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RESEARCH LETTER

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Key Points:

- Highest Ross Sea dFe concentrations are found within 50 m of the seafloor
- Annual dFe efflux from the continental shelf in the Ross Sea is estimated
- Shallower shelf areas supply additional episodic inputs of Fe to surface waters

Supporting Information:

- Readme
- Table S1
- Table S2
- Text S1
- Text S2
- Figure S1

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Estimating the benthic efflux of dissolved iron on the Ross Sea continental shelf

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Abstract Continental margin sediments provide a potentially large but poorly constrained source of dissolved iron (dFe) to the upper ocean. The Ross Sea continental shelf is one region where this benthic supply is thought to play a key role in regulating the magnitude of seasonal primary production. Here we present data collected during austral summer 2012 that reveal contrasting low surface (0.08 ± 0.07 nM) and elevated near-seafloor (0.74 ± 0.47 nM) dFe concentrations. Combining these observations with results from a high-resolution physical circulation model, we estimate dFe efflux of 5.8×10^7 mol yr⁻¹ from the deeper portions (>400 m) of the Ross Sea continental shelf; more than sufficient to account for the inferred “winter reserve” dFe inventory at the onset of the growing season. In addition, elevated dFe concentrations observed over shallower bathymetry suggest that such features provide additional inputs of dFe to the euphotic zone throughout the year.

1. Introduction

Iron plays a major role in regulating primary production over large areas of the surface ocean, where concentrations of this essential micronutrient are low enough to limit phytoplankton growth rates. Subsurface ocean waters are typically depleted in dissolved iron (dFe) relative to macronutrients, with respect to algal growth requirements, such that inputs of “new” iron to surface ocean waters from atmospheric dust, rivers, and continental margin sediments are thought to play an essential role in sustaining marine primary production [Measures *et al.*, 2008; Boyd and Ellwood, 2010]. In this context, there is a pressing need to constrain these source terms in order to understand and model the biogeochemical cycle of iron, its impact on the ocean ecosystem and carbon cycling, and its sensitivity to future environmental changes.

The Antarctic continental margins are among the most productive regions in the Southern Ocean [Arrigo *et al.*, 2008a] and, given the low dust deposition rates and absence of river inputs in these regions, are areas where benthic sources of iron to the euphotic zone hold particular importance [Wagener *et al.*, 2008; Sedwick *et al.*, 2011; Measures *et al.*, 2012; Wadley *et al.*, 2014]. In this communication, we focus on the benthic sources of dFe in the Ross Sea, an Antarctic continental shelf sea that covers an area of almost 500,000 km² and sustains annual primary production of around 20 Tg C [Arrigo *et al.*, 2008a; Smith *et al.*, 2012]. This high regional production, combined with a relatively high export efficiency [Asper and Smith, 1999], and the formation of oceanic bottom waters in the western Ross Sea [Orsi and Wiederwohl, 2009] imply that the Ross Sea constitutes a major regional CO₂ sink [Arrigo *et al.*, 2008b].

Despite high seasonal production in the Ross Sea, surface macronutrient concentrations are seldom depleted, and shipboard incubation experiments have demonstrated that low dFe concentrations limit phytoplankton growth rates during austral summer [Martin *et al.*, 1990; Sedwick and DiTullio, 1997; Sedwick *et al.*, 2000; Coale *et al.*, 2003]. The limited iron data from this region suggest that there is a seasonal decrease in surface dFe concentrations following the vertical resupply by convective mixing over winter, with biological uptake and export responsible for the depletion of early spring concentrations (>0.2 nM) to growth-limiting concentrations (~0.1 nM) by late spring/early summer [Sedwick and DiTullio, 1997; Fitzwater *et al.*, 2000; Sedwick *et al.*, 2000; Coale *et al.*, 2005; Sedwick *et al.*, 2011]. However, satellite observations indicate continued accumulation of phytoplankton biomass throughout the summer, implying that significant inputs of new dFe to surface waters of this region occur during the growing season. The major sources of dFe to surface waters in this region are thought to include vertical resupply of iron-rich bottom waters by winter convective mixing, year-round

benthic inputs from shallow banks and nearshore sediments, inputs from melting sea ice and glacial ice, and shelfward intrusions of Circumpolar Deep Water, with aerosol inputs thought to be a minor contribution [Mahowald *et al.*, 2005; Sedwick *et al.*, 2011; de Jong *et al.*, 2013; Smith *et al.*, 2014].

The Processes Regulating Iron Supply at the Mesoscale in the Ross Sea study aimed to use water column dFe data collected during austral summer 2012 and numerical model simulations to quantify the hypothesized source terms. Here we make use of these new data with a focus on the vertical distribution of dFe near the seafloor. By combining the dFe data with physical parameters derived from a high-resolution physical circulation model, we estimate the flux of dFe from the benthos on the Ross Sea continental shelf.

2. Methods

Hydrographic data and seawater samples were collected in austral summer 2012 aboard Research Vessel/Icebreaker (RVIB) *Nathaniel B Palmer* (cruise NBP12-01, 24 December 2011 to 8 February 2012). Seawater samples for dFe analysis were collected in Teflon-lined 5 L Niskin-X samplers (General Oceanics) modified for trace metal sampling, deployed on a trace metal clean carousel unit (SeaBird Electronics) using a Kevlar line. Hydrographic data and ancillary samples were collected in separate casts at each station using a standard rosette sampler fitted with 10 L Niskin bottles, an SBE 911*plus* conductivity-temperature-depth (CTD) sensor (SeaBird Electronics), and a C-Star transmissometer sensor (WET Labs).

Seawater samples for dFe analysis were filtered through 0.2 μm pore AcroPak Fluorodyne II filter capsules (Pall) into acid-cleaned 125 mL low-density polyethylene bottles (Nalgene) within 4 h of collection and acidified to pH 1.7 with 6 N Optima ultrapure hydrochloric acid (Fisher). Subsequent shore-based determinations of dFe were performed by flow injection analysis with in-line preconcentration and colorimetric detection [Sedwick *et al.*, 2005, 2011] using a method modified after Measures *et al.* [1995]. Determinations of dFe in SAFe (Sampling and Analysis of Iron) seawater reference materials S and D2 [Johnson *et al.*, 2007] during the period of analyses yielded mean concentrations of $0.108 \pm 0.008 \text{ nmol kg}^{-1}$ ($n = 12$) and $0.947 \pm 0.033 \text{ nmol kg}^{-1}$ ($n = 2$), respectively, which agree with consensus mean concentrations of $0.093 \pm 0.008 \text{ nmol kg}^{-1}$ (SAFe S) and $0.933 \pm 0.023 \text{ nmol kg}^{-1}$ (SAFe D2) as of May 2013. Subsamples of selected water column samples were filtered through 0.4 μm pore polycarbonate track-etch membranes, which were subsequently analyzed for particulate iron by energy-dispersive X-ray fluorescence spectroscopy as described by Barrett *et al.* [2012].

Estimates of station-specific vertical eddy diffusivity coefficients (k_z) for the austral summer were extracted from a Regional Ocean Modeling System physical circulation model of the Ross Sea, similar to that described by Dinniman *et al.* [2007, 2011], with the addition of a dynamic sea ice component [Budgell, 2005], tidal forcing [Padman *et al.*, 2002], and a bottom boundary layer parameterization addition to the base K Profile Parameterization (KPP) vertical mixing scheme [Durski *et al.*, 2004]. The vertical eddy diffusivity is computed at every time step between every model vertical layer from the KPP parameterization. The model domain extends from north of the shelf break at approximately 67.5°S, south to 85°S, including most of the cavity beneath the Ross Ice Shelf, with horizontal grid spacing of 5 km and 24 vertical levels of varying thickness, with finer depth resolution toward the sea surface and the seafloor. For this study, a hindcast simulation was performed for the period 15 September 2010 to 27 February 2012, with daily average k_z values extracted for a 90 day summertime period from 29 November 2011 to 26 February 2012 (i.e., including the period of cruise NBP12-01). Further details of the model are described in Text S1.

3. Analysis and Discussion

Water column profiles of dFe concentration were obtained from 47 stations over the Ross Sea continental shelf during cruise NBP12-01 (Figure 1a and Figure S1 in the supporting information). Twenty-six of these profiles include water samples collected within 20 m of the seafloor, and an additional 10 include samples collected within 25 m of the seafloor (Table 1). To our knowledge, this data set represents the first detailed sampling of near-bottom waters for dFe over the Ross Sea shelf and thus represents a significant contribution to the water column iron data that have been collected from this region.

Measured dFe concentrations ranged from 0.03 to 2.19 nM (Table S1), in general agreement with the range of previous dFe measurements from the Ross Sea [Sedwick and DiTullio, 1997; Fitzwater *et al.*, 2000;

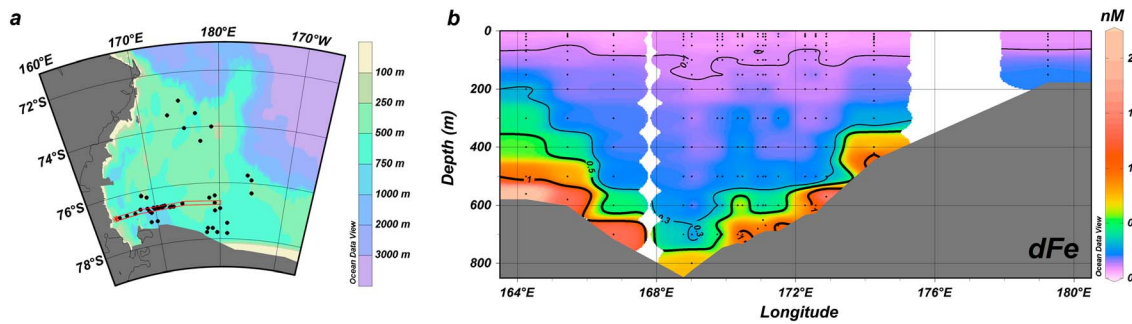


Figure 1. (a) Map showing Ross Sea stations sampled for dissolved iron during cruise NBP12-01: data from stations outlined in red are shown in (b) a zonal section of dFe concentration in the south-west Ross Sea, illustrating the contrast between low surface values and relatively high and variable benthic dFe concentrations. Contours define concentrations of 0.1, 0.3 (thin lines), 0.5, and 1.0 (thick lines) nM dFe. Dots indicate water samples. Figure prepared using Ocean Data View [Schlitzer, 2012].

Sedwick et al., 2000; Coale et al., 2005; Sedwick et al., 2011]. The lowest dFe concentrations were measured in the upper 50 m of the water column (Figures 1b and S1), with an average concentration of 0.084 ± 0.074 nM ($n = 169$). A small number of stations showed slightly elevated dFe concentrations in near-surface waters (~10 m depth), most notably at the three easternmost stations that were in, or adjacent to, melting pack ice, which has previously been identified as a source of iron to surface waters in this region [Sedwick and DiTullio, 1997].

Below 100 m depth, the profiles typically showed an increase in dFe concentration with depth. For the majority of stations ($n = 37$), with seafloor depths greater than 400 m, the dFe profiles displayed a quasi-exponential increase in concentration with depth, with a pronounced concentration gradient toward the sea floor. The dFe concentrations of samples collected within 50 m of the seafloor were variable, but generally high relative to upper ocean concentrations (Figure 1b and Figure S1), with an average value of 0.74 ± 0.47 nM ($n = 55$). These deep waters account for a substantial proportion of the total water column dFe inventory over the Ross Sea continental shelf: based on median concentrations of 50 m depth intervals, approximately 35% of this inventory resides within 100 m of the seafloor (Figure 2).

Some of the increase in dFe concentration with depth may reflect the progressive remineralization of particulate matter exported from overlying surface waters. However, this increase is much sharper than observed in open-ocean settings [e.g., Johnson et al., 1997; Tagliabue et al., 2012], suggesting that the concentration gradient is instead maintained by the upward diffusion of dFe from benthic sources, as it has been similarly interpreted in other continental shelf settings [Nédélec et al., 2007; Cullen et al., 2009; de Jong et al., 2012]. In a study focused on the sources of dissolved iron to the Atlantic sector of the Southern Ocean, de Jong et al. [2012] attributed high dFe concentrations in bottom waters to diffusion of iron-rich pore water across the sediment-water interface and/or by mobilization of these pore waters into the water column by resuspension of seafloor sediments. By using the observed near-seafloor gradients in dFe from four water column profiles, together with a literature estimate of the deep sea vertical eddy diffusivity coefficient, they estimated dFe fluxes of $1.3\text{--}15.5 \mu\text{mol m}^{-2} \text{d}^{-1}$.

Here we apply a similar approach to estimate the vertical diffusive flux of dFe from the benthos to overlying waters, using our considerably larger dFe data set and location-specific summertime k_z values derived from the physical circulation model hindcast. In doing so, we apply a one-dimensional approach to each station and assume that the observed profiles of water column dFe concentration, with low “background” subsurface values of ~0.1 nM and elevated near-seafloor concentrations, represent a steady state feature during the

summer season that is maintained by turbulent diffusion of dFe from the benthos into the low-iron overlying waters. Here the benthic dFe sources are likely to include both sedimentary inputs and the remineralization of organic matter near the seafloor, although our data do not allow us to discriminate between the two. For k_z , we use mean values from the top surface of the deepest model

Table 1. Proximity of Deepest Hydrocast Sample to the Seafloor at Each Station

Height Above Seafloor (m)	Number of Stations
≤20	26
21–25	10
26–30	4
31–40	2
41–50	2
>50	3

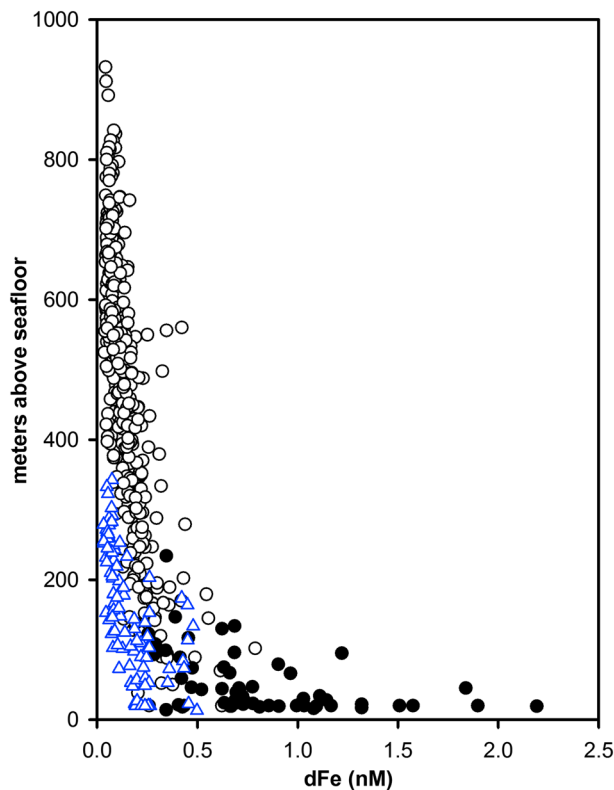


Figure 2. Measured dFe concentration as a function of height above seafloor for all stations sampled on cruise NBP12-01. Circles and triangles represent measurements made at “deep” (>400 m) and “shallow” (<400 m) stations, respectively; filled symbols indicate samples collected within the benthic nepheloid layer, as determined by transmissometer readings from accompanying hydrographic CTD casts.

was applied to dFe concentration data below 200 m depth (to avoid influence from any near-surface features) for each profile, using the general exponential formula:

$$[dFe] = 0.1 \text{ nM} + Ae^{Bz} \tag{2}$$

where [dFe] is the dFe concentration at depth z meters, 0.1 nM is the assumed ambient subsurface dFe concentration in the absence of benthic input, and A and B are adjustable parameters that are calculated to yield the best fit for each individual profile. The form of equation (2) has no physical basis, other than that the dFe concentration profiles appear to follow an exponential increase with depth; the inclusion of parameters A and B allows the flexibility to obtain reasonable fits to all of the dFe profiles considered. Differentiation of equation (2) with respect to z yields

$$\partial[dFe]/\partial z = BAe^{Bz} \tag{3}$$

For each station with water depth greater than 400 m, the resulting best fit expressions for equations (2) and (3) were extrapolated to calculate [dFe] and $\partial[dFe]/\partial z$ near the seafloor. The estimated seafloor dFe concentrations vary from 0.26 to 2.68 nM, which are similar to near-bottom concentrations in samples collected near the Celtic Sea shelf edge [Nédélec et al., 2007] and over the Kerguelen Plateau [Blain et al., 2007], although lower than concentrations in near-bottom samples collected off the west coast of Canada (up to ~6 nM; Cullen et al. [2009]) or in off-shelf, near-seafloor samples from the Atlantic sector of the Southern Ocean (~2–20 nM) [de Jong et al., 2012]. Applying our approach to calculate seafloor dFe concentration gradients for these other locations, where data allow, yields values of 11×10^{-4} to $33 \times 10^{-4} \mu\text{mol m}^{-4}$ for the Kerguelen Plateau [Blain et al., 2007; Gerringa et al., 2008], which are near the lower end of our Ross Sea range (7×10^{-4} to $732 \times 10^{-4} \mu\text{mol m}^{-4}$;

layer at each station (3.8–10.7 m above the seafloor, depending on water column depth), averaged over the 90 day summer hindcast period of 29 November 2011 to 26 February 2012. These model-derived k_z values range from 1.1×10^{-4} to $57.7 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ (Figure 3a and Table S2), with a median value of $6.7 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$; this value is roughly an order of magnitude lower than the abyssal value used by de Jong et al. [2012], but is in accord with estimates made in other regions of the Southern Ocean and Antarctic continental margin [Law et al., 2003; Blain et al., 2007; Gerringa et al., 2012], and with near-bottom k_z estimates derived from radon concentrations (2×10^{-4} to $50 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$) measured in various oceanic locations [Broecker et al., 1968].

We calculate the upward diffusive flux of dFe from the benthos, F_{dFe} , using Fick’s first law of diffusion:

$$F_{dFe} = k_z \partial[dFe]/\partial z \tag{1}$$

where $\partial[dFe]/\partial z$ is the vertical gradient in dFe concentration near the seafloor. In doing so, we assume that vertical and horizontal advection can be neglected.

To estimate $\partial[dFe]/\partial z$, a least squares fit

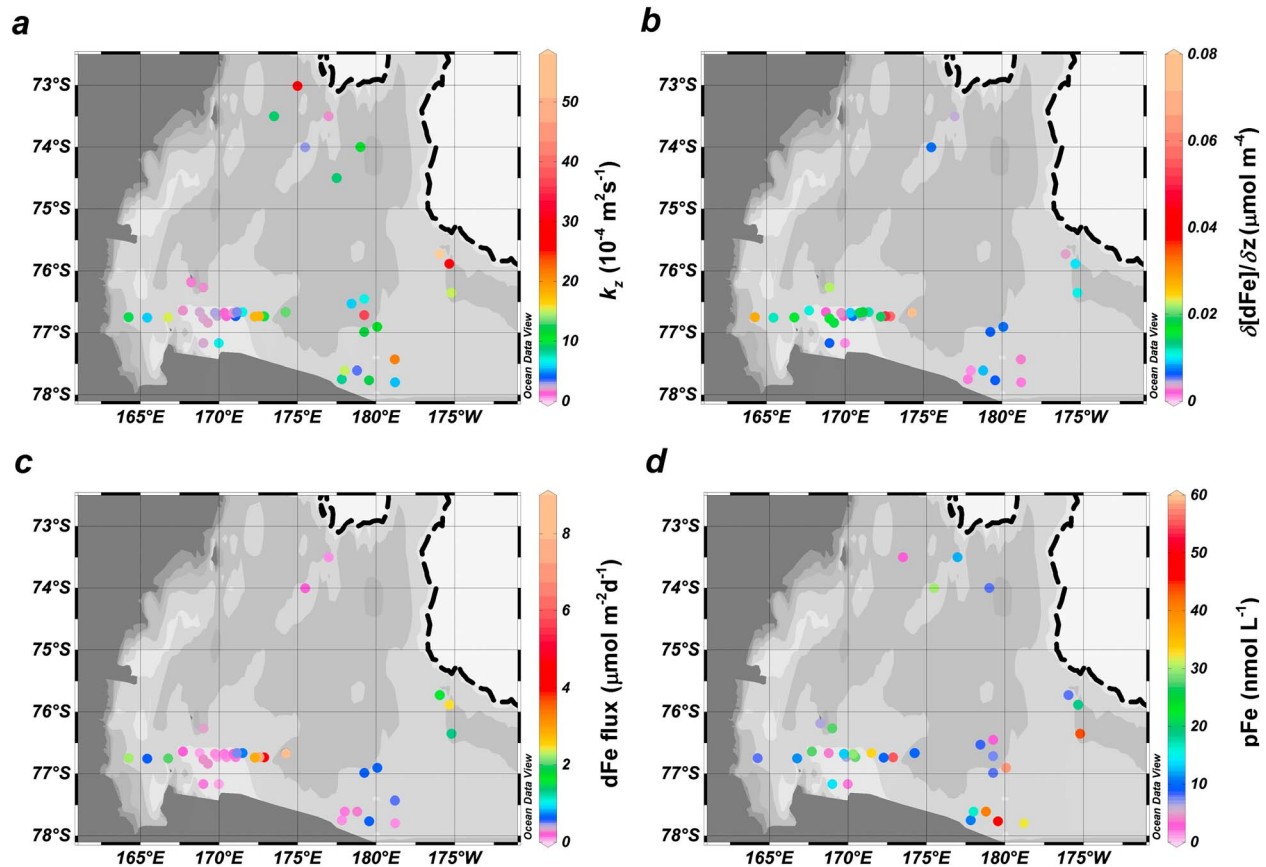


Figure 3. Distribution by station of (a) average summertime benthic k_z values for all stations, based on the bottom vertical layer of the physical circulation model; (b) vertical gradient of dFe concentration at the seafloor; (c) calculated benthic efflux of dFe for stations in water depths >400 m; and (d) particulate iron concentration in the deepest water column samples (not measured at all stations). Dashed line represents the 1000 m isobath, with on-shelf isobaths at every 250 m and at 100 m depth. Figure prepared using Ocean Data View [Schlitzer, 2012].

Figure 3b), and a larger range of 2×10^{-4} to $1490 \times 10^{-4} \mu\text{mol m}^{-4}$ for the Atlantic sector of the Southern Ocean [Löscher *et al.*, 1997; de Jong *et al.*, 2012].

Calculated benthic dFe fluxes at the Ross Sea stations span 0.028 – $8.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Figure 3c), with a geometric mean of $0.36 \mu\text{mol m}^{-2} \text{d}^{-1}$. Integrating this mean flux over the $4.48 \times 10^{11} \text{m}^2$ of Ross Sea continental shelf that is deeper than 400 m [Smith *et al.*, 2012] yields a cumulative input for the 90 day summertime period of $\sim 1.4 \times 10^7$ moles dFe. Assuming that the same conditions can be extrapolated to the entire year, which assumes both that the average k_z values at each station are representative of annual averages and that there is no seasonal change in dFe gradient at the seafloor, this would give an annual benthic efflux of $\sim 5.8 \times 10^7$ moles dFe. Fluxes of dFe calculated both for individual stations and for the regional mean depend on the k_z value used at each station and the calculated dFe concentration gradient near the seafloor. As discussed, the choice of fitting data to equation (2) has no physical basis other than to allow estimation of the dFe concentration gradient near the seafloor. Using the alternate method of a straight line fit to dFe concentrations of the two deepest samples, the calculated dFe fluxes cover a similar range (0.002 – $3.33 \mu\text{mol m}^{-2} \text{d}^{-1}$), with a geometric mean of $0.15 \mu\text{mol m}^{-2} \text{d}^{-1}$, approximately half of the mean value derived from the fitted profiles. This approach, along with other variations on estimating $\partial[\text{dFe}]/\partial z$ at the seafloor and the effect of varying the k_z value are discussed in Text S2: in each case the calculated mean dFe flux for the shelf lies within the range 0.12 – $0.52 \mu\text{mol m}^{-2} \text{d}^{-1}$, giving annual benthic Fe supply estimates of between 2×10^7 and 8.5×10^7 moles.

Our flux estimates are generally lower than values estimated by de Jong *et al.* [2012] but greater than that estimated by Blain *et al.* [2007] for the Kerguelen Plateau ($0.03 \mu\text{mol m}^{-2} \text{d}^{-1}$), with some of the differences clearly due to the choice of k_z values. Our dFe benthic flux estimates are at the lower end of published estimates for other shelf regions, which were derived from in situ incubations or pore water dFe profiles,

and range from <0.02 to $1000 \mu\text{mol m}^{-2} \text{d}^{-1}$ [Elrod *et al.*, 2004; Pakhomova *et al.*, 2007; Severmann *et al.*, 2010; Homoky *et al.*, 2012, 2013]. Elrod *et al.* [2004] suggested a global mean benthic dFe efflux of $8.16 \mu\text{mol m}^{-2} \text{d}^{-1}$, based on a global mean carbon oxidation rate of $12 \text{mmol m}^{-2} \text{d}^{-1}$ and an average Fe/C flux ratio of $0.68 \mu\text{mol Fe/mmol oxidized carbon}$. This is over 20 times greater than our geometric mean estimate of $0.36 \mu\text{mol m}^{-2} \text{d}^{-1}$ for the Ross Sea. However, DeMaster *et al.* [1996] calculated a much lower flux of remineralized carbon from Ross Sea sediments of $0.2\text{--}2.7 \text{mmol m}^{-2} \text{d}^{-1}$. Substituting these values into the Elrod algorithm gives a benthic flux of iron from the Ross Sea shelf of $0.16\text{--}1.86 \mu\text{mol m}^{-2} \text{d}^{-1}$, which brackets the values estimated using our approach. Thus, assuming that the California coast Fe/C ratio used by Elrod *et al.* [2004] can be broadly applied, the application of their algorithm is supported by our data and suggests that a low rate of benthic carbon oxidation is responsible for the relatively low dFe fluxes estimated for the Ross Sea.

Alternatively, the relatively low values of our dFe flux estimates may reflect the well-oxygenated nature of subsurface waters on the Ross Sea continental shelf relative to the other regions [Elrod *et al.*, 2004; Severmann *et al.*, 2010]. Microbial reduction of Fe(III) to the more soluble Fe(II) leads to the release of dFe into sediment pore waters during the early stages of diagenesis [Burdige, 2006]. This Fe(II) is then transferred from the sediment pore waters into the overlying water column via diffusion and sediment resuspension, where its residence time in solution is largely determined by the oxygen content of the near-bottom waters [Lohan and Bruland, 2008; Homoky *et al.*, 2012]. In well-oxygenated waters, unless stabilized by organic complexation, dissolved Fe(II) will be oxidized to Fe(III), which may then be removed to the sediments via precipitation, aggregation, and/or particle scavenging. Indeed, a recent study of benthic dFe exchange suggests that resuspended particulate material may regulate the benthic efflux of dFe, both through mobilizing high-iron pore waters and by removal of released dFe [Homoky *et al.*, 2012]. Such processes may occur in our study region, where nearly all of the stations sampled in waters deeper than 400 m showed evidence of a benthic nepheloid layer (Figure 2), based on CTD transmissometer profiles and elevated particulate iron concentrations (often $>10 \text{nM}$) in near-seafloor samples (Figure 3d). Verification of whether sediment resuspension represents an additional source of dFe to the water column or a sink for dFe released by diffusion from sediments is beyond the scope of the current study. Such processes would undoubtedly perturb the dFe concentration gradient, although higher-resolution measurements of near-bottom dFe concentrations and/or direct characterization of iron biogeochemical cycling within the benthic nepheloid layer would be required to assess such effects.

At 10 stations with relatively shallow bathymetry ($<400 \text{m}$), the dFe concentration profiles did not show the same quasi-exponential increase in concentration with depth; rather, dFe concentrations either increased in an approximately linear fashion with depth from a near-surface minimum or varied little between the deepest two or three samples. Studies of the distribution of seafloor sediments in the Ross Sea suggest that the banks and shoals are typically characterized by coarse glacial-marine sediments, rather than the siliceous muds and oozes that dominate deeper areas of the shelf [Dunbar *et al.*, 1985; Anderson, 1999]. As such, sediments in these shallower areas would be expected to contain a smaller proportion of organic matter, thereby creating conditions that are less effective at reducing and releasing iron into pore fluids and overlying bottom waters, and explaining the smaller gradients in dFe concentration at these stations. Nonetheless, middepth dFe concentrations at these shallower stations were often elevated relative to the same depths at stations in deeper areas of the shelf: over the 100–300 m depth interval, the median dFe concentration for samples collected at the 10 shallow stations was significantly greater than that for the 37 deeper stations ($>400 \text{m}$ depth), based on the Mann-Whitney Rank Sum Test (0.19nM versus 0.13nM ; $p < 0.001$).

During the winter months, deep convective mixing vertically redistributes benthic dFe throughout the water column, providing a “winter reserve” of dFe in the euphotic zone at the onset of the growing season. Using a water column dFe inventory estimated from the mean concentrations over 100 m depth intervals, and assuming that winter mixing homogenizes the water column over most of the shelf (as indicated by the model hindcast), yields 0.22nM as an estimate of the water column dFe concentration at the start of the growing season, consistent with values reported for early spring [Coale *et al.*, 2005]. Assuming an average summer mixed layer depth of 25 m (based on the climatology at <http://www7320.nrlssc.navy.mil/nmld/nmld.html>), and using our observed mean late summer dFe concentration for the upper 25 m (0.08nM) as a post growth season surface mixed layer concentration, suggests an annual shelf-wide winter resupply of 1.6×10^6 moles dFe into the surface mixed layer ($3.5 \mu\text{mol m}^{-2} \text{yr}^{-1}$). This represents only one tenth of our calculated summertime

benthic input of 1.4×10^7 moles dFe for the deeper areas of the shelf. Assuming that the winter benthic dFe flux is similar to our summertime estimate, the annual benthic efflux of 5.8×10^7 moles dFe appears to be far in excess of the winter vertical resupply to surface waters and may thus constitute a significant supply of dFe to offshore regions of the Southern Ocean via lateral advection from the Ross Sea shelf, a process that has been described for other regions [Elrod et al., 2004; Lam et al., 2006; Tagliabue et al., 2009]. In addition, some fraction of the efflux of dFe from the shallower areas of the Ross Sea shelf will presumably enter the euphotic zone episodically during the summer, as a result of tidal, eddy, and wind-driven mixing, thereby providing a further source of benthic dFe to phytoplankton during the growing season.

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