1 **Distribution of planktonic biogenic carbonate organisms in the Southern Ocean south of**

2 **Australia: a baseline for ocean acidification impact assessment**

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14

15 **Abstract**

16 The Southern Ocean provides a vital service by absorbing about one sixth of humankind's annual

17 emissions of CO_2. This comes with a cost – an increase in ocean acidity that is expected to have

18 negative impacts on ocean ecosystems. The reduced ability of phytoplankton and zooplankton to

19 precipitate carbonate shells is a clearly identified risk. The impact depends on the significance of

20 these organisms in Southern Ocean ecosystems, but there is very little information on their abundance

21 or distribution. To quantify their presence, we used coulometric measurement of particulate inorganic

22 carbonate (PIC) on particles filtered from surface seawater into two size fractions: 50-1000 μm to

23 capture foraminifera (the most important biogenic carbonate forming zooplankton) and 1-50 μm to

24 capture coccolithophores (the most important biogenic carbonate forming phytoplankton). Ancillary

25 measurements of biogenic silica (BSi) and particulate organic carbon (POC) provided context, as

26 estimates of the biomass of diatoms (the highest biomass phytoplankton in polar waters), and total

27 microbial biomass, respectively. Results for 9 transects from Australia to Antarctica in 2008-2015

28 showed low levels of PIC compared to northern hemisphere polar waters. Coccolithophores slightly

29 exceeded the biomass of diatoms in Subantarctic waters, but their abundance decreased more than 30-

30 fold poleward, while diatom abundances increased, so that on a molar basis PIC was only 1% of BSi

31 in Antarctic waters. This limited importance of coccolithophores in the Southern Ocean is further

32 emphasized in terms of their associated POC, representing less than 1 % of total POC in Antarctic

33 waters and less than 10% in Subantarctic waters. NASA satellite ocean colour based PIC estimates

34 were in reasonable agreement with the shipboard results in Subantarctic waters, but greatly over-

35 estimated PIC in Antarctic waters. Contrastingly, the NASA Ocean Biogeochemical Model (NOBM)

36 shows coccolithophores as overly restricted to Subtropical and northern Subantarctic waters. The

37 cause of the strong southward decrease in PIC abundance in the Southern Ocean is not yet clear.

38 Poleward decrease in pH is small and while calcite saturation decreases strongly southward it remains

39 well above saturation (>2). Nitrate and phosphate variations would predict a poleward increase.

40 Temperature and competition with diatoms for limiting iron appear likely to be important. While the

41 future trajectory of coccolithophore distributions remains uncertain, their current low abundances

42 suggest small impacts on overall Southern Ocean pelagic ecology.

1. Introduction

Production of carbonate minerals by planktonic organisms is an important and complex part of the global carbon cycle and climate system. On the one hand, carbonate precipitation raises the partial pressure of CO_2 reducing the uptake of carbon dioxide from the atmosphere into the surface ocean; on the other hand, the high density and slow dissolution of these minerals promotes the sinking of associated organic carbon more deeply into the ocean interior increasing sequestration [*P.W. Boyd and Trull*, 2007b; *Buitenhuis et al.*, 2001; *Klaas and Archer*, 2002; *Ridgwell et al.*, 2009; *Salter et al.*, 2014]. Carbonate production is expected to be reduced by ocean acidification from the uptake of anthropogenic CO_2, with potentially large consequences for the global carbon cycle and ocean ecosystems [*Orr et al.*, 2005; *Pörtner et al.*, 2005].

The low temperature and low alkalinity of Southern Ocean waters make this region particularly susceptible to ocean acidification, to the extent that thresholds such as undersaturation of aragonite and calcite carbonate minerals will be crossed sooner than at lower latitudes [*Cao and Caldeira*, 2008; *McNeil and Matear*, 2008; *Shadwick et al.*, 2013]. Carbonate forming organisms in the Southern Ocean include coccolithophores (the dominant carbonate forming phytoplankton; e.g. [*Rost and Riebesell*, 2004]), foraminifera (the dominant carbonate forming zooplankton; e.g. [*Moy et al.*, 2009; *Schiebel*, 2002]), and pteropods (a larger carbonate forming zooplankton, which can be an important component of fish diets; e.g. [*Doubleday and Hopcroft*, 2015; *Roberts et al.*, 2014]). However, the importance of carbonate forming organisms relative to other taxa is unclear in the Southern Ocean [*Watson W. Gregg and Casey*, 2007b; *Holligan et al.*, 2010]. Satellite reflectance observations, mainly calibrated against northern hemisphere PIC results, suggest the presence of a "Great Calcite Belt" in Subantarctic waters in the Southern Ocean, and also show high apparent PIC values in Antarctic waters [*W M Balch et al.*, 2016; *W M Balch et al.*, 2011]. Our surveys were designed in part to evaluate these assertions for waters south of Australia.

As a simple step towards quantifying the importance of planktonic biogenic carbonate forming organisms in the Southern Ocean, we determined the concentrations of particulate inorganic carbonate (PIC) for two size classes, representing coccolithophores (1-50 μm, referred to as PIC01) and foraminifera (50-1000 μm, referred to as PIC50), from surface water samples collected on 9 transects between Australia and Antarctica. We provide ecological context for these observations based on the abundance of particulate organic carbon (POC) as a measure of total microbial biomass, and biogenic silica (BSi), the other major phytoplankton biogenic mineral, as a measure of diatom biomass. This provides a baseline assessment of the importance of calcifying plankton in the Southern Ocean south of Australia, against which future levels can be compared.

80   In the discussion of our results, we interpret BSi as representative of diatoms, PIC50 as representative

81   of foraminifera, and PIC01 as representative of coccolithophores, including a tendency to equate this

82   with the distribution of the most cosmopolitan and best studied coccolithophore, *Emiliania huxleyi*.

83   These assumptions need considerable qualification. Most BSi is generated by diatoms (~90%), with

84   only minor contributions from radiolaria and choanoflagellates in the upper ocean, making this

85   approximation reasonably well supported [*Hood et al.*, 2006]. Similarly, but less certainly,

86   foraminifera are a major biogenic carbonate source in the 50-1000 μm size range, but pteropods,

87   ostrocods, and other organisms are also important [*Schiebel*, 2002]. We do not discuss the PIC50

88   results in any detail because of this complexity, because controls on foraminifera distributions appear

89   to involve strongly differing biogeography of several co-dominant taxa, rather than dominance by a

90   single species [*Be and Tolderlund*, 1971], because the numbers of these organisms collected by our

91   procedures were small, and because assessing these issues is beyond the scope of this paper.

92   Attributing all the PIC01 carbonate to coccolithophores relies on the assumption that fragments of

93   larger organisms are not important. This seems reasonable given that the larger PIC50 fraction

94   generally contained 10-fold lower PIC concentrations (as revealed in the Results section).

95

96   Our tendency to equate the PIC01 fraction with the abundance of *Emiliania huxleyi* is probably the

97   weakest approximation. It is not actually central to our conclusions, except to the extent that we

98   compare our PIC01 distributions to expectations based on models that use physiological results

99   mainly derived from experiments with this species. That said, this is a poor approximation in

100 Subtropical waters where the diversity of coccolithophores is large, but improves southward where

101 the diversity decreases (see Smith et al. 2017 for recent discussion), and many observations have

102 found that *Emiliania huxleyi* was strongly dominant in Subantarctic and Antarctic Southern Ocean

103 populations, generally >80% [*Boeckel et al.*, 2006; *Eynaud et al.*, 1999; *Findlay and Giraudeau*,

104 2000; *Gravalosa et al.*, 2008; *Mohan et al.*, 2008]. Of course, *Emiliania huxleyi* itself comes in

105 several strains even in the Southern Ocean, with differing physiology, including differing extents of

106 calcification [*Cubillos et al.*, 2007; *M. N. Muller et al.*, 2015; *M.N. Muller et al.*, 2017; *Poulton et al.*,

107 2013; *Poulton et al.*, 2011]. All these approximations are important to keep in mind in any

108 generalization of our results. We also note that our technique does not distinguish between living and

109 non-living biomass, and thus is more representative of the history of production than the extent of

110 extant populations at the time of sampling.

111

112 **2. Methods**

113 Sub-sections 2.1 and 2.2 present the sampling and analytical methods, respectively, used for the 8

114 transits across the Southern Ocean since 2012. Sub-section 2.3 details the different methods used

115 during the earlier single transit in 2008 and assesses the comparability of those results to the later

116 voyages. Sub-section 2.4 details measurements of water column dissolved nutrients, inorganic carbon

117 and alkalinity. Sub-section 2.5 provides details of satellite remote sensing data and the NASA Ocean

118 Biogeochemical Model used for comparison to the ship results.

119

120 **2.1. Voyages and sample collection procedures**

121 The locations of the voyages, divided into north and south legs, are shown in Figure 1. Voyage and

122 sample collection details are given in Table 1, where for ease of reference we have numbered the legs

123 in chronological order and refer to them hereafter as VL1, VL2, etc. Samples were collected from the

124 Australian icebreaker *RV Aurora Australis* for 4 voyages and from the French Antarctic resupply

125 vessel *l'Astrolabe* for 1 voyage. All samples were collected from the ships' underway "clean"

126 seawater supply lines with intakes at ~4 m depth. These supply lines are separate from the engine

127 intakes, have scheduled maintenance and cleaning, and are only turned on offshore (to avoid possible

128 contamination from coastal waters). Samples were collected primarily while underway, except during

129 VL1 and VL3, which were operated as WOCE/CLIVAR hydrographic sections with full depth CTDs,

130 with samples collected on station.

131

132 For all voyages (except VL1, discussed in section 2.3 below), separate water volumes were collected

133 for the PIC, POC, and BSi analyses. The POC samples also yielded particulate nitrogen results -

134 referred to here as PON. The POC/PON and BSi samples were collected using a semi-automated

135 system that rapidly, ~ 1 minute, and precisely filled separate 1 L volumes for each analyte - thus these

136 samples are effectively point samples. In contrast, PIC samples were collected using the pressure of

137 the underway seawater supply to achieve filtration of large volumes (10's to 100's of litres) over ~2

138 hours. Thus these samples represent collections along ~20 miles of the ship track (except when done

139 at stations).

140

141 POC/PON samples were filtered through pre-combusted 13 mm diameter quartz filters (0.8 μm pore

142 size, Sartorius Cat#FT-3-1109-013) that had been pre-loaded in clean (flow-bench) conditions in the

143 laboratory into in-line polycarbonate filter holders (Sartorius #16514E). The filters were preserved by

144 drying in their filter holders at 60°C for 48 hours at sea, and returned to the laboratory in clean dry

145 boxes.

146

147 Biogenic silica samples were filtered through either 13 mm diameter nitrocellulose filters (0.8 μm

148 pore size, Millipore Cat#AAWP01300) or 13 mm diameter polycarbonate filters (0.8 μm pore size,

149 Whatman Cat#110409), pre-loaded in clean (flow-bench) conditions in the laboratory into in-line

150 polycarbonate filter holders (Sartorius #16514E). Filters were preserved by drying in their filter

151 holders at 60°C for 48 hours at sea, and returned to the laboratory in clean dry boxes.

152

5

153   PIC samples were collected by sequential filtration for two size fractions. After pre-filtration through

154   a 47 mm diameter 1000 μm nylon mesh and supply pressure reduction to 137 kPa, seawater was

155   filtered through a 47 mm diameter in-line 50 μm nylon filter to collect foraminifera, and then through

156   a 47 mm diameter in-line 0.8 μm GF/F filter (Whatman Cat#1825-047) to collect coccolithophores.

157   The flow path was split using a pressure relief valve set to 55 kPa, so that large volumes (~200 L)

158   passed the 50 μm filter, and only a small fraction of this volume (~15 L) passed the 0.8 μm filter.

159   Filtration time was typically 2 hours. Volume measurement was done by either metering or

160   accumulation. Based on visual examination, the high flow rate through the 50 μm nylon mesh was

161   sufficient to disaggregate faecal pellets and detrital aggregates. The flow rate data also suggests that

162   filter clogging was uncommon (see the Supplementary Information for expanded discussion). While

163   still in their holders, the filters were rinsed twice with 3 mL of 20 mM potassium tetraborate buffer

164   solution (for the first couple of voyages and later degassed deionized water) to remove dissolved

165   inorganic carbon, and blown dry with clean pressurised air (69 kPa). We consider that the short

166   contact time of this rinse did not dissolve PIC, based on the sharp (non-eroded) features of

167   coccolithophores collected in this way and examined by scanning electron microscopy (Cubillos et al.,

168   2007). The filters were then removed from their holders, folded, and inserted into Exetainer glass

169   tubes (Labco Cat #938W) and dried at 60 °C for 48 hours for return to the laboratory. In the

170   following text, we refer to the GF/F filter sample results (which sampled the 0.8 (~ 1) to 50 μm size

171   fraction) as PIC01, and the nylon mesh sample fraction (which sampled the 50-1000 μm size fraction)

172   as PIC50.

173

174   **2.2 Sample analyses**

175   **2.2.1 Particulate Organic Carbon and Nitrogen analysis**

176   The returned filter holders were opened in a laminar flow bench. Zooplankton were removed from the

177   filters and the filters were then cleanly transferred into silver cups (Sercon Cat#SC0037), acidified

178   with 50 μL of 2 N HCl and incubated at room temperature for 30 minutes to remove carbonates, and

179   dried in an oven at 60 °C for 48 hours. The silver cups were then folded closed and the samples, along

180   with process blanks (filters treated in the same way as samples, but without any water flow onboard

181   the ship) and casein standards (Elemental Microanalysis OAS standard CatNo. B2155, Batch 114859)

182   were sent to the University of Tasmania Central Sciences Laboratory for CHN elemental analysis

183   against sulphanilamide standards. Repeat samples collected sequentially at approximately 2 hour

184   intervals while the ship remained on station (station replicates) had a standard error of 7% (1 sd n=

185   10) and 8% (1 sd n= 10) for POC and PON respectively. Importantly the processing blanks were large

186   and variable, and were corrected for separately for each voyage. For VL2 and VL3, POC process

187   blanks averaged 25± 6 μg C (1 sd, n=2) equating to 20% of the average sample value. For VL4 and

188   VL5, POC process blanks averaged 14 ± 2 μg C (1 sd, n=4) equating to 18% of the average sample

189   value. For VL6 and VL7, POC process blanks averaged 23 ± 3 µg C (1 sd n=4) equating to 28 % of

190   the average sample value. For VL8 and VL9 POC process blanks averaged 14 ± 1 µg C (1 sd n=4)

191   equating to 14 % of the average sample value.

192

193   **2.2.2 Biogenic Silica analysis**

194   Biogenic silica was dissolved by adding 4 mL of 0.2 M NaOH and incubating at 95 °C for 90 minutes,

195   similar to the method of [*Paasche*, 1973]. Samples were then rapidly cooled to 4 °C and acidified with

196   1 mL of 1 M HCl. Thereafter samples were centrifuged at 1880 g for 10 minutes and the supernatant

197   was transferred to a new tube and diluted with 36 g L^{-1} sodium chloride. Biogenic silica

198   concentrations were determined by spectrophotometry using an Alpkem model 3590 segmented flow

199   analyser and following USGS Method I-2700-85 with these modifications: ammonium molybdate

200   solution contained 10 g L^{-1} $(NH_4)_6Mo_7O_{24}$, 800 µl of 10% sodium dodecyl sulphate detergent replaced

201   Levor IV solution, acetone was omitted from the ascorbic acid solution, and sodium chloride at the

202   concentration of seawater was used as the carrier solution. Station replicates had a standard error of

203   9% (1 sd n=9). The average blank values were 0.002 ± 0.003 µmoles per filter (1 sd, n=13) for

204   nitrocellulose filters and 0.002 ± 0.002 µmoles per filter (1 sd, n=2) for polycarbonate filters, equating

205   to 0.16 % and 0.01 % of average sample values, respectively.

206

207   **2.2.3 Particulate Inorganic Carbon analysis**

208   Particulate inorganic carbon samples were analysed by coulometry using a UIC CM5015 coulometer

209   connected to a Gilson 232 autosampler and syringe dilutor. The samples were analysed directly in

210   their gas tight Exetainer collection tubes, by purging for 5 minutes with nitrogen gas, acidification

211   with 1.6 mL (PIC50 - 50 µm nylon filters) or 2.4 mL (PIC01 - GF/F filters) of 1 N phosphoric acid,

212   and equilibration overnight at 40°C. Samples were analysed the following day with a sample analysis

213   time of 8 minutes and a dried carrier gas flow rate of 160 mL min^{-1}. Calcium carbonate standards

214   (Sigma Cat#398101-100G) were either weighed onto GF/F filters or weighed into tin cups (Sercon

215   Cat# SC1190) and then inserted into Exetainer tubes (some with blank nylon filters). Station

216   replicates had standard errors of 18% (1 sd n=11) and 13% (1 sd n=11) for PIC01 and PIC50

217   respectively. The average GF/F filter blank value was -0.07 ± 0.27 µg C (1 sd, n=47) equating to --

218   0.21% of average sample values, and for nylon filters was 0.04 ± 0.27 µg C (1 sd, n=46) equating to

219   0.05% of average sample values.

220

221   **2.3 Distinct sample collection and analytical methods used during V1**

222   **2.3.1 Distinct sample collection procedures for VL1**

223   For VL1, single samples were collected at each location by both sequential filtration and

224   centrifugation of the underway supply over 1-3 hours. Despite the long collection times these

225   samples are effectively point samples because they were collected on station.

226

227   Sequential filtration was done using in-line 47 mm filter holders (Sartorius, Inc.) holding 3 sizes of

228   nylon mesh (1000 μm, 200 μm, 50 μm) followed by a glass fibre filter (Whatman GF/F, 0.8 μm

229   nominal pore size, muffled before use). These size fractions were intended to collect foraminifera (50-

230   200 μm) and coccolithophores (0.8-50 μm), and pteropods (200-1000 μm), but the largest size

231   fraction had insufficient material for analysis. The flow rate at the start of filtration was 25-30 L hour^{-1}

232   and typically dropped during filtration. The 0.8 μm filter was replaced if flow rates dropped below 10

233   L hour^{-1}. Sampling typically took 3 hours. Quantities of filtered seawater were measured using a flow

234   meter (Magnaught M1RSP-2RL) with a precision of +/-1%. After filtration, remaining seawater in the

235   system was removed using a vacuum pump. Filters were transferred to 75 mm Petri dishes inside a

236   flow bench, placed in an oven (SEM Pty Ltd, vented convection) for 3-6 hours to dry at 60 ^{o}C and

237   stored in dark, cool boxes for return to the laboratory.

238

239   A continuous flow Foerst type centrifuge [*Kimball Jr and Ferguson Wood*, 1964], operating at 18700

240   rpm, was used to concentrate phytoplankton from the underway system at a flow rate of 60 L per

241   hour, measured using a water meter with a precision of +/-1% (Arad). Sampling typically took 1-3

242   hours. After centrifugation, 500 mL of de-ionized water was run through the centrifuge to flush away

243   remaining seawater and associated dissolved inorganic carbon. This was followed by 50 mL of

244   ethanol to flush away the de-ionized water, ensure organic matter detached from the cup wall, and

245   speed subsequent drying. Inside a laminar flow clean bench, the slurry in the centrifuge head was

246   transferred into a 10 mL polypropylene centrifuge tube (Labserve) and the material on the wall of the

247   cup was transferred using 3 mL of ethanol and a rubber policeman. The sample was then centrifuged

248   for 15 minutes and 3200 rpm, and the supernatant (~7 mL) removed and discarded. The vial was

249   placed in the oven to dry for 12 hours at 60 ^{o}C and returned to the laboratory.

250

251   **2.3.2 Distinct analytical procedures for VL1 samples**

252   POC/PON analyses for the 0.8 μm size fraction collected by filtration were done by packing five 5

253   mm diameter aliquots (punches) of the 47 mm diameter GF/F filters into acid-resistant 5x8 mm silver

254   cups (Sercon SC0037), treating these with two 20 μl aliquots of 2 N HCl to remove carbonates [*P

255   King et al.*, 1998], and drying at 60 ^{o}C for at least 48 hours. For the 50 μm mesh filtration samples,

256   and the centrifuge samples, 0.5-1.0 mg aliquots of the dried (72 hours at 60 ^{o}C) centrifuge pellet

257   remaining after PIC coulometry were encapsulated in 4x6 mm silver cups (Sercon SC0036).

258   Analyses of all these sample types was by catalytic combustion using a Thermo-Finnigan Flash 1112

259   elemental analyzer calibrated against sulphanilamide standards (Central Sciences Laboratory,

260   University of Tasmania). Precision of the analysis was +/- 1 %. A blank correction for of 0.19 ± 0.09

261   ug C was applied which represented 1.6 % of an average sample.

262

263   PIC concentrations were determined for subsamples of the 0.8 µm GF/F filters (half of the filter), the

264   whole 50 µm mesh screens, and the whole centrifuge samples by closed system acidification and

265   coulometry using a UIC CM5011 CO_2 coulometer. The samples were placed in glass vials (or in the

266   case of the centrifuge tubes connected via an adaptor), connected to a manual acidification unit and

267   condenser and maintained at 40^oC after acidification with 4mL of 1N HCl, and swept with a nitrogen

268   gas-flow (~100 mL min^{-1}) via a drier and aerosol filter (Balston) into the coulometry cell. Calibration

269   versus calcium carbonate standards (200 to 3000ug) provided precision of $\pm$ 0.3%. However, for the

270   0.8 µm filter, precision was limited to 10 % by sub-sampling of the filter due to uneven distribution.

271   Blank corrections were applied to the 0.8 µm size fraction, being 2.4 $\pm$ 1.8 ug C representing 8.8 % of

272   an average sample. The 50 µm fraction blank correction was 3.3 $\pm$ 0.1 ug C, representing 22 % of an

273   average sample. Centrifuge pellet coulometry blank subtraction was 2.0 $\pm$ 0.1 ug C, equivalent to 2.8

274   % of an average sample.

275

276   Biogenic silica analysis of the residues remaining after PIC analysis of the centrifugation samples,

277   was by alkaline digestion (0.2 N NaOH) in a 95^oC water bath for 90 minutes, similar to the method

278   described by Paasche (1973) and as described in section 2.2.2. with the variation that 4 mL of each

279   sample was transfered from the centrifuge tubes and filtered using a syringe filter before dilution to

280   10mL.

281

282   **2.3.3 Comparison of VL1 to other voyages**

283   The first survey on VL1 in 2008 differed from later efforts in two important ways: i) POC and PIC

284   samples were collected by both filtration and centrifugation, ii) separate BSi samples were not

285   collected - instead BSi analyses were carried out only on the sample residues from PIC coulometric

286   sample digestions of the centrifuge samples. Comparison of POC and PIC results from the

287   centrifugation samples (effectively total samples without size fractionation) and the filtration samples

288   (separated into the PIC01 0.8-50 µm and PIC50 50-1000 µm size fractions) shows (Figure 2) that

289   filtration collected somewhat more PIC (order 20-30 %) and considerably more POC (order 200-300

290   %) than centrifugation. This fits with the possibility of loss of material from the continuous

291   centrifuge cup, with greater loss of lower density organic matter (and possible additional loss of

292   organic matter via dissolution in the ethanol rinsing step). Thus for comparison of VL1 POC and PIC

293   to the other voyages we use only the filtration results, thereby avoiding methodological biases. For

294   BSi, we do not have this possibility. Based on the low centrifuge yields for PIC and POC we can

295   expect that the VL1 BSi values are also too low. This is confirmed by comparison to the other

296   voyages which reveals that VL1 BSi values were lower than those of other voyages, especially in the

297   far south where BSi values were generally highest (data shown below), but nonetheless had similar

298   north-south latitudinal trends. For this reason, our further interpretation of the VL1 BSi results is only

299   in terms of these latitudinal trends.

300

301   **2.4 Analysis of nutrients, DIC, alkalinity, and calculation of pH and calcite saturation**

302   Nutrients were analysed onboard ship for VL1 to VL5, and on frozen samples returned to land for

303   VL6-9, all by the CSIRO hydrochemistry group following WOCE/CLIVAR standard procedures,

304   with minor variations [*Eriksen*, 1997], to achieve precisions of ~1% for nitrate, phosphate, and silicate

305   concentrations. Dissolved inorganic carbon (DIC) and alkalinity samples were collected in gas tight

306   bottles poisoned with mercuric chloride and measured at CSIRO by coulometry and open cell

307   titration, respectively [*Dickson et al.*, 2007]. Comparison to certified reference materials suggests

308   accuracy and precision for both DIC and alkalinity of better than ± 2 μmol kg^{-1}. Full details were

309   recently published [*Roden et al.*, 2016]. Calculation of pH (free scale) and calcite saturation were

310   based on the Seacarb version 3.1.2 software (https://CRAN.R-project.org/package=seacarb), which

311   uses the default selection of equilibrium constants given in [*Van Heuven et al.*, 2011].

312

313   **2.5 Satellite derived ocean properties and the NASA Ocean Biogeochemistry Model**

314   The locations of oceanographic fronts in the Australian sector were estimated from satellite altimetry,

315   following the approach of [*S. Sokolov and Rintoul*, 2002], updated as follows. Absolute sea surface

316   height (SSH) was calculated by adding the sea surface height anomaly from AVISO+ [*Pujol et al.*,

317   2016] to the 2500 dbar reference level mean dynamic topography of [*Olbers et al.*, 1992]. The

318   positions of the fronts were then identified using the sea surface height contours corresponding to the

319   positions of the Southern Ocean fronts identified by [*S. Sokolov and Rintoul*, 2007a] in the region

320   100-180 °E. From this analysis, we show 8 fronts from north to south consisting of:

321   Fronts 1-3: north, middle, and south branches of the Subantarctic Front (SAF), which bound the

322   highest velocity jets of the ACC. Fronts 4-6: north, middle, and south branches of the Polar Front

323   (PF), associated with subsurface temperature features related to the strength of the ACC and with the

324   shoaling of CDW in the overturning circulation. The Polar Frontal Zone (PFZ) lies between the

325   northernmost of these branches and the SAF to its north. Fronts 7-8: north and south branches of the

326   Southern Antarctic Circumpolar Current Front (sACCf) front, marking weaker flows in Antarctic

327   waters of the ACC and occurring near where upwelling of old nutrient rich and relatively acidic

328   Circumpolar Deep Water comes closest to the surface.

329

330   We do not show the Subtropical Front (STF) that marks the northern boundary of the Southern Ocean,

331   or the Southern Boundary Front, which marks the southern edge of the ACC (separating it from

332   westerly flow in Antarctic shelf waters). This is because both features have weak, discontinuous SSH

333   signatures south of Australia: mesoscale eddies rather than the STF dominate the weak SSH field in

334   the Subantarctic Zone (SAZ; between the STF and the SAF), and detection of the Southern Boundary

335   Front is confounded by proximity to the Antarctic shelf where altimetry is impacted by other

336   processes, including sea-ice cover for much of the year [*S. Sokolov and Rintoul*, 2007a].

337

338   We considered using these dynamic heights and front locations as ordinates for the spatial

339   distributions of POC, PIC and BSi. In the core of the ACC (50-60 °S), this did help explain some

340   departures from monotonic north-south trends as resulting from meanders of the fronts, but latitude

341   was more strongly correlated with PIC abundance in the SAZ and with BSi in southern ACC waters

342   and Antarctic shelf waters, where dynamic height contours were only weakly varying. Accordingly,

343   there was no overall advantage of replacing latitude by dynamic height as a predictor of biogenic

344   mineral concentrations, and we have used latitude as the ordinate in our figures and discussion.

345

346   Sea surface temperatures (°C) were obtained from the NASA MODIS Aqua 11 μm night-only L3m

347   product available on-line:

348   https://giovanni.gsfc.nasa.gov/giovanni/#service=TmAvMp&starttime=&endtime=&data=MODISA_

349   L3m_SST_2014_nsst&variableFacets=dataFieldMeasurement%3ASea%20Surface%20Temperature

350   %3B

351   We chose the night values to avoid shallow ephemeral structures arising from daytime solar heating.

352   We refer to these estimates simply as SST values.

353

354   Phytoplankton chlorophyll concentrations (Chl in mg m^{-3} = ug L^{-1}) were obtained from the NASA

355   MODIS Aqua L3m product available on-line:

356   https://giovanni.gsfc.nasa.gov/giovanni/#service=TmAvMp&starttime=&endtime=&data=MODISA_

357   L3m_CHL_2014_chlor_a&variableFacets=dataFieldMeasurement%3AChlorophyll%3B

358   The full citation for this data is:

359   NASA Goddard Space Flight Center, Ocean Ecology Laboratory, Ocean Biology Processing Group.

360   Moderate-resolution Imaging Spectroradiometer (MODIS) Aqua Chlorophyll Data; 2014

361   Reprocessing. NASA OB.DAAC, Greenbelt, MD, USA.

362   doi:10.5067/AQUA/MODIS/L3M/CHL/2014.

363   The algorithm relies on the blue/green reflectance ratio for Chl values above 0.2 ug L^{-1} and

364   incorporates stray light correction based on the difference between red and blue light reflectances at

365   lower Chl levels. This product has been suggested to underestimate chlorophyll in the Southern Ocean

366   south of Australia (Johnson et al., 2013), but has the advantage of ongoing ready availability. For this

367   reason, we use it only for context and not for any detailed comparisons to shipboard observations. We

368   refer to these estimates as SChl values.

369

370   Particulate inorganic carbonate concentrations (mol m^{-3}) based on backscatter magnitudes [*W M Balch*

371   *et al.*, 2005] were obtained from the NASA MODIS/AQUA ocean colour product available on-line:

372   https://oceancolor.gsfc.nasa.gov/cgi/l3/A20111212011151.L3m_MO_PIC_pic_9km.nc.png?sub=img

373   The full citation for this data is:

374   NASA Goddard Space Flight Center, Ocean Ecology Laboratory, Ocean Biology Processing Group.

375   Moderate-resolution Imaging Spectroradiometer (MODIS) Aqua Particulate Inorganic Carbon Data;

376   2014 Reprocessing. NASA OB.DAAC, Greenbelt, MD, USA. doi:

377   10.5067/AQUA/MODIS/L3M/PIC/2014.

378   We refer to these estimates as SPIC values. The veracity of these estimates in the Southern Ocean

379   remains an active area of research. PIC sampling in the Subantarctic South Atlantic found levels 2-3

380   times lower than the satellite estimates [*W M Balch et al.*, 2011], and the algorithm also produces

381   surprisingly high estimates in Antarctic waters, where limited shipboard surveys suggest that

382   coccolithophore abundances drop strongly (work summarized in Balch et al., 2005). Our data

383   provides the most extensive PIC observations for comparison to SPIC values in Antarctic waters yet

384   available, and is discussed in detail below. Comparison of PIC and SPIC values at individual

385   sampling sites was based on combined data from MODIS Aqua and Terra 9km daily products. SPIC

386   values were an average of pixels within 25 km of PIC sampling sites on the same day.

387

388   Modeled coccolithophore distributions were obtained from the data-assimilating general circulation

389   model NASA Ocean Biogeochemical Model (NOBM) available on-line:

390   https://giovanni.gsfc.nasa.gov/giovanni/#service=TmAvMp&starttime=&endtime=&data=NOBM_M

391   ON_R2014_coc&variableFacets=dataFieldDiscipline%3AOcean%20Biology%3BdataFieldMeasure

392   ment%3APhytoplankton%3B

393   The phytoplankton function type model is based on [*Watson W Gregg and Casey*, 2007a]. Details of

394   particular relevance to comparisons with our observations are discussed in section 3.4.

395

396   **3. Results and Discussion**

397

398   **3.1 Representativeness of oceanographic sampling**

399   As shown in Figure 1, sampling covered all Southern Ocean zones from sub-tropical waters in the

400   north to seasonally sea-ice covered waters in the south (covering SST ranging from -1 to 23 °C).

401   Almost all samples were representative of high-nutrient low-chlorophyll Southern Ocean waters,

402   indicative of iron limitation. Exceptions occurred near Tasmania, where moderate levels of SChl

403   were occasionally present, and over the Antarctic shelf where locally very high levels of SChl were

404   present. Individual maps for each voyage leg of SChl are provided in the Supplementary Material and

405   of satellite reflectance based estimates of PIC (SPIC) below, and reveal that higher values of SChl and

406   SPIC are often associated with mesoscale structures, especially in the Subantarctic and Polar Frontal

407   Zones. This means that mesoscale variability makes satellite versus shipboard comparisons difficult,

408   and this problem is exacerbated by frequent cloud cover. Both techniques characterize the very upper

409   water column, with ship samples from ~4m depth and the satellite ocean colour observations

410   reflecting the e-folding penetration depth of ~10-15 m [*Grenier et al.*, 2015; *Morel and Maritorena*,

411   2001].

412

413   It appears likely that our single-depth sampling can be considered as representative of upper water

414   column phytoplankton concentrations, because pigment samples and profiles of beam attenuation and

415   night-time fluorescence from some of these voyages as well as previous work show that biomass is

416   generally well mixed in the upper water column, and that when subsurface chlorophyll maxima are

417   present they primarily reflect increased chlorophyll levels rather than increased phytoplankton

418   abundances [*Andrew R. Bowie et al.*, 2011a; *A.R. Bowie et al.*, 2011b; *Parslow et al.*, 2001; *Rintoul*

419   *and Trull*, 2001; *Shadwick et al.*, 2015; *Trull et al.*, 2001b; *S. W. Wright et al.*, 1996; *S.W. Wright and*

420   *van den Enden*, 2000]. This perspective is also consistent with the limited information on the depth

421   distributions of coccolithophores in the Southern Ocean, which generally exhibit relatively uniform

422   and maximal values (especially for the most abundant species, *Emiliania huxleyi*) within the surface

423   mixed layer [*Findlay and Giraudeau*, 2000; *Holligan et al.*, 2010; *Mohan et al.*, 2008; *Takahashi and*

424   *Okada*, 2000]. There is some evidence that this conclusion can also be applied to the PIC50

425   foraminiferal fraction, in that the most abundant of these organisms tend to co-locate with

426   phytoplankton in the mixed layer in the Southern Ocean [*Mortyn and Charles*, 2003].

427

428   **3.2 Latitudinal distributions of BSi, PIC, and POC**

429   All the Voyage Legs exhibited similar latitudinal variations of the measured chemical components

430   (Figure 3). BSi, predominantly derived from diatoms, was clearly the dominant biogenic mineral in

431   the south in Antarctic waters. PIC01 concentrations, predominantly derived from coccolithophores,

432   were highest in northern Subantarctic waters, although even there BSi was often present at similar

433   levels. Interestingly, PIC50 concentrations, predominantly derived from foraminifera, often exhibited

434   maxima in the middle of the Southern Ocean at latitudes of 55-60 °S. The latitudinal variations in all

435   these biogenic mineral concentrations were quite strong, exceeding two orders of magnitude. In

436   contrast, variations in POC were 10-fold smaller, and often quite uniform across the central Southern

437   Ocean, with maxima sometimes in the far north near Tasmania and sometimes in the far south over

438   the Antarctic shelf (Figure 3). Variations in BSi, PIC, and POC concentrations among the voyages, at

439   a given latitude, were smaller than these north-south trends. It seems likely that these smaller

440   variations were partly seasonal, in that the earliest seasonal voyage leg (VL4 in September) had lower

441   concentrations of every component. But across the other voyages, ranging from mid-November

442   (VL5) to mid-April (VL1) no clear seasonal cycle was exhibited, perhaps owing to variations in

443   sampling location, and the known importance of inter-annual and mesoscale structures in Southern

444   Ocean phytoplankton distributions (e.g. [*Moore et al.*, 1999; *Moore and Abbott*, 2002; *S. Sokolov and*

445   *Rintoul*, 2007b]). As noted in the Methods section (2.3), the BSi values for VL1 stand out as being too

446 low, in that they were well below those of other voyages, while the POC, PIC01, and PIC50 values
447 were similar.
448
449 The latitudinal dependence of the relative importance of diatoms and coccolithophores is revealed by
450 viewing the BSi/PIC01 ratios as an ensemble for all the voyages (use of the ratio helps to remove
451 seasonal and interannual variations in their abundances which tend to track each other at a given
452 latitude). The BSi/PIC01 ratio reaches values of 200 in the far south and decreases north of 50 °S to
453 values near 1 (Figure 4a). Approximate equivalence of BSi and PIC01 occurs relatively far north in
454 the Southern Ocean, near 50 °S, and thus near the southern edge of the Subantarctic Zone. This
455 persistence of the importance of diatoms as a major component of the phytoplankton community in
456 northern waters of the Southern Ocean must reflect the winter-time renewal of silica supply from
457 upwelled deep waters in the Southern Ocean that are carried north by Ekman transport, combined
458 with recycling of biogenic silica within surface waters, given that by mid-summer silicate is largely
459 depleted north of the Subantarctic Front [*Nelson et al.*, 2001; *Trull et al.*, 2001b]. Accordingly the
460 relative dominance of diatoms and coccolithophores in the SAZ may be quite sensitive to changes in
461 the overturning circulation and westerly wind field. How this might translate into impacts on the
462 biological carbon pump remains far from clear. Interestingly, deep ocean sediment traps in the SAZ
463 south of Australia reveal strong dominance (4-fold) of PIC over BSi in the export flux to the ocean
464 interior, reminding us that export can be selective (and also that foraminifera can contribute a
465 significant fraction of total PIC, estimated to vary from ~1/3 to 2/3; [*A L King and Howard*, 2003]).
466 The POC flux recovered by these deep sediment traps was close to the global median and similar to
467 that of biogenic silica dominated fluxes in the Polar Frontal Zone to the south [*Trull et al.*, 2001a].
468
469 The importance of diatoms across the entire Southern Ocean, relative to coccolithophores is further
470 emphasized by expressing their biogenic mineral abundances in terms of associated POC, using
471 average values for the POC/BSi ratio of iron-limited diatoms (3.35, equivalent to a Si/N ratio of 2 and
472 Redfield C/N ratio of 6.7 [*Olivier Ragueneau et al.*, 2006; *Takeda*, 1998]) and the POC/PIC ratio of
473 coccolithophores (1.5, for *Emiliania huxleyi* morphotype A, the dominant Southern Ocean species,
474 [*Bach et al.*, 2015; *M. N. Muller et al.*, 2015]). As shown in Figure 4b, this suggests that diatoms
475 dominate the accumulation of organic carbon throughout the Southern Ocean, with coccolithophores
476 generally contributing less than half that of diatoms in the SAZ and less than a tenth of that in
477 Antarctic waters. This statement is of course limited to POC captured by our small volume, size
478 limited (1-1000 μm), sampling procedure, and variability in the extent of dominance and the
479 scaling of POC to biogenic minerals still allows significant contributions from other POC sources.
480 The relatively small POC contribution from coccolithophores is only weakly sensitive to the ~3-fold
481 variation [*M. N. Muller et al.*, 2015] of POC/PIC ratios among *Emiliania huxleyi* morphotypes. Using

482   the lower value of 0.83 observed for over-calcified forms that occur in the northern SAZ would

483   reduce the POC contribution there but still leave it co-dominant with diatoms, and using the higher

484   value of 2.5 observed for polar morphotype C would increase the POC contribution in Antarctic

485   waters, but still leave it overwhelmed by the diatom contribution (Figure 4b). The relative

486   contributions to total POC are also sensitive to the POC/PIC ratio chosen for diatoms (which vary

487   significantly across genera; [*O. Ragueneau et al.*, 2002; *Olivier Ragueneau et al.*, 2006]). For these

488   reasons, the relative dominance is best viewed on the log scale of Figure 4b, and while keeping in

489   mind the considerable scatter.

490

491   Figure 4b also emphasizes that total POC contents can be largely explained by diatom biomass in

492   Antarctic waters (south of 50 °S), whereas in the SAZ (north of 50 °S), total POC often exceeds the

493   sum of contributions from diatoms and coccolithophores. This serves as an important reminder that

494   other organisms are important to the carbon cycle in the SAZ, and phytoplankton functional type

495   models should avoid over-emphasis on diatoms and coccolithophores just because they have

496   discernable biogeochemical impacts (on silica and alkalinity, respectively) and satellite remote

497   sensing signatures [*Hood et al.*, 2006; *Moore et al.*, 2002]. Finally, we note that the relatively low

498   levels of PIC across the Southern Ocean as observed here means that POC/PIC ratios are high, greater

499   than 4 in the SAZ and ranging up to 20 in Antarctic waters (Figure 4a). This suggests calcification

500   has a negligible countering impact on the reduction of surface ocean CO_2 partial pressure by

501   phytoplankton uptake, even smaller than the few to ~10% influence identified earlier from deep

502   sediment trap compositions in HNLC [*P. W. Boyd and Trull*, 2007a] and iron-enriched waters,

503   respectively [*Salter et al.*, 2014].

504

505   Notably, our Southern Ocean PIC01 estimates are smaller than those found in northern hemisphere

506   polar waters. As compiled by Balch et al. (2005), concentrations were 100-fold higher (~10 μM) in

507   the north Atlantic south of Iceland (60-63 °N) than any of our values, and 1000-fold higher than our

508   values in the same southern hemisphere latitude range. Values collected over many years from the

509   Gulf of Maine [*W M Balch et al.*, 2008] were ~ 1 μM, and thus 5-10 times higher than our SAZ values

510   (Gulf of Maine summer temperatures are similar to the SAZ, and colder in winter). This difference

511   between hemispheres is also evident in observations from the South Atlantic, where PIC values

512   estimated from acid labile backscatter for 6 voyages between 2004 and 2008 and latitudes 40-50 °S

513   were ~0.1-0.5 μM in remote waters [*W M Balch and Utgoff*, 2009], increasing to 1-2 μM in the

514   Argentine Basin with a few values reaching 4 μM [*W Balch et al.*, 2014]. These high South Atlantic

515   observations are the highest of the "Great Calcite Belt" identified as a circumpolar feature of

516   Subantarctic waters based on SPIC values [*W Balch et al.*, 2014; *W M Balch et al.*, 2011]. Notably,

517   shipboard PIC measurements in this feature are 2-3 times lower than the SPIC estimates in the South

518   Atlantic [*W M Balch et al.*, 2011], and ship collected samples from two voyages across the South

519   Atlantic and Indian sectors [*W M Balch et al.*, 2016] exhibit PIC concentrations (actual PIC values

520   accessed online at http://www.bco-dmo.org/dataset/560357, rather than the PIC estimates from acid-

521   labile backscatter shown in the paper) that decrease eastwards in this feature to reach values close to

522   our observations in the Australian sector of ~ 0.1 μM (Figure 3).

523

524   **3.3 Comparison to satellite PIC (SPIC) estimates**

525   As is very evident from the limited observations we have achieved from our efforts over many years,

526   it will never be possible to characterize Southern Ocean phytoplankton population dynamics from

527   ship based sampling – the influences of mesoscale circulation, ephemeral inputs of the limiting

528   nutrient iron, and food web dynamics produce variability that cannot be adequately assessed in this

529   way, leaving sparse sampling open to potentially large biases. Use of satellite observations is clearly

530   the path forward to alleviate this problem, and development of algorithms for global coccolithophore

531   distributions has been a major advance [*W M Balch et al.*, 2005; *Brown and Yoder*, 1994]. Until

532   recently the calibration of these SPIC values has been based primarily on North Atlantic observations.

533   Work to check these efforts for the Southern Ocean has begun, but remains sparse. Early work in the

534   South Atlantic found that SPIC values appeared to exceed ocean PIC by a factor of 2-3 [*W M Balch et

535   al.*, 2011], and based on a handful of samples it was suggested that this might reflect a lower amount

536   of PIC per coccolith [*Holligan et al.*, 2010], and it has since been confirmed that polar

537   coccolithophores can have low PIC contents [*Charalampopoulou et al.*, 2016; *M. N. Muller et al.*,

538   2015; *Poulton et al.*, 2011]. Two dedicated voyages to investigate the "Great Calcite Belt" in the SAZ

539   and PFZ across the South Atlantic and South Indian Oceans, attempted comparison of acid-labile

540   backscatter (as a proxy for PIC) and MODIS SPIC values, but there were no match-ups in the South

541   Atlantic owing to cloudy conditions [*W M Balch et al.*, 2016]. Results from the South Indian sector,

542   and from other voyages in the South Atlantic show high acid-labile backscatter which translates into

543   high SPIC estimates in the SAZ and PFZ (especially in naturally iron-fertilized waters), but also high

544   values further south which are not in agreement with ship observations [*W M Balch et al.*, 2016; *Smith

545   et al.*, 2017].

546

547   Comparison of our ship observations to MODIS SPIC estimates are shown in Figure 5 for each

548   voyage leg. These reveal some agreement in the SAZ in terms of identifying moderate levels of PIC,

549   often in association with higher levels of total SChl (Supplementary Material), but differ strongly in

550   Antarctic waters where all ship observations reveal low PIC values, whereas the SPIC estimates in

551   Antarctic waters reach and often exceed those in the SAZ, especially over the Antarctic shelf. Both

552   cloudy conditions and strong mesoscale variability limit the number of direct comparisons (match-

553   ups) that can be made. Using a match-up length scale of 25 km (i.e. the ship and satellite observations

554   must be within 25 km of each other on the same day), which is somewhat larger than the correlation

555   length scale for chlorophyll in the Southern Ocean of 10-15 km [*Haëntjens et al.*, 2017], allowed us to

556   retain 116 match-ups. These results, shown in Figure 6, confirm that the satellite SPIC values are

557   reasonable estimates in Subantarctic waters, within a factor of 2-3 [*W M Balch et al.*, 2011], but very

558   much too high in Antarctic waters.

559

560   **3.4 Comparison to possible environmental controls on coccolithophore growth rates**

561   The ship observations provided here offer a significant advance in quantifying the distributions of

562   coccolithophores in the Southern Ocean south of Australia, but much less understanding of why these

563   distributions arise and therefore how they might change in response to climate, circulation, and

564   biogeochemical changes in the future. Coccolithophores, especially the most common species

565   *Emiliania huxleyi*, have been studied sufficiently in the laboratory to allow possible important

566   controls on their niches and especially their calcification rates to be proposed, including temperature,

567   pH, pCO_2, calcite saturation state, light, and macro- and micro-nutrient availability [*Bach et al.*, 2015;

568   *Feng et al.*, 2016; *Mackinder et al.*, 2010; *M. N. Muller et al.*, 2015; *Müller et al.*, 2017; *Schlüter et*

569   *al.*, 2014; *Schulz et al.*, 2007; *Sett et al.*, 2014; *Zhang et al.*, 2015]. We collected observations of many

570   of these properties in parallel with our PIC observations, and now briefly examine whether they

571   present correlations that might contribute to understanding why coccolithophores are found mainly in

572   northern Subantarctic waters, and not further south. For illustrative purposes, we focus on VL3 (the

573   mid- to late summer I9 northward hydrographic section from Antarctica to Perth) and VL6 (the early

574   to mid-summer southward Astrolabe transit from Tasmania to Antarctica). VL3 covered the widest

575   range of physical properties, and exhibited PIC01 concentrations that remained elevated further south

576   than any other voyage (Figure 3). VL6 exhibited the more typical PIC01 distribution of a close to

577   continuous decrease southward (Figure 3). The results from the other Voyage Legs were very similar

578   to VL3 (figures not shown; data available in Supplementary Materials).

579

580   Many properties that might influence coccolithophore productivity decreased strongly and close to

581   monotonically from north to south across the Southern Ocean for our voyages (Figure 7). These

582   include temperature (from 23 to -0.4 C for our samples), salinity (from 35.6 to 33.6, with tight

583   correlation with alkalinity, not shown - data available in the Supplementary Material), pH (from 8.20

584   to 8.08 on the free scale), and the saturation state of calcite (from 5.22 to 2.12). The strong correlation

585   of these properties means that it is not easy to separate their possible influences on coccolithophore

586   distributions, without relying on specific thresholds or quantitative response models. This problem of

587   correlations among drivers has been noted before in examining transect data across Drake passage,

588   where more detailed measurements of coccolithophore properties augmented with incubation studies

589   found temperature and light were the most probable drivers of coccolithophore abundance and

590   calcification rates [*Charalampopoulou et al.*, 2016]. Our lack of information on the availability of

591   light (mixed layer depth was determined only on the two hydrographic sections), iron, or individual

592 species and strains, makes deducing a possible influence of ocean acidification on coccolithophore

593 distributions from our spatial distribution data even more difficult. Nonetheless, we offer a few

594 pertinent observations. Firstly, the change in PIC01 abundances with latitude is much larger than

595 expected from models of the responses of calcification rates (normalized to maximum rates) to

596 inorganic carbon system variations (Figure 7). Two models are shown:

597

598   1.   The "Bach model" based on independent terms for sensitivity to bicarbonate, CO_2, and pH. It

599   fits quite well the results from many laboratory incubations of *Emiliania huxleyi* strains under

600   conditions of modern and elevated pCO_2 [*Bach et al.*, 2015], and we have used values for the

601   constants (a, b, c, d) obtained from incubations of a strain isolated from Subantarctic waters

602   south of Tasmania [*Müller et al.*, 2017] to provide what might be considered the best current

603   model for the calcification rate response to changing inorganic carbon abundance and

604   speciation, following Eq. (1):

605

606   Bach relative calcification rate = $a\,[HCO_3^-] / (b+[HCO_3^-]) - e^{-c[CO2]} - d[H^+]$ (1)

607

608   2.   The "Langdon model" based on a simple, inorganic precipitation motivated parameterization

609   of calcification as a function of calcite saturation state Ω [*Gattuso et al.*, 1998; *Langdon et al.*,

610   2000], which has been shown to apply in an approximate way to many corals [*Anthony et al.*,

611   2011; *Silverman et al.*, 2007], and perhaps to Southern Ocean foraminifera [*Moy et al.*, 2009].

612   We have chosen the simple linear form (n=1) and a sensitivity at the top end of the observed

613   range (a =1/4, so that calcification rate varies linearly from 0 to 1 for Ω=1 to 4), following Eq.

614   (2):

615

616   Langdon relative calcification rate = $a\,(\Omega-1)^n$ (2)

617

618 As shown in Figure 7, both these calcification rate models exhibit limited variations with latitude in

619 the Southern Ocean. The Bach model suggests negligible change in calcification rate. This is

620 essentially because the Southern Ocean variations in bicarbonate, CO_2, and pH are very small

621 compared to the future expected values used in incubation experiments. In addition, southward

622 cooling causes pH to rise, offsetting the impact of southward decrease in salinity and alkalinity, thus

623 reducing the southward decrease of pH and the associated drop in modeled calcification rate. The

624 Langdon model suggests approximately 3-fold decrease in calcification rate, which is considerably

625 smaller than the more than 10-fold drop in PIC01 (shown on a linear scale in Figure 7 and a

626 logarithmic scale in Figure 3). The shape of the Langdon model decrease shows some agreement with

627 that of PIC01 for VL6, but none for VL3 (which exhibits relatively constant significant PIC01

18

628   concentrations in the 40-50 °S latitude range where the Langdon model shows a strong decrease in

629   calcification rate, and then a strong drop in PIC01 south of 60 °S where the Langdon model shows no

630   change). Thus, and unsurprisingly, coccolithophore abundances are clearly not controlled by

631   inorganic carbon chemistry alone. This perspective has been strongly emphasized previously,

632   including by Bach et al., (2015), who noted " …great care must be taken when correlating carbonate

633   chemistry with coccolithophore dispersal because this is by no means the only parameter controlling

634   it. Physical (e.g. temperature), other chemical (e.g. nutrient concentrations), or ecological (e.g. grazing

635   pressure) factors will under many if not most circumstances outweigh the influence of carbonate

636   chemistry conditions…".

637

638   Many laboratory studies have emphasized the importance of temperature on coccolithophore growth

639   rates, as compiled recently [*Feng et al.*, 2016], and warming has been suggested as a possible cause of

640   decadal northward apparent range expansion in the North Atlantic [*Rivero-Calle et al.*, 2015] and the

641   occurrence of unusual blooms in the Bering Sea [*Merico et al.*, 2004]. To provide a brief visualization

642   of the expected univariate response, we fit the "Norberg" thermal optimum envelope model [*Norberg*,

643   2004] to growth rate data for 5-25 °C with modern pCO_2 and nutrient replete conditions for a

644   Southern Ocean morphotype A strain of *Emiliania huxleyi*, isolated from south of Tasmania [*M. N.*

645   *Muller et al.*, 2015], with optimum temperature z=15, thermal window w=10, and scaling constant *a*,

646   in which the exponential term represents the broad global temperature dependence of generic

647   phytoplankton growth rates [*Eppley*, 1972] and produces the known skewed form of organismic

648   thermal tolerances, following Eq. (3):

649

650        $$\text{Norberg growth rate (d}^{-1}) = a\,[1 - ((T-z)/w)^2]\,e^{0.0633T} \tag{3}$$

651

652   As shown in Figure 7, this predicts a drop from ~0.5 d^{-1} at the northern edge of the Southern Ocean to

653   zero growth near ~53 °S, whereas PIC01 concentrations fall off more slowly further south. The

654   presence of other morphotypes with lower thermal optima [*Cubillos et al.*, 2007] is an easy possible

655   way to explain this difference. Overall the Norberg temperature model has an advantage of the

656   calcification rate models – it does predict a strong decrease to negligible PIC01 values in the south.

657   There are of course many other possible explanations (as noted at the start of this section).

658

659   Interestingly, these uncertainties regarding the roles of inorganic carbon chemistry and temperature on

660   Southern Ocean coccolithophore distributions contrast with the possible role of macro-nutrients, in

661   that phosphate and nitrate increase southward across the Southern Ocean (e.g. [*Trull et al.*, 2001b]),

662   and were everywhere abundant during our surveys (nitrate > 3 μM , with phosphate/nitrate close to

663   Redfield expectations, data in Supplementary Material), and thus would be expected to lead to

664   southward increases in coccolithophore abundances which were not observed. For this reason we

665   suggest nitrate and phosphate availability is not an obvious driver of the southward decrease in

666   coccolithophore abundances in Southern Ocean HNLC waters (i.e. these nutrients are sufficient

667   everywhere), although these nutrients may be important in determining the success of

668   coccolithophores in oligotrophic waters at the northern edge of the Southern ocean, given the high

669   half-saturation constant for nitrate uptake observed in some laboratory studies (~13 μM ; [*Feng et al.*,

670   2016]), and the possibility that high temperature and low nutrient conditions may non-linearly amplify

671   phytoplankton stresses [*Thomas et al.*, 2017].

672

673   Importantly, in addition to multivariate environmental control of coccolithophore distributions via

674   their growth rates, there is the possibility of control by resource competition with other autotrophs

675   (presumably mainly for iron) and/or stronger loss terms to grazers in Antarctic than Subantarctic

676   waters ([*Assmy et al.*, 2013] has suggested preferential grazing as a control on community structure;

677   but we have no data to allow us to evaluate this). These are difficult issues to evaluate, and we provide

678   just one comment. Diatom abundances as estimated from BSi concentrations show a stronger

679   latitudinal relationship to silicon availability than coccolithophores do to carbonate availability

680   (Figure 7). Diatoms abundances drop strongly near the SAF, north of which summer time $Si(OH)_4$

681   concentrations drop below 1 μM , i.e. close to the 'residual" concentration which it appears diatoms

682   cannot access [*Paasche*, 1973]. Surveys of coccolithophores and diatoms in the SAZ in the South

683   Atlantic and South Indian sectors have previously suggested that coccolithophore distributions may be

684   linked to competition with diatoms [*W M Balch et al.*, 2016; *Smith et al.*, 2017], and this view is

685   compatible with our observations, although it remains unproven. Further progress in understanding

686   the controls on coccolithophore abundances in the Southern Ocean is clearly needed. At present

687   temperature, light, and competition with diatoms for iron appear to be the strongest candidates (at

688   least for southward expansion [*Charalampopoulou et al.*, 2016; *Gafar et al.*, 2017]; with nitrate a

689   strong influence on the location of the northern oligotrophic boundary; [*Feng et al.*, 2016]).

690

691   **3.5 Comparison to the NASA Ocean Biogeochemical Model**

692   Many of these ideas about the roles of environmental conditions and ecological competition have

693   been included in models for global coccolithophore distributions, e.g. [*Watson W Gregg and Casey*,

694   2007a; *Le Quere et al.*, 2005]; and we provide a brief comparison to one model – the NASA Ocean

695   Biogeochemical Model (NOBM) for which simulation results are available on-line (see the Methods

696   section). In brief, the NOBM predicts coccolithophore abundances (in Chl units) that are restricted to

697   the far northern reaches of the Southern Ocean (Figure 8). This is also true for the Dynamic Green

698   Ocean Model [*Le Quere et al.*, 2005]. This contrasts with our PIC results (Figures 3, 4, 7) and with

699   PIC and coccolithophore cell counts from other sampling efforts which have found coccolithophore

700   abundances to extend with similar concentrations right across the SAZ and sometimes the PFZ, e.g.

during VL6 south of western Australia (Figures 3 and 7), south of Tasmania [*Cubillos et al.*, 2007], in the Scotia Sea [*Holligan et al.*, 2010], and in the South Atlantic and South Indian Oceans, especially in regions of natural iron fertilization [*W M Balch et al.*, 2016; *Smith et al.*, 2017]. In the NOBM, diatoms are also simulated and show (Figure 8) the expected high abundance in Antarctic waters in the southern third of the Southern Ocean, decreasing northward as in our results (but also show a band of elevated diatom concentrations in the Subantarctic, which we did not observe).

Competition for nutrients in the NOBM favours the ability of coccolithophores over diatoms to get by on limited resources (half-saturation constants for nitrate and iron of 0.5 and 0.67 versus 1.0 and 1.0 μM) including light (half saturation constant of 56 versus 90 μmol photons m^{-2} s^{-1} under Southern Ocean low light conditions). But diatoms are specified to have higher growth rates when all resources are non-limiting (maximum growth rate at 20 °C 1.50 versus 1.13, both with the same Eppley dependence on temperature). Thus in the model, diatoms dominate silicon replete Southern Ocean waters, outcompeting other species for the limiting iron, and only give way to other species when silicon is depleted. Notably these other species then do best when additional Fe is supplied from either atmospheric sources (in the north where continental dusts are not shielded by ice) or island oases such as Crozet or Kerguelen. This view is compatible with our observations and those carried out in the northern half of the Southern Ocean during the "Great Calcite Belt" voyages [*W M Balch et al.*, 2016; *Smith et al.*, 2017]. It suggests that potential expansion of coccolithophores southward might be linked to decreasing supply of silicon from reduced upwelling of Circumpolar Deep Water in a progressively more stratified global ocean. A cautionary note to this conclusion is provided by the NOBM simulation of significant concentrations of diatoms in the SAZ where silicon is low, which arises from their specified higher maximum growth rate, emphasizing the importance of this parameter, and its temperature dependence, in modeling phytoplankton distributions. In specifying this temperature dependence, this model and most others still rely on the global compilation from nearly 50 years ago [*Eppley*, 1972]. Clearly better understanding of the controls on maximum growth rates and their temperature tolerance for key phytoplankton taxa is needed, first to understand current distributions and then to explore possible future changes.

4. Conclusions

Our surveys of PIC concentrations as a proxy for coccolithophores in the Southern Ocean south of Australia suggest:

- The concentrations of coccolithophores were much smaller (at least 10-fold) in the open Southern Ocean south of Australia than in northern hemisphere oceans.

737   •   Coccolithophores were most abundant in the SAZ, and occasionally in the PFZ.

738

739   •   The contribution of coccolithophores to total phytoplankton biomass (estimated from POC)

740   was small, less than 10% in Subantarctic waters and less than 1% in Antarctic waters.

741

742   •   The "Great Calcite Belt" characterization of SAZ and PFZ waters is overstated south of

743   Australia, because both the satellite (SPIC) estimates and our in-situ PIC measurements show

744   lower values than in the South Atlantic and South Indian where this feature was first

745   suggested.

746   •   The satellite PIC (SPIC) algorithm provides a good estimate, within a factor of 2-3, of PIC

747   values in Subantarctic waters south of Australia, but erroneously suggests large

748   agglomerations of PIC in polar waters, where little to none is present south of Australia.

749

750   •   Our PIC results and ancillary measurements of biogenic silica, particulate organic carbon,

751   dissolved nutrients, and inorganic carbon system status may be useful in the testing of models

752   of limiting conditions and ecological competitions that affect coccolithophore distributions.

753   Preliminary considerations suggest that temperature, iron, and competition with diatoms may

754   be stronger influences than pH or calcite saturation state.

755

756 Despite the considerable effort required to obtain these survey results, much remains to be done just to

757 define coccolithophore distributions, for example their seasonality, especially when the complexities

758 of differing responses of individual species and strains are considered.

773 **References**

774

775 Anthony, K., J. A Kleypas, and J. P. Gattuso (2011), Coral reefs modify their seawater
776   carbon chemistry–implications for impacts of ocean acidification, *Global Change Biology*,
777   *17*(12), 3655-3666.

778 Assmy, P., V. Smetacek, M. Montresor, C. Klaas, J. Henjes, V. H. Strass, J. M. Arrieta, U.
779   Bathmann, G. M. Berg, and E. Breitbarth (2013), Thick-shelled, grazer-protected diatoms
780   decouple ocean carbon and silicon cycles in the iron-limited Antarctic Circumpolar
781   Current, *Proceedings of the National Academy of Sciences*, *110*(51), 20633-20638.

782 Bach, L. T., U. Riebesell, M. Gutowska, L. Federwisch, and K. G. Schulz (2015), A unifying
783   concept of coccolithophore sensitivity to changing carbonate chemistry embedded in an
784   ecological framework, *Progress in Oceanography*, *135*, 125-138.

785 Balch, W., D. Drapeau, B. Bowler, E. Lyczkowski, L. Lubelczyk, S. Painter, and A. Poulton
786   (2014), Surface biological, chemical, and optical properties of the Patagonian Shelf
787   coccolithophore bloom, the brightest waters of the Great Calcite Belt, *Limnol. Oceanogr*,
788   *59*(5), 1715-1732.

789 Balch, W. M., N. R. Bates, P. J. Lam, B. S. Twining, S. Z. Rosengard, B. C. Bowler, D. T.
790   Drapeau, R. Garley, L. C. Lubelczyk, and C. Mitchell (2016), Factors regulating the Great
791   Calcite Belt in the Southern Ocean and its biogeochemical significance, *Global
792   Biogeochemical Cycles*, *30*(8), 1124-1144.

793 Balch, W. M., D. T. Drapeau, B. C. Bowler, E. S. Booth, L. A. Windecker, and A. Ashe
794   (2008), Space–time variability of carbon standing stocks and fixation rates in the Gulf of
795   Maine, along the GNATS transect between Portland, ME, USA, and Yarmouth, Nova
796   Scotia, Canada, *Journal of plankton research*, *30*(2), 119-139.

797 Balch, W. M., D. T. Drapeau, B. C. Bowler, E. Lyczskowski, E. S. Booth, and D. Alley
798   (2011), The contribution of coccolithophores to the optical and inorganic carbon budgets
799   during the Southern Ocean Gas Exchange Experiment: New evidence in support of the
800   "Great Calcite Belt" hypothesis, *Journal of Geophysical Research*, *116*, C00F06,
801   doi:10.1029/2011JC006941.

802 Balch, W. M., H. R. Gordon, B. C. Bowler, D. T. Drapeau, and E. S. Booth (2005), Calcium
803   carbonate measurements in the surface global ocean based on Moderate-Resolution
804   Imaging Spectroradiometer data, *Journal of Geophysical Research*, *110*, C07001; doi:
805   07010.01029/02004jc002560.
806 Balch, W. M., and P. E. Utgoff (2009), Potential interactions among ocean acidification,
807   coccolithophores, and the optical properties of seawater, *Oceanography*, *22*(4), 146-159.
808 Be, A. W. H., and D. Tolderlund (1971), Distribution and ecology of living planktonic
809   foraminifera in surface waters of the Atlantic and Indian Oceans, in *Micropaleontology of*
810   *Oceans* edited by B. M. Funnel and W. R. Riedel, pp. 105-149, Cambridge University
811   Press, New York.
812 Boeckel, B., K.-H. Baumann, R. Henrich, and H. Kinkel (2006), Coccolith distribution
813   patterns in South Atlantic and Southern Ocean surface sediments in relation to
814   environmental gradients, *Deep Sea Research Part I: Oceanographic Research Papers*,
815   *53*(6), 1073-1099, doi:http://dx.doi.org/10.1016/j.dsr.2005.11.006.
816 Bowie, A. R., F. B. Griffiths, F. Dehairs, and T. W. Trull (2011a), Oceanography of the
817   subantarctic and Polar Frontal Zones south of Australia during summer: Setting for the
818   SAZ-Sense study, *Deep-Sea Research II*, *58*(21-22), 2059-2070,
819   doi:10.1016/j.dsr2.2011.05.033.
820 Bowie, A. R., T. W. Trull, and F. Dehairs (2011b), Estimating the Sensitivity of the
821   Subantarctic Zone to Environmental Change: the SAZ-Sense project., *Deep Sea Research*
822   *II*, *58*(21-22), 2051-2058.
823 Boyd, P. W., and T. Trull (2007a), Understanding the export of biogenic particles in oceanic
824   waters: Is there consensus?, *Progress in Oceanography*, *72*(4), 276-312,
825   doi:10.1016/j.pocean.2006.10.007.
826 Boyd, P. W., and T. W. Trull (2007b), Understanding the export of marine biogenic particles:
827   is there consensus?, *Progress in Oceanography*, *4*, 276-312,
828   doi:210.1016/j.pocean.2006.1010.1007.
829 Brown, C. W., and J. A. Yoder (1994), Coccolithophore blooms in the global ocean,, *Journal*
830   *of Geophysical Research*, *104C*, 1541-1558.
831 Buitenhuis, E., P. van der Wal, and H. J. W. de Baar (2001), Blooms of Emiliania huxleyi are
832   sinks of atmospheric carbon dioxide: a field and mesocosm study derived simulation,
833   *Global Biogeochemical Cycles*, *15*(3), 577-587.
834 Cao, L., and K. Caldeira (2008), Atmospheric CO2 stabilization and ocean acidification,
835   *Geophysical Research Letters*, *35*(19), n/a-n/a, doi:10.1029/2008GL035072.
836 Charalampopoulou, A., A. J. Poulton, D. C. E. Bakker, M. I. Lucas, M. C. Stinchcombe, and
837   T. Tyrrell (2016), Environmental drivers of coccolithophore abundance and calcification
838   across Drake Passage (Southern Ocean), *Biogeosciences*, *13*(21), 5917-5935,
839   doi:10.5194/bg-13-5917-2016.
840 Cubillos, J. C., S. W. Wright, G. Nash, M. F. d. Salas, B. Griffiths, B. Tilbrook, A. Poisson,
841   and G. M. Hallegraeff (2007), Calcification morphotypes of the coccolithophorid
842   Emiliania huxleyi in the Southern Ocean: changes in 2001 to 2006 compared to historical
843   data, *Marine Ecology Progress Series*, *348*, 47-54, doi: 10.3354/meps07058.
844 Dickson, A. G., C. L. Sabine, and J. R. Christian (2007), Guide to Best Practices for Ocean
845   CO2 Measurements*Rep.*, Sidney, British Columbia.
846 Doubleday, A. J., and R. R. Hopcroft (2015), Interannual patterns during spring and late
847   summer of larvaceans and pteropods in the coastal Gulf of Alaska, and their relationship to
848   pink salmon survival, *Journal of Plankton Research*, *37*(1), 134-150,
849   doi:10.1093/plankt/fbu092.
850 Eppley, R. W. (1972), Temperature and phytoplankton growth in the sea, *Fisheries Bulletin*,
851   *70*, 1063-1085.

852 Eriksen, R. (1997), A practical manual for the determination of salinity, dissolved oxygen,
853   and nutrients in seawater*Rep. 11*, 83 pp, Hobart, Tasmania, Australia.
854 Eynaud, F., J. Giraudeau, J. J. Pichon, and C. J. Pudsey (1999), Sea-surface distribution of
855   coccolithophores, diatoms, silicoflagellates and dinoflagellates in the South Atlantic
856   Ocean during the late austral summer 1995, *Deep Sea Research Part I: Oceanographic*
857   *Research Papers*, *46*(3), 451-482, doi:http://dx.doi.org/10.1016/S0967-0637(98)00079-X.
858 Feng, Y., M. Y. Roleda, E. Armstrong, P. W. Boyd, and C. L. Hurd (2016), Environmental
859   controls on the growth, photosynthetic and calcification rates of a Southern Hemisphere
860   strain of the coccolithophore Emiliania huxleyi, *Limnology and Oceanography*, *62*, 519-
861   540, doi:10.1002/lno.10442.
862 Findlay, C. S., and J. Giraudeau (2000), Extant calcareous nannoplankton in the Australian
863   Sector of the Southern Ocean (austral summers 1994 and 1995), *Marine*
864   *Micropaleontology*, *40*(4), 417-439, doi:http://dx.doi.org/10.1016/S0377-8398(00)00046-
865   3.
866 Gafar, N. A., B. D. Eyre, and K. G. Shulz (2017), A conceptual moel for projecting
867   coccolithophorid growth, calcification, and photosynthetic carbon fixation rates in
868   response to global change (carbonate chemistry, temperature, and light) based on
869   *Gephyrocapsa oceanica*, *Progress in Oceanography*, *in review*.
870 Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine, and R. Buddemeier (1998), Effect of
871   calcium carbonate saturation of seawater on coral calcification, *Global and Planetary*
872   *Change*, *18*(1), 37-46.
873 Gravalosa, J. M., J.-A. Flores, F. J. Sierro, and R. Gersonde (2008), Sea surface distribution
874   of coccolithophores in the eastern Pacific sector of the Southern Ocean (Bellingshausen
875   and Amundsen Seas) during the late austral summer of 2001, *Marine Micropaleontology*,
876   *69*(1), 16-25, doi:http://dx.doi.org/10.1016/j.marmicro.2007.11.006.
877 Gregg, W. W., and N. W. Casey (2007a), Modeling coccolithophores in the global oceans,
878   *Deep Sea Research Part II: Topical Studies in Oceanography*, *54*(5), 447-477.
879 Gregg, W. W., and N. W. Casey (2007b), Modeling coccolithophores in the global oceans,
880   *Deep Sea Research Part II: Topical Studies in Oceanography*, *54*(5–7), 447-477,
881   doi:http://dx.doi.org/10.1016/j.dsr2.2006.12.007.
882 Grenier, M., A. Della Penna, and T. W. Trull (2015), Autonomous profiling float
883   observations of the high biomass plume downstream of the Kerguelen plateau in the
884   Southern Ocean, *Biogeosciences 12*, 1–29, doi:10.5194/bg-12-1-2015.
885 Haëntjens, N., E. Boss, and L. D. Talley (2017), Revisiting Ocean Color algorithms for
886   chlorophyll a and particulate organic carbon in the Southern Ocean using biogeochemical
887   floats, *Journal of Geophysical Research: Oceans*, *122*(8), 6583-6593,
888   doi:10.1002/2017JC012844.
889 Holligan, P., A. Charalampopoulou, and R. Hutson (2010), Seasonal distributions of the
890   coccolithophore, Emiliania huxleyi, and of particulate inorganic carbon in surface waters
891   of the Scotia Sea, *Journal of Marine Systems*, *82*(4), 195-205.
892 Hood, R. R., E. A. Laws, R. A. Armstrong, N. R. Bates, C. W. Brown, C. A. Carlson, F.
893   Chai, S. C. Doney, P. G. Falkowski, and R. A. Feely (2006), Pelagic functional group
894   modeling: Progress, challenges and prospects, *Deep Sea Research Part II: Topical Studies*
895   *in Oceanography*, *53*(5), 459-512.
896 Kimball Jr, J., and E. Ferguson Wood (1964), A simple centrifuge for phytoplankton studies,
897   *Bulletin of Marine Science*, *14*(4), 539-544.
898 King, A. L., and W. R. Howard (2003), Planktonic foraminiferal flux seasonality in
899   Subantarctic sediment traps: A test for paleoclimate reconstructions, *Paleooceanography*,
900   *18*(1), 1019, doi:1010.1029/2002PA000839, 002003.

901   King, P., H. Kennedy, P. P. Newton, T. D. Jickells, T. Brand, S. Calvert, G. Cauwet, H.
902   Etcheber, B. Head, and A. Khripounoff (1998), Analysis of total and organic carbon and
903   total nitrogen in settling oceanic particles and a marine sediment: an interlaboratory
904   comparison, *Marine Chemistry*, *60*(3), 203-216.
905   Klaas, C., and D. E. Archer (2002), Association of sinking organic matter with various types
906   of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochemical*
907   *Cycles*, *16*(4), doi:10.1029/2001GB001765.
908   Langdon, C., T. Takahashi, C. Sweeney, D. W. Chipman, and J. Goddard (2000), Effect of
909   calcium carbonate saturation state on the calcification rate on an experimental coral reef,
910   *Global Biogeochemical Cycles*, *14*(2), 613C-DIC, 615N-NO613 and 618O-NO613 639-
911   654.
912   Le Quere, C., S. P. Harrison, I. Colin Prentice, E. T. Buitenhuis, O. Aumont, L. Bopp, H.
913   Claustre, L. Cotrim Da Cunha, R. Geider, and X. Giraud (2005), Ecosystem dynamics
914   based on plankton functional types for global ocean biogeochemistry models, *Global*
915   *Change Biology*, *11*(11), 2016-2040.
916   Mackinder, L., G. Wheeler, D. Schroeder, U. Riebesell, and C. Brownlee (2010), Molecular
917   mechanisms underlying calcification in coccolithophores, *Geomicrobiology Journal*,
918   *27*(6), 585-595.
919   McNeil, B. I., and R. J. Matear (2008), Southern Ocean acidification: A tipping point at 450-
920   ppm atmospheric CO2, *Proceedings of the National Academy of Sciences 105*(48), 18860-
921   18864, doi: 18810.11073/pnas.0806318105.
922   Merico, A., T. Tyrrell, E. J. Lessard, T. Oguz, P. J. Stabeno, S. I. Zeeman, and T. E.
923   Whitledge (2004), Modelling phytoplankton succession on the Bering Sea shelf: role of
924   climate influences and trophic interactions in generating Emiliania huxleyi blooms 1997–
925   2000, *Deep Sea Research I*, *51*(12), 1803-1826, doi:1810.1016/j.dsr.2004.1807.1003.
926   Mohan, R., L. P. Mergulhao, M. V. S. Guptha, A. Rajakumar, M. Thamban, N. AnilKumar,
927   M. Sudhakar, and R. Ravindra (2008), Ecology of coccolithophores in the Indian sector of
928   the Southern Ocean, *Marine Micropaleontology*, *67*(1–2), 30-45,
929   doi:http://dx.doi.org/10.1016/j.marmicro.2007.08.005.
930   Moore, J. K., M. R. Abbot, J. G. Richman, W. O. Smith, T. J. Cowles, K. H. Coale, G. W.D.,
931   and R. T. Barber (1999), SeaWiFS satellite ocean color data from the Southern Ocean,
932   *Gephysical Research Letters*, *26*(10), 1465-1468.
933   Moore, J. K., and M. R. Abbott (2002), Surface chlorophyll concentrations in relation to the
934   Antarctic Polar Front: seasonal and spatial patterns from satellite observations, *Journal of*
935   *Marine Systems*, *37*, 69-86.
936   Moore, J. K., S. C. Doney, J. A. Kleypas, D. M. Glover, and I. Y. Fung (2002), An
937   intermediate complexity marine ecosystem model for the global domain, *Deep-Sea*
938   *Research II*, *49*, 403-462?
939   Morel, A., and S. Maritorena (2001), Bio-optical properties of oceanic waters- A reappraisal,
940   *Journal of Geophysical research*, *106*(C4), 7163-7180.
941   Mortyn, P. G., and C. D. Charles (2003), Planktonic foraminiferal depth habitat and δ18O
942   calibrations: Plankton tow results from the Atlantic sector of the Southern Ocean,
943   *Paleoceanography*, *18*(2).
944   Moy, A. D., W. Howard, S. G. Bray, and T. Trull (2009), Reduced calcification in modern
945   Southern Ocean planktonic foraminifera, *Nature Geoscience*, *2*(April), 276-280,
946   doi:10.1038/NGEO460.
947   Muller, M. N., T. Trull, and G. M. Hallegraeff (2015), Differing responses of three Southern
948   Ocean Emiliania huxleyi ecotypes to changing seawater carbonate chemistry, *Marine*
949   *Ecology Progress Series*, *531*, 81-90, doi:10.3354/meps11309.

950 Muller, M. N., T. W. Trull, and G. Hallegraeff (2017), Independence of nutrient limitation
951   and carbon dioxide impacts on Southern Ocean coccolithophore Emiliania huxleyi, *Nature*
952   *- Microbial Ecology*, *in press*
953 Müller, M. N., T. W. Trull, and G. M. Hallegraeff (2017), Independence of nutrient limitation
954   and carbon dioxide impacts on the Southern Ocean coccolithophore Emiliania huxleyi,
955   *The ISME Journal*, 1-11, doi:10.1038/ismej.2017.53.
956 Nelson, D. M., M. A. Brzezinski, D. E. Sigmon, and V. M. Frank (2001), A seasonal
957   progression of Si limitation in the Pacific sector of the Southern Ocean, *Deep-Sea*
958   *Research II*, *48*, 3973-3995.
959 Norberg, J. (2004), Biodiversity and ecosystem functioning: a complex adaptive systems
960   approach, *Limnology and Oceanography*, *49*(4part2), 1269-1277.
961 Olbers, D. J., V. Gouretski, and G. S. J. Schroter (1992), *Hydrographic Atlas of the Southern*
962   *Ocean*, 99 pp., Alfred Wegener Institute for Polar and Marine Research, Bremerhaven.
963 Orr, J. C., et al. (2005), Anthropogenic ocean acidification over the twenty-first century and
964   its impact on calcifying organisms, *Nature 437*, 681-686, doi:610.1038/nature04095.
965 Paasche, E. (1973), Silicon and the ecology of marine plankton diatoms. I. Thalassiosira
966   pseudonana (Cyclotella nana) grown in a chemostat with silicate as limiting nutrient,
967   *Marine biology*, *19*(2), 117-126.
968 Parslow, J., P. Boyd, S. R. Rintoul, and F. B. Griffiths (2001), A persistent sub-surface
969   chlorophyll maximum in the Polar Frontal Zone south of Australia: seasonal progression
970   and implications for phytoplankton-light-nutrient interactions, *Journal of Geophysical*
971   *Research*, *106*, 31543-31557.
972 Pörtner, H. O., M. Langenbuch, and B. Michaelidis (2005), Synergistic effects of temperature
973   extremes, hypoxia, and increases in CO2 on marine animals: From Earth history to global
974   change, *Journal of Geophysical Research, Oceans*, *110*, doi:10.1029/2004JC002561.
975 Poulton, A. J., S. C. Painter, J. R. Young, N. R. Bates, B. Bowler, D. Drapeau, E.
976   Lyczsckowski, and W. M. Balch (2013), The 2008 Emiliania huxleyi bloom along the
977   Patagonian Shelf: Ecology, biogeochemistry, and cellular calcification, *Global*
978   *Biogeochemical Cycles*, *27*(4), 1023-1033.
979 Poulton, A. J., J. R. Young, N. R. Bates, and W. M. Balch (2011), Biometry of detached
980   Emiliania huxleyi coccoliths along the Patagonian Shelf, *Marine Ecology Progress Series*,
981   *443*, 1-17.
982 Pujol, M.-I., Y. Faugère, G. Taburet, S. Dupuy, C. Pelloquin, M. Ablain, and N. Picot (2016),
983   DUACS DT2014: the new multi-mission altimeter data set reprocessed over 20 years,
984   *Ocean Science*, *12*(5), 1067-1090.
985 Ragueneau, O., N. Dittert, P. Pondaven, P. Treguer, and L. Corrin (2002), Si/C decoupling in
986   the world ocean: is the Southern Ocean different?, *Deep-Sea Research II*, *49*, 3127-3154.
987 Ragueneau, O., S. Schultes, K. Bidle, P. Claquin, and B. Moriceau (2006), Si and C
988   interactions in the world ocean: Importance of ecological processes and implications for
989   the role of diatoms in the biological pump, *Global Biogeochemical Cycles*, *20*(4),
990   GB4S02.
991 Ridgwell, A., D. N. Schmidt, C. Turley, C. Brownlee, M. T. Maldonado, P. Tortell, and J. R.
992   Young (2009), From laboratory manipulations to Earth system models: scaling
993   calcification impacts of ocean acidification, *Biogeosciences*, *6*, 2611–2623.
994 Rintoul, S. R., and T. Trull (2001), Seasonal evolution of the mixed layer in the Subantarctic
995   Zone south of Australia, *Journal of Geophysical Research*, *106*(C12), 31447-31462,
996   doi:10.1029/2000JC000329.
997 Rivero-Calle, S., A. Gnanadesikan, C. E. Del Castillo, W. M. Balch, and S. D. Guikema
998   (2015), Multidecadal increase in North Atlantic coccolithophores and the potential role of
999   rising CO2, *Science*, *350*(6267), 1533-1537.

1000 Roberts, D., W. R. Howard, J. L. Roberts, S. G. Bray, A. D. Moy, T. Trull, and R. R.
1001   Hopcroft (2014), Diverse trends in shell weight of three Southern Ocean pteropod taxa
1002   collected with Polar Frontal Zone sediment traps from 1997 to 2007, *Polar Biology*,
1003   *37*(10), 1445-1458, doi:10.1007/s00300-014-1534-6.
1004 Roden, N. P., B. Tilbrook, T. W. Trull, P. Virtue, and G. D. Williams (2016), Carbon cycling
1005   dynamics in the seasonal sea-ice zone of East Antarctica, *Journal of Geophysical*
1006   *Research: Oceans*, doi:10.1002/2016JC012008.
1007 Rost, B., and U. Riebesell (2004), Coccolithophores and the biological pump: responses to
1008   environmental changes, in *Coccolithophores*, edited, pp. 99-125, Springer.
1009 Salter, I., R. Schiebel, P. Ziveri, A. Movellan, R. Lampitt, and G. A. Wolff (2014), Carbonate
1010   counter pump stimulated by natural iron fertilization in the Polar Frontal Zone, *Nature*
1011   *Geosci*, *7*(12), 885-889, doi:10.1038/ngeo2285.
1012 Schiebel, R. (2002), Planktic foraminiferal sedimentation and the marine calcite budget,
1013   *Global Biogeochemical Cycles*, *16*(4), 1065.
1014 Schlüter, L., K. T. Lohbeck, M. A. Gutowska, J. P. Gröger, U. Riebesell, and T. B. Reusch
1015   (2014), Adaptation of a globally important coccolithophore to ocean warming and
1016   acidification, *Nature Climate Change*, *4*(11), 1024-1030.
1017 Schulz, K. G., B. Rost, S. Burkhardt, U. Riebesell, S. Thoms, and D. Wolf-Gladrow (2007),
1018   The effect of iron availability on the regulation of inorganic carbon acquisition in the
1019   coccolithophore *Emiliania huxleyi* and the significance of cellular compartmentation for
1020   stable carbon isotope fractionation, *Geochimica et Cosmochimica Acta*, *71*(22), 5301-
1021   5312.
1022 Sett, S., L. T. Bach, K. G. Schulz, S. Koch-Klavsen, M. Lebrato, and U. Riebesell (2014),
1023   Temperature modulates coccolithophorid sensitivity of growth, photosynthesis and
1024   calcification to increasing seawater pCO2, *PLoS One*, *9*(2), e88308.
1025 Shadwick, E. H., B. Tilbook, N. Cassar, T. W. Trull, and S. R. Rintoul (2015), Summertime
1026   physical and biological controls on O2 and CO2 in the Australian Sector of the Southern
1027   Ocean, *Journal of Marine Systems*, *147*, 21-28, doi:10.1016/j.jmarsys.2013.12.008.
1028 Shadwick, E. H., T. Trull, H. Thomas, and J. A. E. Gibson (2013), Vulnerability of Polar
1029   Oceans to Anthropogenic Acidification: Comparison of Arctic and Antarctic Seasonal
1030   Cycles, *Scientific Reports*, *3*(August), 1-7, doi:10.1038/srep02339.
1031 Silverman, J., B. Lazar, and J. Erez (2007), Effect of aragonite saturation, temperature, and
1032   nutrients on the community calcification rate of a coral reef, *Journal of Geophysical*
1033   *Research: Oceans*, *112*(C5).
1034 Smith, H. E., A. J. Poulton, R. Garley, J. Hopkins, L. C. Lubelczyk, D. T. Drapeau, S.
1035   Rauschenberg, B. S. Twining, N. R. Bates, and W. M. Balch (2017), The influence of
1036   environmental variability on the biogeography of coccolithophores and diatoms in the
1037   Great Calcite Belt, *Biogeoscience Discussions*, *in review*, doi:10.5194/bg-2017-5110.
1038 Sokolov, S., and S. R. Rintoul (2002), Structure of Southern Ocean fronts at 140E, *Journal of*
1039   *Marine Systems*, *37*(1-3), 151-184.
1040 Sokolov, S., and S. R. Rintoul (2007a), Multiple jets of the Antarctic Circumpolar Current
1041   south of Australia, *Journal of Physical Oceanography*, *37*, 1394-1412,
1042   doi:1310.1175/JPO3111.1391.
1043 Sokolov, S., and S. R. Rintoul (2007b), On the relationship between fronts of the Antarctic
1044   Circumpolar Current and surface chlorophyll concentrations in the Southern Ocean, *J.*
1045   *Geophys. Res. – Oceans*, *112*(C07030), doi: 10.1029/2006JC004072.
1046 Takahashi, K., and H. Okada (2000), Environmental control on the biogeography of modern
1047   coccolithophores in the southeastern Indian Ocean offshore of Western Australia, *Marine*
1048   *Micropaleontology*, *39*(1–4), 73-86, doi:http://dx.doi.org/10.1016/S0377-8398(00)00015-
1049   3.

1050   Takeda, S. (1998), Influence of iron availability on nutrient consumption ratio of diatoms in
1051   oceanic waters, *Nature*, *393*, 774-777.
1052   Thomas, M. K., M. Aranguren Gassis, C. T. Kremer, M. R. Gould, K. Anderson, C. A.
1053   Klausmeier, and E. Litchman (2017), Temperature–nutrient interactions exacerbate
1054   sensitivity to warming in phytoplankton, *Global Change Biology*, doi:10.1111/gcb.13641.
1055   Trull, T., S. G. Bray, S. J. Manganini, S. Honjo, and R. Francois (2001a), Moored sediment
1056   trap measurements of carbon export in the Subantarctic and Polar Frontal Zones of the
1057   Southern Ocean, south of Australia, *Journal of Geophysical Research*, *106*(C12), 31489-
1058   31509, doi:10.1029/2000JC000308.
1059   Trull, T., S. R. Rintoul, M. Hadfield, and E. R. Abraham (2001b), Circulation and seasonal
1060   evolution of polar waters south of Australia: Implications for iron fertilization of the
1061   Southern Ocean, *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, *48*(11-12),
1062   2439-2466, doi:10.1016/s0967-0645(01)00003-0.
1063   Van Heuven, S., D. Pierrot, J. Rae, E. Lewis, and D. Wallace (2011), MATLAB program
1064   developed for CO2 system calculations, ORNL/CDIAC-105b, Carbon Dioxide Inf, *Anal.*
1065   *Cent., Oak Ridge Natl. Lab., US DOE, Oak Ridge, Tenn.*
1066   Wright, S. W., D. P. Thomas, H. J. Marchant, H. W. Higgins, M. D. Mackey, and D. J.
1067   Mackey (1996), Analysis of phytoplankton of the Australian sector of the Southern Ocean:
1068   comparisons of microscopy and size frequency data with interpretations of pigment HPLC
1069   data using the 'CHEMTAX' matrix factorisation program, *Marine Ecology Progress*
1070   *Series*, *144*, 285-298.
1071   Wright, S. W., and R. L. van den Enden (2000), Phytoplankton community structure and
1072   stocks in the East Antarctic marginal ice zone (BROKE survey, Jan.-Mar.1996)
1073   determined by CHEMTAX analysis of HPLC pigment signatures, *Deep-Sea Research II*,
1074   *47*(12), 2363-2400.
1075   Zhang, Y., L. T. Bach, K. G. Schulz, and U. Riebesell (2015), The modulating effect of light
1076   intensity on the response of the coccolithophore Gephyrocapsa oceanica to ocean
1077   acidification, *Limnology and Oceanography*, *60*(6), 2145-2157.
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Figure Captions

1. Map of sample sites (dots) relative to major Southern Ocean fronts (lines) and satellite SST (means

for productive months, October-March, over the sample collection period 2008-2014). Front

abbreviations: SAF = Subantartic Front, PF = Polar Front, sACCf = Southern Antarctic Circumpolar

Current Front, N = North, M= Middle, S= South.

2. Comparison of centrifugation versus filtration size-fraction results for Voyage Leg 1, a)

centrifugation total POC versus filtration POC (0.8-50 μm fraction): b) centrifugation total PIC versus

filtration PIC01 (0.8-50 μm) and PIC50 (50-1000 μm) fractions.

3. Latitudinal variations in POC, BSi, PIC50, PIC01 concentrations for each voyage leg. See Table 1

for Voyage Leg details and Figure 1 for sample sites.

4. Latitudinal variations in the dominance of diatoms versus coccolithophores and their contributions

to total POC, for results combined from all voyages: a) BSi/PIC01 and POC/(PIC50+PIC01) ratios, b)

Percent contributions to total POC attributable to diatoms (assuming POC/BSi=3.35) and

coccolithophores (assuming POC/PIC01=0.833).

5. Maps comparing ship based distributions of coccolithophore PIC distributions (PIC01, coloured

dots) with satellite PIC estimates (SPIC; background colours) for each voyage leg. The SPIC

estimates are averages for the month preceding the start of each voyage leg. Contour lines indicate

dynamic height determined frontal positions for the week preceding the each voyage leg (see Figure 1

for front nomenclature).

6. Comparison of satellite SPIC and ocean PIC concentrations for the 116 match-ups for which

satellite SPIC estimates were available within 25 km of the ocean PIC sample sites, on the same day.

Colours indicate sample latitudes and show that good correlation occurs in Subantarctic waters, but

strong overestimation by the satellite technique in Antarctic waters.

7. Latitudinal environmental conditions for voyage leg VL3 (left panels) and voyage leg VL6 (right

panels): a, b) T, S, pH (free scale), calcite saturation, c, d) PIC01, Bach and Langdon relative

calcification rate (dimensionless) and Norberg growth rate (d^{-1}) models, e, f) BSi and Si(OH)$_4$

concentrations (μM).

1114   8. Maps of NASA Ocean Biogeochemical Model results for coccolithophore and diatom

1115   distributionsResults are means for productive month, October-March for 2008-2012, the last year

1116   available on-line: a) diatoms, b) coccolithophores.

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Table 1. Sample Collection

#	Voyage Name	Leg	Dates	PIC50[3]	PIC01[3]	POC & PON[3]	BSi[3]
VL1	AA2008_V6 (SR3)	North	28/03/2008–15/04/2008	57/0	59/0	59/0	59/0
VL2	AA2012_V3 (I9)	South	05/01/2012–20/01/2012[1]	4/16	4/16	9/25	7/22
VL3	AA2012_V3 (I9)	North	20/01/2012–09/02/2012	62/0	62/0	59/0	53/0
VL4	AA2012_VMS (SIPEXII)	South	13/09/2012–22/09/2012	0/20	0/19	0/24	0/24
VL5	AA2012_VMS (SIPEXII)	North	11/11/2012–15/11/2012	0/24	0/24	0/27	0/28
VL6	AL2013_R2 (Astrolabe)	South	10/01/2013–15/01/2013	0/25	0/25	0/23	0/25
VL7	AL2013_R2 (Astrolabe)	North	25/01/2013–30/01/2013	0/27	0/27	0/26	0/27
VL8	AA2014_V2 (Totten)	South	05/12/2014–11/12/2014	0/36	0/36	0/32	0/37
VL9	AA2014_V2 (Totten)	North	22/12/2014–24/01/2015[2]	6/44	6/44	8/27	8/39

[1] 18/01/2012-20/01/2012 east to west traverse from approximately 65^0 S 144^0 E to 65^0 S 113^0 E included in South leg, see Figure 1

[2] 22/12/2014-11/1/2015 west to east traverse from approximately 65^0 S 110^0 E to 65^0 S 140^0 E included in North leg, see Figure 1

[3] Numbers of samples collected on station / underway

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Figure showing two panels (a) and (b) of chlorophyll-a concentration (Chla µg · L⁻¹) maps over the Southern Ocean south of Australia, with ocean front contours labelled SAF-N, SAF-M, SAF-S, PF-N, PF-M, PF-S, sACCf-N, and sACCf-S. Axes show Latitude and Longitude.