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Bioactive trace metal distributions and biogeochemical controls in the Southern Ocean

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Bioactive Trace Metal Distributions and Biogeochemical Controls in the Southern Ocean

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(ABOVE) Rosette with GOFLOs on a Kevlar wire for clean sampling. (LEFT) Shipboard analysis of trace metals in the trace metal container van. (RIGHT) Subsampling GOFLOs in the trace metal container van. *Photos © Chris Linder*

ABSTRACT. Extensive sampling in many regions of the Southern Ocean has demonstrated that surface water concentrations of dissolved Fe are low enough to limit phytoplankton growth. In contrast, there is currently no evidence that other bioactive elements (e.g., Mn, Zn, Co) are similarly limiting. Although atmospheric input of dissolved Fe to Southern Ocean surface waters appears to be low, resuspension of sediments from shallow regions around islands and the Antarctic coastline can inject significant amounts of Fe into the surrounding waters, stimulating primary production and providing a natural laboratory for studying the response of biological systems to natural Fe fertilization processes. Future work using a multitracer approach across seasonal transitions would be particularly beneficial to quantifying input processes and fluxes. However, it would require the design of new sampling platforms that can accommodate trace metal sampling under extreme weather conditions.

INTRODUCTION

Ironically, it was a pair of manuscripts about trace element distributions in the Northeast Pacific, specifically in the Gulf of Alaska, that stimulated much of the recent interest in trace element distributions in the Southern Ocean. The essence of those manuscripts (Martin and Fitzwater, 1988; Martin et al., 1989) was that the surface waters of the Gulf of Alaska contained such low levels of dissolved Fe that this limited the ability of phytoplankton to grow in these waters and to remove the readily available macronutrients, NO_3, PO_4, and $Si(OH)_4$. This hypothesis, initially suggested by Gran (1931) and Hart (1934), was confirmed by showing that the addition of Fe to deckboard incubations resulted in increased chlorophyll *a* and depletion of NO_3 and PO_4 over that in the controls. The conclusion that the biological state of this area, which had long been recognized as a High Nutrient Low Chlorophyll (HNLC) region, was due to the scarcity of dissolved Fe, and the suggestion that the Southern Ocean, another HNLC region, was similarly Fe limited provoked a lively debate within the oceanographic community (see Chisholm and Morel, 1991).

Understanding the circumstances that lead to incomplete biological utilization of macronutrients in HNLC regions had been of great interest to oceanographers for some time for several reasons. One of the most pressing topical reasons was the relationship between HNLC regions and the global carbon cycle. The "fixing" of oceanic dissolved CO_2 into particulate organic carbon by phytoplankton in oceanic surface waters and its subsequent export via vertical particle settling results in a net transfer of carbon from the surface to the deep ocean. Because CO_2 in the atmosphere and dissolved CO_2 in the surface ocean are constantly equilibrating, this removal of surface carbon by the "biological pump" has the net effect of reducing atmospheric CO_2 levels. Thus, it had been recognized that the excess macronutrients in Southern Ocean surface waters represented a large inefficiency in the ocean's nutrient cycling, limiting the ocean's ability to take up atmospheric CO_2. This realization led Martin (1990) to postulate the "glacial Fe hypothesis," which explicitly suggested that enhanced Fe delivery to Southern Ocean surface waters as a result of increased atmospheric dust loads during the last glacial maximum could have been responsible for a 2–4 Gt C yr^{-1} increase in primary productivity, resulting in lowered atmospheric CO_2. Martin's calculation that the addition of Fe to contemporary Southern Ocean surface waters could support the removal of 3 Gt C yr^{-1} provoked immediate interest among those who were seeking CO_2 sinks to ameliorate the effects of anthropogenic CO_2 production (see Chisholm and Morel, 1991). At a more fundamental scientific level though, the inability to explain the factors that led to the formation of these unique oceanic ecosystems indicated a profound gap in our understanding of how biological, chemical, and physical processes operate and interact in large parts of the contemporary ocean. This lack of knowledge in turn limits our ability to make meaningful biogeochemical models of the ocean that can be used to predict oceanic responses to future climate forcing.

But, we are getting ahead of the story in many ways, as it is important first to discuss the evolution of the determination of trace elements in seawater before focusing on the particular interest of establishing their distribution patterns in the Southern Ocean. This history will help us understand the background to the development of the Fe hypothesis and the problems that subsequent investigators faced in the Southern Ocean.

Starting in the early 1970s, chemical oceanographers turned their attention to determining elements and isotopes in seawater that were far less abundant than the commonly measured species, allowing them to explore new regions

of the periodic table for useful oceanographic tracers. Pure scientific curiosity fueled much of this initial work, which was made possible by advances in the design of analytical equipment that reduced detection limits and the development of materials that permitted metal-free handling of samples. Another very important stimulus was the development and implementation of the GEOSECS (Geochemical Ocean Sections Study) program in the 1970s (Craig and Turekian, 1980), which provided the very first global sampling program, and brought samples from remote regions to laboratories that were not equipped to mount their own seagoing research programs. At first, the race to "fill in" the periodic table with what came to be called "trace elements and isotopes" focused on obtaining representative profiles of each element in different ocean basins to delineate their types of behavior (e.g., nutrient-like, scavenged, conservative) and to determine their oceanic residence times. This "chemical prospecting" phase reached maturity by the late 1980s, and attention then turned to using these elements to identify and constrain oceanic processes.

Focusing on a restricted number of trace elements that yielded important oceanic insights provided an impetus to improve analytical techniques to expand the database and to permit shipboard determinations. As the analytical frontiers were pushed back and interest focused on ubiquitous elements such as Fe, Zn, and Pb, it became clear that there were major issues with contamination of water samples during either collection or analysis. The realization that much early data for contamination-prone elements was compromised by blanks motivated a community-wide reassessment of sampling and handling methodologies. Claire Patterson's drive to determine the pre-anthropogenic concentration of Pb in deep Pacific seawater led him to develop a specialized clean sampling system (Schaule and Patterson, 1977). Although obtaining only one sample per deployment, this sampler showed, for the first time, that the vertical distributions of contamination-prone trace species were not highly variable as had been previously thought, but had "oceanographically consistent" distributions (Sclater et al., 1976).

The first oceanographically consistent distributions of dissolved Fe were published by Landing and Bruland (1987) as a result of adopting nonmetallic hydrowires (Kevlar) and GO-FLO sampling bottles with no internal springs (Bruland et al., 1979). This work indicated that dissolved Fe levels in the eastern Pacific surface ocean were ~ 0.1–0.7 nM, an order of magnitude lower than previously reported. Martin's group, which was particularly interested in the effect of trace elements on phytoplankton primary production, extended this work to the sub-Arctic Pacific, and it ultimately led to the development of the "glacial Fe hypothesis" described above. These findings inspired scientists to investigate the much larger HNLC region of the Southern Ocean to see if low Fe was also limiting production in this region. The story of trace element work in the Southern Ocean is therefore heavily focused on the distribution of dissolved Fe and other bioactive trace elements. Although the Antarctic Treaty defines the Southern Ocean as being south of 60°S, we will discuss data sets that include more northern regimes, up to the Subtropical Front where the transition between subtropical and sub-Antarctic surface waters occurs (Orsi et al., 1995), and where we observe large changes in the chemistry of the surface water, particularly the availability of unused macronutrients (such as NO_3), a central part of our story. See Figure 1; figures were created using Ocean Data View software (Schlitzer, 2011).

Fe CONCENTRATIONS IN THE SOUTHERN OCEAN

The phenomenon of Fe limitation arises from its low solubility in oxygenated seawater. The vertical transport and decomposition of biological material leads to the transport and release of nutrients from the surface to the oceanic interior. The insolubility of the remineralized dissolved Fe makes it susceptible to removal from the water column by scavenging processes, thereby fractionating it from the macronutrients that are not scavenged. For this reason, when nutrient-rich deep water is returned to the sunlit ocean via upwelling, the ratio of Fe to the accompanying nutrients is below that required for biological uptake. In most regions of the ocean, surface water dissolved Fe concentrations are "topped up" by addition from external sources. However, in the Southern Ocean, the combination of very high rates of ventilation producing large fluxes of macronutrients to surface waters and weak external sources of Fe to facilitate "topping up" results in surface waters that are deficient in Fe relative to macronutrients needed to sustain primary production.

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The Atlantic and Drake Passage Sectors of the Southern Ocean

The Atlantic and Drake Passage sectors of the Southern Ocean, which are the most accessible, are by far the most studied areas of the Southern Ocean to date with respect to Fe (Figure 1). John Martin's group was the first to provide direct evidence that Southern Ocean phytoplankton growth was limited by this Fe deficiency, thus supporting the Fe hypothesis. They incubated samples and observed enhanced phytoplankton growth and nutrient drawdown in those with Fe addition over the unamended controls (Martin et al., 1990a,b). Much of the early work still suffered from sample contamination issues that bedeviled earlier trace element work in other places. The earliest work that produced reliable results that have been replicated by later investigators used GO-FLO or homemade plastic bottles suspended individually on Kevlar or other nonmetallic line.

Westerlund and Öhman (1991) reported a small number of upper water column dissolved Fe values in the Weddell Sea that were mostly less than 1 nM, similar to values reported for raft collected samples by Sanudo-Wilhelmy et al. (2002) and consistent with Fe limitation in this macronutrient rich area. Croot et al. (2004) reported values along 6°E between ~ 50° and 60°S that are generally 0.3 nM or less in upper waters. Chever et al. (2010) similarly show dissolved Fe values of < 0.25 nM in the upper waters between 42° and 58°S along 0° during the International Polar Year BONUS-GOODHOPE cruise. Recently, Klunder et al. (2011) using a custom-built titanium rosette deployed using a Kevlar cable, show values of < 0.25 nM throughout the latitude range 40°–70°S along 0°.

The Pacific Sector of the Southern Ocean

The first systematic seasonal study of dissolved Fe in Southern Ocean waters was undertaken during US JGOFS (Joint Global Ocean Flux Study), which mounted six research cruises between October 1996 and March 1998 along 170°W from 53°S into the Ross Sea. This project pioneered the use of GO-FLO bottles on an uninstrumented, polymer-covered rosette frame (Hunter et al., 1996), a technique later extended to fully instrumented commercial rosettes (Measures et al., 2008). The results from US JGOFS work (Measures and Vink, 2001; Coale et al., 2005) showed that, despite the ~ 0.1 nM difference between the two data sets, there was general agreement that Fe concentrations dropped dramatically from up to 0.34 nM near the retreating ice edge in the Antarctic Circumpolar Current at 64°S to 0.075 nM in the northern Ross Sea at 71°S in March at the end of the growing season. Coale et al. (2005) found dissolved Fe values in the upper waters of the southern part of the Ross Sea (0.05–0.4 nM) to be significantly higher than those they had seen in the Antarctic Circumpolar Current, and they attributed this higher number to melting sea ice

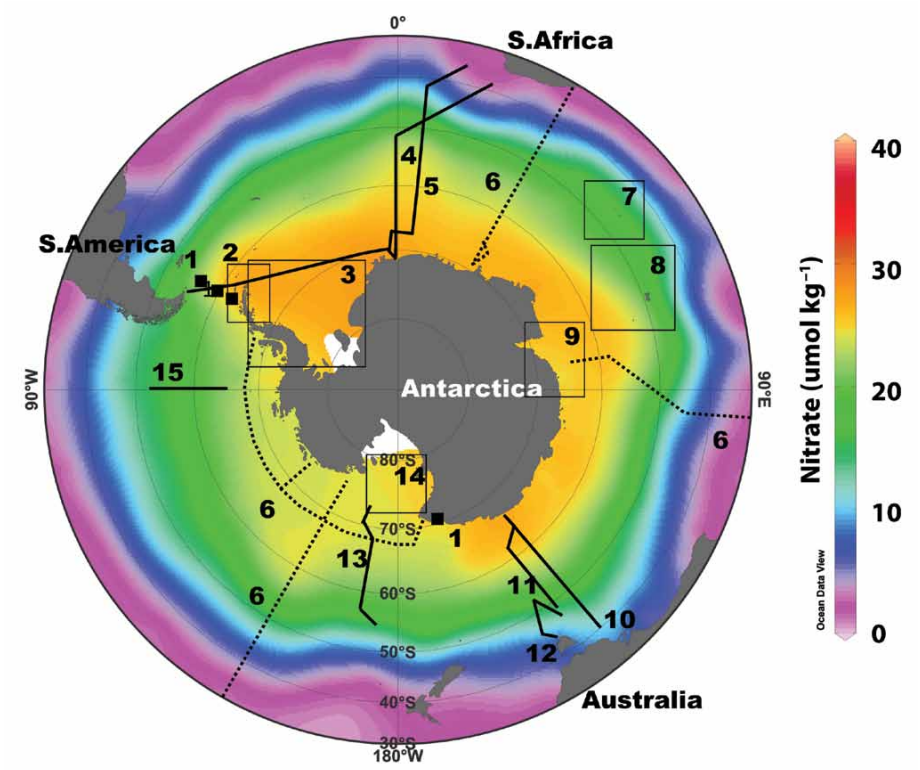

Figure 1. Southern Ocean map showing the sampling locations of the Fe data discussed in this paper with surface nitrate concentrations overlaid (µmol kg^{-1}; eWOCE, http://www.ewoce.org). 1 Martin et al. (1990a,b); 2 Hatta et al. (2008); 3 Westerlund and Öhman (1991), Sanudo-Wilhelmy et al. (2002), Smith et al. (2007); 4 Chever et al. (2010); Bown et al. (2011), Klunder et al. (2011); 5 Croot et al. (2004); 6 Measures et al. (2010); 7 Bucciarelli et al. (2001); 8 Planquette et al. (2007); 9 Lannuzel et al. (2007); 10 Sedwick et al. (1997; 2008); 11 Sohrin et al. (2000); 12 Bowie et al. (2009); 13 Hunter et al. (1996), Measures and Vink (2001), Coale et al. (2005); 14 Martin et al. (1990b), Sedwick and DiTullio (1997), Sedwick et al. (2000), Coale et al. (2005); 15 de Baar et al. (1999).

from Fe-rich nearshore areas or release of aerosols accumulated on sea ice.

Sedwick et al. (2000) also found southern Ross Sea Fe values that were significantly higher than those in the Antarctic Circumpolar Current. Their spring upper 300 m dissolved Fe values ranged from 0.45–3.8 nM. They suggest that the highest value might reflect sedimentary inputs from nearby Franklin Island and other elevated values from melting ice. The summer values were much lower, ranging from 0.09–0.57 nM, but two stations exhibited significantly higher values ascribed to melting ice. A station near one occupied by Coale et al. (2005) showed similar values in the 0.2–0.3 nM range. At stations where surface water Fe was 0.17 nM, incubation work showed that both growth and nutrient removal were stimulated by Fe addition compared to controls.

In the area south of Tasmania, Sedwick et al. (1997), using custom-built polycarbonate bottles mounted on a Polybraid nonmetallic line, reported the first consistent data for the Australian sector of the Southern Ocean. Their data, collected along 140°E, showed values dropping from 0.59 nM in offshore subtropical surface waters at 40°S to 0.1–0.2 nM in the upper 50 m south of 50°S. They also speculated that resuspension of sediments might contribute to the higher values over the Tasman shelf, a subject we return to later. They also concluded that the low levels of Fe seen south of 50° could result in Fe limitation of production.

Additional sampling along the CLIVAR (Climate Variability and Predictability) SR3 cruise track (Sedwick et al., 2008) showed Fe values decreasing from 0.8 nM in the Subtropical Front region during fall to < 0.1 nM at 64°S in spring. Similar values (< 0.3 nM) were obtained for labile Fe (i.e., unfiltered) by Sohrin et al., (2000) using a conventional rosette lowered on a titanium wire. While Sedwick et al. (2008) suggest that aerosol deposition might play a role in supplying Fe to the region, they also invoke southward advection of Fe-enriched subtropical waters and input from marginal sediments as likely to be more important. Bowie et al. (2009) also invoke shelf processes as a supply mechanism at their stations southeast of Tasmania.

The EU JGOFS program in 1995 sampled between 52° and 68°S along ~ 90°W using GO-FLO bottles mounted on a Kevlar cable (de Baar et al., 1999). Dissolved Fe values ~ 0.3 nM north of the Subantarctic Front dropped to 0.2 nM or less in the Antarctic Circumpolar Current, similar to those reported for the other regions of the Pacific sector of the Southern Ocean.

Thus, when all the reliable data sets throughout the Southern Ocean are combined, Fe concentrations are extremely low south of the Subtropical Front, coincident with the onset of HNLC conditions with little in the way of zonal gradients, and complementary incubation experiments have always demonstrated a growth response to added Fe above that of the controls.

SOURCES OF Fe TO THE SOUTHERN OCEAN

The spatial distribution of dissolved Fe in combination with other tracers has been used to identify the principal sources of Fe to the Southern Ocean. As discussed above, external sources are needed to provide an additional source of Fe. There are three main external sources of trace elements to the Southern Ocean (Figure 2): (1) from the atmosphere via deposition and partial dissolution of mineral dust in surface waters, (2) resuspension of sediments

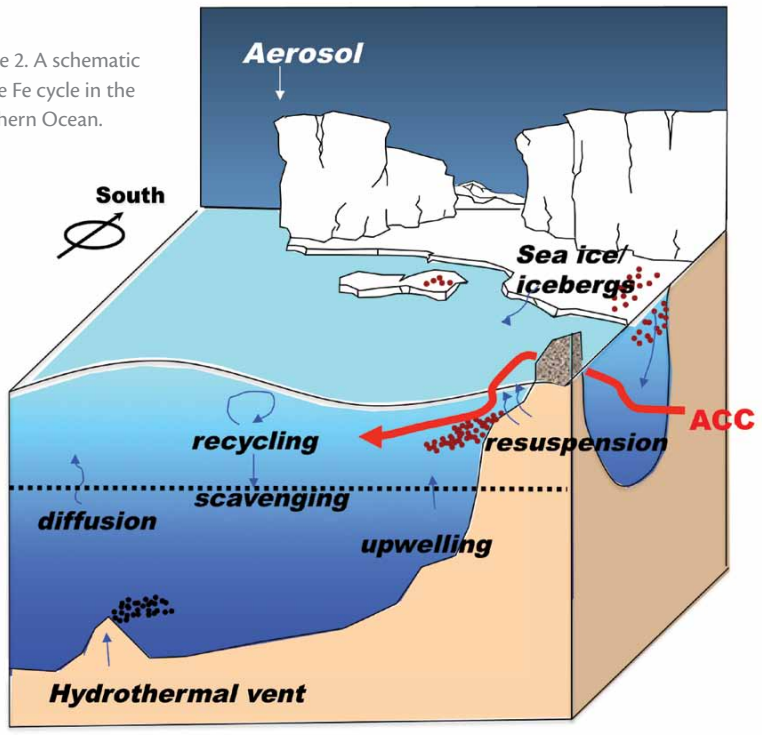

Figure 2. A schematic of the Fe cycle in the Southern Ocean.

in coastal regions releasing pore waters and particulate material into the water column, and (3) melting of sea ice or icebergs. Although hydrothermal vents provide an important Fe flux to intermediate and deep waters of the Southern Ocean (Tagliabue et al., 2010), it is not clear whether hydrothermal Fe reaches the euphotic zone, thereby impacting phytoplankton growth. Recent advances in the analysis of Fe isotopes in open ocean seawater (Lacan et al., 2010) may help constrain the magnitude of this hydrothermal flux to Southern Ocean surface waters.

ESTIMATING ATMOSPHERIC DEPOSITION TO THE SOUTHERN OCEAN

The amount of crustal material deposited on the surface ocean from the atmosphere has been the subject of significant research over many years. It is of particular importance to understanding of HNLC regions because average crustal materials contain high levels of Fe, ~ 1 mmol g^{-1} (Wedepohl, 1995). Duce et al. (1991) showed atmospheric deposition values ranging from > 20 g mineral dust m^{-2} yr^{-1} in regions near the Sahara to less than 0.1 g m^{-2} yr^{-1} over the remote Southern Ocean, which has little or no nearby ice-free land masses to generate mineral aerosols. However, these estimates were made using the mass of aerosols collected on sampling towers situated on land that were then extrapolated out over the ocean. In other words, there were no actual data from the ocean, and regional coverage was limited in oceanic areas without landmasses. Although there are now sampling programs that regularly collect aerosol samples from research vessels (Buck et al., 2010), the short duration of oceanic cruises means that these data represent only brief time periods, and thus, given the highly sporadic nature of dust deposition events, it is hard to generate reliable annual estimates from these extrapolated values. An alternate approach by Measures and Brown (1996) uses the concentration of dissolved Al in surface waters as a recorder of the input and partial dissolution of crustal aluminosilicates. The estimated residence time of dissolved Al in surface waters implies that these values represent a five-year running average of dust deposition. Recent work has shown that other elements, such as ^{232}Th, can also be used as tracers for mineral dust deposition (Hsieh et al., 2011).

Using US JGOFS data (Measures and Vink, 2001) and our unpublished dissolved Al data from the surface samples of several CLIVAR cruises (Measures et al., 2010), we can calculate mineral aerosol deposition to the surface ocean. We convert this number to an estimate of annual dissolved Fe deposition by assuming the Fe content of mineral dust is equivalent to average crustal material (1 mmol g^{-1} Fe by weight; Wedepohl, 1995) and that 5% of this material will dissolve in the surface waters (Figure 3). While these particular values are reasonable, they are not sacrosanct because there will be variations in both the Fe content of the mineral dust and its fractional solubility. Nevertheless, these values can serve as rough estimates of the amount of dissolved Fe addition to Southern Ocean surface waters from this process. Figure 3 suggests that over most of the Southern Ocean, dissolved Fe deposition is < 5 µmol Fe m^{-2} yr^{-1}, which is close to the snow sample values of Edwards and Sedwick (2001). If added

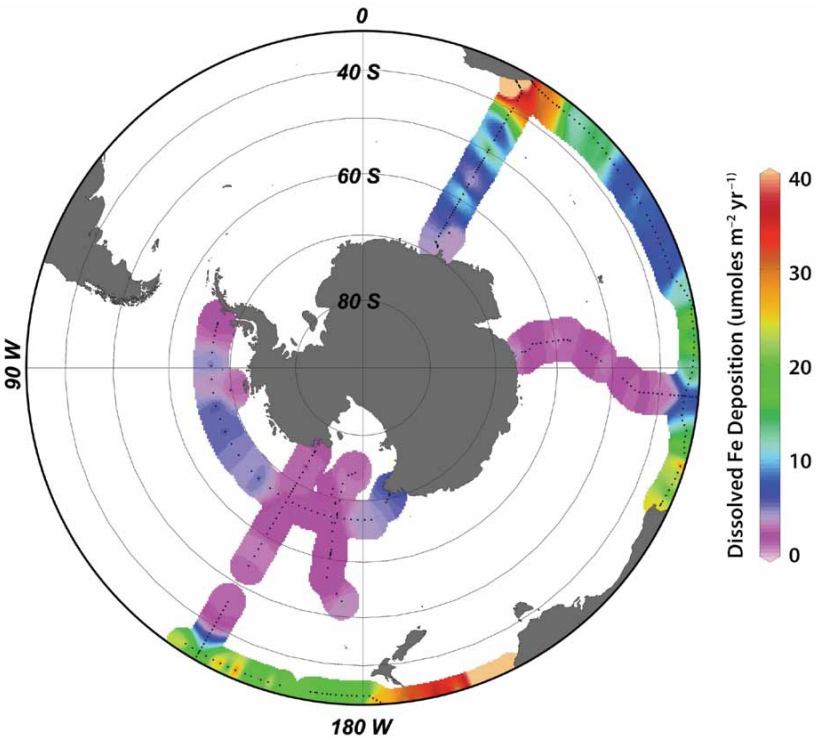

Figure 3. Calculated deposition of dissolved Fe (µmol m^{-2} yr^{-1}) to the surface waters of the Southern Ocean (see text for details).

to a 50 m mixed layer, it would result in a ~ 0.1 nM dissolved Fe increase. Despite these generally low deposition rates, there is evidence of enhanced deposition near 20°E downwind of South America's Patagonian plateau, which has been suggested as a potential source of bioactive metals (Chever et al., 2010; Bown et al., 2011).

Fe INPUT FROM SEA ICE AND ICEBERGS

Observation of blooms and elevated Fe levels near retreating ice edges has led several workers to suggest that the input of iron derived from melting sea ice may be an important factor in their development (Martin, 1990; Sedwick and DiTullio, 1997). However, melting sea ice also promotes water-column stratification and mixed-layer shoaling, which are also necessary preconditions for the initiation of spring blooms. It is now well established that the concentration of Fe in sea ice and icebergs may be up to two orders of magnitude higher than that measured in surrounding Southern Ocean waters, so that ice melt may constitute a non-negligible source of Fe into Southern Ocean surface waters in austral spring and summer (Lannuzel et al., 2007; Smith et al., 2007). However, estimating the relative importance of ice-derived Fe in the Southern Ocean is difficult because the concentration of Fe measured in sea ice and icebergs appears to be extremely variable from place to place, within the ice itself and also across seasons. For example, Fe in icebergs may vary from 4 to 600 nM (Lin et al., 2011), and Fe in sea ice was found to vary seasonally between 2 nM in summer and 18 nM in winter (Lannuzel et al., 2010). For this reason, current estimates of the Fe flux originating from ice melt have large uncertainties. Future climate change may increase the abundance of icebergs and decrease the extent of Antarctic sea ice. This change will likely affect the magnitude and timing of Fe delivery to certain regions of the Southern Ocean, with possible implications for the productivity of Antarctic ecosystems. More data are thus required to improve estimates of meltwater Fe to surface waters of the Southern Ocean and to assess its impact on productivity.

SUSPENDED SEDIMENTS AS A SOURCE OF DISSOLVED Fe

The occurrence of anomalously productive regions within the HNLC Southern Ocean, notably downstream of islands and the Antarctic Peninsula, suggests that natural processes may be adding Fe to these regions (Sullivan et al., 1993). Bucciarelli et al. (2001) and Planquette et al. (2007) were the first to measure the distribution of dissolved Fe near the islands of Kerguelen and Crozet (Figure 1). Both surveys concluded that these island systems were a significant source of Fe to surrounding surface waters on the basis of the positive dissolved Fe gradients measured from the islands' coastal zones (up to 12.6 nM) to downstream offshore HNLC waters (up to 0.71 nM). While it is clear that these Fe values are elevated relative to typical Southern Ocean levels described previously, identifying the dominant mechanism supplying Fe to these regions is a difficult endeavor based on Fe distributions alone and no winter observations. To better characterize the source terms, the KEOPS (KErguelen: compared study of the Ocean and the Plateau in Surface water) and CROZEX (CROZet natural iron bloom and EXport experiment) expeditions employed a multitracer approach using rare earth elements (Zhang et al., 2008) and short-lived radium isotope activities (Charette et al., 2007; van Beek et al., 2008). These data suggest that the Fe enrichment in both regions mainly results from the lateral advection of water masses that were in contact with shallow lithogenic sediments of the island shelf systems rather than vertical or atmospheric inputs.

Recent data from the Drake Passage region (Hatta et al., 2008) show a dramatic increase in dissolved Fe where the Antarctic Circumpolar Current impinges on the shelf of the South Shetland Islands (Figure 4). The accompanying increase in d-transmissometer signal (a proxy for suspended particle load) and dissolved Al and Mn (not shown) all suggest that the observed Fe increase results from resuspension of lithogenic and biogenic sediments and release of reducing pore waters. The offshore advection of this naturally Fe-fertilized water then leads to a broad plume of enhanced biomass visible in satellite imagery downstream of Drake Passage. We thus conclude that suspended sediments and pore waters are most likely the dominant sources of dissolved Fe that fuel the productivity hotspots observed in the wake of Southern Ocean landmasses. More data, particularly seasonal, would further our understanding of the process of natural Fe fertilization in these remote, anomalously productive regions of the Southern Ocean.

OTHER BIOACTIVE TRACE METALS

Several other dissolved metals, notably Co and Zn, exhibit vertical distributions that resemble those of macronutrients, suggesting that their distribution is partly controlled by biological processes.

Because Zn, Mn, and Co are all cofactors of metalloenzymes that are essential for phytoplankton metabolism, and are present in the pico-to-nanomolar range in open ocean surface water, it has been speculated that these elements could, along with Fe, exert an important control on macronutrient cycles and phytoplankton production in the Southern Ocean.

Zn and Mn have received the most attention, as early laboratory studies indicated that cultured coastal diatoms were Zn limited at concentrations comparable to those found in surface waters of the Central Pacific (Morel et al., 1994) and that Mn limitation, albeit less clear, was detected at Mn levels less than 0.1 nM (Brand et al., 1983). These results, however, were never unequivocally confirmed during bottle incubation experiments of ambient Southern Ocean water subjected to enrichments of Zn (Scharek et al., 1997; Coale et al., 2003; Ellwood, 2004) or Mn (Martin et al., 1990a, Buma et al., 1991; Scharek et al., 1997; Sedwick et al., 2000). In retrospect, the lack of evidence for Zn limitation of Southern Ocean waters during incubation experiments is not surprising because dissolved Zn in Southern Ocean surface waters is two to three orders of magnitude higher than the free Zn^{2+} concentration (~ 2 pM) that limited growth of cultured coastal diatoms (Martin et al., 1990b; Morel et al., 1994; Sanudo-Wilhelmy et al., 2002; Coale et al., 2005; Ellwood, 2008; Croot et al., 2011). In addition, the most comprehensive Zn speciation data set from the Atlantic sector of the Southern Ocean indicates that most dissolved Zn in this region is labile, with free Zn^{2+} concentrations greater than 0.1 nM (Baars and Croot, 2011). Clearly, Zn availability is not limiting phytoplankton growth in the Southern Ocean. Irrespective of the sampling season or longitude, the range of dissolved Zn concentrations reported in the Southern Ocean is ~ 0.2–6.5 nM. Surface Zn concentrations generally increase with increasing latitude in the Southern Ocean, suggesting that the dominant supply of Zn to Southern Ocean surface waters occurs through the upwelling and mixing of Zn-rich deep waters (Martin et al., 1990b; Coale et al., 2005; Ellwood, 2008; Croot et al., 2011). Dissolved Zn and Si are generally strongly correlated in the Southern Ocean, even though a physiological mechanism connecting Si and Zn uptake in marine diatoms remains elusive (Ellwood, 2008; Croot et al., 2011). However, given that

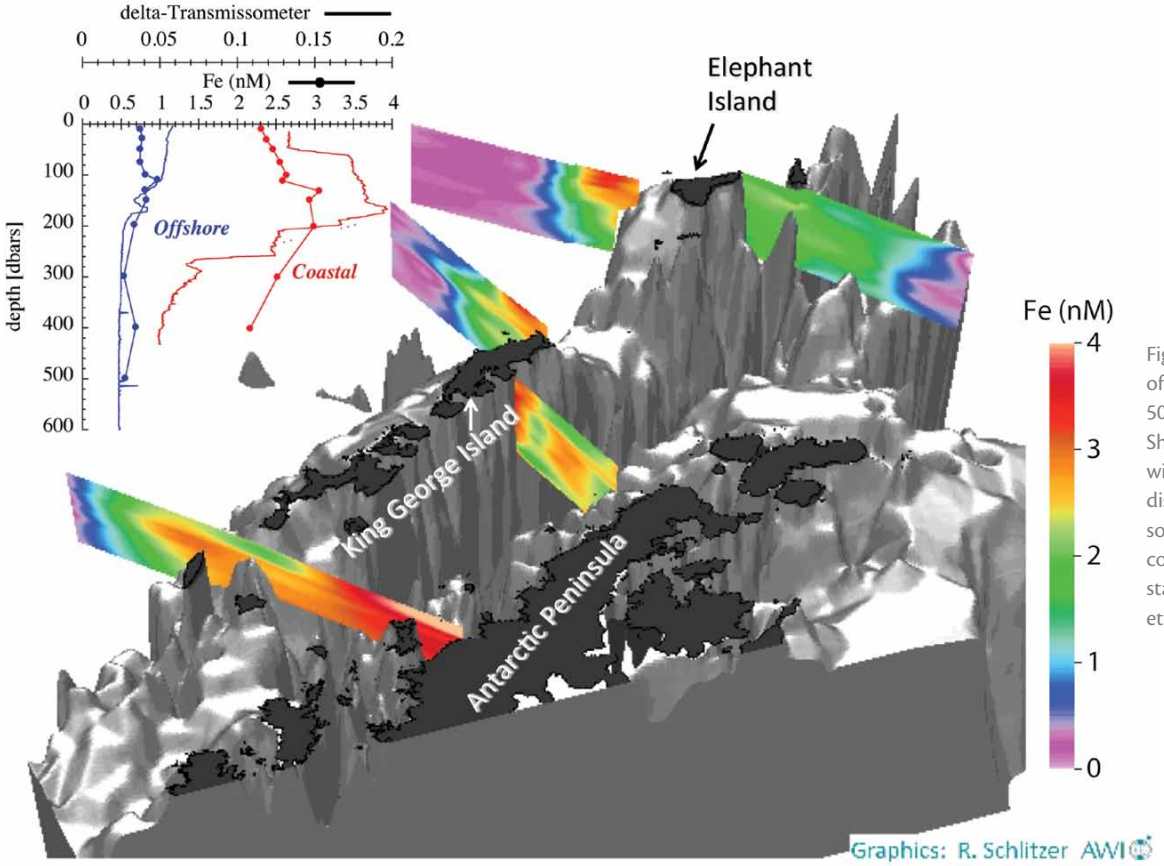

Figure 4. The distribution of dissolved Fe in the upper 500 m around the South Shetland Islands during winter 2006. The inset shows dissolved Fe and d-transmissometer voltage profiles at coastal (red) and offshore stations (blue), from Hatta et al. (2008).

diatoms are a dominant taxonomic group in the Southern Ocean, they potentially dictate the cycling of Zn in these waters (Ellwood, 2008).

Dissolved Mn concentrations in the Southern Ocean range from 0.04–0.83 nM (Westerlund and Öhman, 1991; Sedwick et al., 1997, 2000; Middag et al., 2011), with values greater than 1 nM near productive shelves (Martin et al., 1990b) and in the vicinity of hydrothermal vent systems (Middag et al., 2011). Although dissolved Mn profiles do suggest biological uptake and regeneration in some Southern Ocean regions (Sedwick et al., 1997, 2000; Middag et al., 2011), there is still no convincing evidence of algal growth limitation in Southern Ocean waters due to Mn deficiency alone.

The biogeochemical cycle of dissolved Co is linked to that of Zn and Cd, because Co is capable of substituting for these metals in some carbonic anhydrase enzymes (Saito et al., 2010). Published dissolved Co measurements in the Subantarctic Zone southwest of New Zealand (Ellwood, 2008) in the Ross Sea (Saito et al., 2010) and in the Atlantic sector of the Southern Ocean (Martin et al., 1990b; Bown et al., 2011) range from 5–85 pM. In the Ross Sea, Saito et al. (2010) showed that while biological uptake affected the Co distribution seasonally, the dissolved Co pool was never saturated by Co binding ligands and thus remained bioavailable year-round, in contrast to lower latitudes where Co is often completely bound. This finding is consistent with earlier bottle incubation experiments, which showed that the addition of Co alone did not yield significant phytoplankton growth over controls from the Ross Sea (Bertrand et al., 2007). However, it has been shown that the addition of Fe and the Co-containing vitamin B_{12} together can enhance phytoplankton growth and alter community composition compared to Fe-only amendments (Bertrand et al., 2007). Vitamin B_{12} is produced by specific prokaryotes and is required by most eukaryotic phytoplankton species (Bertrand et al., 2007). The finding that, under conditions replete with Fe, availability of vitamin B_{12} may limit production in the Southern Ocean suggests that the efficiency of the biological pump in HNLC regions may not be solely affected by Fe availability.

In summary, incubations of natural phytoplankton assemblages from the Southern Ocean subjected to Zn, Mn, or Co enrichments have not shown increased primary production. Additionally, published data show that dissolved Zn and Co are more bioavailable in the Southern Ocean relative to lower latitudes. Therefore, at this stage, it appears that Fe is the only bioactive trace element that limits phytoplankton productivity in the Southern Ocean. Whether the distribution and availability of bioactive compounds other than Fe (such as vitamin B_{12}) may influence eukaryotic community composition in the Southern Ocean warrants further investigations.

FUTURE RESEARCH

Mesoscale artificial Fe fertilization experiments have unequivocally confirmed that primary productivity in various HNLC regions is Fe limited (Martin et al., 1994; Boyd et al., 2004; Coale et al., 2004). However, the long-term impacts of such perturbations on ecosystem structure and whether they can export carbon to the ocean's interior have been difficult to ascertain due to the limited observational period that followed the initiation of the blooms. In addition, the intermittent infusion approach using acidified $FeSO_4$ that had to be adopted in these experiments to create and sustain the blooms is undoubtedly a limited analog of the large-scale Fe fertilization of the Southern Ocean that may have contributed to the reduced atmospheric CO_2 levels recorded at glacial maxima.

Regardless of how you feel about deliberate fertilization of the ocean as a means of reducing contemporary atmospheric CO_2 levels, it is nevertheless important to gain a deeper understanding of how Fe-stimulated growth processes operate because natural perturbations to the Fe delivery rate to these regions may have been one of several global physical and biogeochemical switching systems that played a role in the planetary response to glacial/interglacial cycles.

The places within the Southern Ocean where natural Fe fertilization processes are occurring from sediment resuspension do provide an opportunity to study the response to the fertilization process beyond the timescales normally available to research cruises. The sustained nature of Fe addition in these regions and its advection away from the source means that the surface waters downstream of the input represent a time series of the response to the addition. Thus, by sampling strategically downstream of a sustained natural Fe input, it may be possible to see the longer-term results of fertilization and any resulting carbon export processes that are beyond the scale that can be achieved with artificial fertilization and normal research cruise logistics. In this regard, the Drake Passage region, one of the more accessible parts of the Southern

Ocean that could yield these data, may make an attractive site for such studies, as would the Kerguelen Plateau and the Crozet Islands.

To be successful though, such studies would need to include a full suite of physical and biological parameters and sampling over the seasonal cycle. To date, few regions have been subjected to seasonal studies. Also, future geochemical sampling would need to adopt a multitracer approach. For example, radium isotopes could be used to estimate the time since Fe infusion; Th isotopes can be used to estimate removal processes; and a variety of other geochemical tracers including Fe isotopes, rare earth elements, and their isotopes can be used to provide clues as to the sources of the Fe infusion. The use of multiple trace elements and isotopes to understand and constrain biogeochemical systems is at the core of the international GEOTRACES project (http://www.geotraces.org), which will play an important role in improving our understanding of the processes that deliver vital trace elements to all parts of the ocean.

A multitracer approach would be particularly beneficial in the Southern Ocean. However, a particular problem associated with this kind of work at high latitudes is the need to quickly remove sampling equipment from the open deck of the ship to avoid potential freezing problems for both samples and equipment. Current research vessels, designed before the advent of trace metal clean sampling equipment, often lack the specialized handling equipment needed for this kind of work. While it is relatively simple to obtain and install the necessary winches, cables, and sampling platforms, the design of the interior sampling (Baltic) rooms on high-latitude ships will usually only accommodate a single rosette system, and there are no suitable laboratories within the body of the ship that permit clean handling of samples. A new generation of sampling platforms designed to house this specialized equipment will be needed if we are to exploit the potential that the distributions of trace elements and isotopes offer in understanding the biogeochemistry of the Southern Ocean.

In addition to surface platforms, future research efforts need to be directed toward the development of methods for determination of trace elements in seawater that can be adapted for use on autonomous platforms such as moorings, gliders, and Argo floats. These platforms, by extending the reach of sampling beyond traditional ships, would give the geochemical community access to data in regions that are logistically inaccessible, and also provide invaluable time-series information on oceanic distributions during sparsely sampled periods such as the winter when weather conditions can make surface sampling extremely difficult. In summary, despite pioneering efforts by many groups to study the role that bioactive metals play in modulating primary production, species composition, and carbon export in the Southern Ocean, there is much still to be learned.

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