1	Surface water iron supplies in the Southern Ocean sustained by deep winter mixing
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22	Iron regulates Southern Ocean primary productivity and due to geographically restricted
23	surface inputs (e.g. local dust supply), most dissolved iron (DFe) is supplied at a basin-scale to
24	surface waters from subsurface reservoirs (remineralisation and sediment/hydrothermal
25	inputs). The main physical processes are deep winter mixing (entrainment) and year-round

26 diffusion across density surfaces (diapycnal diffusion). The relative importance of each

27 remains observationally poorly constrained, yet ultimately governs the climate sensitivity of regional productivity. Here we show that winter entrainment determines the DFe supply to 28 29 Southern Ocean phytoplankton to a greater extent than diapycnal diffusion, necessitating a 30 strong seasonal reliance on biologically recycled iron. DFe observations are combined with 31 hydrography from Argo floats and biological utilisation estimates to determine basin-scale, observationally constrained DFe fluxes. Weak vertical gradients reduce the importance of 32 33 diapycnal diffusion to seasonal re-supply and instead, a 'one off' deep wintertime entrainment 34 pulse annually replenishes surface DFe stocks. Following DFe depletion, biological observations from the sub-Antarctic sector suggest intense upper-ocean DFe recycling that 35 36 sustains productivity. Accordingly, entrainment and recycling are likely important drivers of temporal variations in Southern Ocean primary production. Our results are underpinned by 37 38 the nature of vertical DFe gradients, making these features important constraints on ocean 39 models.

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The micronutrient iron (Fe) is an important regulator of primary productivity and therefore the 41 strength of the biological carbon pump in the Southern Ocean<sup>1,2</sup>. This region is of key importance to 42 both the global carbon cycle and air-sea carbon dioxide fluxes<sup>3,4</sup> and the impact of future or past 43 climate variability is mediated to a large degree by modifications to Fe supply to the biota<sup>5</sup>. Despite 44 a marked expansion of DFe observations in the 'GEOTRACES' era<sup>6</sup> and several investigations<sup>7,8</sup> 45 into the magnitude of exogenous inputs of dissolved Fe (DFe,  $t<0.2\mu m$ ), little attention has been 46 47 focussed on the physical processes that supply DFe at the basin-scale from subsurface reservoirs, enriched in DFe from both external inputs<sup>1,8</sup> and remineralisation<sup>9</sup>. In general, wintertime deep 48 49 mixing (or entrainment), year-round vertical diapycnal diffusion and Ekman upwelling/downwelling are the major physical processes involved in the vertical supply of DFe to 50 phytoplankton<sup>10-12</sup>. The maximum depth of mixing over the year (MLD<sub>MAX</sub>) and the DFe inventory 51 52 within this stratum control the degree of DFe entrainment. Diapycnal diffusion depends on the

53 vertical diffusivity ( $k_z$ ) and the vertical DFe gradient at the base of the MLD ( $\partial Fe/\partial z_{MLD}$ ), while the 54 Ekman upwelling/downwelling of DFe depends on the wind stress curl and the concentration of 55 DFe at the base of the mixed-layer. In terms of their drivers, entrainment is primarily controlled by 56 air-sea surface buoyancy fluxes, while Ekman upwelling/downwelling responds to momentum 57 forcing from winds, and near-surface diapycnal diffusion extracts its energy from a range of sources including winds and buoyancy. As each of these factors will be differentially altered by climate 58 change<sup>5,13</sup>, understanding the climate sensitivity of vertical DFe supply to Southern Ocean 59 60 phytoplankton depends upon the relative role played by different physical input pathways. Despite prior attempts<sup>10,11</sup>, the importance of each physical pathway is poorly quantified due to historically-61 62 sparse data coverage and this shortcoming hampers efforts to constrain the response of Southern 63 Ocean biogeochemical cycling to climate change.

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65 A key influence on the vertical input of DFe to the mixed-layer is exerted by its water column profile and in particular, the location and magnitude of vertical concentration gradients ( $\partial Fe/\partial z$ ). 66 The depth at which  $\partial Fe/\partial z$  is maximal is termed the 'ferricline' (hereafter:  $Z_{Fe}$  supplementary figure 67 1), and as for nitrate (and the 'nitracline'), is critical in understanding how changes in winds and 68 69 buoyancy fluxes will impact physical DFe supply processes. Like nitrate stocks in the North 70 Atlantic, DFe concentrations are typically depleted (not necessarily to zero) in Southern Ocean surface waters during spring/summer<sup>6</sup> due to biological consumption and prevailing DFe 71 limitation<sup>14</sup>, with greater subsurface concentrations from organic matter remineralisation. However, 72 73 unlike nitrate, Fe is also lost from the dissolved pool due to particle scavenging, has important subsurface inputs from ocean sediments and hydrothermal vents<sup>1,8</sup> and is likely remineralised more 74 slowly<sup>15,16</sup>, such that  $Z_{Fe}$  can be deeper than both the nitracline and MLD<sup>15,17-19</sup>. However, the 75 76 nature of the depth offset between Z<sub>Fe</sub> and MLD across the wider Fe-limited Southern Ocean and its relation to physical DFe supply processes remains uncertain. If Z<sub>Fe</sub> were to be consistently deeper 77 78 than the MLD at basin scales, this would have important implications for the magnitude of vertical

DFe supply and its seasonal variability, highlighting the unique nature of Fe cycling. Here we use a novel approach that synthesises recent DFe observations (including recent GEOTRACES field campaigns)<sup>6</sup>, co-localised MLDs from the Argo float archive<sup>20</sup> and satellite phytoplankton Fe utilisation estimates<sup>7</sup> (see Methods) to quantify the processes responsible for the seasonal supply of DFe in the Southern Ocean for the first time. Our goals were to document  $Z_{Fe}$  depths, their relation to MLDs and to quantify the spatial variability in the supply of DFe from entrainment, diapycnal mixing and Ekman upwelling/downwelling across the Southern Ocean.

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## 87 Ferricline Depth and Quantifying Vertical Iron Supply

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Due to its fundamental role in regulating DFe inputs, we first determined Z<sub>Fe</sub> across the Southern 89 90 Ocean. The mean depth of Z<sub>Fe</sub> was 333m (median of 350m) across the 140 unique determinations 91 (Figure 1a). Much of the variability in  $Z_{Fe}$  in absolute depth is eliminated when the potential density anomaly ( $\sigma_{\theta}$ , kg m<sup>-3</sup>; referenced at the ocean surface) at the depth of Z<sub>Fe</sub> is plotted 92 93 (determined from Argo profiling floats; Figure 1b). Consistent across all sampled Southern Ocean sectors, we find that  $Z_{Fe}$  is typically associated with denser waters south of the Polar Front ( $\sigma_{\theta}$  > 94 27.5 kg m<sup>-3</sup>) and with lighter waters ( $\sigma_{\theta}$  < 27.5 kg m<sup>-3</sup>) further north, with a striking decline in  $\sigma_{\theta}$  at 95  $Z_{Fe}$  from south to north (Figure 1b). Since  $\sigma_{\theta}$  declines at any depth from south to north, 96 97 modifications to isopycnal depths likely drive a large part of the variability in the absolute depth of Z<sub>Fe</sub> (Figure 1, especially at relatively adjacent locations) probably following some 'preconditioning' 98 99 from Fe-specific biogeochemical processes (encapsulated by longer remineralisation length scales<sup>15</sup>). The vertical gradient at  $Z_{Fe}$  ( $\partial Fe/\partial z_{ZFe}$ ) is generally much greater than that at the MLD 100  $(\partial Fe/\partial z_{MLD})$ , which indicates that  $Z_{Fe}$  is the most significant vertical gradient in the upper 1000m 101 102 (Supplementary Figure 2). Moreover,  $\partial Fe/\partial z_{ZFe}$  is greatest (meaning a 'sharper' ferricline) in the south Atlantic sector, illustrating the signature of DFe subsurface lateral transfer from numerous 103 regional islands<sup>1,7</sup> in the DFe profiles. On average,  $Z_{Fe}$  is deeper than the co-located MLD by 245m 104

105 (median = 210m, Figure 2a), with no seasonal bias where data are available (Figure 1c). As a 106 measure of MLD variability, the offset changes to 199m or 288m using MLDs at  $\pm 2\sigma$  or  $-2\sigma$ , 107 respectively (see methods for details on the computation of the standard deviation,  $\sigma$ ). Thus 108 irrespective of the time of year, we demonstrate that  $Z_{Fe}$  is robustly and significantly deeper than the 109 MLD across much of the Southern Ocean. That nitracline and phosphocline depths are more closely 110 coupled to the MLD illustrates unique behaviour of DFe in this regard (Supplementary Figure 3).

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That Z<sub>Fe</sub> is almost always much deeper than the concomitant MLD indicates limited input of DFe 112 113 from diapycnal diffusion due to weak  $\partial Fe/\partial z_{MLD}$  (supplementary Figure 2b). For example, applying typical Southern Ocean  $k_z$  values<sup>18,21-23</sup> of 10<sup>-5</sup> to 10<sup>-4</sup> m<sup>2</sup> s<sup>-1</sup> results in 1.6-15.7 nmol DFe m<sup>-2</sup> d<sup>-1</sup> 114 from diapycnal diffusion input. Across all combinations of MLD and  $k_z$  (i.e.  $\pm 2\sigma$  for MLD and  $10^{-5}$ -115  $10^{-4}$  for k<sub>z</sub>), diapycnal diffusion is 0.25-7.7 µmol DFe m<sup>-2</sup> yr<sup>-1</sup> (Figure 2b; consistent with estimates 116 from occasional *in situ* studies<sup>14,16,17,24</sup>). The highest rates of diapycnal diffusion DFe input are 117 found near the Antarctic Peninsula and are comparable to recent regional observations<sup>24</sup>. However 118 such values do not appear generally representative of the offshore Southern Ocean, where diapycnal 119 diffusion inputs of <0.2 umol DFe m<sup>-2</sup> yr<sup>-1</sup> generally prevail (Figure 2b). 120

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122 In contrast to diapycnal diffusion, the winter entrainment pulse can supply much more DFe. Entrainment is quantified using winter mixed-layer depths (MLD<sub>MAX</sub>) from ARGO profiles, 123 alongside estimated winter Z<sub>Fe</sub> (Z<sub>FeMAX</sub>, see methods). While winter mixing depths exceed Z<sub>FeMAX</sub> 124 more often, the mean offset remains 212m (median = 143m, Figure 2a), similar to the sole winter 125 DFe section<sup>25</sup>. At  $\pm 2\sigma$  on MLD<sub>MAX</sub>, mean offsets are 114m and 311m. To correctly compute net 126 entrainment inputs also requires a consideration of the DFe stocks that are detrained during 127 128 springtime mixed-layer shallowing, which can be estimated using Argo profiling data at each DFe profile location. Ultimately, the mean entrainment Fe input is 21.1  $\mu$ mol DFe m<sup>-2</sup> yr<sup>-1</sup>, or 9.5-33.2 129  $\mu$ mol DFe m<sup>-2</sup> yr<sup>-1</sup> at  $\pm 2\sigma$  on MLD<sub>MAX</sub>. This is more than 10-fold greater (on average) than the 130

annual diapycnal diffusion inputs estimated above. Spatially (Figure 2c), entrainment inputs are higher than average around the Antarctic Peninsula and some parts of the Indian and Pacific sectors of the Southern Ocean. Much lower entrainment fluxes are present in many other regions due to weak vertical gradients in DFe persisting down to MLD<sub>MAX</sub>. That appreciable entrainment fluxes DFe arise despite ~200m offsets persisting between  $Z_{FeMAX}$  and MLD<sub>MAX</sub> highlights the smaller vertical gradients in DFe at the top of the ferricline (but shallower than  $Z_{FeMAX}$ ) that are captured by winter mixing.

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139 Ekman upwelling and downwelling is computed using DFe concentrations at the mixed-layer base 140 and the wind stress curl (Figure 2d). Ekman fluxes are strongly latitude-dependent, switching from net losses to gains of DFe as the sign of the wind stress curl changes across the atmospheric 141 142 subtropical jet (Figure 2d). In general, Ekman fluxes are comparable to those associated with 143 diapycnal diffusion, rather than entrainment, and on average are a slight net loss of DFe from the system (-0.7 umol DFe  $m^{-2} vr^{-1}$  or a median of -0.4 umol DFe  $m^{-2} vr^{-1}$ ), although this is likely 144 sensitive to the sampling frequency north and south of the atmospheric subtropical jet. Finally, 145 146 transient MLD deepening during the phytoplankton growth season might entrain additional Fe, but 147 using the rate of change in the MLD from Argo floats 10 days either side of the sampling date, we 148 found this process to be negligible.

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Additional regional or localised sources of DFe to the mixed layer are provided from dust deposition<sup>26</sup> and melting of sea ice<sup>27</sup> or icebergs<sup>28,29</sup> and glaciers<sup>29,30</sup>. Estimates of their supply rates are difficult to generalise as they are usually derived from models or point-source observations that are not easily extrapolated to basin scales. Upper limits<sup>7</sup> for dust deposition, sea ice melting and icebergs are on the order of 20 µmol DFe m<sup>-2</sup> yr<sup>-1</sup>, making them comparable to entrainment. However, it is notable that many of these additional DFe fluxes are extremely localised<sup>7</sup> and these upper limits will only be realised close to sources (i.e. nearshore waters). Therefore over much of

157 the offshore Southern Ocean that is the focus of this study, their contribution to DFe supply will be 158 greatly reduced. The major basin-scale role we find for entrainment is similar to a recent study 159 conducted at one station in the, oceanographically very different, western North Pacific<sup>31</sup>.

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### 161 Iron Supply and Utilisation

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163 We now consider how diapycnal diffusion and entrainment DFe sources can meet estimates of 164 biological Fe utilisation. Basin-scale quantifications of phytoplankton Fe utilisation rely on 165 combining estimates of net primary production with algal Fe utilisation from laboratory culture 166 experiments<sup>7</sup>. Direct comparison with our physical input terms is complicated as much of the Fe utilisation is met from recycled Fe, illustrated by *f*e-ratios (proportion of Fe uptake from 'new' 167 sources<sup>17</sup>) that range between 0.06 and 0.5 from low to high DFe waters<sup>14,16,17,32</sup>. Moreover, 168 169 phytoplankton only represent about half of total Fe utilisation associated with microbial and metazoan assemblages<sup>1</sup>. Lastly, the quantification of diapycnal diffusion and entrainment are 170 sensitive to assumptions regarding  $k_z$  and (to a lesser extent) the degree of detrainment, 171 respectively. Nevertheless, by exploring the plausible parameter space for the *f*e-ratio, k<sub>z</sub> and 172 173 detrainment we can assess the capacity for diapycnal diffusion and entrainment to meet phytoplankton Fe utilisation (where DFe data are presently available). When k<sub>z</sub> is low, diapycnal 174 175 diffusion cannot match utilisation in >50% of locations, regardless of *f*e-ratios (Figure 3a). Even when  $k_z$  approaches its upper limit of  $10^{-4}$  m<sup>2</sup> s<sup>-1</sup>, diapycnal diffusion meets utilisation in >50% of 176 177 cases only when the fe-ratio reaches unrealistically low levels (i.e., minimal reliance on new Fe, Figure 3a). In contrast, it is only when the detrainment term is greatest (~3-fold higher than the 178 Argo float data average of 3.1) and the *f*e-ratio is maximal (i.e. greatest reliance on new Fe) that 179 180 entrainment cannot meet utilisation in >50% of cases (Figure 3b). As more DFe data are collected 181 in the offshore Southern Ocean then the importance of diapycnal diffusion would likely further 182 decline. When examined spatially, even in locations where diapycnal diffusion is strong (e.g. near

the Antarctic Peninsula, Figure 2b), it only provides ~10-20% of total DFe inputs from physicallymediated fluxes (Figure 3c). In contrast, entrainment always provides >60% of total DFe input (Figure 3d) and is often able to offset regional losses of DFe due to Ekman downwelling (Figure 2d). Thus it seems diapycnal diffusion is rarely a significant component of seasonal DFe supply in the Southern Ocean, which we suggest is dominated by a 'one-off' pulse of new DFe via winter entrainment. It is noteworthy in this context that entrainment can always match available estimates of iron utilisation (supplementary material).

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191 Our results permit an illustration of the key processes involved in the supply and cycling of DFe 192 over the Southern Ocean phytoplankton growth season (Figure 4). Deep winter mixing maximises 193 access to subsurface DFe reservoirs and re-stocks the mixed-layer. During spring, this inventory is depleted rapidly (days to weeks) by both the upper ocean biota<sup>14</sup> and abiotic scavenging onto 194 195 settling particles. Diapycnal diffusion will therefore become the major DFe supply term from late spring onwards, but its low rates ( $\sim$ 7-21 nmol DFe m<sup>-2</sup> d<sup>-1</sup>) cannot be reconciled with measured 196 mixed-layer phytoplankton utilisation<sup>14,16,17,32,33</sup> of ~2-6  $\mu$ mol DFe m<sup>-2</sup> d<sup>-1</sup>. Phytoplankton are 197 198 therefore heavily reliant on DFe from pelagic recycling, with *fe*-ratios declining accordingly over summer<sup>14</sup>. This highlights the importance of the 'ferrous wheel'<sup>33</sup> in late spring and summer when 199 DFe inputs to the mixed-layer are weak. Indeed, measured Fe regeneration rates of 5-10  $\mu$ mol m<sup>-2</sup> d<sup>-</sup> 200 <sup>1</sup> more closely match phytoplankton requirements<sup>14</sup>. We suggest that an increasing importance of 201 202 recycled Fe due to low diapycnal diffusion inputs would cause a shift from initially high *fe*-ratios to 203 lower *fe*-ratios over the year. This may prove disadvantageous to larger phytoplankton such as diatoms and favour smaller phytoplankton cells<sup>14</sup>. The relative magnitudes of winter DFe 204 205 replenishment of the mixed-layer by entrainment and on-going diapycnal diffusion is mediated by 206 the degree of coupling between Z<sub>Fe</sub> and the MLD over the year (e.g. Figures 1c, 2a). However, due to the persistent offsets between Z<sub>Fe</sub> and the MLD (Figure 2a), winter entrainment dominates DFe 207 208 supply over much of the Southern Ocean (Figure 3d), with little vertical DFe input to the biota from spring onwards (Figure 4). This emphasises the role of Fe recycling by herbivory, bacterivory and virally-mediated microbial mortality in regulating the mixed-layer DFe pool until the mixed-layer deepens again in autumn. Accordingly, better understanding the dynamics of DFe turnover rates and the associated bioavailability of recycled DFe would be an important future focus.

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214 Our conceptual model posits that because Z<sub>Fe</sub> is so deep, recycling is crucial in maintaining mixed-215 layer DFe stocks following the pulse of DFe from entrainment (Figure 4). The detailed biological 216 rate data supporting this view has been obtained from detailed process studies conducted in the Sub Antarctic Zone of the Southern Ocean<sup>15-17,32,33</sup>. Turning to the silicate-rich waters of the Antarctic 217 218 Zone, our analysis suggests that the paradigm of significant winter entrainment input of DFe 219 followed by little subsequent 'irrigation' from diapycnal iron supply is also true (Figure 3c d). But 220 in addition to Fe recycling, it is also plausible that additional biological factors might influence the 221 seasonal cycle of biological productivity south of the Polar Front in the Antarctic Zone. For example, heavily-silicified diatoms are more common here and their 'luxury uptake' of DFe<sup>34,35</sup> 222 early in the spring (when mixed layer DFe stocks remain high) may help sustain diatom cell 223 224 division once this wintertime DFe pulse has been depleted. Nevertheless, any region-specific 225 additional processes, such as luxury uptake of iron, would only serve to complement recycling as a key determinant of phytoplankton growth once the influence of entrained iron ceases in 226 227 spring/summer (Figure 4).

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### 229 Implications for Southern Ocean Carbon Cycling

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231 DFe regulates phytoplankton growth throughout the Southern Ocean<sup>1,2</sup>, hence basin-scale

fluctuations in Southern Ocean primary productivity<sup>36</sup> should be linked to changing DFe inputs.

233 Our initial results would suggest an important role for entrainment, as mediated by winter mixing in

this context (Figure 3d). Indeed, using a scale analysis we find inter-annual variation in DFe supply

from entrainment is 9.1-33  $\mu$ mol m<sup>-2</sup> yr<sup>-1</sup>, as compared to 1.2-3.6 or -1.9-0.4  $\mu$ mol m<sup>-2</sup> yr<sup>-1</sup> from 235 diapycnal diffusion or Ekman, respectively. Inter-annual modifications to dust deposition<sup>37,38</sup>, or the 236 melting of sea ice<sup>39</sup> might also be important locally (perhaps ranging 2 to 8 fold<sup>7</sup>), but these inputs 237 238 cannot readily be extrapolated to basin scales. Inter-annual basin-scale changes in Southern Ocean primary production presently can only be assessed by satellite and are estimated<sup>36</sup> at ~ $\pm 11\%$  (from 239 1997-2006). This variability is relatively small in contrast to the large changes in wintertime DFe 240 241 inputs we estimate and the widely demonstrated role DFe supply plays in setting regional productivity<sup>2</sup>. Robust attribution of causality to the driver(s) of observed fluctuations in remotely-242 sensed basin-scale primary productivity is so far lacking for the Southern Ocean<sup>36</sup>. Such attribution 243 244 may be further masked by the unique bio-optical properties of Southern Ocean waters that likely hinder the utility of remotely-sensed productivity datasets<sup>40</sup>. Satellite estimates may be further 245 confounded by the complicated inter-play between physical DFe supply, external DFe inputs and 246 physiological plasticity in phytoplankton DFe utilisation<sup>7</sup>. Nevertheless, our results show winter 247 entrainment is pivotal to regional DFe supply and must be part of a future appraisal of the 248 sensitivity of Southern Ocean productivity to basin-scale environmental fluctuations, which has 249 been overlooked in previous assessments<sup>36,41</sup>. 250

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252 Properly accounting for the role of winter entrainment DFe inputs requires the parallel 253 consideration of winter mixing depths and their connection to subsurface DFe reservoirs (Figure 2a). An improved understanding of the distribution of ferricline depths across the Southern Ocean, 254 255 as part of the GEOTRACES programme, and how they change on seasonal scales would permit a 256 more widespread identification of regions where entrainment dominates. This would, in turn, highlight locations where primary productivity might be more sensitive to variability in buoyancy 257 258 fluxes rather than winds. In addition, appraising the sensitivity of Fe recycling to environmental 259 factors on seasonal scales is also crucial since it is clearly the major resupply process over spring-260 summer once entrainment ceases, with probable implications for ecosystem structure (Figure 4).

Finally, climate models seeking to represent the evolution of the Southern Ocean carbon cycle or productivity<sup>42-46</sup> must pay careful attention to their representation of vertical distributions of DFe. The degree of coupling between  $Z_{Fe}$  and the MLD in the model will dictate the relative role played by different physical DFe supply mechanisms, as well as the importance of mixed-layer recycling of Fe in sustaining productivity over seasonal and inter-annual periods.

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### 267 Methods Summary

A global DFe database<sup>6</sup> was re-gridded into 1° x 1° longitude and latitude bins (south of 40°S) by 268 269 month of sampling and on a depth axis with a 25m resolution in the upper 1000m. The compiled Fe 270 profiles were scrutinised in a number of ways. We firstly required there to be at least one observation shallower than 50m, one observation deeper than 500m and at least five observations in 271 272 total per profile. The remaining profiles were then interpolated on the vertical axis (see supplementary material) to determine Z<sub>Fe</sub>. We decided on the most objective definition possible for 273  $Z_{\text{Fe}}$ , i.e., the depth at which the  $\partial \text{Fe}/\partial z$  gradient was maximal (see also:<sup>18</sup>), which avoided assigning 274 a subjective threshold concentration. Alternative methods might be imagined that would allow the 275 capturing of the 'top' and 'bottom' of the ferricline using deviations in  $\partial Fe/\partial z$  from zero 276 277 (Supplementary Figure 1), however they are not easily applied with confidence to such a large 278 dataset. As such our work identifies the 'core' of the ferricline. To avoid deep ocean gradients 279 associated with point sources (e.g., hydrothermal vents) being misidentified as the upper ocean 280 ferricline we restricted our analysis to the upper 1000m where hydrothermal tracers show minimal gradients<sup>8</sup>. Finally, since in coastal systems Z<sub>Fe</sub> might be very close to the seabed due to sediment 281 282 input, we decided to remove data where Z<sub>Fe</sub> was more than 80% of the bottom depth. The total 283 number of unique determinations was 140 or by month: 25 in January, 18 in February, 14 in March, 284 46 in April, 10 in July, 2 in October, 20 in November and 5 in December. The DFe dataset used in 285 this study is archived and updated here: http://pcwww.liv.ac.uk/~atagliab/LIV WEB/Data.html.

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We calculated the MLD for every Southern Ocean profile with a surface-density difference criterion of  $\Delta \sigma_{\theta} \leq 0.03$  kg m<sup>-3 47,48</sup> (Supplementary Figure 1d). The correspondence between Z<sub>Fe</sub> and MLD was then examined by co-locating MLDs from either in situ CTD profiles and/or Argo profiles<sup>20</sup> (Supplementary Figure 2d) for the same month and year within 2.5 degrees of a Z<sub>Fe</sub> determination and weighted by 1/d<sup>4</sup> (where d is the distance from the Z<sub>Fe</sub> determination). We also use the maximum MLDs associated with each location for the specific year. Uncertainty in each MLD determination is assessed using a climatology at ±2 standard deviation.

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295 Diapycnal input is calculated by taking  $\partial Fe/\partial z$  at the MLD (Supplementary Figure 2b) from Argo and multiplying by an estimate of vertical diffusivity ( $k_z$ , see main text). Winter entrainment is 296 297 computed by integrating DFe down to the MLD<sub>MAX</sub> from Argo. The proportion of the DFe stock 298 entrained in the ML during winter that is detrained during springtime mixed-layer shallowing can 299 be estimated using the MLD<sub>MAX</sub>:MLD<sub>MIN</sub> ratio from Argo at each DFe profile location (average = 300 3.16±1.86, see Supplementary Figure 2c for a representation of this term). Finally, the Ekman 301 upwelling/downwelling of DFe requires the mean mixed layer DFe from DFe observations and 302 Argo alongside the wind stress curl. For windstress we used the Quick Scatterometer Mean Wind 303 Field (QuickSCAT MWF) gridded product (this global half degree-resolution product is processed 304 and distributed by the Centre European Remote Sensing Satellite (ERS) d'Archivage et de 305 Traitement (CERSAT); available online at http://www.ifremer.fr/cersat/). We used weekly maps of 306 wind stress between 1999 and 2009 to produce monthly mean maps over a period consistent with the Argo data. The stated error of the product is less than  $7 \times 10^{-3}$  Pa over the area studied. 307

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309 To estimate  $Z_{FeMAX}$ , we used the robust relationship between  $Z_{Fe}$  and density (Figure 1b) and since 310  $Z_{Fe}$  is below the diabatic surface layer for most profiles we determined  $Z_{FeMAX}$  by assuming that  $Z_{Fe}$ 311 conserves its density. Thus the change in the density profile between the time of measurement and 312 the time of MLD<sub>MAX</sub> drives the 'winter' DFe profile. The resulting profiles are illustrated for four 313 case study regions in Supplementary Figure 4.

315	The i	ron utilisation estimates combine regionally optimised NPP determinations from ocean
316	colou	ur <sup>36</sup> with combination with estimates of the biogeography in algal Fe/C ratios to arrive at
317	annua	al Fe utilisation estimates (1996 to 2007). The algal Fe/C ratios are applied using laboratory
318	data 1	from Southern Ocean isolates <sup>7,49</sup> . For reference, the median annual Fe utilisation map from
319	ref(7)	) is reproduced in Supplementary Figure 5a.
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473

# 474 Author Contributions

- 475 Led design of the study and writing of the manuscript (A.T), assembly of the iron and Argo datasets
- 476 and data analysis (A.T and J-B.S), additional physical flux analyses (A.T., J-B.S, M.L and S.S),
- 477 biological rate measurements (P.W.B) and additional iron observations (A.R.B). All authors
- 478 contributed to the overall experimental work, discussion of the results and their implications, as
- 479 well as commenting on the manuscript.

480 Figure Legends:

481

482 Figure 1. Depths and potential density of the ferricline and its seasonal evolution. a) The depth 483 of the ferricline (m, black and grey triangles denote the mean and median, respectively), b) the potential density anomaly ( $\sigma_{\theta}$ , kg m<sup>-3</sup>) associated with the ferricline depth and c) box and whisker 484 plots of the seasonal cycle in MLD, Z<sub>Fe</sub> and Z<sub>Fe</sub>-MLD (the size of the box represents the 1st to 3rd 485 486 quartiles, with the vertical bar corresponding to the median and the whiskers representing 1.5 times 487 the inter-quartile range). While calculations for panels a and b are performed on a 1° grid, they are shown using a 3° grid for clarity, the 3000m isobath and the mean Polar Front position (black line<sup>6</sup>) 488 489 are also displayed.

490

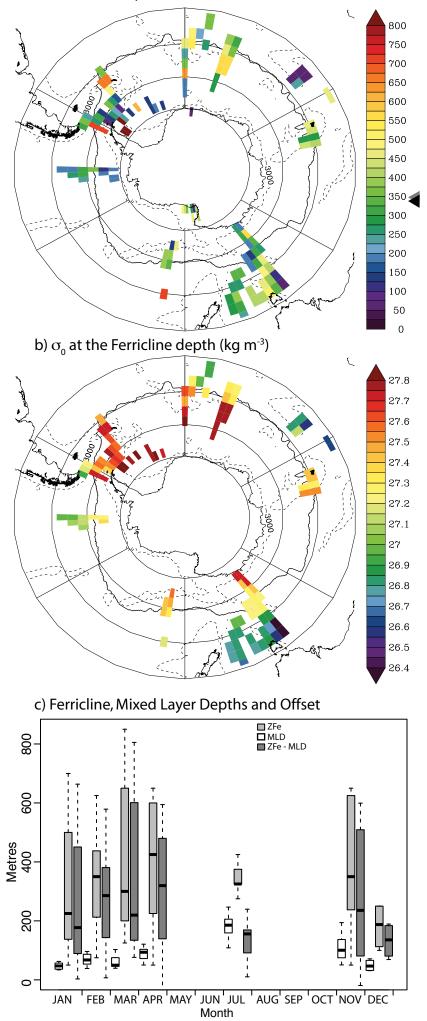
Figure 2. The relationship between the ferricline and mixed layer depths and calculations of physically-mediated iron fluxes. a) A histogram of the offset (m) between the depth of the ferricline and the mixed layer depth (blue and red for concomitant and winter MLDs, respectively), b) annual diapycnal diffusion flux of Fe across the mixed-layer (mmol  $m^{-2} yr^{-1}$ ), c) annual entrainment flux of Fe (mmol  $m^{-2} yr^{-1}$ ) and d) annual Ekman DFe term (mmol  $m^{-2} yr^{-1}$ ), with a negative/positive values indicating downwelling/upwelling of DFe. In panels b-d black and grey triangles denote the mean and median, respectively. Gridding for panels b-d as for Figure 1a.

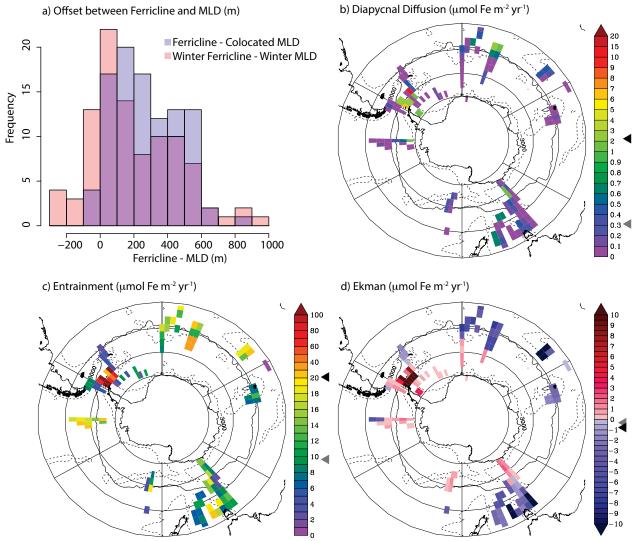
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Figure 3. Assessments of how different physically-mediated iron supply mechanisms compare
to utilisation and their contribution to total iron fluxes. The percentage of locations where a)
diapycnal diffusion and b) entrainment can match iron utilisation over different scenarios regarding
the *f*e-ratio and k<sub>z</sub> (panel a) and detrainment (panel b). The proportional contribution of c) diapycnal
diffusion and d) entrainment to total physical DFe supply (see supplementary Figure 3b). Gridding
for panels c and d as for Figure 1a.

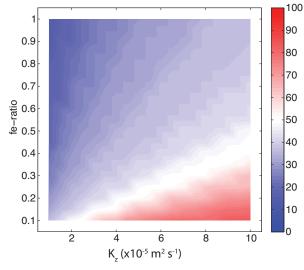
506	Figure 4. A schematic representation of the seasonal variability in Southern Ocean Fe cycling.
507	We emphasise seasonal changes in the physical supply of Fe (blue arrows), mixed layer depth and
508	the mixed layer DFe inventory, as well as the magnitude of recycling (orange-red arrows) and
509	pelagic community composition. The dominant physical processes over the season is conceptualised
510	at the bottom of the figure. We note that some recycling likely occurs below the mixed-layer and
511	can be entrained the following winter.
510	

a) Ferricline Depth (m)



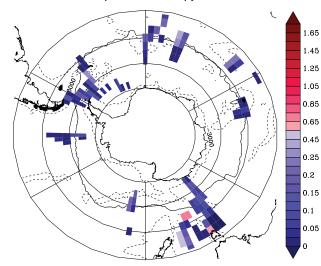


#### a) Offset between Ferricline and MLD (m)



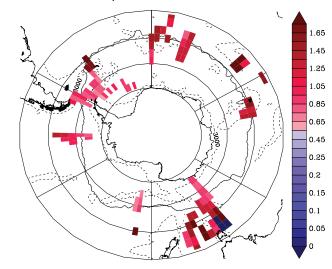
a) Percent of Locations where Diapycnal Diffusion Matches Iron Utilisation

c) Relative Importance of Diapycnal Diffusion



100 1 90 0.9 80 0.8 70 0.7 60 9.0 fe-ratio 50 40 0.4 30 0.3 20 0.2 10 0.1 0 2 4 6 8 Detrainment

d) Relative Importance of Entraiment



b) Percent of Locations where Entrainment Matches Iron Utilisation

