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# Phytoplankton responses to dust addition in the FeMn co-limited eastern Pacific sub-Antarctic differ by source region

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- 23

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#### 36 Abstract.

The seasonal availability of light and micronutrients strongly regulates productivity in the Southern 37 Ocean, restricting biological utilization of macronutrients and CO<sub>2</sub> drawdown. Mineral dust flux is a 38 key conduit for micronutrients to the Southern Ocean and a critical mediator of multi-millennial-scale 39 atmospheric CO<sub>2</sub> oscillations. Whilst the role of dust-borne iron (Fe) in Southern Ocean 40 biogeochemistry has been examined in detail, manganese (Mn) availability is also emerging as a 41 potential driver of past, present, and future Southern Ocean biogeochemistry. Here we present results 42 43 from fifteen bioassay experiments along a north-south transect in the under-sampled eastern Pacific sub-Antarctic Zone. In addition to widespread Fe limitation of phytoplankton photochemical 44 45 efficiency, we found further responses following the addition of Mn at our southerly stations, supporting the importance of Fe-Mn co-limitation in the Southern Ocean. Moreover, addition of 46 47 different Patagonian dusts resulted in enhanced photochemical efficiency with differential responses linked to source region dust characteristics in terms of relative Fe/Mn solubility. Changes in both the 48 49 relative magnitude of dust deposition, combined with source region mineralogy, could hence determine whether Fe or Mn limitation control Southern Ocean productivity under future as well as 50 51 past climate states.

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## 53 Significance statement.

54 Atmospheric dust supply of micronutrients to the Southern Ocean is an important regulator of phytoplankton productivity, impacting the global carbon cycle. Understanding how phytoplankton 55 respond to changes in dust supply has become increasingly important, with supply predicted to alter 56 with future climate change. We show that Patagonian dusts, which differ in characteristics by source 57 region, can supply different amounts of the essential micronutrients iron and manganese to the 58 Southern Ocean and subsequently drive different responses in the resident phytoplankton. Changes in 59 dust supply, including shifts in source regions, could therefore be an important factor controlling 60 phytoplankton productivity in the past and future Southern Ocean. 61

62

# 63 Introduction.

Productivity in the modern Southern Ocean is restricted by low iron (Fe) and potentially manganese
(Mn) availability (1-4) owing to upwelling of macronutrient-rich deep waters depleted in these
scavenged trace metals (5, 6), combined with low atmospheric supply (1, 7).

Both Fe and Mn are essential requirements in oxygenic photosynthesis, with multiple Fe binding 67 68 components required to enable photosynthetic electron flow, while the oxygen-evolving complex of photosystem II requires 4 bound Mn atoms (8). Surface uptake by phytoplankton leads to a scarcity of 69 both Fe and Mn in Southern Ocean surface waters, which can subsequently limit productivity, leading 70 to underutilization of macronutrients and net release of deep-ocean carbon (4, 7, 9). Enhanced 71 micronutrient supply, including through increased atmospheric dust fluxes, thus has the potential to 72 73 drive increased macronutrient utilization, export production and atmospheric  $CO_2$  drawdown (1, 7). Indeed, the higher supply of lithogenic Fe to Southern Ocean phytoplankton during glacial climate 74 75 periods correlates with increased nitrate removal and productivity and is a critical mediator of millennial-scale atmospheric CO<sub>2</sub> oscillations (7, 10-12). Dust fluxes to the Sub-Antarctic Zone (SAZ) 76 in particular have been associated with a significant fraction of atmospheric  $CO_2$  drawdown during the 77 last glacial cycle (9, 13), with isolation of the deep Southern Ocean by enhanced stratification the other 78 major contributor (13-15). 79

80 Although there is still uncertainty as to whether global dust deposition rates will increase or decrease due to anthropogenic climate change (16, 17), the expansion of deserts could result in a three-fold 81 greater atmospheric dust loading by the end of the 21<sup>st</sup> century (18). Regionally, this expansion, 82 coupled with climate related increased storminess, could result in a ten-fold increase in dust loading 83 over the Southern Hemisphere compared with a minimal increase over much of the Northern 84 Hemisphere (18). Any future increase in dust flux may enhance the delivery of Fe and other co-limiting 85 nutrients such as Mn (4, 19), which could be particularly important should warming and freshening of 86 Southern Ocean surface waters increase stratification, and hence reduce supply from subsurface 87 reservoirs (5, 20). The delivery of dust-borne nutrients may be further supported by an increased 88 contribution from wildfire aerosols (21-24), which can relieve nutrient limitation and significantly 89 increase Southern Ocean productivity following exceptional individual events (25). 90

91 Despite the potential importance of Southern Ocean dust inputs for modern productivity and glacialinterglacial cycles, relatively few studies have investigated the ecophysiological response of natural 92 93 Southern Ocean phytoplankton communities to direct dust addition. In situ and shipboard bottle experiments of Fe fertilization have typically assessed responses to the addition of inorganic Fe (e.g., 94 95 dissolved chloride salts or ferrous sulphate) (26-30). Such addition of Fe may fail to mimic the responses from complex natural substrates, where the (bio-)availability of multiple micronutrients may 96 97 vary. For example, naturally Fe-limited Southern Ocean phytoplankton have been shown to respond differently to dust addition compared with inorganic Fe (31). Moreover, the increasing evidence that 98 Mn may be co-limiting with Fe in certain settings and regions of the Southern Ocean (4, 19, 32) needs 99

100 consideration in the context of multiple-micronutrient supply from natural particulates. This is 101 particularly interesting due to the high abundance of both elements in crustal material (sediments, 102 airborne dusts) and similar short oceanic residence times. Indeed, the supply of volcanic ash to 103 Southern Ocean phytoplankton communities has been shown to produce a stronger response than 104 addition of Fe alone, potentially due to relief of Mn (co-)limitation (33). Understanding biological 105 responses to complex natural sources of trace-metal-nutrients may thus be essential for realistic 106 projections of the Southern Ocean biological carbon pump under past and future climates (4).

- 107 The composition of dust will vary with source provenance (34, 35) and processing both at source and 108 during atmospheric transport (36, 37). In particular, Fe within glaciogenic versus non-glaciogenic dust 109 sources appears to be both more labile and bioavailable due to a higher  $Fe^{2+}$  content (35, 38). This 110 higher  $Fe^{2+}$  content of glaciogenic dust has been shown to significantly increase growth and 111 photosynthetic efficiency compared with non-glaciogenic dust in a cultured diatom (35). Similarly, the 112 relative abundance, solubility and bioavailability of the multiple trace metals in dust deposition may 113 be key in determining the overall ecosystem response (4).
- South America is the largest source of dust to the modern Southern Ocean contributing ~60 % of the 114 flux, with Australia the other key source, particularly for the Pacific sector (39, 40). However, 115 increased circumpolar transport of South American dust sources potentially dominated the >3-fold 116 higher dust fluxes and >15-fold higher  $Fe^{2+}$  fluxes to the Pacific SAZ during glacial periods (34, 41). 117 Understanding the fertilization potential of this increased glacial bioavailable  $Fe^{2+}$  flux, alongside other 118 potentially co-limiting trace-metals for natural phytoplankton communities in the Pacific SAZ, may 119 thus be crucial for determining the likely response of the glacial-interglacial system and more broadly 120 121 understanding the role of variable dust fluxes and source regions in Southern Ocean biogeochemistry.
- We thus combined in situ observations with a series of shipboard bottle experiments in the undersampled eastern Pacific SAZ (3), the region of the modern sub-Antarctic with the lowest annual mean dust flux (Fig. 1A). Experiments were conducted to assess the potential role of natural sources of Fe and Mn in regulating phytoplankton ecophysiology in the region and the broader Southern Ocean.

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#### 127 Results and discussion.

# 128 Phytoplankton responses to Fe and Mn amendment.

Eight smaller volume (2-6 day, denoted Ex-S1-S8) and seven larger volume (6 day, denoted Ex-L1L7) nutrient addition experiments were conducted using various factorial combinations of inorganic

Fe and Mn (alongside silicate (Si) and zinc (Zn)), in addition to three different Patagonian dust sources 131 (35) (see Methods). Phytoplankton responses to amendment with Fe and/or Mn showed clear spatio-132 temporal patterns coincident with in situ variability in the concentration of these metals and prevailing 133 phytoplankton bloom conditions, as influenced by physical setting (Fig. 1B) and indicated by 134 macronutrient drawdown and chlorophyll-a concentrations (Fig. 1C-E). Surface chlorophyll-a 135 concentrations (Fig. 1C, D) indicated a substantial bloom peaking shortly after the start of the cruise 136 137 in the southern half of the study region. Correspondingly, surface dissolved silicate (dSi) and Mn (dMn) concentrations (Fig. 1E, F) decreased over time as the bloom progressed, particularly to the 138 139 south of the region. In contrast, dissolved Fe (dFe) concentrations (Fig. 1G) were more uniformly low  $(<0.1 \text{ nmol } L^{-1})$  in surface waters over the observation period. 140

141 The supply of Fe to incubation experiments significantly increased values of the fluorescence derived 142 parameter  $F_{\nu}/F_m$  in all experiments (Fig. 2 and Figs. S1, S4, S6), indicating widespread Fe limitation of the efficiency with which extant phytoplankton were converting absorbed light energy to chemical 143 144 energy during photosynthesis (42). No serial responses (i.e., greater secondary or tertiary effects following the addition of a second or third nutrient in combination, see Methods (43)) were observed 145 at the lower biomass northern OOI station, where dMn remained relatively high  $(dMn > 0.1 \text{ nmol } L^{-1})$ 146 (Figs. 1, 2 and Figs. S1-S6). In contrast, at stations TN and TS, toward the south of the SAZ, which 147 were characterized by elevated chlorophyll-a and rapidly depleting dMn and dSi concentrations (Fig. 148 149 1 E, F), phytoplankton experimental responses indicated Mn serial/co-stress within all experiments, i.e.,  $F_{\nu}/F_m$  was significantly increased following combined Fe and Mn addition compared with Fe alone 150 (irrespective of further addition of Si (i.e.,  $\pm$ Si)). Importantly, the observed significant differences in 151  $F_{\nu}/F_{m}$  between Fe(±Si) and FeMn(±Si) treatments were characterized by a drop in  $F_{\nu}/F_{m}$  within Fe(±Si) 152 treatments from day 2 to day 6 (e.g., Fig. 2E). Moreover, a small but statistically significant increase 153 154 in  $F_{\nu}/F_m$  following sole addition of Mn(±Si) was observable after 6 days at TS in Ex-L4 and in TN Ex-155 L7 (Fig. 2F and S1).

Chlorophyll-a concentrations (Fig. 2 and Figs. S2, S5) and DIN drawdown (Fig. S3) increased 156 alongside  $F_{\nu}/F_m$  following Fe addition to all experiments. Serial responses to the further addition of 157 158 Mn and/or Si were always observed to the south of the study region at TN and TS, with the highest 159 chlorophyll-a increases and DIN drawdown occurring following the combined FeMnSi addition to these experiments, despite no evidence of primary Si limitation. Our experiments thus indicated Fe-160 161 Mn-Si serial limitation of the phytoplankton community in the south of our study region. In contrast to Fe and Mn, that have an absolute requirement in photosynthesis (8, 19) no change in  $F_{\nu}/F_m$  or 162 biomass was observed following the addition of Zn within the two experiments where this was tested 163

(Fig. 3 and Figs. S4, S5). The absence of a Zn response may be potentially due to elevated in situ dZn
concentrations (Table S2) or the potential for metabolic substitution of some of the Zn requirement
with Co or Cd in carbonic anhydrase (44, 45).

167 Overall, our experimental data were consistent with serial Fe-Mn-Si limitation developing as both the natural in situ bloom (Fig. 1) and artificially induced blooms within the experiments (Fig. 2) depleted 168 169 ambient Mn, expanding the growing evidence of an important role for Mn availability in Southern Ocean productivity (4, 19, 32). Moreover, the spatial-temporal patterns observed in the experimental 170 171 responses were broadly predictable on the basis of the relative availability of dMn and dFe compared with phytoplankton cellular requirements, as calculated using  $Mn_{Fe}^*$  (=  $dMn - dFe/R_{FeMn}$ , where  $R_{FeMn}$ , 172 the assumed cellular molar stoichiometry of Fe:Mn, was taken as 2.67) (3, 4). Specifically, serial Fe-173 Mn responses were only observed in the low (negative) Mn<sub>Fe</sub>\* (signifying Mn deficiency) waters to 174 175 the south (Fig. 1), particularly following the peak of the bloom.

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#### 177 Phytoplankton responses to Patagonian dust addition.

178 Response to Patagonian dust addition revealed insights into the potential role of dust supply in 179 Southern Ocean phytoplankton ecophysiology across naturally occurring biogeochemical gradients. 180 For this study, dust samples included a subset of previously investigated glaciogenic (SMD13-3 and 181 PMG) and non-glaciogenic (CAR19) sources from Patagonia (35). After both 2 and 6 days incubation, 182 the addition of dust resulted in pronounced but varying responses in both  $F_{\nu}/F_m$ , biomass accumulation 183 and nutrient drawdown, with the glaciogenic SMD13-3 generally providing a stronger response than 184 either the other glaciogenic PMG or non-glaciogenic CAR19 sources (Figs. 2, 3, S4 and S5).

Addition of all the dust sources significantly increased  $F_{\nu}/F_m$  and chlorophyll-a after 2 days in all 185 except one experiment (Station OOI Ex-S8) (Figs. S4, S5). Of the three dusts, SMD13-3 promoted the 186 strongest responses, which were frequently comparable to the 2 nmol L<sup>-1</sup> inorganic Fe addition from 187 the same experiments (Figs. 2, 3). The stronger response to SMD13-3 addition corresponded with this 188 dust having the highest Fe content by mass (10% compared with 1.3 and 3.7% for PMG and CAR19, 189 respectively, Table S3), a significant fraction of which is comprised of Fe<sup>2+</sup> silicates (35). Hence, Fe 190 mineralogy and solubility likely contributed to the stronger short-term (2-day) experimental responses, 191 as serial Mn responses were less apparent over these timescales (Fig. 2). 192

After 6 days, the addition of SMD13-3 to station OOI Ex-L5 increased  $F_{\nu}/F_m$  (Fig. 2) to values comparable to the Fe additions, with no apparent serial Mn response. In contrast, the response to

195 SMD13-3 addition in station TN Ex-L7 was elevated above that of Fe(±Si) treatments and equal in magnitude to the combined FeMn(±Si) additions. Moreover, unlike in the Fe(±Si) treatments, no drop 196 in  $F_{\nu}/F_m$  from 2 to 6 days was observed in the SMD13-3 dust treatment for TN Ex-L7. These 197 experimental biotic responses thus indicated that Mn released from SMD13-3 particles could alleviate 198 199 the observed serial Fe-Mn limitation of photochemical energy conversion. Similarly, and in contrast with previous responses of a cultured diatom grown under Fe-deplete, Mn replete conditions (35), the 200 201 photophysiological response to the glaciogenic PMG dust source in station TN Ex-L7 was lower relative to the non-glaciogenic CAR19 source. Dust addition also stimulated chlorophyll-a 202 203 accumulation (Fig. 2) and DIN drawdown after 6 days in a similar fashion to that observed for  $F_{\nu}/F_m$ , with differences in response again related to dust source. Specifically, the SMD13-3 dust provided the 204 largest change in biomass with lower responses to CAR19 and PMG additions. The change in biomass 205 was either comparable or less than that from Fe addition in all experiments. Decreasing biotic 206 responses to dust additions (SMD13-3 >> CAR19 > PMG), in particular within the serial Fe-Mn 207 limited Ex-L7 experiment (Fig. 2E, F), thus indicated variable amounts and/or kinetics of release of 208 209 both Fe and Mn.

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#### 211 Differential phytoplankton responses linked to source region dust characteristics.

212 To assess how Fe and Mn were released into seawater and how this may have driven the observed biotic responses, we determined total element contents of the different dust sources and conducted 213 214 controlled abiotic leaching experiments designed to simulate the shipboard bottle experiments as 215 closely as possible. Measurable dissolved Fe and Mn was leached from each dust source by the 2-day time point (Fig. 4). No further significant increase in measurable dFe or dMn occurred between days 216 217 2 and 6 (Fig. 4), consistent with the majority of labile Fe and Mn mobilizing rapidly following contact with seawater (46-48). Typical crustal Mn/Fe ratios of less than 0.02 mol mol<sup>-1</sup> are expected to be 218 partially offset by fractional Mn solubility in atmospheric aerosols being around one order of 219 magnitude greater than for Fe (47, 49-51), due to much of the Fe in mineral particles being located 220 within refractory phases (52), combined with leached  $Fe^{2+}$  rapidly oxidizing to  $Fe^{3+}$  under oxygenic 221 conditions. Consistent with this, fractional solubilities within our experimental setup for Fe and Mn 222 223 were around 0.23 and 1.79 %, respectively, for the glaciogenic PMG source (Table S3), but were even more extreme for the other two sources, with values of 0.05 % (Fe) and 7.29 % (Mn) for the glaciogenic 224 SMD13-3 source and 0.05 % (Fe) and 8.82 % (Mn) for the non-glaciogenic CAR19 source. The 225 SMD13-3 and PMG glaciogenic dust sources used in this study were more highly reduced (35), which 226

in addition to providing soluble  $Fe^{2+}$ , could also provide highly soluble reduced  $Mn^{2+}$  species. However, the reason for the higher apparent Mn solubility for non-glaciogenic CAR19 is less clear.

Consistent with the SMD13-3 dust driving the strongest biotic experimental responses (Fig. 2), it was 229 the strongest source of both leachable dissolved Fe and Mn, releasing 0.84 and 4.64  $\mu$ mol g<sup>-1</sup>, 230 respectively (Fig. 4), equating to dissolved additions of 0.21 and 0.42 nmol  $L^{-1}$  dFe and 1.16 and 2.32 231 nmol L<sup>-1</sup> dMn to our large and small volume experiments, respectively. Addition of dFe from SMD13-232 233 3 to Ex-L7 at station TN was thus one order of magnitude lower than that of the inorganic Fe addition, providing further support for the elevated  $F_{\nu}/F_m$  compared with that of Fe after 6 days incubation being 234 due to simultaneous Mn release (Fig. 2E, F). Indeed, the dissolved Mn/Fe leach ratio of 5.52 mol mol<sup>-</sup> 235 <sup>1</sup> for SMD13-3 would have provided an excess of Mn relative to Fe and biotic requirements (3, 4, 53), 236

with an estimated  $Mn_{Fe}^*$  increase of 1.03±0.09 (1SD) nmol L<sup>-1</sup>.

A similar dissolved Mn/Fe leach ratio of 3.86 mol mol<sup>-1</sup> was observed for the non-glaciogenic CAR19, 238 however the lower concentrations of both Fe and Mn released would have produced an Mn<sub>Fe</sub>\* of 239 0.31±0.02 nmol L<sup>-1</sup>. In contrast, glaciogenic PMG released more Fe than Mn with a Mn/Fe leach ratio 240 of 0.32 mol mol<sup>-1</sup> corresponding to a  $Mn_{Fe}^*$  of 0.00±0.03 nmol L<sup>-1</sup>. The relative release of Fe and Mn 241 from these natural dust sources was thus decoupled from the total mass content, due to highly variable 242 243 solubilities (Table S3), with the relative strengths of the biotic responses, particularly after 6 days (Figs. 2, 3) SMD13-3 >> CAR19 > PMG, being relatable to the same sequence of higher absolute Fe 244 245 and Mn additions and higher Mn<sub>Fe</sub>\* (Fig. 4).

Previous laboratory experiments that observed stronger responses to SMD13-3 and PMG than CAR19 under Mn replete, Fe deficient conditions were largely driven by the higher  $Fe^{2+}$  content of the physically weathered glaciogenic sources (35, 38). However, within the Mn deficient (Mn<sub>Fe</sub>\* < $\approx$ 0) waters of the southeast Pacific SAZ (Fig. 1H), the enhanced Mn supply from the glaciogenic SMD13-3 and non-glaciogenic CAR19 drove the stronger response, highlighting the importance of both in situ nutritional status of the community and the multi-trace-metal characteristics of any inputs in determining system responses.

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## 254 Extrapolating experimental responses to wider scales.

Care must clearly be taken in extrapolating experimental responses such as those presented here to
natural system responses to similar drivers (i.e., dust inputs) over different time and space scales (3, 4,
54-56). Our experimental dust additions were of comparable magnitude to modern total annual inputs

to the South Atlantic sector of the Southern Ocean, which are around two orders of magnitude higher 258 than deposition to the study region (Fig. 1A). Moreover, these experiments were monitored over a 6-259 day time period in a closed system, which is very different to an in situ open system (54). Indeed, 260 differences in the extent to which the strongest combined Fe and Mn dust source (SMD13-3) could 261 fully reproduce the physiological (e.g.,  $F_{\nu}/F_m$ ) and biomass (e.g., chlorophyll) related biotic responses 262 to direct FeMn(±Si) addition from 2 to 6 days, were likely due to the order of magnitude lower Fe 263 input from the dust, combined with progressive responses, as artificial blooms proceeded in the bottles. 264 However, combined with other recent observations (4, 32), the progressive in situ development of Mn 265 266 (co-)deficiency (Fig. 1H) and serial limitation (Fig. 1J, K) during the bloom to the south of our study region and clear biotic responses to dust related Mn inputs (Figs. 2, 3), clearly argue for consideration 267 of larger scale biogeochemical consequences. 268

269

# 270 Biogeochemical implications.

The flux of mineral dust into Southern Ocean waters is among the lowest found on Earth (50). Present day dust inputs to the Southern Ocean from South America, South Africa and Australia follow the circumpolar flow of the westerly winds, predominantly fertilizing surface waters of the Atlantic, Indian, and Pacific sectors, respectively (40, 50, 57). The peak of dust deposition occurs during austral spring and summer (24, 39), contributing to the SAZ mixed layer Fe and Mn inventories that already hold the potential for FeMn (co-)limitation due to Mn deficiency relative to Fe, i.e.,  $Mn_{Fe}^* \le 0$  (4, 6).

For the Southeast Pacific sector of the SAZ, we observed near zero or negative post-bloom Mn<sub>Fe</sub>\* values (Fig. 1H) similar to the Mn (co)-limited central Drake Passage (4). The source of dust, and by association mineralogy, is therefore likely to be an important influence on productivity in the SAZ. Specifically, the deposition of dust with high Mn/Fe leach ratios (e.g., SMD13-3, CAR19) would be expected to strengthen regional Fe limitation and/or prevent development of Mn (co-)limitation, whilst deposition of sources with lower Mn/Fe leach ratios (e.g., PMG) could strengthen Mn (co-)limitation, particularly towards the end of seasonal growth.

Dust-derived Fe to the SAZ has been associated with atmospheric  $CO_2$  drawdown during the last glacial cycle (9, 13). In contrast to modern/Holocene dust transport, South America was the dominant source of dust to the Pacific Southern Ocean during glacial periods (34). Such changes in source provenance could directly affect the relative magnitude of Fe and Mn delivery, with cascading effects on macronutrient utilization and  $CO_2$  drawdown. Indeed, reconstructions estimate a ~15-fold increase in Fe<sup>2+</sup> supply to regions of the glacial Southern Ocean in comparison with interglacial periods,

suggesting a role for glacier-derived Fe fertilization in the observed declines in atmospheric  $CO_2$  (41). However, our data suggest that dust may be significant in providing both Fe and Mn as biologically essential and potentially co-limiting micronutrients. The efficiency of dust-induced increases in glacial macronutrient utilization and hence ultimately atmospheric  $CO_2$  drawdown may thus have depended on source region influences on both Fe and Mn supply (4, 19).

Despite uncertainty as to how anthropogenic climate change will modify global dust deposition rates (16, 17), it has been proposed that the expansion of deserts and strengthening of winds could increase Southern Hemisphere atmospheric dust loading by the end of the 21<sup>st</sup> century (18). Ocean biogeochemical models also predict strengthening and poleward displacement of westerly winds over the 21<sup>st</sup> century (58-60), further influencing dust mobilization and source regions. Given the proximity to Southern Hemisphere dust source regions, any increase in deposition rates would likely be greatest between 40 and 60° S.

302 The net effect of altered dust flux on Southern Ocean biogeochemistry further depends on additional climate related changes. The balance between intensification and poleward displacement of westerly 303 winds acting to increase upwelling and subsurface nutrient supply versus warming and freshening of 304 surface waters that can act to increase stratification (58, 61) should determine whether mixed layer 305 productivity increases or decreases (20, 62). The relative importance of dust-borne supply of Fe and 306 Mn to the SAZ can thus be influenced by circulation related changes in the sub-surface entrainment 307 flux of both macro- and micronutrients. For example, the deficiency of both Fe and Mn in upwelling 308 circumpolar deep-waters (6) means that any regionally reduced sub-surface supply of these scavenged 309 micronutrients, potentially coupled with any increased atmospheric dust deposition, might be expected 310 311 to result in a higher biological pump efficiency, as defined by macronutrient utilization (3, 15, 63). Changes in the magnitude of dust deposition, variations in source regions, and altered circulation 312 patterns could hence all combine to determine whether Fe or Mn limitation control productivity and 313 314 biological CO<sub>2</sub> uptake potential of the Southern Ocean under future as well as past climate states. However, ocean biogeochemical models currently typically only consider dust deposition from the 315 316 perspective of Fe supply (9, 19, 64). Our results suggest that dust-borne Mn can have a significant influence on Southern Ocean phytoplankton ecophysiology, emphasizing the need for the 317 318 incorporation of multi-element dust-driven fluxes in both past and future climate predictions.

319

## 320 Materials and methods.

Voyage and seawater collection. Experiments and sample collection were carried out on the *R.R.S. Discovery* DY111 cruise (December 2<sup>nd</sup> 2019 – January 9<sup>th</sup> 2020), a component of the UK Carbon
Uptake and Seasonal Traits in Antarctic Remineralisation Depth (CUSTARD) project (Fig. 1). A total
of fifteen nutrient and dust addition experiments (Fig. 1 and S6) were conducted along the 89°W
meridian at 54°S (Station OOI), 57°S (Station TN) and 60°S (Station TS).

326 Nutrient amendment experiments. Eight smaller volume (2-6 day, denoted Ex-S1-S8) and seven larger volume (6-day, denoted Ex-L1-L7) factorial nutrient amendment experiments were conducted 327 328 (Fig. S6), using similar methods to those employed previously in the HNLC Southern Ocean and elsewhere (28-30, 43). Surface seawater (2-3 m) for experiments was pumped directly into a class-329 1000 clean air laboratory container using a Teflon diaphragm pump (A-15, Almatec) connected by 330 acid-washed PVC tubing to a towed "Fish" sampler. For each experiment, seawater from the towed 331 332 fish was collected into either 2 L (Ex-S) or 4 L (Ex-L) acid-washed polycarbonate bottles. Bottles were first filled in random order up to  $\sim$ 50% of total volume, before then being topped up, again in random 333 334 order. Samples for initial measurements (photophysiology, chlorophyll-a and macronutrients) were collected at the beginning, middle (i.e., after all experimental bottles were ~50% full) and end of the 335 filling process. Separate replicate bottles were amended with single or combination additions of Fe, 336 Mn, Zn, and Si to final concentrations of 2 nmol  $L^{-1}$  for each trace metal and 10  $\mu$ mol  $L^{-1}$  for Si. Control 337 bottles, with no added nutrients, were collected in parallel. Fe, Mn, and Zn were added as FeCl<sub>3</sub>, MnCl<sub>2</sub> 338 and  $ZnCl_2$ , respectively, prepared from  $\geq 99\%$  purity salts (Sigma-Aldrich) and stabilized in 0.024 M 339 340 HCl (SpA, Romil). The Si solution was prepared from Na<sub>2</sub>SiF<sub>6</sub> salt (Sigma-Aldrich) and passed through a column of cation exchange resin (Chelex-100, BioRad) to remove trace metal impurities. 341

342 Three small volume and two large volume experiments were chosen to investigate the physiological 343 response of resident phytoplankton communities to Patagonian dust amendment. Sediment samples were prepared and sterilized per the methods described in Shoenfelt et al. (2017) (35) with the current 344 345 study also adopting the same sample names. Glaciogenic (SMD13-3 and PMG) and non-glaciogenic (CAR19) sediment was added to separate incubation bottles by triple rinsing (using filtered surface 346 347 seawater) of the material from sterile 0.5 mL micro-centrifuge vials and was accompanied by replicate 348 controls whereby identical empty vials were rinsed into separate incubation bottles. No significant differences were observed between controls and these separate dust treatment controls (Fig. 2 and Figs. 349 S4, S5). The addition of a fixed 1 mg mass of each dust source resulted in final additions of 0.5 and 350 0.25 mg L<sup>-1</sup> for small and large volume experiments, respectively. All experimental incubations were 351 conducted as biological triplicates, apart from Ex-S6 (all duplicates) and the dust additions to Ex-S8, 352 Ex-L5, and Ex-L7 that were also duplicates. Following nutrient amendment, the bottles were externally 353

sealed with film (Parafilm<sup>TM</sup>) and incubated in a temperature-controlled container set to local sea surface temperature (5.5 - 7.0 °C during the study) and surrounded by daylight simulation LED light banks with ~200 µmol photons m<sup>-2</sup> s<sup>-1</sup> flux and set to an approximate local day/night cycle of 16 and 8 h, respectively.

Sub-sampling. All experimental bottles in every experiment were sub-sampled for the same set of 358 variables measured for initial conditions (photophysiology, chlorophyll-a and macronutrients) after 48 359 hours (2 days) in the clean air laboratory, at which point six of the eight small volume experiments 360 (Ex-S1-S3 and S6-S8) were terminated. To allow for any potentially slower photophysiological and 361 growth response to Zn addition, Ex-S4 and Ex-S5 were allowed to incubate for a further 4 days at 362 which point (i.e., day 6) they were sampled for a second and final time. All the larger volume 363 experiments (Ex-L1-L7) were sub-sampled at 2 days and terminated after 6 days following a second 364 365 and final sampling.

Phytoplankton photosynthetic physiology. Variable chlorophyll fluorescence was measured using a 366 Chelsea Scientific Instruments Fastracka<sup>TM</sup> Mk II Fast Repetition Rate fluorimeter (FRRf) integrated 367 with a FastAct<sup>TM</sup> laboratory system. Samples (~125 mL) were dark-acclimated for 30 minutes in 368 opaque bottles (Nalgene) and FRRf measurements were blank corrected using carefully prepared 0.2 369 370  $\mu$ m filtrates and 18.2 M $\Omega$ -cm ultrapure water for each experiment (28). Blanks contributed 2±1 % (n=15) of the maximum fluorescence signal during this study. Protocols for FRRf measurements and 371 data processing were similar to those detailed elsewhere (28). Data from the FRRf was analyzed to 372 derive values of the minimum and maximum fluorescence ( $F_0$  and  $F_m$ , respectively) and the apparent 373 photochemical efficiency of photosystem II (PSII),  $F_v/F_m$  (where  $F_v=F_m-F_o$ ) (65). A phytoplankton 374 375 response from the nutrient or dust amendment experiments was represented by a significant increase 376 in  $F_v/F_m$  over that of the control bottles.

377 Chlorophyll. Samples for Chlorophyll-*a* analysis (~100 mL) were filtered onto 0.7 μm nominal
378 porosity GF/F filters and extracted into 90% acetone for 24 hours in the dark at 4 °C prior to
379 measurement. Chlorophyll-*a* concentration was determined on a pre-calibrated Turner Designs Trilogy
380 fluorometer (66) whilst at sea within 48 hours of collection.

Macronutrients. The dissolved concentrations of macronutrients phosphate ( $PO_4^{3-}$ ), silicate (SiO<sub>2</sub>; as Si hereafter), and nitrate (determined as nitrate + nitrite) were measured onboard ship within 24 h of sample collection using a SEAL QuAAtro 39 segmented flow auto-analyser following colorimetric procedures provided by SEAL Analytical (Q-064-05, Q-066-05, Q-068-05). Certified Reference Materials (CRM Lots CJ and CB, KANSO, Japan) were used to check for accuracy of the method with
 excellent agreement.

387 Trace metals. Seawater samples for ambient dissolved trace metal determination were collected from the towed "Fish" sampler during the "filling" stage of each experiment, alongside experimental initial 388 samples. Seawater was filtered through 0.2 µm porosity membrane cartridge filters (Sartobran, 389 Sartorius) into trace metal-clean 125 mL low density polyethylene bottles and acidified to pH 1.7 390 (0.024 M) by addition of 12 M ultrapure HCl (UpA, Romil) under a class-100 laminar flow hood in 391 392 the clean air container. Samples were double bagged in polyethylene bags and stored for analysis. Dissolved trace metal concentration was determined using a standard addition method (67, 68) with 393 off-line pre-concentration and subsequent high resolution ICP-MS (69, 70) at the National 394 Oceanographic Centre, Southampton, UK. Certified values for SAFe (S and D2) reference material 395 396 compared well with our measured values (Table S1).

397 **Dissolution experiments.** Dust leaching experiments were designed to replicate dust addition to the bioassay experiments as closely as possible. Leaching experiments were performed after the cruise 398 inside a class-1000 clean air laboratory at the National Oceanographic Centre, Southampton, UK, 399 under controlled physico-chemical conditions (12 h light/dark cycles, ~ 25° C) using filtered Southern 400 Ocean surface seawater collected from the "Fish" sampler during DY111 (-56.9° S, -88.7° E). 401 Glaciogenic (SMD13-3 and PMG) and non-glaciogenic (CAR19) sediment was added to 1.5 L of 402 seawater in 2 L acid-washed and well rinsed polycarbonate bottles according to the methods outlined 403 for the nutrient amendment experiments. Sub-samples for dissolved trace metal analysis were taken 404 405 after 2 and 6 days by filtration through acid-washed 0.2 µm pore size, 25 mm polycarbonate track-406 etched membrane filters (Nuclepore, Whatman) before acidification (0.024 M) by addition of 12 M 407 ultrapure HCl (UpA, Romil). The filtration manifold consisted of acid-cleaned PTFE manifold tubing and PVC peristaltic pump tubing. A new filter was used for each sub-sample. Dissolved trace metals 408 409 in sub-samples from the dissolution experiment were analyzed at the same time as for the DY111 ambient samples. Whilst metal adsorption to bottle walls may occur over a 2-day period (71), this 410 411 effect would have been minimized through the large surface area to volume ratio of our experiment 412 bottles, whilst reasonably rapid establishment of equilibrium occurred, as we measured no significant 413 change in either Fe or Mn between two and 6-day time points.

**Dust particle digestion.** Dust samples were fully digested after the cruise following recommended GEOTRACES protocols (72). Briefly, the samples were transferred into trace metal-clean perfluoroalkoxy vials (Savillex) under a laminar flow fume hood in a class-100 clean laboratory, into

which 1 mL of digest solution (50% HNO<sub>3</sub> + 10% HF, v/v, Optima Grade, Romil) was pipetted. Vials were refluxed at 135 °C for 4 hours and then evaporated to near dryness. Once cooled, 100  $\mu$ L of concentrated HNO<sub>3</sub> was added to each vial and the samples dried down again. Samples were redissolved in 3 mL of 5% HNO<sub>3</sub> solution (spiked with 1 ppb indium as a drift monitor) and refluxed at 135 °C for 1 hour. A 0.5 mL aliquot of each sample was diluted to 3 mL with the same 5% HNO<sub>3</sub> solution in trace metal-clean, polyethylene Omni-vials (DWK Wheaton<sup>TM</sup>), for analysis by HR-ICP-MS (Element XR – Thermo Scientific<sup>TM</sup>) at the National Oceanography Centre, Southampton, UK.

- Statistical analysis of experimental results and interpretation of '(co-)limitation'. Differences 424 between the various response variables within the experiments were assessed using ANOVA followed 425 by a Bonferroni means comparison test (p<0.05). We adopt a similar definition framework for different 426 'types' of '(co-)limitation' as previously (3, 43, 73), noting that evidence of both serial and independent 427 428 responses frequently occurred, sometimes within the same experiment (e.g., Fig. 2 and Figs. S1-S3). Moreover, we differentiate at points in the text between stress (a physiological response to 429 430 environmental change, e.g.,  $F_v/F_m$  increasing following amendment with a nutrient indicating lower nutrient stress) and 'limitation' (e.g., biomass or equivalently net growth rate increases following 431 amendment with a nutrient indicating lowered nutrient limitation) (43). We note that although the 432 former (i.e., a physiological response) is clearly a necessary precursor for the latter, they are not 433 434 synonymous and are timescale dependent (3). However, all provide evidence for multi-nutrient influence on phytoplankton ecophysiology. 435
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Figure 1. **Biogeochemical setting and spatiotemporal development of Fe and Mn (co-)limitation.** (A) Annual mean dust deposition  $(g m^{-2} y^{-1})$  in and around the Southern Ocean (24) alongside (B) December 2019 mean sea surface temperature and (C) chlorophyll-*a* concentration (Modis AQUA at 4 km resolution) for the study region (red trapezoid in 1A). (D-I) Hovmöller diagrams (time against latitude) showing in situ biogeochemical progression during the DY111 cruise for sea surface chlorophyll-*a* (D), silicate (E), dMn (F), dFe (G), Mn<sub>Fe</sub>\* (H), *Fv/Fm* (I). (J-K) Summarized experimental responses (larger volume experiments after 6-days) to nutrient addition as indicated by 606 changes in Fv/Fm (J) and chlorophyll-*a* (K). Symbol colors indicate the identity and type of limitation, 607 see Figs. S1-S3 (43). Locations of the larger type experiments are labelled in J, see Fig. S6 for all 608 experimental times / locations.

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Figure 2. Example responses of phytoplankton ecophysiology to nutrient and dust additions. (A-610 611 B, E-F) Apparent photochemical efficiency of PSII (Fv/Fm) and (C-D, G-H) chlorophyll-a response to nutrient and dust amendment in Ex-L5 at OOI (A-D) and Ex-L7 at TN (E-H), respectively. For 612 clarity only a subset of the nutrient and dust additions are shown in the time series A, C, E, G, with the 613 614 day 6 data for all treatments included in B, D, F, H. Symbols for all panels are indicated in C. Large 615 open circles in A, C, E, G indicate initial values. Means (± 1 standard deviation) are indicated in all panels, with individual data points also provided (small symbols) for B, D, F, H. Statistically 616 617 indistinguishable means evaluated across all treatments in full factorial manner are labelled with the 618 same letter (analysis of variance (ANOVA) followed by Bonferroni post-hoc means comparison test 619  $P \le 0.05$ ).

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Figure 3. Change in apparent photochemical efficiency of PSII ( $\Delta Fv/Fm$ ) and net growth rates ( $\mu$ ) in response to nutrient and dust amendment across all experiments. Delta notation ( $\Delta$ ) indicates change relative to the values in control bottles. Data shown here correspond to the mean responses (*n*=2-3) from all treatments across all bioassay experiments.

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Figure 4. **Patagonian dust dissolution.** Mean ( $\pm 1$  standard deviation) of dissolved (0.2 µm) trace metal concentrations per unit mass added resulting from leaching of glaciogenic (SMD13-3, PMG) and non-glaciogenic (CAR19) Patagonian dusts into ambient Southern Ocean seawater. Colored circles represent experimental duplicates.

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