Title: Multi-decadal trend of increasing iron stress in Southern Ocean phytoplankton

Authors: Thomas J. Ryan-Keogh[1*†], Sandy J. Thomalla[1,2†], Pedro M. S. Monteiro[1,2], Alessandro Tagliabue[3]

1. Southern Ocean Carbon-Climate Observatory, CSIR; Cape Town, 7700, South Africa
2. Marine and Antarctic Research for Innovation and Sustainability, University of Cape Town; Cape Town, 7700, South Africa
3. Department of Earth, Ocean and Ecological Sciences, School of Environmental Sciences, University of Liverpool; Liverpool, L69 3GP, UK

*Corresponding author. Email: tryankeogh@csir.co.za

† These authors contributed equally to this work.

Abstract: Southern Ocean primary productivity is primarily controlled by adjustments in light and iron limitation, but the spatial and temporal determinants of iron availability, accessibility and demand are poorly constrained, hindering accurate long-term projections. We present here a unique multi-decadal record of phytoplankton photophysiology between 1996 – 2022, from historical *in situ* datasets collected by BGC-Argo floats and ship-based platforms. We find a significant multi-decadal trend in irradiance-normalised non-photochemical quenching due to increasing iron stress, with concomitant declines in regional net primary production. The observed trend of increasing iron stress results from changing Southern Ocean mixed layer physics, as well as complex biological and chemical feedbacks that are indicative of important ongoing changes to the Southern Ocean carbon cycle.

Summary Sentence: Southern Ocean phytoplankton exhibit a significant multi-decadal increase in iron stress with climate implications.

28   **Main Text**

29

30   The Southern Ocean acts as the climate flywheel of the planet, buffering the impacts of climate

31   change by accounting for half of the total oceanic uptake of anthropogenic CO_2, absorbing three

32   quarters of the excess heat generated by anthropogenic CO_2 ([1], [2]), whilst also regulating the

33   supply of nutrients in support of low latitude productivity ([3]). Net primary production (NPP) is a

34   major contributor to biological carbon export, ~2 Pg C year^{-1} ([4]), in the Southern Ocean and

35   supports rich marine ecosystems ([5]), driven in part by high macronutrient availability and

36   summertime light levels, but ultimately constrained by seasonal changes in light and a scarce

37   supply of the essential micronutrient iron (Fe) ([6], [7]). Substantial progress has been made in

38   understanding the range of Southern Ocean Fe supply mechanisms and biogeochemical cycling

39   processes that act to govern contemporary NPP ([8], [9]). Fe availability in the surface ocean is a

40   complex mix of concurrent biotic and abiotic processes that rapidly consume and recycle Fe, as

41   well as remove it from solution by particle scavenging and colloidal pumping ([9]). A central role

42   is played by the mixed layer depth, which influences seasonal and sub-seasonal Fe supply ([8], [10])

43   simultaneously altering light availability, which affects phytoplankton growth and Fe demand

44   ([11], [12]). It is likely that anthropogenic forcing will affect all of these supply and removal terms

45   ([13]) in a complex manner, impacting Fe availability, NPP, ecosystem function and the transfer of

46   carbon, energy and nutrients through pelagic and benthic food webs ([5]). Observational

47   constraints on how climate variability impacts Fe availability for phytoplankton is, therefore, a

48   crucial component of Southern Ocean environmental change.

49

50   The Southern Ocean experiences climate variability associated with the Southern Annular Mode

51   (SAM) (*14–16*), with the recent increase in the positive phase of the SAM due to ozone depletion

52   and greenhouse gases driving an intensification and poleward shift of the westerly winds (*15*).

53   This is considered the clearest and most persistent change in Southern Hemisphere climate in the

54   last half century (*17*). Changes in Southern Ocean winds associated with the SAM elicit

55   widespread alterations of ocean vertical stratification and mixed layer depth (*18–20*), affecting

56   nutrient supply and the light environment, which interact seasonally to influence phytoplankton

57   growth (*5*). The poleward shift of the westerly winds may also impact atmospheric dust

58   deposition further altering Fe supply to the surface ocean (*21*). Any observable climate

59   adjustments will integrate changes associated with the SAM such as altered ocean stratification,

60   mixing and atmospheric deposition, with stronger projected changes in warming, carbonate

61   chemistry and ocean transport (*22*). Crucial to both contemporary and future trends in NPP, is

62   the response of Fe supply, availability and demand, which will be a key driver. However, there

63   are presently poor constraints on changing Fe supply and demand, and little consensus on the

64   impact of ocean warming and altered carbonate chemistry on Fe bioavailability in the Southern

65   Ocean (*5, 13*). Earth System Models tend to predict increased Southern Ocean NPP by the end of

66   the 21st century but are typified by significant inter-model disagreement (*23*). These

67   uncertainties in NPP trends are amplified by poor constraints on the Fe cycle components of

68   earth system models themselves (*24*), especially regarding projected changes in Fe stress (*25*),

69   for which there are no observation-based datasets presently available.

70

71   It is not possible to directly infer Fe stress from observed ambient concentrations, as standing

72   stocks are severely depleted by biological uptake (*26*) being maintained by recycling (*10*) and

4

73   there is substantial plasticity of phytoplankton cellular contents and requirements (*11*, *12*), which

74   necessitates experimental approaches (*27*). Manipulation experiments of natural or cultured

75   communities incubated in bottles (*6*) or via *in situ* open ocean fertilization (*28*, *29*) provide

76   insight regarding the role of Fe addition, while proteomic techniques quantify cellular responses

77   to *in situ* resource stresses of specific organisms (e.g., 30). Results from decades of research have

78   identified various responses in the probability of energy allocation of photons from a net balance

79   perspective in response to varying Fe and light conditions that stem from the central role that Fe

80   plays in photosynthesis (Fig. 1). For example, under optimal light and Fe replete conditions (Fig.

81   1A) phytoplankton photochemistry is at maximum capacity with any remaining energy being

82   dissipated as either fluorescence or non-photochemical quenching (NPQ; the dissipation of

83   excess energy in the form of heat; 31). Under nutrient replete conditions with high light stress

84   (Fig. 1B) there is a reduction in photochemistry to prevent photodamage to photosystem II and a

85   reduction in fluorescence (i.e., the common scenario of suppressed fluorescence measured during

86   daylight hours) with the dominant sink of excess energy being NPQ. Phytoplankton can adjust to

87   low average light levels by synthesizing additional photosynthetic reaction centres for increased

88   light absorption (*32*). However, because of the high Fe requirement of reaction centres, Southern

89   Ocean phytoplankton have evolved a photoacclimation strategy in response to their typically low

90   light and Fe environment (*7*, *27*) that economizes their Fe use by enhancing light absorption

91   through increased light harvesting antennae size (with additional pigment complexes) rather than

92   the number of reaction centres (*12*). Selective pressure for this strategy however reduces the

93   efficiency of excitation energy transfer (from light harvesting pigments to reaction centres) and

94   can result in a bottleneck and buildup of protons under low Fe conditions (*33*). The result of this

95   scenario (under optimal light and Fe deplete conditions, Fig. 1C) is an equal allocation of energy

5

96   to photochemistry (as in an optimal light and Fe scenario, Fig. 1A) but with a greater proportion

97   of energy being dissipated as fluorescence. This drives the universal and readily observed

98   increase in fluorescence to chlorophyll ratios under low Fe conditions (*34*, *35*). If we consider a

99   Fe limited but high light environment (Fig. 1D), phytoplankton avoid overexcitation and damage

100   to their photosystems by reducing photochemistry and fluorescence with the dominant energy

101   sink being NPQ. This is further supported by an increase in the synthesis of photoprotective

102   pigments involved in the xanthophyll cycle under Fe limiting conditions (*36*). An observed

103   increase in NPQ (in surface sunlit waters) is thus expected to reflect an increase in Fe stress

104   under high light conditions. Although this photophysiological plasticity may not be common to

105   all Southern Ocean phytoplankton, with a few exceptions exhibiting limited NPQ capacity to the

106   same stressors (Table S1), experiments that expressed a measurable increase in NPQ from excess

107   energy diversion were always in response to Fe limiting conditions (Table S1). These

108   photophysiological responses to Fe and light have a well-founded mechanistic basis and the

109   potential to provide a diagnostic appraisal of environmental conditions (*37*).

110

111   **Changing Photophysiology in the Southern Ocean**

112

113   A novel *in vivo* approach developed by Ryan-Keogh & Thomalla (*38*) quantifies the degree of

114   NPQ (which manifests as a measurable decrease in the ratio of photons emitted as fluorescence

115   to those absorbed by pigments) as a function of available light (irradiance-normalised NPQ,

116   referred to as α_{NPQ} in Ryan-Keogh & Thomalla (*38*)). Since the dominant influence of

117   "instantaneous" environmental light conditions on the degree of quenching are accounted for in

118   the determination of irradiance-normalised NPQ (as the slope of NPQ against *in situ* irradiance;

6

119   see Materials and Methods), this approach uniquely fingerprints the photophysiological response

120   of phytoplankton to their environment, independent of current light conditions and inclusive of

121   pigment configuration. A particular strength of this approach is that it can be applied to any

122   ocean profile with coincident measurements of fluorescence, photosynthetically active radiation

123   and backscatter or beam attenuation (e.g., ship-based, BGC-Argo profiling floats or autonomous

124   gliders), providing a unique opportunity to deliver a long-term time series by taking advantage of

125   historical measurements (see Materials and Methods). Here, we quantify irradiance-normalised

126   NPQ from a data set of 47 BGC-Argo floats and 194 cruises comprising a total of 5795 profiles

127   spanning 26 years (Fig. 2; see Materials and Methods), to produce the first multi-decadal (1996 –

128   2022) *in situ* assessment of irradiance-normalised NPQ in the Southern Ocean biome (defined

129   here as the spatial extent of the subpolar and ice biomes (*39*). We find a significant (Table 1; F-

130   statistic = 260.50, p<0.001, r^2 = 0.92) positive linear trend in irradiance-normalised NPQ (Fig. 2)

131   in the Southern Ocean (4.69% yr^{-1}) which is robust (p<0.001 – <0.05) across different seasons

132   (Fig. S1A–D), ocean basins (Fig. S1E–G) and frontal zones (Fig. S1H–J). Moreover, this trend is

133   not affected by an unequal distribution of observations by year, with no change in trend when the

134   sample size is retained at a minimum (n = 3) over time (Fig. S2A) or using a Monte Carlo

135   experiment where the years were randomly sampled (i.e., a jackknife resampling of 75% of the

136   1996 to 2022 range: Fig. S2B). These additional tests are indicative of the robustness of the

137   detected trend in irradiance-normalised NPQ that is not significantly affected by seasonal, spatial

138   or temporal bias in data coverage. The link between Southern Ocean contemporary climate

139   variability and the trend in annual mean irradiance-normalised NPQ is highlighted by its

140   significant correlation with the decadal rolling mean of the SAM index (Fig. S3, r^2 = 0.62,

141   p<0.001), which implies that Southern Ocean phytoplankton are experiencing a multi-decadal

7

142   photophysiological adjustment, via their irradiance-normalised NPQ, to changes in nutrient and

143   light availability from altered stratification,   mixed layer dynamics and dust deposition. If this

144   trend were driven primarily by increasing Fe stress, it would suggest significant implications for

145   adjustments in regional NPP and the effectiveness of the biological carbon pump.

146

147   The likelihood that variability in irradiance-normalised NPQ is primarily reflecting Fe stress is

148   supported by the fact that this proxy was significantly higher in control versus Fe addition

149   incubation experiments in the sub-Antarctic Southern Ocean (*38*) that it is well correlated with

150   elevated fluorescence to Chl ratios in Fe limited regions of the Southern Ocean (*35*) and it

151   reproduces known gradients in Southern Ocean Fe limitation, from both natural and artificial Fe

152   fertilization experiments. For example, BGC-Argo profiles upstream and downstream of the

153   Kerguelen Plateau (Fig. 3A), a region with a well characterised island mass Fe fertilization effect

154   (*40*), show significantly lower irradiance-normalised NPQ values (t-statistic = -12.74, $p < 0.001$,

155   df = 1011) in Fe fertilized downstream waters (mean = 16.6×10^{-3}, SE = 0.41×10^{-3}, n = 525)

156   compared to Fe-limited upstream locations (mean = 23.3×10^{-3}, SE = 0.44×10^{-3}, n = 470).

157   Similarly, ship-based profiles in and out of Fe addition patches during the SOIREE (*28*) and

158   SOFEx (*29*) mesoscale Fe fertilization experiments (Fig. 3A) are typified by irradiance-

159   normalised NPQ values that are significantly lower (t-statistic = 2.95 & 2.66, $p < 0.05$, df = 12 &

160   18, respectively) in patch (mean = 3.0×10^{-3}, SE = 1.24×10^{-3}, & 3.3×10^{-3}, SE = 0.97×10^{-3}, n

161   = 6 & 8, respectively) compared to out of patch (mean = 9.1×10^{-3}, SE = 1.72×10^{-3}, & 21.6 ×

162   10^{-3}, SE = 4.79×10^{-3}, n = 4 & 16, respectively). Finally, across all available Southern Ocean

163   data, irradiance-normalised NPQ values in spring (Fig. 3B) and summer (Fig. 3C) are

164   significantly higher than those from autumn (Fig. S4A; spring = t-statistic = 2.10, $p < 0.05$, df =

8

165 2392; summer = t-statistic = 3.29, p<0.001, df = 3555) and winter (Fig. S4B; spring = t-statistic

166 = 3.92, p<0.001, df = 2236; summer = t-statistic = 4.89, p<0.001, df = 3399), in accordance with

167 expected spring and summer time Fe depletion from biological utilisation (*7*, *10*). Since a

168 photoacclimation response to seasonal variability in light would drive the opposite relationship,

169 this further supports the role of Fe-stress in driving irradiance-normalised NPQ.

170

171 Although the effect of instantaneous light is accounted for when deriving irradiance-normalised

172 NPQ, longer term photoacclimation strategies may also impact the trend (and seasonal

173 characteristics) observed in irradiance-normalised NPQ. These photophysiological adjustments

174 can also be detected through changes in cellular chlorophyll to carbon (Chl:C) ratios, however it

175 is important to note that these reflect phytoplankton's combined photoacclimation and nutrient

176 allocation response. Chl:C ratios are expected to increase in response to low light (*41*), however

177 photoacclimation occurs more effectively during Fe replete conditions (*42*), such that the degree

178 of response in Chl:C is primarily dependent on Fe availability. Particulate backscatter (b_{bp}) (from

179 both satellite and in situ sensors) can act as proxies for phytoplankton carbon (*43–45*), and their

180 proportion relative to chlorophyll can be used to infer cellular Chl:C ratios. The positive trend

181 observed in Chl:C from satellite remote sensing (r^2 = 0.62, 0.81% yr^{-1}, p<0.001; Fig. S5) for the

182 coincident period (1998 – 2021), suggests that phytoplankton are responding to a reduction in

183 available light by increasing cellular packaging of chlorophyll. This is supported by a spatially

184 coherent trend of a significant decrease in mixed layer light across the Southern Ocean (Fig. S6).

185 As such, photoacclimation/photoadaptation to low light conditions may contribute to the

186 observed trend in irradiance-normalised NPQ. That said, any reduction in available light in the

187 typically iron stressed Southern Ocean (7, 27) would increase Fe demand (*12*, *46*) and increase

188   Fe stress in the absence of sufficient increases in Fe supply. When the trend in Chl:C is

189   investigated *in situ* (2015 – 2021) (restricted to BGC-Argo as, unlike irradiance-normalised

190   NPQ, fluorescence derived estimates of chlorophyll and optical proxies for carbon cannot be

191   merged across different sensors from the ship-based dataset due to differences in sensors and

192   manufacturer calibration coefficients), the integrated mixed layer trend (although insignificant) is

193   instead negative ($r^2 = 0.50$, -3.59% yr^{-1}, $p = 0.07$) reflecting a more typical response to Fe stress

194   (i.e., a decrease in Chl:C with a decrease in growth rates under Fe limiting conditions), with no

195   evidence of photoacclimation/photoadaptation. Moreover, a significant a negative relationship is

196   observed between *in situ* increasing irradiance-normalised NPQ and decreasing Chl:C (2015 –

197   2021) (Fig. S7A-C; $r^2 = 0.51 – 0.54$, $p<0.001$), which strongly suggests that the

198   photophysiological trend in irradiance-normalised NPQ is in response to iron stress (rather than

199   low light). Similarly, when the seasonal characteristics are interrogated, Chl:C ratios are

200   significantly higher in winter than in summer (Fig S8; t-statistic = 18.7 – 21.9, $p<0.001$, df =

201   2019 – 2113) reflecting typical photoacclimation in response to low light conditions (*41*). Were

202   photoacclimation the dominant driver of seasonal variability in NPQ it would elicit an increase in

203   irradiance-normalised NPQ in winter. The opposite response however (Fig. 3B,C) suggests that

204   Fe stress is instead most likely to be the dominant driver of seasonal variability in irradiance-

205   normalised NPQ.

206

207   **Trends in Primary Productivity**

208

209   Any trend of increasing Fe stress should reflect in concurrent reductions in photosynthetic

210   capacity and a decline in overall productivity, with large implications for biogeochemical cycling

10

211 and carbon drawdown (*47*). We note however that a decline in NPP, although expected in

212 response to an increase in Fe stress, is not a certainty (or a necessary requirement to verify Fe

213 stress), as indeed an increase in standing stocks (from increasing NPP) could drive an increase in

214 Fe stress. Similarly, trends in NPP may also reflect top-down controls of grazing that are

215 independent of Fe stress. Nonetheless, when we apply two models of NPP (*48*, *49*) to the

216 Southern Ocean BGC-Argo data set (restricted to this platform for the same reason as described

217 above, 2014 – 2021; see Materials and Methods), we observe a decrease in NPP for both models

218 (Fig. 4). While the decline in NPP from the CbPM model is significant (Fig. 4A, 10% yr^{-1}, r^2 =

219 0.81, p<0.01; Table 1), the decreasing trend from the VGPM model is insignificant (Fig. 4A, 8%

220 yr^{-1}, r^2 = 0.43, p = 0.08), but both are on a similar order of magnitude as the increase in

221 irradiance-normalised NPQ for the same time period (4.72% yr^{-1}, r^2 = 0.56, p<0.05). When we

222 apply the same two NPP models in combination with an additional two NPP models (*50*, *51*) to a

223 concomitant 24 year time series (1998 – 2021) from the Ocean Colour Climate Change Initiative

224 product (*52*) (see Materials and Methods), we see dominant declines in NPP for the subpolar and

225 ice biomes (*39*) from the carbon-based CbPM models and absorption-based CAFE model (with

226 61 – 80% of the trends being negative and 10 – 29% positive; Fig. 4B-D). Although the VGPM

227 model shows an increase in NPP (77% positive and 13% negative; Fig. 4C) this can be explained

228 by its strong dependence on trends in chlorophyll that are augmented by Southern Ocean

229 warming (*5*, *53*). Similar results were observed in a recent study by Pinkerton et al. (*54*) (with

230 different satellite data and trend detection methods) but with all trends in NPP from the CbPM

231 model being negative with an overall negative but insignificant trend of -0.15% yr^{-1} (p = 0.17),

232 whereas NPP from the VGPM model were positive and significant (0.8% yr^{-1}, p < 0.001).

233 However, when we investigate trends in NPP for the same period (1996 – 2021) from earth

234   system models of the Coupled Model Intercomparison Project phase 6 (CMIP6) we see very

235   little multi-decadal variability, with trends in NPP that range from -0.22% to 0.21% yr^{-1} ($r^2 = 1.5$

236    $\times 10^{-3} – 0.42$, Fig. 4F; Table 1). While most earth system models show insignificant trends in

237   NPP, three display significant positive trends ($0.10 – 0.15\%$ yr^{-1}, $p<0.05$, Table 1) while two

238   others depict significant negative trends (-0.01% and -0.22% yr^{-}1, $p<0.05$, Table 1). Once

239   projected to the end of the century however, the majority of CMIP6 models (>80%) agree on an

240   increasing trend in NPP (23) at odds with trends currently observed to be ongoing.

241

242   **Sensitivity of Fe limitation to climate drivers**

243

244   The progressive trend of increasing *in situ* irradiance-normalised NPQ observed here over the

245   past 26 years reflects the impact of a suite of concurrent physical, chemical and biological

246   processes on the Southern Ocean Fe cycle and the response of phytoplankton production

247   (inclusive of physiological plasticity and adaptability), ranging from changing Fe supply,

248   speciation and recycling to adjustments in phytoplankton Fe demands and interactions with other

249   microbes (9, 55). The key challenge is that large scale *in situ* datasets are largely concerned with

250   ocean physics at spatio-temporal scales that are not matched by biological and chemical process

251   experiments (9). Overall, the trend in irradiance-normalised NPQ showed moderate correlations

252   with the dominant climate trends of reduced pH and surface warming (Fig. S9A,B, Table S2; $r^2 =$

253   0.42 and 0.36, respectively; $p<0.001$). This relationship with pH would agree with previous

254   studies that exhibit reduced Fe uptake under ocean acidification scenarios (56) due to potential

255   inhibition of the Fe uptake mechanisms (57). Moreover, ocean acidification is likely to impact

256   the availability of Fe bound to organic ligands as a lower pH will affect both Fe adsorption and

257 complexation (*58*, *59*). Direct impacts of a reduced pH on NPQ is also likely as this mechanism

258 relies upon a trans-thylakoid membrane pH gradient (*60*), which would be impacted by a buildup

259 of intracellular hydrogen ions (*61*). The relationship with surface warming more likely reflects

260 independent changes to Fe delivery (e.g., 14) or poorly constrained impacts on Fe speciation,

261 bioavailability and demand (*13*). Relating the trend in irradiance-normalised NPQ to the

262 dominant SAM driven response of altered wind (namely vertical mixing and stratification)

263 showed some linkages, with a significant correlation between deeper summer mixed layer depths

264 (Fig. S9C, $r^2 = 0.39$, $p<0.05$), but no correlation with autumn, winter or spring mixed layer

265 depths (Fig. S9D-F, $p>0.05$). Recent evidence (24) has shown that in the Southern Ocean

266 summer there is a deepening of the mixed layer ($-3.4\% \pm 1.5\%$ decade^{-1}), which could increase

267 Fe demand (by decreasing light availability) and a significant increase in stratification ($8.1\% \pm$

268 4.1% decade^{-1}), which could negatively impact subseasonal Fe supply (e.g., from storm driven

269 entrainment, 8). Furthermore, it is also likely that for some key regions of the Southern Ocean,

270 local signals linked to changing Fe supply from dust, margins, glaciers or sea ice may be

271 important (*5*).

272

273 Adjustments in irradiance-normalised NPQ are fingerprinted by the well understood response of

274 phytoplankton photophysiology to Fe limitation. If the trend in irradiance-normalised NPQ

275 observed here is indeed reflecting a long-term increase in Fe stress, with an amplitude

276 adjustment in time (Fig. 2) similar to that observed from natural Fe fertilisation (Fig. 3A),

277 alongside a concomitant decrease in NPP (from *in situ* BGC-Argo floats 2014 – 2021; Fig. 4A

278 and CbPM satellite derived Fig. 4B), the implications are that earth system models may be

279 underestimating ongoing change in the Southern Ocean. Both CMIP5 and CMIP6 earth system

13

280 models tend to project a trend of increasing NPP and reducing Fe stress in the Southern Ocean

281 by the end of the 21st century in response to climate change (*23*), which is opposite to the

282 observed trend emerging across the region in this study. Improved knowledge of how Fe stress

283 interacts with other limiting factors and the role of parallel changes in phytoplankton species

284 composition and top-down control by grazers would enable us to link changing climate drivers,

285 growing Fe stress and altered NPP more robustly in the Southern Ocean and improve confidence

286 in projections. A major strength of irradiance-normalised NPQ is that it is a photophysiological

287 *in situ* measurement that can be applied retrospectively to appropriately equipped platforms to

288 span timeframes that reflect an integrated response to climate change and may help provide

289 emergent constraints for earth system models for improved climate projections.

290

291 **References:**

292 1.   T. L. Frölicher, J. L. Sarmiento, D. J. Paynter, J. P. Dunne, J. P. Krasting, M. Winton,

293   Dominance of the Southern Ocean in Anthropogenic Carbon and Heat Uptake in CMIP5

294   Models. *Journal of Climate*. **28**, 862–886 (2015).

295 2.   N. Gruber, P. Landschützer, N. S. Lovenduski, The Variable Southern Ocean Carbon

296   Sink. *Annual Review of Marine Science*. **11**, 159–186 (2019).

297 3.   J. L. Sarmiento, N. Gruber, M. A. Brzezinski, J. P. Dunne, High-latitude controls of

298   thermocline nutrients and low latitude biological productivity. *Nature*. **427**, 56–60 (2004).

299 4.   R. Schlitzer, Carbon export fluxes in the Southern Ocean: results from inverse modeling

300   and comparison with satellite-based estimates. *Deep Sea Research Part II: Topical Studies*

301   *in Oceanography*. **49**, 1623–1644 (2002).

302   5.   S. F. Henley, E. L. Cavan, S. E. Fawcett, R. Kerr, T. Monteiro, R. M. Sherrell, A. R.

303   Bowie, P. W. Boyd, D. K. A. Barnes, I. R. Schloss, T. Marshall, R. Flynn, S. Smith,

304   Changing Biogeochemistry of the Southern Ocean and Its Ecosystem Implications .

305   *Frontiers in Marine Science* . **7** (2020), p. 581.

306   6.   J. H. Martin, R. M. Gordon, S. E. Fitzwater, Iron in Antarctic waters. *Nature*. **345**, 156–

307   158 (1990).

308   7.   P. W. Boyd, Environmental factors controlling phytoplankton processes in the Southern

309   Ocean. *Journal of Phycology*. **38**, 844–861 (2002).

310   8.   S.-A. Nicholson, M. Lévy, J. Jouanno, X. Capet, S. Swart, P. M. S. Monteiro, Iron supply

311   pathways between the surface and subsurface waters of the Southern Ocean: from winter

312   entrainment to summer storms. *Geophysical Research Letters*. **46**, 14567– 14575 (2019).

313   9.   A. Tagliabue, A. R. Bowie, P. W. Boyd, K. N. Buck, K. S. Johnson, M. A. Saito, The

314   integral role of iron in ocean biogeochemistry. *Nature*. **543**, 51–59 (2017).

315   10.   A. Tagliabue, J. B. Sallée, A. R. Bowie, M. Lévy, S. Swart, P. W. Boyd, Surface-water

316   iron supplies in the Southern Ocean sustained by deep winter mixing. *Nature Geoscience*.

317   **7**, 314–320 (2014).

318   11.   W. G. Sunda, S. A. Huntsman, Iron uptake and growth limitation in oceanic and coastal

319   phytoplankton. *Marine Chemistry*. **50**, 189–206 (1995).

320   12.   R. F. Strzepek, P. W. Boyd, W. G. Sunda, Photosynthetic adaptation to low iron, light, and

321   temperature in Southern Ocean phytoplankton. *Proceedings of the National Academy of*

322   *Sciences*. **116**, 4388–4393 (2019).

323   13.   D. A. Hutchins, P. W. Boyd, Marine phytoplankton and the changing ocean iron cycle.

324   *Nature Climate Change*. **6**, 1072–1079 (2016).

325   14.   S. A. Henson, J. L. Sarmiento, J. P. Dunne, L. Bopp, I. Lima, S. C. Doney, J. John, C.

326   Beaulieu, Detection of anthropogenic climate change in satellite records of ocean

327   chlorophyll and productivity. *Biogeosciences*. **7**, 621–640 (2010).

328   15.   N. C. Swart, J. C. Fyfe, O. A. Saenko, M. Eby, Wind-driven changes in the ocean carbon

329   sink. *Biogeosciences*. **11**, 6107–6117 (2014).

330   16.   A. G. Marshall, M. A. Hemer, H. H. Hendon, K. L. McInnes, Southern annular mode

331   impacts on global ocean surface waves. *Ocean Modelling*. **129**, 58–74 (2018).

332   17.   L. M. Polvani, D. W. Waugh, G. J. P. Correa, S.-W. Son, Stratospheric Ozone Depletion:

333   The Main Driver of Twentieth-Century Atmospheric Circulation Changes in the Southern

334   Hemisphere. *Journal of Climate*. **24**, 795–812 (2011).

335   18.   N. S. Lovenduski, N. Gruber, Impact of the Southern Annular Mode on Southern Ocean

336   circulation and biology. *Geophysical Research Letters*. **32** (2005),

337   doi:https://doi.org/10.1029/2005GL022727.

338   19.   J. B. Sallée, K. G. Speer, S. R. Rintoul, Zonally asymmetric response of the Southern

339   Ocean mixed-layer depth to the Southern Annular Mode. *Nature Geoscience*. **3**, 273–279

340   (2010).

341   20.   J.-B. Sallée, V. Pellichero, C. Akhoudas, E. Pauthenet, L. Vignes, S. Schmidtko, A. N.

342   Garabato, P. Sutherland, M. Kuusela, Summertime increases in upper-ocean stratification

343   and mixed-layer depth. *Nature*. **591**, 592–598 (2021).

344   21.   C. M. Laluraj, M. Thamban, K. Satheesan, Dust and associated geochemical fluxes in a

345   firn core from coastal East Antarctica and its linkages with Southern Hemisphere climate

346   variability over the last 50 years. *Atmospheric Environment*. **90**, 23–32 (2014).

347 22. M. Meredith, M. Sommerkorn, S. Cassotta, C. Derksen, A. Ekaykin, A. Hollowed, G.

348   Kofinas, A. Mackintosh, J. Melbourne-Thomas, M. M. C. Muelbert, G. Ottersen, H.

349   Pritchard, E. A. G. Schuur, "Polar Regions" in *IPCC Special Report on the Ocean and*

350   *Cryosphere in a Changing Climate*, H.-O. Pörtner, D. C. Roberts, V. Masson-Delmotte, P.

351   Zhai, M. Tignor, E. Poloczanska, K. Mintenbeck, A. Alegría, M. Nicolai, A. Okem, J.

352   Petzold, B. Rama, N. M. Weyer, Eds. (2019).

353 23. A. Tagliabue, L. Kwiatkowski, L. Bopp, M. Butenschön, W. Cheung, M. Lengaigne, J.

354   Vialard, Persistent Uncertainties in Ocean Net Primary Production Climate Change

355   Projections at Regional Scales Raise Challenges for Assessing Impacts on Ecosystem

356   Services. *Frontiers in Climate*. **3** (2021), (available at

357   https://www.frontiersin.org/article/10.3389/fclim.2021.738224).

358 24. A. Tagliabue, O. Aumont, R. DeAth, J. P. Dunne, S. Dutkiewicz, E. Galbraith, K. Misumi,

359   J. K. Moore, A. Ridgwell, E. Sherman, C. Stock, M. Vichi, C. Völker, A. Yool, How well

360   do global ocean biogeochemistry models simulate dissolved iron distributions? *Global*

361   *Biogeochemical Cycles*. **30**, 149–174 (2016).

362 25. A. Tagliabue, N. Barrier, H. Du Pontavice, L. Kwiatkowski, O. Aumont, L. Bopp, W. W.

363   L. Cheung, D. Gascuel, O. Maury, An iron cycle cascade governs the response of

364   equatorial Pacific ecosystems to climate change. *Global Change Biology*. **26**, 6168–6179

365   (2020).

366 26. T. J. Ryan-Keogh, L. M. DeLizo, W. O. Smith, P. N. Sedwick, D. J. McGillicuddy, C. M.

367   Moore, T. S. Bibby, Temporal progression of photosynthetic-strategy in phytoplankton in

368   the Ross Sea, Antarctica. *Journal of Marine Systems*. **166**, 87–96 (2017).

369   27.   C. M. Moore, M. M. Mills, K. R. Arrigo, I. Berman-Frank, L. Bopp, P. W. Boyd, E. D.

370   Galbraith, R. J. Geider, C. Guieu, S. L. Jaccard, T. D. Jickells, J. La Roche, T. M. Lenton,

371   N. M. Mahowald, E. Marañón, I. Marinov, J. K. Moore, T. Nakatsuka, A. Oschlies, M. A.

372   Saito, T. F. Thingstad, A. Tsuda, O. Ulloa, Processes and patterns of oceanic nutrient

373   limitation. *Nature Geoscience*. **6**, 701–710 (2013).

374   28.   P. W. Boyd, A. J. Watson, C. S. Law, E. R. Abraham, T. Trull, R. Murdoch, D. C. E.

375   Bakker, A. R. Bowie, K. O. Buesseler, H. Chang, M. Charette, P. Croot, K. Downing, R.

376   Frew, M. Gall, M. Hadfield, J. Hall, M. Harvey, G. Jameson, J. LaRoche, M. Liddicoat, R.

377   Ling, M. T. Maldonado, R. M. McKay, S. Nodder, S. Pickmere, R. Pridmore, S. Rintoul,

378   K. Safi, P. Sutton, R. Strzepek, K. Tanneberger, S. Turner, A. Waite, J. Zeldis, A

379   mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron

380   fertilization. *Nature*. **407**, 695–702 (2000).

381   29.   K. H. Coale, K. S. Johnson, F. P. Chavez, K. O. Buesseler, R. T. Barber, M. A.

382   Brzezinski, W. P. Cochlan, F. J. Millero, P. G. Falkowski, J. E. Bauer, R. H. Wanninkhof,

383   R. M. Kudela, M. A. Altabet, B. E. Hales, T. Takahashi, M. R. Landry, R. R. Bidigare, X.

384   Wang, Z. Chase, P. G. Strutton, G. E. Friederich, M. Y. Gorbunov, V. P. Lance, A. K.

385   Hilting, M. R. Hiscock, M. Demarest, W. T. Hiscock, K. F. Sullivan, S. J. Tanner, R. M.

386   Gordon, C. N. Hunter, V. A. Elrod, S. E. Fitzwater, J. L. Jones, S. Tozzi, M. Koblizek, A.

387   E. Roberts, J. Herndon, J. Brewster, N. Ladizinsky, G. Smith, D. Cooper, D. Timothy, S.

388   L. Brown, K. E. Selph, C. C. Sheridan, B. S. Twining, Z. I. Johnson, Southern Ocean Iron

389   Enrichment Experiment: Carbon Cycling in High- and Low-Si Waters. *Science*. **304**, 408–

390   414 (2004).

391   30.   M. A. Saito, M. R. McIlvin, D. M. Moran, T. J. Goepfert, G. R. DiTullio, A. F. Post, C. H.
392   Lamborg, Multiple nutrient stresses at intersecting Pacific Ocean biomes detected by
393   protein biomarkers. *Science*. **345**, 1173–1177 (2014).

394   31.   M. A. van Leeuwe, J. Stefels, Photosynthetic responses in Phaeocystis antarctica towards
395   varying light and iron conditions. *Biogeochemistry*. **83**, 61–70 (2007).

396   32.   P. G. Falkowski, J. La Roche, Acclimation to spectra irradiance in algae. *Journal of*
397   *Phycology*. **27**, 8–14 (1991).

398   33.   J. A. Raven, Predictions of Mn and Fe use efficiencies of phototrophic growth as a
399   function of light availability for growth and C assimilation pathway. *New Phytologist*.
400   **116**, 1–18 (1990).

401   34.   P. S. Schrader, A. J. Milligan, M. J. Behrenfeld, Surplus photosynthetic antennae
402   complexes underlie diagnostics of iron limitation in a cyanobacterium. *PLoS ONE*. **6**,
403   e18753 (2011).

404   35.   C. Schallenberg, R. F. Strzepek, S. Bestley, B. Wojtasiewicz, T. W. Trull, *Geophysical*
405   *Research Letters*, in press, doi:https://doi.org/10.1029/2021GL097616.

406   36.   R. J. Geider, J. la Roche, R. M. Greene, M. Olaizola, Response of the photosynthetic
407   apparatus of Phaeodactylum tricornutum (Baccilariophyceae) to nitrate, phosphate or iron
408   starvation. *J Phycol*. **29**, 755–766 (1993).

409   37.   M. J. Behrenfeld, A. J. Milligan, Photophysiological Expressions of Iron Stress in
410   Phytoplankton. *Annual Review of Marine Science*. **5**, 217–246 (2013).

411   38.   T. J. Ryan-Keogh, S. J. Thomalla, Deriving a proxy for iron limitation from chlorophyll
412   fluorescence on buoyancy gliders. *Frontiers in Marine Science*. **7**, 275 (2020).

413   39.   A. R. Fay, G. A. McKinley, Global open-ocean biomes: mean and temporal variability.

414   *Earth Syst. Sci. Data*. **6**, 273–284 (2014).

415   40.   S. Blain, B. Queguiner, T. Trull, The natural iron fertilization experiment KEOPS

416   (KErguelen Ocean and Plateau compared Study): An overview. *Deep-Sea Research Part*

417   *Ii-Topical Studies in Oceanography*. **55**, 559–565 (2008).

418   41.   K. H. Halsey, B. M. Jones, Phytoplankton Strategies for Photosynthetic Energy

419   Allocation. *Annual Review of Marine Science*. **7**, 265–297 (2015).

420   42.   C. M. Moore, S. Seeyave, A. E. Hickman, J. T. Allen, M. I. Lucas, H. Planquette, R. T.

421   Pollard, A. J. Poulton, Iron-light interactions during the CROZet natural iron bloom and

422   EXport experiment (CROZEX) I: Phytoplankton growth and photophysiology. *Deep-Sea*

423   *Research Part II: Topical Studies in Oceanography*. **54**, 2045–2065 (2007).

424   43.   G. Dall'Olmo, T. K. Westberry, M. J. Behrenfeld, E. Boss, W. H. Slade, Significant

425   contribution of large particles to optical backscattering in the open ocean. *Biogeosciences*.

426   **6**, 947–967 (2009).

427   44.   V. Martinez-Vicente, G. Dall'Olmo, G. Tarran, E. Boss, S. Sathyendranath, Optical

428   backscattering is correlated with phytoplankton carbon across the Atlantic Ocean.

429   *Geophysical Research Letters*. **40**, 1154–1158 (2013).

430   45.   J. R. Graff, T. K. Westberry, A. J. Milligan, M. B. Brown, G. Dall'Olmo, V. van Dongen-

431   Vogels, K. M. Reifel, M. J. Behrenfeld, Analytical phytoplankton carbon measurements

432   spanning diverse ecosystems. *Deep-Sea Research Part I: Oceanographic Research*

433   *Papers*. **102**, 16–25 (2015).

434   46.   R. F. Strzepek, K. A. Hunter, R. D. Frew, P. J. Harrison, P. W. Boyd, Iron-light

435   interactions differ in Southern Ocean phytoplankton. *Limnol Oceanogr*. **57**, 1182–1200

436   (2012).

437   47.   K. Petrou, M. A. Doblin, P. J. Ralph, Heterogeneity in the photoprotective capacity of

438   three Antarctic diatoms during short-term changes in salinity and temperature. *Marine*

439   *Biology*. **158**, 1029–1041 (2011).

440   48.   M. J. Behrenfeld, P. G. Falkowski, Photosynthetic rates derived from satellite-based

441   chlorophyll concentration. *Limnology & Oceanography*. **42**, 1–20 (1997).

442   49.   M. J. Behrenfeld, E. Boss, D. A. Siegel, D. M. Shea, Carbon-based ocean productivity and

443   phytoplankton physiology from space. *Global Biogeochem Cycles*. **19**, GB1006 (2005).

444   50.   T. Westberry, M. J. Behrenfeld, D. A. Siegel, E. Boss, Carbon-based primary productivity

445   modeling with vertically resolved photoacclimation. *Global Biogeochem Cycles*. **22**

446   (2008), doi:https://doi.org/10.1029/2007GB003078.

447   51.   G. M. Silsbe, M. J. Behrenfeld, K. H. Halsey, A. J. Milligan, T. K. Westberry, The CAFE

448   model: A net production model for global ocean phytoplankton. *Global Biogeochem*

449   *Cycles*. **30**, 1756–1777 (2016).

450   52.   S. Sathyendranath, R. J. W. Brewin, C. Brockmann, V. Brotas, B. Calton, A. Chuprin, P.

451   Cipollini, A. B. Couto, J. Dingle, R. Doerffer, C. Donlon, M. Dowell, A. Farman, M.

452   Grant, S. Groom, A. Horseman, T. Jackson, H. Krasemann, S. Lavender, V. Martinez-

453   Vicente, C. Mazeran, F. Mélin, T. S. Moore, D. Müller, P. Regner, S. Roy, C. J. Steele, F.

454   Steinmetz, J. Swinton, M. Taberner, A. Thompson, A. Valente, M. Zühlke, V. E. Brando,

455   H. Feng, G. Feldman, B. A. Franz, R. Frouin, R. W. Gould, S. B. Hooker, M. Kahru, S.

456   Kratzer, B. G. Mitchell, F. E. Muller-Karger, H. M. Sosik, K. J. Voss, J. Werdell, T. Platt,

457 An Ocean-Colour Time Series for Use in Climate Studies: The Experience of the Ocean-

458 Colour Climate Change Initiative (OC-CCI). *Sensors* . **19** (2019), ,

459 doi:10.3390/s19194285.

460 53. M. Auger, R. Morrow, E. Kestenare, J.-B. Sallée, R. Cowley, Southern Ocean in-situ

461 temperature trends over 25 years emerge from interannual variability. *Nat Commun*. **12**

462 (2021), doi:10.1038/s41467-020-20781-1.

463 54. M. H. Pinkerton, P. W. Boyd, S. Deppeler, A. Hayward, J. Höfer, S. Moreau, Evidence for

464 the Impact of Climate Change on Primary Producers in the Southern Ocean . *Frontiers in*

465 *Ecology and Evolution* . **9** (2021), p. 134.

466 55. P. W. Boyd, M. J. Ellwood, A. Tagliabue, B. S. Twining, Biotic and abiotic retention,

467 recycling and remineralization of metals in the ocean. *Nature Geoscience*. **10**, 167–173

468 (2017).

469 56. D. Shi, Y. Xu, B. M. Hopkinson, F. M. M. Morel, Effect of ocean acidification on iron

470 availability to marine phytoplankton. *Science*. **327**, 676–679 (2010).

471 57. J. B. McQuaid, A. B. Kustka, M. Oborník, A. Horák, J. P. McCrow, B. J. Karas, H.

472 Zheng, T. Kindeberg, A. J. Andersson, K. A. Barbeau, A. E. Allen, Carbonate-sensitive

473 phytotransferrin controls high-affinity iron uptake in diatoms. *Nature*. **555**, 534–537

474 (2018).

475 58. X. Liu, F. J. Millero, The solubility of iron in seawater. *Marine Chemistry*. **77**, 43–54

476 (2002).

477 59. K. L. Wilde, J. L. Stauber, S. J. Markich, N. M. Franklin, P. L. Brown, The Effect of pH

478 on the Uptake and Toxicity of Copper and Zinc in a Tropical Freshwater Alga (Chlorella

479 sp.). *Archives of Environmental Contamination and Toxicology*. **51**, 174 (2006).

22

480   60.   P. Müller, X.-P. Li, K. K. Niyogi, Non-photochemical quenching. A response to excess

481   light energy. *Plant Physiology*. **125**, 1558–1566 (2001).

482   61.   L. T. Bach, L. C. M. Mackinder, K. G. Schulz, G. Wheeler, D. C. Schroeder, C. Brownlee,

483   U. Riebesell, Dissecting the impact of CO2 and pH on the mechanisms of photosynthesis

484   and calcification in the coccolithophore Emiliania huxleyi. *New Phytologist*. **199**, 121–134

485   (2013).

486   62.   J. Holte, L. D. Talley, J. Gilson, D. Roemmich, An Argo mixed layer climatology and

487   database. *Geophysical Research Letters*. **44**, 5618–5626 (2017).

488   63.   A. Olsen, N. Lange, R. M. Key, T. Tanhua, H. C. Bittig, A. Kozyr, M. Àlvarez, K.

489   Azetsu-Scott, S. Becker, P. J. Brown, B. R. Carter, L. Cotrim da Cunha, R. A. Feely, S.

490   van Heuven, M. Hoppema, M. Ishii, E. Jeansson, S. Jutterström, C. S. Landa, S. K.

491   Lauvset, P. Michaelis, A. Murata, F. F. Pérez, B. Pfeil, C. Schirnick, R. Steinfeldt, T.

492   Suzuki, B. Tilbrook, A. Velo, R. Wanninkhof, R. J. Woosley, GLODAPv2.2020 – the

493   second update of GLODAPv2. *Earth Syst. Sci. Data Discuss.* **2020**, 1–41 (2020).

494   64.   S. A. Good, M. J. Martin, N. A. Rayner, EN4: Quality controlled ocean temperature and

495   salinity profiles and monthly objective analyses with uncertainty estimates. *J Geophys Res*

496   *Oceans*. **118**, 6704–6716 (2013).

497   65.   C. Schmechtig, A. Poteau, H. Claustre, F. D'Ortenzio, G. Dall'Olmo, E. Boss, Processing

498   Bio-Argo particle backscattering at the DAC level (2015).

499   66.   C. Roesler, J. Uitz, H. Claustre, E. Boss, X. Xing, E. Organelli, N. Briggs, A. Bricaud, C.

500   Schmechtig, A. Poteau, F. D'Ortenzio, J. Ras, S. Drapeau, N. Haëntjens, M. Barbieux,

501   Recommendations for obtaining unbiased chlorophyll estimates from in situ chlorophyll

23

502   fluorometers: A global analysis of WET Labs ECO sensors. *Limnology and*

503   *Oceanography: Methods*. **15**, 572–585 (2017).

504 67.   G. E. Kim, M.-A. Pradal, A. Gnanadesikan, Quantifying the biological impact of surface

505   ocean light attenuation by colored detrital matter in an ESM using a new optical

506   parameterization. *Biogeosciences*. **12**, 5119–5132 (2015).

507 68.   X. Xing, N. A. B. Riggs, E. M. B. Oss, H. Ervé, C. Laustre, Improved correction for non-

508   photochemical quenching of in situ chlorophyll fluorescence based on a synchronous

509   irradiance profile. *Optics Express*. **26**, 2111–2125 (2018).

510 69.   C. de Boyer Montégut, G. Madec, A. S. Fischer, A. Lazar, D. Iudicone, Mixed layer depth

511   over the global ocean: An examination of profile data and a profile-based climatology.

512   *Journal of Geophysical Research: Oceans*. **109** (2004), doi:10.1029/2004JC002378.

513 70.   B. S. Sackmann, M. J. Perry, C. C. Eriksen, Fluorescene quenching from Seaglider

514   Seaglider observations of variability in daytime fluorescence quenching of chlorophyll-a

515   in Northeastern Pacific coastal waters Fluorescence quenching from Seaglider.

516   *Biogeosciences Discussions*. **5**, 2839–2865 (2008).

517 71.   X. Xing, H. Claustre, S. Blain, F. D'Ortenzio, D. Antoine, J. Ras, C. Guinet, Quenching

518   correction for in vivo chlorophyll fluorescence acquired by autonomous platforms: A case

519   study with instrumented elephant seals in the Kerguelen region (Southern Ocean).

520   *Limnology and Oceanography: Methods*. **10**, 483–495 (2012).

521 72.   S. Swart, S. J. Thomalla, P. M. S. Monteiro, The seasonal cycle of mixed layer dynamics

522   and phytoplankton biomass in the Sub-Antarctic Zone: A high-resolution glider

523   experiment. *Journal of Marine Systems*. **147**, 103–115 (2015).

524 73. T. Coleman, Y. Li, An Interior Trust Region Approach for Nonlinear Minimization

525 Subject to Bounds. *SIAM Journal on Optimization*. **6**, 418–445 (1996).

526 74. T. F. Coleman, Y. Li, On the convergence of interior-reflective Newton methods for

527 nonlinear minimization subject to bounds. *Mathematical Programming*. **67**, 189–224

528 (1994).

529 75. F. Pedregosa, G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel,

530 P. Prettenhofer, R. Weiss, V. Dubourg, J. Vanderplas, A. Passos, D. Cournapeau, M.

531 Brucher, M. Perrot, É. Duchesnay, Scikit-learn: Machine Learning in Python. *Journal of*

532 *machine learning research*. **85**, 2825–2830 (2011).

533 76. M. M. Hussain, I. Mahumd, pyMannKendall: a python package for non parametric Mann

534 Kendall family of trends tests. *Journal of Open Source Software*. **4**, 1556 (2019).

535 77. A. H. Orsi, T. Whitworth, W. D. Nowlin, On the meridional extent and fronts of the

536 Antarctic Circumpolar Current. *Deep Sea Research Part I: Oceanographic Research*

537 *Papers*. **42**, 641–673 (1995).

538 78. A. E. Allen, J. LaRoche, U. Maheswari, M. Lommer, N. Schauer, P. J. Lopez, G. Finazzi,

539 A. R. Fernie, C. Bowler, Whole-cell response of the pennate diatom Phaeodactylum

540 tricornutum to iron starvation. *Proceedings of the National Academy of Sciences*. **105**,

541 10438–10443 (2008).

542 79. A. Pankowski, A. McMinn, Iron availability regulates growth, photosynthesis, and

543 production of ferredoxin and flavodoxin in Antarctic sea ice diatoms . *Aquatic Biology*. **4**,

544 273–288 (2009).

545 80. A.-C. C. Alderkamp, G. Kulk, A. G. J. Buma, R. J. W. Visser, G. L. Van Dijken, M. M.

546 Mills, K. R. Arrigo, The Effect of Iron Limitation on the Photophysiology of Phaeocystis

547 Antarctica (Prymnesiophyceae) and Fragilariopsis Cylindrus (Bacillariophyceae) under

548 Dynamic Irradiance. *Journal of Phycology*. **48**, 45–59 (2012).

549 81. C. J. M. Hoppe, C. S. Hassler, C. D. Payne, P. D. Tortell, B. Rost, S. Trimborn, Iron

550 Limitation Modulates Ocean Acidification Effects on Southern Ocean Phytoplankton

551 Communities. *PLOS ONE*. **8**, e79890 (2013).

552 82. K. Petrou, S. Trimborn, B. Rost, P. J. Ralph, C. S. Hassler, The impact of iron limitation

553 on the physiology of the Antarctic diatom Chaetoceros simplex. *Marine Biology*. **161**,

554 925–937 (2014).

555 83. S. Trimborn, S. Thoms, K. Bischof, S. Beszteri, Susceptibility of Two Southern Ocean

556 Phytoplankton Key Species to Iron Limitation and High Light . *Frontiers in Marine*

557 *Science* . **6** (2019), p. 167.

558 84. F. Koch, S. Beszteri, L. Harms, S. Trimborn, The impacts of iron limitation and ocean

559 acidification on the cellular stoichiometry, photophysiology, and transcriptome of

560 Phaeocystis antarctica. *Limnology and Oceanography*. **64**, 357–375 (2019).

561 85. C. Schallenberg, R. F. Strzepek, N. Schuback, L. A. Clementson, P. W. Boyd, T. W. Trull,

562 Diel quenching of Southern Ocean phytoplankton fluorescence is related to iron

563 limitation. *Biogeosciences*. **17**, 793–812 (2020).

564 86. D. Bozzato, T. Jakob, C. Wilhelm, S. Trimborn, Effects of iron limitation on carbon

565 balance and photophysiology of the Antarctic diatom Chaetoceros cf. simplex. *Polar*

566 *Biology*. **44**, 275–287 (2021).

567

568 **Acknowledgements:**

569

584

585   **Author contributions:**

586

587   Conceptualization: TJRK, SJT

588   Formal analysis: TJRK, AT

589   Investigation: TJRK

590   Methodology: TJRK, SJT, AT

591   Funding Acquisition: TJRK, SJT, PMSM

592   Visualisation: TJRK

27

593　Writing - original draft: SJT

594　Writing - review & editing: TJRK, PMSM, AT

595

596　**Competing Interests:**

597

598　Authors declare that they have no competing interests.

599

600　**Data availability:**

601

602　BGC-Argo data were made available through the biogeochemical argo database (Table S3;

603　https://biogeochemical-argo.org/). Ship-based data were downloaded from various online

604　repositories (Table S4). Southern Annular Mode data were retrieved from

605　https://climatedataguide.ucar.edu/climate-data/. Core Argo mixed layer depth data were retrieved

606　from http://mixedlayer.ucsd.edu/. GLODAPv2.2021 data were retrieved from

607　https://www.glodap.info/index.php/merged-and-adjusted-data-product/. Ocean colour climate

608　change initiative data were retrieved from https://esa-oceancolour-cci.org/, with ocean colour

609　PAR data retrieved from http://www.globcolour.info/. Hadley EN4.2.2 temperature and salinity

610　data were retrieved from https://www.metoffice.gov.uk/hadobs/en4/download-en4-2-2.html. Sea

611　surface temperatures were retrieved from https://www.ghrsst.org/. CMIP6 data were obtained

612　from https://esgf.llnl.gov/.

613

614　**Supplementary Materials:**

615

616   Material and Methods

617   References (*62-86*)

618   Figs. S1 to S11

619   Tables S1 to S4

620

29

622

Fig. 1. Schematic of the proportional energy allocation at photosystem II (PSII) under different

iron (Fe) and light scenarios that phytoplankton may encounter, where PC means

photochemistry, FL means fluorescence and NPQ means non-photochemical quenching.

Scenario A represents the optimal light and iron scenario where PC is at its maximum with any

remaining energy dissipated as FL or NPQ. Scenario B represents a high light stress scenario

where there is a reduction in PC to prevent damage to PSII and a reduction in FL, with NPQ

acting as the dominant energy sink. Scenario C represents an iron limiting scenario with an

increased light harvesting antenna size to maintain PC as in scenario A, but with an increase in

FL. Scenario D represents both a high light stress and iron limiting scenario, where both PC and

FL will be reduced with NPQ again acting as the dominant energy sink. The opaque background

units in panels A and B represent complete reaction centres with light harvesting antennas,

whereas the opaque background units in panels C and D represent the synthesis of energetically

decoupled light harvesting antennas, which may absorb light with only FL and potentially NPQ

acting as energy sinks.

637

Fig. 2. Distribution and trend of irradiance-normalised NPQ. Seasonal and annual means, with

an Ordinary Least Squares regression on the annual mean, of irradiance-normalised NPQ

determined from the combined BGC-Argo and ship-based dataset. (Inset) Map showing

distribution of BGC-Argo and ship-based profiles (1996 – 2022).

642

Fig. 3. Robustness of irradiance-normalised NPQ as a proxy for Fe stress demonstrated through

natural and artificial Fe gradients and seasonal Fe depletion. (A) Mean irradiance-normalised

Commented [JHS1]:

Commented [TRK2R1]: We unsure what the issue is here with this word is. Can you please elaborate further.

We are open to the idea of changing it to Graphic/Simplified representation instead of Schematic.

645   NPQ ± standard errors from BGC-Argo profiles upstream and downstream of the Kerguelen

646   plateau and from ship-based profiles in and out of Fe-fertilized patches during SOIREE and

647   SOFEX. Maps of irradiance-normalised NPQ based on combined BGC-Argo and ship-based

648   profiles (1996 – 2021) for (B) Spring (SON: September, October, and November) and (C)

649   Summer (DJF: December, January, and February) gridded to 5° × 5°. The dashed line represents

650   the spatial extent of the Southern Ocean defined as the subpolar and ice biomes from Fay &

651   McKinley (*39*). See Fig. S4 for Winter and Autumn.

652

653   **Fig. 4.** Comparing net primary production (NPP) for the Southern Ocean from BGC-Argo,

654   remote sensing, and earth systems models. (A) Normalised annual means of NPP derived BGC-

655   Argo using 2 different NPP models (2014 – 2021) and derived from remote sensing using 4

656   different NPP models (1998 – 2021) averaged across the sub-polar and ice biomes from Fay &

657   McKinley (*39*), decadal trends (1998 – 2021) from remote sensing using (B) CbPM1, (C)

658   CbPM2, (D) CAFE and (E) VGPM, and (F) normalised annual means of NPP from CMIP6

659   model outputs (1996 – 2021). Statistics of the normalised annual trends of NPP models from

660   panels A and F can be found in Table 1. Normalisation was performed by dividing the data by

661   the mean value. Note that CbPM1 refers to the Behrenfeld et al. (*49*) model and CbPM2 refers to

662   the Westberry et al. (*50*) model. The dashed line represents the spatial extent of the Southern

663   Ocean defined as the subpolar and ice biomes from Fay & McKinley (*39*).

31

Platform	Date range	Parameter	Slope	Intercept	R^2	F-statistic	p-value
in situ	1996 – 2022	Irradiance-normalised NPQ	4.69×10^{-2}	-93.18	0.92	260.49	2.18×10^{-14}
	2014 – 2021	VGPM	-0.08	172.29	0.43	4.45	0.08
		CbPM1	-0.10	197.73	0.81	25.60	2.31×10^{-3}
Remote Sensing	1998 – 2021	VGPM	0.01	-15.79	0.55	26.97	3.30×10^{-5}
		CbPM1	-0.02	32.85	0.61	34.13	7.05×10^{-6}
		CbPM2	-0.01	25.80	0.57	29.08	2.05×10^{-5}
		CAFE	-0.01	19.47	0.46	18.75	2.69×10^{-4}
Earth System Models	1996 – 2021	CMIP6 Median	7.96×10^{-4}	-0.60	0.10	2.83	0.15
		CMIP6 Range	$-2.25 \times 10^{-3} - 2.19 \times 10^{-3}$	$-0.38 - 5.51$	$1.54 \times 10^{-3} - 0.42$	$0.04 - 17.53$	$7.92 \times 10^{-3} - 0.98$

664

665 **Table 1**: Normalised Ordinary Least Squares regression results of irradiance-normalised NPQ

666 (1996 – 2022), NPP from 2 production models applied to BGC-Argo data (2014 – 2021), NPP

667   from 4 production models applied to Remote Sensing data (1998 – 2021) and NPP from CMIP6

668   outputs (1996 – 2021). Note that CbPM1 refers to the Behrenfeld et al. (*49*) model and CbPM2

669   refers to the Westberry et al. (*50*) model.