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

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Abstract: Iceberg-hosted sediments and atmospheric dusts transport potentially bioavailable iron to the Arctic and Southern Oceans as nanoparticulate ferrihydrite (the most soluble and potentially bioavailable iron (oxyhydr)oxide mineral). 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 1.4-11 and 3.2-25 Gmoles yr^{-1} to the Arctic and Southern Oceans respectively. Atmospheric dust 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 sediment content of icebergs and samples of atmospheric dust delivered to the polar regions.

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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). Contributions from hydrothermal activity and shelf sediments are based on estimates and/or measurements of dFe (see Tagliabue et al., 2010; Dale et al., 2015) but quantifying dFe contributions from atmospheric dusts 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; 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 dusts entering seawater were 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

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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. (2015) 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., 2015; 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 in Antarctica (Pritchard et al., 2012; Depoorter et al., 2013; 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

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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., 2015). 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 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).

The Fe budgets for the AO use the area >60ºN (a larger area than that >66º33′39″N which is conventionally used to define the Arctic Ocean; Pabi et al., 2008) and the SO budget is based on the area >60ºS. The 60ºS latitude lies close to the Antarctic Polar Front (the boundary between cold Antarctic waters and warmer sub-Antarctic waters), which runs clockwise from 140ºE to 60ºW, beyond which the front moves out to 48ºS (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

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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 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 or organic complexes (see later) 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). These aerosol samples 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). 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

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149 Eastern Mediterranean; one from a dust collector located in Crete and the other from deposition
150 on to a clean glass surface at Rosh Pina, Israel. (Table S2). Relevant data from the literature
151 (Table S2) are also included for 3 additional dry deposition samples from the Eastern
152 Mediterranean and China (Table S2).
153
154 2.3 Analytical Methodology

155 Each sample of air-dried sediment was treated for 24 hours by an ascorbic acid solution
156 buffered at pH 7.5. The extractant was a deoxygenated solution of 0.17M sodium citrate and
157 0.6M sodium bicarbonate to which ascorbic acid was added to produce a concentration of
158 0.057M. Approximately10-40 mg of sample were mixed with 10 ml of the ascorbate solution,
159 shaken for 24 hrs at room temperature and then filtered through a 0.45 μm cellulose nitrate
160 membrane filter (Kostka and Luther, 1994; Hyacinthe and Van Cappellen, 2004; Raiswell et al.,
161 2010). The Fe removed by ascorbic acid is hereafter termed FeA and reported as dry wt. %. This
162 technique quantitatively removes the Fe from fresh 2-line ferrihydrite and partially dissolves the
163 Fe from aged 2-line and 6-line ferrihydrite and schwertmannite with negligible effects on other
164 Fe (oxyhydr)oxides or clay minerals (Raiswell et al., 2010). The measurement of nanoparticulate
165 ferrihydrite is important because this mineral phase is directly or indirectly bioavailable (Wells
166 et al., 1983; Rich and Morel, 1990; Kuma and Matsunga, 1995; Nodwell and Price, 2001). The
167 delivery of ferrihydrite to the open ocean thus has the potential to stimulate productivity in Fe-
168 limited areas (Raiswell et al., 2008; Raiswell, 2011).

169 The residual sediment was treated for 2 hrs with a solution of 0.29M sodium dithionite in
170 0.35M acetic acid and 0.2M sodium citrate, buffered at pH 4.8 (Raiswell, et al., 1994). Following
171 the ascorbic acid extraction step, the dithionite extracts the remaining (oxyhydr)oxide Fe (aged
172 ferrihydrite, goethite, lepidocrocite and hematite; Raiswell et al., 1994). Dithionite-soluble Fe is
173 hereafter termed FeD and is reported as dry wt. %. Both the FeA and FeD extractant solutions
174 were analysed for Fe either by Atomic Absorption Spectrometer with an air-acetylene flame or
175 by spectrophotometry using ferrozine (Stookey, 1980). Replicate analysis of a river sediment
176 internal laboratory standard gave analytical precisions of 3% for FeA and 10% for FeD using this
177 sequential extraction. Errors associated with sampling glacial sediments are examined below.
178 Blank corrections were negligible.

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2.4 Approach

Estimates of the solubility of Fe in atmospheric dusts have utilised a variety of extraction techniques 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 range from 0.2 to 80%, depending on time, pH and the extractant (Baker and Croot, 2010). Few of these extractions 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). Our ascorbic acid extraction is more selective for ferrihydrite than the Baker et al. (2006) extraction but weaker than the Chen and Siefert (2003) extract (compared to which the ascorbic extract is at a higher pH, and is selective for ferrihydrite).

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 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

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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; 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.

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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. 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 are log normally 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 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

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266 sampled, and part of the differences in FeA and FeD may result from mineralogical/geochemical
267 variations in the glacial bedrock. An alternative explanation for the high wt. % FeA and FeD
268 values is that iceberg sediments have undergone alteration during post-calving transport as
269 temperature fluctuations induced melting and weathering. The slightly acidic pH (5.5-6.0) of
270 snow and glacial icemelt (Meguro et al., 2004; Tranter and Jones, 2001) accompanied by the
271 presence of extracellular polymeric substances (Lannuzel et al., 2014; Lutz et al., 2014) is able to
272 accelerate the production of Fe (oxyhydr)oxides by weathering. Furthermore, Kim et al. (2010)
273 has observed that UV radiation causes the photoreductive dissolution of Fe (oxyhydr)oxides
274 (goethite, hematite) encased in ice to ferrous Fe. Photoreductive dissolution was significantly
275 faster in ice than in aqueous solutions at pH 3.5 and was not influenced by the presence of
276 electron donors. Acids are concentrated by several orders of magnitude at the ice-grain boundary
277 due to freeze concentration effects and the resulting low pH (~1.5) further enhances
278 photoreductive dissolution. Lin and Twinning (2012) have found elevated concentrations of
279 ferrous Fe within 1 km of a melting iceberg in the Southern Ocean which they suggest could be
280 derived by the photoreduction of FeA in melt pools. However, most ferrous Fe is likely to be
281 rapidly re-oxidised and precipitated as (oxyhydr)oxide minerals once exposed to the atmosphere
282 by melting, which dilutes the acids and increases pH. The redox recycling effects of repeated
283 melting/freezing events are explored below, as they might apply to any sediments (including
284 atmospheric dusts, see later) encased in ice.

285 Fig. 1 shows an idealised melting/freezing reaction scheme for any sediment in which Fe
286 (oxyhydr)oxides are initially absent and that only contains silicate Fe. Dissolution is initiated in
287 acidic snow melt where Fe is leached slowly by silicate dissolution (Step 1). Subsequent freezing
288 (Step 2) halts dissolution and induces the precipitation and aggregation of Fe (oxyhydr)oxides as
289 FeA and FeD. The transformation of ferrihydrite (FeA) to goethite/hematite (FeD) has a half-life
290 of several years at $T < 5^{o}C$ (Schwertmann et al., 2004; Brinza, 2010) and hence a proportion of
291 FeA can be preserved over the life time of an iceberg. A new phase of melting (Step 3) causes
292 the rapid dissolution or disaggregation of the newly formed FeA and FeD and also restarts the
293 slow dissolution of silicate Fe, until renewed freezing (Step 4) again produces FeA and FeD in
294 amounts that have now been increased by the Step 3 dissolution of silicate Fe. Provided there is
295 insufficient time for the transformation of FeA to FeD to be completed then FeA and FeD will
296 both accumulate at the expense of silicate Fe. A comparison of the mean FeA contents of the

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297 glacial (0.03 wt. %) and iceberg (0.076 wt. %) sediments and their errors suggests that
298 melting/freezing effects, hereafter termed 'ice processing', could increase FeA contents by factor
299 of 2.5, assuming similar initial FeA contents. This data provides the first, semi-quantitative
300 estimate of how deposition on to sea ice might enhance the FeA delivery from atmospheric dust.
301 These changes may also be accompanied by other, poorly understood chemical mechanisms that
302 may further enhance Fe delivery from sea ice (Vancoppenolle et al., 2013).

303 3.3 Iceberg-Hosted FeA Fluxes

304 The iceberg-hosted FeA flux (Table 4) is based on sediment encased in icebergs and
305 excludes sediments associated with seasonal ice (see later). The solid ice discharge from
306 Antarctica has been determined as 1321±144 km^3 yr^{-1} by Depoorter et al. (2013) for the period
307 1979-2010 and from Greenland as 524±51 km^3 $yr^{-1}$for the period 1958-2010 by Bamber et al.
308 (2012). Van Wychen et al. (2015) estimate that the contribution from other ice masses in Alaska,
309 Svalbard, and the Russian and Canadian Arctic is 34.4 km^3 yr^{-1} for which we assume a 10% error
310 (roughly the same as for the Greenland flux). Hence the total ice loss from the Arctic is 558±55
311 km^3 $yr^{-1}$and from the Antarctic is 1321±144 km^3 yr^{-1}. Raiswell et al. (2006) and Death et al.
312 (2014) point out that the sediment content of icebergs is poorly constrained but use a value of 0.5
313 g $litre^{-1}$, similar to the mean sediment content of river water. A value in the range 0.6-1.2 g $litre^{-1}$
314 has been inferred by Shaw et al. (2011) based on the sediment load needed to produce the excess
315 ^{224}Ra activity in the vicinity of icebergs in the Weddell Sea. Here we use the conservative
316 estimate of 0.5 g $litre^{-1}$ of sediment but the asterix in Table 4 indicates that this value may be a
317 significant source of error. The mean wt. % FeA content of icebergs is 0.076% with a variability
318 of 0.030 to 0.194% (Table 3). Deriving the product of the ice mass loss, sediment load and FeA
319 content (Table 4) shows that the flux of iceberg-hosted FeA to the AO ranges from 1.4 to 11
320 Gmol $yr^{-1}$with a mean of 3.8 Gmol yr^{-1}, and to the SO is 3.2 to 25 Gmol yr^{-1} with a mean of 9.0
321 Gmol yr^{-1}. All flux values hereon are quoted to two significant figures. These ranges overlap
322 because the same data have been used for the sediment and FeA contents of icebergs and because
323 the iceberg discharge values to the AO and the SO only differ by a factor of 2.

324 3. 4 Atmospheric Dust Composition

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Mineralogy is a key factor in comparing particulate sources and use of the ascorbic acid extraction technique for the iceberg sediments and atmospheric dusts 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 dusts and the other dusts analysed here. Consistent with this we note that the range of total Fe values (2.9 to 4.3 wt. %) for the Patagonian aeolian dusts analysed by Gaiero et al. (2007) overlaps the range in our dusts (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 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) have fractional solubility data based on the ratio between Fe extracted at pH 5.3 by meltwater and total Fe. A median value of 6% was found for dusts (deposited during the LGM on ice at Dome C, East Antarctica) that were high in total Fe (8%), 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 on these atmospheric dusts has been to produce Fe (oxyhydr)oxides 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

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(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 dusts 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 dusts. Further data from atmospheric dusts delivered to the polar regions are clearly needed to substantiate this conclusion.

3.5 Atmospheric Dust FeA Fluxes

This FeA flux is based on dusts transported through the atmosphere (where there is potential for cloud processing) 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 dusts are representative 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 dusts delivered to the SO with an FeA wt. % ranging 0.018 to 0.081% produce a flux of< 0.01 to 0.01 (mean 0.01) Gmol yr^{-1} (Table 5).

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 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 several sources, including 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;

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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 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 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

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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. These values are numerically comparable to the fluxes from iceberg-hosted sediments although shelf dFe (largely colloidal or nanoparticulate Fe of unknown composition) and FeA as nanoparticulate ferrihydrite may not be of similar bioavailability.

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.
(2) The atmospheric dust sample set is small and may not be representative of dusts 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

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patterns of upwelling and turbulence 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 lasts for longer than a month (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 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 dusts (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). The important features of the new FeA and FeD 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 dusts 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. 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.

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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

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Table 3. Composition of Iceberg, Glacial Ice and Atmospheric Dust Samples.

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 $km^3\ yr^{-1}$	558±55[a]	1321±144[b]	a. Bamber et al. (2012) and Van Wychen et al. (2014). b. Depoorter et al (2013).
Sediment Content g $litre^{-1}$	0.5*	0.5*	Estimated 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}	1.4-3.8-11	3.2-9.0-25	

*Indicates a poorly constrained value.

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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.
FeA Flux Gmol yr^{-1}	0.02-0.03-0.07	<0.01-0.01-0.01	
FeA wt. % (With ice processing)	0.045-0.095-0.203*	0.045-0.095-0.203*	Assuming ice processing increases concentrations by 2.5x
FeA Flux Gmol yr^{-1}	0.03-0.05-0.12	<0.01-0.01-0.03	

*Indicates poorly constrained values

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	1.4 – 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

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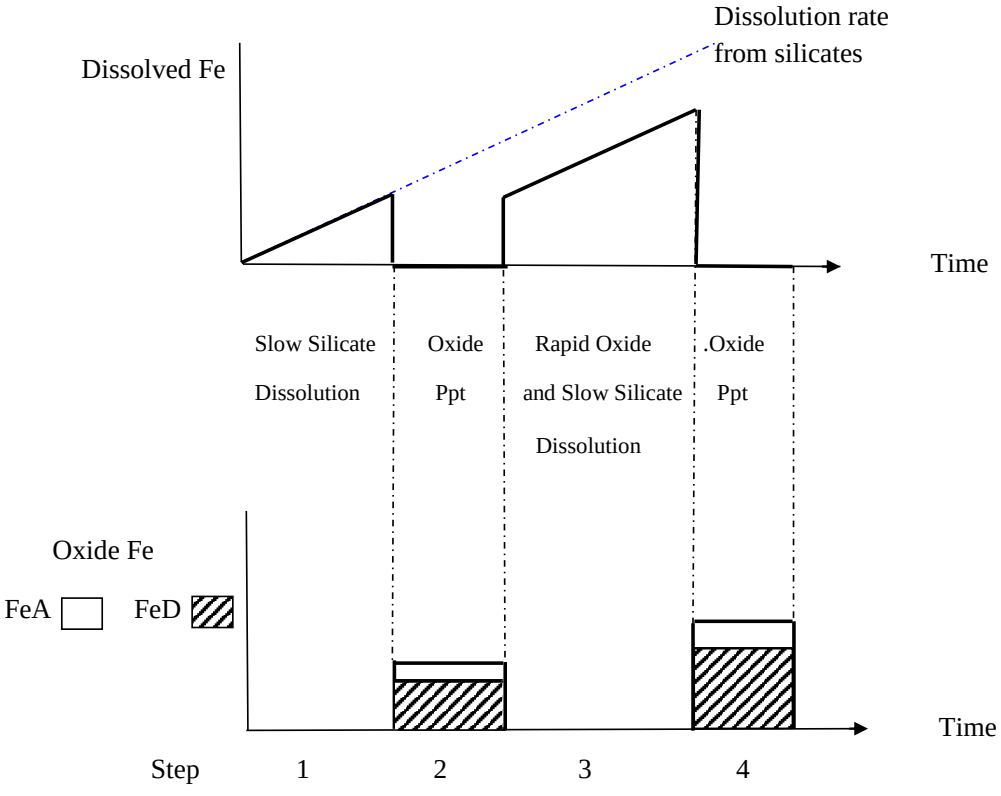
Figure 1. Simplified reaction scheme for the reactions of ice-hosted sediments during melting/freezing cycles.



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

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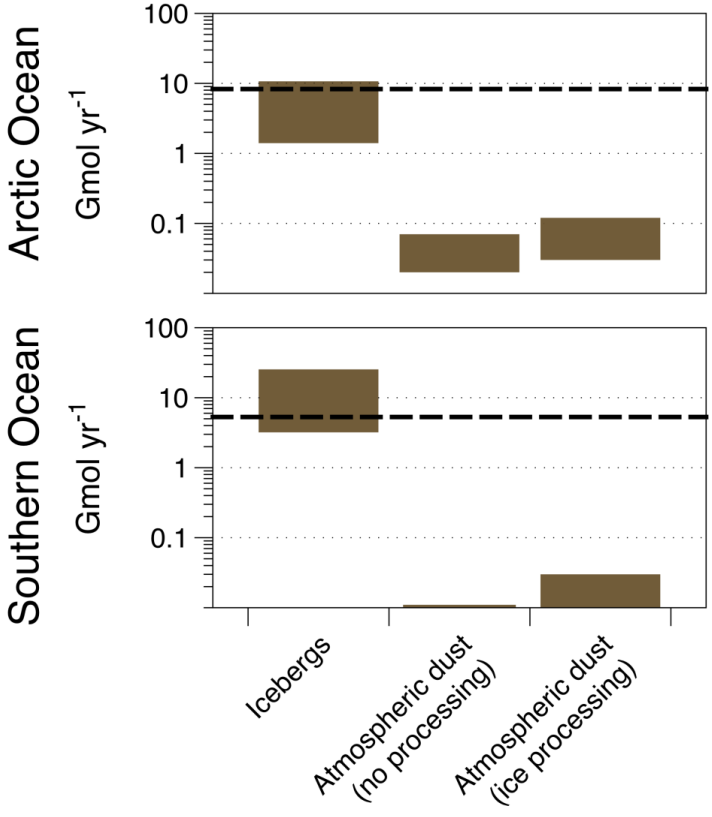

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