16.4	19.1	39.0	110.6
	600	2.0	463.0	5.81	228464	3800	9064.9	182.8	2042.1	65203	25.4	37.4	52.3	175.2
	835	1.9	394.9	3.50	171405	3309	6547.3	138.2	2102.4	54734	19.2	25.6	41.6	122.6
	10	18.4	309.7	5.78	176062	33485	5936.1	121.2	1057.3	44398	15.9	29.9	58.2	421.3
11	20	16.7	264.7	4.80	148554	45269	4934.0	98.8	996.7	37558	13.4	23.5	62.9	296.4
	111	25.5	271.0	4.37	140098	28367	5114.0	97.0	1106.5	37097	13.2	22.8	53.5	314.9

	202	3.3	278.4	4.24	142286	4423	4795.1	98.9	1643.1	34418	13.2	18.9	37.6	127.7
	271	11.0	265.7	3.00	114569	10192	4321.5	91.5	1407.0	32367	12.8	19.1	41.2	163.7
	339	10.8	302.4	3.32	130081	4808	5053.0	103.6	1454.1	38351	14.2	18.0	35.3	131.1
	388				143125	3755	6872.0	139.3	2064.5	52556	19.3	25.4	42.8	145.9
	437	3.2	415.8	4.20	181173	3395	7265.3	160.8	2520.5	68869	21.3	31.0	47.7	149.9
	693	2.9	367.1	2.97	115025	2964	4313.8	104.5	1933.8	36663	14.7	20.7	44.0	
	739	4.4	541.2	4.39	162644	3997	6551.8	150.1	2750.7	54176	21.3	27.6	53.8	120.8
	1028	2.6	567.0	3.11	123736	3423	4408.0	113.1	3353.9	37515	17.7	23.9	53.8	
	1069	2.1	910.6	4.71	183720	4279	7109.8	146.0	2605.0	58693	19.9	35.9	52.0	154.8
	10	36.1	98.2	0.67	17962	88429	589.5	18.8	250.8	4089	3.7	33.4	60.5	474.7
	20	50.6	146.4	0.91	25463	123684	859.1	27.9	438.5	5716	5.6	49.9	94.1	598.0
	30	30.1	162.0	1.12	35150	64579	1182.0	30.9	416.0	8179	5.4	34.0	78.6	457.3
	50	21.2	99.2	0.67	20219	39736	697.3	19.2	308.9	4755	3.5	19.2	38.9	221.7
	72	22.2	159.5	0.87	26892	37884	960.4	25.3	437.1	6459	4.3	18.5	47.6	227.0
11	105	7.6	166.5	0.92	32880	10052	1360.4	36.1	664.3	9969	5.2	7.5	28.8	97.7
14	125	7.6	173.8	1.25	54449	6579	1931.5	43.8	819.1	13108	6.5	8.9	22.9	85.6
	150	7.7	263.7	2.07	83548	6467	2992.5	72.8	1206.9	21588	9.5	13.1	32.5	112.0
	175	6.8	232.3	1.73	77560	5563	2647.0	62.3	1107.7	18796	8.9	11.0	28.8	90.1
	200	6.2	307.2	2.72	125253	4802	4555.4	101.6	1544.6	32654	13.3	18.3	39.4	127.4
	250	6.8	557.3	5.26	232315	5417	8169.0	177.4	2338.6	63888	21.5	31.4	44.7	168.2
	285	7.0	538.0	5.28	248584	5232	8774.7	172.4	2182.0	64030	22.3	32.2	43.0	168.4
	10	89.0	124.7	1.08	28914	180100	933.0	38.7	402.2	6495	7.6	118.8	172.9	986.0
	20	90.6	127.7	1.18	29184	181444	1340.4	41.7	360.4	6881	6.9	159.6	210.0	976.6
	35	41.8	149.4	0.89	22121	82409	701.1	25.2	298.5	5039	5.2	68.5	132.2	545.9
	50	39.1	141.2	0.83	23831	71185	892.6	25.3	303.8	6052	5.0	61.5	127.7	464.9
	75	126.4	537.8	0.60	17209	114084	589.9	33.7	692.8	4279	8.1	44.7	112.0	1028.5
15	100	6.0	176.0	1.02	40209	12844	1453.4	36.1	584.6	9267	5.1	9.5	29.7	99.1
	180	5.7	221.7	1.76	68084	5151	2252.5	72.7	1393.1	17633	9.1	11.0	28.6	92.0
	240	6.6	274.8	2.44	97442	4250	3646.1	89.4	1890.6	26645	12.9	16.6	35.2	95.0
	310	7.9	307.5	2.26	105567	3657	3803.9	94.7	1839.3	29332	13.7	18.1	37.0	105.4
	350	6.2	246.6	1.22	64494	3080	2234.8	54.3	1493.0	15649	9.6	11.0	29.5	69.9
	416	2.7	418.0	2.08	97529	4141	3023.5	84.9	2955.4	24903	12.7	20.6	44.3	106.8

	10	144.7	138.6	0.70	12411	561164	415.5	37.0	562.3	3443	10.1	165.4	244.8	1392.8
	18	99.7	126.5	0.72	16353	245907	558.7	29.9	515.3	11006	7.6	118.0	204.4	1216.1
	28	104.3	170.2	0.96	20994	224807	713.5	39.3	510.3	5090	7.8	130.3	216.2	1227.4
	50	36.2	154.2	0.97	29360	100975	990.3	30.0	464.5	6900	5.8	54.8	137.9	523.8
	80	19.6	175.0	0.97	32090	50112	1155.8	34.8	531.5	7860	5.3	28.7	81.5	216.4
17	100	8.6	176.3	1.14	35671	19446	1278.2	38.1	636.4	8636	5.0	14.3	45.8	91.7
17	130	16.0	95.7	0.62	20191	31346	735.1	19.5	262.5	4575	3.2	20.9	64.7	296.8
	160	11.2	314.3	2.31	88091	12333	3003.4	90.4	1686.5	20746	11.2	15.2	61.2	112.3
	200	3.7	195.1	1.46	53654	3932	1766.3	58.9	1369.1	13777	7.7	8.5	29.7	83.7
	260	7.1	191.6	1.45	55812	3434	2065.0	55.2	1372.1	13746	7.7	8.7	24.3	75.3
	350	7.2	329.1	2.74	109281	4034	4063.6	103.2	2115.7	31317	14.6	20.0	41.1	129.2
	398	8.3	459.3	2.69	123804	4592	4127.1	105.2	2862.6	33609	14.7	36.5	43.1	139.1
	10	75.9	111.9	0.72	22805	146244	727.3	30.8	230.9	5482	4.9	121.5	173.2	960.1
	13	83.5	134.2	1.48	40185	153387	970.3	40.9	332.5	7284	5.4	165.0	197.6	1240.9
	33	86.5	127.4	0.94	28194	167892	1136.1	36.6	338.0	6783	6.8	170.3	205.7	794.6
	60	35.8	133.2	0.79	18941	58447	757.5	22.2	278.5	4995	4.6	51.1	107.8	537.1
	80	28.3	164.2	0.67	21457	48946	719.0	21.1	347.5	5247	4.3	33.6	83.8	328.7
21	120	7.8	151.3	0.77	23983	14657	853.3	25.5	555.9	6264	3.7	11.7	43.4	104.5
21	200	3.2	168.2	1.57	64305	3786	2212.2	55.4	1501.0	16593	8.1	12.5	27.0	66.4
	280	7.5	215.7	1.82	72292	3755	2463.1	66.6	1822.0	19500	9.4	11.9	30.5	80.4
	330	9.6	261.5	2.16	93893	3788	3381.8	76.5	1959.5	25539	11.8	16.4	36.5	105.4
	360	8.1	251.4	1.92	77863	5336	3092.0	75.9	1894.1	24234	11.2	14.9	37.4	105.2
	410	6.5	699.3	3.12	129755	4776	4534.0	105.8	2748.6	36020	15.0	26.0	44.0	129.8
	420	6.0	799.6	4.46	169306	4657	6313.5	159.7	3491.1	56066	19.5	35.0	53.4	174.2
	10	111.7	144.4	1.94	45830	210555	1851.5	63.3	551.2	11804	9.4	208.1	201.9	1856.4
	25	83.0	147.3	2.09	53239	159176	2145.3	61.5	537.1	13506	8.4	144.2	192.3	1174.0
	50	12.2	162.1	2.26	73742	34015	2803.3	60.6	482.2	18396	7.9	22.8	82.3	318.6
24	75	16.1	213.3	3.22	88912	31305	3519.4	75.6	574.8	22375	9.9	36.0	109.8	577.4
24	115	7.8	239.0	2.66	101954	19583	4334.5	93.6	1121.3	27778	12.3	21.4	59.2	191.6
	150	7.6	172.1	2.47	84391	12494	3110.1	72.8	1400.6	20511	10.2	16.8	44.5	151.3
-	170	7.0	203.2	2.42	88692	8808	3011.7	70.8	1637.9	20203	10.0	15.4	39.2	113.5
	320	7.5	202.5	1.85	67343	6757	2419.3	82.1	1916.0	17996	9.5	12.3	35.6	106.8

	500	3.5	344.3	2.16	87742	3676	3202.8	84.2	2122.6	25116	12.3	15.9	40.8	92.6
	650	5.7	189.2	1.46	57086	3500	2106.2	61.1	1466.2	14955	8.0	10.2	27.0	76.6
	850	2.2	352.8	1.58	74681	3283	2835.8	66.1	1576.0	21301	9.6	13.8	36.9	72.8
	1031	2.5	923.7	3.30	138549	4741	5131.8	115.7	2386.9	38976	16.4	27.9	47.8	121.1
	10	34.5	145.1	2.33	74816	85364	2835.5	70.9	655.4	21072	9.6	51.5	134.6	881.5
	30	50.5	176.1	2.86	92298	179028	3465.3	83.6	995.7	24681	12.2	60.8	147.3	1090.2
	60	43.5	153.1	2.69	86171	122304	3023.6	74.3	808.0	20228	9.7	56.2	124.8	696.9
	100	22.9	118.5	1.48	48096	44753	1821.9	41.3	415.8	12780	5.7	34.9	98.4	541.1
	140	15.2	181.6	2.57	85297	28949	3309.0	74.8	1202.4	23137	11.0	25.3	151.7	321.0
20	200	5.2	373.0	4.02	151757	7938	6504.2	143.8	2168.9	50157	18.5	24.7	48.7	160.1
26	240	4.1	381.5	3.50	173300	5277	6325.1	127.7	2194.6	50788	19.1	23.8	42.2	131.9
	300	6.2	466.5	4.41	208593	5640	8274.2	177.9	2546.5	71206	23.3	30.5	53.0	210.7
	400	4.8	402.3	3.13	168107	3836	6363.1	130.6	2274.7	51851	18.5	24.4	41.4	132.5
	500	2.6	509.6	4.45	224301	3816	8155.3	171.9	2909.3	72557	24.1	33.5	50.9	155.0
	680	1.1	181.3	1.35	66976	1518	2473.9	59.2	1367.0	20735	8.1	10.7	21.7	56.7
	735	2.1	627.8	2.91	140734	4282	5462.3	121.9	3046.0	41960	16.8	29.6	49.5	129.9
	10	31.5	204.7	4.21	128862	65525	4557.2	93.5	1108.5	34936	12.1	28.4	70.9	599.5
	40	31.5	325.4	4.96	144985	49833	5801.4	118.0	1373.8	39968	15.2	25.7	65.0	463.0
	70	4.0	392.9	5.79	178055	5431	7140.6	143.6	1584.8	52576	17.9	22.8	38.0	124.3
	150	3.3	523.1	7.16	252918	5126	10269.4	211.8	2714.2	88638	25.8	34.2	52.1	151.9
	180				270359	4602	10881.0	217.1	2440.8	84880	27.7	37.2	51.6	180.7
20	200	2.3	562.2	6.71	310059	4538	12031.6	230.4	2515.6	92437	30.6	37.8	54.4	203.7
29	240	2.7	584.9	7.91	275834	5175	13489.7	244.3	2288.5	88105	32.4	38.5	57.1	206.9
	260	2.5	592.8	7.60	310544	5025	13168.3	232.2	2385.5	87477	31.9	39.6	55.6	207.2
	300	2.4	559.3	6.32	291566	4253	11482.1	219.6	2760.8	90094	30.8	40.6	57.9	224.5
	400	2.4	544.6	7.51	260598	4196	10451.4	227.2	2340.5	79754	30.0	45.6	54.9	202.3
	500	2.6	613.5	7.51	256655	4272	11670.7	245.3	2479.5	82920	31.5	49.4	56.0	200.7
	615	2.5	527.4	6.12	237444	4077	10190.8	215.1	2469.1	75921	26.9	42.1	53.7	177.0
	20	52.8	128.6	1.98	56787	157780	2224.7	58.4	899.9	15434	9.4	80.6	139.0	786.1
20	100	8.5	279.0	3.38	132995	12364	5048.9	102.5	1522.9	43172	14.1	23.7	52.9	176.8
30	150	3.9	293.0	3.03	144116	6342	5451.6	108.1	1833.5	40664	15.9	23.7	45.8	142.3
	200	3.5	457.8	4.38	216609	5088	8111.3	168.3	2625.5	71557	22.7	31.1	52.1	195.9

	227	5.5	420.5	3.70	190314	6275	6686.6	142.8	2611.4	55744	19.9	27.6	48.7	160.8
	236	5.1	483.6	5.12	228506	5819	8531.7	181.0	2618.1	80653	24.2	33.2	55.0	168.0
	280	5.6	224.9	2.18	97090	3728	3228.4	82.4	2317.6	25591	12.1	14.6	33.6	92.6
	305	6.2	210.4	1.70	71112	7162	2528.4	68.1	2096.3	20223	10.1	11.2	30.0	85.4
	340	6.0	320.9	2.58	128244	4189	4703.9	100.9	2291.6	35290	15.7	20.8	38.0	136.1
	450	3.8	362.4	2.93	132499	3197	4554.4	101.9	2257.2	37903	16.0	21.8	39.7	117.1
	546	2.5	353.4	1.83	92552	3476	3479.4	82.1	2499.1	25603	11.8	16.1	38.4	82.7
	640	1.6	496.0	2.33	109985	3426	4178.0	86.7	2213.1	33503	13.2	26.5	41.5	108.3
	100	12.8	237.9	3.47	116685	22300	4984.8	102.4	1271.1	34620	14.0	23.2	59.8	241.2
	140	14.3	281.0	3.72	138684	19558	5460.6	112.0	1712.1	38432	15.7	27.1	60.3	213.4
	175	4.9	516.8	5.05	249250	7050	9604.5	201.2	2827.5	86774	26.7	37.2	61.5	216.2
	197	5.2	354.3	3.90	158272	7794	6664.1	134.7	2083.9	47953	18.1	26.8	47.4	143.9
	235	7.9	438.9	4.80	210449	8576	7609.1	199.1	2623.1	63136	22.4	32.1	55.6	190.6
21	278	3.1	242.7	1.91	83713	4350	5001.7	115.1	2062.7	36216	15.0	19.8	37.4	114.4
31	290	4.9	312.5	3.08	139320	5335	5016.7	113.5	2341.3	39979	15.3	23.0	41.6	114.8
	301	4.3	376.0	3.65	154264	4075	6289.9	137.1	2436.7	53595	18.8	25.4	43.9	146.3
	332	5.2	447.1	4.52	232425	5766	9664.6	174.6	2585.3	78416	25.6	35.3	53.4	197.9
	360	3.3	430.7	4.05	224499	4585	9070.6	169.9	2674.8	79664	25.2	33.2	51.3	171.0
	400	4.2	440.5	4.21	199554	4690	8694.1	177.1	2386.8	70901	24.4	33.9	52.3	168.8
	500	2.7	408.7	3.13	153085	3436	5881.0	134.6	2343.1	59994	19.9	30.0	46.3	137.4
	10	85.1	108.4	0.99	24907	144248	1078.1	34.9	470.8	5799	6.8	162.7	210.5	1049.2
	25	66.0	127.3	1.16	35565	154986	1252.0	38.8	473.0	8060	6.8	176.7	218.0	917.3
	40	7.7	101.7	1.16	40402	22868	1763.4	40.3	381.5	10252	5.2	7.6	29.5	133.0
	60	12.9	162.2	1.70	42879	43046	1630.1	42.1	464.3	10096	5.2	38.3	98.4	332.9
	100	9.5	193.8	1.73	58468	23644	2348.3	62.0	980.8	15136	7.4	29.5	74.8	207.0
24	150	12.9	162.2	3.84	66333	7789	2609.8	70.6	1518.8	17736	8.9	15.7	40.0	93.4
34	200	3.5	40.0	0.45	13783	10560	618.5	15.4	157.1	3741	1.8	3.3	14.3	47.3
	300	5.4	170.1	1.32	44886	3363	2014.3	63.5	1618.5	13487	8.2	7.9	27.2	68.2
	380	7.3	225.0	1.86	67051	4791	2567.1	83.8	1955.7	17546	10.1	12.0	33.2	82.7
	500	6.4	281.3	2.00	80243	3773	3255.8	75.7	1648.5	21941	11.5	14.9	34.0	124.1
	610	2.5	431.6	1.35	58840	4089	2177.8	46.9	1270.0	15232	8.3	14.0	38.7	65.3
	640	1.9	1074.4	3.24	134768	4242	5243.7	101.7	2540.0	36428	16.5	40.2	53.2	131.2

ТМ	Depth (m)	Cd	Ва	Th	Al	Р	Ti	v	Mn	Fe	Со	Ni	Cu	Zn
	10	0.0	-1.4	0.0	-82.5	227.1	-0.4	0.0	-1.9	1.3	0.0	-0.6	5.0	9.0
	50	6.7	150.1	0.5	24291.9	6547.2	156.1	54.4	3047.4	18044.5	14.1	25.7	43.5	175.6
F	100	9.4	84.0	0.0	284.1	3905.7	0.4	8.9	352.8	315.5	1.8	5.4	15.4	51.5
5	250	4.3	83.2	0.2	4156.2	2167.3	50.6	20.0	1260.9	3235.8	5.1	6.6	18.1	79.4
	460	1.6	130.9	0.2	5465.1	2048.4	63.8	14.7	867.4	3608.1	5.8	11.8	29.1	67.0
	636	8.3	95.0	0.1	3140.6	5035.2	20.1	10.3	573.0	2136.7	4.4	11.1	27.6	58.4
	15	22.6	57.7	0.2	7799.3	38860.7	34.8	16.8	341.1	2724.5	3.5	57.3	61.9	384.6
	40	11.7	135.9	0.2	9778.0	21487.6	83.5	24.8	981.8	6215.8	6.7	39.0	52.6	307.5
0	140	5.7	52.4	0.3	5343.6	4025.4	52.3	18.8	958.7	3868.1	3.8	9.1	18.4	93.8
0	320	11.5	84.4	0.5	8251.8	3187.6	97.9	33.5	2100.4	5960.4	7.2	9.4	23.7	96.0
	525	2.7	107.1	0.4	8585.5	2264.9	104.3	24.3	1452.4	6288.9	6.0	9.5	20.0	59.7
	760	1.9	214.7	0.4	12956.0	2162.0	100.3	24.6	1568.9	9028.3	8.6	18.0	29.4	59.4
	10	7.2	64.9	0.1	1603.2	7530.6	6.7	8.4	412.6	1074.4	2.0	9.3	14.8	74.5
	100	0.0	-0.8	0.0	10170.2	2745.3	122.7	29.4	1798.9	7651.1	7.1	11.5	23.6	77.3
0	240	17.0	39.3	0.1	737.9	20408.2	3.1	4.4	98.2	395.4	1.2	27.1	20.8	263.8
9	320	12.1	138.0	0.4	26160.9	3093.4	296.0	50.4	2286.2	18340.1	13.4	18.1	39.2	112.1
	440	4.0	118.2	0.4	26469.9	3115.6	308.5	47.3	2169.5	17511.8	12.6	17.7	40.5	130.6
	740	3.1	169.3	0.3	16558.1	2505.4	132.5	46.5	3491.7	12491.7	11.2	21.9	35.6	84.3
	13	131.1	54.3	0.4	1987.8	157396.3	18.7	23.0	404.6	1207.1	6.8	243.1	148.6	1707.1
	60	26.3	95.0	1.6	30227.2	21661.6	202.8	67.6	2168.0	21926.3	18.7	35.5	67.6	297.8
21	120	2.7	299.0	1.3	51333.1	4654.1	1129.5	79.8	2777.3	32923.5	21.4	29.4	55.7	198.1
21	280	8.3	92.1	0.4	6743.7	2240.2	98.5	23.8	1504.3	4973.0	6.1	7.7	20.4	108.9
	360	9.3	112.8	0.4	10962.7	2203.6	175.1	31.0	1672.6	8040.5	8.5	11.0	27.0	77.6
	420	7.5	240.7	0.5	18901.0	3679.6	127.8	53.1	4334.1	14041.2	12.9	25.3	38.9	132.9
	40	38.4	45.8	0.0	230.3	21725.7	-0.5	5.9	218.9	240.6	1.8	13.7	18.2	208.2
	150	40.0	59.3	0.6	15094.8	51925.9	163.6	34.1	1334.0	9498.8	8.7	24.1	44.1	589.6
20	200	2.4	169.8	0.3	42797.7	3863.4	564.9	66.6	2161.6	28337.3	18.3	24.5	46.8	166.3
29	300	2.6	166.6	0.4	43199.2	3514.5	620.3	67.2	2247.6	29572.7	18.7	26.0	46.0	178.9
	500	2.6	135.5	0.3	29776.9	2819.6	362.7	55.4	2062.9	22266.3	16.2	25.3	40.2	203.3
	615	2.6	140.7	0.4	35285.5	3423.5	419.9	62.8	2655.1	24930.1	17.7	26.0	44.4	133.8

**Table A2**. The labile particulate element concentrations (pM) at selected stations and depths in the Amundsen Sea Polynya, as determined by weak acid chemical leaching. Negative values represent blank overcorrection. Station locations and sampling times are given in Table A3.

Sta. TM	Date	Time GMT	Latitude	Longitude
5	12/13/10	14:09:36	-71.952	-118.474
7	12/15/10	5:47:32	-73.967	-118.035
8	12/15/10	21:24:11	-73.170	-115.000
9	12/17/10	8:20:19	-74.220	-112.002
10	12/17/10	16:02:08	-74.186	-113.251
11	12/18/10	1:40:39	-74.209	-112.507
14	12/20/10	5:19:53	-73.541	-110.582
15	12/21/10	20:22:56	-72.998	-113.312
17	12/23/10	0:59:56	-73.121	-112.000
21	12/26/10	20:43:08	-73.278	-112.105
24	12/29/10	16:25:37	-73.416	-115.250
26	12/31/10	22:41:57	-73.800	-113.172
29	1/2/11	8:27:50	-74.176	-113.341
30	1/2/11	23:06:29	-73.649	-113.224
31	1/3/11	6:19:25	-73.650	-113.610
34	1/5/11	23:08:03	-72.741	-116.017

**Table A3.** Summary of APIRE station number, date and time of sampling, and latitude and longitude (decimal degrees, negative means south Latitude and west longitude) for each station at which particulate trace metals were determined.