



Iron in sea ice: Review and new insights

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Abstract

The discovery that melting sea ice can fertilize iron (Fe)-depleted polar waters has recently fostered trace metal research efforts in sea ice. The aim of this review is to summarize and synthesize the current understanding of Fe biogeochemistry in sea ice. To do so, we compiled available data on particulate, dissolved, and total dissolvable Fe (PFe, DFe and TDFe, respectively) from sea-ice studies from both polar regions and from sub-Arctic and northern Hemisphere temperate areas. Data analysis focused on a circum-Antarctic Fe dataset derived from 61 ice cores collected during 10 field expeditions carried out between 1997 and 2012 in the Southern Ocean. Our key findings are that 1) concentrations of all forms of Fe (PFe, DFe, TDFe) are at least a magnitude larger in fast ice and pack ice than in typical Antarctic surface waters; 2) DFe, PFe and TDFe behave differently when plotted against sea-ice salinity, suggesting that their distributions in sea ice are driven by distinct, spatially and temporally decoupled processes; 3) DFe is actively extracted from seawater into growing sea ice; 4) fast ice generally has more Fe-bearing particles, a finding supported by the significant negative correlation observed between both PFe and TDFe concentrations in sea ice and water depth; 5) the Fe pool in sea ice is coupled to biota, as indicated by the positive correlations of PFe and TDFe with chlorophyll *a* and particulate organic carbon; and 6) the vast majority of DFe appears to be adsorbed onto something in sea ice. This review also addresses the role of sea ice as a reservoir of Fe and its role in seeding seasonally ice-covered waters. We discuss the pivotal role of organic ligands in controlling DFe concentrations in sea ice and highlight the uncertainties that remain regarding the mechanisms of Fe incorporation in sea ice.

1. Introduction

Marine phytoplankton use light and nutrients including nitrogen, phosphorus and trace metals to convert dissolved carbon dioxide (CO₂) into organic matter through photosynthesis. Phytoplankton growth is often limited by the availability of the micro-nutrient iron (Fe) in remote oceanic regions where external inputs of this nutrient are low (Martin et al., 1990; de Baar et al., 1995). Iron clearly limits primary productivity in large regions of the Southern Ocean (de Baar et al., 1990). Iron limitation has also been suggested in some parts of the Arctic Ocean (Aguilar-Islas et al., 2007; Taylor et al., 2013).

Several studies have reported considerable enrichment of Fe in sea ice (Grotti et al., 2005; Lannuzel et al., 2007, 2008, in press; Aguilar-Islas et al., 2008; Tovar-Sánchez et al., 2010; van der Merwe et al., 2011a, 2011b; de Jong et al., 2013, 2015; Kanna et al., 2014), but the processes driving these high concentrations are not well understood (Janssens et al., 2016). The majority of Fe inputs to sea ice are believed to originate from the seawater (Lannuzel et al., 2007). The co-occurrence of high concentrations of Fe and organic matter in the ice suggests a coupling leading to their enrichment (Grotti et al., 2005; Lannuzel et al., 2007, in press; Schoemann et al., 2008). Iron released by sea-ice melting during spring, in combination with increasing

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light availability and surface-water stratification, can trigger ice-edge phytoplankton blooms (Arrigo et al., 1997; Sedwick and DiTullio, 1997; Measures, 1999; Lannuzel et al., 2010; Kanna et al., 2014). The global (Arctic and Antarctic) seasonal ice zone, where sea ice completely melts and reforms every year, covers about 22.5 million km². Hence, sea ice constitutes the dominant and most widespread source of Fe in polar waters during seasonal melting (Lannuzel et al., 2007; de Jong et al., 2015) and therefore may play a key role in drawing down atmospheric CO₂ levels through the stimulation of primary production in these climatically-important areas.

However, despite sampling and analytical advances, the number of Fe measurements on sea ice is vanishingly small compared to the vast area that sea ice covers. Considering all field measurements to date, the total number of cores extracted for trace metal analysis amounts to only 131 (Table 1), and covers a combined area of a few square meters, widely distributed over the Southern and Arctic Oceans. This lack of data is due, in part, to the logistical difficulties of accessing remote areas of the polar oceans and the difficulties in trace metal-clean sampling of sea ice. Specialized trace metal-clean sampling equipment for sea ice has been developed and used in only a few laboratories around the world. Furthermore, the highly saline, organic-rich and highly variable nature of the sea-ice sample matrix provides analytical challenges to effectively quantify trace metals. In recent years, these challenges have been overcome, and together with international intercalibration exercises (e.g., GEOTRACES program), new information on the distribution of trace elements in the world's oceans, and more specifically in the most remote and Fe-limited oceanic areas, has become available.

Table 1. List of sea-ice Fe data currently available in the literature

Ocean	Voyage ID	Sector	Year	Months	Number of cores	Type of ice	Water depth (m)	[DFe] (nmol L ⁻¹)	[PFe] (nmol L ⁻¹)	[TDFe] (nmol L ⁻¹)
Arctic	Transdrift III ^a	Laptev Sea	1995	Oct	19	fast	10–40	281–10,585	n.a.	n.a.
	Bering Ecosystem Study ^b	Bering Sea	2007	Apr–May	6	fast	40–80	2.92–376	n.a.	111–75,100
	ATOS-Arctic ^c	Fram Strait	2007	July	10	fast	100–2,500	n.a.	n.a.	220–3,599
Sub-Arctic	n.a. ^{d,e}	Baltic Sea	1999	Jan–Apr	23	fast	5–20	n.a.	n.a.	1,323–11,839
	P/V <i>Soya</i> ^f	Sea of Okhotsk	2010, 2011	Feb	9	fast	100–1,000	< DL ^g –5.8	n.a.	33.6–3,821
Southern	PNRA ^g	Ross Sea	1997, 1998	Nov	1	fast	430	n.a.	718–7,091	n.a.
	PNRA ^h	Ross Sea	2000, 2001	Nov–Dec	5 (2 for DFe)	fast	430	1.07–5.98	26–1,162	n.a.
	CASEY ⁱ	South Pacific	2009	Nov	7	fast	17	2.1–81	40.2–6,828	33.8–4,240
	Scott Base ^j	Ross Sea	2003	Jan	6	fast	50–450	2.2–109	9–1,854	10–1,178
	ARISE ^k	South Pacific	2003	Sept–Oct	6	pack	> 1,000	2.6–26.0	n.a.	3.3–65.8
	ISPOL ^l	Weddell Sea	2004–2005	Nov–Jan	7	pack	> 500	0.7–36.8	2.0–141.2	2.3–97.8
	SIPEX ^m	South Pacific	2007	Sept–Oct	8	pack and fast	> 1,000	0.2–14.4	n.a.	1.2–378
	McMurdo ⁿ	Ross Sea	2009	Nov	3	fast	600	n.a.	12–9,318	n.a.
	SIPEX2 ^o	South Pacific	2012	Sept–Nov	6	pack	> 1,000	0.9–17.4	0.04–990	n.a.
	SIMBA ^p	Bellingshausen Sea	2007	Oct	10	pack	> 1,000	1.1–30.2	n.a.	2.8–77.7
AWECS ^q	Weddell Sea	2013	July	5	pack	500–4,000	1.0–3.2	20.1–254.1	n.a.	

^aHölemann et al. (1999)

^bAguilar-Islas et al. (2008)

^cTovar-Sánchez et al. (2010)

^dn.a. indicates not available

^eGranskog and Virkanen (2001)

^fKanna et al. (2014)

^gGrotti et al. (2001)

^hGrotti et al. (2005)

ⁱvan der Merwe et al. (2011b)

^jde Jong et al. (2013)

^kLannuzel et al. (2007)

^lLannuzel et al. (2008)

^mvan der Merwe et al. (2011a)

ⁿNoble et al. (2013)

^oLannuzel et al. (in press)

^pde Jong et al. (2015)

^qJanssens et al. (2016)

^rDL indicates detection limit.

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Global climate models currently do not incorporate active biogeochemical ice-related processes (e.g., Vancoppenolle et al., 2013). Some biogeochemical ocean models have included the role of sea ice as a source of Fe to surface waters (Lancelot et al., 2009; Wang et al., 2014), demonstrating how Fe released from sea ice may boost phytoplankton growth in the marginal ice zones during spring. However, very simple parameterizations were used in the models, because the mechanisms of Fe incorporation into and release from sea ice remain poorly understood. This review summarizes and synthesizes the current understanding on Fe biogeochemistry in sea ice in order to inform emerging modeling efforts. The data compiled in this work provide a first step in making quantitative estimates of the impact of sea ice-bearing Fe on primary productivity in polar waters, in particular the Southern Ocean.

2. Iron in Arctic and Antarctic sea ice

2.1. Sampling and analytical methods – an overview

Several techniques have been used to retrieve ice samples suitable for trace metal analysis successfully. The use of non-contaminating ice corers renders the collection of sea-ice samples for trace-metal analysis easier and logistically less challenging, resulting in more samples with larger volumes, leading to an increase in sea-ice trace metal data over the last 10 years. Recommendations for the collection of contamination-free samples in the sea-ice environment are made in Miller et al. (2015). Once collected, the samples are placed into acid-cleaned plastic containers and allowed to melt, before filtration through 0.2 or 0.4 μm membrane filters to obtain the fractions of dissolved Fe (DFe, smaller than 0.2 or 0.4 μm) and particulate Fe (PFe, larger than 0.2 or 0.4 μm). An unfiltered sample aliquot can be collected as well, and acidified at pH 1.8 for at least 6 months to obtain the total dissolvable Fe (TDFe) fraction.

Particulate trace metals retained on the filters are generally digested in a mixture of strong acids ($\text{HCl} + \text{HNO}_3 + \text{HF}$, supra- or ultrapure-grade quality) before being dry-evaporated, redissolved and analysed (Grotti et al., 2001; Bowie et al., 2010; de Jong et al., 2013). Several instrumental techniques are used to determine the Fe concentrations ($[\text{Fe}]$) in the solutions resulting from the sample preparation step, including flow injection analysis with chemiluminescence detection (Lannuzel et al., 2006; van der Merwe et al., 2011a, 2011b; Kanna et al., 2014); inductively coupled plasma mass spectrometry, either following pre-concentration (Aguilar-Islas et al., 2008; de Jong et al., 2008) or directly (Tovar-Sánchez et al., 2010; Noble et al., 2013; Lannuzel et al., 2014, in press); inductively coupled plasma optical emission spectrometry (Grotti et al., 2005); and electrothermal atomic absorption spectrometry (Granskog and Virkanen, 2001; Grotti et al., 2005; Kanna et al., 2014).

2.2. Historical data compilation and analysis

2.2.1. Data description and methods

Under the auspices of the Scientific Committee on Oceanographic Research (SCOR) working group 140 (BEPSII), we have extended the effort of the Antarctic Sea Ice Processes and Climate (ASPeCt) program to compile the first circum-Antarctic and Arctic sea-ice Fe database (ASPeCt-Fe), following the template protocols of ASPeCt (Worby et al., 2008) and ASPeCt-Bio (Meiners et al., 2012). Iron data from 131 sea-ice cores over 16 campaigns from 1995 to 2013 in Arctic, sub-Arctic and Antarctic waters are currently available (Table 1). Because of the lack of ancillary information (ice thickness, sampling depth and location) for a significant part of these studies, only 71 of these cores can be used for consistent statistical analysis. Only 10 of these samples originate from the northern hemisphere (ATOS, Tovar-Sánchez et al., 2010; Table 1), and these data are not really comparable to the Antarctic dataset due to a lack of vertical resolution and the report of total Fe concentrations rather than DFe, TDFe and PFe concentrations. We therefore focused subsequent analyses on 61 ice cores collected in the Southern Ocean and Antarctic coastal marine systems (Figure 1).

We separated the coastal (land-fast sea ice) from offshore free-drifting pack ice data based on the ETOPO 1 Arc-minute global relief model (Amante and Eakins, 2009), giving water column depth at the coring location. Cores collected in waters shallower than 200 m were considered as coastal. We expected to find an Fe concentration gradient from the continental shelf to deeper water regions.

Iron concentrations were integrated vertically to obtain the Fe inventory (I , $\mu\text{mol m}^{-2}$), using the following procedures: 1) convert nmol L^{-1} into $\mu\text{mol m}^{-3}$; 2) sum the products (concentration \times section depth); and 3) divide the result by the total length of the sections and multiply by core length. Step 3 accounts for the effect of missing ice-core sections (i.e., when only a few sections, rather than full cores were analysed). Cores with less than 25% of sampled fractions were excluded from further analyses.

To derive mean concentration profiles, the Fe concentration profiles from ice cores with more than four sampled sections were estimated on a grid with four layers of equal thickness, imposing the conservation of Fe content. Mean profiles were obtained by averaging the estimated concentrations on each vertical layer.

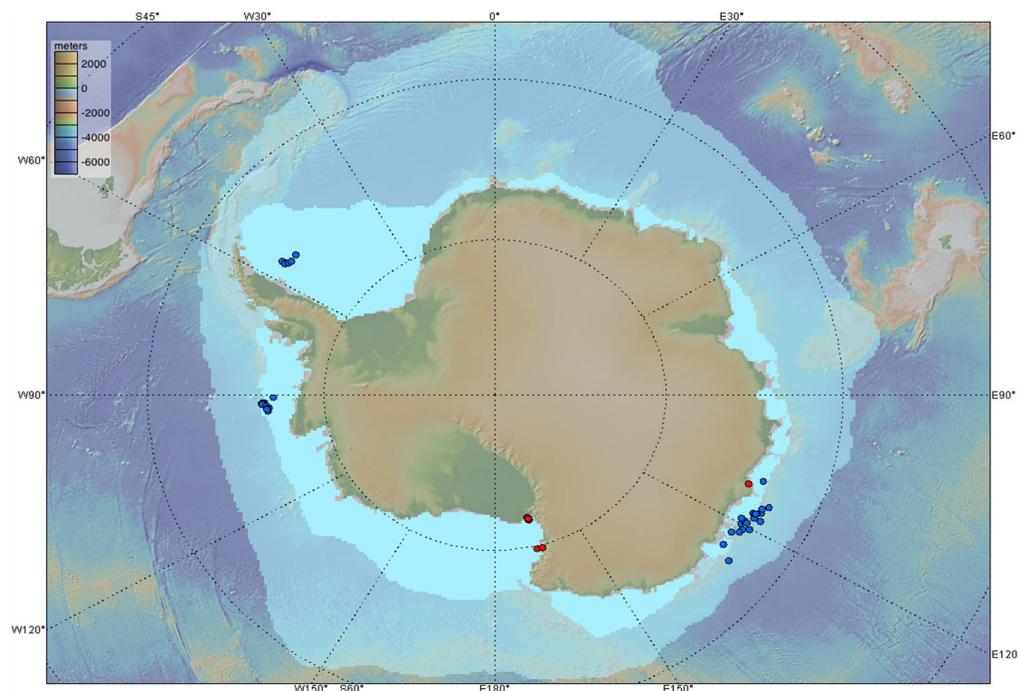


Figure 1

Map showing the locations of pack (blue) and fast (red) ice cores (<http://www.geomapapp.org/>).

The blue-shaded overlays represent mean (1979–2007) maximal (September) and minimal (March) sea-ice extent ($\geq 15\%$ ice cover).

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For each Fe profile, corresponding profiles of salinity (S), *in situ* temperature (T), chlorophyll *a* (Chl-*a*) and particulate organic carbon (POC) were obtained from the database (same date and geographical coordinates of extraction, ice thickness within 0.2 m). Note that the core sections between profiles of two different parameters rarely matched, because Fe data and the auxiliary parameter data often derived from two separate cores. When both sea-ice S and T were available, we computed brine salinity (S_{br}) and brine volume fractions (Φ_{br}) following Notz (2005). Summary statistics for the Antarctic data analyses are given in Table 2 and visualized in Figures 2–8.

Table 2. Summary statistics for Fe concentrations in Antarctic sea ice

Parameter	DFe	TDFe	PFe
Number of cores with valid data	56 (11 fast, 45 pack)	50 (9 fast, 41 pack)	44 (14 fast, 30 pack)
Number of core sections with valid data	275	280	181
Mean fraction of core length sampled (%)	50	50	43
Concentration range (nmol L ⁻¹)	0.2–110	0.04–6,800	0.9–7,100
Mean concentration \pm S.D. ^a (nmol L ⁻¹)	9.8 \pm 15.0	210 \pm 660	310 \pm 770
Median concentration (nmol L ⁻¹)	4.4	23	39
Mean inventory \pm S.D. ($\mu\text{mol m}^{-2}$)			
All	12 \pm 21	250 \pm 460	310 \pm 480
Fast ice	22 \pm 20	1,100 \pm 500	930 \pm 450
Pack ice	9.6 \pm 20	70 \pm 150	80 \pm 220
Median inventory ($\mu\text{mol m}^{-2}$)			
All	4.7	14	21
Fast ice	14	1,100	840
Pack ice	2.9	11	9.6

^aS.D. indicates standard deviation of the mean.

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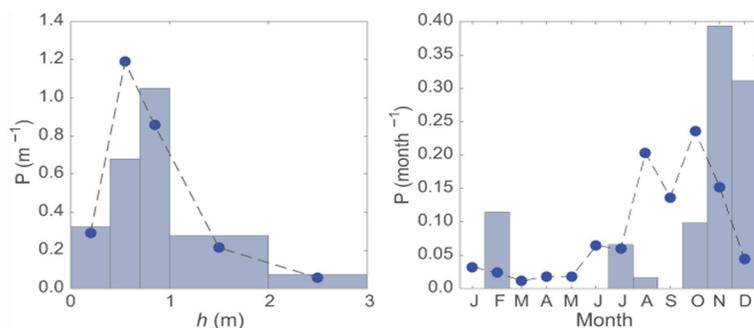


Figure 2

Probability density distributions of ice thickness (left) and sampling month (right).

About half of the Fe ice cores analysed (grey bars) have an ice thickness, h , of < 1 m, which is comparable to the ASPeCt-BIO database (blue circles; Meiners et al., 2012).

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2.2.2 Spatial representativity and variability

In contrast to seawater which is well-mixed in most areas of the globe, sea ice is a very heterogeneous medium to sample. Many sea-ice biogeochemical studies have highlighted the need for highly spatially resolved sampling efforts (both vertically, along the depth of the ice core, and horizontally, from centimeters to meters to regional to global scale). We also agree that there is a need for a spatially resolved sampling of Fe in sea ice. This aim has yet to be achieved. Ideally, the trace metal cores need to be collected in replicate a few meters away from each other to assess the effect of horizontal variability on metal distribution. Also, because of the logistical challenges posed by such a heterogeneous, changing and extreme environment, sea-ice biogeochemists tend to sample thin and undeformed areas of sea-ice cover. This sampling plan makes the comparison of Fe to other parameters and the interpretation of the dataset easier. However, recent autonomous underwater vehicles have shown that on average 57% of the Antarctic pack-ice cover is deformed (Williams et al., 2015). This contribution far exceeds previous drilling (12%) and shipboard (43%) observations (Williams et al., 2015). Dynamic processes of ridging and rafting are therefore a significant part of the sea-ice environment and deserve to be more consistently sampled and studied. Data presented here focus on undeformed first-year ice and associated Fe distributions.

Iron sampling around Antarctica is generally sparse (Figure 1). Data are available from four Antarctic sectors (Weddell Sea, Bellingshausen Sea, Ross Sea and Pacific), with the highest sampling effort in the Pacific sector (four field programs). Pack ice samples dominated the collated dataset (i.e., 68% of the total number of cores for PFe, 80% for DFe and 82% for TDFe; Table 2). Coastal ice cores comprised only land-fast sea-ice cores (PNRA, Casey and McMurdo; Table 1). We can therefore use the term “land-fast” (or simply “fast”) as an equivalent for coastal sea ice. About half of the ice cores analysed have an ice thickness of < 1 m, which is comparable to the ASPeCt-BIO database (Figure 2; Meiners et al., 2012). Iron distributions are heavily skewed, with a large proportion of small values and few very large values (Figure 3). This explains why the median Fe concentrations are generally lower than the mean concentrations (Table 2).

Our analysis of existing data confirms that Antarctic sea ice contains high levels of Fe, in all forms, for both pack and fast ice (Table 2). For example, the DFe mean concentration in pack ice ($[\text{DFe}] = 9.8 \pm 15.0$ nmol L^{-1} , $n = 56$ cores) is an order of magnitude higher than Southern Ocean surface seawater concentrations (compilation from Tagliabue et al., 2012: mean $[\text{DFe}] = 0.61 \pm 1.14$ nmol L^{-1} in shelf waters and 0.38 ± 0.55 nmol L^{-1} in off-shelf waters). Because Fe concentrations are higher in coastal than in open

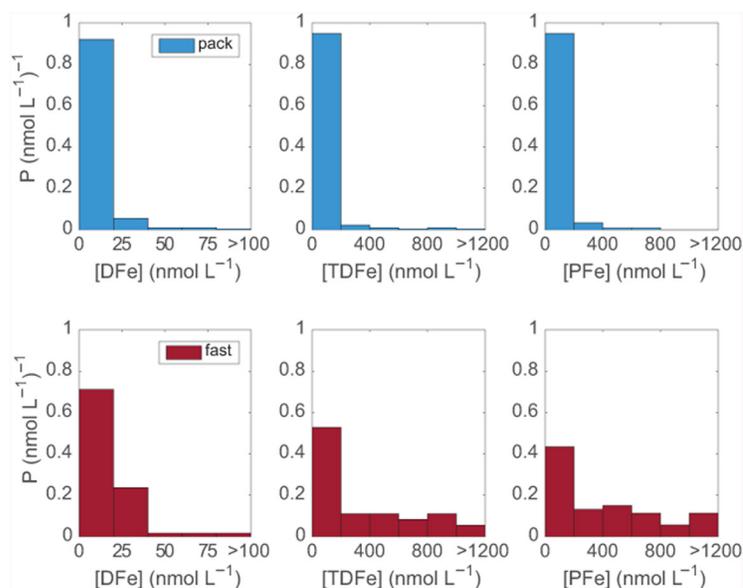


Figure 3

Probability distributions for DFe, TDFe and PFe concentrations in pack (blue) and fast (red) ice.

The distributions of the Fe concentrations (nmol L^{-1}) are heavily skewed. Large Fe values are usually observed in the bottom of the ice because sea-ice algae scavenge Fe from seawater or Fe is transported downwards from the upper sea-ice layer during brine drainage.

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water, fast ice should be more concentrated in Fe than pack ice. Overall, and as expected, we do find an [Fe] gradient in sea ice from the continental shelf, where fast-ice floes are composed predominantly of congelation ice and coastal inputs of Fe are high, to the deep-water regions, where pack-ice floes are composed of frazil ice and snow ice and external Fe inputs are low (Table 2; Figure 4). This enrichment in fast ice compared to pack ice is especially obvious in the TDFe and PFe fractions (Table 2; Figure 4). Inverse relationships ($p < 0.05$) are observed TDFe, PFe and DFe contents and water column depth (Figure 5; Spearman's rank correlation coefficients = 0.65, 0.58 and 0.43, respectively). The increase in Fe inventories (especially TDFe and PFe forms) in sea ice when the water column depth decreases indicates the importance of sedimentary and coastal inputs in supplying Fe-bearing particles to land-fast sea ice (Grotti et al., 2005; van der Merwe et al., 2011b; de Jong et al., 2013; Noble et al., 2013). Sediment entrainment in sea ice has been observed in shallow waters of the Kara and Laptev Seas (Lindemann et al., 1999; Dethleff and Kuhlmann, 2009), suggesting that this process could entrain PFe (and therefore TDFe) into sea ice.

The vertical distribution of Fe in Antarctic sea ice is usually C-shaped in pack ice and L-shaped in fast ice (Grotti et al., 2001, 2005; Lannuzel et al., 2008; van der Merwe et al., 2011b). The highest Fe concentrations in pack ice are found in the uppermost parts of the ice cover, presumably because of entrainment of Fe during rapid growth of frazil ice, or snow ice formation during flooding events (also known as infiltration

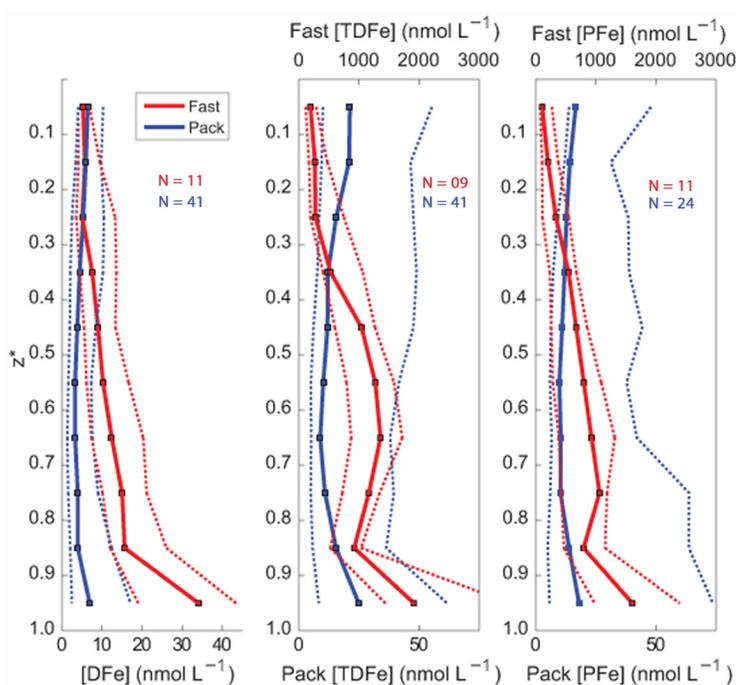


Figure 4

Vertical profiles of DFe, TDFe and PFe concentrations for pack (blue) and fast (red) ice.

The Fe concentrations (nmol L^{-1}) have been normalized to depth (z^*), with medians (solid lines) and interquartile ranges (dotted lines) indicated. There is significantly more Fe in fast ice than in pack ice, which holds true for all forms of Fe (DFe, TDFe and PFe).

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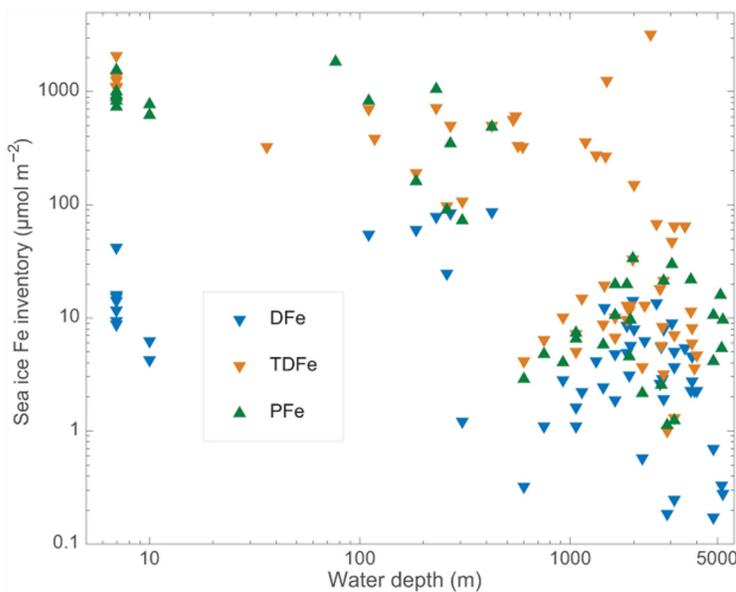


Figure 5

Iron inventories in Antarctic sea ice versus water column depth.

Inverse relationships ($p < 0.05$) were observed between TDFe, PFe and DFe inventories ($\mu\text{mol m}^{-2}$) and water column depth (m) (Spearman's rank correlation coefficients = 0.65, 0.58 and 0.43, respectively). The increase in Fe inventories (especially in the case of TDFe and PFe forms) in sea ice when the bathymetry decreases suggests the importance of sedimentary and coastal inputs in supplying Fe-bearing particles to land-fast ice.

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ice). These processes are less prevalent in fast ice, which tends to consolidate at slower growth rates, under quiescent and less snowy conditions, to form columnar ice. Iron is generally more concentrated towards the bottom of the ice because sea-ice algae scavenge Fe from seawater (Grotti et al., 2005; Lannuzel et al., 2010) or Fe is transported down from the upper sea-ice layer during brine drainage (de Jong et al., 2015). Interestingly, the compiled vertical Fe profiles are quite homogeneous, except for a slight increase of DFe concentrations with depth, especially in land-fast sea ice (Figure 4). The absence of the characteristic C- or L-shaped profiles in these averaged data is most likely due to the spatial and temporal variability masking/diluting the Fe maxima of individual ice cores.

As observed in fast ice collected on the Antarctic shelf, floes forming in the far south are expected to have a high lithogenic Fe content because of their proximity to land sources, as well as a high biogenic Fe content due to extended light exposure that allows biomass accumulation (Grotti et al., 2005; van der Merwe et al., 2011b; de Jong et al., 2013). Although the signal is diluted in our dataset, extremely high Fe levels can also be found in the pack ice zone (up 990 nmol L⁻¹ PFe during SIPEX2; Lannuzel et al., in press) and are considered to be the result of ice forming at higher latitudes early in the season with subsequent advection to the north. These dynamics would result in older ice with a higher Fe content occurring in the pack ice zone which is maintained at favourable light and temperature conditions during the seasonal ice consolidation and drift.

2.2.3 Seasonal variability in Fe concentrations in Antarctic sea ice

Data available to date are strongly seasonally biased towards spring and summer, with no data available for the autumn season and only a few data points available for late winter (Figure 2). One recent study reports high Fe concentrations in newly formed sea ice compared to seawater collected in the Weddell Sea in austral winter (Janssens et al., 2016). Three Antarctic time series have investigated the seasonal distribution of Fe during the melt season, the strategy employed being to repeatedly collect ice cores at one site every 3 to 5 days for several weeks (Lannuzel et al., 2008; van der Merwe et al., 2011b; de Jong et al., 2015). The time-varying nature of these studies highlighted the key role of biological uptake and halo-thermodynamics in the drawdown of DFe concentrations in sea ice and release into seawater.

Similar fieldwork should be pursued in both hemispheres, over extended periods of time, ideally over a whole year. Ultimately, there is a need for long-term observing platforms (for example, station-based) to investigate the interannual and decadal variability, which will aid in the identification of future trends in sea-ice mediated iron cycling.

2.3. Fe correlations in sea ice

2.3.1. Iron and ice thickness

The co-variance of mean DFe concentrations ([DFe], in nmol L⁻¹) with ice thickness h is represented in Figure 6. The sharp decrease of salinity (S) with ice thickness h in first-year ice is well documented (e.g., Kovacs, 1996). If DFe were a passive solute, purely driven by brine dynamics, then [DFe] would decrease with thickness in the same manner as S . If DFe were incorporated into forming sea ice without being expelled, then [DFe] would remain constant with h for constant seawater concentrations. The significant increase in [DFe] with ice thickness h (Figure 6) illustrates the continuous pumping of seawater DFe into sea ice. Similar correlations are weak for [TDFe] and [PFe] (Figure 6), hence they must be driven by different processes, i.e., processes that are likely independent of DFe dynamics.

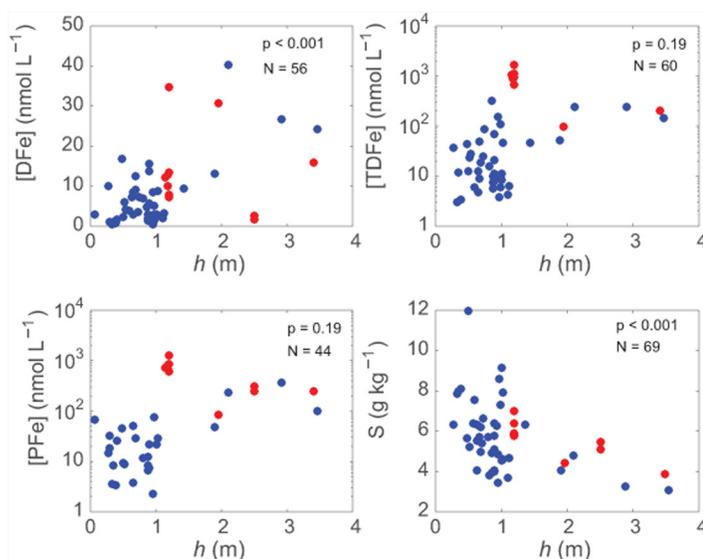


Figure 6

Mean iron concentrations and salinity versus ice thickness for pack (blue) and fast (red) ice.

Mean concentrations of DFe (upper left), PFe (upper right), TDFe (lower left) and salinity (S , lower right) are plotted as a function of ice thickness (h) and analysed for non-parametric Spearman's rank correlation. The statistical parameters apply to all data points in a given panel. The significant increase in [DFe] with ice thickness illustrates the continuous pumping of seawater DFe into sea ice. If DFe were a passive solute, [DFe] would decrease with thickness in the same manner as S . The correlations are weak for [TDFe] and [PFe], hence they must be driven by different processes from DFe.

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2.3.2. Iron and ice thermodynamics

Temperature and salinity are the main thermodynamic sea-ice state variables, from which other relevant quantities such as brine fraction or permeability derive (e.g., Hunke et al., 2011). In this subsection, how Fe relates to the thermodynamic state of sea ice is analysed.

If Fe were a passive solute, then the concentration of DFe in sea ice would be controlled by the composition of the seawater from which the ice forms (Meiners and Michel, in press), and [DFe] would change in direct proportion to salinity. Yet no correlation is observed in sea ice between [DFe] and salinity (Table 3). No correlation is observed in the dataset between [DFe] and *in situ* ice temperatures either (Table 3). Several field studies mention a decrease in DFe concentrations as sea ice warms and summer progresses (Lannuzel et al., 2007, 2008; van der Merwe et al., 2011b; de Jong et al., 2015), a feature that is less clear in the present study when multiple data sets with large variability in DFe concentrations are averaged.

Table 3. Correlation statistics based on non-parametric Spearman-rank tests to explore correlations between Fe concentrations and other variables^a for Southern Ocean ice-core sections

Form of Fe	Statistics	S	T	S _{br}	Φ _{br}	[Chl-a]	[POC]	[PFe]	[TDFe]
[DFe]	r ²	0.01	0.01	0.01	0.11	0.11	0.22	0.19	0.18
	p	0.1	0.2	0.1	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	N	42	35	35	35	42	44	34	49
[PFe]	r ²	0.07	0.05	0.06	0.36	0.49	0.48	-	0.92
	p	< 0.001	0.02	< 0.001	< 0.001	< 0.001	< 0.001	-	< 0.001
	N	34	27	27	27	34	26	-	33
[TDFe]	r ²	0.04	0.04	0.04	0.32	0.4	0.42	0.92	-
	p	0.003	0.02	0.007	< 0.001	< 0.001	< 0.001	< 0.001	-
	N	47	34	34	34	39	43	33	-

^aBulk sea-ice salinity (S), sea-ice temperature (T), brine salinity (S_{br}), brine fraction (Φ_{br}), and concentrations of chlorophyll *a* ([Chl-a]), particulate organic carbon ([POC]), dissolved iron ([DFe]), particulate iron ([PFe]) and total dissolvable iron ([TDFe]). If from a different core, the profiles of the investigated parameter were first interpolated onto the corresponding Fe core.

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Using *in situ* ice temperature and salinity, brine volume fraction can be calculated. A brine volume fraction greater than 5% is considered to indicate that sea ice is permeable to fluid transport (Golden et al., 1998). Brine fraction correlates significantly and positively with [DFe], [TDFe] and [PFe] (Table 3). A greater brine fraction is also associated with elevated biological synthesis of organic matter due to: (i) greater nutrient supply, (ii) more space for growth, and (iii) lower brine salinity and higher temperature, closer to seawater conditions (Becquevort et al., 2009; Vancoppenolle et al., 2010; Arrigo et al., 2014; Saenz and Arrigo, 2014). Autotrophic processes responsible for the formation of POM in sea ice when the brine fraction is greater will also lead to higher concentrations of PFe and TDFe in sea ice (see section 2.4.). This hypothesis is supported by the significant positive correlations of both [PFe] and [TDFe] with POC and Chl-a concentrations (Table 3, Figure 7).

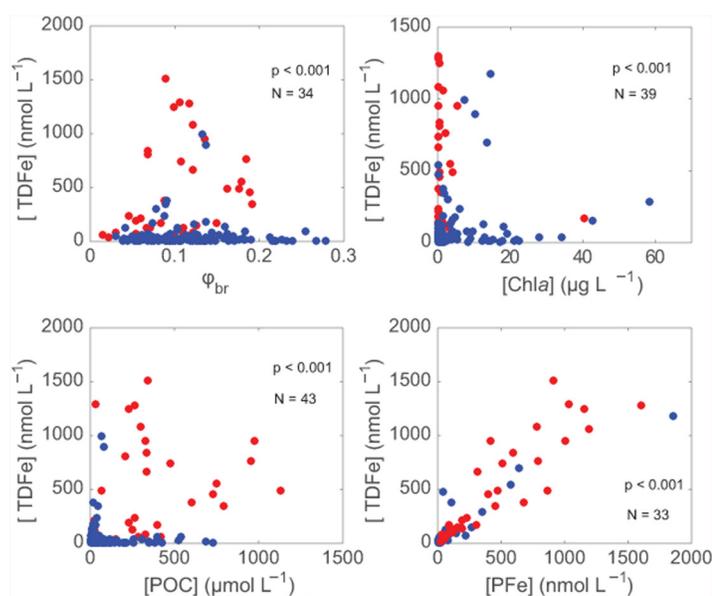


Figure 7

Selected scatter plots for [TDFe] for pack (blue) and fast (red) ice.

Mean concentrations of total dissolved Fe (TDFe) are plotted as a function of brine volume fraction (Φ_{br}, upper left), chlorophyll *a* (Chl-a, upper right), particulate organic carbon (POC, lower right) and particulate Fe (PFe, lower right), and analysed for non-parametric Spearman's rank correlation. The statistical parameters apply to all data points in a given panel. The positive and significant correlations of TDFe concentrations with brine volume fraction Φ_{br} and biological parameters such as [POC] and [Chl-a] suggest a coupling between the Fe pool and the biota. The strongest correlation shown (lower right), between [TDFe] and [PFe], indicates that particulate Fe largely explains the total dissolvable Fe in sea ice.

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2.4. Biological controls on Fe distribution

Besides the role of thermodynamic processes, the distribution of Fe phases within sea ice is also controlled by biological processes. Autotrophic activity can lead to a decrease in DFe concentrations via uptake and a parallel increase in biogenic PFe concentrations. Conversely, activity by marine heterotrophs tends to remineralise Fe, transforming it from PFe into DFe. Recent work has shown the complex interplay of competition and synergy between bacteria and phytoplankton in the Fe and C cycles in Fe-fertilized waters downstream of the Kerguelen Plateau (Fourquez et al., 2015). The same interactions between the heterotrophic and autotrophic communities likely occur in the sea-ice environment. The effect of autotrophic activity on the Fe cycle is usually visible in basal sea ice in spring when [PFe], [Chl-a] and [POC] increase, suggesting a bio-accumulation of PFe (Grotti et al., 2005; van der Merwe et al., 2009; de Jong et al., 2013). Our compilation of circum-Antarctic data confirms positive and significant relationships of both [PFe] and [TDFe] with [POC] and [Chl-a] (Table 3, Figure 7).

Iron isotopic fractionation can be used to trace sources and biogeochemical processes in the marine environment. The role of autotrophic and heterotrophic activity in the sea-ice Fe cycle has been further described using Fe isotopes (de Jong et al., 2007). In Antarctic pack ice, de Jong and co-authors showed that the isotopic composition of PFe is lighter in the uppermost part of the ice cover where bacteria and heterotrophic flagellates dominate, and tends to increase deeper in the sea-ice cover where large autotrophs, in particular diatoms, are more abundant. The isotopic composition of DFe contrasts with PFe, with lighter DFe isotopes in basal ice and heavier DFe isotopes in the internal layers. The authors contend that heterotrophs and autotrophs have different Fe uptake mechanisms, with heterotrophs favouring the uptake of light DFe isotopes and the autotrophs favouring the uptake of heavy DFe isotopes (de Jong et al., 2007). Furthermore, physical processes may also fractionate Fe, with the level of isotopic fractionation depending on sea-ice temperatures and/or sea-ice formation mechanisms (de Jong et al., 2007). Clearly, detailed research on the role of autotrophs and heterotrophs in the sea-ice Fe cycle is required.

2.5. Iron speciation in sea ice: An indicator of Fe bio-availability

2.5.1. Size fractions of Fe

Iron can exist in the marine environment in different forms, physically (i.e., size) and chemically (i.e., redox species Fe^{2+} or Fe^{3+} , free Fe or organically bound Fe). The form in which Fe exists dictates how easily accessible or “bio-available” it is for phytoplankton and other microorganisms. Most studies distinguish between the operationally defined particulate (greater than 0.2 or 0.4 μm) and dissolved (smaller than 0.2 or 0.4 μm) forms to estimate this Fe bio-availability. In fact, the dissolved fraction contains a continuum of small soluble and large colloidal species within which Fe may partition. Although one would assume that the smallest size is easier for phytoplankton to access, no direct link exists between soluble and bio-available Fe. In fact, colloidal Fe seems to be an important pool to sustain Fe bio-availability (Hassler and Schoemann, 2009). One study has reported operationally defined soluble (smaller than 0.02 μm) and colloidal (0.02–0.2 μm) Fe concentrations from Antarctic fast ice (Lannuzel et al., 2014). The colloidal Fe fraction represented on average 75% of the dissolved fraction. This contribution is well above Southern Ocean studies, where 37% of DFe was found to be colloidal in surface waters (0.03–0.2 μm ; Boye et al., 2010).

There is much more TDFe and PFe than DFe in sea ice, which seems true both for fast ice and pack ice (Table 2). The median PFe concentration (38.7 nmol L^{-1}) is similar to TDFe (23.0 nmol L^{-1}), which are both about 7 times higher than DFe (4.4 nmol L^{-1}). Antarctic fast ice contains much more Fe than pack ice, especially in the case of the TDFe and PFe fractions (Table 2).

The partitioning of Fe between the dissolved and particulate pools is especially important since DFe and PFe are released sequentially during spring melt, therefore potentially extending the time over which phytoplankton can benefit from sea-ice Fe fertilization (Grotti et al., 2001; van der Merwe et al., 2011a). Laboratory-based observations have confirmed that DFe is released into seawater first together with salts and dissolved organic material, while PFe is released at a later stage together with particulate organic matter and low salinity waters (Lannuzel et al., 2013). A study by Janssens and co-authors (2016) also showed size selective incorporation of PFe and DFe during the early stages of sea-ice formation.

2.5.2. Retention of Fe within sea ice

Field-based (van der Merwe et al., 2011a) and laboratory-based (Lannuzel et al., 2013) studies have both indicated a temporal decoupling between the release of DFe and PFe into the water column during spring melt. The later release of PFe compared to DFe suggests that PFe is somehow retained within the sea-ice matrix, whether via physical constrictions within the brine network (Krembs et al., 2011) or possible adhesion to the walls of the brine channels. This retention of PFe is likely to involve the complexation of Fe with extracellular polymeric (or exopolymeric) substances (EPS; see section 2.5.5), gel-like material in the brine phase of the sea-ice matrix (Krembs et al., 2002). Exopolymers in seawater can be two to four orders of magnitude more adhesive than other particles (Passow, 2002), which in sea ice could aid in the attachment of PFe to other particulate surfaces possibly including the walls of the brine channels. Although similar

retention processes for nutrients have been suggested in the case of dissolved phosphate (Becquevort et al., 2009; Fripiat et al., 2016), no data have suggested that such retention is the case for DFe.

To evaluate the level of retention of DFe within sea ice, we compared the DFe and salinity (S) data from sea-ice cores (AsPeCt-Fe, 275 sections) with DFe and S data collected in 28 sackhole brines. To collect sackhole brines, incomplete holes were drilled to a desired depth (above and below the -5°C isotherm; Tison et al., 2008). The brines were then allowed to drain into the sackholes and collected using a peristaltic pump and acid-clean silicone tubing. Bulk sea-ice and sackhole samples were collected during the same cruises (ARISE, ISPOL, SIPEX, CASEY). We then calculated the theoretical DFe concentrations in the brines ($[\text{DFe}]^{\text{br}}$):

$$[\text{DFe}]^{\text{br}} = \frac{[\text{DFe}]}{\Phi_{\text{br}}}$$

where $[\text{DFe}]$ is the concentration of DFe in the bulk sea-ice sample and Φ_{br} is the brine fraction. If DFe is dissolved in brine, there should be no difference between theoretical $[\text{DFe}]^{\text{br}}$ and measured Fe concentration in the sackhole samples.

However, the results show that the theoretical DFe concentrations in the brines are systematically much higher (median of 57.2 nmol L^{-1} ; Figure 8) than the actual measurements from sackhole samples (median of 4.36 nmol L^{-1} ; Figure 8). We therefore argue that:

- (1) most of the DFe is not truly dissolved in brine, but rather adsorbed onto surfaces, including possibly ice, or organic matter such as EPS or algae within the ice matrix;
- (2) the sample processing for bulk sea-ice Fe concentration (e.g., melting of ice core sections and/or filtration) appears to release the “adsorbed” Fe more effectively than the sackhole method for brine sampling.

Our findings highlight the strength of the Fe pumping process in Antarctic sea ice. The median ratio between the theoretical and measured brine Fe concentration can be used as an approximation of the adsorption coefficient of DFe in sea ice; nearly 90% of DFe is adsorbed onto something in sea ice. The retention of Fe within the sea-ice matrix is especially relevant for evaluating the residence time of Fe in sea ice and therefore its bio-availability for sea-ice and pelagic algae.

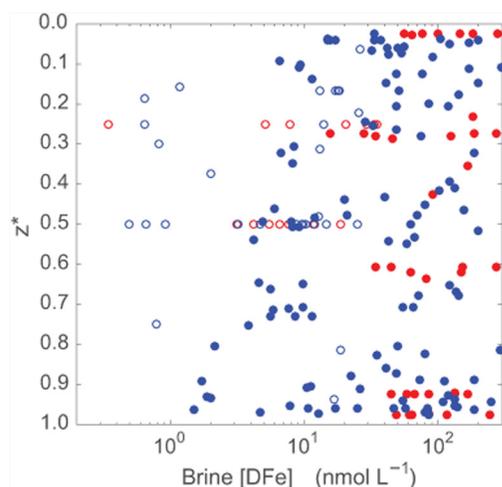


Figure 8

Theoretical and measured DFe concentrations in sea-ice brines for pack (blue) and fast (red) ice.

The theoretical DFe concentrations (filled circles) in the brines ($[\text{DFe}]^{\text{br}}$) were calculated as $[\text{DFe}]^{\text{br}} = \frac{[\text{DFe}]}{\Phi_{\text{br}}}$, where $[\text{DFe}]$ is the concentration of DFe in the bulk sea-ice sample and Φ_{br} is the brine fraction. The measured DFe concentrations (open circles) are from sackhole samples. Samples were collected during the ARISE, ISPOL, SIPEX and CASEY expeditions (Table 1). All data are plotted by normalized ice-core depth (z^*). The theoretical DFe concentrations are found systematically higher (median 57.2 nmol L^{-1}) than the measurements from the sack-hole samples (median 4.36 nmol L^{-1}) collected during the same cruises. The ratio between the median theoretical and measured brine Fe concentration can be used as an approximation of the adsorption coefficient of DFe in sea ice; nearly 90% of DFe in sea ice is adsorbed onto something.

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2.5.3. Iron redox species

No data have been reported yet on Fe redox species in sea ice. The reduced form Fe^{2+} is often considered more bio-available than Fe^{3+} (Shaked and Lis, 2012). Although the half-life of Fe^{2+} is extended in polar waters because of the cold temperatures and low H_2O_2 concentrations (Wells et al., 1995), Fe^{2+} oxidation still occurs in a matter of minutes (half-life of Fe^{2+} is 94 min at O_2 saturation and 4°C ; Croot and Laan, 2002), which poses a challenge for analysis considering the time required to collect, melt, filter and analyse sea-ice cores. Alternatively, immediate analysis of liquid brine samples can limit the time for oxidation to occur and therefore help preserve the redox state. Available measurements show that both O_2 undersaturation and oversaturation with respect to equilibrium with air are found in sackhole brines (Papadimitriou et al., 2007), with hyperoxic conditions ($[\text{O}_2] > 300\text{--}350 \mu\text{mol kg}^{-1}$) being common in predominantly autotrophic-dominated sea-ice habitats. In seawater below sea ice, experimental and observational studies show that growing sea ice releases brine enriched in O_2 , while melting ice is under-saturated in O_2 (Mock et al., 2003; Glud et al., 2014; Moreau et al., 2015). This transition from higher to lower O_2 concentrations in seawater could favour the formation of Fe^{2+} species as spring arrives.

Sudden changes in light exposure, salinity and temperature during sample collection and processing can also affect Fe redox chemistry in melted ice samples. Laboratory-based and field-based work suggests that the photochemical reduction and dissolution of Fe oxides can be enhanced significantly in the ice compared to the liquid phase (Kim et al., 2010). The only currently available Fe²⁺ data in the field for the sea-ice environment are for under-ice seawater, with values below 10 pmol L⁻¹, and do not suggest that sea ice supplies detectable amounts of Fe²⁺ to Antarctic surface waters (Schallenberg et al., in press). As one meter of sea ice attenuates over 97% of UV-B radiation reaching the underlying seawater (Perovich, 1993), photochemical production of Fe²⁺ is expected to be minimal or absent, consistent with these measurements. The photochemical reduction of Fe³⁺ into Fe²⁺ requires the presence of electron donors such as colored dissolved organic matter (CDOM), which is produced either actively or as a bi-product by marine microbes (Nelson et al., 1998, 2004; Barbeau et al., 2001; Rochelle-Newall and Fisher, 2002; Gerringa et al., 2004; Rijkenberg et al., 2005). A pulse of CDOM released from melting sea ice (Norman et al., 2011) and/or biological activity could enhance Fe²⁺ production in under-ice seawater and particularly in sunlit surface layers close to receding ice-edges in spring and summer (Schallenberg et al., in press). This process, however, has not yet been reported.

2.5.4. Effect of CO₂ and pH on Fe chemistry

It has been suggested that ocean acidification could increase Fe bio-availability by “dissolving” more Fe as well as favouring the more bio-available species of Fe, Fe²⁺ (Breitbarth et al., 2010). In this scenario, ocean acidification would increase primary productivity in Fe-enriched areas, potentially leading to a stimulation of the biological pump of carbon (Breitbarth et al., 2010; Hoppe et al., 2013). Conversely, other studies suggest that ocean acidification may decrease the bio-availability of DFe (Shi et al., 2010). Sea ice can exhibit high levels of CO₂ compared to the atmosphere, e.g., from oversaturation ($\Delta p\text{CO}_2 = p\text{CO}_{2(\text{brines})} - p\text{CO}_{2(\text{air})} = 525$ ppm) during early spring to a marked undersaturation ($\Delta p\text{CO}_2 = 335$ ppm) during summer (Delille et al., 2014). Recent work on modeled Arctic sea ice has shown that during ice growth, due to CO₂ flux from sea ice to the atmosphere, sea ice is likely basic (pH > 9). During ice melt, due to the flux of CO₂ from the atmosphere to sea ice, melting sea ice becomes likely acidic (pH < 6.5), which can lead to acidic melt ponds in the Arctic (Bates et al., 2014). The acidification of the sea-ice environment has not yet been observed in Antarctica, but it is possible that net primary productivity can change the sea surface pH and therefore Fe bio-availability over a seasonal growth/melt cycle.

2.5.5. Complexation of Fe

Inorganic Fe is the preferred form for biological uptake, but the organically bound fraction is also accessible for some phytoplankton and bacteria (Maldonado and Price, 1999; Maldonado et al., 2005). Two studies report the level of organic complexation of Fe in sea ice, and they both agree that over 99% of Fe in sea ice is bound to organic ligands (Boye et al., 2001; Lannuzel et al., 2015). Similar to what has been reported historically in the case of DFe, the dissolved organic ligands are also enriched in sea ice and in sackhole brines compared to ice-free waters (i.e., 4.5–72.1 nmol L⁻¹ in sea ice and 5.9–41.4 nmol L⁻¹ in brines, against a mean of 0.72 ± 0.23 nmol L⁻¹ in seawater in Boye et al., 2001). Lannuzel et al. (2015) highlight a positive linear relationship between DFe and dissolved ligand concentrations in sea ice and brines collected off the East Antarctic coast. This finding suggests that organic ligands control the concentration of DFe in sea ice. When DFe occurs in excess to the concentration of organic ligands, DFe may form less bio-available Fe oxyhydroxides in the particulate size range. Organic ligands can be produced *in situ* by sea-ice (or planktonic) algae and bacteria (Lannuzel et al., 2015) or supplied externally from sediment resuspension (Croot and Johansson, 2000; Buck et al., 2007). Organic ligands ultimately maintain Fe in solution for longer than would otherwise occur, thereby delaying the adsorption of DFe onto particles and likely increasing the residence time of bio-available forms of Fe in sea ice. It has been hypothesized that in sea ice, EPS carrying carbohydrate backbones with large amounts of negatively charged uronic acid functional groups can also act as Fe-binding organic ligands (van der Merwe et al., 2009; Benner, 2011; Hassler et al., 2011; Lannuzel et al., 2015). These weak organic ligands would then be released with Fe into seawater in spring, and could help trigger and sustain ice-edge phytoplankton blooms by increasing the residence time of DFe in surface waters (van der Merwe et al., 2009; Lannuzel et al., 2015) and its bio-availability for microorganisms (Hassler and Schoemann, 2009; Hassler et al., 2011).

2.5.6. Bio-availability of PFe

There is evidence that PFe can become accessible to some organisms (Maranger et al., 1998; Hurst and Bruland, 2007; Rubin et al., 2011), and certain fractions of PFe can also leach dissolved and soluble Fe over time (Schroth et al., 2009). Particulate Fe can also be solubilized by protozoan and metazoan grazing, lysis (including virally induced), bacterial remineralization and phytoplankton exudation (Barbeau et al., 1996). Recent data on the solubility of sea-ice particles collected in the Sea of Okhotsk suggest that 1.0–6.8% of sea-ice PFe can become soluble in seawater within 48 hours (Kanna et al., 2016). The speciation of PFe can also be approximated by applying a suite of selective chemical digestions, e.g., using acetic acid, hydroxylamine hydrochloride and hydrogen peroxide to sequentially remove 1) the exchangeable ions and the metals bound

to the carbonate phases, labile oxides and organic matter; 2) metals associated with Fe oxides; and 3) elements associated with sulphides and organic matter (Grotti et al., 2005). Results of this work showed that PFe is essentially present as oxides or bound to an oxidisable fraction, especially in bottom sea ice where organic matter is more abundant. In addition to spatial variability along the core, Grotti and co-authors also observed a seasonal increase in the fraction of oxidisable PFe. The authors attribute this finding to the seasonal increase in organic ligand (e.g., humic acid) concentration in sea ice, or the growth of algae at the ice-water interface.

Some studies have quantified the partitioning of PFe between the lithogenic (i.e., refractory) and biogenic (i.e., potentially bio-available) fractions by using the Fe/Al (aluminium) ratio in the Earth's crust to trace the origin and therefore approximate bio-availability of PFe. In the Sea of Okhotsk, a linear relationship between sea-ice [TDFe] and [TDAI] suggests a general lithogenic origin of Fe (Kanna et al., 2014). This suggestion also applies to Antarctic fast ice where a high fraction of lithogenic PFe from sedimentary or crustal origin is observed (Grotti et al., 2005; de Jong et al., 2013; Noble et al., 2013; Lannuzel et al., 2014). However, biogenic Fe dominates the PFe pool in Antarctic pack ice, because the lithogenic inputs are much smaller offshore compared to near-shore (Lannuzel et al., in press).

3. Sources of Fe to sea ice

Iron can be delivered to the surface ocean, and therefore sea ice, from several external sources: dusts (continental, extraterrestrial and volcanic), rivers including glacial outflow, hydrothermal vents, continental shelves, and cryospheric elements including glaciers, ice shelves and icebergs. The magnitude of these fluxes depends on the location and, in certain cases, the time of year (e.g., glacier run-off and river outflow increases in spring-summer). Flux estimates of some of these Fe sources have been published for the Southern Ocean. Atmospheric dust input to the Southern Ocean is generally low compared to other sources (Mahowald et al., 2005; Wagener et al., 2008; Gao et al., 2013). The dust contribution, however, can be more important in localized areas; for example, in McMurdo Sound where exposed bedrock, desert soil from the McMurdo Dry Valleys, and the Mount Erebus volcano may supply substantial amounts of DFe ($0.001\text{--}4.7 \mu\text{mol m}^{-2} \text{d}^{-1}$, depending upon the source and location) to surface waters or to sea-ice and snow surfaces if present (de Jong et al., 2013). Apart from regional exceptions, it is inferred that most of the Fe found in Antarctic sea ice must come from below, either by entrainment of Fe into the mixed layer from deeper waters or from biogenic matter and associated Fe remaining in seawater from the preceding summer season (see section 4; Janssens et al., 2016). The magnitude of these fluxes varies between pack ice and fast ice, with fast ice experiencing enhanced Fe inputs due to its proximity to the sedimentary sources and higher productivity in the water column (see section 2.2.2; Grotti et al., 2005; van der Merwe et al., 2011b; de Jong et al., 2013).

4. Mechanisms of Fe incorporation into sea ice

The mechanisms that drive the incorporation of dissolved and particulate Fe into forming sea ice remain unclear, which explains in part why the parameterization of Fe processes in sea-ice biogeochemical models remains difficult. Several incorporation mechanisms have been suggested and are summarised in Janssens et al. (2016). The potential pathways for incorporation of particulate material (organisms and detritus) include: 1) nucleation where marine particles serve as ice-condensation nuclei; 2) scavenging of particles, also referred to as suspension freezing, by frazil ice crystals rising through the water column; and 3) sieving of particle-containing seawater through layers of newly-forming or established sea ice, trapping particles into the sea-ice matrix (Ackley and Sullivan, 1994; Spindler, 1994; Gradinger and Ikävalko, 1998). In addition, bio-accumulation of Fe through algal growth in the bottom layers has been suggested as an important pathway of Fe accumulation in sea ice (Grotti et al., 2005; Lannuzel et al., 2010; van der Merwe et al., 2011a; de Jong et al., 2013). The underlying physical processes driving bio-accumulation of dissolved species have been modeled by Vancoppenolle et al. (2010), using silicate as an example. Living organisms, bio-detritus and sediments contain elevated concentrations of Fe, therefore any process that favours their incorporation into sea ice, will also lead to the incorporation of Fe.

As sea ice is a highly heterogeneous and difficult environment to sample in a repeated manner, there is mounting interest in the development of experimental ice-tanks that are trace-metal clean. These facilities would allow replication of sea-ice conditions and to isolate processes thought to drive the incorporation and release of Fe in sea ice by “switching off” their relative contribution to the formation (and melting) of artificial sea ice. These experiments can hopefully provide new information on coupled physical-biogeochemical processes in the sea-ice matrix and at the sea ice/seawater interfaces but need to be carried out in tandem with modeling and field-studies.

5. Fate of Fe when sea ice melts

Several studies have reported fluxes of Fe from melting sea ice, either in Antarctic fast ice (van der Merwe et al., 2011b; de Jong et al., 2013), Antarctic pack ice (Lannuzel et al., 2007, 2008, 2014; van der Merwe et al., 2011a; de Jong et al. 2015), or sub-Arctic sea ice (Kanna et al., 2014). They all highlight that melting sea ice results in a significant temporal redistribution of Fe in surface waters in the marginal ice zone. The magnitude of spring Fe release is comparable to major sources of Fe in low latitude areas including dust and rivers in the case of the Sea of Okhotsk, or dust and sedimentary inputs around Antarctica. Melting sea ice is a “pulsed source” in that it supplies Fe to surface waters over a relatively short period in spring and summer (70% of sea-ice DFe was lost in 10 days during a time-series experiment in Weddell Sea pack ice; Lannuzel et al., 2008), while other Fe sources can potentially supply Fe all year round. Antarctic sea ice stores $4.7 \mu\text{mol m}^{-2}$ of DFe (median value; Table 2). Our data compilation also highlights the importance of sea ice as a reservoir of PFe (median = $20.6 \mu\text{mol m}^{-2}$; Table 2). However, it is not clear how bio-available this sea ice-derived PFe is and how long PFe remains in the water column.

The size fractionation and organic speciation of Fe may dictate the fate of sea ice-derived Fe upon release into seawater. Dissolved Fe can either be taken up by phytoplankton or scavenged onto particles. The concentration of organic ligands present in seawater or seeded from sea ice, potentially in the form of EPS (Hassler et al., 2011), may ultimately control the solubility of Fe and its residence time in seawater. Once released into seawater, PFe can remain in suspension, be remineralized by bacteria or zooplankton grazing or exported to the seafloor. According to Stokes' law, large lithogenic particles of Fe will sink faster than small particles (Lannuzel et al., 2014; van der Merwe et al., 2015). Also, because of greater densities, lithogenic particles will tend to sink faster than biogenic particles (Klaas and Archer, 2002; Sarmiento and Gruber, 2006). Ice algae, however, have a high coagulation potential resulting in rapid export of this biogenic material (Boetius et al., 2013; Riebesell et al., 1991). All these parameters need to be included in sea-ice biogeochemical models to gauge the effectiveness of Fe inputs from melting sea ice.

6. Role of Fe-bearing sea ice in the productivity of the Southern Ocean

Sea ice seasonally covers up to 40% of the Southern Ocean. Growing evidence suggests that phytoplankton blooms in the seasonal ice zone may play a significant role in carbon uptake and export (Smith and Nelson, 1985, 1986; Lancelot et al., 1993; Sedwick and DiTullio, 1997; Buesseler et al., 2010). Given the large interannual variability in terms of both the sea-ice coverage and onset of melt (Massom et al., 2013), as well as the large spatial variability of the physical sea-ice environment (Zwally et al., 1983; Meiners et al., 2012; Stammerjohn et al., 2012; Williams et al., 2015), understanding what controls the onset of primary productivity in the seasonal ice zone is an essential first step in assessing its contribution to the biological pump of carbon.

The seasonal ice zone is the ideal environment to test the long-standing paradigm of light versus Fe limitation in the Southern Ocean. A simplistic approach would be to suggest that primary productivity is controlled by Fe availability in open waters (mean [DFe] = $0.31 \pm 0.45 \text{ nmol L}^{-1}$, $n = 999$; Tagliabue et al., 2012) and by light availability in shelf waters (mean [DFe] = $0.61 \pm 1.14 \text{ nmol L}^{-1}$, $n = 382$; Tagliabue et al., 2012). The large standard deviation on compiled DFe measurements in the Southern Ocean, however, highlights the variability in DFe concentrations measured on the shelf and in open waters, therefore implying that the distribution of [DFe] highly varies seasonally and regionally.

Seasonally, sea ice only fertilizes seawater when it melts, while other sources may supply Fe to surface waters all year-round. Although decaying sea ice and subsequent Fe release is most common in spring and summer, phytoplankton blooms have also been associated with disintegrating ice in autumn (Lieser et al., 2015). Spatially, the role of sea ice as reservoir of Fe matters most in areas where other Fe inputs are low (e.g., open waters). In the Ross Sea, melting sea ice and wintertime mixing equally supply most of the DFe to surface waters, with lesser input from the intrusion of Circumpolar Deep Water and glacial ice meltwaters (McGillicuddy et al., 2015). The Ross Sea contrasts with other areas of the Antarctic continental margin, like the Amundsen Sea where melting glacial ice has been identified as the major source of DFe to surface waters (Gerringa et al., 2012; Sherrell et al., 2015), and melting sea ice supplies less than 3% of the Fe necessary to support the phytoplankton bloom (Gerringa et al., 2012). In the Atlantic sector of the Southern Ocean, horizontal advection dominates DFe supply in summer by representing 54% of the total flux (de Jong et al., 2012). The significance of this mode of supply on the Antarctic shelf is supported by an exponential decrease of DFe concentrations as a function of distance from the Antarctic coast (de Jong et al., 2012).

In open waters, the role of Fe-bearing sea ice as a fertilizing agent becomes more prominent than on the coast, because lithogenic Fe contribution to surface waters decreases as we move northwards. When spring arrives and light conditions improve, pack ice starts to melt and releases Fe to the water column in a matter of days (70% Fe loss over 10 days; Lannuzel et al., 2008). This high seeding of Fe occurs while the ice cover is still present and stabilizes the water column. This ideal timing of Fe input from melting pack ice can play a pivotal role in triggering algal blooms in the seasonal ice zone (Sedwick and DiTullio, 1997; Measures, 1999; Arrigo et al., 2008).

Seawater sampling at the ice/water interface has been carried out in parallel with sea-ice measurements for the last 10 years, using a peristaltic pump and acid-clean tubing deployed as several depths below the ice cover (e.g., 0 m, 1 m, 5 m, down to 30 m deep). The fertilization potential of melting sea ice in these studies is clear, with measured Fe concentrations in under-ice seawater well above those generally measured in ice-free waters ($[DFe] = 0.1\text{--}4.5 \text{ nmol L}^{-1}$; see overview table in de Jong et al., 2013). Deeper under-ice seawater (15–1,000 m deep) and sea-ice Fe concentrations have also been measured in parallel in the sea-ice zone (Schallenberg et al., in press). Although Fe concentrations in sea ice were high, no obvious Fe input from melting sea ice was observed in seawater collected using the trace metal rosette (TMR). To avoid contamination from the ship, TMR seawater sampling starts at 15–30 m deep, i.e., potentially below the pivotal depths where rapid seeding, uptake and remineralization of Fe may occur. Exchanges of nutrients and organic matter take place at the ice/water interface, and high vertical resolution in this shallow body of water is needed to record the fertilization event from sea-ice melt. Underway surface sampling using a clean surface pump sipper/tow fish system could be the way forward to collect the water depths (2–25 m) where the fertilizing role of sea ice could be the most pronounced.

It should be noted that although most studies focused on Fe biogeochemistry, other trace elements such as manganese (Mn), copper (Cu), zinc (Zn) and cobalt (Co) play a key role in the biological pump of carbon through co-limitation of physiological processes. Despite the ecological significance of these trace elements, our understanding of their global distribution, biogeochemical cycling and supply in sea ice is still very limited. Overall most studies show that, although DFe is clearly enriched in sea ice relative to seawater, enrichment is not the case for other trace metals which tend to be coupled with macro-nutrients and salinity (Frache et al., 2001; Grotti et al., 2005; Hendry et al., 2010; Lannuzel et al., 2011). This difference raises questions on the fertilization potential of melting sea ice in polar waters. Sea ice may well supply substantial amounts of Fe and alleviate Fe limitation in Antarctic surface waters during spring, but other trace elements such as Co and Mn may then become in short supply relative to Fe and potentially limit primary productivity in these waters.

7. Effects of climate change on the cycle of Fe in Antarctic waters

The development of biogeochemical models may help identify and quantify which Fe sources are likely to change in the future, and whether primary productivity in polar waters will respond positively or negatively to these changes. Satellite data presented in Arrigo et al. (2015) suggest that melting ice shelves are a primary supplier of Fe to coastal Antarctic polynyas, with basal melt rates of nearby ice sheets explaining 59% of the variance in mean Chl-a concentrations between polynyas. Since glacier calving is expected to increase in the future (Bell, 2008), producing more icebergs, we can expect an increase in glacial Fe supply to surface waters (Smith et al., 2007; Raiswell et al., 2008; Raiswell, 2011; Gerringa et al., 2012; Bhatia et al., 2013; Death et al., 2014; Hawkings et al., 2014; Duprat et al., 2016). It has also been suggested that increased ice-shelf melt favours the expansion of sea ice in certain locations around Antarctica (Bintanja et al., 2013). These glacial melt waters being Fe-rich, they constitute an increasingly important source of Fe to expanding Antarctic sea ice. Overall, apart from the obvious role of sea ice as a foraging and feeding ground for animals such as krill, penguins, seals and whales, the predicted long-term sea-ice reduction will allow more light to penetrate the upper ocean. This increase in light availability would favour phytoplankton blooms (Arrigo et al., 2008; Ardyna et al., 2014) and intensify biological drawdown of oceanic CO₂. However, if sea ice is not present, the Fe delivered from glaciers, land masses and sediments will not have the opportunity to be stored over winter and released into surface waters in spring, at a time ideal for phytoplankton growth; i.e., the link that sea ice makes between the continental sources (where Fe is replete) and the offshore high-nutrient low-chlorophyll surface ocean (where Fe is needed) would be cut. Also, higher trophic levels, such as krill and whales that rely on sea ice and its associated food web, have been recognized to play a role in remineralizing Fe in surface waters (Tovar-Sánchez et al., 2007; Lavery et al., 2010; Nicol et al., 2010; Ratnarajah et al., 2014). As such, it will be difficult to predict what effect a predicted reduction in sea-ice extent and volume will have on the Fe cycle given the multiple interlinked positive and negative feedback loops. It appears critical to use models to quantify how the changes in Fe delivery to surface waters will affect polar ecosystems.

8. Conclusion: Challenges and future directions

Sea ice is a challenging environment to sample without contaminating trace metals; as a result, only a limited amount of data is currently available (Table 1). Most of the data come from the Southern Ocean, yet it remains difficult to tease out the main processes driving the spatial and seasonal Fe variability in Antarctic sea ice. Given the dynamic, heterogeneous and ephemeral nature of sea ice, reducing the uncertainties illustrated in Table 2 and Figure 4 would take a large international effort. Additional field observations in the Atlantic and Pacific sectors of the Southern Ocean (Figure 1) and austral autumn and winter (Figure 2) are crucial to address the spatial and seasonal variability in DFe, PFe and TDFe distributions in the sea-ice

zone. Future field investigations should include measurements of other trace metals (e.g., Al, Mn, Co), as well as macro-nutrients, Chl-a, POC, dissolved organic carbon and basic physical parameters such as snow and ice thicknesses, air temperature, PAR, *in situ* ice temperature and salinity, ice textures and, if possible, $\delta^{18}\text{O}$ to differentiate snow ice from frazil ice. In parallel with field observations on Fe concentrations and distributions, laboratory-based experiments and modeling studies should be carried out to isolate specific processes. Investigating the mechanisms of Fe incorporation into artificial sea ice is an example. Information on the effect of heterotrophic activity on the Fe cycle in sea ice, the competition between sea-ice algae and bacteria for Fe and C substrates and the variability in Fe:C molar uptake ratios in samples of natural sea ice, brine and under-ice water is also highly encouraged. Another avenue for future research is to quantify the solubility of sea-ice particles in sea ice and seawater, as well as the effect of CO_2 , O_2 , UV radiation, temperature and salinity gradients on Fe chemistry in the seasonal ice zone. This information is crucial to accurately predict how future changes will affect marine productivity in polar waters.

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Contributions

- Contributed to conception and design: DL, MV, PvdM, VS
- Contributed to acquisition of data: DL, MV, PvdM, JdJ, KM, MG, JN, VS
- Contributed to analysis and interpretation of data: DL, MV, PvdM, VS
- Drafted and revised the article: DL, MV, PvdM, JdJ, KM, MG, JN, VS
- Approved the submitted version for publication: DL, MV, PvdM, JdJ, KM, MG, JN, VS

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Competing interests

The authors declare they have no competing interest of any kind with this research and the publication of this manuscript.

Data accessibility statement

All data are available on PANGAEA, Data Publisher for Earth & Environmental Science.

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