



# Organic ligands control the concentrations of dissolved iron in Antarctic sea ice



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## ARTICLE INFO

### Article history:

Received 8 October 2014

Received in revised form 30 April 2015

Accepted 12 May 2015

Available online 3 June 2015

### Keywords:

Sea ice

Seawater

Iron

Organic ligands

Complexation

Antarctica

## ABSTRACT

The organic complexation of dissolved iron (DFe) was assessed in 5 snow, 34 sea ice, 12 brine and 24 under-ice seawater samples collected during a 22 day time series in the East Antarctic sector in austral summer 2009. Similar to seawater, over 99% of DFe was bound to organic ligands in snow, sea ice and brines throughout the study. Dissolved organic ligand and Fe concentrations were higher in the brines and sea ice than in snow and seawater samples. In sea ice, [DFe] ranged from 2.1 to 81.0 nM and organic Fe complexing ligands ([Lt]) ranged from 4.5 to 72.1 nM, with complex stability  $\log K_{\text{FeL}} = 21.0\text{--}23.0$ . Estimated concentrations of inorganic Fe ([Fe']) in sea ice ranged from 0.1 to 98.2 pM. In brines, [DFe] ranged from 0.3 to 34.6 nM and [Lt] ranged from 5.9 to 41.4 nM, with complex stability  $\log K_{\text{FeL}} = 21.0\text{--}22.0$ . Estimated concentrations of inorganic Fe (Fe') in brines ranged from 0.70 to 7.2 pM. Organic ligands were nearly saturated with Fe in both sea ice and brines, with positive linear relationships observed between [DFe] and [Lt]: [Lt] = 0.90 [DFe] + 4.24 ( $R^2 = 0.93$ ,  $n = 34$ ) in sea ice and [Lt] = 1.08[DFe] + 4.86 ( $R^2 = 0.98$ ,  $n = 12$ ) in brines. Our results therefore suggest that the organic ligands produced by sea ice algae and bacteria keep Fe in the dissolved phase therefore enhancing its availability for the sea ice algal community. When DFe concentrations become higher than the ligand concentrations, non-organically bound Fe is transferred into the particulate phase by scavenging, biological uptake or precipitation processes. As sea ice starts to melt, DFe is released into seawater together with organic ligands, potentially increasing the residence time of Fe in Antarctic surface waters and its bio-availability for the phytoplankton community.

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## 1. Introduction

It has been demonstrated that iron (Fe) plays a crucial role in 40% of the world's oceans, where low inputs of Fe limit marine productivity. High rates of productivity have however been reported in the Antarctic marginal ice zone (e.g., Arrigo and van Dijken, 2003; Hales and Takahashi, 2004; Arrigo et al., 2008), where sea ice has been shown to accumulate and store Fe during the unproductive winter months, only to release it upon melting during the highly productive spring/summer months (e.g., Grotti et al., 2005; Lannuzel et al., 2007; van der Merwe et al., 2009). Through this storage capability, Antarctic sea ice has the potential to seasonally supply more Fe to Antarctic surface waters in spring/summer than other sources such as atmospheric deposition, extraterrestrial iron, vertical diffusion, and upwelling (Lannuzel et al., 2007). Several recent process studies in fast ice have shown the Fe fertilization potential of sea ice at the local scale. Measurements of both dissolved and particulate Fe in fast ice near Casey station (East Antarctica) allowed estimates of the biological carbon drawdown that

could be fuelled by the seasonal melting of fast ice (van der Merwe et al., 2011b; Lannuzel et al., 2014a). Recent work in the Ross Sea has made similar progress in estimating the seasonal release of Fe from melting fast ice and suggests that this short-term source to the water column may support up to 85% of the local primary production (de Jong et al., 2013). While these efforts have done much to improve our understanding of the sources and magnitudes of the Fe supply and their potential to support primary production in the marginal ice zone, considerable uncertainty remains with respect to the bio-availability of this Fe input.

It is well accepted that dissolved Fe (DFe, 0.2 or 0.4  $\mu\text{m}$  filtrate) has a greater relative proportion available for phytoplankton uptake than particulate Fe (PFe > 0.2 or 0.4  $\mu\text{m}$  size pore filters). Thus, processes which help maintain Fe in the dissolved form in the euphotic zone will therefore increase its bio-availability, and potentially improve the functioning of the biological pump of carbon. Within the dissolved fraction, Fe can exist under the inorganic form (Fe'), which is the most bio-available (Brand et al., 1983), or be organically complexed (FeL). Oceanographic research over the past two decades has shown that more than 99% of the DFe present in the ocean is bound to organic ligands (Gledhill and van den Berg, 1994; van den Berg, 1995; Rue and Bruland, 1995; Boyé et al., 2001; Gledhill et al., 1998). The almost

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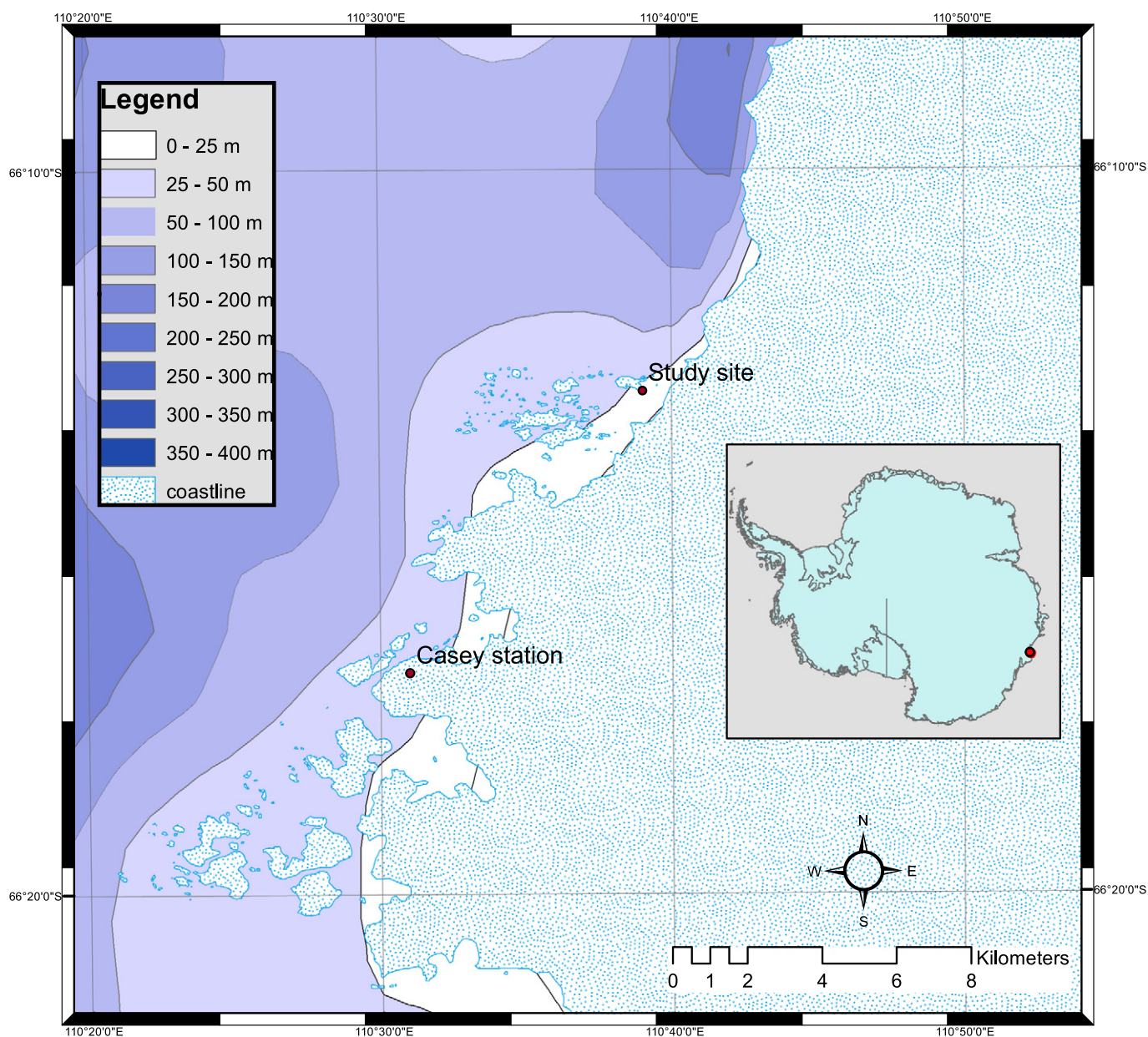
complete organic complexation of Fe increases its solubility and minimizes the formation of less-soluble and negatively-buoyant Fe (oxy)hydroxide particles, therefore increasing DFe residence time in seawater and its availability for phytoplankton growth (Johnson et al., 1997; Sunda, 1997). Although sea ice covers 40% of the Southern Ocean at maximum extent and is recognized as the main source of Fe to surface waters in spring (Lannuzel et al., 2007), only one study has opportunistically measured Fe-binding organic ligands in Antarctic sea ice. Boyé et al. (2001) highlighted a >99% organic complexation of Fe in three sea ice samples collected near 70°S/6°E. Although precise information regarding the collection method and type of sea ice was not stated in the report, these results were the first to indicate that organic complexation may be as important in sea ice as in seawater. The goal of our paper is to build on the pilot work from Boyé et al. (2001) and to evaluate whether organic ligands control the concentrations of DFe in sea ice. To do so, we document and discuss the level of organic

complexation of DFe in 5 snow samples, 34 sea ice sections, 12 brine solution and 24 under-ice seawater samples. The samples were collected every 3 days over a 22 day time series in East Antarctic fast ice during late Austral spring (November–December 2009) during the sea ice melt season.

## 2. Material and methods

### 2.1. Collection of samples

Samples were collected during an Australian Antarctic fieldwork expedition in November–December 2009, near Casey station (Fig. 1). Contamination-free ice coring and water sampling equipment developed by Lannuzel et al. (2006) was used. A full description of the sampling procedure was given in van der Merwe et al. (2011b). Briefly, snow was first collected with an acid-cleaned polyethelene shovel,



**Fig. 1.** Bathymetry and location of the fast ice site visited near Casey station.

All data were provided by the Australian Antarctic Data Centre (<https://data.aad.gov.au/>). Bathymetry data were supplied by IBCSO project Arndt et al. (2013). Coastal polygon supplied by SCAR, Antarctic Digital Database is copyright © 1993–2014 Scientific Committee on Antarctic Research.

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