1   **Authors Overall Response**

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

8   **Overview:**

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

17   The extraction has been thoroughly tested in Raiswell et al (2010).It is not an assumption that
18   ascorbic acid extracts only ferrihydrite. Table 3 from Raiswell et al. (2010) is shown below and
19   clearly shows high selectivity for fresh 2 line ferrihydrite which was also characterised by XRD
20   (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

21

22   See also Reyes and Torrent (1997), Soil Sci Soc. Am. J., 61, 1647-1654, Hyacinthe and Van
23   Cappellen (2004), Mar Chem., 91, 225-251 and Kostka and Luther (1994), Geochim.

24 Cosmochim Acta, 58, 1701-1710 for similar results that clearly state ascorbate specificity for
25 ferrihydrite under conditions similar to those used here (pH 7.5-8).

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

29 Please see below for details.

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

33 Agreed this is an important gap in our data (and in other datasets) that needs attention in the
34 future, as we clearly recognise in lines 328-330, and 428. It is common practice in Southern
35 Ocean Fe models to use a range of values for fractional solubility (as we discuss in lines 44-71),
36 with 1-2% being a frequent but poorly justified choice based on widely varying extraction data.
37 We could have adopted this approach. However Boyd et al (2010) are emphatic that 'close
38 reading, including the original references, does not support the 1-2% solubility value.' Instead
39 we have analysed a small, but geographically wide-spread set of dusts to estimate a solubility
40 value based on an ascorbic acid extraction. We proceed cautiously on the basis that our samples
41 are representative of those delivered to the polar regions (lines 368-370). This data provides
42 some support for the 1-2% fractional solubility estimate (a valuable result that enhances the
43 credibility of models using this value) and thus provides preliminary proof of concept based on
44 measurements of dusts that are related to mineralogy. Crucially, this methodology also allows
45 iceberg and dust particulate sources to be compared (lines 325-327)

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

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

49 There are high resolution photographs and selected area electron diffraction (TEM and SAED) of
50 iceberg-hosted ferrihydrite (that were also characterised by bulk XRD) in the Raiswell et
51 al.(2008) Geochemical Trans. Paper, and the same mineral in suspended particulate matter
52 derived from subglacial environments (the Hawkings et al paper). This is the principal mineral
53 extracted by ascorbic acid, as detailed above, and all ferrihydrite is nanoparticulate (see below).

54 *Given that recent FEG-TEM analysis identifies only a small proportion of the iron as 6-line*
55 *ferrihydrite (Hawkings et al., 2014) and instead classified it mostly as amorphous Fe or poorly*
56 *crystalline 2-line ferrihydrite, also significant amounts of Fe(II) were also identified therefore it is*
57 *more realistic to provide a more accurate description of the iron rather than refer to it as*

58   *ferrihydrite throughout the mansucript. Indeed the description in the Hawkings et al. work of*
59   *reactive nanparticulate iron would seem to be optimal.*

60   Hawkings et al makes no mention of 6-line ferrihydrite nor either of Fe(II). They do describe the
61   iron on p.2 of their paper as 'poorly ordered ferrihydrite'. The term 'reactive nanoparticulate
62   iron' is only used in the title. However if the editor deems it appropriate we can change the
63   description to 'reactive nanoparticulate iron', but see above.

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

69   The International Mineralogical Association (IMA) Commission on New Minerals lists
70   ferrihydrite as a mineral. HFO is not so listed. Our only reference to 6-line ferrihydrite is in line
71   163 and it is not here described as a mineral although in fact it was so recognised by the IMA in
72   1973. See below.

73   *While both 2-line and 6-line ferrihydrite are only found as nanoparticles, thus using the term*
74   *"nanoparticle ferrihydrite" is somewhat redundant, even if it does include the 'buzz' term*
75   *nanoparticle.*

76   Agreed. There are different views on this issue. Some reviewers take the view that it is not
77   commonly understood that all ferrihydrite is nanoparticulate, and hence this is useful emphasis.
78   We are happy to put in a simple statement to this effect, and remove the nanoparticulate
79   adjective. although non-specialist readers may find it useful to retain 'nanoparticulate

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

83   Yes the reactivity of the two phases are considerably different, as we show in their extraction
84   with ascorbic acid (see lines 162-3 and the above Table).

85   *The assay used here is very much an operational definition (Raiswell et al., 2010) and it is well*
86   *known that the dissolution of iron from different iron oxide phases is dependent on a number of*
87   *factors including pH (Deng and Stumm, 1994), surface complexation by ligands (Shimizu et al.,*
88   *2013; Eusterhues et al., 2014) and dissolved Fe(II) (Pedersen et al., 2005), most importantly the*
89   *dissolution is time dependent.*

90   Agreed but selectivity can be obtained by carefully controlling the extraction conditions. The
91   above Table shows that there are marked variations in the dissolution rates of different Fe

92   minerals. Raiswell et al. (2010) dealt with the effects of ascorbic concentration and pH and show
93   that it is important to control these conditions to obtain reproducible results (as we have done).

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

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

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

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

110 **Presenting data as %Fe/dry sediment.**

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

114 See lines 155-159. FeA weights of 10-40 mg in 10 ml of ascorbic produce concentrations of < 1
115 ppm which were analysed mainly by AAS . We can add these details to the amended ms . We
116 have found no variation in FeA for different weights under these conditions. Raiswell et al.
117 (2010) considered the effects for different ratios of extractant concentration/sample weight and
118 found no significant variations. We have considered the effects of grain size through analysis of
119 different size fractions of iceberg sediment and concluded that such effects are small (see lines
120 237-244).

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

124 The samples were air-dried at room temperature which does not give complete water loss. The
125 samples are relatively coarse and loss of water was always less than 10 % when compared to

126 over-dried samples. Actually air-drying was used in the Larsen et al paper which the reviewer
127 cites.

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

130 Agreed. This is a large source of uncertainty as we acknowledge in lines 311-313. The Shaw et
131 al reference (lines 313- 314) does give a range. The issue has most recently been discussed by
132 Death et al. (see our refs) who cites ranges of 0.4-0.8 g litre^{-1}for Antarctic icebergs. Dowdeswell
133 and Dowdeswell (1990, J. Geol., 97, 221-231) give a range of 0.2-200 g litre^{-1} in icebergs from
134 Spitzbergen. We are happy to add these additional data if the editor supports their inclusion.

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

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

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

150 Glaciers (and large Antarctic ice stream) are frozen rivers that freeze-on sediment produced from
151 the subglacial comminution (physical weathering) of bedrock. Glacial meltwaters studied by
152 Gurnell (1997, in Glacial-Fluvial Sediment Transfer, published by Wiley) have mean suspended
153 sediment concentrations of 1 g litre^{-1}. We use a conservative value of 0.5 g litre^{-1}, which finds
154 support as we note in lines 313-317.

155 **Missing experimental information and lack of statistical information:**

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

158 The details presented here are as used in the Raiswell Geochem. Trans and Chem Geol papers,
159 and the Hawkings papers that we cite. Earlier papers (see the refs cited in lines 22-24 of this
160 response) give additional detail and we can add this.

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

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

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

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

170 **Recent papers of relevance to this work:**

171 *The introduction and discussion section were missing a number of key recent papers of*
172 *relevance to the current work. This included recent work showing the role of seasonal physical*
173 *mixing on iron concentrations in the surface waters of the Southern Ocean (Tagliabue et al.,*
174 *2014), thus an alternative supply route to those proposed here.*

175 We agree that the Tagliabue et al study is an important contribution but it deals with deep water
176 mixing of dissolved Fe into surface waters. There is no mention of particulate Fe sources and
177 discussion of the paper would be outside our scope (see lines 112-114).

178 *Additionally an evaluation of the impact of giant icebergs on marine productivity (Duprat et al.,*
179 *2016) has also been published.*

180 We discuss this but have incorrectly cited this as the Luis paper in press in line 448. This will be
181 rectified in an amended version of our ms.

182 *Similarly a number of papers connected to Greenland ice melt and iceberg flux (Wilton et al.,*
183 *2015), and in particular to the iron flux with one suggesting it could be important (Bhatia et al.,*
184 *2013), though another study thought it was less so (Hopwood et al., 2015).*

185 We deal with the Wilton paper below. The Bhatia and Hopwood papers deal with meltwaters
186 fluxes of dissolved Fe and particulate Fe which are substantially outside our scope of particulate
187 iceberg and dust sources. Furthermore the Bhatia paper examines meltwaters that transit > 10 km
188 of a proglacial plain (including a lake where there is evidence of considerable post-melting
189 additions of Fe). There is a more relevant recent Hopwood paper (Frontiers in Earth Science,
190 4:15, doi:10.3389/feart.2016.0015) that discusses oceanographic features which may minimise

191 iceberg escape to the ocean from long Greenlandic fjords (> 100 km). However Hopwood et al
192 also point out that their study may not be typical of other Greeenlandic fjords. We agree with
193 Hopwood that this issue is important and we will add relevant discussion. We have been in
194 contact with Hopwood (and others) and ascertained that there are no currently no estimates of
195 iceberg losses in fjords.

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

198 The Jeong studies are excellent and make the point that dissolution is not a reductive process and
199 requires the presence of a liquid-like ice boundary region. This adds valuable support for our
200 suggested ice-processing model (lines 285-299). We will add material from these papers to the
201 amended version. The Guerra paper deals with acid mine drainage and the Kim paper with
202 Mn.chemistry and are therefore less relevant.

203 **Specific comments:**

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

207 The Moore et al paper was published as a Review article, which makes it appropriate to illustrate
208 the well-known point that the SO is an HNLC area. But we can add additional references as
209 requested.

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

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

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

218 Our choice of differences in lines 98-100 relates to particulate supplies but this could be a useful
219 addition, as being another difference between the polar oceans.

220 *P3 line 88: The source of the icebergs is also important as currently icebergs are predominantly*
221 *from Eastern Canada, though a switch to western Greenland may be anticipated (Wilton et al.,*
222 *2015).*

223 There are no icebergs sourced from Eastern Canada (see the Wilton paper, page 197) although
224 there are important sources from Western Greenland, Eastern Greenland and from glaciated
225 islands in northern Canada, along with Svalbard and the Russian Arctic Islands (Wilton, page
226 197 and see also the Bamber and Van Wychen papers that we cite). These studies conclude that
227 most Arctic icebergs are sourced from Greenland. Wilton et al. conclude that the principal
228 sources prior to 1930 were from southern Greenland and only since then is the major source from
229 western Greenland.

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

233 Bhatia et al do not predict that meltwaters will be more important than icebergs. They state on p.
234 277 that 'Icebergs may provide yet another source of glacially derived Fe, a mechanism known
235 to occur in the SO but not yet investigated around Greenland. This may be another significant,
236 and under-represented input…'This is a justification for our own study. Our response to the
237 Hopwood work is given above.

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

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

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

244 The Klunder paper is a study of deep water dissolved Fe in the AO, and it does indeed show that
245 concentrations are high. However the authors state that 'strong stratification prevents mixing
246 between the deep water concentrations and the surface waters…'.We do not wish to deal with
247 dissolved Fe in surface waters (and with the complex processes associated with the release of
248 dissolved Fe from particulates in seawater; see lines 112-114) and would be reluctant to extend
249 still further into surface and deep water mixing processes.

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

252 We acknowledge that here are different definitions. The IHO defines the AO as lying roughly
253 within the quadrangle formed by N. Greenland, Prince Patrick Island, Point Barrow, Koteni
254 Islands and Wrangel Island but this is a small area much of which lies within 80°N. There are
255 other definitions. For example the CIA Factbook defines the Arctic as the region within 57°N;
256 our Pabi reference is to about 66°N (which is the Arctic Circle). We have defined the area >

257 60°N which incorporates the southern tip of Greenland and lies close to the region defined by the
258 Pabi reference. This latitude limit is also the same as that used for the SO (see lines 104-108)

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

262 Our extraction is very specific. See above.

263 *P5 line 136: There is a problem here with the operational definitions and the descriptors used.*
264 *Iceberg sediment is typically much coarser than what is derived from sea ice (Goldschmidt et al.,*
265 *1992) and don't meet the formal defintion of a nanoparticle (1-100 nm).*

266 Iceberg sediment is an assortment of both coarse and fine particles but this does not prevent iron
267 nanoparticles being present in any fraction (see below). We have high resolution microscopy
268 images that show the presence of ferrihydrite in iceberg sediments (see cited references to
269 Raiswell et al, Deep Sea Res and Geochemical Transactions) and in glacial sediments (see the
270 cited Raiswell reference in Geochim. Cosmochim Acta and also the Hawkings et al paper).

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

273 Samples were gently disaggregated (line 140) but not crushed in a pestle and mortar.

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

278 This dust sample was collected from a glass window cleaned with water. It had not rained.since
279 cleaning. We can add this information. This sampling methodology has been used elsewhere for
280 bulk samples where contamination is an unlikely to be a major influence. See Herut et al (a glass
281 panel, no cleaning information provided, Limon. Oceanog., v. 47, p.871 and Shi et al (a cleaned
282 solar panel, Env. Sci Tech., v. 43, p.6592).

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

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

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

291   See above.

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

294   Air-dried at room temperature. The samples are coarse and the subsequent weight losses to oven
295   dryness ($110^{o}C$) are <10%. This approach is common practice (see the Larsen et al. paper cited
296   by the reviewer, p. 4829).

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

298   De-oxygenation was carried out by bubbling with nitrogen. Reyes and Torrent (ref above)
299   conclude that excessive de-oxygenation can be prevented during the extraction by minimising
300   the air space in the extraction vessel. We used 10 ml centrifuge tubes that were capped. We can
301   also add this information to the methodology.

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

305   The missing information is not substantially relevant. Lines 173-174 state that the Fe extracted as
306   FeA and FeD was measured either by ferrozine or by AAS after each extraction step. In fact only
307   the reproducibility and sampling data in Tables 1 and 2 were measured by ferrozine. We can add
308   this detail.

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

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

320   *P6 line 164: Goethite and hematite are also partly soluble under this approach though the*
321   *dissolution is significantly slower (Deng and Stumm, 1994; Smolen et al., 2003). Also- P6 line*

322 *164: This is assuming that what dissolves is ferrihydrite – as a pure sample of goethite or*
323 *magnetite would also give a similar result.*

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

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

328 Dithionite does not remove all the Fe present in silicates (see Raiswell et al, 1994, Chem Geol,
329 111, 101-111 . The total Fe data in Table S3 of this ms are literature data and the appropriate
330 references are given in Table S2.

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

332 We define Fe (oxyhydr)oxides as ferrihydrite, lepidocrocite, goethite and hematite in line 194.

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

335 It would be incorrect to describe all Fe (oxyhydr)oxides as HFO. HFO refers only to hydrous
336 ferric oxide which is considered to be equivalent to ferrihydrite (see p.316 in the Heimstra ref
337 cited by the reviewer). Oxides such as hematite contain no structural water and should not be
338 described as HFO.

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

342 Yes we can add these references (and could add many others) to the potential bioavailability
343 citations in lines 164-166 and 200-207. Editorial advice would be helpful.

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

347 Yes direct uptake has been shown for protozoa. The Shaked and Lis paper (see refs) discusses
348 how cyanobacteria are able to mediate dust dissolution and access iron directly, as can
349 mixotrophic plankton (see our Nodwell and Price reference) Our statement 'directly or
350 indirectly' is intended only to be inclusive.

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

353 We will cite the additional primary sources suggested by the reviewer (above) in an amended
354 version of the ms

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

357 The extractions were done sequentially (see lines 169-172) so different phases have been
358 extracted. Dissolution of FeD would be slow but may occur, for example, by siderophores.
359 Detailing these processes in seawater are outside our scope (see above).

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

363 We disagree but are happy to accept editorial guidance. The sampling and reproducibility issues
364 are important, as the reviewer clearly realises. As such, the sieving belongs in the results section.

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

368 The student 't' test requires the numbers of samples and their means and standard deviations (see
369 for example Paradine and Rivett, Statistics for Technologists, page 112). The data are all given in
370 Table 1 and discussed in lines 219-223.

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

378 Ascorbic acid is highly specific for ferrihydrite which is always present in a nanoparticulate form
379 (see above).We do not know whether the nanoparticles are free-standing (and possibly
380 aggregated) or attached (lines 442-444). Aggregated or attached nanoparticles could be
381 associated with grains of any size. Attachment may or may not continue to exist after delivery
382 into seawater. In any event, whether attached or not, our FeA can only be ferrihydrite and can
383 only be nanoparticulate.

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

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

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

392   Inevitably there is variability in sampling coarse iceberg sediment consisting of material ranging
393   from comminuted material to bedrock grains (lines 241-244). But there is a much bigger
394   variability between samples, which is the reason for needing a large, geographically diverse
395   database.

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

398   The hypothesis is given in line 239. We test the probability that there is no significant difference
399   between the single sample and the sample group. The z test is described in Russell Langley,
400   Practical Statistics, page152-4.

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

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

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

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

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

412   The previous line (251) states that this is a logarithmic mean but we are happy to make this
413   alteration in the final text.

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

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

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

421 No. The data were plotted on probability paper which showed improved linearity with a
422 logarithmic transformation, particularly for the FeA data. For the sake of consistency all the data
423 were treated logarithmically. We can add this detail.

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

427 Agreed, there is an typographical error here and 'production' should read 'dissolution' in line
428 271. Lannuzel et al state with regard to sea ice that 'EPS have a high affinity for metal cations
429 and could bind metals in sea ice, therefore increasing their solubility and bioavailability by
430 slowing the production of scarcely soluble Fe oxyhydroxides'. The Hassler references refer to
431 the role of EPS extracted from plankton in seawater, rather than sea ice, but they provide good
432 support for the role of EPS in solubilizing Fe and we can cite in this context.

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

435 Two excellent papers which add further support to the mechanism described in lines 270-278.
436 We will certainly add text based on these two papers (see above).

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

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

444 *P10 line 287: Cooling the sample to the freezing point of water also induces redox changes for*
445 *the solution phase as has been shown for studies linking sea ice and water on Mars (Horne,*
446 *1963;Marion et al., 2003;Marion et al., 2005;Marion et al., 2008;Marion et al., 2010). There is*
447 *also the high ionic strength to consider. Again see the recent work by Jeong et al regards*
448 *freeze/thaw cycles.*

449 Studies on these other planets with regard to redox transitions are likely to be affected by low
450 pO$_2$. But the Jeong references are excellent (see above).

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

452 Yes we will change this.

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

455 Yes, we have clearly stated that there could be differences between the two sample groups (see
456 lines 266-268). All the ice samples must be subject to at least one freeze/thaw event and it is
457 highly likely multiple events would arise from temperature fluctuations during iceberg transport.

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

461 We deal with this issue above.

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

464 We believe it is; see Table and discussion above.

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

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

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

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

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

477 The cited reference to Lannuzel et al 2014 clearly states that there were 2-3 orders of magnitude
478 enrichment in sea ice compared to underlying seawater. We will alter the text to state this.

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

481 This is correct here. See response to line 271.

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

486 We are comparing sea ice and icebergs only on the basis that both undergo one or more
487 freeze/thaw cycles. Our discussion starts out by recognising that there are different Fe sources in
488 sea ice and icebergs (see line 382-384). We then move on to suggest that the dust deposited on
489 sea ice may be processed in the same way as we suggest for icebergs. However we can re-write
490 these few line to emphasise the differences and stress that our estimate refers only to the
491 freeze/thaw effects.

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

496 The shelf flux discussion (lines 414-421) offers a comparison in magnitude (only) with the
497 iceberg data in both the AO and the SO. The De Jong paper points out the paucity of data for SO
498 sediment pore water fluxes. They have four profiles in the Atlantic sector of the SO (within our
499 defined SO area) that have a mean Fe diffusive flux of ~9 μmol/m^2/day (range 1-15), comparable
500 to the mean shelf flux derived by Dale et al (7.3μmol/m^2/day) which forms the basis of their 72
501 Gmol/yr shelf estimate. The modelling community (see lines 44-71) assumes that shelf sources
502 make important Fe contributions in the SO and the Dale estimate is a simple way of providing an
503 order of magnitude comparison with our own iceberg data-entirely appropriate in our AO and SO
504 context. The proportions of oxygen-depleted sediments on the shelf in the AO and SO are
505 unknown but we are happy to add a statement that the Dale values may be an overestimate.

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

511 We argue that the presence of large bergs may act to prolong the residence time, relative to
512 smaller icebergs. But it is useful to add the water column effects suggested here.

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

516 Agreed, see lines 301-302 and the discussion in lines 382-384 which points out that there are
517 multiple Fe sources to sea ice.

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

520 Wet deposition is thought to be the main deposition mechanism (see Mahowald et al, 2011,
521 Quaternary Science Reviews, 30, 7-8, 832-854) but fluxes are poorly known in remote areas
522 (see for example p. 1077 in the Breitbarth reference that we cite). Line 468 simply makes the
523 uncontentious point that more data are needed but we will add the Mahowald reference as
524 suggested.
525
526 *Table 1: Please include the number of samples that this analysis was constructed from.*

527 This data is in the text but can certainly be added to the Table.

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

532 Total Fe data are not available but the comparison is correctly constructed to examine the
533 reproducibility in FeA, which is the subject of this ms. Each line in the table tests whether the
534 single sample ($<63\mu m$) could be drawn from the same population as the 5 ($< 1mm$) samples.
535 This is fully explained in lines 220-236.

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

541 The suggested additional data would be interesting but not necessarily helpful in dealing with the
542 FeA and FeD sample sets, especially in the context of dealing with processes in the source areas,
543 for example bedrock geology, and weathering (see lines 266-267) either subglacially or in the
544 dust source area or during iceberg transport and melting

545

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547