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# 1 The interplay between regeneration and scavenging fluxes drives ocean iron cycling

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## 18 **Abstract:**

19  
20  
21 **Despite recent advances in observational data coverage, quantitative constraints on**  
22 **how different physical and biogeochemical processes shape dissolved iron**  
23 **distributions remain elusive, lowering confidence of future projections in iron-**  
24 **limited regions. Here we show that dissolved iron is cycled rapidly in Pacific mode**  
25 **and intermediate water and accumulates at a rate controlled by the strongly**  
26 **opposing fluxes of regeneration and scavenging. Combining new datasets within a**  
27 **watermass framework shows that the multidecadal iron accumulation is much lower**  
28 **than expected from a meta-analysis of iron regeneration fluxes. This mismatch can**  
29 **only be reconciled by invoking significant rates of iron removal operating on multi-**  
30 **decadal timescales, which imply generation of authigenic iron pools. Consequently,**  
31 **the rapid internal cycling of iron, rather than its physical transport, is the main**  
32 **control on observed iron stocks within intermediate waters globally and upper**  
33 **ocean iron limitation will be strongly sensitive to subtle changes to the internal**  
34 **cycling balance.**

## 35 36 **Introduction**

37  
38 Upper ocean primary production is limited by the availability of iron (Fe) over much of the  
39 ocean<sup>1</sup>. Even where nitrogen (N) and phosphorus (P) are the main limiting factors, Fe  
40 continues to play a key role by driving rates of N fixation<sup>2</sup> and acquisition of dissolved  
41 organic P<sup>3</sup>. Fe limitation ultimately arises due to a deficiency in the supply of Fe, relative to  
42 N and P<sup>4</sup>. Away from regions of dust deposition, the dominant component of Fe delivery,  
43 relative to N or P, is its relative concentration in thermocline waters<sup>5</sup>. This is particularly  
44 apparent across the south Pacific Ocean, where transport by sub-Antarctic mode water  
45 (SAMW) and Antarctic Intermediate water (AAIW) plays a key role in setting thermocline  
46 nutrient levels<sup>6</sup>. Accordingly, any fluctuations in the relative balance between Fe and major  
47 nutrients N and P in mode and intermediate waters in response to changes in climate will  
48 influence upper ocean Fe limitation and consequently modify global carbon and nitrogen  
49 cycles.

50  
51 At present, there is low confidence in model projections of how modulations to climate will  
52 affect Fe supply to the upper ocean, as models generally show poor skill and substantial

53 disagreement in their representation of the present-day ocean iron cycle. This lack of  
54 fundamental understanding of iron biogeochemistry is well illustrated by the order of  
55 magnitude inter-model variability in the residence time of iron in global models, despite  
56 aiming to reproduce the same ocean distributions and patterns from state of the art  
57 datasets<sup>7</sup>. Thus, despite a relatively long legacy of modelling the ocean iron cycle<sup>8,9</sup>,  
58 significant uncertainties in the magnitude of the major processes remain<sup>1,10</sup>. This means  
59 that while shifts in Fe inventories may indeed drive end-of-century trends in simulated  
60 productivity across much of the global ocean<sup>11-15</sup>, confidence in model projections is  
61 diminished by the lack of mechanistic constraints on their behaviour.

62  
63 The ocean iron cycle is affected by an array of processes that interact together to set the  
64 dissolved iron concentrations in different parts of the ocean<sup>16</sup>. In the past decade,  
65 continental margins and hydrothermal vents have been acknowledged to augment dust  
66 deposition as important external iron sources<sup>17,18</sup>. Perhaps most striking has been the  
67 recognition that the internal cycling of iron is typified by a range of biotic and abiotic  
68 transformations linked to Fe uptake, recycling, regeneration, scavenging and colloidal  
69 dynamics<sup>10,19</sup>. These processes act to shuttle dissolved iron between soluble and colloidal  
70 phases<sup>20-22</sup> and drive transitions of particulate iron between biogenic, lithogenic and  
71 authigenic (i.e., the residual particulate Fe not accounted for by lithogenic and algal  
72 biogenic pools) components<sup>23,24</sup>. Despite these new insights, the relative magnitude of  
73 regeneration and scavenging, and crucially, the realised rate of net regeneration, is  
74 unknown at the spatial and temporal scales of mode and intermediate water transport. In  
75 part due to these missing constraints, global ocean models used to assess the response  
76 of ocean ecology, biogeochemistry and the carbon cycle to environmental change are free  
77 to tune their internal iron cycle with residence times that vary from a few tens to a few  
78 hundreds of years<sup>7</sup>.

79  
80 Newly expanded datasets of dissolved Fe (DFe) distributions from international ocean  
81 survey efforts within the GEOTRACES programme<sup>25,26</sup> should facilitate model  
82 improvement, but only if quantitative insights into the governing processes can be  
83 determined. A particular challenge is to disentangle the balance between biogeochemical  
84 and physical processes in setting nutrient levels in the oceans' interior. For example, total  
85 phosphate ( $\text{PO}_4$ ) at depth is made up of up of two components: one associated with physical  
86 transport to depth (preformed  $\text{PO}_4$ ) and the other from the regeneration of P from organic  
87 matter degradation (regenerated  $\text{PO}_4$ ) which is quantified using apparent oxygen utilisation  
88 (AOU)<sup>27,28</sup>. A similar framework can be outlined for Fe, but Fe may be decoupled from P  
89 as it is affected by additional processes, such as extra Fe inputs onto intermediate water  
90 surfaces, unique regeneration of Fe, or Fe removal by scavenging<sup>1,10,29</sup>. While scavenging  
91 of Fe will add complexity to the two component model used for P, its magnitude remains  
92 an unknown quantity. This lack of understanding is encapsulated by our evolving view of  
93 the ocean iron residence time<sup>7,30,31</sup>.

94  
95 Here we use observations to quantify the modification of DFe, benchmarked to  $\text{PO}_4$ , within  
96 the mode and intermediate waters of the south Pacific Ocean, using AOU to derive the  
97 role played by physics, regeneration and scavenging for the first time. We focus on mode  
98 and intermediate waters as they support the majority of global productivity through nutrient  
99 supply to surface waters<sup>6</sup>. This approach illuminates a highly dynamic interior ocean Fe  
100 cycle is, within which the commonly measured DFe pool is only a small residual  
101 component. Consequently, additional measurements of the ocean iron cycle pools beyond  
102 DFe and in particular fluxes are necessary to better constrain internal cycling and reduce  
103 uncertainty in global climate model projections.

## 105 Results

106

### 107 **Tracking South Pacific iron and phosphate accumulation**

108

109 Pacific Ocean SAMW and AAIW form in the southeast Pacific Ocean<sup>32,33</sup> and their  
110 equatorward transport is well sampled by the southern part of the CLIVAR P16 cruise track  
111 along 150W (Figure 1, Supplementary Figure 1). We targeted the region 46-10S of the  
112 transect within a potential density window of 26.8-27.2 that broadly encompasses both  
113 SAMW and AAIW (hereafter defined as intermediate water)<sup>32,34</sup>. In this density window,  
114 salinity was relatively well conserved at 34.3-34.5 (indicating negligible mixing from  
115 multiple end-members), and enough parallel observations of DFe, PO<sub>4</sub> and oxygen  
116 needed for our analysis were available (n=89). As intermediate water moves equatorward  
117 its core depth varies between 200m to 800m and AOU increases from 20 to 160 mmol m<sup>-3</sup>  
118 as the constituents transported within the watermass, or delivered via sinking from above,  
119 undergo further remineralisation (Supplementary Figure 1). Using an age tracer within a  
120 data-constrained ocean circulation inverse model (OCIM)<sup>35</sup> that reproduces P16 salinity  
121 measurements, intermediate water in this density window aged by ~190 years (from 69 to  
122 260 years) during this part of the P16 transect (Figure 1, see also Supplementary Figure  
123 2).

124

125 As expected from our understanding of P biogeochemistry, PO<sub>4</sub> is well correlated with  
126 AOU within the intermediate water layer (R=0.96, Figure 2a) and the slope of 11.48±0.71  
127 mmol P mol C<sup>-1</sup> is very close to that expected from the organic matter content<sup>36</sup>. The  
128 intercept indicates a preformed PO<sub>4</sub> concentration of 1.04±0.04 mmol m<sup>-3</sup> at the  
129 intermediate water outcrop in the Fe-limited Southern Ocean. More surprising is the  
130 broadly linear relationship between DFe and AOU within intermediate water (R=0.66,  
131 Figure 2b), with a slope of 3.92±0.99 μmol Fe mol C<sup>-1</sup> and a preformed DFe concentration  
132 of 0.16±0.06 μmol m<sup>-3</sup>. The Fe/C ratios estimated from the slope of the linear regression  
133 between Fe and AOU within AAIW are similar to those previously estimated from vertical  
134 profiles across the North Pacific Ocean<sup>37,38</sup>. However, the profile-based estimates cannot  
135 strictly be used to quantify the accumulation of dFe since the zero AOU intercept that  
136 should represent the surface water outcrop of the isopycnal layer is instead the directly  
137 overlying surface water. This means that the values reported here are the first estimates of  
138 the temporal accumulation of DFe alongside concomitant oxygen consumption in Pacific  
139 intermediate waters. Indeed, we can use the watermass age estimate from OCIM to derive  
140 rates of accumulation of 6.75 μmol PO<sub>4</sub> m<sup>-3</sup> yr<sup>-1</sup> and 2.34 nmol dFe m<sup>-3</sup> yr<sup>-1</sup> between 46S  
141 and 10S.

142

143 While the accumulation of PO<sub>4</sub>, relative to C, conforms our prior understanding based on  
144 observations of P/C ratios from organic matter<sup>36</sup>, DFe accumulation appears very low,  
145 even for the Fe-poor South Pacific. Estimates of median phytoplankton Fe content from  
146 available synchrotron measurements (Table 1) range from 11.7 to 31.3 μmol Fe mol C<sup>-1</sup>,  
147 with a median value of ~15.7 μmol Fe mol C<sup>-1</sup> typical of the South Pacific. This indicates  
148 that only around a quarter (25%) of phytoplankton Fe is accumulating as DFe in  
149 intermediate waters due to regeneration. It is possible that living phytoplankton are not  
150 representative of the sinking detrital pool<sup>39</sup>, which could be addressed by examining Fe/C  
151 ratios within bulk particulate matter. However, particulate Fe also includes relatively inert  
152 lithogenic Fe, which would overestimate the labile (i.e. biotic) Fe content. To account for  
153 this, we estimated lithogenic Fe (see methods) from the only GEOTRACES particulate Fe  
154 dataset from the Pacific Ocean (stations west of the east Pacific rise on the zonal GP16  
155 transect between Ecuador and Tahiti) using three different lithogenic models accounting  
156 for a range of end members from the Pacific basin<sup>23,24,40</sup>. After this correction, median

157 non-lithogenic Fe/C ratios within all particulate samples, shallower than the lightest  
158 intermediate water isopycnal, range from 48.2-196.4  $\mu\text{mol Fe mol C}^{-1}$ , while the median  
159 P/C ratio is 12.73  $\text{mmol P mol C}^{-1}$  (Table 1). This particulate analysis shows that the  
160 accumulation of dFe along the intermediate water pathway is only 2-8% of the non-  
161 lithogenic particulate Fe or ~25% of phytoplankton Fe. In contrast, as expected from the  
162 two-component preformed-regenerated model of P cycling, 90% of the median particle P/C  
163 ratio accumulates as  $\text{PO}_4$  along the intermediate water pathway. This suggests that the  
164 simple two component balance between regenerated and preformed pools that explains  
165 the internal cycling of  $\text{PO}_4$  is not applicable for Fe and the balance of subsurface  
166 solubilisation and scavenging processes that control the net observable Fe  
167 remineralisation remain unconstrained.

168

### 169 **Controls on dissolved iron accumulation in intermediate waters**

170

171 There are three main hypotheses to explain the mismatch between accumulation of DFe  
172 and the magnitude of phytoplankton and particulate Fe stocks that fuel DFe  
173 replenishment. The first hypothesis states that particulate Fe is not exported from the  
174 surface ocean and instead retained in the zone shallower than the upper bound of  
175 intermediate waters. The second hypothesis states that particulate Fe is exported out of  
176 the upper ocean but is not regenerated. Finally, the third hypothesis states that ample Fe  
177 is exported and regenerated, but strong scavenging of regenerated Fe leads to minor  
178 accumulation of DFe.

179

180 The first hypothesis can be rejected since although recycling of Fe in the upper ocean is  
181 significant, ample particulate Fe is exported from the surface ocean. Significant recycling  
182 of Fe in the upper mixed layer has been demonstrated from a variety of field studies and  
183 budget calculations<sup>5,10,19,41-43</sup>, which indicate substantial turnover of the particulate Fe pool.  
184 Measurements of particulate Fe exported from the upper ocean from trace metal clean  
185 sediment traps are very rare, but, where available, also support substantial export of  
186 particulate Fe. Sinking particulate Fe flux data from the SAZ-Sense and FeCycle I and II  
187 (at ~100m depth and either directly accounting for lithogenic Fe or taking a conservative  
188 80% estimate of the lithogenic fraction<sup>44</sup>) results in non-lithogenic Fe/C export ratios of  
189 between 30-400  $\mu\text{mol Fe mol C}^{-1}$  and P/C export ratios of around 6-8.5  $\text{mmol P mol C}^{-1}$   
190 across all data<sup>44-46</sup> (all broadly similar to those from non-lithogenic mixed layer particles,  
191 Table 1). Median values from both datasets produce flux ratios of 141.6  $\mu\text{mol Fe mol C}^{-1}$   
192 and 5.6  $\text{mmol P mol C}^{-1}$ , compared to accumulation ratios of 3.9  $\mu\text{mol Fe mol C}^{-1}$  and 11.5  
193  $\text{mmol P mol C}^{-1}$  (Table 1). Thus, despite intense recycling in the surface mixed layer,  
194 export fluxes of non-lithogenic Fe out of the base of the surface mixed layer are significant  
195 relative to the accumulation of DFe during regeneration along mode water pathways in the  
196 oceans' interior (Table 1), leading us to reject hypothesis one.

197

198 The second hypothesis can be rejected in light of previous assessments of solubilisation of  
199 Fe from particles below the mixed layer (at between 100-200m) through a set of  
200 experiments that incubated a subsurface particle assemblage resuspended from McLane  
201 pump 142mm filters and monitored the release of DFe, as well as by iron budget  
202 calculations. These estimates are sparse, but for two distinct field experiments, dFe  
203 release rates range between 511-1,314, and 120-460  $\text{nmol m}^{-3} \text{yr}^{-1}$  from particles from  
204 below the mixed layer<sup>47,48</sup>. Budget based calculations are similar, producing subsurface  
205 dFe regeneration rates of 190-2,630  $\text{nmol m}^{-3} \text{yr}^{-1}$  at 100m<sup>45</sup>. Across all estimates we find  
206 a median of 485  $\text{nmol m}^{-3} \text{yr}^{-1}$ , two orders of magnitude greater than the dFe accumulation  
207 rate of ~2  $\text{nmol m}^{-3} \text{yr}^{-1}$  we find within intermediate water (Table 1). These rates are  
208 clearly substantial, and we are required to reject hypothesis two.

209

210 Based on our rejection of the first two hypotheses, we are required to invoke a significant  
211 loss of regenerated Fe from either scavenging or bacterial removal when considering  
212 hypothesis three. This would reconcile the low rates of dFe accumulation within  
213 intermediate waters with the significant export of non-lithogenic Fe and large rates of dFe  
214 solubilisation from sinking particles. The potential role of the removal of regenerated algal  
215 biogenic Fe has been previously observed using synchrotron-mapping of particles derived  
216 from sediment traps<sup>49</sup> and would also explain new observations of an increasing  
217 association of sinking non-lithogenic particulate Fe with authigenic phases in deep-moored  
218 sediment traps (between 500, 1,500 and 3,200m) in the Atlantic<sup>50</sup>. For the Pacific, we  
219 calculate that 20-40% of the particulate Fe within the intermediate water in the western  
220 portion of the GP16 Pacific section cannot be accounted for by the sum of lithogenic and  
221 algal biogenic components. This implies a non-negligible authigenic particulate Fe  
222 component that would be consistent with removal of regenerated Fe by scavenging.  
223

## 224 **Discussion**

225

226 Our results point to continual removal of regenerated iron, resulting in only a small  
227 accumulation of DFe within intermediate waters. The combination of the constant rain of  
228 new material and the disaggregation of sinking particles in the ocean interior may be able  
229 to maintain scavenging of released Fe as the increasing surface area:volume ratio  
230 provides new surfaces for scavenging. Indeed, the increase in the flux of small particles  
231 (11-64  $\mu\text{m}$ , equivalent spherical diameter, ESD) off Bermuda, and the concomitant  
232 opposite trend for large (> 64  $\mu\text{m}$  ESD) particles at depth<sup>51</sup>, highlights the important role  
233 this may play in producing small particles. Similarly, number spectrum analyses (using  
234 underwater video cameras) across the upper 200 m of the water column in the S. Pacific  
235 Gyre reveal much higher abundances of small particles than larger ones<sup>52</sup>. As scavenging  
236 of trace metals like Fe is highly dependent on surface area<sup>53-55</sup>, these particle  
237 disaggregation/fragmentation processes can catalyse further scavenging of the dFe  
238 released by regeneration. Scavenging of regenerated Fe into authigenic phases may also  
239 enhance particle sinking rates by increasing the specific gravity of particles (as noted for  
240 lithogenic Fe<sup>56</sup>). These abiotic processes may act in concert with the removal of solubilised  
241 Fe by heterotrophic bacteria operating within particle microenvironments<sup>57,58</sup>. If we take  
242 our median estimated regeneration rate of dFe and the estimated accumulation rate of  
243 dFe (Table 1), and then combining these with a typical intermediate water layer thickness  
244 of 300m at 10S, requires net downward removal fluxes of around  $0.39 \mu\text{mol m}^{-2} \text{d}^{-1}$ .  
245 Although these fluxes would be inconspicuous in the measurements spanning around 0.4-  
246  $10 \mu\text{mol m}^{-2} \text{d}^{-1}$  from trace metal clean sediment traps<sup>44,45</sup>, they are crucial in shaping the  
247 basin scale internal cycling of dFe in intermediate water layers.  
248

249 We observe a small, but significant, accumulation of DFe with time (Figure 2b), suggesting  
250 that the net regeneration quantified by the slope of the DFe versus AOU relationship  
251 integrates the regeneration and scavenging fluxes. Observed concentrations of weak Fe-  
252 binding ligands are typically well in excess of DFe levels, which would imply an ample  
253 capacity to stabilise regenerated Fe at much higher levels<sup>59-62</sup> and is not in agreement with  
254 our analysis. However, the muted increase in DFe we observe is very consistent with the  
255 apparent saturation of strong Fe-binding ligands by DFe pools in the south Pacific  
256 Ocean<sup>60</sup>. This would imply that strong Fe-binding ligands, rather than their weaker  
257 counterparts, may play a key role in shaping the dissolved Fe distribution in the oceans'  
258 interior. An additional role may be played by the interplay between soluble and colloidal  
259 iron pools, which can also be part of the ligand pools<sup>20-22</sup>. For instance, in the future it may  
260 be useful to compare the net regeneration from the DFe-AOU slope to observations of

261 colloidal iron. Finally, we emphasise that the putative production of authigenic Fe from the  
262 DFe solubilised during regeneration, that we term here as scavenging, might not occur in  
263 the water column, but instead within particles and their associated microenvironments<sup>57,58</sup>  
264 in a manner disconnected from the wider water column ligand pool.

265  
266 The DFe-AOU slope of  $2.7 \mu\text{mol DFe mol AOU}^{-1}$  from our analysis (Figure 2b) permits us  
267 to examine what proportion of the DFe pool might be controlled by the net interplay  
268 between regeneration and scavenging (termed 'internal cycling' hereon). Roughly two-  
269 thirds of the interior  $\text{PO}_4$  signal is preformed (controlled by physical transport), with the  
270 remaining one-third due to regeneration<sup>27,28</sup>. In contrast to  $\text{PO}_4$ , the proportion of the DFe  
271 pool controlled by internal cycling in intermediate waters (within the 26.8-27.2 isopycnal  
272 layer) across the entire available GEOTRACES dataset<sup>26</sup> of DFe and AOU has a median  
273 value of 0.57 (Figure 3). This implies that over half of the DFe concentration in  
274 intermediate water is in fact set by internal cycling (i.e. the interplay between regeneration  
275 and scavenging), with the remainder controlled by physical transport of preformed DFe  
276 (either from the ocean surface or laterally). The stronger role played by preformed  $\text{PO}_4$   
277 than preformed DFe arises due to the higher unused  $\text{PO}_4$  levels in the, typically Fe-limited,  
278 watermass outcrop regions. Thus, because DFe is drawn down to very low levels in  
279 regions of intermediate water formation, internal cycling has a larger imprint on the interior  
280 DFe concentrations across much of the globe than for  $\text{PO}_4$ . This view agrees with the lack  
281 of clear water mass signals in large scale ocean DFe sections<sup>63</sup> and is at odds with  
282 simulations from early iron models that retained a large physically transported component.

283  
284 Overall, the strong mismatch we find between the internal basin scale Fe cycle fluxes and  
285 the residual DFe pool that accumulates from their interplay explains why Fe models can  
286 produce such divergent residence times while trying to reproduce the same dFe datasets.  
287 Our analysis finds DFe to be rapidly cycled by regeneration and scavenging, which  
288 supports those models parameterised with short residence times. The net regeneration  
289 that shapes the multi-decade accumulation of DFe in intermediate waters is likely  
290 controlled by some combination of strong iron binding ligands, colloidal dynamics and  
291 authigenic iron pools. Because of the dominance of internal cycling, the concentration of  
292 Fe, relative to major nutrients N and P, and hence upper ocean iron limitation, will be  
293 strongly sensitive to small changes in the gross fluxes of regeneration and scavenging. For  
294 instance, the iron content of upper ocean phytoplankton is highly variable and fluctuations  
295 due to changing iron supply or phytoplankton species composition will affect the gross  
296 regeneration fluxes. Alternatively, biological and chemical transformations of particles,  
297 strong iron-binding ligands and/or iron speciation will modify gross scavenging rates. Both  
298 these examples would change the net regeneration rate and hence the relative to supply  
299 of DFe to the upper ocean biota. Our isopycnal framework provides a mechanistic  
300 methodology to assess ocean biogeochemical models more rigorously in future model  
301 evaluation efforts. A new generation of in situ processes studies<sup>1</sup>, tracking the evolution of  
302 Fe biogeochemistry, measuring both fluxes and particulate and dissolved Fe pools within a  
303 coherent physical framework would offer the potential to further constrain the internal  
304 cycling mechanisms for inclusion into global biogeochemical models. This improved  
305 mechanistic understanding of the ocean Fe cycle is required to reduce uncertainties in  
306 how changes in climate will affect surface ocean Fe limitation of primary productivity.

## 307 308 **Methods**

### 309 310 **Field sampling and data processing**

311 Sampling along the CLIVAR P16 section was conducted during two cruises, from Tahiti to  
312 Kodiak, Alaska aboard the R/V Thomas Thompson (9<sup>th</sup> January – 22 February 2005;

313 P16N), and from Tahiti to Antarctica aboard the R/V Roger Revelle (15<sup>th</sup> February – 25<sup>th</sup>  
314 March 2006; P16S). Samples for dFe were analysed following previously published  
315 protocols<sup>64</sup>. Briefly, 15 mL aliquots of acidified (0.024 M, HCl) sample were spiked with  
316 100 µL of an <sup>57</sup>Fe isotope enriched solution (Fe concentration of 177 nM) and UV-oxidised  
317 (>1 h). After cooling overnight, samples were buffered with ammonium acetate to pH 6.4 ±  
318 0.2 prior to being passed through a column packed with Toyopearl AF-Chelate-650M.  
319 Extracted Fe was subsequently eluted with 1 M HNO<sub>3</sub> into 1 mL aliquots and analysed by  
320 High Resolution-Inductively Coupled Plasma-Mass Spectrometry (Thermo Finnigan  
321 Element 1). dFe concentrations were quantified using a standard isotope dilution  
322 equation. The analytical limit of detection (LOD; 3xSD of blank) averaged 0.019 nM (n=20)  
323 during the analysis period, while the procedural LOD (based on 3xSD of replicate analysis  
324 of SAFe S1) averaged 0.034 nM (n=29). Accuracy and precision was assessed through  
325 the replicate extraction and analysis of SAFE and GEOTRACES seawater reference  
326 materials<sup>64</sup>. Typical within run precision averaged 2.2% (1RSD, n=27) at iron  
327 concentrations around 1 nM and 11.8% (1RSD, n=29) at lower iron concentrations (~0.1  
328 nM). AOU was calculated from oxygen saturation (derived using temperature and salinity).  
329 DFe, PO<sub>4</sub> and AOU were binned within the intermediate water density layers (28.6-27.2)  
330 and between latitudes of 46S and 10S. Statistics were performed using Type II  
331 regressions via the R package 'lmodel2'. The net regeneration (Fe<sub>REG</sub>) that results from  
332 the near-balance between regeneration and scavenging is derived by combining the Fe /  
333 AOU slope from the P16 with AOU using oxygen, temperature, salinity and DFe data from  
334 IDP2017<sup>26</sup> between the 26.8-27.2 isopycnal layer that represents intermediate water. Field  
335 data from the P16 voyage is available from BCO-DMO.

336

### 337 **Corrections for Lithogenic and algal Biogenic Fe**

338 Presuming that total particulate Fe in any sample is the sum of algal biogenic (PFeBio, P-  
339 associated), lithogenic (PFeLith, Al- or Ti-associated), and scavenged sub-fractions, we  
340 estimate scavenged Fe (PFeScav) by sequentially subtracting estimated lithogenic  
341 (PFeLitho), non-lithogenic (PFeNonLitho) and authigenic (PFeAuth) fractions via the  
342 following three balances: PFeTotal = PFeLitho + PFeBio + PFeScav, PFeNonLitho =  
343 PFeTotal – PFeLitho and PFeAuth = PFeNonLitho – PFeBio. In this study we based  
344 lithogenic Fe corrections on two assumptions: 1) lithogenic material in the ocean is  
345 ultimately derived from a crustal source(s) with estimable, fixed composition(s), and 2)  
346 lithogenic particles are refractory, meaning that elemental exchange with dissolved or  
347 other particulate pools during their marine residence times (weeks to years)<sup>24</sup> does not  
348 significantly alter their composition. To estimate and correct for lithogenic Fe we quantify  
349 the number and composition of potential lithogenic end-members. Via the ratios of Al, Ti  
350 and Th we address the compositional gradients of lithogenic particles in the GP16 transect  
351 and estimate the fractional composition of each end-member (see Supplementary Note  
352 and Supplementary Figures 3 and 4). We then correct for lithogenic Fe using Fe/Al or  
353 Fe/Ti ratio(s) from one or more end-member(s) in turn for a total of three lithogenic Fe  
354 estimates. Finally, algal biogenic Fe (PFeBio), is derived from particulate phosphorus (PP)  
355 concentrations and estimates of the algal biogenic Fe/P ratio. This analysis is performed  
356 using data from the GP16 section from the GEOTRACES IDP2017<sup>26</sup>.

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### **Author Contributions**

The study was designed by A.T and P.W.B, with input from M.J.E and A.R.B. A.T conducted the analysis. W.M.L and A.M provided datasets from P16. B.S.T and D.C.O analysed phytoplankton and particulate datasets. T.D performed the ocean circulation model inversion. The paper was written by A.T and P.W.B, with contributions from all co-authors.

### **Competing interests**

The authors declare no competing interests.

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**Figure Captions:**

**Figure 1. Study Area.** The southern part of the CLIVAR P16S line in the south Pacific Ocean, on a backdrop of water age (years) from the OCIM model for the intermediate water isopycnal layer ( $\sigma_0=26.8-27.2$ ). The individual stations used in this analysis are marked with red crosses.

**Figure 2. Linking phosphate and dissolved iron to apparent oxygen utilisation.** Plots of  $\text{PO}_4$  (phosphate) and DFe (dissolved iron) observations against AOU (apparent oxygen utilisation) observations between the  $\sigma_0= 26.8-27.0$  isopycnal layers along the P16 transect through the South Pacific Ocean, performed with a Type II regression

**Figure 3. Origins of dissolved iron in IDP2017.** The fraction of the dissolved iron concentration from the IDP2017 explained by the regeneration – scavenging balance between the  $\sigma_0= 26.8-27.0$  isopycnal layers is quantified here. The magnitude of the regeneration – scavenging balance (in  $\text{Fe}_R$ ,  $\text{mol m}^{-3}$ ) can be derived by using the slope of the apparent oxygen utilisation – dissolved iron relationship from the P16 transect ( $2.7 \mu\text{mol dissolved iron mol apparent oxygen utilisation}^{-1}$ ) and the independent apparent oxygen utilisation and dissolved iron datasets from the GEOTRACES IDP2017. The net regeneration of dissolved iron ( $\text{Fe}_R$ ) is then divided by the observed total dissolved iron to quantify the fraction explained by the regeneration – scavenging balance. The median value of 0.57 is indicated with a vertical dashed line. This indicates that over half of the observed dissolved iron is explained by the regeneration – scavenging balance.

413 **Table 1.** Meta-analysis of median and inter-quartile ranges (IQR) stoichiometric ratios from  
 414 phytoplankton, particles (with different lithogenic corrections applied), sediment trap fluxes  
 415 (with local estimates of lithogenic Fe or applying a conservative 80% lithogenic correction)  
 416 and below mixed layer regeneration rates from process studies. Median ratios and slopes  
 417 are in units of  $\mu\text{mol/mol}$  (Fe/C) or  $\text{mmol/mol}$  (P/C), while rates are either  $\text{nmol dFe m}^{-3} \text{yr}^{-1}$   
 418 or  $\mu\text{mol PO}_4 \text{m}^{-3} \text{yr}^{-1}$   
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	<b>Detail</b>	<b>Fe/C Median</b>	<b>IQR</b>	<b>P/C Median</b>	<b>IQR</b>
<b>Phyto- plankton</b>	South tropical Pacific	16.0	7.8-40.7		
	South Pacific <sup>65</sup>	15.3	9.7-26.5		
	Equatorial Pacific <sup>66</sup>	11.7	6.9-20.4		
	North Pacific	20.2	9.8-55.0		
	North Atlantic <sup>67</sup>	31.3	19.8-59.9		
<b>Marine Particles*</b>	Ti endmember	48.21	2.67-204.76	12.73	11.38-14.55
	Al endmember	196.4	105.5-396.7		
	Al/Ti endmember	103.35	56.69-175.83		
		<b>Fe/C Median</b>	<b>IQR</b>	<b>P/C Median</b>	<b>IQR</b>
<b>Export^</b>	SAZ-Sense, FeCycle I and II sediment traps <sup>44-46</sup>	141.6	190.6	5.6	3.6
		<b>Fe rate Median</b>	<b>IQR</b>		
<b>Regener- ation~</b>	Experiments and budgets <sup>45,47,48</sup>	485.5	855.9		
		<b>Fe/C</b>	<b>Fe Rate</b>	<b>P/C</b>	<b>P Rate</b>
<b>Dissolved</b>	Intermediate water	3.92 $\pm 0.99$	2.34	11.48 $\pm 0.71$	6.75

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422 \*particles collected from bottles during GEOTRACES GP16 voyage between Ecuador and  
 423 Tahiti in the south Pacific above the intermediate water layer and west of station 23 to  
 424 avoid influence of low oxygen waters (n=54).  
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427 ^Calculated non-lithogenic flux from sediment traps from the SAZ-Sense, FeCycle I and  
 428 FeCycle II process studies, either by using local corrections or a conservative estimate of  
 429 80% lithogenic Fe (n=14 for Fe and 11 for P).

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431 ~Regeneration rates are compiled from all direct measurements of solubilization of  
 432 particles collected from below the mixed layer and iron budget calculations of iron  
 433 regeneration (n=6).

434

#### 434 **Data Availability**

435 All the data used in this research are freely available and may be downloaded through the  
 436 links detailed in the Methods section.

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