



## Sources of iron in the Ross Sea Polynya in early summer



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### ARTICLE INFO

#### Article history:

Received 29 January 2015

Received in revised form 27 May 2015

Accepted 2 June 2015

Available online 5 June 2015

#### Keywords:

Ross Sea

Fe

Dissolved Fe

Fe fluxes

Antarctica

GEOTRACES

### ABSTRACT

Dissolved Fe (DFe) was measured in the Ross Sea Polynya (RSP), Antarctica, during a GEOTRACES cruise between 20 December 2013 and 5 January 2014. DFe was measured over the full water column with special emphasis on samples near the seafloor. In the upper mixed layer, DFe was very low everywhere ( $<0.10$  nM). DFe increased with depth to values between 0.60 and 2.76 nM near the seafloor. The highest DFe concentrations were found at stations where a bottom nepheloid layer (BNL) was present (28 out of 32 stations). Deep DFe was lower (0.24–0.38 nM) at stations with no BNL. The main DFe supply to the upper mixed layer was vertical diffusive transport from the seafloor sediments, with a mean flux of  $3.3 \times 10^{-8}$  mol DFe  $m^{-2} day^{-1}$ . DFe fluxes showed large spatial variability of three orders of magnitude and were positively correlated to DFe concentrations near the sediment and vertical turbulent eddy diffusivity ( $K_z$ ) and negatively correlated to water depth. The greatest fluxes were observed above the shallow banks such as Ross and Pennell Banks, and sediments with a BNL. We studied the horizontal diffusive transport from Franklin Island as an example of horizontal DFe transport from landmasses. No DFe transport was detected in the upper 100 m of the water column, probably due to uptake by phytoplankton. However, at 200 and 300 m depth, the DFe transport at distances between 50 and 100 km from Franklin Island was as large as the mean diffusive upward transport, indicating the potential importance of landmasses as a local source of DFe. Conversely, no horizontal transport of DFe from banks was detected. In addition, the Ross Ice Shelf (RIS) was a negligible source of DFe. Only the Ice Shelf Water (ISW), a water mass formed under the RIS, contained slightly elevated DFe (0.18–0.26 nM) compared to the surrounding waters. However, this elevated DFe did not reach into the RSP. Icebergs were not encountered and were not evaluated as a DFe source. Overall, we conclude that DFe from the seafloor and land mass sediments are the main DFe sources of DFe that support phytoplankton in the upper mixed layer of the Ross Sea Polynya in early summer.

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### 1. Introduction

Antarctic shelf waters are a strong sink for atmospheric  $CO_2$  due to high biological productivity, intense winds, high air–sea gas exchange, formation of bottom water and extensive winter ice cover (Arrigo et al., 2008a; Jones et al., 2015-in this issue). These factors make these regions important for the biogeochemical cycling of elements, particularly that of carbon (Sarmiento et al., 2004; Arrigo et al., 2008a). Specifically, coastal polynyas (areas of open water surrounded by ice) are hot spots for energy and carbon transfer between the atmosphere and ocean (Smith and Barber, 2007). The reduced ice cover increases air–sea gas exchange and results in enhanced light availability in the near surface waters in early spring, thereby increasing primary productivity through phytoplankton photosynthesis. In addition to its importance for the global carbon cycle, phytoplankton productivity on Antarctic shelves supports the biota of higher trophic levels such as krill,

penguins, and whales (Arrigo et al., 2003; Arrigo and Van Dijken, 2003a; Ainley et al., 2006).

In the Southern Ocean, phytoplankton productivity is often limited by the availability of iron (Fe) (de Baar et al., 1990; Martin et al., 1990, 1994; Boyd et al., 2007 and references therein), although light limitation due to deep vertical mixing may also limit phytoplankton growth (Mitchell et al., 1991; De Baar et al., 2005). Fe exists in both dissolved and particulate forms in seawater. Dissolved Fe (DFe) is considered to be the preferred form for phytoplankton, but since Fe has a low solubility in seawater, it easily precipitates or is scavenged, and sinks out of the euphotic zone as particulate Fe (Millero, 1998; Liu and Millero, 2002). The concentrations of DFe in Antarctic waters are controlled by a balance between Fe input from various sources, processes like organic complexation that keep Fe in solution, and removal processes (Gledhill and Van den Berg, 1994; Boyd et al., 2012; Klunder et al., 2011; Thuróczy et al., 2011, 2012). Dissolved organic ligands are molecules that bind trace metals such as Fe. In this way, the ligands increase the solubility of Fe, retard the precipitation of Fe (hydr-) oxides, and increase Fe availability for biological uptake in the upper ocean. As such, the binding by dissolved organic ligands may play an important role

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in the dissolution of Fe and keeping Fe in the dissolved phase. It is unknown which fraction of the organically complexed Fe pool can be directly utilized by phytoplankton and how it is taken up (Hassler et al., 2011; Gledhill and Buck, 2012).

Potential sources of DFe in Antarctic waters are upwelling of DFe-rich deep waters (De Baar et al., 1995; Löscher et al., 1997; Croot et al., 2004; Klunder et al., 2011), melting glaciers, ice sheets, and icebergs (De Baar et al., 1995; Raiswell et al., 2006, 2008; Gerringa et al., 2012; Wadham et al., 2013), melting sea ice (Sedwick and DiTullio, 1997; Lannuzel et al., 2010, 2014; van der Merwe et al., 2011), atmospheric dust deposition either directly into surface waters or onto sea ice (Croot et al., 2007; Sedwick et al., 2008, 2011; de Jong et al., 2013), hydrothermal vents (Tagliabue et al., 2010; Klunder et al., 2011; Hawkes et al., 2013; Aquilina et al., 2014), and sediment resuspension and reductive dissolution (Fitzwater et al., 2000; Sedwick et al., 2011; De Jong et al., 2012; Hatta et al., 2013; Marsay et al., 2014). Sediment resuspension and reductive dissolution are particularly important when a bottom nepheloid layer (BNL) is present, a layer above the sediment that contains significant amounts of suspended sediment, as it is important for exchange of DFe between sediment and water (Bacon and Rutgers van der Loeff, 1989; Klunder et al., 2012). Horizontal and vertical advection and diffusion determine the distribution of DFe from these sources (Blain et al., 2007, 2008; Gerringa et al., 2012; de Jong et al., 2012; Bowie et al., 2014), which is facilitated by complexation with dissolved organic ligands (Thuróczy et al., 2011, 2012; Boye et al., 2001; Croot et al., 2004; Gerringa et al., 2008).

The Ross Sea is one of the most studied coastal regions of Antarctica and the most productive sector of the Southern Ocean (Arrigo and Van Dijken, 2003a; Arrigo et al., 2008b). Low DFe concentrations have been reported in the surface waters, which may limit phytoplankton growth (Martin et al., 1990; Sedwick and DiTullio, 1997; Fitzwater et al., 2000; Coale et al., 2005; Sedwick et al., 2011; Marsay et al., 2014). Traditionally, it was thought that DFe concentrations in surface waters were high during the winter and early spring due to remineralization of Fe and vertical mixing that brings deep DFe-rich water to the surface (Sedwick and DiTullio, 1997; Fitzwater et al., 2000; Coale et al., 2005). This winter stock of DFe would then be taken up by phytoplankton over the course of the spring and summer, resulting in seasonal Fe-limitation of phytoplankton growth (Sedwick et al., 2000; Coale et al., 2005). However, Sedwick et al. (2011) showed that even in early spring, before the seasonal peak in phytoplankton abundance, DFe concentrations were already extremely low in surface waters of the Ross Sea Polynya (RSP). These low DFe concentrations were potentially limiting phytoplankton growth and suggest that bioavailable Fe must be supplied throughout the growing season in order to sustain phytoplankton blooms. However, the source of this DFe is unclear. The Ross Ice Shelf (RIS) does not appear to be a major source of DFe to surface waters of the RSP since DFe is relatively low at stations close to the edge of the RIS (Sedwick et al., 2011; Marsay et al., 2014). This contrasts with the Amundsen Sea, where the Pine Island Glacier was the main Fe source for the phytoplankton bloom in the Pine Island Polynya (Gerringa et al., 2012; Alderkamp et al., 2012), and the Dotson Ice Shelf was a major DFe source for phytoplankton in the Amundsen Sea Polynya (Sherrell et al., submitted; Alderkamp et al., 2015). Sedwick et al. (2011) suggested that the main Fe sources to surface waters of the Ross Sea were dust deposition, sea ice melt, and vertical exchange of DFe through reductive dissolution of sediments. Marsay et al. (2014) also suggested that sediment-derived Fe was the most important DFe source. De Jong et al. (2013) acknowledged the importance of dust and sea ice melt but also proposed that sediment-derived Fe from the melting of icebergs and ice sheets was an important DFe source. In contrast, Coale et al. (2005) concluded that DFe transport from the sediment through vertical mixing did not bring DFe to surface waters.

The research presented here aims to identify and quantify the sources of DFe that support phytoplankton blooms in the Ross Sea.

We present water column DFe concentrations related to water masses in the Ross Sea during December and January when the phytoplankton bloom typically reaches its highest biomass levels (Arrigo and Van Dijken, 2003a, 2004). In particular, we use high spatial resolution DFe concentration data from waters near suspected Fe sources, such as the Ross Ice Shelf, sea ice, sediments, Modified Circumpolar Deep Water (MCDW), and land masses (e.g., Franklin Island), to calculate DFe fluxes from these sources to surface waters where it supports phytoplankton growth.

## 2. Methods

### 2.1. Sampling

The cruise NBP13-10 of the RVIB *Nathaniel B. Palmer* took place from December 2013 to January 2014 as part of the Phantastic project. We entered the Ross Sea from the north-east on 20 December and left on the north-western side on 5 January (Fig. 1). We sampled a total of 33 stations, two stations in the eastern Ross Sea and 31 stations in the RSP (Fig. 1). Twenty-five stations made a circle section through the RSP that was sampled starting at station 20, going south to the RIS, and then counter-clockwise (Fig. 1).

The following sections will be discussed in detail:

- 1) The south–north central RSP transect along the 177.5°E meridian from a distance of 10 km from the RIS at 77.74°S to the north crossing one trough up to the Ross Bank and crossing a second trough to the Pennell Bank at 74.5°S. Along this section, we studied surface DFe in relation to water properties in the central RSP and potential DFe sources from the RIS and Ross Bank.
- 2) The east–west Pennell Bank transect along 74.5°S from the Pennell Bank at 177.5°E to the Joides Trough at 172.5°E. Here we studied potential DFe sources from the Pennell Bank.
- 3) The west–east Franklin Island transect along 76.1°S from 9.5 km east of Franklin Island at 168.7°E to 169°E. Along this section, we studied potential DFe sources from Franklin Island.
- 4) The western RSP transect, from station 75 (74.5°S, 172.5°E) moving to the south-west to station 87 (76°S, 170°E) and from there to the south-east (via st. 91, 101, 111, 112, 113) to station 114 (77.33°S, 177.5°E) which is the same position as station 31 of the central RSP transect. At this section, we studied surface DFe in relation to water properties in the western RSP.

All trace metal clean (TMC) water samples were collected using modified 12 L GO-FLO (Oceanics) samplers provided by the Royal NIOZ (The Netherlands) which were attached to a TMC frame provided by the United States Antarctic Program. Temperature, depth, and salinity were measured with a SBE 9/11plus conductivity–temperature–depth (CTD) system (SeaBird Electronics). The frame also included a C-star transmissometer (WET Labs) and a chlorophyll *a* (Chl *a*) fluorometer (WET Labs). Temperature and salinity were transformed into conservative temperature ( $\Theta$  in °C) and absolute salinity ( $S_A$  in g kg<sup>−1</sup>) according to McDougall et al. (2009).

Typical sample depths were 10, 25, 50, 75, 100, and every 100 m, thereafter depending on water depth. Full water column profiles were sampled at 33 stations where the deepest sample was  $6 \pm 4.19$  m above the bottom and an additional sample 10 m above the deepest sample. Occasionally, surface waters were sampled at 4–5 m depth.

Water was filtered (Sartorius®, 0.2 µm; Satrobran 300) prior to DFe analysis (see below) inside a trace metal clean van.

### 2.2. Analyses

#### 2.2.1. DFe determination with Flow Injection Analysis

Trace metal clean work was done free from contamination in a plastic bubble on the ship. Overpressure in the bubble was achieved by

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