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The heterogeneous nature of Fe delivery from melting icebergs

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Abstract

The micronutrient iron (Fe) can be transported from marine terminating glaciers to the ocean by icebergs. There are however few observations of iceberg Fe content, and the flux of Fe from icebergs to the offshore surface ocean is poorly constrained. Here we report the dissolved Fe (DFe), total dissolvable Fe (TdFe) and ascorbic acid extractable Fe (FeAsc) sediment content of icebergs from Kongsfjorden, Svalbard. The concentrations of DFe (range 0.63 nM – 536 nM, mean 37 nM, median 6.5 nM) and TdFe (range 46 nM – 57 μM, mean 3.6 μM, median 144 nM) both demonstrated highly heterogeneous distributions and there was no significant correlation between these two fractions. FeAsc (range 0.0042 to 0.12 wt. %) was low compared to both previous measurements in Kongsfjorden and to current estimates of the global mean. FeAsc content per volume ice did however, as expected, show a significant relationship with sediment loading (which ranged from < 0.1 – 234 g L^{-1} of meltwater). In the Arctic, icebergs lose their sediment load faster than ice volume due to the rapid loss of basal ice after calving. We therefore suggest that the loss of basal ice is a potent mechanism for the reduction of mean TdFe and FeAsc per volume of iceberg. Delivery of TdFe and FeAsc to the ocean is thereby biased towards coastal waters where, in Kongsfjorden, DFe (18 ± 17 nM) and TdFe (mean 8.1 μM, median 3.7 μM) concentrations were already elevated.

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Introduction

Icebergs contain higher Fe concentrations than seawater, both in the dissolved (<0.2 μm) (Martin *et al.*, 1990; De Baar *et al.*, 1995; Loscher *et al.*, 1997) and particulate (>0.2 μm) phases (Hart, 1934; Lin *et al.*, 2011; Shaw *et al.*, 2011). Icebergs should thus constitute a source of the micronutrient Fe to offshore polar waters (Raiswell *et al.*, 2008). As the rate of iceberg calving in polar seas oscillates on glacial to inter-glacial timescales (Bond *et al.*, 1992), and recent climate change has increased the discharge of calved ice volume from both the Antarctic (Paolo *et al.*, 2015) and Greenlandic (Bamber *et al.*, 2012) ice sheets, Fe delivery from icebergs may also change. Particularly in the Southern Ocean, where DFe deficiency extensively limits primary production (Martin *et al.*, 1990, 1991; Moore *et al.*, 2013), and icebergs cause chemical and biological enrichment of surrounding waters (Smith Jr. *et al.*, 2007; Schwarz and Schodlok, 2009; Smith *et al.*, 2011), a change in iceberg Fe supply could significantly affect marine primary productivity. Yet there remain large uncertainties concerning the magnitude of iceberg Fe supply and its effect(s) on marine ecosystems. For example, calculated phytoplankton Fe utilisation is considerably less than present estimates of iceberg Fe supply to the Weddell Sea (Boyd *et al.*, 2012). The reason for this is unclear, yet it demonstrates the difficulty in isolating the contribution of icebergs to the marine Fe cycle.

Observations of DFe concentrations in iceberg meltwater are sparse, but the available data does suggest a heterogeneous distribution, with DFe ranging 4–600 nM in Antarctic (Lin *et al.*, 2011) and 3–300 nM in Greenlandic (Hopwood *et al.*, 2016) iceberg melt. The distribution of particulate Fe (which includes FeAsc) is also expected to be heterogeneous due to the presence of embedded sediment-rich layers that account for only a small fraction of total iceberg volume (Lin *et al.*, 2011; Raiswell, 2011; Raiswell *et al.*, 2016). Whilst TdFe data for icebergs is sparse, iceberg FeAsc content has previously been estimated in multiple catchments worldwide (Raiswell *et al.*, 2016) producing a mean global content of 2.7–17 μM. However, FeAsc content and offshore iceberg FeAsc fluxes are normally calculated using a mean sediment loading (0.5 g L^{-1} is widely used as outlined in Raiswell *et al.* (2016)) with considerable uncertainty generally acknowledged in this value. Here we combine the analysis of DFe, TdFe, FeAsc and iceberg sediment load in order to provide a well constrained assessment of iceberg-Fe content within a single catchment.

Methods

A FeAsc dataset was compiled for icebergs in Kongsfjorden with visible embedded or surface sediment sampled from small boats in July 2015 and August 2016. Sediment from pro-glacial streambeds in the catchment, embedded sediment from Kongsvegen glacier surface, and embedded sediment ~100 m inside an ice crevasse (on Midtre Lovénbreen glacier) was also collected (Fig. 1) for comparative purposes. FeAsc leaches were conducted on wet sediment as per Raiswell *et al.* (2010), with leached Fe determined by measuring absorbance (λ = 562 nm) before and after the addition of ferrozine (as detailed in Supplementary Information Methods).

Separately, ice samples (1–2 kg) were randomly collected from small boats (July 2015). The meltwater was acidified to pH < 2. After storage for 12 months, DFe and TdFe were measured by inductively coupled plasma mass spectroscopy (further details in Supplementary Information Methods).

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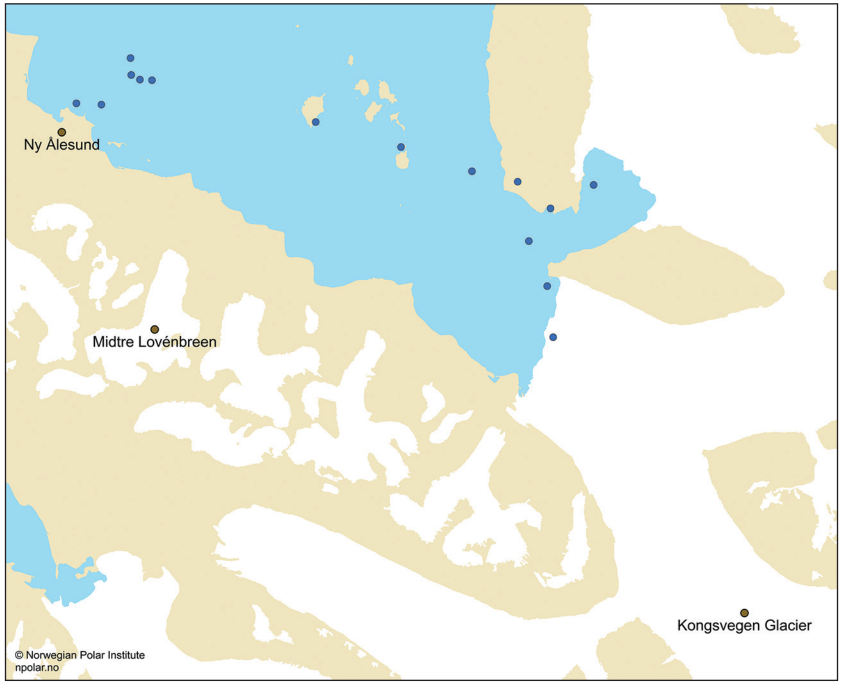

Figure 1 Surface fjord sample locations in Kongsfjorden.

Results

The FeAsc concentration is reported for 116 different sediment samples (Table S-2) including 58 iceberg samples collected from ice with visible embedded sediment. FeAsc ranged from 0.0042 to 0.12 wt. % in iceberg embedded sediment (Fig. 2). Ice sediment content ranged from <0.1 to 234 g L^{-1} of meltwater, close to the 0.2–200 g L^{-1} range previously reported in Svalbard by Dowdeswell and Dowdeswell (1989). Combining FeAsc (wt. %) and sediment load (g L^{-1} of melted ice) produced a median FeAsc ice content of 2.5 μM. Given that our sampling strategy was to target sediment-rich ice, this should thereby be an over-estimate of median iceberg FeAsc content (L^{-1} of melted ice) in Kongsfjorden.

The DFe and TdFe concentrations are reported in parallel for 28 randomly collected iceberg samples (Table S-4). TdFe ranged from 46 nM to 57 μM (mean 3.6 μM, median 144 nM) and the range of 0.63 nM – 536 nM for DFe was similarly broad (mean 37 nM, median 6.5 nM). There was no significant correlation between particulate Fe (TdFe minus DFe) and DFe in these samples (Fig. 3), suggesting that DFe was not specifically associated with sediment laden ice. For comparison, DFe in surface fjord waters averaged 18 ± 17 nM (15 surface stations, Fig. 1) and TdFe ranged widely from 1.1 to 52 μM (mean 8.1 μM, median 3.7 μM) (Table S-3).

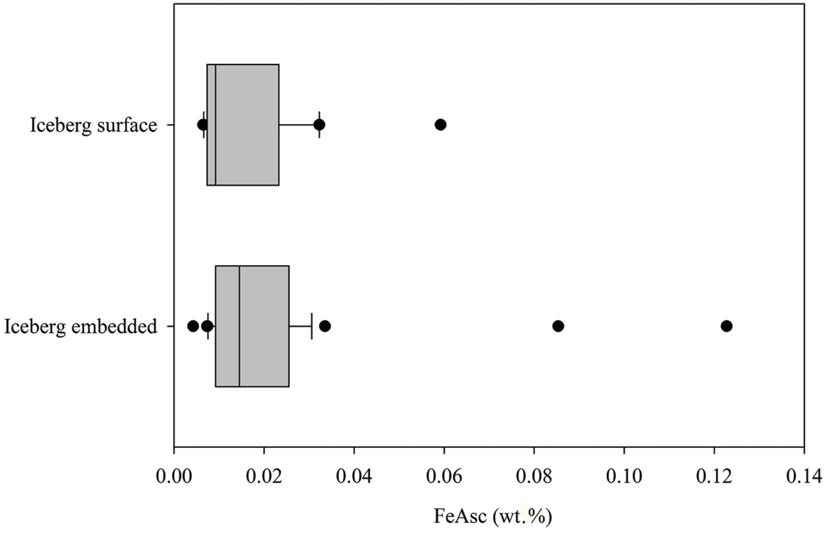

Figure 2 Median FeAsc (wt. %) with 25/75th (boxes) and 10/90th (whiskers) percentiles (outliers also shown) for iceberg embedded (n = 34) and iceberg surface (n = 20) sediment.

Discussion

As has been demonstrated in this study and elsewhere (*e.g.*, Markussen *et al.*, 2016), surface waters in stratified, glaciated fjords can exhibit extremely high TdFe concentrations due to the presence of glacially derived particle plumes. TdFe concentrations in surface waters of Kongsfjorden (mean 8.1 μM, median 3.7 μM) exceeded those in icebergs (3.6 μM and 144 nM, respectively). In the Arctic, a large fraction of iceberg melt occurs in these inshore, high TdFe waters before icebergs are able to deliver Fe to the offshore environment. Accounting for this near-shore loss in flux calculations for iceberg derived Fe supply to the open ocean is difficult. In two Greenlandic catchments, Ilulissat Fjord and Sermilik Fjord, overall in-fjord iceberg volume losses were estimated to be >50 % (Enderlin *et al.*, 2016), tentatively supporting the 50 % inshore iceberg volume loss used to estimate offshore FeAsc fluxes by Raiswell *et al.* (2016). However this assumes that changes in total iceberg Fe content are directly proportional to changes in total ice volume.

All measured Fe phases (DFe, TdFe and FeAsc) in Kongsfjorden were very heterogeneously distributed within the ice. For TdFe and FeAsc (but not DFe, Fig. 3), this can specifically be attributed to the heterogeneous distribution of ice embedded sediment. In the Arctic, iceberg-borne sediment is known to be lost from icebergs faster than ice volume (Mugford and Dowdeswell, 2010) due to its association with basal ice. Thus we expect that the mean TdFe content per volume of an iceberg should decline with time after calving. A model for Kangerdlugssuaq Fjord (Greenland) shows that whilst icebergs lose 20–30 % ice volume within this fjord, the corresponding in-fjord sediment loss is 70–85 % (Mugford and Dowdeswell, 2010). Only a relatively small iceberg volume loss (<20 %) is thereby likely required for the majority of TdFe content to be lost from icebergs. In Kongsfjorden, where summer melting of calved ice is quite rapid due to relatively warm surface seawater (4–5 °C throughout July-August 2016), the post-calving age of an iceberg is therefore likely a critical factor in determining its TdFe content. Sediment loss should also affect mean FeAsc content in the same way, however FeAsc losses may be offset from TdFe losses if significant processing of surface sediment occurs on the timescale of iceberg Fe delivery (Raiswell *et al.*, 2016).

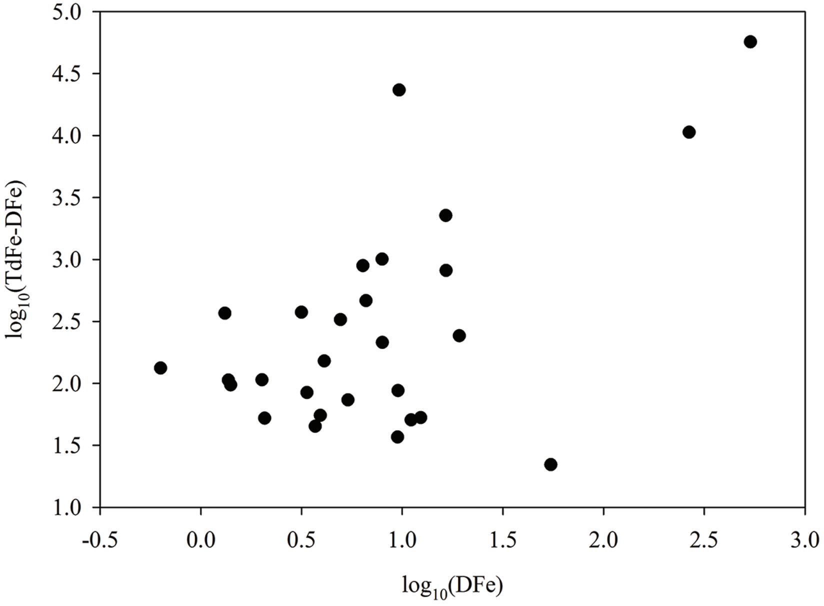

Figure 3 DFe and TdFe (both nM, plotted as $\log_{10}$, TdFe shown minus DFe) for 28 discrete iceberg samples showed no clear relationship.

In Kongsfjorden, Raiswell *et al.* (2016) reported a FeAsc range of 0.016–0.37 wt. % (n = 14), with a mean of 0.14 wt. % and median of 0.092 wt. %; equivalent to 1.4–33 µM, 12 µM and 8.2 µM, respectively when using the suggested mean sediment loading of 0.5 g L^{-1}. Comparing our data both as wt. % and as a µM concentration (calculated using measured sediment loading for each sample, range 0.1–234 g L^{-1}, Table S-2), our FeAsc (wt. %) is consistently lower. Yet our mean FeAsc per volume is much higher (51 µM), because our measured sediment loadings were often greater than the assumed mean of 0.5 g L^{-1}. These differences generally highlight the very high spatial variability in iceberg sediment load and thus TdFe and FeAsc content even within a single fjord.

Table 1 Comparing data for Kongsfjorden from this and prior work suggests a critical difference in both FeAsc (wt. %) and in the scaling of FeAsc to iceberg sediment load (g L^{-1} of ice melt). *The suggested 0.5 g L^{-1} sediment loading is used for data from Raiswell *et al.* (2016). ** For our study, measured sediment loadings were used for each sample. As sediment-rich ice was specifically targeted, the calculated mean/median should be over-estimates.

		a This study	b Raiswell *et al.* (2016)	a/b %
FeAsc / wt. %	Mean	0.021	0.14	16
	Median	0.015	0.092	17
FeAsc / µM (per litre of ice melt)*	Mean	<59 **	12	480
	Median	<2.5 **	8.2	31

Some methodological differences between this study and previous work could be important for the difference in FeAsc (wt. %) (Table 1). In our study, the sediment was not sieved to remove anomalous large particles. Yet a relatively large sub-sample mass was used with good reproducibility demonstrated. For glacial flour particles of <1 mm, it has previously been demonstrated that the change in FeAsc (wt. %) with particle size is not pronounced (Hopwood *et al.*, 2014; Raiswell *et al.*, 2016), but this may not be the case for larger particles. Moreover, in this study sediment was processed in Svalbard with no prolonged storage between collection and analysis. Whilst dried sediment exhibits a rapid decline in FeAsc wt. % (Raiswell *et al.*, 2010), it is not clear how storage of ice or wet sediments affects FeAsc.

Furthermore, there are the critical issues of heterogeneity and of the non-linearity between iceberg sediment and iceberg volume losses. In-fjord iceberg volume loss should correspond to a disproportionately high loss of iceberg embedded sediment (Mugford and Dowdeswell, 2010), and thereby also FeAsc and TdFe. There are no quantitative measures of iceberg age or volume loss for our dataset and the residence time of ice in Kongsfjorden is strongly affected by meteorological conditions and thus subject to high short-term variability. Nonetheless, a difference in the post-calving age of ice sampled between different datasets could correspond to large shifts in iceberg FeAsc and TdFe content. Increased iceberg age would be expected to correspond to lower mean sediment load, and thereby lower TdFe and FeAsc per volume. A reduction in basal sediment load could also explain a difference in FeAsc (wt. %) content if FeAsc (wt. %) is enriched in basal ice compared to non-basal ice. FeAsc (µmol L^{-1}) is correlated with sediment load (Fig. 4), but assessing whether changes in sediment load affect FeAsc (wt. %) is complicated by the lack of any parameter to account for the post-calving age of ice and by the highly variable bedrock composition across Kongsfjorden (see for example Hjelle, 1993).

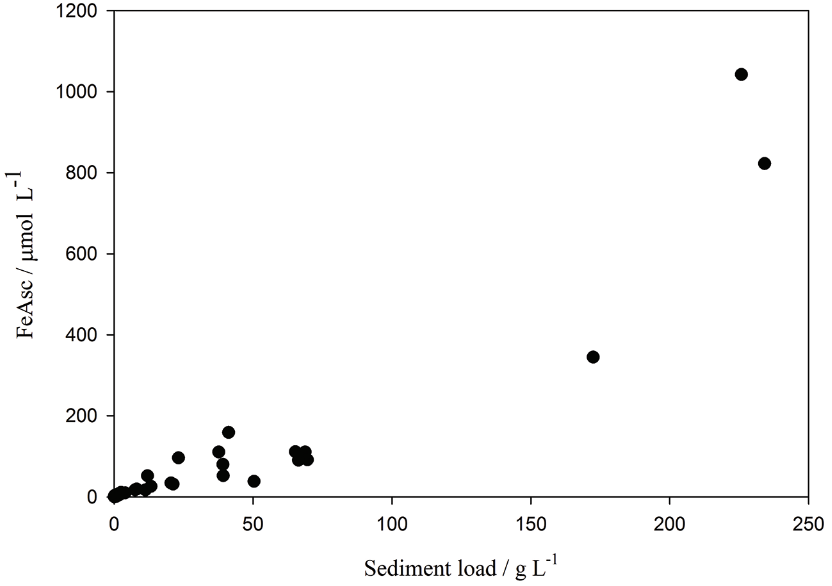

Figure 4 FeAsc (µmol L^{-1} melted ice) increased with sediment load (g L^{-1} melted ice), but it is unclear if the relationship remains linear at high (>50 g L^{-1}) loadings.

Conclusions

Whilst median DFe (6.5 nM) and TdFe (144 nM) concentrations in Kongsfjorden were within the range of concentrations reported elsewhere globally, the median FeAsc concentration (2.5 µM) measured was considerably lower than that reported previously in Kongsfjorden, and compared to present estimates of the global mean, despite the very high sediment loadings observed (<0.1 – 234 g L^{-1}). Generally in the Arctic, a sharp decline in the mean FeAsc and TdFe per volume of meltwater from icebergs with time after calving would be expected due to the preferential loss of iceberg basal ice, as modelled by Mugford and Dowdeswell (2010). Iceberg derived fluxes of TdFe and FeAsc are thereby biased towards delivery in near-shore waters and offshore fluxes are likely much less than if TdFe and FeAsc were homogeneously distributed throughout icebergs.

Glossary

'Fe' refers to all iron phases.

'DFe', dissolved Fe, refers to all Fe phases <0.2 µm.

'FeAsc' is the ferrihydrite content of sediment, defined by Raiswell *et al.* (2010).

'TdFe' is all Fe soluble at pH < 2, inclusive of DFe and should also include any FeAsc present in unfiltered meltwater.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1723

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