

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. 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 a samples was collected without contamination). The lack of aerosol data from the Arctic is a major gap and the use of Mediterranean samples instead is not appropriate as these can not be considered representative of what will be deposited in the Arctic or the Southern Ocean.

General comments:

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. 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 manuscript. Indeed the description in the Hawkings et al. work of reactive nanoparticulate iron would seem to be optimal.

The descriptors used in the present work confuse this issue at present – 6 line Ferrihydrite is classified as a mineral despite it having an indeterminate 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). 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. 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.

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. More crystalline phases are also soluble with ascorbic acid so it is not specific for ferrihydrite (Smolen et al., 2003; Larsen et al., 2006). Indeed in terms of reduction of only ferrihydrite, hydroxylamine is probably a more appropriate reductant (Croot and Hunter, 2000; Chen et al., 2013).

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. 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.

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. 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. 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.

Missing experimental information and lack of statistical information:

The methods section is missing key information about how aspects of the analysis were performed. There is also a lack of important ancillary information with regard to the samples analysed, no particle size information or organic content is provided. 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).

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. Additionally an evaluation of the impact of giant icebergs on marine productivity (Duprat et al., 2016) has also been published. Similarly a number of papers connected to Greenland ice melt and ice berg 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).

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).

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)).

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).

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.

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).

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).

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. 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).

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

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.

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 definition of a nanoparticle (1-100 nm).

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.

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)?

P6 line 149: The Eastern mediterranean does not seem an appropriate representative sample for either the Arctic or Antarctic.

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?

P6 line 151-152: As for line 149, neither the Eastern mediterranean or China seem appropriate samples for the Arctic or Antarctic.

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

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

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.

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.

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).

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.

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?

P7 line 186: What would Fe (oxyhydr)oxides be under the terminology used for the sediments? Normally they are commonly described as HFO, which is analogous to 2 line ferrihydrite in many cases. See the general comment on this above.

- 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).
- 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.
- P8 line 211: Neither of these two references show any data on grazing of dithionate soluble iron – please provide a proper reference for this.
- 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?
- 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.
- 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.
- 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. This also then suggests that sieving may produce an artefact in helping to disaggregate the samples?
- 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.
- 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.
- P9 line 247: How was the significance ascertained? Please provide statistical data for this.
- 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.
- P9 line 253: Please state this as the logarithmic mean and not refer to it as the mean.
- 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? Did you apply Pearson's sample skewness test to check the t-test assumption of normality for the log transformed data.
- 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.
- P10 line 272: See also the recent work of Jeong et al. regarding this (Jeong et al., 2012;Jeong et al., 2015).

- 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.
- 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.
- P10 line 296: This is the logarithmic mean and should be stated as such.
- P11 line 298: Grain size could also explain this difference and what evidence is there that these samples have undergone freeze/thaw cycles?
- 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.
- P12 line 326: It is not clear that the assay as used here determine only ferrihydrite and not other iron phases.
- 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.
- P12 line 333: See also the recent work by Simonella et al. (2014).
- P13 line 380: 1-2 orders of magnitude but not more than that.
- P14 line 388: This contradicts the statement on line 272 where there was precipitation in the presence of EPS.
- 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.
- 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.
- 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.
- 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.
- 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.
- Table 1: Please include the number of samples that this analysis was constructed from.
- 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.

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.

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