Title: A "shallow bathtub ring" of local sedimentary iron input maintains the Palmer Deep
 biological hotspot on the West Antarctic Peninsula shelf.

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25 ABSTRACT

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27 Palmer Deep is one of several regional hotspots of biological productivity along the inner 28 shelf of the western Antarctic Peninsula. Proximity of hotspots to shelf-crossing deep troughs has led to the "canyon hypothesis", which proposes that circumpolar deep water flowing shoreward 29 30 along the canyons is upwelled on the inner shelf, carrying nutrients including iron (Fe) to surface 31 waters, maintaining phytoplankton blooms. We present here full-depth profiles of dissolved and 32 particulate Fe and manganese (Mn) from eight stations around Palmer Deep, sampled in January 33 and early February of 2015 and 2016, allowing the first detailed evaluation of Fe sources to the 34 area's euphotic zone.

We show that upwelling of deep water does not control Fe flux to the surface; instead, shallow sediment-sourced Fe inputs are transported horizontally from surrounding coastlines, creating strong vertical gradients of dissolved Fe within the upper 100m that supply this limiting nutrient to the local ecosystem. The supply of bioavailable Fe is therefore not significantly related to the canyon transport of deep water. Nearshore time-series samples reveal that local glacial meltwater appears to be an important Mn source but, surprisingly, is not a large direct Fe input to this biological hotspot.

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44 Media Summary:

45 Situated in nearshore waters of the western Antarctic Peninsula, Palmer Deep is one of 46 several regional hotspots of biological productivity. High phytoplankton growth suggests a

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notably strong source of the limiting nutrient iron (Fe). Here, we provide the first measurements 47 with which to test this hypothesis. We show that upwelling of deep water does not control Fe 48

49 supply to the surface; instead, shallow sediments provide Fe inputs are transported horizontally

50 from surrounding coastlines, at depths just below the surface, creating strong vertical gradients

51 of dissolved Fe within the upper 100m, and supplying Fe to the local ecosystem.

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KEYWORDS: iron, manganese, biogeochemistry, Antarctic, sediment, phytoplankton, nutrient

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1. Introduction

57 58 59 The Southern Ocean south of the Polar Front is widely considered to be a High Nutrient Low 60 Chlorophyll (HNLC) region, where phytoplankton biomass is limited in part by availability of 61 the micronutrient Fe [1, 2]. Phytoplankton abundance increases with proximity to the Antarctic 62 continent [3], leading to the presumption that Fe limitation is at least to some extent relieved by 63 continental sources [4]. The Western Antarctic Peninsula (WAP) continental shelf region is 64 characterized by high phytoplankton concentrations, as assessed by remote sensing, though with considerable spatial, seasonal, and interannual variability characterizing summertime blooms [5-65 9]. On the WAP shelf, phytoplankton biomass in summer (January) is higher generally on the 66 67 inner shelf than on the outer shelf and seaward of the shelf break [5-9]. In particular, several inner shelf biological "hotspots" have been identified, where organisms at all trophic levels from 68 69 phytoplankton [10] to penguins [11] are more abundant than in other coastal regions of the WAP. 70 These hotspots, including Palmer Deep (PD), occur adjacent to the inner shelf termini of cross-71 shelf canyons, geological features resulting from ice scour during the last Glacial period. The 72 hypothesis that the concentrated activity of higher organisms is driven by bottom-up mechanisms 73 such as nutrient flux is supported by recent observations that phytoplankton biomass is indeed 74 significantly higher in these regions [10], and that diatoms, critical prev and bottom-up controls 75 on krill populations [12], compose an anomalously high fraction of the phytoplankton 76 assemblage [10]. Recent work with autonomous gliders supports this view, and locates the high 77 phytoplankton regions and coincident penguin foraging locales to the flanks of the canyon along

78 sharp bathymetric gradients [11].

79 Only recently have data become available to support earlier hypotheses that the 80 availability of Fe in the euphotic zone exerts a key control on the distribution of phytoplankton 81 production over the WAP shelf [13-15]. These new findings were preceded by earlier work that 82 focused on control of phytoplankton growth by mixed layer depth and light availability over the 83 WAP shelf, with the implicit assumption that macro- and micronutrients were replete 84 everywhere, but with no explicit mention of Fe [6]. A competing hypothesis argued that 85 upwelling of Upper Circumpolar Deep Water (UCDW), which is variable in space and time on 86 the WAP, determined which regions experienced high primary production and high fractions of 87 diatoms, but did not speculate on a connection to Fe supply [16]. Garibotti et al. [8, 17] 88 suspected that the seasonal progression of phytoplankton assemblages, expressed geographically 89 in WAP surface waters, may result from Fe removal by early-blooming diatoms following sea 90 ice retreat. A quarter century of data collected as part of the Palmer-LTER program [18] indicate

91 that macronutrients are seldom exhausted in the WAP region [19]. This suggests that trace 92 elements and/or light control the distribution of primary producers on the shelf as a whole, as93 well as within the hotspots.

94 The "canyon hypothesis" posits that the locations of the biological hotspots [11] on the 95 WAP are determined by the preferential upwelling of UCDW at the nearshore termini of the 96 several canvons or troughs that traverse the shelf from the shelf break to the inner coastal 97 regions. The implication is that the relatively high nutrient content of UCDW provides bottom-98 up support for high productivity in regions of upwelling, including the nearshore hotspots. Given 99 the abundance of macronutrients in surface water throughout the WAP, including at PD, it is 100 reasonable to assume that Fe is the critical nutrient supplied by the upwelled deep water. 101 However, until the present work, no measurements of subsurface Fe concentrations in PD were 102 available to test this idea.

103 Recently, the first description of the spatial distribution of potentially-limiting dissolved 104 Fe (dFe) concentrations in surface waters on the WAP was presented for January of 2010, 2011 105 and 2012 [12]. It was found that, while in general the inner shelf regions are relatively rich in 106 dFe, large regions of the mid- and outer-shelf have surface dFe concentrations low enough to 107 potentially limit productivity of at least some members of the phytoplankton assemblage (<0.15 108 nmol kg⁻¹; similar to surface waters of the off-shelf polar Southern Ocean HNLC region [13]). A 109 complementary study of springtime dFe distributions confirmed relatively high concentrations 110 inshore, increasing with depth [14]. However, neither study included investigation of a nearshore

hotspot with sufficient spatial resolution and sampling density to identify the specific
mechanisms that could lead to high dFe flux to surface waters, or whether Fe delivery to hotspots

113 is indeed related to UCDW upwelling.

Here we report an intensive study of dissolved and particulate distributions of Fe and Mn in the region of the PD hotspot, in the northern WAP adjacent to Palmer Research Station, in January of 2015 and 2016 (Fig. 1). This targeted investigation of hotspot micronutrient distribution refutes the canyon hypothesis that UCDW upwelling supplies the critical limiting nutrient. Instead, the results indicate that vertical mixing of laterally transported Fe derived from relatively shallow local sediments, at dFe concentrations exceeding those found in deep waters, provides the Fe flux that maintains the biological hotspot at PD.

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2. Methods

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a) Trace metal clean seawater collection:

Water column profile samples for this study were collected during the annual cruises of the
RV *Laurence M. Gould* as part of the Palmer LTER program. The two 2015 cruise stations were
collected on January 6 and 8, 2015 (15-24 and 15-48). During the 2016 cruise, three PD stations
were sampled early in the cruise on January 11-12, 2016 (16-15, 16-24 and 16-31) and three
were sampled late in the cruise on February 6-8, 2016 (16-394, 16-414 and 16-445; Fig. 1).
The methods employed for clean seawater collection were very similar to those used in the

132 GEOTRACES program [20]. Seawater samples for iron analysis were collected using a trace

133 metal clean (TMC) rosette composed of twelve Teflon-coated Niskin-X bottles mounted on a

polyurethane-coated frame free of metal anodes. The rosette was deployed using a plastic-coated

135 custom-designed winch and an aramid conducting cable through an anodized aluminum sheave.

136 The Niskin-X bottles were stored and prepared in a metal-free clean room in the ship's

137 laboratory, constructed of plastic sheeting over an unpainted wooden frame and inflated

138 continuously with HEPA-filtered air to avoid metal contamination. Immediately before a cast,

139 each bottle was carried individually from the clean room and mounted on the rosette on deck.

140 Bottles were cocked and open for the minimum possible duration before deployment, to

141 minimize deck contamination. Bottles were closed on ascent while the package moved upward at

142 <10 m min⁻¹ to ensure that the seawater sample was collected as the rosette moved into clean

143 seawater. Filled Niskin bottles were returned to the clean room as soon as possible after 144 recovery.

145 Once racked in the clean room, each Niskin-X bottle was pressurized to ~0.5 atm using an air 146 pump and manifold fed by HEPA-filtered air and re-filtered just before entering each Niskin

147 bottle. An acid-cleaned piece of Bev-A-Line tubing was secured in the stopcock and rinsed with

148 sample seawater before an acid-cleaned Acropak-200 (0.2 µm) capsule filter was attached to the

149 line. After the filter was flushed with ~1 L of seawater, acid-cleaned LDPE bottles were filled

150 with filtered seawater following three $\sim 10\%$ -volume bottle rinses. Samples were acidified to

151 0.012 M HCl (pH ~2) using concentrated ultrapure acid (Optima grade, Fisher Scientific) and 152 stored until analysis.

153 Particulate samples were pressure-filtered at ~0.5 atm from 2-7 L of seawater using a Niskin-154 mounted filter holders containing acid-washed 25mm Supor filters (0.45 µm), following the 155 methods of Planquette and Sherrell [21]. Excess seawater was removed by gentle suction, and

156 filters were then frozen in acid-cleaned polystyrene Petrislides until analysis. All equipment was 157 acid washed prior to use.

158 Surface water was collected at LTER Station E (6.5 km NE of the head of PD; Figure 1), 159 using an acid-cleaned all-polypropylene syringe and 0.45 µm pore size Supor syringe filter. Sampling was completed while leaning over the side of a slowly-moving inflatable Zodiac boat, 160 161 as detailed in Carvalho et al. [22]. Samples were collected in duplicate during 11 one-day 162 expeditions between January 5 and March 9, 2015. The mean of the duplicates is reported if they 163 agree within $\pm 15\%$ (difference about the mean), otherwise the lower of the two values is reported.

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b) Dissolved and particulate trace metal analysis:

167 Stored acidified filtered seawater samples were analyzed for Fe and Mn (as well as Zn, Cu, 168 Ni, Cd, and Pb; to be reported elsewhere) using an offline commercial version of the isotope 169 dilution-inductively coupled plasma mass spectrometry (ICP-MS) method of Lagerström, Field 170 [23], using procedures similar to those described in detail in Annett et al. [13]. In short, 10 mL 171 aliquots of seawater samples were automatically extracted using the commercially available 172 SeaFAST pico system (Elemental Scientific, Inc.) after online buffering to pH ~6.5 using 173 ammonium acetate and a 25-fold pre-concentration into 10% v/v ultrapure nitric acid (Optima 174 grade, Fisher Scientific). The standardization of Fe employed the method of isotope dilution, 175 while Mn was standardized using external matrix-matched standards that were extracted and pre-176 concentrated identically to samples. Extracts were analyzed using an Element 1 sector-field ICP-177 MS (Finnigan MAT). Accuracy was assessed by repeated measurements of SAFe surface (SAFe 178 S) and deep (SAFe D2) Pacific Ocean reference seawater samples. Our measurements of SAFe S 179 gave Fe=0.102±0.021 (n=29 over a 2-month period; consensus 0.093±0.008) and Mn=1.00±0.05 180 (n=34 over a 2-month period; consensus 0.79±0.06). Our measurements of SAFe D gave 181 Fe=0.968±0.066 (n=39 over 1 year; consensus 0.933±0.023) and Mn=0.48±0.02 (n=37 over 1 182 year; consensus 0.35±0.05). Consensus values are from the most recent May 2013 compilation

183 (http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials). 184 Precision, determined by replicated analysis of two different in-house large-volume reference seawater samples within each analytical session, was typically $\pm 3\%$ or better. 185

186 In a trace-metal clean laminar flow hood, particulate filters were cut in half to provide 187 samples for both total particulate digestion and leachable metal content, using a new surgical 188 stainless steel razor blade for each profile. Filter halves were digested for total particulate metals 189 using an HNO₃/HF solution and ICP-MS analysis for a large suite of elements, following the 190 method of Planquette and Sherrell [21]. Filter halves for leachable metals (LpFe and LpMn) 191 were heated (~90°C) for 10 minutes in 25% (v/v) ultrapure acetic acid solution (Optima grade, 192 Fisher Scientific) with a small addition of hydroxyl amine reducing agent [24], left to cool 193 slowly for 2 hours, and centrifuged. The supernatant was removed with an acid-rinsed pipette to 194 a clean Teflon PFA vial, 100 uL concentrated HNO₃ was added with 30 ng of Cs as a vield 195 tracer, and the sample dried down on a Teflon-coated hotplate in a HEPA filtered-air fume hood. 196 Another 100 uL concentrated HNO₃ (Optima grade, Fisher Scientific) was added and the sample 197 was dried down again to digest and drive off remaining leaching solution organic compounds. 198 The residues were re-dissolved in a 5% (v/v) HNO₃ solution (Optima grade, Fisher Scientific) by

199 heating at 95°C for 2 hours with vial caps tightened. Samples were then analyzed by ICP-MS as 200 for total particulate digests.

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c) Seawater oxygen isotope ratio analysis:

202 Samples were collected from the ship's CTD/rosette (deployed at the same stations and 203 204 typically within 2 hours of the TMC CTD deployment) during the annual cruises of the RV 205 Laurence M. Gould as part of the Palmer LTER program. Samples were also collected from the surface and/or 10m at Station E during quasi-weekly water column profiling, as described above. 206 207 Samples were stored in 50mL glass bottles, which were sealed with stoppers and aluminum 208 crimps, and subsequently transported to the Natural Environment Research Council (NERC) 209 Isotope Geosciences Laboratory at the British Geological Survey, UK, for determination of the ratio of stable oxygen isotopes in seawater (δ^{18} O, being standardized values relative to Vienna 210 211 Standard Mean Ocean Water, VSMOW). A VG Isoprep 18 and SIRA 10 mass spectrometer was 212 used for analysis, with duplicate analyses revealing a precision better than 0.02‰. Paired δ^{18} O 213 and salinity data were used in a simple 3-endmember mass balance to quantify separately the 214 contribution to the freshwater budget from sea ice melt (%SIM) and that from meteoric water 215 (%MET; the sum of glacial discharge and precipitation into the ocean). This endmember balance 216 method was developed originally by Östlund and Hut [25], and has been implemented at the 217 WAP for both coastal and shelf-wide freshwater studies (e.g. Meredith et al. [26]). The values of 218 the endmembers used here (i.e. the values of the "pure" forms of oceanic water, sea ice melt and 219 meteoric water prior to these endmembers mixing to form the waters sampled) were, respectively, salinity = 34.73, 7, 0 and $\delta^{18}O = 0.1, 2.1, -16$; typical errors in the derived 220 221 freshwater contributions are better than 1%. Full details are provided in Meredith et al. [26]. 222

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3. Results

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a) Hydrographic variables

227 The potential temperature and salinity profiles are within the range of those observed 228 previously at this inner shelf region [22]. The temperature is generally variable in surface waters, 229 depending on local variations in the recent history of solar warming, heat and water flux, sea ice

230 melting, and mixing (Fig. 2). Below this lies a Winter Water (WW) layer with potential 231 temperature about -1.2°C for most stations. Station 15-48, furthest from shore (Fig. 1), had the 232 thickest and deepest WW within the interval 50-100 m (unfortunately because of competing 233 sampling demands, no metals samples were taken in this depth interval). Late season 2016 234 profiles on the shallow flanks at the head of the canvon (16-414 and 16-445) had the warmest 235 upper water column profiles overall, and the strong temperature minimum evident at 20-50 m at 236 the nearby earlier stations 16-24 and 16-31 was apparently eroded by mixing with warmer water 237 above and below, even to a greater degree than observed with glider data at the flank stations 238 collected just 3-4 days prior (compare Fig. 2 to Fig. 6 of Carvalho et al. [22]). The regionally 239 modified UCDW endmember is generally found at depths >400 m, and is characterized by 240 potential temperature ~1.4°C and salinity ~34.7.

241 242

b) Dissolved Fe

243 Dissolved Fe concentration profiles at the eight PD CTD stations were relatively similar 244 except at the most coastal station, located south of PD (16-394), and displayed modest but 245 significant differences reflecting geographical position and temporal variation (Fig. 3a,e; Table 246 S1). The dFe was moderately low in the upper 20m (most values 0.2-0.5 nmol kg⁻¹ up to 0.8 247 nmol kg⁻¹ at two stations; Fig. 3a,e) and increased approximately linearly to maxima as high as 3.5 nmol kg⁻¹ found at depths ranging from 75-200m, then decreased to 1.8-2.5 nmol kg⁻¹ near 248 249 400 m. The two 2015 stations near the middle of the canyon (15-24 and 15-48) showed slight 250 increases in dFe from 400 m to the bottom (1200-1300 m), with maximum concentrations as 251 high as 2.6 nmol kg⁻¹ at 10 m off the bottom. Station 16-15 was unique in showing the deepest 252 maximum (200 m), anomalously high concentrations from 400-700m, and lower concentrations 253 below 700 m than the 2015 deep stations, with no increase to the sediments. Overall most 254 samples in the core of the UCDW (>400 m) had dFe concentrations of 2.0-2.5 nmol kg⁻¹.

255 Among the stations in the NE sector of the sampling region in the vicinity of the head of 256 the canyon and closest to Palmer Station (Fig. 1), the stations over the northern flank, 16-24 and 257 16-414, had relatively deep dFe maxima between 100 m and 200 m. These maxima also had 258 higher concentrations than those over the southern flank (16-31 and 16-445) which occurred 259 shallower, at 75-100m. In addition, the canyon head stations that were occupied 27 days later in 260 the cruise (16-414 and 16-445) had lower dFe overall through the upper 200 m than the nearby 261 but earlier-occupied stations (16-24 and 16-31, respectively), representing apparent temporal 262 variability in dFe concentrations in this region, although a role for short spatial gradients cannot 263 be ruled out.

Notably, the southern coastal Station 16-394 differed strongly in dFe distribution from all other stations, with high concentrations of 1.1 nmol kg⁻¹ in surface waters (5 m), increasing strongly to a local maximum of 7.3 nmol kg⁻¹ at 50 m (Fig. 4). This maximum was followed by a slight decrease to 6.9 nmol kg⁻¹ at 65 m, and thereafter a linear increase to the very high value of 12.4 nmol kg⁻¹ near the bottom at 289 m. These results suggest a strong nearshore Fe source throughout the upper 300 m in this PD region south of the canyon.

- 270 271
- c) Dissolved Mn

While dFe which varied spatially by <3-fold in the surface waters, dMn was much more variable, exhibiting a 10-fold range in surface waters (Fig. 3c,g; Table S1). Surface maxima were observed only at Stations 15-24 and 15-48, where surface dMn was 4.1 and 2.6 nmol kg⁻¹, respectively. The 2015 surface value of 4.1 nmol kg⁻¹ over the middle of the canyon (LTER grid

276 station 600.040; Fig. 1) was the highest surface water dMn measured in the region, despite the distance from coastal sources. The surface dMn variations at the other stations (0.6-2.9 nmol kg⁻¹ 277 278 at 5-10 m depth) reflected varying degrees of local surface minima. All stations except three (15-279 24, 15-48 and 16-394) showed similar local subsurface dMn maxima of 3.0-4.2 nmol kg⁻¹ at 280 similar depths (50-65 m) and isopycnals, shallower and stronger than the dFe maxima. Below 281 these maxima, dMn decreased rapidly and similarly for most profiles to values near 1.0 nmol kg⁻ 282 ¹ at 400 m, though 15-24 was a higher outlier. Stations 15-24 and 15-48 showed nearly vertical dMn profiles at ~ 1.0 nmol kg⁻¹ from 400 m to the bottom, while dMn at 16-15 was also nearly 283 homogenous in this depth interval, but was significantly lower at ~0.8 nmol kg⁻¹. Coastal station 284 285 16-394 was anomalous in having a very strong subsurface maximum of 8.8 nmol kg⁻¹ at 35 m, 286 coincident with particulate Fe and Mn peaks (Fig. 4). Below this maximum, dMn decreased very 287 rapidly to 5.3 nmol kg⁻¹ at 50 m, and more slowly below that to a minimum of 3.3 nmol kg⁻¹ near 288 the bottom, remaining at roughly twice the concentrations found in the canvon stations (Fig. 3c). 289

d) Particulate Fe

291 Much higher concentrations of Fe were observed in suspended particulate form than in 292 dissolved form, over the entire water column at all stations. Total suspended particulate Fe (total 293 particulate Fe; TpFe) showed very strong variability with depth and between stations (Fig. 3b,f; 294 Table S1). In general, TpFe was at minimum concentrations in surface waters, though the 295 minimum varied from 1.2 to 12.4 nmol kg⁻¹ at the open water sites. A surface local minimum as 296 also observed at coastal Station 16-394, but it was much higher at 127 nmol kg⁻¹. Subsurface 297 local maxima in TpFe, of strongly varying intensity, occur within the interval 75-200 m (except 16-394, which had a shallower maximum at 35m). Concentrations of TpFe at the 75-200 m 298 299 subsurface maximum varied from ~ 20 nmol kg⁻¹ at 15-48 and 16-24, to a very sharp peak of 155 300 nmol kg⁻¹ at 78 m at 16-445, to a volumetrically huge peak centered at 35 m at the south coastal 301 station 16-394, with maximum TpFe at the highest value found in this study (230 nmol kg⁻¹). 302 This southern coastal station had the highest Fe concentrations at all depths (Figs. 3, 4), even 303 though concentrations decreased from the 35 m maximum to a minimum of 100 nmol kg⁻¹ near 304 the bottom. For comparison, the highest TpFe found in the Amundsen Sea embayment, ~120 305 nmol kg⁻¹, was observed in near-surface waters adjacent to the Crossen Ice Shelf [27]. At the 306 deep canyon stations of PD. TpFe increased roughly 2-fold from 500 m to the bottom, to 307 maximal values for these stations of 50-65 nmol kg⁻¹ at 1210-1320 m. These deep and thick 308 nepheloid layer signals were either not observed or were very subtle in the shallower stations to 309 northeast and south, with bottom depths at \leq 500 m.

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290

e) Particulate Mn

312 Suspended particulate Mn (total particulate Mn; TpMn) showed strong spatial variability 313 in the upper 50 m, with profiles from 50-400 m that were similar in shape to TpFe, but much 314 lower in concentration (Fig. 3d,h; Table S1). Opposite to the Fe speciation, dMn exceeded TpMn 315 at most near-surface locations, and TpMn was at a minimum in near-surface waters of most 316 stations. The canyon head stations 16-414 and 16-445 and also the coastal 16-394 were 317 exceptions in having a local TpMn maxima at or near the surface (Figs. 3d, 4). Subsurface 318 maximum TpMn concentrations occurred in the 75-150 m interval, generally corresponding in 319 depth to the TpFe maxima at the same stations, with maximum values <4 nmol kg⁻¹ (except for 320 coastal station 16-394; Fig 4). For deep stations near the center of PD, a second and larger 321 maximum occurred at or near the bottom, with an increasing gradient to this maximum starting at 500 m, though with a lesser relative gradient to the bottom than for TpFe. As for TpFe, these
near-bottom increases in TpMn were absent (or nearly so) for canyon slope stations 16-24 and
16-31.

- 325 326
- f) Comparison of dissolved and particulate pools

327 The relative profiles of dissolved and particulate Fe and Mn, including the weak acid 328 leachable fraction (LpFe, LpMn), are displayed for three characteristic stations in Fig. 5. The 329 labile fraction of Fe (LpFe) generally accounts for less than half the total particulate Fe (TpFe) 330 but its relative contribution increases in offshore near-surface waters as in Station 15-24. In 331 contrast, LpMn accounts for more than half of TpMn in the upper 50-100m and nearly 100% in 332 the upper 20m of Stations 16-414 and 16-445 (Fig. 5; Table S1). However, the contribution of 333 LpMn decreases to less than half of TpMn in the deeper waters of all stations at which labile 334 particulate metals were determined (Fig. 5; Table S1).

335 336

g) Glacial meltwater and precipitation

337 The distribution of oxygen isotopes of seawater indicated a strong maximum in the 338 fraction %MET in surface waters at all stations (Fig. 2). Meteoric water contributed 3-4% 339 volumetrically in the upper 20 m at all stations, when calculated relative to the CDW 340 endmember. Despite its location in the center of PD, well offshore, Station 15-24 had high 341 %MET in surface water and the highest meteoric fraction mixed down to 200 m, with ~1% at 342 200 m. Occupied one year later at the same location, Station 16-15 had significantly lower 343 %MET throughout the upper 200m. In contrast, at the coastal station 16-394 the %MET decreased rapidly from a surface maximum just over 4% to <0.5% at 50 m, with a slight decrease 344 345 thereafter to the bottom. The other profiles fell between these bounds, although the late-cruise 346 2016 stations near the canyon mouth (16-414 and 16-445) showed essentially no meteoric 347 component below 100 m, within the errors of the calculation.

348 349

h) Sea ice melt

The profiles of %SIM show values in the range -1 to $\pm 1\%$ over most of the water column sampled (Fig. 2). Negative values here denote waters that were subject to net sea ice formation prior to being sampled, though the low values observed are generally not significantly different from zero. The exception to this pattern is the upper 20-30 m, over which there is often a modest increase towards the surface, with some values exceeding $\pm 2\%$, indicative of variable summerseason sea ice melt at the surface. There does not appear to be a consistent relationship between %SIM and trace metal distributions.

- 357
- 358 i) Station E surface dissolved metals

359 In the surface waters of Station E, roughly 3 km south of Palmer Station (Fig. 1), dFe varied 360 widely from 0.6-6.9 nmol kg⁻¹ (previously reported in [22]), and dMn from 0.7-3.8 nmol kg⁻¹ 361 (Fig. 6). The temporal variations in dFe and dMn displayed an anti-correlation overall; dMn was 362 lowest when dFe was highest, and vice versa. The CTD profiles taken at each sampling event 363 allowed mixed layer depth (MLD) to be calculated, using the methods of Carvalho et al. [22]. 364 The dFe concentrations were low through much of January, and MLD shallow. When MLD 365 deepened to 39 m at the onset of a windy February [22] dFe increased sharply to its maximal value of 6.9 nmol kg⁻¹, while dMn fell to its minimum value of 0.76 nmol kg⁻¹. The MLD 366 deepened to 76 m on the next sampling occasion, and dFe fell to 3.8 nmol kg⁻¹. Through the rest 367

of the sampling period, dFe continued to fall and dMn to rise slightly, until the last sampling date
when MLD shoaled and dFe dropped to near the January levels. The %MET in these surface
waters (sampled at 0 m or 10 m) remained between 3% and 4% over the entire sampling period,

- 371 with a broad subtle maximum centered in late January.
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- 374 DISCUSSION
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- 376 377
- 4. A shallow sub-surface dissolved Fe maximum.

378 The PD region has been described as one of three regional WAP hotspots of biological 379 productivity at all trophic levels, with maximum phytoplankton productivity typically in January 380 [10]. The high productivity has been described as resulting from upwelling, driven by winds and 381 the regional canyon bathymetry [11] with the implication that nutrient supply from below makes 382 this region especially productive, encouraging krill growth [28], supporting seabirds and 383 mammals [29] and maintaining a local penguin colony near Palmer Station [30]. At the same 384 time, because macronutrients are rarely drawn down to limiting concentrations in this region and 385 on the WAP shelf overall, it was inferred that the supply of micronutrients (e.g. Fe; [2]) from 386 upwelled UCDW allowed the PD euphotic zone to be more productive than surrounding inner 387 shelf regions (though see an alternative view, [31]). From previous studies of trace metal 388 distributions in the off-shelf deep Southern Ocean, it was realized that dFe was more 389 concentrated in UCDW than in surface waters of the Southern Ocean overall [14, 32], and 390 incursions of UCDW along cross-shelf canyons were thought to supply the hotspots, including 391 PD, with Fe sourced from deeper off-shelf waters, brought to the PD euphotic zone by upwelling 392 following the long transit to the inner shelf [33]. However, none of these earlier studies had 393 access to water column Fe data with which to test this hypothesis.

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395 The data presented here show that modified UCDW (potential temperature ~ 1.4 °C), found in 396 the deeper regions of PD (>400 m at most stations), carries about 2.0 nmol kg⁻¹ dFe, indicating 397 that it is certainly enriched during its transit across the shelf, relative to the off-shelf open ACC 398 UCDW endmember (dFe ~0.4 nmol kg⁻¹ [14]). However, our results reveal a shallower dFe 399 maximum of \sim 2-4 nmol kg⁻¹, centered at 75-200m, falling in the upper part of the mixing zone 400 between UCDW and WW, and much shallower than the core of the UCDW. The proximity of 401 this relatively shallow dFe maximum to the euphotic zone indicates that this feature is the 402 primary driver of the strong upper water column gradient in dFe that supplies the PD euphotic 403 zone with the limiting micronutrient through vertical diffusion and wind-driven mixing events. The surface dFe concentrations of 0.2-0.8 nmol kg⁻¹ are substantially higher than those found in 404 405 surface waters of the outer shelf or seaward of the shelf break in the open Southern Ocean [13]. 406 The details of Fe availability and biological response are beyond the scope of this paper, but the 407 relatively high surface dFe concentrations are consistent with the PD hotspot phytoplankton 408 being Fe-replete overall in January, allowing variations in productivity to be controlled largely 409 by light availability and MLD (F. Carvalho pers. comm.). Overall, we see very little resemblance 410 between dFe or TpFe concentrations and endmember water masses as defined by 411 temperature/salinity characteristics (Fig. 2, inset), consistent with our interpretation that Fe 412 distributions that are controlled by local sources and sinks rather than by mixing of water masses 413 with well-defined Fe concentrations.

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- 5. A dominant sedimentary Fe source is indicated by suspended particle distributions.

416 417 The source of the upper water column dFe maxima is informed by the distribution and composition of suspended particles. At every station measured in this study, TpFe shows a sub-418 419 surface maximum at 75-200m, the magnitude of which decreases in general with distance from 420 shore (Fig. 3b,f). The comparison of leachable particulate Fe (LpFe) to total particulate Fe 421 (TpFe) suggests that suspended Fe exists mostly within refractory terrigenous particles (LpFe 422 ~12-36% of TpFe; Fig. 5, Table S1), an assertion reinforced by total particulate Fe/Al ratios that 423 are very close to the crustal mean value (data not shown). While the depth of the peak varies by 424 station, the range of seawater densities at which the TpFe maxima appear is fairly narrow, at σ_{θ} = 425 27.44-27.71. In particular, stations sampled close to each other in time tend to have TpFe peaks 426 falling at very similar densities even if they are at different depths; for example, the shallow 427 sharp peak at 16-445 (southern flank; Fig. 1) occurs on almost exactly the same density surface $(\sigma_{\theta} = 27.61 \text{ at } 78 \text{ m})$ as the broader deeper peak at 16-414 (northern flank; $\sigma_{\theta} = 27.63 \text{ at } 100 \text{ m})$. 428 429 The TpFe peaks increased sharply from the PD center and slope to the shallower flanks near the 430 mouth of the canyon (16-24 vs. 16-414 and 16-31 vs. 16-445 in Fig. 3b,f) and even more so to 431 the very coastal station 16-394 (Fig. 4). While there is a possibility of substantial temporal 432 variation over the period of the cruise, especially in the upper water column and in association 433 with the early February wind mixing event, the characteristics described here overall suggest 434 strongly that the TpFe peaks resulted from lateral advection of fine resuspended sediment 435 occurring along the coast or near proximal islands, at 50m or shallower. The resulting suspended 436 particles then roughly followed isopycnals during horizontal eddy diffusion and advection, the peaks broadening and attenuating under the influence of vertical mixing and particle sinking 437 438 during transport to the sampling sites. Consistent with a coastal source and lateral dispersal, we 439 note that the lowest TpFe concentrations in the upper 300m are found at the most distal Station 440 15-48 (Fig. 3f).

441 At all stations, the dFe maximum occurs at or just below the upper water column TpFe 442 maximum. The depth relationships are illustrated by three representative stations where TpFe 443 peaks range in magnitude and occur at different depths (Fig. 5). In each case, the dFe peak was 444 vertically broader than the corresponding TpFe peak, maintaining high values for tens of meters below the peak, whereas the TpFe decreased with depth below the maximum. For example, at 445 PD Station 15-24 (Fig. 5a), the TpFe maximum of 34 nmol kg⁻¹ occurred at 75m, and peaks of 446 447 10 nmol kg⁻¹ LpFe and 2.8 nmol kg⁻¹ dFe were centered one sampling depth deeper (100m). As 448 well, down to 500m, the dFe and TpFe profile shapes follow each other fairly closely, at a 449 dFe:TpFe molar ratio of ~1:10. This suggests a strong relationship between TpFe and dFe, and 450 that both derive from a common sedimentary source. At Stations 16-414 and 16-445, the TpFe 451 peaks are much larger than at 15-24 but dFe remains in the 2-3 nmol kg⁻¹ range. A reasonable 452 assumption is that the concentration of dFe is controlled by the concentration of soluble organic 453 ligands and by the presence of $<0.2 \,\mu m$ colloidal Fe particles. It is also reasonable to assume that 454 dFe has a much longer residence time than TpFe, and thus integrates any temporal variations in 455 the depths at which sedimentary sources are injected into the water column at some distance 456 from the measured stations. The main source of Fe to the upper water column can thus be viewed 457 as a "shallow bathtub ring" of coastal sediment inputs surrounding PD to the north, east and 458 south, that are mixed and advected into the central canyon region of this biological hotspot. The 459 dominance of a sedimentary source is similar to recent findings showing efficient vertical mixing of a sedimentary Fe sources to feed phytoplankton blooms over a shallow bank on the outer RossSea shelf [34, 35].

462 The mechanistic relationship between dFe and sediment resuspension is difficult to 463 determine from the available data. The dFe may be sourced from shallow porewaters with high 464 dFe concentrations that are "mined" during resuspension events and released into the water 465 column. These porewaters may be highly enriched in soluble Fe(II) through shallow anaerobic 466 respiration [32, 36], or may be enriched in Fe(III) stabilized by high concentrations of dissolved 467 strong organic ligands resulting from the early diagenesis of organic matter at the sediment 468 surface. A second potential source mechanism is that surface sediment LpFe (likely some form 469 of Fe(III)) is resuspended along with refractory TpFe, and upon exposure to excess Fe ligands in 470 the water column or to sufficient energy to physically disaggregate a subset of these particles 471 into the colloidal size fraction ($<0.2 \mu m$), releases Fe(III) the dFe pool.

472 It is informative to note the unique dFe profile shape at Station 16-394, which has a local 473 maximum just below the TpFe maximum, as at other stations, but then displays a linear increase to very high near-bottom concentrations of >12 nmol kg⁻¹ (Fig. 4). This suggests that the nearby 474 475 deeper coastal sediments are a very strong source of dFe that does not scale with resuspension 476 intensity. This same profile type is common in Ryder Bay, another very coastal site that does not 477 impinge directly on a biological hotspot [37], but at that site dMn increases in parallel to dFe, 478 while at 16-394 dMn decreases to the bottom (Fig. 4). Thus, different metal source processes are 479 at play at Ryder Bay and 16-394; more generally, the mechanisms governing the Fe:Mn ratio of 480 dissolved inputs from sediments are not well understood [36]. We speculate that both dFe and 481 stabilizing dissolved ligands are released from coastal sediments at this station and likely from 482 shallower sediments shoreward of the station. Station 16-394 is unique in displaying a nearly 483 vertical density distribution from 100m to the bottom ($\sigma_{\theta} = 27.62-27.68$), within the range of 484 densities at which the dFe peak is seen offshore, and is therefore a possible source for the 485 offshore dFe maxima. The divergence of the pFe and TpFe profiles below ~75m suggests that 486 dFe sources need not be associated strictly with sediment resuspension. The details of processes 487 occurring proximal to the coastal Fe sources deserve further study.

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6. Glacial meltwater is a minor source of Fe to the Palmer Deep hotspot euphotic zone.

491 At most stations, dMn exhibited upper water column maxima that were considerably 492 shallower than the dFe peaks (Figs. 3-5). This difference can be interpreted as a result of the 493 relative importance of glacial meltwater as a source of dFe vs. dMn to the upper water column in 494 the PD region. While it is tempting to suggest that these dMn peaks also derive from shallow 495 sediments, they are often shallower by one or two sampling depths than the TpMn peaks (Fig. 3 496 c,d,g,h) that in turn tend to match the depths of the TpFe peaks, suggesting a combined TpMn 497 and TpFe source from sediment resuspension. As well, the dMn is quite variable in surface 498 waters, and 4 of the 8 profiles have local or absolute maxima at or near the surface (15-24, 15-499 48, 16-15 and 16-394; Figs. 3, 4). We hypothesize that the distribution of dMn in the upper 100m 500 results primarily from a meteoric water source (assumed dominated locally by glacial meltwater; 501 [38]), which we have shown is maximal at the surface (Fig. 2c,g), followed by variable 502 drawdown of dMn by biological and scavenging processes occurring in the upper 50m, inducing 503 a subsurface dMn peak as a byproduct of dMn removal in the uppermost water column, rather 504 than as a reflection of a subsurface lateral source of dMn at that depth. By this reasoning, the 505 stations with dMn maxima at the surface are the least altered from their near-shore source.

presumably a result of minimal biological removal relative to other stations (as for 15-24 and 15-48), or by virtue of being very close to a meltwater source (as for 16-394). The Station 16-15 profile suggests that removal of a meltwater source had only affected the shallowest sampled depth; otherwise the profile in the upper 75m is quite similar to the profile taken a year earlier in the same location (15-24; Fig. 3g). Some of the profiles show TpMn increases to surface or nearsurface maxima within the upper 50m (16-24,16-414 and 16-445, Fig. 3d; 16-394, Fig. 4), that

are not accompanied by TpFe peaks. In these near-surface waters, LpFe increases to the surface

- and becomes the major fraction of TpFe (Fig. 5). We speculate that the near-surface LpMn (and
- 514 TpMn) thus represents the complementary manifestation of the near-surface conversion of
- 515 meltwater-sourced dMn into the labile particulate phase, probably by a combination of
- 516 phytoplankton uptake and bacterial oxidation [39]. Homogeneous oxidation of Mn(II) by O_2 517 takes many years (~10⁷ times slower than Fe(II) oxidation; [40]) but a role for heterogeneous 518 inorganic oxidation in the catalyzing presence of MnO₂ particles cannot be ruled out in this 519 environment [41, 42].
- 520 Importantly, dFe shows none of this sort of behavior; it is uniformly low in surface 521 waters at all stations. This contrast in the behavior of dMn and dFe is consistent with the 522 combined effects of a high dissolved Mn:Fe ratio in glacial meltwater and relatively greater dFe 523 removal after input and during lateral transport within the surface layer. Indeed, measurements of 524 glacial meltwater streams from Marr Glacier, adjacent to Palmer Station (Fig. 1) show strong 525 variability but average dMn ~1600 nmol kg⁻¹ (possibly reflecting anoxia in the subglacial 526 hydrologic system) and a mean dMn:dFe molar ratio of ~7 (full meltwater data to be presented 527 elsewhere). The single sample reported in Annett et al. [13] turns out to be atypical in having 528 anomalously low dMn and a dMn:dFe ratio <1. We conclude that glacial meltwater has a large 529 effect on dMn but a small effect on dFe distributions in the broader PD region.

530 This conclusion is at odds with the recent description of surface water dFe and dMn 531 spanning three summers over the whole WAP shelf region [13], which showed evidence of a 532 broad, imperfect and variable, but significant, correlation between dFe and %MET for surface 533 waters of the entire WAP shelf region, but no such correlation for dMn. One possible 534 reconciliation of these observations is that on the larger regional scale, shallow vertical mixing 535 and variable biologically-mediated removal of both metals combines the δ^{18} O and dMn signal of 536 meltwater with the initially deeper dFe signal to result in inter-relationships among these 537 quantities that are highly variable and when measured in offshore waters may not reveal clearly 538 the controlling processes at and near the coastal sites of input. It is also possible that glacial 539 meltwater composition near Palmer Station is not typical of inputs to the wider WAP. Further 540 measurements of various glacial meltwater streams and proximal coastal waters will be required 541 to better understand the effects of glacial melt on the WAP as a whole. Nonetheless, the data 542 presented here strongly suggest that for the PD region, glacial meltwater inputs have little effect 543 on dFe distributions.

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7. Further clues from time-series sampling of coastal surface water.

The fundamental findings of this work, a strong meltwater source of dMn and a subsurface sedimentary source for dFe for the PD region, are supported by the early 2015 timeseries sampling of dissolved metals in surface water at Sta. E, located ~3km south of Palmer Station in ~100m of water. Surface water dFe through much of January varies about a mean of

about 1 nmol kg⁻¹(Fig. 6) only slightly higher than the highest surface water seen at the more

552 offshore stations (Fig. 3a) and very similar to surface waters at coastal Station 16-394. Over the same period, dMn is relatively high, averaging ~3 nmol kg⁻¹. However, an increase in mixed 553 554 layer depth from 13 m to 39 m on the 9 February 2015 sampling was accompanied by a strong increase in dFe to near 7 nmol kg⁻¹, similar to the value of the peak dFe at 50m depth at Station 555 556 16-394 (Fig. 4). At the same time, dMn fell to 0.8 nmol kg⁻¹. Upon subsequent deepening of the 557 MLD to 76 m, dFe fell to 3.8 nmol kg⁻¹, while dMn increased slightly. Over late February into 558 March, surface dFe continued to decrease while dMn rose slowly. Overall for the time-series dFe 559 and dMn are negatively correlated.

560 We interpret this temporal sequence to indicate a surface enrichment of dMn, but little 561 dFe, from nearby meltwater sources when MLD was shallow. When a wind event mixed the 562 water column to several tens of meters depth, we suspect that the sharp increase in surface dFe 563 resulted from upward mixing of a strong pre-existing gradient to high dFe in the subsurface, 564 while at the same time the pre-mixing-event surface enrichment of dMn was diluted with lower-565 dMn water from below, assuming dMn was maximal at the surface before the mixing event 566 (profile similar to 15-24 in shape; Fig. 3g). Over the subsequent sampling period, deep mixing 567 continued, and dFe was preferentially removed by continued biological uptake and scavenging, 568 while dMn increased somewhat, likely a result of continued surface meltwater inputs. It may 569 seem curious that the fraction of meteoric water varies little (between 3 and 4%) over this 570 sampling period, with no anomaly evident during the mixing event. While only surface water 571 data are available, we speculate that this is because %MET varies comparatively little with 572 depth, a result of accumulation and continuation of meteoric water inputs as reflected by this 573 conservative tracer. The surface time-series, though limited in scope, thus provides a window 574 into nearshore vertical Fe and Mn distribution. While it appears that high dMn can be traced to a 575 meltwater source if MLD remains shallow, this is not true for dFe. Instead, near-shore 576 sedimentary sources provided high dFe within the upper 50m and overwhelmed any meltwater 577 Fe source to this region, though not necessarily over the entire WAP shelf.

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8. Conclusion

582 These new trace metal data strongly suggest that sedimentary inputs in nearshore regions 583 surrounding PD – the "shallow bathtub ring" – are the primary source for bioavailable Fe to the 584 upper water column and thence to phytoplankton in the euphotic zone of the hotspot. The idea 585 that upwelling of deep modified UCDW provides the key micronutrient for this biological 586 hotspot is thus obviated and likely irrelevant, as the vertical dFe gradient to the surface is 587 governed by the sediment-sourced sub-surface maximum at 75-200m, not by the lower Fe 588 content local deep water found at >400 m. Interestingly, this implies that at least some marine-589 terminating glaciers in this region may have grounding lines that are quite shallow, as 590 resuspension would require sediment that is not ice covered. Alternatively, unglaciated islands or 591 regions of the mainland may be preferential sedimentary Fe sources, and glacial meltwater may 592 also transport fine sediment into coastal waters; clearly, better knowledge of regional circulation 593 [31] and the depths of glacial termini grounding lines within the upper 200 m near PD [43, 44] 594 would be helpful in identifying specific sedimentary Fe source regions. 595 These findings suggest that a critical characteristic of the subsurface Fe source is that it is

below the zone of rapid biologically-driven removal within the surface mixed layer, likely enhancing the broad dispersal and relatively continuous nature of the Fe input. Also, wind-driven

598 vertical mixing events may be crucial to provide sufficient Fe flux to the phytoplankton 599 assemblage to maintain the uniquely high productivity of the PD hotspot [10]. Therefore, the 600 existence of the hotspot does not result from upwelling of deep water, driven by canyon 601 bathymetry, but instead seems dependent on bottom shear stress in shallow sedimentary regions 602 surrounding the PD. On the basis of the PD example, we propose that canyons *per se* may be less 603 relevant to hotspot location than previously thought, although the bathymetry of their flanks may 604 encourage the necessary upward mixing of the strong local subsurface Fe supply. Further, the 605 continuing retreat of marine-terminating glaciers on the peninsula [43] may enhance Fe delivery 606 to this and possibly other coastal regions, not via the commonly assumed mechanism of 607 increasing meltwater flux, but rather by exposing additional regions of shallow sediments, which 608 could then serve as important new Fe sources to the upper water column of WAP inner shelf. 609 610 COMPETING INTERESTS: We have no competing interests. 611 AUTHOR CONTRIBUTIONS 612 613 614 RS conceived the study, supervised the 2015 field work and all of the data production, and drafted the manuscript. AA collected field samples in 2016 and analyzed the particulate samples. 615 616 JF collected field samples in 2015 and supervised the field effort in 2016. VR analyzed the 617 dissolved trace element samples. MM provided the oxygen isotope data, conducted the mass 618 balance calculations, and interpreted the results. All authors critically edited the manuscript and 619 gave final approval for publication. 620 621 622 623 624 **ACKNOWLEDGEMENTS** 625 626 We thank the Captain and crew of the R/V L.M. Gould, as well as the USAP and the logistics 627 support team for their expert assistance at sea. Thanks to Hugh Ducklow and Oscar Schofield for 628 their LTER leadership and useful discussion, to Laramie Jensen and Chervl Zurbrick for 629 assistance with trace metal sampling, to Nicole Waite, Jim Fiorendino, Rachel Caplan and Conor 630 Sullivan for help with Zodiac sampling, to Filipa Carvalho for providing glider data that 631 informed our sampling locations, to Ryan Bu for assistance with ICP-MS analyses, to Nicole 632 Waite for assistance with archived LTER data and with MLD calculations, to Laura Nazarro for 633 creating Fig. 1, and to Stanley Ko for his comments on an earlier version of the manuscript. This 634 work was supported by NSF ANT-1142250 to R.M.S. The participation of Michael Meredith in 635 this research was funded by the Natural Environment Research Council via awards 636 NE/N018095/1 and NE/P003060/1. 637 638 639 DATA ACCESSIBILITY 640 641 Data are made available in the attached Excel file "Sherrell Table S1-Dataset+legend". 642

643 ELECTRONIC SUPPLEMENTARY MATERIAL

644 645 Excel file "Sherrell Table S1-Dataset+legend". 646 647 648 REFERENCES 649 650 [1] de Baar, H. J. W. 2005 Synthesis of iron fertilization experiments: From the Iron Age in the 651 Age of Enlightenment. Journal of Geophysical Research 110. (DOI:10.1029/2004jc002601). 652 [2] Tagliabue, A., Bowie, A. R., Boyd, P. W., Buck, K. N., Johnson, K. S. & Saito, M. A. 2017 653 The integral role of iron in ocean biogeochemistry. Nature 543, 51-59. 654 (DOI:10.1038/nature21058). 655 [3] Arrigo, K. R., van Dijken, G. L. & Strong, A. L. 2015 Environmental controls of marine 656 productivity hot spots around Antarctica. Journal of Geophysical Research: Oceans 120, 657 5545-5565. (DOI:10.1002/2015jc010888). [4] Bovd, P. W., Arrigo, K. R., Strzepek, R. & van Dijken, G. L. 2012 Mapping phytoplankton 658 659 iron utilization: Insights into Southern Ocean supply mechanisms. Journal of Geophysical 660 Research: Oceans 117, n/a-n/a. (DOI:10.1029/2011jc007726). [5] Prezelin, B. B., Hofmann, E. E., Mengelt, C. & Klinck, J. M. 2000 The linkage between 661 662 Upper Circumpolar Deep Water (UCDW) and phytoplankton assemblages on the west 663 Antarctic Peninsula continental shelf. J Mar Res 58, 165-202. 664 [6] Vernet, M., Martinson, D., Iannuzzi, R., Stammerjohn, S., Kozlowski, W., Sines, K., Smith, 665 R. & Garibotti, I. 2008 Primary production within the sea-ice zone west of the Antarctic 666 Peninsula: I—Sea ice, summer mixed layer, and irradiance. Deep Sea Research Part II: 667 Topical Studies in Oceanography 55, 2068-2085. (DOI:10.1016/j.dsr2.2008.05.021). 668 [7] Smith, R. C., Martinson, D. G., Stammerjohn, S. E., Iannuzzi, R. A. & Ireson, K. 2008 669 Bellingshausen and western Antarctic Peninsula region: Pigment biomass and sea-ice 670 spatial/temporal distributions and interannual variability. Deep Sea Research Part II: Topical 671 Studies in Oceanography 55, 1949-1963. (DOI:10.1016/j.dsr2.2008.04.027). 672 [8] Garibotti, I. A., Vernet, M., Smith, R. C. & Ferrario, M. E. 2005 Interannual variability in the 673 distribution of the phytoplankton standing stock across the seasonal sea-ice zone west of the 674 Antarctic Peninsula. Journal of Plankton Research 27, 825-843. (DOI:10.1093/plankt/fbi056). 675 [9] Schofield, O., Brown, M., Kohut, J., Nardelli, S., Saba, G. & Waite, N. 2018 Changing upper 676 ocean mixed layer depth and phytoplankton productivity along the West Antarctic Peninsula. 677 Philosophical Transactions of the Royal Society A in press. 678 [10] Kavanaugh, M. T., Abdala, F. N., Ducklow, H., Glover, D., Fraser, W., Martinson, D., 679 Stammerjohn, S., Schofield, O. & Doney, S. C. 2015 Effect of continental shelf canvons on 680 phytoplankton biomass and community composition along the western Antarctic Peninsula. 681 Marine Ecology Progress Series 524, 11-26. (DOI:10.3354/meps11189). [11] Schofield, O., Ducklow, H., Bernard, K., Doney, S., Patterson-Fraser, D., Gorman, K., 682 683 Martinson, D., Meredith, M., Saba, G., Stammerjohn, S., et al. 2013 Penguin Biogeography 684 Along the West Antarctic Peninsula: Testing the Canyon Hypothesis with Palmer LTER 685 Observationsf. Oceanography 26, 204-206. (DOI:10.5670/oceanog.2013.63). 686 [12] Saba, G. K., Fraser, W. R., Saba, V. S., Iannuzzi, R. A., Coleman, K. E., Doney, S. C., 687 Ducklow, H. W., Martinson, D. G., Miles, T. N., Patterson-Fraser, D. L., et al. 2014 Winter 688 and spring controls on the summer food web of the coastal West Antarctic Peninsula. Nat 689 Commun 5, 4318. (DOI:10.1038/ncomms5318).

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FIGURES & CAPTIONS





Figure 1. Map of Palmer Deep study region off the Antarctic Peninsula. Stations designated YY-# where YY is cruise year and # is event number, were sampled from surface to bottom in 2015 (closed squares and blue triangle) and 2016 (closed circles). The Palmer LTER grid station 600.040 in the deepest part of the canyon was occupied in each year (red circle). Station E (blue triangle) was sampled over a time-series in January-March, 2015, in surface waters only.





818 Figure 2. Hydrographic data from the eight stations, with shallower stations in the top panels and

819 deeper canyon stations in bottom panels. Plotted left to right are (a,e) potential temperature , (b,f)

salinity, (c,g) % meteoric water contribution and (d, h) % sea ice melt. A T-S plot for these
stations is shown as inset on lower salinity graph. Station color designations are consistent with

- 822 Figure 3.



Figure 3. Vertical distribution of (a,e) dissolved Fe (dFe), (b,f) total particulate Fe (TpFe), (c,g)

dissolved Mn (dMn), and (d,h) total particulate Mn (TpMn). Bottom sample collected at ~10m
 off bottom in each profile. Station 16-394 (solid black circles) runs off scale, but is shown in full

detail in Figure 4. Open circles indicate canyon head stations sampled on the north and south

flanks late in the research cruise (February 7-8), 27 days after the nearby stations (Fig. 1)

- 845 indicated by filled circles of the same color.



Figure 4. Vertical profiles of dissolved (open symbols) and particulate (closed symbols) Fe (red squares) and Mn (black circles) at southern coastal Station 16-394. Bottom is at approximately 300m.



Figure 5. Comparison of the vertical profiles of dissolved Fe (dFe), labile particulate Fe (LpFe),

and total particulate Fe (TpFe) at Stations 15-24, 16-414, and 16-445 (top panels). Note

particulate Fe concentrations are much larger than dissolved, and are shown on bottom x-axis.

881 Bottom panels show the same variables for Mn at the same stations, all values on the top x-axis.

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Figure 6. Time series of dissolved Fe and Mn, meteoric water contribution (left y-axis) and mixed layer depth (right y-axis) at Station E in early 2015. Note mixed layer depth is plotted

- increasing down to be more visually intuitive.

SHORT TITLE FOR PAGE HEADINGS: Iron supply to the Palmer Deep hotspot