Authors Overall Response

The reviewer has spent a considerable amount of time on this review and the effort is appreciated and we anticipate an improved ms will result. This review certainly identifies issues of genuine scientific merit along with many requests for more details. Its principal assertion-that our ascorbic acid extraction is not selective- can be easily refuted. Below we respond on a point-by-point basis and we have distinguished the review from our response by using italics for the review. Line numbers correspond to pages in the paper.

Overview:

This work presents a collation of sediment analysis for an operational defined iron lability assay from glacial ice and icebergs and compares this with atmospheric dust in an attempt to evaluate the potential bioavailable iron supply to the Arctic and Southern Oceans for the two different sources. The paper does not make a convincing case for its analysis however as it all hangs on the assumptions that the ascorbic acid based assay only measures ferrihydrite iron and that this iron is bioavailable – these assumptions are not tested in any detail and nor have they been in previous work using this approach – so the whole extrapolation of a few samples to vast regions seems overstated.

The extraction has been thoroughly tested in Raiswell et al (2010).It is not an assumption that ascorbic acid extracts only ferrihydrite. Table 3 from Raiswell et al. (2010) is shown below and clearly shows high selectivity for fresh 2 line ferrihydrite which was also characterised by XRD (see Fig. 2 in that paper). The extraction is therefore well-tested and constrained.

Mineral	**%FeA**	**%FeD**	**% Total Fe**
Fresh 2-line Ferrihydrite	53.8	-	53.8
Aged 2-line Ferrihydrite	9.98	44.0	54.0
Freeze-dried and aged 6-line Ferrihydrite	4.0	47.4	51.4
Schwertmannite	12.2	30.0	42.2
As-rich Schwertmannite	8.4	28.5	43.0
Lepidocrocite	0.42	54.0	62.8
Hematite	0.004	23.5	69.8
Goethite	0.03	42.4	62.8
Magnetite	0.09	5.44	72.3
Illite	0.051	0.41	5.60
Illite/Smectite	0.024	0.26	0.80
Smectite	0.031	0.21	2.60

See also Reyes and Torrent (1997), Soil Sci Soc. Am. J., 61, 1647-1654, Hyacinthe and Van Cappellen (2004), Mar Chem., 91, 225-251 and Kostka and Luther (1994), Geochim. Cosmochim Acta, 58, 1701-1710 for similar results that clearly state ascorbate specificity for ferrihydrite under conditions similar to those used here (pH 7.5-8).

A major weakness at present is the lack of ancillary data for the sediments and a clear explanation of how the samples were prepared or collected (e.g. 'collected from a clean window' is not an adequate description of how samples was collected without contamination).

Details added lines 144-156. Contamination is not a problem with these bulk samples.

The lack of aerosol data from the Arctic is a major gap and the use of Mediterranean samples instead is not appropriate as these cannot be considered representative of what will be deposited in the Arctic or the Southern Ocean.

Agreed this is an important gap in our data (and in other datasets) that needs attention in the future, as we clearly recognise in lines 383-385, 367-369,and 499-500. It is common practice in Southern Ocean Fe models to use a range of values for fractional solubility (as we discuss in lines 46-73), with 1-2% being a frequent but poorly justified choice based on widely varying extraction data. We could have adopted this approach. However Boyd et al (2010) are emphatic that 'close reading, including the original references, does not support the 1-2% solubility value.' Instead we have analysed a small, but geographically wide-spread set of dusts to estimate a solubility value based on an ascorbic acid extraction. We proceed cautiously on the basis that our samples are representative of mineral dust delivered to the polar regions (lines 424-426). This data provides some support for the 1-2% fractional solubility estimate (a valuable result that enhances the credibility of models using this value) and thus provides preliminary proof of concept based on measurements of dusts that are related to mineralogy. Crucially, this methodology also allows iceberg and dust particulate sources to be compared (lines 380-381)

Operationally defined determinations of Fe: Crystalline Ferrihydrite or a mixture of phases

Throughout the manuscript nanoparticulate iron is described as being ferrihydrite, but no evidence is supplied regarding its crystal structure.

There are high resolution photographs and selected area electron diffraction (TEM and SAED) of iceberg-hosted ferrihydrite (that were also characterised by bulk XRD) in the Raiswell et al.(2008) Geochemical Trans. Paper, and the same mineral in suspended particulate matter derived from subglacial environments (the Hawkings et al paper). These are now cited in lines 171-173.

Given that recent FEG-TEM analysis identifies only a small proportion of the iron as 6-line ferrihydrite (Hawkings et al., 2014) and instead classified it mostly as amorphous Fe or poorly crystalline 2-line ferrihydrite, also significant amounts of Fe(II) were also identified therefore it is more realistic to provide a more accurate description of the iron rather than refer to it as ferrihydrite throughout the mansucript. Indeed the *description in the Hawkings et al. work of reactive nanparticulate iron would seem to be optimal.*

Hawkings et al makes no mention of 6-line ferrihydrite nor either of Fe(II). They do describe the iron on p.2 of their paper as ‘poorly ordered ferrihydrite’. The term ‘reactive nanoparticulate iron’ is only used in the title.

The descriptors used in the present work confuse this issue at present – 6 line Ferrihydrite is classfied as a mineral despite it having an indeterminant formula, however 2 line ferrihydrite isn’t a mineral and is commonly referred to as hydrous ferric oxide (HFO), though some authors (Schwertmann and Cornell, 2007) suggest this is erroneous, while others consider it as an essentially amorphous iron oxide (Hiemstra, 2013).

The International Mineralogical Association (IMA) Commission on New Minerals lists ferrihydrite as a mineral. HFO is not so listed. Our only reference to 6-line ferrihydrite is in line 163 and it is not here described as a mineral although in fact it was so recognised by the IMA in 1973. See below.

While both 2-line and 6-line ferrihydrite are only found as nanoparticles, thus using the term “nanoparticle ferrihydrite” is somewhat redundant, even if it does include the ‘buzz’ term nanoparticle.

The text has now been amended in lines 174-176 to explain that all ferrihydrite in nanoparticulate, and we no longer use the term ‘nanoparticulate ferrihydrite’.

More importantly the reactivity and lability of the two phases are considerably different (Wells et al., 1991) and a reaction scheme that could distinguish between the two would be extremely beneficial.

Yes the reactivity of the two phases are considerably different, as we show in their extraction with ascorbic acid (see lines 168-170 and the above Table).

The assay used here is very much an operational definition (Raiswell et al., 2010) and it is well known that the dissolution of iron from different iron oxide phases is dependent on a number of factors including pH (Deng and Stumm, 1994), surface complexation by ligands (Shimizu et al., 2013; Eusterhues et al., 2014) and dissolved Fe(II) (Pedersen et al., 2005), most importantly the dissolution is time dependent.

Selectivity can be obtained by carefully controlling the extraction conditions. The above Table shows that there are marked variations in the dissolution rates of different Fe minerals. Raiswell et al. (2010) dealt with the effects of ascorbic concentration and pH and show that it is important to control these conditions to obtain reproducible results (as we have done).

More crystalline phases are also soluble with ascorbic acid so it is not specific for ferrihydrite (Smolen et al., 2003;Larsen et al., 2006).

Not under the conditions we use. Larsen et al use a pH of 3 and we agree that more crystalline phases would be dissolved under these conditions, which are much more aggressive than our own (at pH 7.5).The Smolen et al paper finds 'significant ferrous iron concentrations can result from goethite dissolution near neutral pH over a period of 400 hours'. Inspection of their Fig 3 shows that dissolution from 2 g/litre of goethite (without pre-treatment) produces a 0.02 mM Fe solution which represents ~0.1% of the goethite Fe. This is consistent with the table above which shows little dissolution of the more crystalline phases (hematite, goethite, magnetite, and Fe-bearing clays) for our 24 hr extraction at pH 7.5.

Indeed in terms of reduction of only ferrihydrite, hydroxylamine is probably a more appropriate reductant (Croot and Hunter, 2000; Chen et al., 2013).

Probably not because it is less selective. Poulton and Canfield (2005), Chem. Geol, 214, 209-221 show that hydroxylamine dissolves all ferrihydrite as well as lepidocrocite (not extracted by ascorbic acid). It is therefore less specific than our extraction. Consistent with this, Marz et al. (2012), Chem. Geol., 330-331, 116-126 show that hydroxylamine extracts slightly more Fe than ascorbic acid.

Presenting data as %Fe/dry sediment.

The way the sediment data is presented is problematic at present as it does not give any information about what the actual iron concentration that was released was and whether there were variations as a function of the amount of dry sediment or grain size in the assay.

There is the usual level of information in lines 164-166. We have found no variation in FeA for different weights under these conditions. Raiswell et al. (2010) considered the effects for different ratios of extractant concentration/sample weight and found no significant variations. We have considered the effects of grain size through analysis of different size fractions of iceberg sediment and concluded that such effects are small (see lines 246-263).

It is also not well explained how the water content of the sediment is removed when the samples are only air dried – if they were not dried completely then porosity of the sediments would clearly be important.

This effect is small, see lines 160-162. Actually air-drying was used in the Larsen et al paper which the reviewer cites.

Also using this approach the flux is highly dependent on the value of sediment per L of ice and this value is poorly constrained and no range is given.

Agreed. This is a large source of uncertainty as we acknowledge in lines 366-373 where we have added ranges.

It is clear that for large icebergs this value should be lower than for small icebergs as if the sediment laden part was simply due to the iceberg being previously grounded then there will be a strong surface area to volume effect and if the contact area is the same larger icebergs will have less sediment per unit volume.

Not necessarily. The processes are complex and relate both to glacial processes (pre-iceberg release) as well as iceberg transport across the shelf and the sediment content of icebergs is therefore poorly constrained. Glacial comminution and deformation of bedrock and basal freeze-on entrains sediment subglacially, whilst sediment can also be found englacially through incorporation of debris along shear zones. Transport across the shelf can also add sediment where icebergs become grounded and can freeze sediment to themselves. This is probably more likely for large icebergs as they transit the shelf than for small icebergs, but we do not know and detailed discussion would be unhelpful.

The analogy to river suspended sediment seems incongruous as it is not like Antarctic icebergs are literally frozen rivers as they are in reality continental ice that was formed from deposited snow over millenia.

Glaciers (and large Antarctic ice stream) are frozen rivers that freeze-on sediment produced from the subglacial comminution (physical weathering) of bedrock. Glacial meltwaters studied by Gurnell (1997, in Glacial-Fluvial Sediment Transfer, published by Wiley) have mean suspended sediment concentrations of 1 g litre^{-1}. We use a conservative value of 0.5 g litre^{-1}, which finds support as we note in lines 369-370.

Missing experimental information and lack of statistical information:

The methods section is missing key information about how aspects of the analysis were performed.

The details presented in Section 2.3 have been considered sufficient in the Raiswell Geochem. Trans and Chem Geol papers, and the Hawkings papers that we cite. Earlier papers (see the refs cited in lines 163-167 give additional detail.

There is also a lack of important ancillary information with regard to the samples analysed, no particle size information or organic content is provided.

We see little merit in this data, given our aim is to use a well-constrained extraction to measure potentially bioavailable Fe.

In the data analysis, basic information is not provided about the statistical parameters (e.g. number of samples) and in some cases the statistical *tests applied do not seem appropriate (e.g. paired t-tests when the data are not paired).*

All the necessary information are given in the Tables. Our *t* and *z* test data are paired. More detail below.

Recent papers of relevance to this work:

The introduction and discussion section were missing a number of key recent papers of relevance to the current work. This included recent work showing the role of seasonal physical mixing on iron concentrations in the surface waters of the Southern Ocean (Tagliabue et al., 2014), thus an alternative supply route to those proposed here.

We agree that the Tagliabue et al study is an important contribution but it deals with deep water mixing of dissolved Fe into surface waters. There is no mention of particulate Fe sources and discussion of the paper would be outside our scope (see lines 114-116).

Additionally an evaluation of the impact of giant icebergs on marine productivity (Duprat et al., 2016) has also been published.

We discuss this but have incorrectly cited this as the Luis paper in press. This correction has been made in lines 45, 81 and 520.

Similarly a number of papers connected to Greenland ice melt and iceberg flux (Wilton et al., 2015), and in particular to the iron flux with one suggesting it could be important (Bhatia et al., 2013), though another study thought it was less so (Hopwood et al., 2015).

We deal with the Wilton paper below. The Bhatia and Hopwood papers deal with meltwaters fluxes of dissolved Fe and particulate Fe which are substantially outside our scope of particulate iceberg and dust sources. Furthermore the Bhatia paper examines meltwaters that transit > 10 km of a proglacial plain (including a lake where there is evidence of considerable post-melting additions of Fe).

There is a more relevant recent Hopwood paper (Frontiers in Earth Science, 4:15, doi:10.3389/feart.2016.0015) that discusses oceanographic features which may minimise iceberg escape to the ocean from long Greenlandic fjords (> 100 km). However Hopwood et al also point out that their study may not be typical of other Greeenlandic fjords. We agree with Hopwood that this issue is important and have added discussion in lines 347-365.. We have been in contact with Hopwood (and others) and ascertained that there are no currently no estimates of iceberg losses in fjords.

There have also been a number of key papers on the effect of freeze/thaw chemistry on iron (Jeong et al., 2012;Jeong et al., 2015;Guerra et al., 2016) and Mn chemistry (Kim et al., 2012).

The Jeong studies are excellent and make the point that dissolution is not a reductive process and requires the presence of a liquid-like ice boundary region. This adds valuable support for our suggested ice-processing model and we have add material from these papers in lines 297-308. The Guerra paper deals with acid mine drainage and the Kim paper with Mn.chemistry and are therefore less relevant.

Specific comments:

P2 line 45: The cited study is a model view, for the purposes of the point being made here it would be more beneficial to use a reference that provided experimental evidence (e.g. (Boyd et al., 2000; Coale et al., 2004).

The Moore et al paper was published as a Review article, which makes it appropriate to illustrate the well-known point that the SO is an HNLC area.

P2 line 46: A key recent paper is missing here and needs to be included as it demonstrates how physical mixing can result in a seasonal resupply of Fe to surface waters in the Southern Ocean (Tagliabue et al., 2014).

This paper is outside our scope of dealing with particulate sources. See above.

P3 line 84: It should be noted however that in the Arctic there is a considerable freshwater input from rivers across the continental shelf regions and considerable Fe supply (Martin et al., 1993; Dai and Martin, 1995 ;Guieu et al., 1996; Pokrovsky et al., 2006; Pokrovsky et al., 2014)– something that does not occur in the Antarctic.

Our choice of differences in lines 100-103 relates to particulate supplies but we have cited Dyurgerov et al to show that river discharge is another difference between the polar oceans.

P3 line 88: The source of the icebergs is also important as currently icebergs are predominantly from Eastern Canada, though a switch to western Greenland may be anticipated (Wilton et al., 2015).

There are no icebergs sourced from Eastern Canada (see the Wilton paper, page 197) although there are important sources from Western Greenland, Eastern Greenland and from glaciated islands in northern Canada, along with Svalbard and the Russian Arctic Islands (Wilton, page 197 and see also the Bamber and Van Wychen papers that we cite). These studies conclude that most Arctic icebergs are sourced from Greenland. Wilton et al. conclude that the principal sources prior to 1930 were from southern Greenland and only since then is the major source from western Greenland.

P4 line 90: It should be noted though that other recent studies have predicted that meltwater will be more important than icebergs (Bhatia et al., 2013), though a later study indicated that the flux of iron to the North Atlantic from meltwater would be small (Hopwood et al., 2015).

Bhatia et al do not predict that meltwaters will be more important than icebergs. They state on p. 277 that ‘Icebergs may provide yet another source of glacially derived Fe, a mechanism known to occur in the SO but not yet investigated around Greenland. This may be another significant, and under-represented input…’This is a justification for our own study. Our response to the Hopwood work is given above.

P4 line 102: The Irminger sea is in the North Atlantic not the Arctic Ocean, it is included in Arctic studies as a high latitude sea – however please correct this error in Geography.

We agree that the Irminger Basin is in the North Atlantic but it lies mostly north of 60^oN and is therefore within our definition of the AO (see below).

For a reference for iron in the Arctic use Klunder et al. (2012) as this shows the high Fe concentration in the Arctic (as opposed to the North Atlantic).

The Klunder paper is a study of deep water dissolved Fe in the AO, and it does indeed show that concentrations are high. However the authors state that ‘strong stratification prevents mixing between the deep water concentrations and the surface waters…’.We do not wish to deal with dissolved Fe in surface waters (and with the complex processes associated with the release of dissolved Fe from particulates in seawater; see lines 112-116) and would be reluctant to extend still further into surface and deep water mixing processes.

P4 line 105: The Arctic Ocean is formally defined by the International Hydrographic Organization (IHO) and is somewhat different to what is described here.

We acknowledge that here are different definitions. The IHO defines the AO as lying roughly within the quadrangle formed by N. Greenland, Prince Patrick Island, Point Barrow, Koteni Islands and Wrangel Island but this is a small area much of which lies within 80^oN. There are other definitions. For example the CIA Factbook defines the Arctic as the region within 57^oN; our Pabi reference is to about 66^oN (which is the Arctic Circle). We have defined the area > 60^oN which incorporates the southern tip of Greenland and lies close to the region defined by the Pabi reference. This latitude limit is also the same as that used for the SO (see lines 108-110)

P4 line 109: This is very specific – “measurements of ferrihydrite Fe” – in fact the measurements are not as specific so please rephrase accordingly. See the general comment above regarding this.

Our extraction is very specific. See above.

P5 line 136: There is a problem here with the operational definitions and the descriptors used. Iceberg sediment is typically much coarser than what is derived from sea ice (Goldschmidt et al., 1992) and don’t meet the formal defintion of a nanoparticle (1-100 nm).

Iceberg sediment is an assortment of both coarse and fine particles but iron nanoparticles could be attached to grains present in any fraction (see below). We have high resolution microscopy images that show the presence of ferrihydrite in iceberg and in glacial sediments (see the cited reference in 171-173).

P5 line 140: Please explain in more detail how the samples were disaggregated – this obviously has an important bearing on the interpretation of the data.

Samples were gently disaggregated but not crushed in a pestle and mortar, see lines 141-142.

P5 line 147: Please explain what is meant in this case by a 'clean window'? How was it cleaned? Was it a glass pane or some other material? Had it rained previously (leaving salts)? Also- P6 line 150: As for line 147 – please explain more about how the sample was collected – as this could be a car windscreen or anything?

This dust sample was collected from a glass window cleaned with water. It had not rained.since cleaning. This sampling methodology has been used elsewhere for bulk samples where contamination is an unlikely to be a major influence. See Herut et al (a glass panel, no cleaning information provided, Limon. Oceanog., v. 47, p.871 and Shi et al (a cleaned solar panel, Env. Sci Tech., v. 43, p.6592). We have added these details in 147-154.

P6 line 149: The Eastern Mediterranean does not seem an appropriate representative sample for either the Arctic or Antarctic. Also P6 line 151-152: As for line 149, neither the Eastern mediterranean or China seem appropriate samples for the Arctic or Antarctic.

We have explained above that our approach was to collect a geographically widespread sample suite that could provide comparative extraction data for the iceberg samples. It should be a priority of future work to attempt to collect more representative samples.

P6, line 150. *P6 line 150: As for line 147 – please explain more about how the sample was collected – as this could be a car windscreen or anything?*

See above.

P6 line 155: So the samples were air-dried – at room temperature? Or were they heated before analysis? Were they dried to constant weight?

Details added in lines 159-161. Air drying is a common practice (see the Larsen et al. paper cited by the reviewer, p. 4829).

P6 line 156: How was the reagent deoxygenated? How was O2 subsequently kept out?

De-oxygenation was carried out by bubbling with nitrogen, see lines 163-164. The Reyes and Torrent reference which we have now added gives more details and concludes that excessive de-oxygenation can be prevented during the extraction by minimising the air space in the extraction vessel.

P6 line 161: How was the Fe removed assessed? By Ferrozine at the end of the assay? It is mentioned later but not specified for which analysis it was used for. There seems to be quite a lot of relevant information missing here.

The missing information is not substantially relevant. Lines 186-188 state that the Fe extracted as FeA and FeD was measured either by ferrozine or by AAS after each extraction step. In fact only the reproducibility and sampling data in Tables 1 and 2 were measured by ferrozine.

P6 line 161: So how was the dry weight assessed, earlier it just says they were air dried but nothing about removing the water content. So it is very hard to see how anyone else can reproduce this approach when so many basic pieces of information are missing.

Oven drying for water loss should be avoided as it produces aggregation and alters ferrihydrite to goethite/hematite. Air drying at room temperature minimises alteration but does not produce complete water loss (normally assessed at ~110^{o}C). It would be possible to measure the complete water loss on a different sub-sample by oven drying. However applying this weight correction for the water loss introduces reproducibility errors from the sub-sampling of coarse sediment. Our approach is satisfactory (see also Larsen et al cited by the reviewer) considering that the failure to remove all the water induces only small variations which would anyway be identified in the errors in Tables 1 and 2.

P6 line 164: Goethite and hematite are also partly soluble under this approach though the dissolution is significantly slower (Deng and Stumm, 1994; Smolen et al., 2003). Also- P6 line 164: This is assuming that what dissolves is ferrihydrite – as a pure sample of goethite or magnetite would also give a similar result.

Dissolution is so slow that only negligible amounts of goethite, hematite and magnetite are removed under our conditions. See the Raiswell et al Table above.

P6 line 172: The dithionite reduction does not remove Fe locked up in silicates though, so how is the total Fe assessed? How then is the data in Table 3 calculated?

Dithionite does not remove all the Fe present in silicates (see Raiswell et al, 1994, Chem Geol, 111, 101-111 . The total Fe data in Table S3 of this ms are literature data and the appropriate references are given in Table S2.

P7 line 186: What would Fe (oxyhydr)oxides be under the terminology used for the sediments?

We define Fe (oxyhydr)oxides as ferrihydrite, lepidocrocite, goethite and hematite in line 216.

Normally they are commonly described as HFO, which is analogous to 2 line ferrihydrite in many cases. See the general comment on this above.

It would be incorrect to describe all Fe (oxyhydr)oxides as HFO. HFO refers only to hydrous ferric oxide which is considered to be equivalent to ferrihydrite. We have added this material in lines 174-177. Oxides such as hematite contain no structural water and should not be described as HFO.

P7 line 201: There are a number of other studies that have looked at the bioavailability of Fe from particulate sources e.g. (Iwade et al., 2006; Yoshida et al., 2006; Ushizaka et al., 2008;Bligh and Waite, 2011).

The references we have chosen relate to HFO and/or ferrihydrite. We could add these references (and many others) to the potential bioavailability but the citations in lines 174-181 and 222-230 are sufficient for our purposes.

P7 line 203: Directly bioavailable? Please explain how this works for bacteria or phytoplankton? It has been shown for protozoan (Barbeau et al., 1996; Barbeau and Moffett, 1998) but not for organisms that don't have a food vacuole or stomach.

We have added the Barbeau reference in line 233. The Shaked and Lis paper (see refs) discusses how cyanobacteria are able to mediate dust dissolution and access iron directly, as can mixotrophic plankton (see our Nodwell and Price reference). These processes are outside our scope (see lines 114-166 and 233).

P8 line 211: Neither of these two references show any data on grazing of dithionate soluble iron – please provide a proper reference for this.

See above.

P8 line 211: The labile part of the dithionite reactive iron pool is presumably the same as the ascorbic acid reactive iron pool so how does dissolution make FeD become more bioavailable?

The extractions were done sequentially (see lines 183-185) so different phases have been extracted. Dissolution of FeD would be slow but may occur, for example, by siderophores. Detailing these processes in seawater are outside our scope (see above).

P8 line 221: The section regarding the sieving of the samples should be in the methods section not the results. It isn't clear reading here whether this is wet or dry sieving that is being performed – this needs to be made clear.

We disagree. The sampling and reproducibility issues are important, as the reviewer clearly realises. As such, the sieving belongs in the results section.

P8 line 224: Please provide all the relevant statistical information for the application of the t-test here, without this it is impossible for the reader to judge the validity of the statement made in the text.

The student ‘t’ test requires the numbers of samples and their means and standard deviations (see for example Paradine and Rivett, Statistics for Technologists, page 112). The data are all given in Table 1.

P8 line 228: These results then ask the question if the reactive iron being measured is truly nanoparticulate in size – clearly there is reactive iron but it is found in all size ranges and not exclusively in the smallest size class – this is important as if you one argument is that this is all nanoparticulate iron stuck together that’s one thing but these particles won’t be made more soluble by dissolution in the surface mixed layer as they will sink out quickly. Similarly, in terms of grazing the particles are clearly too big for ingestion – in both the dissolution and grazing case they require disaggregation before becoming labile.

Ascorbic acid is highly specific for ferrihydrite which is always present in a nanoparticulate form (see above).We do not know whether the nanoparticles are free-standing (and possibly aggregated) or attached (lines 513-515). Aggregated or attached nanoparticles could be associated with grains of any size. Attachment may or may not continue to exist after delivery into seawater.

This also then suggests that sieving may produce an artefact in helping to disaggregate the samples?

If sieving produced an artifact we would expect to differences by sieving through 1mm and through 63µm. These size differences do not produce different FeA contents, outside that expected for sampling. See Table 2.

P8 line 234: The results of these analyses does not give a lot of confidence as the variability in the replicates is similar to the variability between samples. It appears the samples are too inhomogeneous to really be able to make proper comparisons.

Inevitably there is variability in sampling coarse iceberg sediment consisting of material ranging from comminuted material to bedrock grains (lines 237-239). But there is a much bigger variability between samples, which is the reason for needing a large, geographically diverse database.

P9 line 238: Please explain in more detail what the hypothesis that was being tested here is and provide full details of the statistical analysis.

The hypothesis is given in line 246-247. We test the probability that there is no significant difference between the single sample and the sample group. The z test is described in Russell Langley, Practical Statistics, page152-4.

P9 line 247: How was the significance ascertained? Please provide statistical data for this.

The *z* test is based on the sample size, mean and standard deviation (see above) and all the relevant data are given in Table 2 and the text. Values of *z* for different significance levels are tabulated in Russell Langley.

P9 line 251: A Log normal distribution normally indicates it is most likely related to particle size distribution. So it would have been helpful to compare to this.

Grain size data for a single sample often do have a log normal distribution. But the log normal distribution here is for a group of samples from different locations. Geochemical data for elements present in low concentrations often approximate to log normal distributions because the mean is low and there is the potential for high outliers.

P9 line 253: Please state this as the logarithmic mean and not refer to it as the mean.

Alteration made in line 275.

P9 line 257: As previous please provide all the relevant statistical information for the application of the t-test here, without this it is impossible for the reader to judge the validity of the statement made in the text. In this case was a t-test the most appropriate approach?

The relevant samples sizes, means and standard deviations are given in Table 3. The t test is appropriate to examine whether the difference in the means of two sets of samples is significant.

Did you apply Pearson's sample skewness test to check the t-test assumption of normality for the log transformed data.

No. The data were plotted on probability paper which showed improved linearity with a logarithmic transformation, particularly for the FeA data. For the sake of consistency all the data were treated logarithmically.

P10 line 271: Neither of these two citations say anything about EPS being able to accelerate the production of Fe oxyhydroxides, in fact the literature indicates the opposite in that they help to solubilize iron (Hassler et al., 2011; Hassler et al., 2015) and make it bioavailable.

Agreed, there is a typographical error here and 'production' has now been altered to 'dissolution' in line 295.. Lannuzel et al state with regard to sea ice that 'EPS have a high affinity for metal cations and could bind metals in sea ice, therefore increasing their solubility and bioavailability by slowing the production of scarcely soluble Fe oxyhydroxides'. The Hassler references refer to the role of EPS extracted from plankton in seawater, rather than sea ice, but they provide good support for the role of EPS in solubilizing Fe and are now cited in line 295.

P10 line 272: See also the recent work of Jeong et al. regarding this (Jeong et al., 2012; Jeong et al., 2015).

Two excellent papers which add further support to our proposed ice processing mechanism. We have added discussion of these papers in lines 297-308.

P19 line 280: This is more likely to be derived from photoreduction of the dissolved Fe in solution (Croot et al., 2008) – additionally the half-life of Fe(II) in the plume of an ice berg in polar waters would be several hours (Croot et al., 2001;Croot and Laan, 2002;Croot et al., 2005) particularly if the pH was decreased.

Lin and Twining (as cited) suggest that Fe(II) could be sourced from iceberg-hosted Fe (oxyhydr)oxides. Yes this is another possibility but we wish exclude any detailed discussion of seawater processes

P10 line 287: Cooling the sample to the freezing point of water also induces redox changes for the solution phase as has been shown for studies linking sea ice and water on Mars (Horne, 1963;Marion et al., 2003;Marion et al., 2005;Marion et al., 2008;Marion et al., 2010). There is also the high ionic strength to consider. Again see the recent work by Jeong et al regards freeze/thaw cycles.

Studies on these other planets with regard to redox transitions are likely to be affected by low pO_2. But the Jeong references are excellent (see above).

P10 line 296: This is the logarithmic mean and should be stated as such.

Alteration made in line 329.

P11 line 298: Grain size could also explain this difference and what evidence is there that these samples have undergone freeze/thaw cycles?

Yes, we have clearly stated that there could be differences between the two sample groups (see lines 288-290). All the ice samples must be subject to at least one freeze/thaw event and it is highly likely multiple events would arise from temperature fluctuations during iceberg transport.

P11 line 312: How was this value arrived at? Surely a very large iceberg would be less as it had the same grounded area as a smaller berg, e.g. contact with sediments, but has a larger volume of clean ice.

We deal with this issue above.

P12 line 326: It is not clear that the assay as used here determine only ferrihydrite and not other iron phases.

We believe it is; see Table and discussion above.

P12 line 331: Once again please provide the details of the statistical tests being applied – a t-test does not seem appropriate here as the dust samples are not the same.

The details are as above. The null hypothesis is that the Patagonian dusts are drawn from the same population as all the other dusts. It was not rejected.

P12 line 333: See also the recent work by Simonella et al. (2014).

This is a good reference which has fractional solubilities of 0.8 to 8.0 % for a hydroxylamine extraction on soils from South America. However the authors point out that soil samples may not represent atmospheric dust samples due to fractionation effects (in creating dust from soil). Additional effects are also likely during cloud processing, as the authors recognise. Our dust data therefore avoids soil samples and this reference would not represent a fair comparison to our data.

P13 line 380: 1-2 orders of magnitude but not more than that.

The cited reference to Lannuzel et al 2014 states that there were 2-3 orders of magnitude enrichment in sea ice compared to underlying seawater. The text has been amended to state this.in line 447

P14 line 388: This contradicts the statement on line 272 where there was precipitation in the presence of EPS.

This is correct here. See response to line 271.

P14 line 390: The authors are confusing sea ice studies with iceberg studies – these are quite different in terms of the communities that are found in the surface - remember also that phytoplankton/bacterial growth only occur in the surface area of the sea ice which is exposed to sunlight or in brine channels that are fed by organic material from above.

We are comparing sea ice and icebergs only on the basis that both undergo one or more freeze/thaw cycles. Our discussion now starts out by recognising that there different Fe sources in sea ice and icebergs (see lines 445). We then move on to suggest that the dust deposited on sea ice may be processed in the same way as we suggest for icebergs. We have re-written lines 455-456 to stress that our estimate refers only to the freeze/thaw effects.

P14 line 414: The authors are also referred to Antarctic examples (Dulaiova et al., 2009;de Jong et al., 2012;Borrione et al., 2014). The Dale et al. (2015) global value includes release from oxygen depleted sediments and this is not the case in the SO or AO and thus it could be considered an overestimate for those regions when the global average is applied.

The shelf flux discussion (lines 480-490) offers a comparison in magnitude (only) with the iceberg data in both the AO and the SO. The De Jong paper points out the paucity of data for SO sediment pore water fluxes. They have four profiles in the Atlantic sector of the SO (within our defined SO area) that have a mean Fe diffusive flux of ~9 µmol/m^2/day (range 1-15), comparable to the mean shelf flux derived by Dale et al (7.3µmol/m^2/day) which forms the basis of their 72 Gmol/yr shelf estimate. The modelling community (see lines 46-73) assumes that shelf sources make important Fe contributions in the SO and the Dale estimate is a simple way of providing an order of magnitude comparison with our own iceberg data-entirely appropriate in our AO and SO context. The proportions of oxygen-depleted sediments on the shelf in the AO and SO are unknown and we have added a statement that the Dale values may be an overestimate (line 487)

P16 line 449: This is not necessarily true and indeed the residence time for iron here is likely to be shortened due to scavenging. The reason for the prolonged bloom is most likely twofold, stabilization of the water column by melting ice and the slow growth rates at cold temperatures (Boyd, 2004;Borrione and Schlitzer, 2013). The iceberg is of course still supplying the iron but the water column stabilization effect is also critical.

We argue that the presence of large bergs may act to prolong the residence time, relative to smaller icebergs. But it is useful to add that the water column structure is persistent (line 516).

P16 line 462: This estimate however is not so solid as it is based on a comparison between glacial ice and icebergs and not involving sea ice itself – thus if anything it could be a major underestimation of the bioavailability.

Agreed, see lines 333-335 and the discussion in lines 449-450 which points out that there are multiple Fe sources to sea ice.

P16 line 468: It should also be pointed out that the dust flux to the Southern Ocean is most likely dominated by wet deposition as either rain or snow.

We have amended the text as suggested (lines 547-550), citing Mahowald et al, 2011, Quaternary Science Reviews, 30, 7-8, 832-854) but fluxes are poorly known in remote areas (see for example p. 1077 in the Breitbarth reference that we cite.

Table 1: Please include the number of samples that this analysis was constructed from.

Table amended

Table 2: These results don't really address the reproducibility as we are provided with 5 different samples with differing %FeA values and are told that n=5 for one size fraction and n=1 for the other. What we really need to see is the ascorbic acid soluble iron and the total iron and how that varies.

Total Fe data are not available but the comparison is correctly constructed to examine the reproducibility in FeA, which is the subject of this ms. Each line in the table tests whether the single sample (<63µm) could be drawn from the same population as the 5 (< 1mm) samples. This is fully explained in lines 241-245.

Table S3: There is no auxiliary information provided here to put this samples into context, that is what was the O2 concentration in the water? What was the organic content of the sediment? The grain size distribution? The data seems highly variable but no explanation is given why and then the data is all lumped together for the subsequent analysis and interpretation this makes for a very unsatisfactory approach.

The suggested additional data would be interesting but not necessarily helpful in dealing with the FeA and FeD sample sets, especially in the context of dealing with processes in the source areas. Amended text notes that wide variability results from the local geology (see lines 269, 288-289.)

Interactive comment on "Potentially Bioavailable Iron Delivery by Iceberg-hosted Sediments and Atmospheric Dust to the Polar Oceans" by Rob Raiswell et al.

Anonymous Referee #2

Received and published: 2 May 2016

This is a very well and logically written paper which deals with an aspect of the iron cycle which is poorly constrained, namely the flux of iron coming from particulate sources to the polar oceans. I find the paper a comprehensive and informative synthesis of the current knowledge in this area, with useful new data informing the different iron fluxes. A key strength of this paper is that it also establishes the uncertainties on these fluxes and the areas where future research is needed. The end result is pleasingly robust, clearly laying out uncertainties and making good use of statistical tests for determining reproducibility. As such I recommend publication of the manuscript, subject to the authors addressing the following major point and considering the minor changes.

We thank the referee both for the encouraging and supportive comments, as well for the constructive suggestion to consider anthropogenic sources. We accept that our focus on mineral dust alone is likely to underestimate the supply of potentially bioavailable Fe and have added relevant material as follows to estimate potential combustion sources. The referee responses are given in italics to differentiate them from our responses (which use line numbers refer in the new ms).

Major point:

I just have one major comment - The paper assumes all dust to be low in solubility based on their samples. However, there are two issues with this –

Firstly, although dust solubility is open to interpretation, a number of studies have shown that anthropogenic dust sources may be important, and even more important in some areas of the globe - e.g. iron from combustion, biomass burning etc... e.g Sedwick et al., 2007 (10.1029/2007GC001586), Luo et al., 2008 (10.1029/2007GB002964) Ito et al., 2013 (10.1029/2012GB00437), Ito 2015 (10.1021/acs.estlett.5b00007) to name just a few. . ..This delivery of anthropogenic aerosols is likely to be highly variable and as such may not be captured by a small number of samples or from natural sources – that seems especially likely if there is no high Fe solubility in your aerosol samples as would be expected for anthropogenic Fe (e.g. Sedwick et al., 2007; up to 19%; 10.1029/2007GC001586). If this is the case, then dust sources in your paper may be seriously underestimated– indeed a recent study attributed sporadic high deposition of soluble Fe to Antarctica from biomass burning and it could be the dominant particulate dust Fe source to the Southern Ocean (Winton et al., 2016; 10.1002/2015GB005265.; Ito et al 2015). By only assuming low Fe solubilities, the paper seems to miss this possible Fe source.

Secondly, but by using dust samples from other areas of the globe, it may be that you are poorly representing Antarctic dust, especially combustion Fe sources. I would say that the integrated composition of dust delivered to the Southern Ocean is probably not very similar to the dusts sampled in this manuscript. So while I realize that it is difficult to draw any strong conclusions about the effect of anthropogenic sources of dust to the polar oceans based on your dataset, I think it needs discussion in the paper in the context of uncertainties on the dust flux being calculated.

We have discussed the suggested literature with respect to anthropogenic/combustion sources. We will make the point that our ascorbic acid extractable iron data (FeA) probably represents mineral dust that has undergone little atmospheric processing (line 407-419) and has no significant combustion input (line 426).

This FeA data produces a flux of 0.14 to 0.64 µmol/m^2/yr to the SO (assuming an area of19 x 10^6 km^2). This flux data is compared to the Edwards and Sedwick (2007) and Winton et al. (2015) studies in lines 436-444. Both sites are believed to have sampled clean air with little anthropogenic addition and their low flux estimates match our FeA flux data. Comparisons are difficult due to the different methodologies used to determine solubility but our ascorbic acid leach is at a relatively high pH, compared to the other leaches, and has tended to produced lower Fe data compared to estimates from clean and contaminated samples. We suggest that our FeA data provide a reasonable benchmark to compare to mineral dust and iceberg fluxes delivered to the SO, bearing in mind the uncertainties in the solubility methodologies, the analytical data and the flux estimates.

Estimates of combustion iron sources are very dependent on the model assumptions, especially for solubility. Our ms discusses combustion sources in lines 523-536, using the suggested studies by Luo et al. (2008) and Ito (2015). Table 5 notes that our FeA flux represents mineral dust little influenced by combustion sources, and that combustion sources may be similar to the mineral dust fluxes

There are also a small number of minor comments that require the authors attention:

L17 I think 'dusts' could be 'dust' here and in other places. Dust is usually used as a plural. But at authors discretion

Line 17. Dusts are changed to dust.

L23 What about other forms of iron in dust? Think it would be good to make this clearer here. Nanoparticulate Fe is unlikely to be the only bioavailable form.

'

Line 23. We have modified lines 18-20 stating that Ferrihydrite is the most soluble and potentially bioavailable iron (oxyhydr)oxide mineral and in contrast to other forms of iron (lepidocrocite,goethite, hematite). However these may be solubilsed by further processing in seawater (see our line 231-233).

L39 There are recent Fe-isotope informed calculations for multiple sources also –eg. Conway and John 2014 (doi:10.1038/nature13482). I think this would be a valuable citation here, especially as an emerging approach to constraining different sources of dissolved Fe, including dust and particulate bound Fe.

Line 39. Good idea. This citation is added to line 39 to explain that isotopes have potential to constrain the different sources discussed here.

L42 I think you can remove the' prior to iceberg-hosted'

Line 44. 'the' removed, as suggested.

L74 The Tagliabue reference should be 2016?

Line 74. 2015 has amended to 2016.

L79 of' Antarctica would read better.

Line 81. 'of' has replaced 'in' as suggested.

Lines 147-150. Some more detail of collection would be good here. How was the window cleaned etc? There is not detail of how the med samples were collected. It's important to demonstrate that these samples were obtained cleanly.

Material added in ines 147-155. The collection of bulk samples such as these after dust storms from clean surfaces are unlikely to be significantly affected by contamination, and such samples have been utilised in other studies (see for example Shi et al., 2009, Env. Sci Tech., 43, p. 6592 and Herut et al, Limnol. Oceanog., 47, p.871.

L158 Needs a space before 10

Line 164. Space added.

L162 What is 2-line and 6-line ferrihydrate? Might be worth clarification for the reader.

Material added as requested to lines 174178.

L184 This section misses references and coverage of other techniques which post date the Jickells and Spokes work (it is quite an old study now...) for leaching dust – such as ultrapure water leaches or seawater or acidic leaches, as carried out by American groups such as Sedwick et al. or Buck/Landing et al. or the Conway et al study you cite - and as such rather underrepresents the dust solubility literature.

Material on ultra-pure water leaches and seawater leaches added to lines 196-202. (Conway et al., 2015) and the acidic leaches in lines 203-214, using the suggested references.

L325 This is a long sentence, please add a comma after sources

Line 380. Comma added after ‘sources’, as suggested.

L344 Conway et al also appear to show some seawater-leached data for the Dome C samples.

The seawater leach data (0.15±0.13 mg/m^2/yr) were not significantly different from the pH 5.3 meltwater leach data (0.09±0.17 mg/m^2/yr) which does not appear to be important in this context.

The sentence is also a little clunky. . ..perhaps change to have’ to measured’ and remove data’. These samples are a useful citation, but of course miss any modern anthropogenic sources – might be worth making this point.

Line 399 makes the changes suggested and lines 441-444 add the point about missing anthropogenic sources

L353 Double.

Line 409. Added ‘more than double’, as suggested.

L364 See my major point about anthropogenic sources.

Line 425-426. Yes, we should point out that this excludes anthropogenic sources. See above material that we will add.

L376. Can you also present this as an Fe solubility percentage in terms of total Fe, that would make comparison to other work easier. Same for Table 5?

The fractional solubility estimates are given in line 393-395 and are based on an assumed total Fe content of 3.5%, and so are not tabulated.

Reviewer 3 Responses.

The Duprat paper was wrongly cited as Luisn et al and this has now been corrected, see above.

The use of significant figures is clarified in lines 377-378.

The two different percentages are now differentiated, see lines 401-403.

Potentially Bioavailable Iron Delivery by Iceberg-hosted Sediments and Atmospheric Dust to the Polar Oceans

Robert Raiswell,[1] Jon R. Hawkings[2], Liane G. Benning[1,3], Alex R. Baker[4], Ros Death[2], Samuel Albani[5*], Natalie Mahowald[5], Michael ~~ke~~ D. Krom[1,6], Simon W. Poulton[1], Jemma Wadham[2] and Martyn Tranter[2].

[1]Cohen Biogeochemistry Laboratory, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK.

[2] Bristol Glaciology Centre, School of Geographical Sciences, University of Bristol, Bristol BS8 1SS, UK.

[3] GFZ, German Research Centre for Geosciences, Telegrafenberg, D-11473 Potsdam, Germany.

[4]Laboratory for Global Marine and Atmospheric Chemistry, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

[5]Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York, USA.

[6]Department of Marine Biology, Haifa University, Haifa, Israel.

*Now at the Institute for Geophysics and Meteorology, University of Cologne, Cologne, Germany. RR Corresponding Author: email r.raiswell@see.leeds.ac.uk

Abstract: Iceberg-hosted sediments and atmospheric dust~~s~~ transport potentially bioavailable iron to the Arctic and Southern Oceans as ~~nanoparticulate~~ ferrihydrite. Ferrihydrite is nanoparticulate and ~~(the~~ more~~st~~ soluble, and potentially more bioavailable, than other iron (oxyhydr)oxide minerals (lepidocrocite, goethite and hematite)~~)~~. A suite of more than 50 iceberg-hosted sediments contain a mean content of 0.076 wt. % Fe as ~~nanoparticulate~~ ferrihydrite, which produces iceberg-hosted Fe fluxes ranging from 0.7~~1.4~~-5.5~~11~~ and 3.2-25 Gmoles yr^{-1} to the Arctic and Southern Oceans respectively. Atmospheric dust (with little or no combustion products) contains a mean ~~nanoparticulate~~ ferrihydrite Fe content of 0.038 wt. % (corresponding to a fractional solubility of ~ 1%) and delivers much smaller Fe fluxes (0.02-0.07 Gmoles yr^{-1} to the Arctic Ocean and 0.0-0.02 Gmoles yr^{-1} to the Southern Ocean). New dust flux data show that most atmospheric dust is delivered to sea ice where exposure to melting/re-freezing cycles may enhance fractional solubility, and thus fluxes, by a factor of approximately 2.5. Improved estimates for these particulate sources require additional data for the iceberg losses during fjord transit, the sediment content of icebergs and samples of atmospheric dust delivered to the polar regions.

1. Introduction

Iron (Fe) is an essential limiting nutrient for phytoplankton. Its supply exerts a significant impact on marine productivity with important implications for the carbon cycle and climate change (Mackenzie and Andersson, 2013). Quantifying Fe sources to the oceans, especially those that may be influenced by climate change, is therefore critical. Global Fe cycles commonly recognise important supplies of dissolved Fe (dFe, <0.2 or 0.45µm) from atmospheric dust, continental shelf sediments and hydrothermal activity (e.g., Breitbarth et al., 2010). Iron isotopes are a promising novel, approach (e.g., Conway and John, 2014) to quantifying these different sources but past c~~C~~ontributions ~~from hydrothermal activity and shelf sediments ~~have commonly been~~are~~ based~~-~~ on estimates and/or measurements of dFe (see Tagliabue et al., 2010; Dale et al., 2015). However ~~but ~~quantifying dFe contributions from atmospheric dust~~s~~ requires an estimate of the solubility of iron. Estimating the solubility of Fe in particulates is particularly important in understanding the Fe cycle in the polar oceans where~~ the~~ iceberg-hosted sediments are a source of bioavailable Fe (Smith et al., 2007; Raiswell et al., 2008; Hawkings et al., 2014; Duprat~~Luis~~ et al., 2016).

The Southern Ocean (SO) is the largest HNLC (High Nutrient-Low Chlorophyll) area where productivity is limited by the delivery of Fe (e.g. Moore et al., 2013). Recent modelling studies in the SO have focussed on understanding the factors which control spatial variations in productivity but reach different conclusions due to different representations of the Fe cycle and different assumptions as to Fe solubility and scavenging. For example; Tagliabue et al. (2009) modelled measurements of dFe derived from atmospheric dust and shelf sediments. Atmospheric dust~~s~~ entering seawater was~~ere~~ assumed to have a fractional solubility (soluble Fe expressed as a percentage of total Fe) of 0.5% with continued slower dissolution during sinking occurring at a rate of 0.0002% per day. Overall sediments were more important than atmospheric dust, although dust supplies dominated in some regions depending on the model assumptions used. Lancelot et al. (2009) modelled dFe supplies from atmospheric dust, iceberg melt and shelf sediments. Sediments were the major source, iceberg melt was of lesser significance and atmospheric dust (assumed to have fractional solubility of 2%) had little influence. The models gave good agreement with patterns of phytoplankton growth but large uncertainties were acknowledged in the magnitude of these sources. Boyd et al. (2012) compared biological utilisation patterns using four mechanisms of Fe supply (vertical diffusivity in sea ice free areas, iceberg melt, atmospheric dust and shelf sediments) that were found to have substantial areal extent. Phytoplankton Fe utilisation was highest in regions supplied by Patagonian dust (using fractional solubilities varying from 1-10% Fe) and, to a lesser extent, shelf sediments. Wadley et al. (2014) compared the relative magnitudes and variations in supply of dFe from melting icebergs, shelf sediments and atmospheric dust. Sediments were again shown to be the most important source but considerable uncertainty was noted over the flux of Fe from iceberg-hosted sediments. Death et al. (2014) considered a range of sources that included iceberg-hosted sediments and atmospheric dust and found that modelled productivity was significantly enhanced in areas receiving iceberg-hosted sediments and subglacial melt compared to the productivity arising from atmospheric dust (assumed fractional solubility of 2%). However the contribution from iceberg-hosted sediments was based on a suite of only six samples (Raiswell et al., 2008) that contained 0.15 wt. % Fe as ferrihydrite.

These studies show that SO models produce significant differences in the relative magnitudes of the different Fe sources which complicate attempts to isolate overlapping contributions. For example Tagliabue et al. (2016~~5~~) shows that global dust fluxes of dFe range from 1-30 Gmoles yr^{-1} between different models. Few studies also count for iceberg sources of Fe (see Tagliabue et al., 2016~~5~~; Table 1), the importance of which may be particularly sensitive to climate change. Climate change is driving increased loss of ice from ice shelves in the Antarctic Peninsula (Vaughan, 2006; Rignot et al., 2011) and ice-shelf shrinkage has also been reported from other areas of~~in~~ Antarctica (Pritchard et al., 2012; Depoorter et al., 2013; Duprat~~Luis~~ et al., 2016). Ice shelf losses increase the delivery of potentially bioavailable Fe by iceberg-hosted sediments. Iceberg-hosted sediment data are sparse but current estimates indicate Fe delivery appears to exceed meltwater delivery to the SO by at least an order of magnitude (Hawkings et al., 2014).

Increases in iceberg-hosted sediment delivery are also likely in the Arctic Ocean (AO). A relatively high proportion of primary production occurs on the AO shelves (Pabi et al., 2008) where ice-free areas experience intense phytoplankton blooms due to favourable light and nutrient conditions. Nitrate appears to be the primary limiting nutrient otherwise Fe and/or light become limiting (Popova et al., 2010). Hawkings et al. (2014) have estimated Fe delivery by meltwaters from the Greenland Ice Sheet but no data are available for Fe delivery from iceberg-hosted sediments, although marine-terminating glaciers in the AO are likely to respond to climate change, as in the SO, by producing more icebergs (Bamber et al., 2012) and increasing sediment Fe delivery.

Modelling the polar Fe cycles and assessing the impact of climate change requires an improved estimate of the Fe currently released from the particulates present as iceberg-hosted sediments and atmospheric dust. There is a substantial disagreement as to the strength of different sources and reducing their uncertainty is important (Tagliabue et al., 2016~~5~~). This contribution presents new data for potentially bioavailable Fe from iceberg-hosted sediments and atmospheric dust and also shows how ice transport and storage may influence Fe delivery to the polar regions. The AO and the SO differ in several important respects. The AO receives a substantial riverine flux (~ 2400 km^3 yr^{-1}; Dyurgerov et al., 2010), more atmospheric combustion products (Luo et al., 2008), has a proportionately smaller area of winter ice (see later) and is also being disproportionately affected by global warming (IPCC, 2013). Changes in Fe delivery to the SO may influence productivity but this is unlikely in the AO where there is no evidence for Fe limitation (except perhaps in summer in the Irminger Basin; Nielsdottir et al., 2009).

Formatted: Superscript

Formatted: Superscript

The Fe budgets for the AO use the area >60°N (a larger area than that >66°33′39″N which is conventionally used to define the Arctic Ocean; Pabi et al., 2008) and the SO budget is based on the area >60°S. The 60°S latitude lies close to the Antarctic Polar Front (the boundary between cold Antarctic waters and warmer sub-Antarctic waters), which runs clockwise from 140°E to 60°W, beyond which the front moves out to 48°S (Moore et al., 1999). Our new flux estimates are based on measurements of ferrihydrite Fe which are determined by the source and mode of delivery and have a fundamental influence on bioavailability. We are concerned only with glacial and atmospheric particulate sources that can be significantly influenced by terrestrial and/or transport processes prior to entry into seawater. The fate of these sources on entering seawater and their spatial variations are outside this focus although our data may inform these research areas.

2. Methodology

2.1 Ice-hosted Sediment Sampling

Over 60 sediment samples have been collected from icebergs and glaciers at 15 different Arctic and Antarctic locations (Table S1). Data have previously been reported for only 15 of these samples (from 7 localities, see Table S1) and thus the new samples provide a significant expansion of the existing data and now represent a substantial database for Fe in ice-hosted sediments. A set of 41 new iceberg samples were collected from floating icebergs with sediment-bearing layers present in dense, clear blue ice indicating compressed glacier ice rather than accreted frozen seawater. An additional suite of 9 new glacial ice samples was collected from sediment-rich bands in the main body of glaciers (i.e. land-based ice not icebergs). These samples represent basal ice which has been in contact with the ice-rock interface.

Samples were collected with a clean ice axe, geological hammer or chisel. The outer layers of ice that might be contaminated were allowed to melt and drain away before the remaining ice was transferred into a new polyethylene bag and allowed to melt. Some loss of dissolved Fe by adsorption or the precipitation of (oxyhydr)oxides during melting is possible (Conway et al., 2015) but the presence of~~r~~ organic complexes (see later) may~~can~~ stabilise dissolved Fe. In any event, melt dFe concentrations are too low (Hawkings et al., 2014) to produce any significant increase in sediment Fe contents. Sediment samples were collected as soon as melting was complete by filtration through a Whatman 542 (2.7 µm pore diameter) filter paper or through a 0.4/0.45 µm membrane filter (Table S3). There is a significant difference in the size fractions produced by filtration through 2.7 µm and 0.4/0.45µm but the filtered iceberg sediment is dominated by coarser material and variations in the content and masses of the fraction passing through the different filters seem to be too small to produce significant differences in our extractable Fe contents, at least compared to the variations between different samples (see later, Tables 3 and S3). Small pebbles and grit (> 1mm diameter) were removed and the remaining material gently disaggregated but not crushed. Any further separations are as described below.

2.2 Atmospheric Dust Samples.

A suite of 15 atmospheric dust samples (Table S2) have been analysed by the same extraction techniques used for the iceberg and glacial samples to ensure data comparability. Seven new samples were collected during a cruise through the eastern tropical Atlantic and into the Sea of Marmara (Baker et al., 2006). A~~These a~~erosol samples (~ 100 mg) were collected using high volume (1 m^3 min^{-1}) aerosol samplers onto single acid-washed Whatman 41 filters (pore size 20 µm; see Baker et al., 2006) and mainly represent mineral dust from the Sahara. ~~.~~Three new samples of dry deposition were collected from a clean window in Southern Patagonia and two new samples of dry deposition were collected from the Eastern Mediterranean; one from a dust collector located in Crete and the other from deposition on to a clean glass surface at Rosh Pina, Israel. (Table S2). These bulk mineral dust samples were collected after dust storms and are unlikely to be significantly affected by contamination (see Shi et al., 2009). Relevant data from the literature (Table S2) are also included for 3 additional dry deposition samples from the Eastern Mediterranean and China (Table S2).

2.3 Analytical Methodology

Each sample of air-dried sediment was treated for 24 hours by an ascorbic acid solution buffered at pH 7.5. Air-drying at room temperature does not achieve complete water loss but <10 wt. % more water is removed by oven-drying. The extractant was ~~a deoxygenated~~ a solution of 0.17M sodium citrate and 0.6M sodium bicarbonate to which ascorbic acid was added to produce a concentration of 0.057M. This solution was deoxygenated (by bubbling with nitrogen; see Reyes and Torrent, 1997). Approximately10-40 mg of sample were mixed with 10 ml of the ascorbate solution, shaken for 24 hrs at room temperature and then filtered through a 0.45 µm cellulose nitrate membrane filter (Kostka and Luther, 1994; Hyacinthe and Van Cappellen, 2004; Raiswell et al., 2010). The Fe removed by ascorbic acid is hereafter termed FeA and reported as dry wt. %. Controlling these ~~Th~~conditions produces a high degree of selectivity~~is~~. Fe is ~~technique~~ quantitatively removed~~s the Fe~~ from fresh 2-line ferrihydrite and partially dissolved~~s the Fe~~ from aged 2-line and 6-line ferrihydrite and schwertmannite with negligible effects on other Fe (oxyhydr)oxides or clay minerals (Raiswell et al., 2010). The presence of ferrihydrite in iceberg-hosted sediment and subglacial sediment has been confirmed by high resolution photographs and selected area electron diffraction by Raiswell et al. (2008) and Hawkings et al. (2014).

Ferrihydrite only exists as a fine grained and highly defective nanomaterial. The more disordered form (Hiemstra, 2013) contains two diffraction lines (2-line ferrihydrite, often called hydrous ferric oxide, or HFO) and exists as smaller crystallites than in the form with six diffraction lines (6-line ferrihydrite). The measurement of ~~nanoparticulate~~ ferrihydrite is important because this mineral phase is directly or indirectly bioavailable (Wells et al., 1983; Rich and Morel, 1990; Kuma and Matsunga, 1995; Nodwell and Price, 2001). The delivery of fresh ferrihydrite to the open ocean thus has the potential to stimulate productivity in Fe-limited areas (Raiswell et al., 2008; Raiswell, 2011).

The residual sediment was treated for 2 hrs with a solution of 0.29M sodium dithionite in 0.35M acetic acid and 0.2M sodium citrate, buffered at pH 4.8 (Raiswell, et al., 1994). Following the ascorbic acid extraction step, the dithionite extracts the remaining (oxyhydr)oxide Fe (aged ferrihydrite, goethite, lepidocrocite and hematite; Raiswell et al., 1994). Dithionite-soluble Fe is hereafter termed FeD and is reported as dry wt. %. Both the FeA and FeD extractant solutions were analysed for Fe either by Atomic Absorption Spectrometer with an air-acetylene flame or by spectrophotometry using ferrozine (Stookey, 197~~8~~0). Replicate analysis of a river sediment internal laboratory standard gave analytical precisions of 3% for FeA and 10% for FeD using this sequential extraction. Errors associated with sampling glacial sediments are examined below. Blank corrections were negligible.

2.4 Approach

Estimates of the solubility of Fe in atmospheric dust~~s~~ have utilised a variety of extraction techniques which have produced~~that attempt to simulate the complex reactions that may occur during cloud processing. Jickells and Spokes (2001) have summarised the dust extraction data and show that the~~ estimates of fractional solubility ranging~~e~~ from 0.2 to 80%

(Jickells and Spokes, 2001), depending on time, pH and the extractant (Baker and Croot, 2010~~). Few of these extractions have been fully calibrated against different Fe minerals.~~). Recent studies have attempted to recognise a soluble Fe fraction (extracted with ultra-pure distilled water or seawater) and/or a labile or leachable fraction (using a low pH chemical extraction). Distilled water leaches (Sedwick et al., 2007; Berger et al., 2008; Conway et al., 2015) provide a consistent and reproducible result but losses of Fe can occur due to precipitation of Fe(OH)$_3$. Rapid filtration or flow through techniques can be used to minimise such Fe losses. Seawater extractions are thought to be less reproducible due to variations in the concentrations of natural binding ligands (Sedwick et al., 2007).

Formatted: Subscript

Few of the extractions used to determine labile or leachable Fe have been fully calibrated against different Fe minerals. ~~For example~~ Baker et al. (2006) extracted Fe using ammonium acetate at pH 4.7 which dissolves negligible concentrations of Fe (oxyhydr)oxides but significant concentrations of Fe as carbonate (Poulton and Canfield, 2005). Chen and Siefert (2003) extracted Fe with a 0.5 mM formate-acetate buffer at pH 4.5 which was stated to dissolve Fe (oxyhydr)oxides (mineralogy unspecified). Berger et al. (2008) use a pH 2 leach with acetic acid and hydroxylamine hydrochloride followed a 10 min heating step at 90^{o}C. This method (Winton et al., 2015) extracts metals associated with biogenic material, Fe and Mn (oxyhydr)oxides and adsorbed to clay minerals. Our ascorbic acid extraction is ~~more~~ stronger than that by Baker et al. (2006)~~elective for ferrihydrite~~ ~~than the Baker et al. (2006) extraction~~ but weaker than the extractions used by Chen and Siefert (2003) and Berger et al. (2008). The ascorbic acid extraction is, however, selective for fresh ferrihydrite, which is the most soluble, and thus potentially bioavailable, Fe (oxyhydr)oxide mineral.~~) extract (compared to which the ascorbic extract is at a higher pH, and is selective for ferrihydrite).~~

Formatted: Superscript

We recognise two particulate fractions (Raiswell and Canfield, 2012) that contain Fe (oxyhydr)oxide minerals (ferrihydrite, lepidocrocite, goethite and hematite), as described below.

(1) FeA reported as wt. % Fe that is extractable by ascorbic acid and which consists mainly of fresh~~, nanoparticulate~~ ferrihydrite (Raiswell et al., 2011).

(2) FeD reported as wt. % Fe that is extractable by dithionite. Extraction of FeD following removal of FeA mainly dissolves residual, aged ferrihydrite plus lepidocrocite, goethite and hematite (Raiswell et al., 1994).

An important issue concerns the bioavailability of FeA and FeD. Experimental work suggests that some part of sediment Fe can support plankton growth (Smith et al. 2007; Sugie et al., 2013). Sediment Fe present as fresh ferrihydrite (the most soluble Fe (oxyhydr)oxide) is directly or indirectly bioavailable (see above) and is extracted as FeA. FeA mainly comprises nanoparticulate ferrihydrite that ~~but~~ probably encompasses a range in bioavailabilities (Shaked and Lis, 2012) due to variations in the extent of aggregation and associations with organic matter (which may partially or wholly envelope Fe (oxyhydr)oxide minerals; Raiswell and Canfield, 2012). We are concerned with Fe mineral reactivity at the point of delivery to seawater where ferrihydrite measured as FeA is more labile than FeD (the dithionite-soluble (oxyhydr)oxides which are relatively stable and poorly bioavailable). However, Fe present as FeD may become partially bioavailable after delivery to seawater (for example by dissolution and grazing; Barbeau et al., 1996~~Raiswell and Canfield, 2012~~; Shaked and Lis, 2012), but these complex interactions are outside the scope of the present contribution.

3. Results and Interpretation

3.1 Reproducibility of Iceberg Sediment Sampling.

The collection of small samples from heterogeneous sediment with a range of grain sizes (clay up to sand-size and beyond) is difficult to do reproducibly. Our approach has been to examine the variability both within and between different size-fractions. Our previous practice (Raiswell et al., 2008) has been to remove only coarse material >1mm diameter, which might severely affect our ability to analyse sub-samples of 10-40 mg reproducibly. Table 1 compares the composition of different size fractions produced by sieving iceberg sediment (from Wallensbergfjorden, Svalbard) first to <1mm, then by taking two further replicate subsamples: one sieved to <250 µm and the other to <63 µm. Five replicates were analysed from each size fraction to give the means and standard deviations in Table 1.

A student's *t* test showed no significant differences between mean analyses of wt. % FeA in the three different size fractions. In general the wt. % FeA would be expected to be larger in the finer fractions, but the enrichment need not be large. A comparison of the FeA contents of the glacial flours studied by Hopwood et al. (2014) showed that <500 µm fractions contained 40-130% of the FeA content of the <63 µm fraction. Shaw et al. (2011) also found a rather similar wt % of FeA in the 63-125 µm (0.038%) and 125-500µm (0.053%) fractions of iceberg sediment. Thus the finest fractions are not always large enough in mass, or have a high enough wt. % FeA, to produce substantial differences between the different size fractions. We next examined the sampling reproducibility using five different iceberg samples (K1-5) from Kongsfjord, Svalbard (see Table S3) that were sieved through 1mm with a replicate subsample then produced by sieving to <63 µm. Table 2 shows the mean and standard deviation for 5 replicate analyses of these iceberg samples sieved through <1 mm and compared to a single analysis of the <63 µm fraction.

No consistent pattern emerged from the data presented in Table 2. Samples with low wt. % FeA values (K2 and K3) tended to show the most variation. However, the *z* test showed a high probability of there being no significant difference between the <1mm and <63 µm samples for K1, K3 and K5 (p>5%) but a low probability (p<0.2%) that samples K2 and K4 were not significantly different. We conclude that our practice of removing only very coarse material by sieving through <1 mm provides a reasonable compromise that achieves good reproducibility (unless the wt. % FeA is less than 0.05%) in samples that are coarse enough to be representative of the sediments delivered by icebergs.

3.2. Ice-hosted Sediment Composition.

Table 3 summarises the wt. % FeA and FeD contents of the iceberg and glacier sediments and the mean and standard deviations of FeA and FeD. Wide variations mainly result from source area geology but there are no significant differences between the compositions of the Arctic and Antarctic icebergs (if the outlying data for Weddell Sea IRD4 is ignored; see Table S3) and hence we are justified in presenting all the iceberg samples as a single group (Table 3).

The wt. % FeA and FeD data approach a~~re~~ log normal distribution~~ly distributed~~ and hence logarithmic means are used to calculate the mean values and the logarithmic standard deviations are used to derive the low and high values in Table 3. This approach produces a logarithmic mean FeA content of 0.076 wt. % for the iceberg sediments and a range of 0.030% to 0.194%. These new values are based on more than 50 iceberg samples; thus this mean is more reliable than the earlier mean value of 0.15 wt. % FeA (based on only 6 samples from Raiswell et al., 2008) and the large number of samples also permit an estimate of the variation. A student's *t* test on the logarithmic data showed that the iceberg sediments are significantly higher ($p<0.1\%$) than the logarithmic mean and standard deviation of the wt. % FeA contents of the sediments from glacial ice (mean 0.03%, range 0.015% to 0.060%). The logarithmic mean and standard deviation of the values for wt. % FeD in Table 3 are also significantly higher ($p<0.1\%$) in the icebergs (mean 0.377%, range 0.20% to 0.715%) than in the sediments from glacial ice (mean 0.091% range 0.042% to 0.196%).

3.2.1. Ice Processing Effects

The wt. % FeA and FeD contents of the iceberg sediments are significantly higher than the glacier-hosted sediments. The icebergs were not all derived from the land-based glaciers we sampled, and part of the differences in FeA and FeD may result from mineralogical/geochemical variations in the glacial bedrock. An alternative explanation for the high wt. % FeA and FeD values is that iceberg sediments have undergone alteration during post-calving transport as temperature fluctuations induced melting/freezing cycles ~~melting~~ that caused~~and~~ dissolution~~weathering~~ and precipitation. The slightly acidic pH (5.5-6.0) of ~~snow and~~ glacial icemelt (Meguro et al., 2004; Tranter and Jones, 2001) accompanied by the presence of extracellular polymeric substances (Lannuzel et al., 2014; Lutz et al., 2014; Hassler et al., 2011, 2015) is able to accelerate the dissolution~~production~~ of Fe (oxyhydr)oxides ~~by weathering. .~~

Experimental work by Jeong et al. (2012) showed enhanced dissolution rates of goethite and hematite trapped in ice compared to dissolution rates in water. The degree of enhancement depended on the presence of organic ligands and the surface area of the iron (oxyhydr)oxides; the high surface area of ferrihydrite (compared to goethite and hematite) should produce large enhancements. Jeong et al. (2012) found that dissolution was ligand-enhanced and not reductive. Furthermore ~~Furthermore,~~ Kim et al. (2010) has also observed that UV radiation causes the photoreductive dissolution of Fe (oxyhydr)oxides (goethite, hematite) encased in ice to ferrous Fe. Photoreductive dissolution was significantly faster in ice than in aqueous solutions at pH 3.5 (and was 7-8 times faster than the dissolution rates observed by Jeong et al., 2012) and was not influenced by the presence of electron donors. Acids are concentrated by several orders of magnitude at the ice-grain boundary due to freeze concentration effects and the resulting low pH (~1.5) further enhances both ligand and ~~photo~~reductive dissolution (Kim et al., 2010; Jeong et al., 2015).~~.~~ Lin and Twinning (2012) have found elevated concentrations of ferrous Fe within 1 km of a melting iceberg in the Southern Ocean which they suggest could be derived by the photoreduction of FeA in melt pools. However, most ferrous Fe is likely to be rapidly re-oxidised and precipitated as (oxyhydr)oxide minerals once exposed to the atmosphere by melting, which dilutes the acids and increases pH. The redox recycling effects of repeated melting/freezing events are explored below, as they might apply to any sediments (including atmospheric dust~~s~~, see later) encased in ice.

Fig. 1 shows an idealised melting/freezing reaction scheme for any sediment in which Fe (oxyhydr)oxides are initially absent and that only contains silicate Fe. Dissolution is initiated in acidic snow melt where Fe is leached slowly by silicate dissolution (Step 1). Subsequent freezing ~~(Step 2)~~ initially concentrates the acids and accelerates dissolution until complete freezing (or consumption of the acids) halts dissolution and induces the precipitation and aggregation of Fe (oxyhydr)oxides as FeA and FeD (Step 2). The transformation of ferrihydrite (FeA) to goethite/hematite (FeD) has a half-life of several years at T < 5^{o}C (Schwertmann et al., 2004; Brinza, 2010) and hence a proportion of FeA can be preserved over the life time of an iceberg. A new phase of melting (Step 3) causes the ~~rapid~~ dissolution or disaggregation of the newly formed FeA and FeD and also restarts the slow dissolution of silicate Fe.~~ , until~~ R~~r~~enewed freezing ~~(Step 4) again~~ again accelerates dissolution but finally precipitates ~~produces~~ FeA and FeD in amounts (Step 4) that have now been increased by the Step 3 dissolution of silicate Fe. Provided there is insufficient time for the transformation of FeA to FeD to be completed then FeA and FeD will both accumulate at the expense of silicate Fe. A comparison of the logarithmic mean FeA contents of the glacial (0.03 wt. %) and iceberg (0.076 wt. %) sediments and their errors suggests that melting/freezing effects, hereafter termed 'ice processing', could increase FeA contents by factor of 2.5, assuming similar initial FeA contents. This data provides the first, semi-quantitative estimate of how deposition on to sea ice might enhance the FeA delivery from atmospheric dust. These changes may also be accompanied by other, poorly understood chemical mechanisms that may further enhance Fe delivery from sea ice (Vancoppenolle et al., 2013).

3.3 Iceberg-Hosted FeA Fluxes

The iceberg-hosted FeA flux (Table 4) is based on sediment encased in icebergs and excludes sediments associated with seasonal ice (see later). The solid ice discharge from Antarctica has been determined as 1321±144 km^3 yr^{-1} by Depoorter et al. (2013) for the period 1979-2010 and from Greenland as 524±51 km^3 yr^{-1}for the period 1958-2010 by Bamber et al. (2012). Van Wychen et al. (2014~~5~~) estimate that the contribution from other ice masses in Alaska, Svalbard, and the Russian and Canadian Arctic is 34.4 km^3 yr^{-1} for which we assume a 10% error (roughly the same as for the Greenland flux). Hence the total ice loss from the Arctic is 558±55 km^3 yr^{-1}and from the Antarctic is 1321±144 km^3 yr^{-1}. Iceberg-hosted sediment FeA delivery can in theory be estimated from the product of ice mass loss, iceberg-sediment content and FeA concentration but there are significant difficulties.

The ice mass loss does not represent the mass of icebergs delivered into coastal waters, as significant melting may occur for glaciers that calve into long fjords (Hopwood et al., 2016). Such losses are relatively small in Antarctica where most icebergs are calved from massive, marine-terminating ice shelves and the remainder from outlet glaciers that calve directly into the sea (Silva et al., 2006; Diemand, 2008). However the characteristics of Greenlandic glaciers vary. One end-member represents fast moving glaciers where the ice mass loss is mostly by calving into the ocean, and the other end-member represents slower moving glaciers entering long (up to 100 km) fjords where the ice mass loss is mainly by melting in the fjord (Straneo and Cedenese, 2015; Hopwood et al., 2016). For this end member, fjord circulation patterns largely prevent iceberg-hosted sediments from being delivered directly to coastal waters (Hopwood et al., 2015, 2016). However, the five largest ice mass losses from Greenlandic glaciers occur from the Jakobshavn, Koge Bogt, Ikertivaq, Kangerdlugssuaq and Helheim glaciers (representing an ice mass loss of ~135 km^3 yr^{-1}; Enderlin et al., 2014). The first three of these glaciers either calve directly into coastal waters or have relatively short fjord transit times or distances where melting losses should be low, while large icebergs have also been observed to drift >150 km out of Sermilik Fjord (Helheim Glacier; Sutherland et al., 2014).The Jakobshavn, Koge Bogt, Ikertivaq glaciers represent approximately 68% of the 135 km^3 yr^{-1}. Data on fjord mass losses are urgently required but we will proceed by assuming that melting losses are negligible in Antarctica and are 50% in the Arctic. Thus the ice discharge to the AO is estimated as 279±27 km^3 yr^{-1} (Table 4).

Formatted: Superscript

Formatted: Superscript

Raiswell et al. (2006) and Death et al. (2014) point out that the sediment content of icebergs is poorly constrained but use a value of 0.5 g litre^{-1}, similar to the mean sediment content of river water. Death et al. (2014) cite a range of 0.4-0.8 g litre^{-1} for Antarctic icebergs and a~~A value in the~~ range 0.6-1.2 g litre^{-1} has been inferred by Shaw et al. (2011) based on the sediment load needed to produce the excess ^{224}Ra activity in the vicinity of icebergs in the Weddell Sea. Substantially larger and small concentrations (0.2-200 g litre^{-1}) have been found by Dowdeswell and Dowdeswell (1989). Here we use the conservative estimate of 0.5 g litre^{-1} of sediment but~~ the asterix in Table 4 indicates that~~ this value may be a significant source of error. The mean wt. % FeA content of icebergs is 0.076% with a variability of 0.030 to 0.194% (Table 3). Deriving the product of the ice mass loss, sediment load and FeA content (Table 4) shows that the flux of iceberg-hosted FeA to the AO ranges from 0.7~~1.4~~ to 5.5~~11~~ Gmol yr^{-1}with a mean of 1.9~~3.8~~ Gmol yr^{-1}, and to the SO is 3.2 to 25 Gmol yr^{-1} with a mean of 9.0 Gmol yr^{-1}. The estimated ranges span an order of magnitude and hence all ~~All~~ flux values hereon are only quoted to two significant figures. ~~These ranges overlap because the same data have been used for the sediment and FeA contents of icebergs and because the iceberg discharge values to the AO and the SO only differ by a factor of 2.~~

3. 4 Atmospheric Dust Composition

Mineralogy is a key factor in comparing particulate sources, and use of the ascorbic acid extraction technique for the iceberg sediments and atmospheric dust~~s~~ enables their ferrihydrite contents (as the most readily soluble and potentially bioavailable Fe mineral) to be compared. The atmospheric dust sample set is relatively small and mainly includes samples that are unlikely to be delivered to the polar regions although Patagonian dust is a possible source to the SO (e.g. Schulz et al., 2012). Our Patagonian dust sample set is small but a student's *t* test indicates that there are no significant differences in the concentrations of FeA and FeD between the Patagonian dust~~s~~ and the other dust~~s~~ analysed here. Consistent with this we note that the range of total Fe values (2.9 to 4.3 wt. %) for the Patagonian aeolian dust~~s~~ analysed by Gaiero et al. (2007) overlaps the range in our dust~~s~~ (2.8-4.5 wt.%; Table S4) and the mean value of 3.5 wt. % commonly assumed for atmospheric dust (e.g. Gao et al., 2003; Shi et al., 2012).

Our dust wt. % FeA contents are low (mean 0.038%, range 0.018 to 0.081%) and are comparable to the wt. % FeA contents of the sediments present in glacial ice, but significantly lower ($p<1\%$) than the iceberg-hosted sediments (Table 3). Assuming a dust total Fe (FeT) of 3.5 wt. %, the range in wt. % FeA corresponds to a fractional solubility of ~1%. This data provides a justification for the commonly used fractional solubility range of 1-2% (see earlier) which is known to be an arbitrary choice; Boyd et al., 2010). However our ascorbic acid fractional solubility data are difficult to compare with literature values because a wide range of extractions have been used, few of which have been calibrated against ferrihydrite (see earlier). Conway et al. (2015) measure~~have~~ fractional solubility ~~data~~ based on the ratio between Fe extracted at pH 5.3 by meltwater and total Fe. A median fractional solubility value of 6% was found for dust~~s~~ (deposited during the LGM on ice at Dome C, East Antarctica) that were high in total Fe (8 wt. %), possibly due to enrichment in smaller particles as a consequence of long range transport. Rather lower fractional solubility values (~3%) were found at Berkner Island closer to the South American dust sources and these data are comparable to the FeA range of our dust data, assuming similar extraction behaviour.

Dust wt. % FeD values (mean 0.87%, range 0.43 to 1.76 %) are significantly higher ($p <0.1\%$) than in both iceberg and glacial ice sediments. These data suggest that the net effect of weathering and atmospheric/cloud processing (Shi et al., 2015) on our~~these~~ atmospheric dust~~s~~ has been to more than double~~produce~~ Fe (oxyhydr)oxides present as the less reactive FeD.. The influence of weathering effects alone on soils (potential dust precursors) has been studied by Shi et al. (2011), who showed that the ratio (FeA+FeD)/FeT increased from 0.1-0.2 to 0.5-0.6 in highly weathered samples from areas with relatively high rainfall and temperatures. The (FeA+FeD)/FeT values for the atmospheric dust~~s~~ in Table 3 range from 0.24 to 0.52 which are clearly achievable by weathering alone in the source area. Values of (FeA+FeD)/FeT for the glacial (range 0.013 to 0.059) and iceberg (range 0.063 to 0.201) sediments can also be estimated assuming FeT = 4.2% (mean value for glacial sediments from Poulton and Raiswell, 2002). These values also suggest a trend of increasing weathering intensity from the glacial to the iceberg sediments (resulting from ice processing effects, see earlier) and on to the atmospheric dust~~s~~. Further data from atmospheric dust~~s~~ delivered to the polar regions are clearly needed to substantiate this conclusion.

3.5 Atmospheric Dust FeA Fluxes

This FeA flux is based on dust~~s~~ transported through the atmosphere (where there is potential for processing (but see above) and excludes soils. Localised areas of the Ross Sea are subject to large dust inputs from local terrestrial sands and silts but these appear to be only minor contributors to productivity (Chewings et al., 2014; Winton et al., 2014). Here we proceed cautiously on the basis that the FeA content of our atmospheric dust~~s are~~ represents mineral dust (with small to negligible contributions from combustion sources)~~ative of those~~ delivered to the polar regions. Dust deposition fluxes to the SO have been variably estimated as 0.1 to 27 Tg yr^{-1} (Gao et al., 2003; Mahowald et al., 2005; Jickells et al., 2005; Li et al., 2008). The new flux estimates derived here are based on the Community Earth System Model (Albani et al., 2014), which produces a value of 0.84 Tg yr^{-1} for dust deposition to the SO. The model version we use has been extensively compared to observations, with the sources modified to best match dust fluxes at high latitude (Albani et al., 2014). In the absence of ice processing, atmospheric dust~~s~~ delivered to the SO with an FeA wt. % ranging 0.018 to 0.081% produces a flux of< 0.01 to 0.01 (mean 0.01) Gmol yr^{-1} (Table 5). This corresponds to a flux of 0.14 to 0.64 µmol m^{-1} yr^{-1} (assuming an area of 19 x 10^{6} km^{2} for the SO).

Comparisons with other Fe flux estimates are difficult due to the different methodologies used. Edwards and Sedwick (2001) measured Fe

Formatted: Superscript

Formatted: Superscript

Formatted: Superscript

Formatted: Superscript

soluble at pH 2 from snow samples from East Antarctica, deriving a deposition flux of 0.3 to 2.0 µmol m^{-1} yr^{-1}. Winton et al. (2015) used an acetic acid plus hydroxylamine hydrochloride extraction (at pH 2) to estimate a flux of 0.64 to 2.5 µmol m^{-1} yr^{-1} for dust being delivered to a sector of the SO >45^{o}S. Both sites are believed to sample clean air with little addition from combustion sources. Our FeA data are at the low end of these estimates (consistent with the higher pH of our ascorbic acid extraction) and suggest that our FeA data provide a reasonable benchmark to compare mineral dust (in the absence of combustion addition) and iceberg fluxes delivered to the SO.

Formatted: Superscript

However the SO is more than 80% covered by sea ice during winter (declining to a minimum of ~16%) which has residence time of 1-2 years (Vancoppenolle et al., 2013). Studies of sea ice show that it can be enriched in Fe by up to 2-3 ~~several~~ orders of magnitude relative to the underlying seawater and the melting edge is commonly associated with plankton blooms (Lannuzel et al., 2007; 2008; 2014). This Fe is derived from different sources from that in icebergs, and includes atmospheric dust deposited on the ice surface (augmented by lithogenic dust in near-shore regions) and Fe scavenged from seawater during sea ice formation; Vancoppenolle et al., 2013; Wang et al., 2014). Studies of sea ice in Antarctica have shown high concentrations of Fe that are accompanied by extracellular polymeric substances (EPS) able to solubilise and complex Fe (Lannuzel et al., 2014). We suggest that atmospheric dust deposited on sea ice is processed by freeze/thaw cycle(s) in a similar fashion as dust deposited on icebergs ~~-~~by dissolution (at low pH and aided by EPS) and photoreduction~~ (as described earlier)~~. Our comparison between glacier and iceberg wt. % FeA contents (Table 3) indicates that this ice processing has the potential to increase mean wt. % FeA contents by a factor of 2.5 from 0.038 to 0.095 wt. % Simulations with the Community Earth System Model (Albani et al., 2014) representing the annual cycle of sea ice show that 0.6 Tg yr^{-1}of atmospheric dust are deposited on sea ice that melts (enabling ice processing to occur) which produces a mean rate of FeA delivery of 0.01 Gmol yr^{-1} with a range from <0.01 to 0.02 Gmol yr^{-1}. A further 0.24 Tg yr^{-1} are deposited on open water (no ice processing) which supplies only small amounts of FeA (< 0.01 Gmoles yr^{-1}). Together the delivery to sea ice and open water supplies a mean of 0.01 Gmol yr^{-1} with a range from <0.01 to 0.03 Gmol yr^{-1} (Table 5).

New dust Fe flux estimates to the AO (5.1 Tg yr^{-1}) are also derived from the Community Earth System Model (Albani et al., 2014) as before. In the absence of ice processing a mass flux of 5.1 Tg yr^{-1} dust delivers a range of 0.02 to 0.07 (mean 0.03) Gmol yr^{-1} of FeA (Table 5). Sea ice in the Arctic has a maximum extent of <~~-~~60% with a residence time of 1-7 years (Vancoppenolle et al., 2013). That part of the dust flux that falls on sea ice (2.1 Tg yr^{-1}) may be altered by ice processing which increases the wt. % FeA by a factor of 2.5 (see above) before being released by melting, as with the SO. Ice processed dust delivery to the AO provides a mean FeA flux of 0.03 Gmol yr^{-1} with a range of 0.02 to 0.08 Gmol yr^{-1} (Table 5). The 3.0 Tg yr^{-1}of dust delivered to open water supply a mean FeA flux of 0.02 Gmoles yr^{-1} (range 0.01 to 0.04 Gmoles yr^{-1}) and the total delivery (Table 5) to the AO is the sum of both fluxes (mean 0.05 Gmoles yr^{-1}, range 0.03 to 0.12 Gmoles yr^{-1}).

4. Discussion and Synthesis

The new iceberg and atmospheric dust data presented here provide a valuable insight into the iceberg and dust Fe sources to the polar oceans. They substantiate the view that iceberg sediments have the potential to be a significant~~substantial~~ source of bioavailable Fe as ferrihydrite (Table 6). We provide a context for the iceberg sediment flux data by using the global shelf flux value of Dale et al. (2015) to derive an order of magnitude estimate of shelf sources (thought to be a dominant source in the SO, see earlier). The Arctic and Antarctic shelf areas represent 11.5% and 7.3% of the global shelf area (< 200 m depth; Jahnke, 2010). Combining these area percentages with the global shelf flux dFe value of 72 Gmol yr^{-1} (Dale et al., 2015), suggests shelf sources are approximately ~~-~~8.3 Gmol yr^{-1} to the AO and 5.3 Gmol yr^{-1} to the SO. The shelf areas of the AO and SO that are able to source shelf fluxes of iron are unknown and the~~se~~ values suggested here may be an over-estimate~~are numerically comparable to the fluxes from iceberg-hosted sediments although~~. Furthermore shelf dFe (largely colloidal or nanoparticulate Fe of unknown composition) and FeA as ~~nanoparticulate~~ ferrihydrite may not be of similar bioavailability. Nevertheless the ranges of the shelf and iceberg suggest that both are comparably important sources.

Sources of variation in Tables 4 and 5 relate both to the estimates of mass fluxes as well as the Fe analytical data but improved mass flux estimates may be difficult to achieve given their temporal and spatial variability. Table 6 and Figure 2 summarise the flux ranges. At first sight there appear to be broad similarities in the magnitude of these Fe sources to the polar oceans but we list below three limitations to the current data set.

(1) The iceberg FeA fluxes are based on data that is derived mainly from the Arctic. Iceberg melting losses during fjord transit are poorly known and, if underestimated here, might increase differences between the AO and the SO.
(2) The atmospheric dust sample set is small and may not be representative of dust~~s~~ delivered to the polar regions.
(3) FeA is present as ferrihydrite which is potentially bioavailable to phytoplankton although acquisition rates are unknown and may vary substantially between organisms, and with local environmental factors (Shaked and Lis, 2012).

Iceberg derived FeA is a major source of Fe to both the AO and the SO that will likely increase as iceberg delivery increases with climate warming in the polar regions (Table 6 and Figure 2). Our measurements of iceberg FeA contents are based on a substantial data set although Antarctic data are still poorly represented. It is clear that iceberg FeA is a major source of potentially bioavailable Fe as ferrihydrite, unless the errors associated with the estimates of iceberg sediment contents exceed an order of magnitude (Raiswell et al., 2008; Death et al., 2014; Hawkings et al., 2014). Modelling the impact of iceberg FeA delivery on surface water dFe concentrations will be complex and will require kinetic models that incorporate scavenging, complexation, dissolution and sinking (e.g.,Tagliabue and Volker, 2011; Raiswell and Canfield, 2012). FeA attached to coarse material will settle out of surface waters quickly, but FeA present ~~as~~ mainly as fine-grained material (or ~~as~~ nanoparticles) may be held in suspension for long periods in the wake of icebergs. The basal and sidewall melt from icebergs creates complex patterns of upwelling and turbulence producing a persistent water column structure that may last for several weeks and whose influence extends for tens of km, and from the surface to 200-1500 m depth (Smith et al., 2013). Furthermore giant icebergs (>18 km in length) have a disproportionally large areal influence (compared to smaller bergs) which may last~~s~~ for longer than a month (Duprat~~Luis~~ et al., 2016). The proportion of the FeA found within this area of influence will clearly have a prolonged residence time that may be a key factor in its dispersion and utilisation away from iceberg trajectories into areas with where other Fe supplies are limited.

Atmospheric dust fluxes are estimated to be a minor source of FeA to both the AO and the SO, compared to iceberg-hosted sediment, although substantially larger to the AO (Table 6). The dust database used here is small but appears to be globally representative of mineral dust in that the range of wt. % FeD contents (2-5%) overlaps that found in other studies (e.g. Lafon et al., 2004; 2006). There are no comparable data for potential dust sources to the polar regions although Patagonia atmospheric dust~~s~~ (Gaiero et al., 2007) have wt. % total Fe values ranging from 2.9-4.3 wt. % (which overlaps the 3.5 wt. % total Fe value commonly used as a global average). Our mineral dust flux estimates could be significantly increased by combustion sources, estimates of which are very dependent on the flux model assumptions, especially those for Fe solublity. Luo et al. (2008) show global maps of the ratio (soluble Fe from Combustion)/Total soluble Fe which ranges from 10-40% in the SO (>60°S) and 20-60% in the AO (>60°N). Ito (2015) also shows that soluble Fe from dust makes up ~50% of the total soluble Fe. Table 5 acknowledges that combustion sources could be as large as that from dust in some areas of the AO and the SO.

Formatted: Superscript

Formatted: Superscript

The important features of the new FeA and FeD dust data presented here is that they are closely tied to mineralogy, with FeA measuring the content of fresh ferrihydrite, which is the most reactive and potentially bioavailable Fe mineral. Thus these data enable direct comparison with iceberg sediment FeA delivery. Furthermore we have estimated a potential role for ice processing which appears to enhance FeA contents of dust~~s~~ delivered to sea ice. Mean dust FeA concentrations of 0.095 wt. % (if ice processed) approximate to the mean concentration in icebergs (0.076 wt. %), which indicates that the former will dominate in areas where dust mass fluxes exceed iceberg sediment delivery, assuming both types of particulates have similar residence times in the ocean. Additional atmospheric dust samples from the polar regions are needed to support these cautious conclusions and to clarify the role of combustion sources.~~.~~ Wet deposition is thought to be the main mechanism of deposition to the SO but fluxes are poorly known (Mahowald et al. (2011).Very high soluble Fe contents (Heimburger et al., 2013) have been found in wet deposition samples from the Kerguelen Islands (at 48^{o}S which lies outside our SO area) and a similar flux to the area > 60^{o}S would represent a major contribution.

Acknowledgements

RR thanks the School of Earth and Environment for Greenland fieldwork support and MDK acknowledges support from the Leverhulme Foundation with grant RPG-406 and LGB from the UK Natural Environment Research Council grant number NE/J008745/1. JH, MT and JW were funded by the NERC DELVE project (NERC grant NE/I008845/1 and the associated NERC PhD studentship). The authors are grateful to Lyndsay Hilton from the Thomas Hardye School, Dorset, who provided Antarctic glacial ice samples collected during participation on a Fuchs Foundation charity expedition. The Patagonian dust samples were supplied by S. Clerici. We are grateful to Mark Hopwood for drawing out attention to iceberg losses in Greenlandic fjords.
All the data used in this manuscript are included in the Supplementary Information.

Table 1. Comparison of the FeA Content of Different Size Fractions of Iceberg Sediment.

Sample	% FeA
Sieved <1mm	0.175±0.005
Sieved <250 µm	0.172±0.003
Sieved <63 µm	0.162±0.010

Table 2. Reproducibility of the <1mm Fraction of Iceberg Sediments.

Sample	% FeA<1mm	% FeA<63 µm
K1	0.374±0.019	0.377

K2	0.094±0.019	0.056
K3	0.044±0.017	0.058
K4	0.129±0.021	0.102
K5	0.089±0.007	0.134

Table 3. Composition of Iceberg, Glacial Ice and Atmospheric Dust Samples.(number of samples in brackets)

Sample	Wt. %FeA			Wt. %FeD			(FeA+FeD)/FeT
	Low	Mean	High	Low	Mean	High	Estimated Range (see text)
Icebergs (51)	0.03	0.076	0.194	0.20	0.377	0.715	0.063-0.201
Glacial Ice (16)	0.015	0.03	0.060	0.042	0.091	0.196	0.013-0.059
Atmospheric Dust (15)	0.018	0.038	0.081	0.428	0.868	1.76	0.24-0.52

Low and High values each represent one logarithmic standard deviation from the logarithmic mean, except for (FeA+FeD)/FeT.

Table 4. Fluxes of FeA Derived from Iceberg-hosted Sediment by Melting.

	Arctic[1]	Antarctic[2]	Sources/Notes

Ice Discharge km^{3} yr^{-1}	279~~558~~±27~~55~~^{a}	1321±144^{b}	a. Bamber et al. (2012) and Van Wychen et al. (2014), assumes 50% fjord losses.~~.~~ b. Depoorter et al (2013).
Sediment Content g litre^{-1}	0.5^{c}~~*~~	0.5$^{c.}$ ~~*~~	c. Poorly by Raiswell et al. (2006), similar to the mean river load.
FeA wt. %	0.03-0.076-0.194	0.03-0.076-0.194	
FeA Flux Gmol yr^{-1}	0.7~~1.4~~-1.9~~3.8~~-5.5~~11~~	3.2-9.0-25	

~~*Indicates a poorly constrained value.~~

Formatted: Superscript

Table 5. Atmospheric Dust FeA Fluxes

	Arctic	**Antarctic**	**Sources/Notes**
Mass Flux Tg yr^{-1}	5.1	0.84	Community Earth Systems Model (Albani et al., 2014)
FeA wt. % (No ice processing)	0.018-0.038-0.081~~*~~	0.018-0.038-0.081~~*~~	Based on 15 dust samples from the Atlantic, Mediterranean and Patagonia with little combustion inputs.
FeA Flux Gmol yr^{-1}	0.02-0.03-0.07	<0.01-0.01-0.01	Combustion inputs may range up to si
FeA wt. % (With ice processing)	0.045-0.095-0.203^{b}~~*~~	0.045-0.095-0.203~~*~~	Assumi increas 2.5x
FeA Flux Gmol yr^{-1}	0.03-0.05-0.12	<0.01-0.01-0.03	

~~*Indicates poorly constrained values~~

Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold

Formatted: Superscript

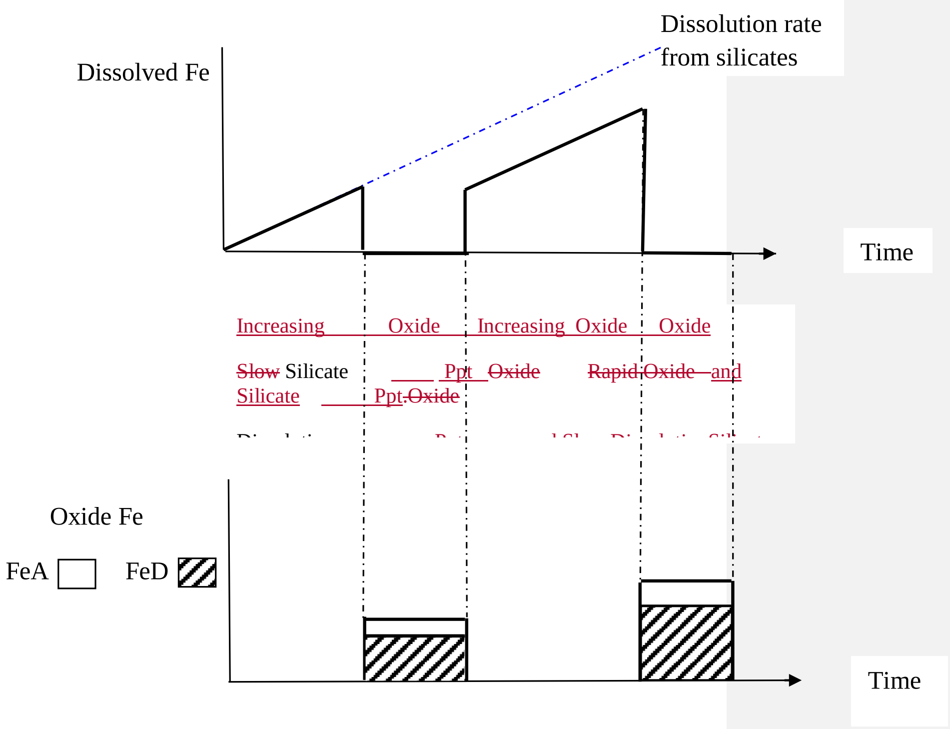
Formatted: Superscript

Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold, Font color: Text 1

Table 6. Summary Data for the Main Sources of Iron to the Arctic and Southern Oceans

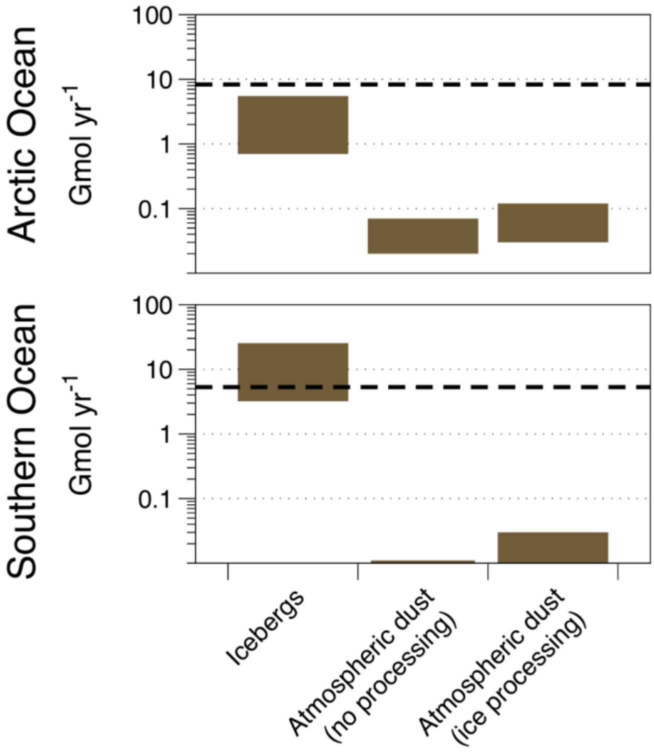
Source	FeA flux range Gmol yr^{-1}	
	Arctic Ocean	Southern Ocean
Iceberg Sediments	0.7~~1.4~~ – 5.5~~11~~	3.2 – 25
Atmospheric dust	0.05 – 0.19	0.01 – 0.05
Ice processed	0.03 – 0.12	<0.01 – 0.03
No ice processing	0.02 – 0.07	<0.01 – 0.02

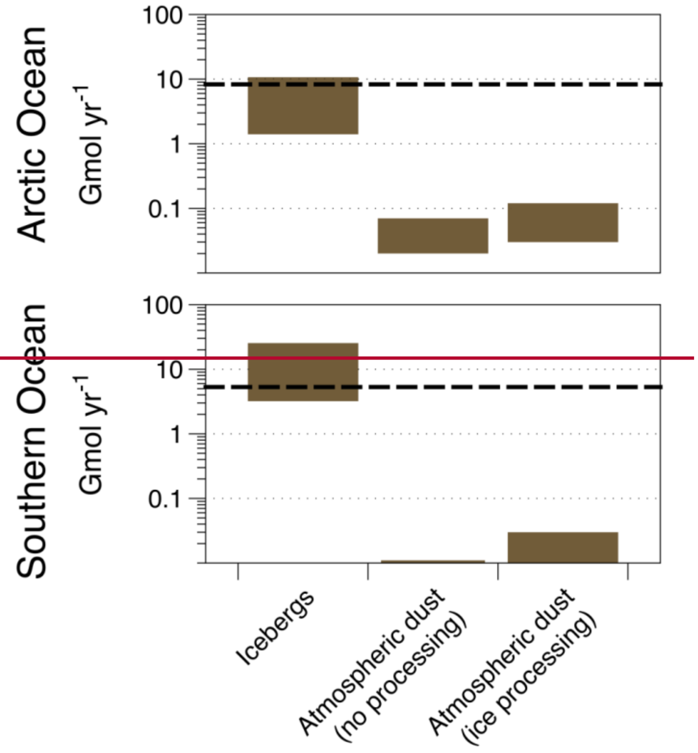
Figure 1. Simplified reaction scheme for the reactions of ice-hosted sediments during melting/freezing cycles.



Step 1 2 3 4

Figure 2. Ranges of FeA fluxes to the Arctic and Southern Oceans. Dashed line shows rough estimates of shelf dFe based on Dale et al. (2015).


Arctic Ocean
Gmol yr-1
100
10
1
0.1
Southern Ocean
Gmol yr-1
100
10
1
0.1
Icebergs
Atmospheric dust (no processing)
Atmospheric dust (ice processing)



References

Albani, S., Mahowald, N. M., Perry, A. T., Scanza, R. A., Zender, C. S., Heavens, N. G., Maggi, V., Kok, J. F., and Otto-Bliesner, B. L.; Improved dust representation in the Community Atmosphere Model, J. Adv. Model. Earth Syst., 6, 541–570, doi:10.1002/2013MS000279, 2014.

Baker, A.R., Jickells, T.D., Witt, M., and Linge, K.L.; Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean, Mar. Chem., 98, 43-58, 2006.

Baker, A.R., and Croot, P.L.; Atmospheric and marine controls on aerosol solubility in seawater, Mar. Chem., 120, 4-13, 2010.

Bamber, J., van den Broeke, M., Ettema, J., Lenarts, J., and Rignot, E.; Recent large increases in freshwater fluxes from Greenland into the North Atlantic, Geophys. Res. Lett., 39, L19501, doi:10.1029/2012/GL050552, 2012.

Barbeau, K., Moffett, J.W., Caron, D.A., Croot, P.L., and Erdner, D.L., Role of protozoan grazing in relieving iron limitation of phytoplankton, Nature, 380, 61-64, 1996.

Boyd, P.W., Arrigo, K.R., Stzepekand, R., and van Dijken, G.L.; Mapping phytoplankton iron utilization: insights into Southern Ocean supply mechanisms, J. Geophys. Res., 117, doi:org/10.1029/2011JC00726, 2012.

Berger, C.J.M., Lippiat, S.M., Lawrence, M.G., and Bruland, K.W.; Application of a chemical leach technique for estimating labile particulate aluminium, iron and manganese in the Columbia River plume and coastal waters off Oregon and Washington; J. Geophys. Res., 113, doi:10.1029/2007/JC004703, 2008.

Boyd, P.W., Mackie, D.S., and Hunter, K.A.; Aerosol iron deposition to the surface ocean-Modes of iron supply and biological responses, ~~-~~Mar. Chem., 120, 128-143, 2010.

Boyd, P.W., Arrigo, K.R., R., Stzepekand, R., and van Dijken, G.L.; Mapping phytoplankton iron utilization: insights into Southern Ocean supply mechanisms, J. Geophys. Res., 117, doi:org/10.1029/2011JC00726, 2012.

Breitbarth, E., ~~E.P.~~ Achterberg, E.P., Ardelan, M.V., Baker,A.R., Bucciarelli, E., Chever, F., ~~-~~Croot, P.L., Duggen, S., Gledhill, M., Hasselhov, M., Hassler, C., Hoffmann, L.J., Hunter, K.A., Hutchins, D.A., Ingri, J., Jickells, T., Lohan, M.C., Nielsdottir, M.C., G. Sarthou, G., ~~.~~ Schoemann, V., Trapp, J.M., Turner, D.R., and Ye, Y.; Iron biogeochemistry across marine systems-Progress from the past decade, Biogeosciences, 7, 1075-1095, 2010~~, 2010~~.

Brinza, L.; Interactions of molybdenum and vanadium and iron nanoparticles, PhD, Department of Earth and Environment, ~~thesis,~~ University of Leeds, 2010.

Formatted: Font: Not Italic

Formatted: Font: Not Bold

Chen, Y., and R.L. Siefert, R.L.; Determination of different types of labile atmospheric iron over remote oceans, J. Geophys. Res., 108, D24, 4774, doi:1029/2003JD003515, 2003.

Chewings, J.M., Atkins, C.B. Dunbar, G.B., and Golledge, N.R.; Aeolian sediment transport and deposition in a modern high-latitude glacial marine environment, Sedimentology, 61, 1535-1557, 2014.

Conway, T.M., and John, S.G.; Quantification of dissolved iron sources to the North Atlantic, Nature, 511, 212-215, 2014.

Conway, T.M., Wolf, E.W., Rothlisberger, R., Mulvaney, R., and Elderfield, H.E.; Constraints on soluble aerosol iron flux to the southern Ocean during the Last Glacial Maximum, Nat. Comms., 6**:**7850 doi:10.1038/ncomms8850, 2015.

Dale, A.W., Nickelsen, L., Scholz, F., Hensen, C., Oschlies, A., and Wallman, K.; A revised global estimate of dissolved iron fluxes from marine sediments, Global Biogeochem. Cy.~~cles~~, doi:10.1002/2014GB005017, 2015.

Death, R., Wadham, J.L., Monteiro, F.,~~-~~ Le Brocq, A.M., Tranter, M., Ridgewell, A., Dutkiewicz, S., and Raiswell, R.; Antarctic ice sheet fertilizes the Southern Ocean, Biogeosciences, 10, 12551-12570, 2014.

Diemand, D.; Icebergs, Encyclopaedia of Ocean Sciences, Edited by Steale, J.H. Turekian, K.K. and Thorpe, S.A., Academic Press, p. 181-190, 2008.

Dowdeswell, J.A., and Dowdeswell, E.K.; Debris in icebergs and rates of glaci-marine sedimentation-observations from Spitzbergen and a simple model; J. Geol., 97, 221-231, 1989.~~.~~

Depoorter, M.A., Bamber, G.L., Griggs, J.A.,T.M. Lenaerts, T.M., Ligtenberg, S.R.M., van den Broeke, M.R., and Moholdt, G.; Calving fluxes and basal melt rates of Antarctic ice shelves, Nature, 502, 89-92, 2013, 2013.

Duprat, L.P.A.M., Bigg, G.R., and Wilton, D.J.; Giant icebergs significantly enhance the marine productivity of the Southern Ocean, Nat. Geosci, 9, 219-221, doi.10.1038NGEO2533, 2016.

Dyurgerov, M., Bring, A., and Destouni, G., Integrated assessment of changes in freshwater inflow to the Arctic Ocean, J. Geophys. Res., 115, doi:10.1029/2009JD013060, 2010.

Edwards, R., and Sedwick, P.; Iron in East Antarctic snow: Implications for atmospheric iron deposition and algal production in Antarctic waters, Geophys. Res. Lett., 28, 3907-3910, 2001.

Enderlin, E.M., Howat, I.M., Jeong, S., Noh, M-J., van Angelen, J.H., and van den Broeke, M.R.; An improved mass budget for the Greenland ice sheet, Geophys. Res. Lett., 41, 866-872, 2014.

Gaiero, D.M., Brunet, F., Probst, J-L., and Depetris, P. J.; A uniform isotopic and chemical signature of dust exported from Patagonia: Rock sources and occurrence in southern environments, Chem. Geol., 238, 107-129, 2007.

Gao, Y., Fan, S-M., and Sarmiento, J.L.; Atmospheric iron input to the ocean through precipitation scavenging: A modeling perspective and its implication for natural iron fertilization in the ocean, J. Geophys. Res., 108~~, 4221~~, doi:10.1029/2002/JD002420, 2003.

Hassler, C.S., Alasonati, E., Mancuso Nichols, C.A., and Slaveykova, V.I.; Exopolysaccharides produced by bacteria isolated from pelagic southern Ocean-Role in Fe binding, chemical reactivity and bioavailability, Mar. Chem., 123, 88-98, 2011.

Hassler, C.S., Norman, L., Mancuso Nichols, C.A., Clementson, L.A., Robinson, C., Schoemann,V., Watson, R.J., and Doblin, M.A.; Iron associated with exopolymeric substances is highly bioavailable to oceanic phytoplankton, Mar. Chem., 173, 136-147, 2015.

Hawkings, J.R., Wadham, J.L., M. Tranter, M., Raiswell, R., Benning, L.G., Statham, P.J., ~~A. ~~Tedstone, A., -Nienow, P., Lee, K., and J. Telling, J.; Ice sheets as a significant source of highly reactive nanoparticulate iron to the oceans, Nat. Comms., 5, 3929, doi:10.1038/ncomms4929, 2014.

Hiemstra, T.; Surface and mineral structure of ferrihydrite, Geochim. Cosmochim. Ac., 105, 316-325, 2013.

Formatted: Font: Not Italic

Heimburger, A., Lusno, R., and S. Triquet, S.; Solubility of iron and other trace elements in rainwater collected on the Kerguelen Islands (South Indian Ocean), Biogeosciences, 10, 6616-6628, 2013.

Hopwood, M.J., Statham, P.J., Tranter, M., and Wadham, J.L.; Glacial flours as a potential source of Fe(II) and Fe(III) to polar waters, Biogeochemistry, doi:10.1007//s10533-013-9945-y, 2014.

Hopwood, M.J., Bacon, S., Arendt, K., Connelly, D.P., and Statham, P.J.; Glacial meltwater from Greenland is not likely to be an important source of Fe to the North Atlantic, Biogeochemistry, 124, 1-11, 2015.

Hopwood, M.J., Connelly, D.P., Arendt, K.E., Jull-Petersen, T., Stinchcombe, M., Meire, L., Esposito, M., and Krishna, R.; Seasonal changes in Fe along a glaciated fjord Greenlandic fjord, Front. Earth Sci., 4, doi:10.3389/feart.2016.00015, 2016.

Hyacinthe, C., and Van Cappellen, P.;~~,~~ An authigenic iron phosphate phase in estuarine sediments: composition, formation and chemical reactivity, Mar. Chem., 91**,** 227-251, 2004.

IPCC; Long-term Climate Change: Projections, Commitments and Irreversibility, 5 th Assessment Report, Chapter 12, 2013.

Ito., A.; Atmospheric processing of combustion aerosols as a source of bioavailable iron, Environ. Sci. Tech. Lett., 2, 70-75, 2015.

Jahnke, R.A~~.~~.; Global Synthesis in Carbon and Nutrient Fluxes in Continental Margins, Global Change-The IGBP Series, Edited by Liu, K.-K et al., Chapter 16. Springer-Verlag, Berlin, 2010.

Jeong, D., Kim, K., and Choi, W.; Accelerated dissolution of iron oxides in ice, Atmos. Chem. Phys., 12, 11125-11133, 2012.

Jeong, D., Kim, K., Min, D.W., and Choi, W.; Freezing-enhanced dissolution of iron oxides; Effects of inorganic acid anions, Env. Sci. Tech., 40, 12816-12822, 2015.

Jickells, T.D., and Spokes, L.J.; Atmospheric inputs to the ocean, in The Biogeochemistry of Iron in Seawater, Edited by Turner, D.R. and Hunter, K.A., pp.123-251.Wiley, New York, 2001.

Jickells, T.D., An, Z.S., Anderson, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawaahata, H., Kubilay, N., LaRoche, J., J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgewell, A., Tegen, I., and Torres, R.; Global iron connections between desert dust, ocean biogeochemistry, and climate, Science, 308, 67-73., 2005.

Kim, K., Choi, W., Hoffmann, M.R., Yoon, H.I., and Park B.K.; Photoreductive dissolution of iron oxides trapped in ice and its environmental implications, Env. Sci., Tech., 44, 4142-4148, 2010.

Kostka, J.E., and Luther III, G.W.; Partitioning and speciation of solid phase iron in saltmarsh sediments, Geochim. Cosmochim. Ac.~~ta~~, 58**,** 1701-1710, 1994.

Kuma, K., and Matsunaga, K.; Availability of colloidal ferric oxides to coastal marine phytoplankton, Mar. Biol., 122, 1-11, 1995.

Lafon, S., Rajot, J-L., Alfaro, S.C. and Gaudichet, S.; Quantification of iron oxides in desert aerosol, Atmos. Env., 38, 1211-1218, 2004.

Lafon, S., Sokolik, I.N., Rajot, J-L., Caquineau, S., and Gaudichet, S.; Characterization of iron oxides in mineral dust aerosols; implications for light absorption, J. Geophys. Res., 111**,** D21207, 2006.

Lancelot, C., de Montey, A., Goose, H., Becquefort, S., Schoemann, V., Basquer, B., and ~~.~~Vancoppenolle, M.; Spatial distribution of the iron supply to phytoplankton in the Southern Ocean: A model study, Biogeosciences, 6, 2861-2878, 2009.

Lannuzel, D., Schoemann, V., de Jong, J., Tison, J-L., and Chou, L.; ~~(2007),~~ Distribution and biogeochemical behavior of iron in the East Antarctic sea ice, Mar.Chem, 106**,** 18-32, 2007.

Lannuzel, D., Schoemann, V., de Jong, J., Chou, L., Delille, B., Becquevort, S., and Tison, J-L.; Iron study in during a time series in the western Weddell Sea pack ice, Mar. Chem., 108, 85-95, 2008.

Lannuzel, D., van der Merwe, P.C., Townsend, A.T., and Bowie, A.R.; Size fractionation of iron, manganese and aluminium in Antarctic fast ice reveals a lithogenic origin and low iron solubility, Mar. Chem., 161, 47-56, 2014.

Li, F.,~~-~~ Ginoux, P., and V. Ramaswamy, V.; Distribution, transport, and deposition of mineral dust in the Southern Ocean and Antarctica: contribution of major sources, J. Geophys. Res., 113, D10207, doi:10.1029/2007JD009190, 2008.

Lin, H., and Twining, B.S.; Chemical speciation of iron in Antarctic waters surrounding free-drifting icebergs, Mar. Chem,,128-129, 81-91, 2012.

~~Luis, P., Duprat, A.M., Bigg, G.R., and Wilton, D.J.; Giant icebergs significantly enhance the marine productivity of the Southern Ocean, Nat. Geosci, doi.10.1038NGEO2533, 2016.~~

Luo, C., Mahowald, N., Bond, T., Chuang, P.Y., Artaxo, P., Siefert, R., Chen, Y., and J. Schauer, J~~.~~.; Combustion iron distribution and deposition, Global Biogeochem.Cy.~~cles~~, 22**,** GB1012, 2008.~~.~~

Lutz, A.M., Arieso, S.E., Villar, J., and Benning, L.G.; Variation in algal communities cause darkening of a Greenland glacier, F.E.M.S., Microbial Ecol., 89, 402-414, 2014.

Mackenzie, F.T., and Andersson, A.J.; The marine carbon cycle and ocean acidification during Phanerozoic time, Geochem. Perspect., 2, 1-227, 2013.

Mahowald, N., Baker, A., Bergametti, G., Brooks, N., Duce, R., Jickells, T.D., Kubilay, N., Prospero, J., and Tegen, I.; The atmospheric global dust cycle and iron inputs into the ocean, J. Geophys. Res., 111**,** D05303, doi:10.1029/2005JD006459, 2005.

Mahowald, N., Albani, S., Engelstaeder, S., Winckler, G., and Goman, M.; Model insight into glacial-interglacial dust records, Quat. Sci. Reviews., 30, 832-854, 2011.

Meguro, H., Toba, Y., Murakami, H., and Kimura, N.; Simultaneous remote sensing of chlorophyll, sea ice and sea surface temperature in the Antarctic waters with special reference to the primary production from ice algae, Adv. Space Res., 33, 116-1172, 2004.

Moore, C.M., Mills, M.M., Arrigo, K.R., Berman-Frank, I., Boyd, P.W., ~~E.D. ~~Galbraith, E.D., Geidler, R.J., Guieu, C., Jaccard, S.L., Jickells, T.D., La Roche, J.,~~-~~ Lenton, T.M., Mahowald, N.M., Marnon, E., Marinov, I., Moore, J.K., Nakatsuka, T., Oschlies, A., Saito, M.A., Thingstad, T.F., Tsuda, A., and Ulloa, O.; Processes and patterns of oceanic nutrient limitation, Nat. Geosci., 6, 701-710, 2013.

Moore, J.K., Abbott, M.R., and ~~J.G.~~ Richman, J.G.; ~~(1999),~~ Location and dynamics of the Antarctic Polar Front from satellite sea surface temperature data, J. ~~-~~Geophys. Res., 104**,** 3059-3073**,** 1999**.**

Nielsdottir, M.C., Moore, C.M., Sanders, R., Hinz D.J., and Achterberg, E.P.; Iron limitation of the postbloom phytoplankton communities in the Iceland Basin. Global Biogeochem.Cy., 23**,** GB3001, 2009.

Nodwell, L.M., and Price, N.M.; Direct use of inorganic colloidal iron by marine thixotrophic phytoplankton, Limnol. Oceanogr., 46, 765-777, 2001.

Pabi, S., van Dijken, G.L., and Arrigo, K.R.; Primary production in the Arctic Ocean, J. ~~-~~Geophys. Res., 113, C08005, doi.org/10.1029/2007JC004578, 2008.

Popova, E. E., Yool, A., Coward, A.C., Aksenov, Y.K., Alderson, S.G., de Cuevas, B.A., and Anderson, T.F.; Control of primary production in the Arctic by nutrients and light: Insights from a high resolution ocean general circulation model, Biogeosciences, 7, 3569-3591, 2010.

Poulton, S.W., and Canfield, D.E.; Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally-derived particulates, Chem. Geol., 214, 209-221, 2005.

Poulton S.W., and Raiswell, R.; The low-temperature geochemical cycle of iron: from continental fluxes to marine sediment deposition, Amer. J. Sci., 302, 774-805, 2002.

Pritchard, H.D., Ligtenberg, S.R.M., Fricker, H.A., Vaughan, D.G., van den Broeke, M.R., and L. Padman, L.; Antarctic ice-sheet loss driven by basal melting, Nature, 484, 502-505, 2012.

Raiswell, R.; Iceberg-hosted nanoparticulate Fe in the Southern Ocean: Mineralogy, origin, dissolution kinetics and source of bioavailable Fe, Deep-Sea Res. Pt. II, 58, 1364-1375, 2011.

Raiswell, R., and Canfield, D.E.; The iron biogeochemical cycle past and present, Geochem. Perspect., 1, 1-220, 2012.

Formatted: Font: Not Italic

Formatted: Font: Not Italic

Formatted: Font: Not Italic

Formatted: Font: Not Italic

Formatted: Font: Not Bold

Raiswell, R., Canfield, D.E., and Berner, R.A.; A comparison of iron extraction methods for the determination of degree of pyritization and recognition of iron-limited pyrite formation, Chem. Geol., 111, 101-111, 1994.

Raiswell R., Tranter, M., Benning, L.G., Siegert, M., Death, R., Huybrechts, R.P., and ~~T.~~ Payne, T.; Contributions from glacially derived sediment to the global iron oxyhydroxide cycle: implications for iron delivery to the oceans, Geochim. Cosmochim. Ac.~~ta~~,70, 2765-2780, 2006.

Raiswell, R., Benning, L.G., Tranter, M., and Tulaczyk, S.; Bioavailable iron in the Southern Ocean: The significance of the iceberg conveyor belt, Geochem. Trans. 9, doi:10:1186/1467-4866-9-7, 2008.

Raiswell, R., Vu, H.P., Brinza, L., and Benning, L.G.; The determination of Fe in ferrihydrite by ascorbic acid extraction: methodology, dissolution kinetics and loss of solubility with age and de-watering, Chem. Geol., 278, 70-79, 2010.

Reyes, I., and Torrent, J.; Citrate-ascorbate as a highly selective extractant for poorly crystalline iron oxides, Soil Sci. Soc. Amer. J., 61, 1647-1654, 1997.

Rich H.W., and Morel, F.M.M.; Availability of well-defined iron colloids to the marine diatom *Thalassiosiraweissflogii*, Limnol. Oceanogr, 35, 652-662, 1990.

Rignot, E., Velicogna, I., van den Broeke, M.R., Monoghan, A., and Lenaerts, J.; Acceleration of the contribution of the Greenland and Antarctic ice sheets to sea level rise, Geophys. Res. Lett., 38, L05503, 2011.

Schulz, M., Prospero, J.M., Baker, A.R., Dentener, F., Ickes,L., Liss, P.S., Mahowald, N., Nickovic, S., Garcia-Pando, C.P., Rodriguez, S., Sarin, M., Tegen, I., and Duce, R.A.; Atmospheric transport and deposition of mineral dust to the ocean: Implications for research needs, Env. Sci. Tech., 46, 10390-10404, 2012.

Schwertmann, U., Stanjek, H., and Becher, H-H.; Long term in vitriol transformation of 2-line ferrihydrite to goethite/hematite at 4, 10, 15 and 25^{o}C, Clay Minerals, 39, 433-438, 2004.

Formatted: Font: Not Italic

Formatted: Font: Not Bold

Sedwick, P.N., Sholkovitz, E.R., and Church, T.M.; Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea, Geochem. Geophys. Geosys., 8, doi:10.1029/2007GC001586, 2007.

Shaked, Y., and Lis, H.; Disassembling iron availability to phytoplankton, Front. Microbiol., 123, 1-26, 2012.

Shaw, T.J., Raiswell, R., Hexel, C.R., Vu, H.P., Moore, W.S., Dudgeon, R., and Smith, K.L.; Input, composition and potential impact of terrigenous material from free-drifting icebergs in the Weddell Sea, Deep-Sea Res. Pt. II, 58**,** 1376-1383, 2011.

Shi, Z., Krom, M.D., Bonneville, S., Baker, A.R., Jickells, T.D., and Benning, L.G.; Formation of iron nanoparticles and increase in iron reactivity in mineral dust during simulated cloud processing, Env. Sci. Tech., 43, 6592-6596, 2009.

Shi, Z., Krom, M.D., Bonneville, S., Baker, A.R., Bristow, C., Mann, G., Carslaw, K., McQuaid, J.B., Jickells, T., and L.G. Benning, L.G.; Influence of chemical weathering and aging of iron oxides on the potential iron solubility of Saharan dust during simulated atmospheric processing, Global Biogeochem. Cy.~~cles~~, 25**,** GB2010, doi:10.1029/2010GBC003837, 2011.

Shi, Z., Krom, M.D., Jickells, T.D., Bonneville, S., Carslaw, K.S., Mihalpoulos, N., Baker, A.R., and Benning, L.G.; Impacts on iron solubility in the mineral dust by processes in the source region and the atmosphere: A review, Aeolian. Res., 5, 21-42, 2012.

Shi, Z., Krom, M.D., Bonneville, S., and Benning, L.G.; Atmospheric processing outside clouds increases soluble iron in mineral dust, Env. Sci. Tech., 49, 1472-1477, 2015.

Silva, T.A.M., Bigg, G.R., and Nicholls, K.W.; Contribution of giant icebergs to the Southern Ocean freshwater flux, J. Geophys. Res., 111, doi:1029/2004JC002843, 2006.

Smith, K.L., Robison, B.H., Helly, J.J., Kaufmann, R.S., Ruhl, H.A., Shaw, T.J., Twining, B.S., and Vernat, M.; Free-drifting icebergs: Hot spots of chemical and biological enrichment in the Weddell Sea, Science, 317, 478-483, 2007.

Smith, K.L.~~ Jr.~~, Sherman, A.D., Shaw, T.J., and Springall, J.; Icebergs as unique Lagrangrian ecosystems in polar seas, Ann. Rev. Mar. Sci., 5, 269-287, 2013.

Stookey, L.L.; Ferrozine- A new spectrophotometric reagent for iron, Anal. Chem., 42, 779-781, 197~~8~~0.

Straneo, F., and Cenedese, C.; The dynamics of Greenland's glacial fjords and their role in climate, Ann. Rev. Mar.Sci., 7, 89-112, 2015.

Sugie, K., Nishioka, J., Kuma, K., Volkov, Y.N., and Nataksuka, T.; Availability of particulate Fe to phytoplankton in the Sea of Okhotsk, Mar. Chem., 152, 20-31, 2013.

Sutherland, D.A., Roth, G.E., Hamilton, G.S., Mernild, S.H., Stearns, L.A., and Straneo, F.; Quantifying flow regimes in a glacial fjord using iceberg drifters, Geophys. Res. Lett., 41, 8411-8420, 2014.

Tagliabue, A., Bopp,L., and Aumont, O.; Evaluating the importance of atmospheric and sedimentary iron sources to Southern Ocean biogeochemistry, Geophys. Res. Lett., 36, L13601, doi:10.1029/2009GL038914, 2009.

Tagliabue, A., Bopp, L., Dupay, J-C., Bowie, A.R., Chever, F., Jean-Bapiste, P., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., and Jeandel, C.; Hydrothermal contribution to the oceanic inventory, Nature Geosci., 3, 252-256, 2010.

Tagliabue, A., and Volker, C., Towards accounting for dissolved iron speciation in global ocean models, Biogeosciences, 8, 3025-3039, 2011.

Tagliabue, A, Aumont, O., Death, R., Dunne, J.P., Dutkiewicz, S., Galbraith, E., Misumi, K., Moore, J.K., Ridgewell, A., Sherman, E., Stock, C., Vichi, M., Volker, C., and Yool, A.; How well do global ocean biogeochemistry models simulate dissolved iron distributions? Global Biogeochem. Cy.~~cles~~, doi:10.1002/2015GB005289, 2016.~~.~~

Tranter, M., and Jones, H.G..; The chemistry of snow: processes and nutrient recycling,The Ecology of Snow, Edited by Jones, H.G., Pomeroy, J.W., Walker, D.A., and Hoham, R., pp. 127-167, Cambridge University Press, 2001.

Vancoppenolle, M., Meiners, K.M., Michel, C., Bopp, L., Brabant, F., Carnat, G., Delille, B., Lannuzel, D., Madec, G., Moreau, S., Tison, J-L., and van der Merwe, P.; Role of sea ice in global biogeochemical cycles: Emerging views and challenges, Quat. Sci. Reviews, 79, 207-230, 2013.

Van Wychen, W., Burgess, D.O., Gray, L., Copland, L., Sharp, M., Dowdeswell, J.A., and Bentham, T.J.; Glacier velocities and dynamic ice discharge from the Queen Elizabeth Islands, Nunavut, Canada. Geophys. Res. Lett, 41, doi 19:1002/2013GL058558, 2014.~~.~~

Vaughan, D.G.; Recent trends in melting conditions on the Antarctic Peninsula and their implications for ice-sheet mass balance and sea level, Arctic Ant. Alpine Res., 38, 147-152, 2006.

Wadley, M.R. Jickells, T.D., and Heywood, K.J.; The role of iron sources and transport for Southern Ocean productivity, Deep-Sea Res. Pt. I, 87, 82-94, 2014.

Wang, S., Bailey, D., Lindsay, K., Moore, J.K., and Holland, M.; Impact of sea ice on the marine iron cycle and phytoplankton productivity, Biogeosciences, 11, 4713-4731, 2014.

Wells, M.L., Zorkin, N.G., and Lewis, A.G.; The role of colloid chemistry in providing a source of iron to phytoplankton. J. Mar. Res., 41**,** 731-746, 1983.

Winton, V.H.L., Dunbar, G.B., Berteler, N.A.N., Millet, M-A., Delmonte, B., Atkins, C.B., Chewings J.M., and Andersson, P.; The contribution of aeolian sand and dust to iron fertilization of phytoplankton blooms in the southwestern Ross Sea, Antarctica, Global Biogeochem. Cy.~~cles~~, 28**,** 423–436, doi: 10.1002/2013GB004574, 2014.

Winton, V.H.L., Bowie, A.R., Edwards, R., Keywood, M., Townsend, A.T., van der Merwe, P., and Bollhofer, A.; Fractional solubility of atmospheric iron inputs to the Southern Ocean; Mar. Chem., 177, 20-32, 2015.

Formatted: Font: Not Italic