[Geophysical Research Letter]

Supporting Information for

Seasonal depletion of the dissolved iron reservoirs in the sub-Antarctic zone of the Southern Atlantic Ocean

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Contents of this file

Introduction

Supporting information of figures, table, full materials and methodology referred to in the manuscript is described here. **Figure S1** shows glider dataset (from surface to 1000m depth) of seasonal characteristics of physical and biological parameters of the water mass (potential temperature, salinity and chlorophyll concentration with the mixed layer depth, euphotic depth and isopycnal of the winter MLD observed at our study area. The glider was deployed from 28 July 2015 to sample continuously and retrieved on 8 February 2016. **Figure S2** display a linear relationship between alpha (α) and maximum rate of photosynthesis (P_{max}) versus Chlorophyll using experimental values from both cruises.

Figure S3 shows the surface PAR from the glider time series using a 7-day rolling mean. **Figure S4** present phytoplankton (C_{phyto}) profiles at the same time as the station occupation obtained by converting glider derived Chlorophyll (assuming an average Chl:C ratio of 0.02 mg Chl mg C^{-1}; Thomalla et al., 2017b). **Figure 5** show the depth-integrated estimates of Fe:C_{phyto} ratios (µmol mol^{-1}) for total and euphotic reservoirs between occupations and over the season. **Table S1** display the results obtained from calculated depth-integrated nutrients inventories from July to February as well as the values for budget calculations between station occupations. **Table S2** show the mean and range of Fe:C ratios reported in literature from Southern Ocean phytoplankton species and community from laboratory cultures (in the presence of only 0.1-0.2nM DFe concentrations) and in-situ measurements, excluding values measured in fertilized patches. **Table S3** shows the total upper water column and euphotic layer Phytoplankton Fe:C_{phyto} ratios between station occupations and over a season. **Text S1** provide full details of materials and methods used (i.e. , nutrients sample collection and analysis methods, primary productivity calculations and depth-integrated PP_{wc}, a description of three methods used to calculate the upper water column depth-integrated nutrients inventories and statistical methods used for significant differences between concentrations and inventories).

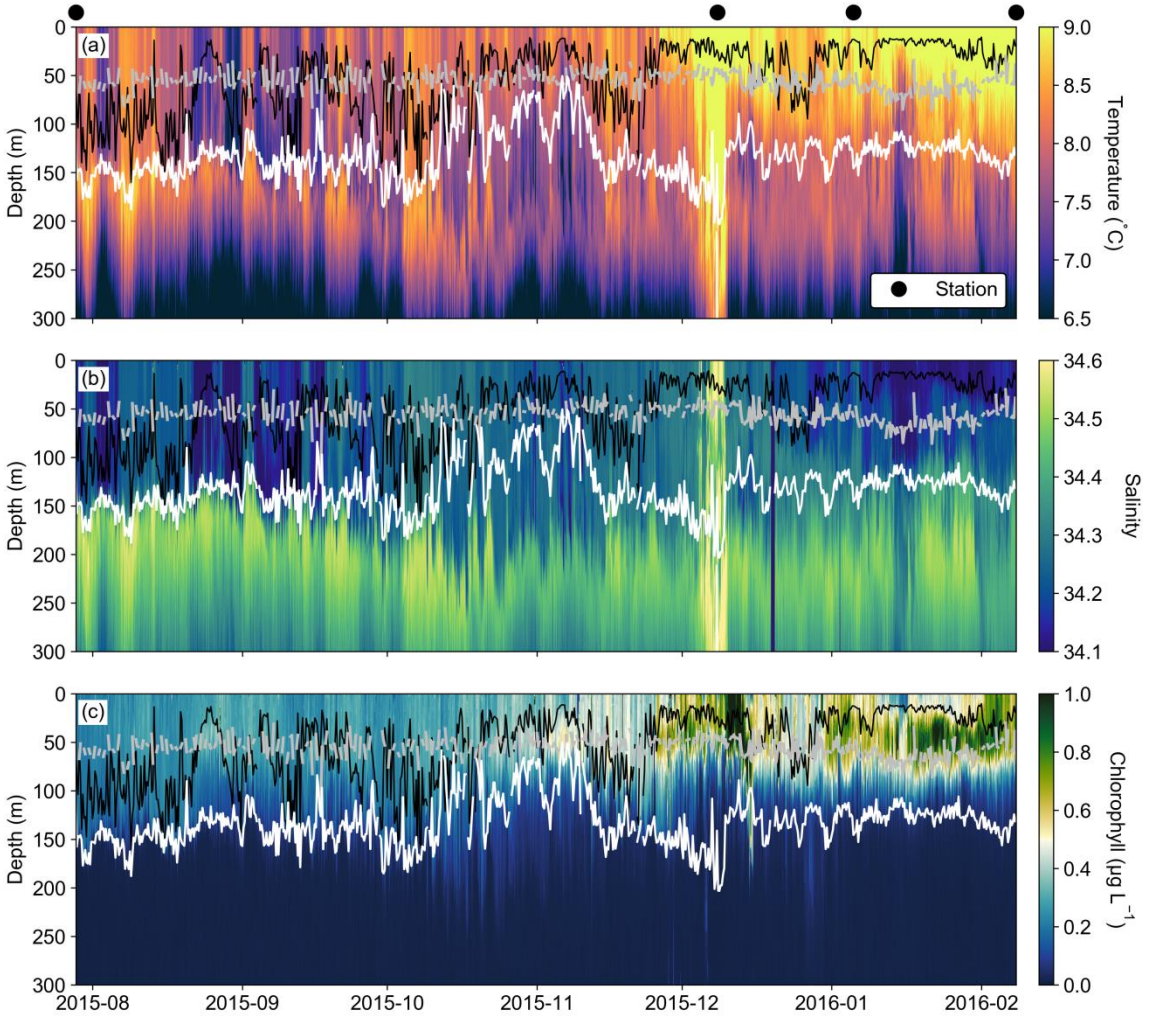

Figure S1: Section plots of the glider time series (surface to 1000 m) from 28 July 2015 to 8 February 2016 of (a) potential temperature (°C), (b) salinity and (c) chlorophyll concentration (µg L^{-1}) with the mixed layer depth (MLD, black line), euphotic depth (grey line) and isopycnal of the winter MLD (white line) overlaid.

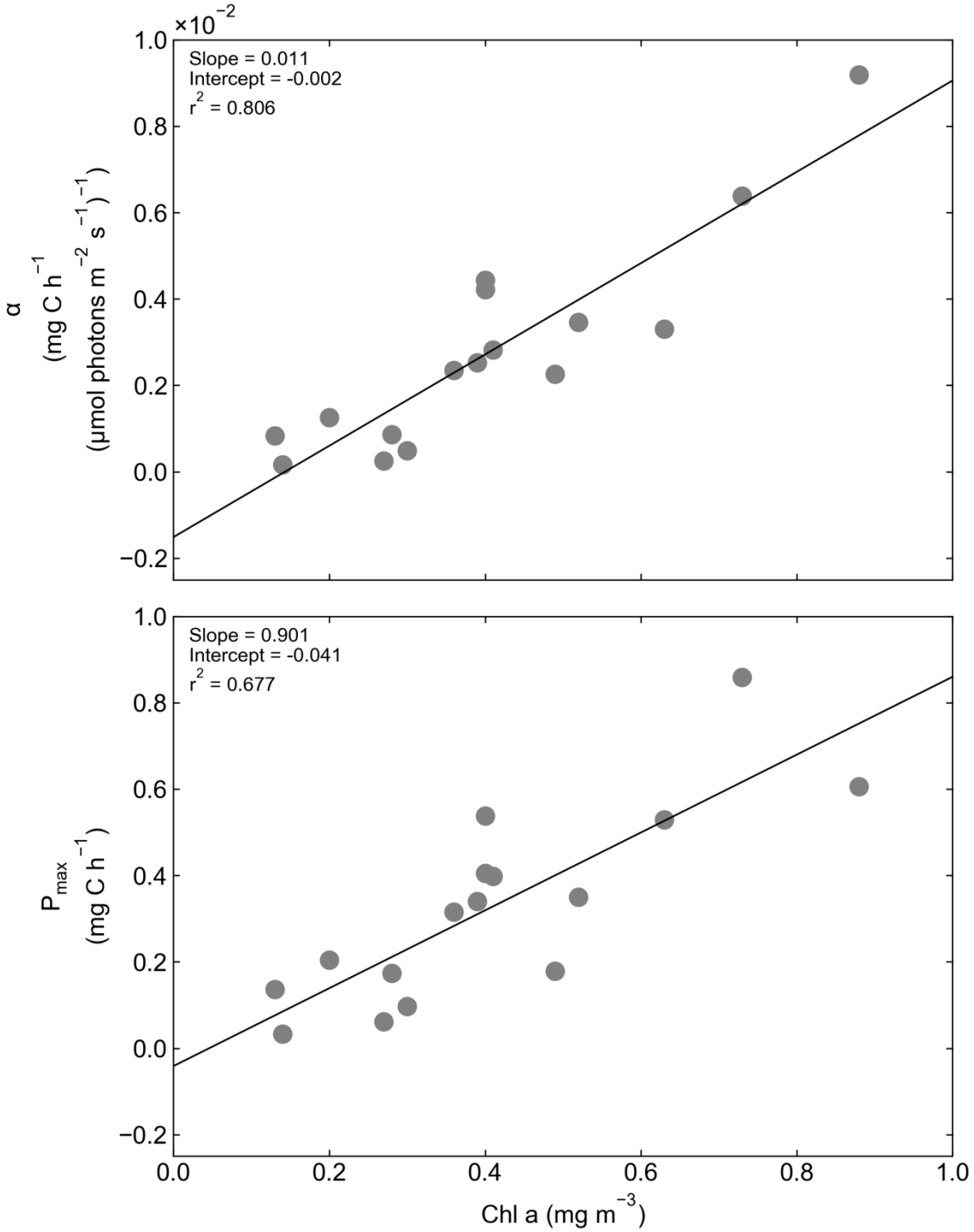

Figure S2: Linear regression between α (mg C h^{-1} (µmol photons m^{-2} s^{-1})$^{-1}$) and chlorophyll a (mg m^{-3}) and P_{max} (mg C h^{-1}) and chlorophyll a based upon photosynthesis irradiance (PE) experiments conducted on both cruises (Ryan-Keogh et al., 2018a).

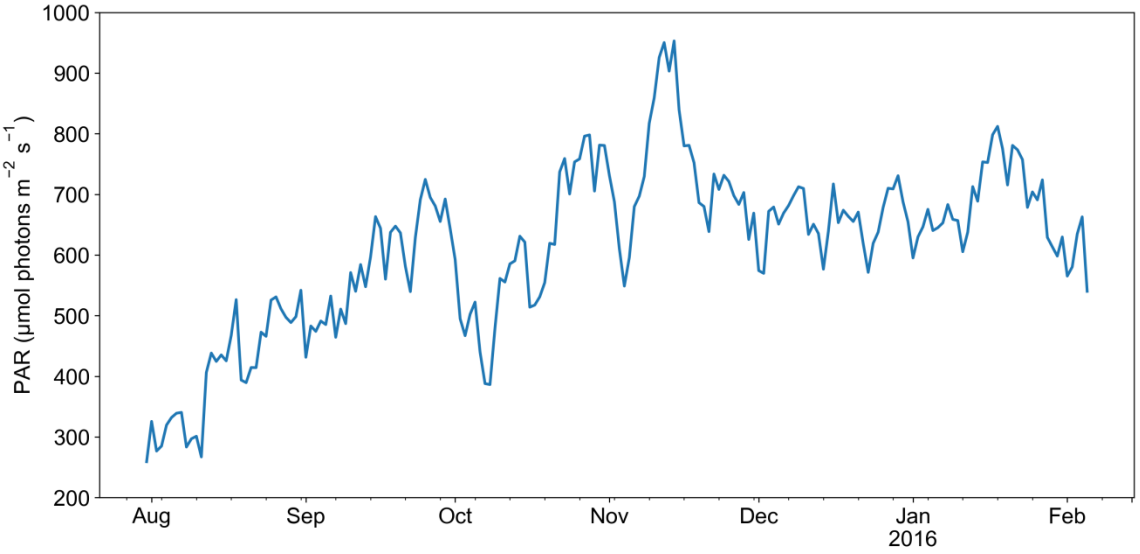

Figure S3: Plots of surface PAR (using a 7-day rolling mean) from glider time series from 28 July 2015 to 8 February 2016**.**

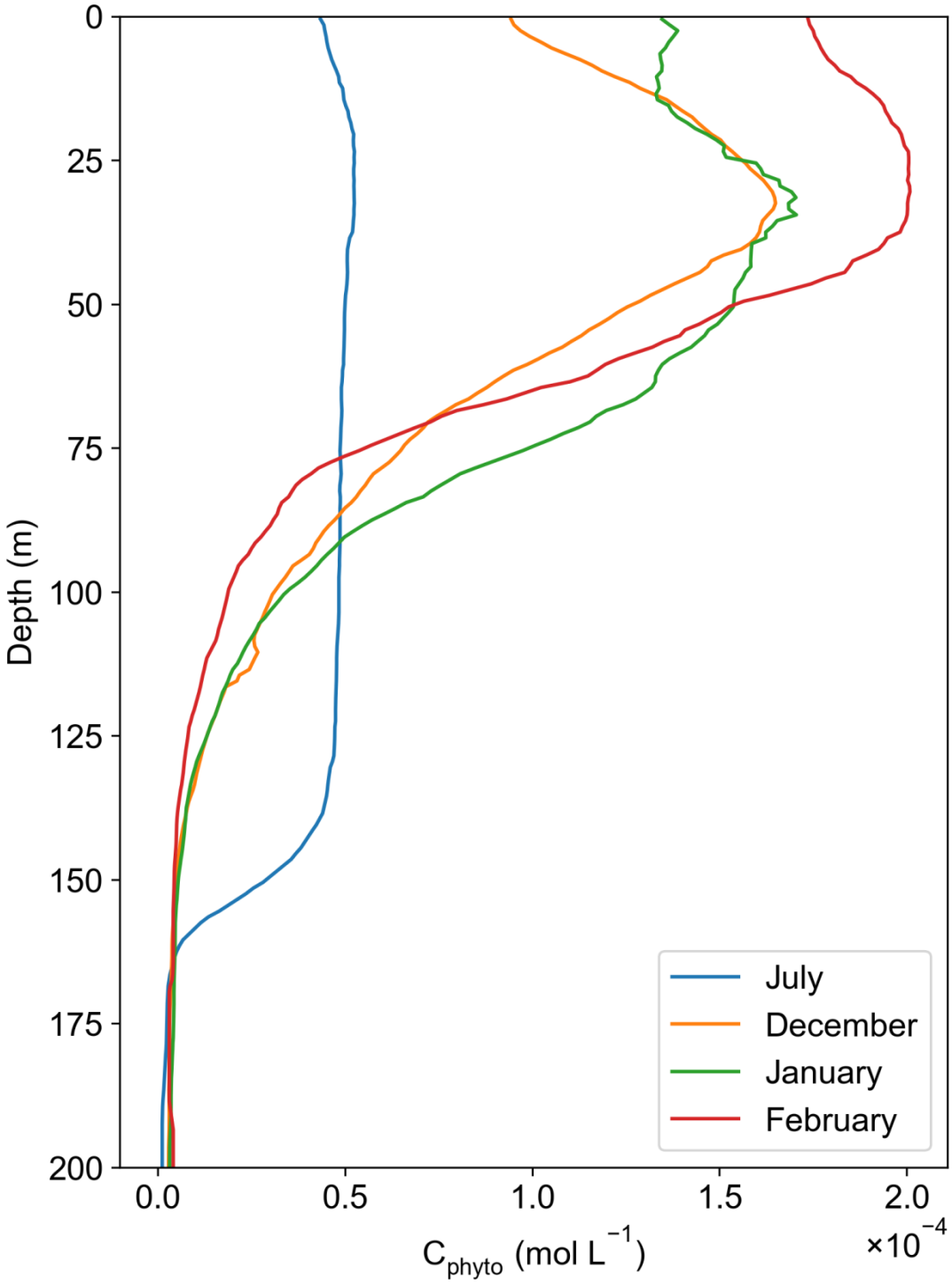

Figure S4: The phytoplankton (C_{phyto}) profiles at the same time as the station occupation obtained by converting glider derived Chlorophyll (assuming an average Chl:C ratio of 0.02 Chl mg C^{-1} taken from Thomalla et al. (2017b).

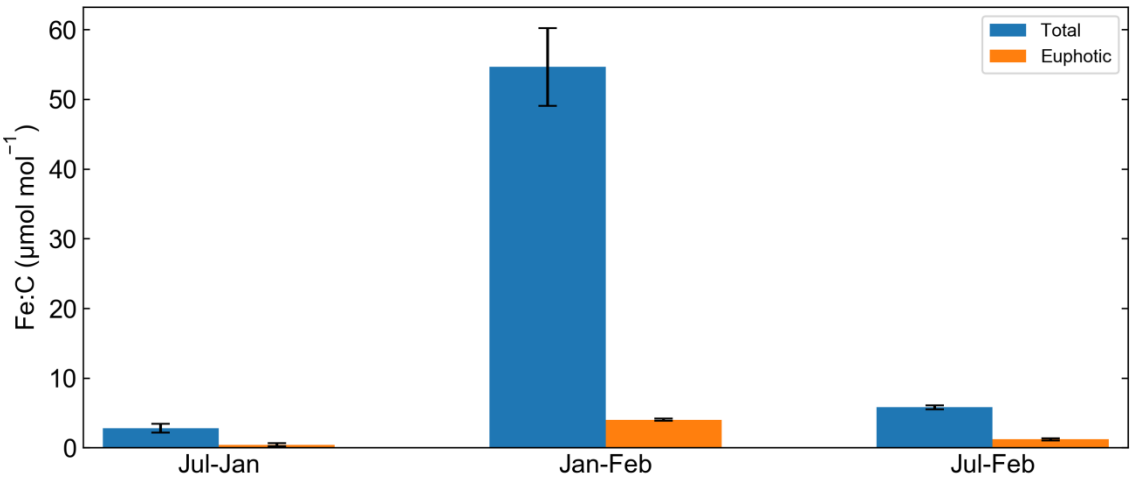

Figure S5: Depth integrated estimates of Fe:C_{phyto} ratios (µmol mol^{-1}) for total and euphotic reservoirs between occupations and over the season.

Table S1: Depth-integrated DFe and DIN inventories, inventory loss rates and estimated Fe:C ratios within the different depth horizons, at each station and between station occupations.

Parameters	**July**	**December***	**January**	**February**
MLD (m)	157	32	16	43
Z_{eu} (m)	58	51	66	66
Winter Isopycnal layer (m)	157	149	134	131
Depth Horizons	**DFe Inventories (µmol m^{-2})**			
Total	45.97 ± 0	32.97 ± 2.17	30.14 ± 3.64	11.27 ± 1.71
Euphotic	14.47 ± 1.29	11.03 ± 1.18	11.67 ± 0.36	4.55 ± 0.08
Aphotic	31.50 ± 1.29	21.95 ± 1.02	18.47 ± 3.83	6.72 ± 1.75
	DIN Inventories (mmol m^{-2})			
Total	3253.49 ± 0.0	2137.87 ± 184	2281.84 ± 341	2283.30 ± 356
Euphotic	1135.23 ± 83	695.61 ± 107	852.48 ± 22	876.36 ± 20.92
Aphotic	2118.26 ± 83	1442.26 ± 80	1429.36 ± 353	1406.94 ± 367
	DFe loss (µmol m^{-2})$^{\#}$			
Depth Horizons	**July – January**	**January - February**	**July – February**	
Total	15.83±3.64	18.87±1.93	34.70±1.71	
Euphotic	2.80±1.41	7.12±0.28	9.92±1.31	
Aphotic	13.03±5.05	11.75±2.08	24.78±3.00	
	DIN loss (mmol m^{-2})$^{\#}$			
Total	971.65±341.16	-1.46±14.54	970.19±355.70	
Euphotic	282.75±89.66	-23.88±0.84	258.87±89.31	
Aphotic	688.90±430.53	22.42±14.14	711.32±444.66	
	Observed DFe loss rate (µmol m^{-2} d^{-1})$^{\#}$			

Number of days between station occupations	161	35	196
Euphotic	0.02±0.01	0.20±0.01	0.05±0.01
Aphotic	0.08±0.03	0.34±0.06	0.13±0.02
	PP estimated Fe:C uptake ratios (µmol mol^{-1})$^{\#}$		
Total	15.86±3.18	43.78 ±7.90	24.20 ±1.96
Euphotic	2.81±1.23	16.52 ±2.65	6.92 ±0.92

* The December nutrients inventories are not used for budget calculation.
$^{\#}$ Values used for budget calculations

1.1. Row "parameters" provide the physical oceanographic context at each station occupation
1.2. Row "DFe and DIN inventories" gives depth-integrated DFe and DIN inventories at each station occupation and within each depth horizon
1.3. Row "DFe and DIN loss inventories" gives DFe and DIN loss inventories between station occupation and within each depth horizon
1.4. Row "DFe and DIN loss rates" gives DFe and DIN loss inventories divided by number of days between station occupations
1.5. Row "PP estimated Fe:C uptake ratios" gives estimated phytoplankton Fe:C uptake ratios calculated based upon the DFe loss between occupations and the cumulative sum of carbon gained via PPwc (corrected for the number of days between occupations).

Table S2: The mean, median and range Fe:C ratios of Southern Ocean phytoplankton species and community from laboratory cultures (in the presence of only 0.1-0.2nM DFe concentrations) and in-situ measurements, excluding values measured in fertilized patches.

	Strzepek et al., 2011[a]	**Strzepek et al., 2012[b]**	**Twining et al., 2004a[c]**	**Twining et al. 2004b[d]**	**Sarthou et al. 2008[e]**	**Fung et al. 2000[f]**	**Abraham et al. 2000[g]**	**Papers combined[h]**
Mean	2.7	3.7	13.7	10.5	4.8	3.0	2.7	4.6
Min	0.4	0.3	6.0	9.0	2.7	2.5		0.3
Max	8.6	10.6	25.0	13.0	8.0	3.5		25.0
n	25.0	17.0	4.0	4.0	4.0	2.0	1.0	57.0

[a] laboratory culture studies of Southern Ocean diatoms (Eucampia antarctica and Proboscia inermis) haptophytes (Phaeocystis Antarctica Clone AA1); [b] Laboratory culture studies of Southern Ocean diatoms (Fragilariopsis Kerguelensis, Eucampia Antarctica and Proboscia inermis) and haptophyte (Phaeocystis Antarctica Clone AA1 and Clone SX9); [c] Diatoms and Autotrophic flagellates (low Fe); [d] Phytoplankton community during SOFeX; [e] Fe:C molar ratios assigned to the N part of the SO (3.5 µmol.mol^{-1}) and to the south (2.5 µmol.mol^{-1}); [f] The mean Fe:C ratio from days 5 and 12 of SOIREE (2.7µmol.mol^{-1}); [g] Microphytoplankton (diatoms) and PNAN from KEOPS (5.7, 3.0, 4.4 and 8.0 µmol.mol^{-1}; [h] The mean and range of all papers combined employed in this study for comparison.

Table S3: Total upper water column and euphotic layer Phytoplankton Fe:C_{phyto} ratios between station occupations and over a season.

Fe:C_{phyto} ratios				
Depth Horizons		**Jul-Jan**	**Jan-Feb**	**Jul-Feb**
Total	Mean	2.8	54.6	5.8
Euphotic		0.4	4.0	1.2
Total	Stdev	0.6	5.6	0.3
Euphotic		0.2	0.2	0.2

Text S1: Materials and methodology

S1.1. Sample collections

DFe samples were collected following GEOTRACES protocols (Cutter, 2013) using a trace metal clean CTD rosette (epoxy coated aluminium frame with titanium bolts) equipped with 24 × 12 L teflon coated GO-FLO bottles (General Oceanics). DFe samples were filtered through 0.2 µm capsule filters with a 0.45 µm Supor membrane pre-filter (Pall AcroPack), drawn into acid washed 125 mL LDPE bottles (Nalgene) and immediately acidified to pH ~1.7 using 25µl of 9.46 M HCl (30% ultrapure; Merck) under a laminar flow hood, double bagged and stored at room temperature for further analysis at LEMAR laboratory (France). Samples for dissolved inorganic nitrate (nitrate + nitrite; DIN) analysis were collected after DFe sample collection, drawn into centrifuge tubes (50 mL; Merck Millipore) and stored at -20^{o}C until analysis at the University of Cape Town (South Africa).

S1.2. Sample analysis

DFe samples were analyzed using Flow Injection Analysis with chemiluminescence detection (FIA-CL) (Obata et al., 1993, modified by Sarthou et al., 2003). Blanks and detection limits of analysis were determined daily (0.006±0.005 nM, n = 11 and 0.005±0.003 nM, n = 11, respectively). Samples were analyzed in triplicate with an average percentage error of 2.2±2.6 % (n = 65). Accuracy and precision of the dataset was certified using GEOTRACES SAFe reference seawater (mean concentration ± standard deviation; D2 = 0.96±0.04 nM; n = 12 and D1 = 0.70±0.01 nM; n = 3), which were in good agreement with consensus values of 0.96±0.02 nM (SAFe D2) and 0.69±0.04 nM (SAFe D1). Dissolved inorganic nitrogen (nitrate + nitrite; DIN) samples were measured using a Lachat Flow Injection Analyser (Egan, 2008; Wolters, 2002).

S1.3. Primary productivity

Depth-integrated PP (PP_{wc}, mol C m^{-2} d^{-1}) was calculated from quenching corrected chlorophyll (Thomalla et al., 2017; surface, mean in the euphotic zone and mean in the MLD) and PAR according to Platt et al. (1980), Platt and Sathyendranath (1993), and Thomalla et al. (2015). α, the light limited slope of photosynthesis, and P_{max}, the maximum rate of photosynthesis, were determined from a linear relationship with chlorophyll using experimental values from both cruises (Supporting Information Figure S2, Ryan-Keogh et al., 2018b).

S1.4. Ancillary dataset

Temperature (°C), salinity and Chlorophyll profiles were obtained from the Seaglider (Supporting Information Figure S1). The mixed layer depth (MLD) was defined as the depth where the density differs from the density at 10 m by more than 0.03 kg m^{-3} following de Boyer Montégut et al. (2004). The euphotic depth (Z_{eu}) calculated from photosynthetically active radiation (PAR) profiles, was defined as the depth at which PAR is 1% of the surface value. The isopycnal depth of the deep winter mixing layer was defined at a density threshold of 26.70 kg m^{-3} and was extended throughout summer to represent remnant winter waters.

S1.5. Upper water column calculations

To understand the processes that control seasonal variability in nutrients concentrations of the upper water column, we calculated the depth-integrated nutrients inventories within different reservoirs in order to construct the seasonal budget calculations. The rationale for choosing euphotic layer as a cut-off is that the surface mixed layer during summer sampling were too shallow, but variable (ranging from 16 to 43 m; Table S1). The euphotic depth did not vary significantly throughout the glider time series, but typically deeper than the surface mixed layer and similarly variable (average = 63±7 m; ranging from 45 to 81 m). We also used the isopycnal depth of the deepest winter ML and extend it throughout summer as a physical barrier cut-off depth for upper water column to represent the winter waters and to allow for high probability of mixing during early season. Seasonal changes in the upper surface water column nutrients inventories were calculated using a trapezoidal rule (Atkins, 1989). Using these depth horizons, the seasonal variation in euphotic and winter mixed layer isopycnals required three different methods to derive the integrated nutrient inventories: i) a fixed mean Z_{eu} and winter isopycnal as reference depths between the euphotic and aphotic reservoirs, ii) using the

observed Z_{eu} and isopycnal depth at each station occupation, and iii) correcting the observed Z_{eu} and winter isopycnal for seasonal variability at each occupation. The biologically active euphotic layer was integrated from the surface to Z_{eu},which was binned separately as changes (i.e. episodic intrusions, biological uptake) in this reservoir over the growing season are not necessarily meaningful from a budgetary perspective. Calculating nutrient budgets requires an ability to quantify gain and loss terms over a seasonal time-frame, this is not possible in the euphotic layer where the dominant processes contributing to gain (i.e. episodic intrusions) and loss (i.e. biological uptake) terms are operating on daily to weekly timescales. The aphotic layer was integrated from Z_{eu} to the winter isopycnal depth, which minimizes the influence of biological uptake in the euphotic zone and entrainment or detrainment of deep nutrient-rich waters from below. As such, changes in this aphotic DFe reservoir can be expected to provide quantitative insight on the seasonal processes affecting it.

S1.6. Statistics

Significant differences were calculated using a t-test of two samples assuming equal variance and one-way ANOVA single factor, with significant results reported at the 95% confidence level ($p < 0.05$).