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Key Points:

- The Southern Ocean Great Calcite Belt (GCB) results from high coccolithophore abundance
- The Great Calcite Belt enhances the ocean source of CO₂ and increases the POC transfer efficiency
- The formation of the Great Calcite Belt is driven by macronutrient and micronutrient effects on phytoplankton growth

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Factors regulating the Great Calcite Belt in the Southern Ocean and its biogeochemical significance

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Abstract The Great Calcite Belt (GCB) is a region of elevated surface reflectance in the Southern Ocean (SO) covering ~16% of the global ocean and is thought to result from elevated, seasonal concentrations of coccolithophores. Here we describe field observations and experiments from two cruises that crossed the GCB in the Atlantic and Indian sectors of the SO. We confirm the presence of coccolithophores, their coccoliths, and associated optical scattering, located primarily in the region of the subtropical, Agulhas, and Subantarctic frontal regions. Coccolithophore-rich regions were typically associated with high-velocity frontal regions with higher seawater partial pressures of CO₂ (*p*CO₂) than the atmosphere, sufficient to reverse the direction of gas exchange to a CO₂ source. There was no calcium carbonate (CaCO₃) enhancement of particulate organic carbon (POC) export, but there were increased POC transfer efficiencies in high-flux particulate inorganic carbon regions. Contemporaneous observations are synthesized with results of trace-metal incubation experiments, ²³⁴Th-based flux estimates, and remotely sensed observations to generate a mandala that summarizes our understanding about the factors that regulate the location of the GCB.

1. Introduction

The pool of particulate inorganic carbon (PIC) is an important reservoir for carbon in the global ocean, with its rates of production, storage, and export providing complex feedback to the global ocean carbon cycle. Estimates of annual PIC production are highly unconstrained, ranging from ~0.4 to 1.8 Pg C yr⁻¹ based on ocean sediment trap estimates [Balch et al., 2007; Berelson et al., 2007; Feely et al., 2004; Milliman, 1993; Morse and Mackenzie, 1990; Wollast, 1994]. Other observational approaches such as satellite remote sensing of PIC [Balch et al., 2005; Iglesias-Rodríguez et al., 2002; Moore et al., 2012], modeling [Pinsonneault et al., 2012], and global alkalinity tracer variability [e.g., Fry et al., 2015] offer further evidence on the location, timing, and magnitude of PIC production, PIC to organic carbon rain ratio, and contributions to the global carbon cycle. The aim of these approaches is to elucidate the climate change-ocean acidification feedback on calcium carbonate (CaCO₃) production and dissolution [Ridgwell et al., 2007; Riebesell et al., 2000; Zondervan et al., 2001] and ultimately carbonate-organic matter ballasting of anthropogenic CO₂ [Tanhua et al., 2013].

Satellite observations enable quantitative estimates of coccolithophore PIC concentrations in the upper ocean through remote sensing algorithms [Balch et al., 2005; Gordon et al., 2001]. The PIC algorithm has been validated previously, mostly in the North Atlantic Ocean. In the Southern Ocean, satellite-derived PIC concentrations suggest that a substantive region of elevated PIC, previously defined as the Great Calcite Belt (GCB) [Balch et al., 2011], occurs each year in the austral summer near the Subtropical Front (STF), Subantarctic Front (SAF), and Polar Front (PF). The GCB appears seasonally in austral summer south of ~38°S and extends poleward to ~60°S with an area of ~52 × 10⁶ km². Ship observations have confirmed that the brightest, highest PIC concentrations are found northeast of the Drake Passage, in the region of the Patagonian Shelf and Falkland Islands [Balch et al., 2014b; Garcia et al., 2011; Painter et al., 2010; Poulton et al., 2013]. Satellite-derived PIC concentrations gradually diminish eastward, remaining discernable throughout the Indian and Pacific sectors of the Southern Ocean (SO).

Satellite estimates indicate that 26% of global suspended PIC is found in the GCB, which represents 16% of the global ocean by area [Balch et al., 2005]. This would suggest that the GCB is arguably the largest ocean

coccolithophore-rich biome. Indeed, supporting evidence of its presence (and domination by the coccolithophore, *Emiliania huxleyi*) has been observed in seawater samples across all sectors of the SO, as far south as 65°S with shipboard observations since the 1960s [see *Holligan et al.*, 2010, their Table 1].

1.1. The Role of Bottom-Up Nutrient Supply on Coccolithophore Production

The spatiotemporal success of one algal group over another group in the GCB is likely related to physical and biogeochemical factors involving the bottom-up supply of nutrients or top-down grazing. Significant portions of the SO in the region of the GCB are considered high nutrient, low chlorophyll (HNLC) [*Minas and Minas*, 1992], with abundant macronutrients and limiting iron [*Boyd et al.*, 1999]. Diatoms usually require Si(OH)_4 and NO_3^- in roughly equal portions [*Brzezinski*, 1985]. Typically, if diatom growth becomes limited by Si (concentrations $< \sim 2 \mu\text{M}$), non-Si users are able to grow faster [*Dugdale and MacIsaac*, 1971; *Egge and Aksnes*, 1992] and can dominate. Moreover, simulation models have suggested that when Si(OH)_4 reaches a critical, low concentration, coccolithophorids can dominate [*Aksnes et al.*, 1994].

Iron availability also influences phytoplankton growth and community structure in large sectors of the ocean [*Boyd et al.*, 2007; *Moore et al.*, 2013], and this, indeed, may influence the GCB. Although coccolithophores generally appear less prone to iron limitation compared to diatoms and other microplankton [*Brand*, 1991; *Lam et al.*, 2001; *Sunda and Huntsman*, 1995], iron has been reported to limit coccolithophore growth in regions of the North Atlantic and Pacific Oceans [*Crawford et al.*, 2003; *Nielsdottir et al.*, 2009]. In the southern hemisphere, higher PIC concentrations are found near continental landmasses and islands, suggesting that associated trace metal supply (either aeolian or upwelled) may help support seasonal coccolithophore production. Furthermore, strong correlations have been noted in sediment records from the SAF zone between fluxes of dust and alkenones (coccolithophore biomarkers) on glacial time scales [*Jaccard et al.*, 2013; *Martínez-García et al.*, 2009, 2014], suggesting that coccolithophores are stimulated by nutrients from dust.

The co-location of the GCB with major oceanographic fronts would suggest that bottom-up supply of upwelled nutrients along these frontal boundaries plays a dominant role in controlling coccolithophore productivity. Because of the importance of nitrate and silicate for phytoplankton growth, several indices have been used to describe their covariability (or lack thereof) in the sea. The Si:N ratio reveals the relative overabundance of silicate in deep waters of the SO [*Sarmiento et al.*, 2007] associated with differences in remineralization of nitrate and silicate and effects of iron on sinking particulate Si and N. Residual nitrate (nitrate–silicate) also has been used to describe the fertility of water masses in coastal waters such as the Gulf of Maine for supporting diatoms versus nonsiliceous phytoplankton [*Townsend et al.*, 2010]. Specifically, in HNLC waters such as the SO, the issue for either of these indices is that for understanding the potential effect of nitrate and silicate on phytoplankton growth, an index is needed that scales the dominant nutrient concentration to the potential growth that they could sustain should growth limitation (e.g., by a trace metal) be removed.

1.2. The Role of the GCB on the Dissolved Inorganic Carbon Cycle and Export Ratio

The seasonal presence of the GCB in the Southern Ocean may have substantive implications for carbon biogeochemistry in the region [*Freeman and Lovenduski*, 2015]. The distribution of coccolithophores in the GCB may affect the efficiency of the biological carbon pump in two opposing ways: (1) as part of the carbonate (PIC) pump, lowering total alkalinity (TA) in the surface ocean during calcification and thereby increasing seawater $p\text{CO}_2$ via changes in CO_2 -carbonate equilibria [e.g., *Bates et al.*, 1996a; *Zeebe and Wolf-Gladrow*, 2001], and (2) through a ballasting effect that increases the magnitude and/or transfer efficiency of the soft tissue (particulate organic carbon (POC)) pump, which would decrease surface ocean $p\text{CO}_2$ [e.g., *Tanhua et al.*, 2013, and references within]. The balance of the POC and PIC pumps determines the net effect of the biological carbon pump on surface $p\text{CO}_2$, exchanges of CO_2 across the air-sea interface, and ultimately feeds back to atmospheric $p\text{CO}_2$. Model studies have shown that atmospheric CO_2 is highly sensitive to the PIC:POC export ratio [*Archer and Maier-Reimer*, 1994; *Archer et al.*, 2000; *Matsumoto et al.*, 2002], particularly in the SO. Halving the global PIC:POC export ratio can lead to an atmospheric CO_2 decrease of 55 ppm [*Sigman et al.*, 1998]. Despite the importance of the PIC:POC export ratio, however, its magnitude is not well constrained. *Sarmiento et al.* [2002] argued that the often-used global PIC:POC export ratio of 0.25 [*Archer et al.*, 2000] is too high. They calculated a global average export ratio of 0.06 ± 0.03 , with the SO (defined

as south of 45°S) having the lowest export ratio ($\text{CaCO}_3:\text{C}_{\text{org}} \sim 0.01$, where C_{org} is equivalent to sinking POC). Measurements of PIC:POC across the GCB would help assess these model findings.

The importance of a ballast effect on atmospheric CO_2 is less clear. Observed correlations between deep (>2000 m) PIC flux and the absolute and relative flux of deep POC have led to hypotheses about the role of PIC in ballasting POC export [François *et al.*, 2002; Klaas and Archer, 2002]. Increasing both the magnitude of POC flux to depth [Volk and Hoffert, 1985] and its remineralization length scale [Kwon *et al.*, 2009] should lower ocean (and ultimately atmospheric) CO_2 . Model studies have shown that atmospheric CO_2 is sensitive to modest changes in remineralization length scales, such that a 24 m increase in the depth at which 63% of sinking carbon is remineralized led to a decrease in atmospheric CO_2 of 10–27 ppm [Kwon *et al.*, 2009].

In this work, we provide ship and satellite comparisons of PIC in the Atlantic and Indian sectors of the SO, comparing them to other data sampled globally to demonstrate the validity of the PIC algorithm for defining the GCB. We use satellite and ship data to show the large-scale pattern of coccolithophores in the GCB and discuss the effects of macronutrient and iron control on the presence of the feature. We describe an index (residual nitrate potential growth (RNPG)) that scales the excess of nitrate versus silicate to the potential growth of phytoplankton, as trace metal limitation is relieved. We then examine the effect of GCB coccolithophores on the CO_2 source/sink balance of the GCB waters and the sinking flux of POC, and we contrast this with regions containing abundant diatoms. Finally, we synthesize these points into a conceptual view on the regulation of GCB growth as well as its biogeochemical significance.

2. Methods

This study was done on research cruises between the Patagonian Shelf and Cape Town, South Africa (January–February 2011; R/V *Melville* no. 1101), and between Durban, South Africa, and Fremantle, Australia (February–March 2012; R/V *Revelle* no. 1202). Underway measurements were made for temperature, salinity, partial pressure of CO_2 ($p\text{CO}_2$), total particulate, and PIC-specific backscattering. Discrete measurements were made for chlorophyll, PIC, POC, biogenic silica (BSi), coccolithophore concentration, calcification, and photosynthesis. Measurements were also made of the seawater CO_2 -carbonate system (i.e., dissolved inorganic carbon (DIC) and total alkalinity (TA)), iron limitation of phytoplankton (via deck experiments), and ^{234}Th -based vertical flux rates. Each of these measurements is described in detail below.

2.1. Underway and Discrete Sampling

A semicontinuous underway sampling system was used to measure hydrographic and bio-optical properties of surface seawater [Balch *et al.*, 2010]. The system measured temperature, salinity, pH, and chlorophyll fluorescence. Total backscattering at 532 nm ($b_{\text{b tot}}$) was measured using a WetLABS ECO-VSF (three angles). Backscattering also was iteratively measured following acidification of seawater with glacial acetic acid, dropping the pH below the pK_1 for dissolution of calcite and the more soluble aragonite [Millero, 1996] ($b_{\text{b acid}}$), and by difference, acid labile backscattering ($b_{\text{b tot}} - b_{\text{b acid}} = b_{\text{b}}^{\text{a}}$) [Balch and Drapeau, 2004], which was calibrated to PIC concentration. About every 3 h, underway, discrete water samples were collected for chlorophyll *a* [Joint Global Ocean Flux Study, 1996], PIC, and POC [Poulton *et al.*, 2006] to calibrate the underway sensor system. Biogenic silica also was sampled using the technique of Brzezinski and Nelson [1989].

2.2. Satellite Data Processing for PIC

Regional PIC concentrations (mol m^{-3}) were estimated by satellite using the merged two-band/three-band algorithm [Balch *et al.*, 2005; Gordon *et al.*, 2001] with Moderate Resolution Imaging Spectroradiometer (MODIS)-Aqua data. The performance of the algorithm in the GCB was assessed by comparing the satellite-derived PIC concentration (mol m^{-3}) to the shipboard-derived PIC concentration (same units, estimated by multiplying the ship-measured acid-labile backscattering (b_{b}^{a} ; units of m^{-1}), by the average coccolithophore backscattering cross section of PIC, currently used in the NASA PIC algorithm ($1.628 \text{ m}^2 \text{ mol}^{-1}$)). This algorithm comparison was made with the data taken in the cruises described here and compared to other global cruises, in which these measurements have been made previously (see Results section). Satellite-derived current velocities were estimated using satellite altimetry from the Jason-2 mission (Ocean Surface Current Analyses–Real Time (OSCAR); <http://www.oscar.noaa.gov/index.html>). Current velocities and directions were downloaded with $1^\circ \times 1^\circ$ resolution between 30°S and 65°S around the entire SO for January 2012, for

comparison to MODIS-Aqua-derived PIC patterns from the same time period, averaged at the same time and space resolutions.

2.3. Microscopy

Total coccolith and coccolithophore abundances were measured by the HA filter/optical-adhesive technique [Poulton *et al.*, 2010] with polarized light microscopy and image analysis [Balch and Utgoff, 2009; Balch *et al.*, 2011]. Discrete water samples were run through a FlowCAM imaging cytometer for measuring particle back-scattering, chlorophyll, phycoerythrin fluorescence, and imaging of nanoplankton and microplankton (4–100 μm). Particle volume was converted to cellular C according to Menden-Deuer and Lessard [2000].

2.4. Calcification/Photosynthesis

Water was sampled at six depths per station, and the microdiffusion technique [Balch *et al.*, 2000; Paasche and Brubak, 1994] was used with simulated in situ, 24 h incubations in deck incubators cooled with ambient surface seawater (Atlantic sector cruise) and a deckboard heater/chiller unit (Indian sector cruise) to estimate net coccolithophore calcification (NCC) and net community organic production. Samples were filtered through 0.4 μm polycarbonate filters, rinsed, and prepared for microdiffusion analysis [Balch *et al.*, 2000].

2.5. Seawater CO₂-Carbonate System Analyses at Sea

Analytical methods followed standardized protocols [Bates *et al.*, 1996b, 2001; Dickson *et al.*, 2007; Knap *et al.*, 1993]. Both DIC and TA samples were sampled shipboard with replicate samples analyzed ashore for QC/QA purposes. TA was determined using a Versatile Instrument for Detection of TA (VINDTA) analytical system (2011 cruise) and Automated Infrared Inorganic Carbon Analyzer (AIRICA). A 25 mL or 10 mL sample volume was used for analysis of DIC analyzer samples on the VINDTA and AIRICA, respectively. Samples were also analyzed ashore using a highly precise (0.02%; 0.4 $\mu\text{mol kg}^{-1}$) VINDTA system [Bates, 2007; Bates and Peters, 2007; Bates *et al.*, 1996b]. Both DIC and TA analyses had a precision and accuracy of $\sim 1 \mu\text{mol kg}^{-1}$ (precision estimates were determined from 300 between-bottle and within-bottle replicates and accuracy assessed using calibrated reference materials for shipboard and lab work from A. Dickson, Scripps Institution of Oceanography, La Jolla, CA). Normalized alkalinity (nTA) is defined as the total alkalinity normalized to a salinity of 35. The ships were outfitted with a flow-through “SAMI” $p\text{CO}_2$ sensor (Sunburst Sensors) based on colorimetric methods (<http://www.sunburstsensors.com/products/oceanographic-carbon-dioxide-sensor.html>). Carbonic acid dissociation constants were appropriate for temperate/polar seas, and temperature, salinity, and depth data were used to compute inorganic carbon parameters (i.e., $p\text{CO}_2$; note that pH, $[\text{CO}_3^{2-}]$, and Ω for aragonite/calcite were not used directly in the paper) using the software, CO2calc [Robbins *et al.*, 2010].

2.6. Export Fluxes of POC, PIC, and BSi

We used the ^{238}U - ^{234}Th disequilibrium technique coupled with measurements of size-fractionated ^{234}Th , POC, PIC, and BSi to determine ^{234}Th -based export fluxes of POC, PIC, and BSi. Samples for ^{234}Th and size-fractionated particles were collected at a subset of stations (Figure 10c). Total ^{234}Th activity profiles were measured using the small-volume technique [Pike *et al.*, 2005]. ^{234}Th export flux from the base of the euphotic zone (“ z_{PAR} ”), defined as the depth of the 0.3% light level, and 100 m below that (“ $z_{\text{PAR}+100}$ ”) were determined by integrating the ^{234}Th activity deficit to those depths. Note that the 0.3% light level was used here because the control of the light levels in our shipboard incubators with neutral-density screen could only be achieved to 0.3%, instead of the more typical definitions of the euphotic zone between the 1% and 0.1% light depths [Marra *et al.*, 2014]. ^{234}Th fluxes were converted to POC, PIC, and BSi fluxes using measured ratios of those components to ^{234}Th in $>51 \mu\text{m}$ particles collected by dual-flow, in situ filtration at z_{PAR} and $z_{\text{PAR}+100}$ [Rosengard *et al.*, 2015; Thomalla *et al.*, 2008]. The PIC:POC export ratio was determined from the PIC:POC ratio of $>51 \mu\text{m}$ particles at z_{PAR} . A dual-flow version of battery-operated pumps by McLane Research, Inc. was used to allow simultaneous collection of particles on precombusted quartz fiber filters (for PIC, POC, and ^{234}Th) and on polyethersulfone filters (for BSi) [Cutter *et al.*, 2010; Lam *et al.*, 2012; Ohnemus and Lam, 2014; Owens *et al.*, 2015]. Total and particulate ^{234}Th activities were counted using low-level Risø beta counters at sea and again after six half-lives on land. Full methodological details are reported in Rosengard *et al.* [2015].

2.7. Calculation of Residual Nitrate Potential Growth

The calculation of residual nitrate potential growth (RNPG) involves recasting the observed nitrate and silicate concentrations into potential algal growth rates, then subtracting the silicate-dependent growth rate

from the nitrate-dependent growth rate, the sign of which determines which algal groups would dominate if relieved from trace metal limitation. If the difference is positive, then this implies that potential nitrate-dependent growth will exceed silicate-dependent growth, should trace-metal limitation be removed. A negative difference implies that potential silicate-dependent (diatom) growth exceeds nitrate-dependent growth as trace metal limitation is relieved. The basic Michaelis-Menten formulation was used to describe nutrient uptake [Caperon, 1967; Dugdale, 1967].

The similarity of half-saturation coefficients for nutrient uptake and growth was noted previously [Eppley and Thomas, 1969], which then allowed potential growth rates to be calculated for nutrient-limited algae as shown in equation (1).

$$\mu = \mu_{\max} (S/(K_s + S)) \quad (1)$$

where μ and μ_{\max} are the specific growth rate and maximum growth rate (both units d^{-1}), respectively; S is the substrate concentration (μM); and K_s is the half-saturation constant for growth (similar to that of uptake; units of μM). Nonetheless, it is well known that species vary in their values of K_s , but in a comparison of the range of K_s values for nitrate uptake by diatoms, dinoflagellates, prymnesiophytes, and chlorophytes, the average K_s for 13 species, with 27 individual determinations, was $\sim 1.77 \mu\text{M}$ ($\text{SE} = \pm 0.46 \mu\text{M}$) [Eppley and Thomas, 1969; Eppley et al., 1969]. The best known estimates of the variability of maximum growth rate of phytoplankton were made as a function of temperature [Bissinger et al., 2008; Eppley, 1972]. In this case, maximum growth rates within the $0\text{--}25^\circ\text{C}$ range varied from 1 to 3d^{-1} for nearly 200 different measurements. A more recent appraisal of 1500 different published estimates of μ_{\max} showed a similar shaped curve but with a slightly larger variability of $1\text{--}4 \text{d}^{-1}$ [Bissinger et al., 2008]. Balch and Byrne [1994] noted that the values of μ_{\max} and K_s were a function of the degree of eutrophy of the environments that the phytoplankton were sampled in, and they used the following simple empirical approximations to predict both parameters:

$$K_{sN} = ([\text{NO}_3]/(3 + [\text{NO}_3])) \times 5.5 \quad (2)$$

$$\mu_{\max N} = ([\text{NO}_3]/(2 + [\text{NO}_3])) \times 3 \quad (3)$$

The subscript, N , in equations (2) and (3) denotes the nitrate-related growth kinetics. It can be seen that in the growth rate prediction of equation (3), the maximal growth rates would asymptote at $\sim 3 \text{d}^{-1}$. Silicate uptake by diatoms differs from phytoplankton nitrate uptake; in that, diatoms typically cannot completely deplete all the silicate. The residual silicate substrate concentration, S_o , averages about $0.7 \mu\text{M}$ and was integrated into the Michaelis-Menten equation [Paasche, 1973a, 1973b] to predict silicate-dependent growth using equation (4).

$$\mu_{\text{Si}} = \mu_{\max\text{Si}} ((S - S_o)/(K_s - \text{Si} + (S - S_o))) \quad (4)$$

where the subscript Si denotes the silicate-specific process. In the absence of comparative data on nitrate and silicate uptake kinetics across a wide spectrum of phytoplankton groups, we here assume that physiological kinetic response to variable substrate concentration will be similar for limiting nutrients, in order to maintain balanced growth [Parslow et al., 1984; Shuter, 1979]. We therefore used the same formulation given in equations (2) and (3) to approximate silicate growth kinetics, but we included S_o in the formulation, the minimal reactive silicate concentration below which diatoms cannot utilize the nutrient (equation (4)) as observed previously by Paasche [1973b].

As a cross-check on the S_o assumption, we examined the number frequency of silicate concentrations measured in our Southern Ocean cruises and found that the most common silicate concentration below $5 \mu\text{M}$ was $0.5\text{--}1 \mu\text{M}$ (7.7% of the 1495 samples), while only 1.1% of the data were a true $0 \mu\text{M}$ (data not shown). This is entirely consistent with Paasche's supposition of S_o of $0.7 \mu\text{M}$. RNPG was then calculated as

$$\text{RNPG} = \mu_N - \mu_{\text{Si}} \quad (5)$$

2.8. Assessment of Iron Limitation

Eight metal incubation experiments were performed along and around the GCB to assess potential for Fe to limit the growth of coccolithophores, diatoms, and other phytoplankton taxa. Mixed-layer water was collected from 20 m with a 30 L GO-FLO bottle deployed on Kevlar line. Bottles were immediately transported into a positive-pressure trace metal clean van, and water was dispensed gently into 10 L low-density polyethylene cubitainers. A $200 \mu\text{m}$ mesh was placed in-line to remove mesozooplankton grazers. All bottles and plastic ware were stringently acid cleaned prior to use, and trace metal clean techniques

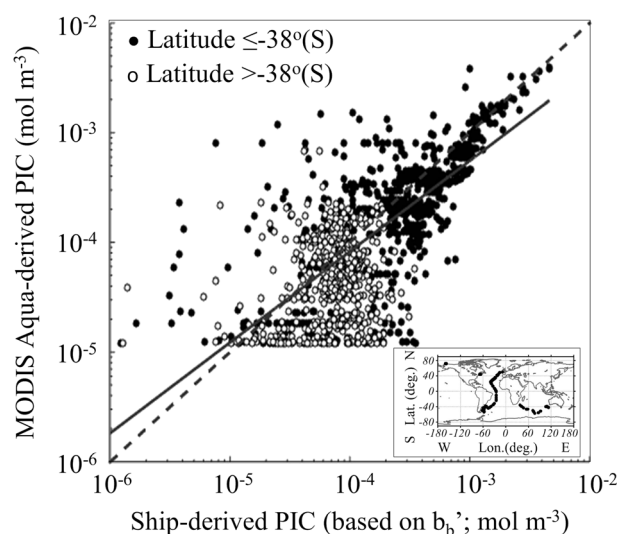


Figure 1. Validation of MODIS-Aqua-derived, merged two-band/three-band PIC algorithm [Balch *et al.*, 2005; Gordon *et al.*, 2001] (only designed for case I waters, where phytoplankton dominate the optical signal [Mobley, 1994]). Dashed line is the 1:1 line. Solid line is the least squares fit. Note that the logarithmic axes allow the performance of the algorithm to be assessed over ~ 3 orders of magnitude of PIC concentration. The least squares fit to the data (95% CI in square brackets) is $\log(Y) = 0.837 [\pm 0.037] \times \log(X) - 0.751 [\pm 0.141]$; $r^2 = 0.575$; RMS error = $\pm 11\%$. Open symbols are the matchup points from latitudes north of the 38°S parallel and closed points are for matchups from south of the 38° parallel (in the GCB). Inset in the bottom right shows the global map of the matchup database, with observations from the GCB cruises described here, plus other cruises where the same technique was applied: Patagonian Shelf COPAS'08 [Balch *et al.*, 2014b], Atlantic Meridional Transect [Robinson *et al.*, 2009], Western Arctic [Balch *et al.*, 2014a], and Gulf of Maine North Atlantic Time Series [Balch *et al.*, 2012]. Note that the Atlantic GCB cruise in 2011 was anomalously cloudy and overcast. There were no synchronous satellite-ship matchups for PIC.

heater/chiller unit was used to control the temperature of recirculating seawater as the ship transited through oceanographic regions with different temperatures. The responses of phytoplankton to added Fe were assessed through measurements of total chlorophyll, biogenic Si, and PIC at the end of the incubation. Incubation experiments lasted between 3 and 6 days.

3. Results

3.1. Spatiotemporal Satellite Determination of PIC

The accuracy of the MODIS-Aqua estimates of PIC concentrations was assessed using cruise data, collected from the world ocean since 2002, the year of the launch of MODIS-Aqua (see inset to Figure 1). Satellite-derived PIC was compared to shipboard measurements of acid-labile backscattering (b_{6}^{-1} ; units m^{-1}) that were converted to equivalent PIC concentration using the average PIC backscattering cross section ($1.628 m^2 (mol PIC)^{-1}$; value currently implemented in the official NASA PIC algorithm). The matchups (which include data from the Southern Ocean) are shown in Figure 1. The results show an RMS error of $\pm 11\%$ for the algorithm globally.

The highest PIC concentrations in the algorithm comparison were found south of 38°S in the GCB (Figure 1). Moreover, satellite-derived PIC and shipboard measurements of acid-labile backscattering showed highest concentrations within the Atlantic sector of the SO, decreasing eastward into the Indian sector of the GCB (Figures 2a–2c). Diversity of coccolithophore populations increased to the east: scanning electron microscope and light microscopy showed that the number of coccolithophore species increased from 1 (*E. huxleyi*) off Patagonia to 8 off Africa and 13 SW of Australia [Smith, 2014]. In both Atlantic and Indian sectors, PIC and

[Bruland *et al.*, 1979] were employed for all steps including conducting the work in a trace metal clean van. Cubitainers and polycarbonate incubation bottles were soaked in 1% Micro detergent for several days, then rinsed copiously with ultrapure >18.2 megohm water, and soaked in 1 M reagent HCl for several more days before being rinsed again and dried before use. Cubitainers were spiked with a Fe solution produced from a traceable AAS standard diluted into 0.01 M Optima HCl. The first two incubation experiments (experiments 1 and 2) inadvertently involved Fe additions of 0.02 nM, due to a calculation error. Experiments 3 through 8 involved Fe additions of 2 nM. Treatment cubitainers were gently homogenized, and water was decanted into triplicate 2.5 L polycarbonate bottles. Bottles were filled completely (minimizing headspace) and sealed with parafilm and vinyl tape, then placed in deckboard incubators at 50% surface irradiance. For experiments 1 through 4 (Atlantic sector cruise), incubator temperature was maintained with surface water circulated through the ship's through-hull system. There were some situations where variations in surface temperature (as we transited north or south) changed the temperature from initial conditions at which the phytoplankton community was collected. For experiments 5 through 8 (Indian sector cruise), a deckboard

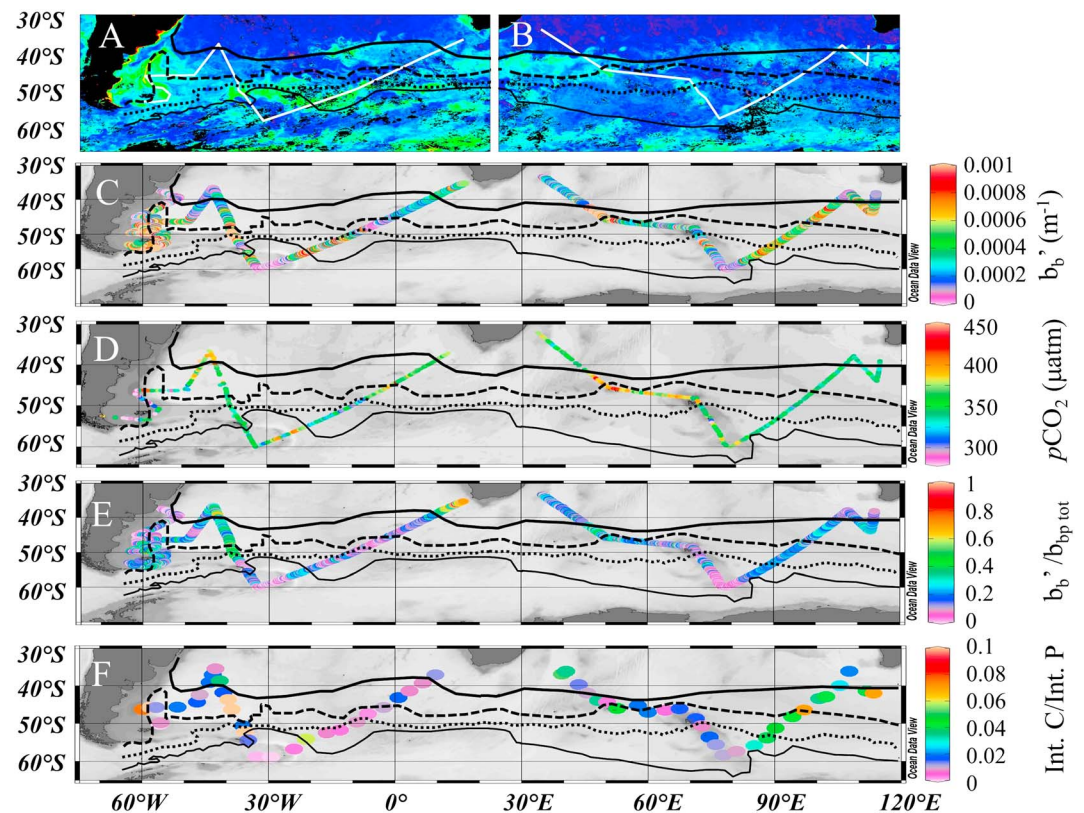


Figure 2. Geographic distribution of surface properties. (a) Cruise track of *Melville* no. 1101 overlaid on the monthly MODIS-Aqua PIC product for January 2011 (9 km binned; mol m^{-3}). (b) Cruise track of *Revelle* no. 1202 overlaid on average satellite-derived PIC for February 2012 (same spatial bins as in Figure 2a). (c) Acid-labile backscattering (backscattering from CaCO_3) of surface mixed layer for both GCB cruises, as well as COPAS'08 cruise over the Patagonian Shelf [Balch *et al.*, 2014b]. (d) Regions with $p\text{CO}_2 > 390 \mu\text{atm}$ (ochre to red colors) represent a source of CO_2 to the atmosphere. Anything $\leq 390 \mu\text{atm}$ (ochre to indigo) represents a CO_2 sink. (e) Fraction of total backscattering contributed by PIC. (f) Integrated calcification/integrated photosynthesis measured using microdiffusion technique. For all plots, the climatological positions of the frontal boundaries are indicated with various black lines: heavy solid = Subtropical Front, medium dash = Subantarctic Front, fine dash = Polar Front, thin solid = ACC boundary [Orsi *et al.*, 1995].

coccolithophore concentrations were generally, but not always, elevated near the climatological and actual positions of the STF, SAF, PF, and the Antarctic Circumpolar Current (ACC) front (Figures 2a–2c; see overlaid density isopleths in Figure 3 for actual locations of fronts). RNPG was highest between the STF and SAF frontal regions and north of the PF. It was lowest south of the PF and in ACC waters (Figure 3a). Diatom concentration was highest inshore of the shelf front on the Patagonian Shelf, in PF and SAF waters in the Atlantic sector of the SO, and PF and ACC waters of the Indian sector SO. Lowest diatom concentrations were observed north of the STF (Figure 3b). Diatom abundance was not exclusively low in regions of positive RNPG. There were a few regions (section B and the northernmost part of section F) where there were both elevated diatoms and coccolithophores in a region of positive RNPG. However, south of the PF in both Atlantic and Indian sectors, regions of negative RNPG were characterized by a stronger diatom (than coccolithophore) response.

Satellite-derived PIC and shipboard measurements of coccolithophore concentration showed highest values within the fast-moving waters of the ACC (Figure 4), in moderate salinity Atlantic sector waters, decreasing eastward into the Indian sectors of the GCB (Figures 3c and 4). The regression between altimetry-based water velocity and PIC concentration is given in Figure 4b. There was a highly significant relationship between the binned current velocity (m s^{-1}) and binned PIC concentration (mol m^{-3} ; Figure 4) ($Y [\pm 0.078] = 6.93 \times 10^{-4} [\pm 2.8 \times 10^{-5}] X^{0.202 [\pm 0.0175]}$; $r^2 = 0.759$; $p < 0.001$).

3.2. Spatial Variability of RNPG and Coccolithophore Abundance

To assess the potential for relative growth of diatoms versus nonsilicifying phytoplankton, we examined the potential for growth (RNPG) on nitrate versus silicate in the absence of trace metal limitation. RNPG was

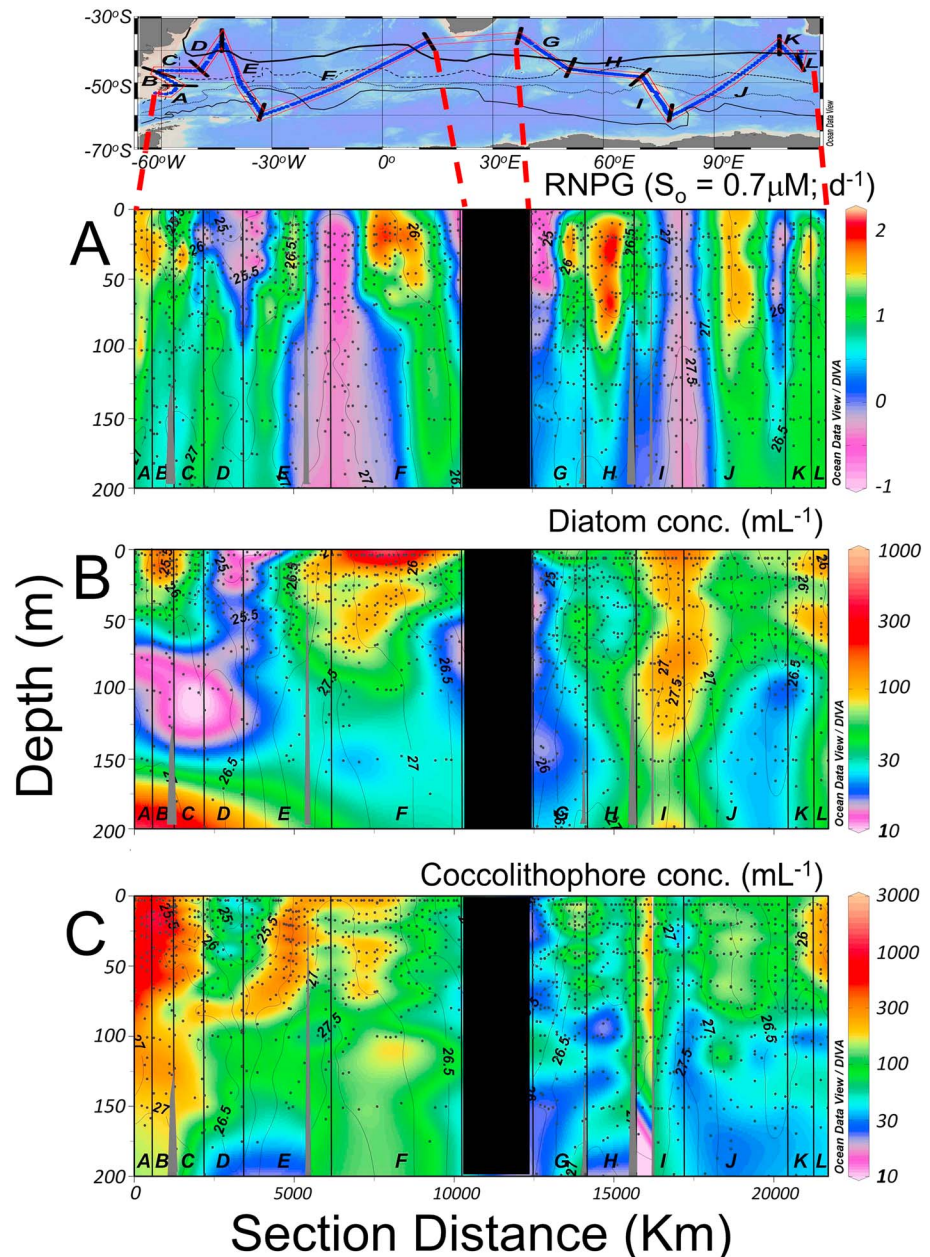


Figure 3. Vertical sections from *Melville* no. 1101 and *Revelle* no. 1202 cruises. The top inset shows the cruise track with letters designating sections of the cruise track. (a) Sections of RNPG (d^{-1}) where positive values are regions where nonsiliceous phytoplankton growth would be expected to be favored, while negative values represent regions and depths where potential diatom growth would be expected. (b) Diatom abundance (mL^{-1}) as determined with the FlowCAM. (c) Sections of coccolithophore concentration (mL^{-1}) as determined with polarized light microscopy. In all plots, vertical lines and letters designate the sections shown in inset. Frontal climatologies are indicated in top inset with different line patterns (from north to south): thick solid line = Subtropical Front, dashed line = Subantarctic Front, fine dash = Polar Front, thin solid line = ACC boundary [Orsi *et al.*, 1995]. Density isopleths overlaid onto Figures 3a–3c.

greatest in waters with temperatures of 5 to 7°C (SAF) and 10 to 12°C (STF). RNPG values were lowest south of the PF and north of the STF (Figures 3a, 5a, and 10b). Coccolith backscattering (b_b' ; also called acid-labile backscattering [Balch *et al.*, 2001]; only measured along track in surface waters) increased with RNPG (Figure 5b). Coccolithophore concentration within the euphotic zone was highest in areas of positive RNPG, but silicifiers exceeded calcifiers (low PIC:BSi ratios) when RNPG was negative (Figures 3a, 3c, and 5c). In contrast, negative RNPG occurred north of the STF (where reduced nitrate concentrations limited diatom growth

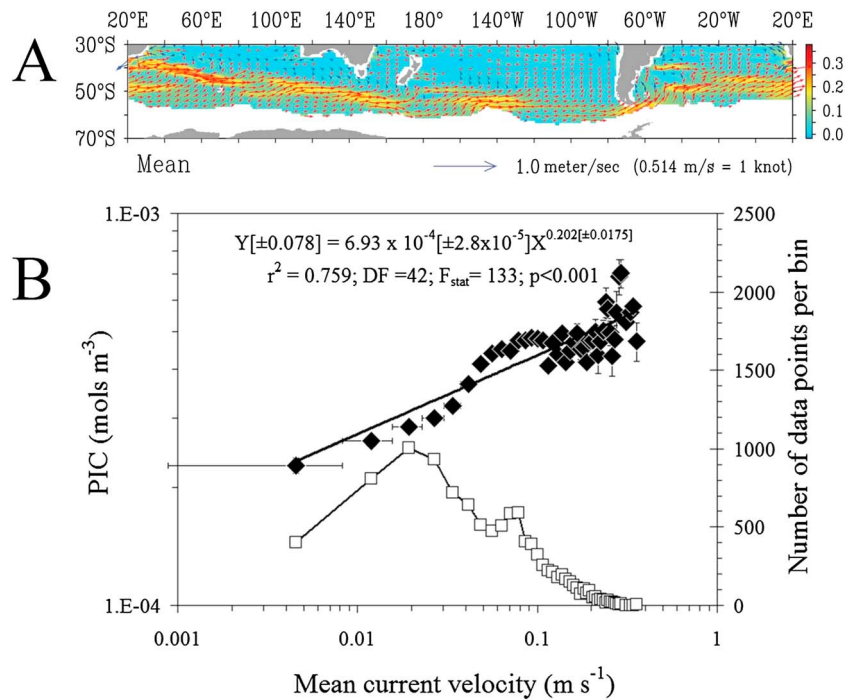


Figure 4. (a) Altimetry-based currents of Southern Ocean (from OSCAR program) color coded to velocity (scale bar on the right). (b) Average PIC concentration from MODIS-Aqua plotted against altimetry-derived current velocity (black diamonds, left y axis). Numbers of data points in each binned average shown as open squares (right y axis). Data show that highest PIC concentration is associated with fastest currents (which lie along frontal boundaries). Least squares power fit to the data also is shown.

more than growth of nonsilicious phytoplankton) and south of the PF waters (where high silicate allowed more diatom growth relative to calcifiers; Figures 5a and 5c). As shown in Figure 3, diatoms cooccurred with coccolithophores near the STF off Australia (near sections K and L) and in the SE Atlantic (along section F) but were most abundant south of the PF (Figure 3b; between sections I and J), where silicate-rich water reached the surface and RNPG was zero or negative, with diatoms increasing relative to coccolithophores (Figure 3c).

3.3. Spatial Variability of Seawater $p\text{CO}_2$

Seawater $p\text{CO}_2$ was highly variable in SAF waters, ranging from <300 to >420 μatm (Figure 2d). Large regions of the SAF zone (e.g., near the Falklands, Crozet, Kerguelen, and Heard Islands—with elevated coccolithophore biomass during January and February) had $p\text{CO}_2$ values up to 100 μatm higher when compared to adjacent low coccolithophore biomass areas in regions of similar temperature in the SAF. Near the Crozet Islands, a multiple linear regression of nTA as a function of b_b' and $p\text{CO}_2$ showed a moderate correlation ($r^2 = 0.52$; $p < 0.01$; Figure 6a). In this same region, the fraction of backscattered light contributed by PIC ($b_b'/b_{b\text{ptot}}$, i.e., PIC:POC; Figure 2e) was accompanied by elevated surface seawater $p\text{CO}_2$ in a number of cases (Figure 2d). These areas also coincided with low-salinity normalized TA values and TA:DIC ratios, suggestive of alkalinity uptake due to calcification (temperature effects on $p\text{CO}_2$ are minimal and do not contribute to this contrast). These biogeochemical and optical features were also pronounced near the Falklands (Figure 6b) and Kerguelen (not shown here) in the SAF. Superimposing the $p\text{CO}_2$ concentrations over the 12 year climatological PIC concentrations generally showed highest $p\text{CO}_2$ concentrations in regions with historically elevated PIC concentrations (Figure 7b). Moreover, the boundaries of the elevated PIC regions near Crozet corresponded to the streamlines of current velocity [Pollard *et al.*, 2007b]. The regions of highest surface seawater $p\text{CO}_2$ observed during the Great Belt cruise are also co-located with regions of higher $p\text{CO}_2$ collected in January and February from 2010 to 2015. In Figure 7b, gridded Southern Ocean CO_2 Atlas (SOCAT) data set (version 3 [Bakker *et al.*, 2014; Pfeil *et al.*, 2013]) corresponds to mean $p\text{CO}_2$ in each $1^\circ \times 1^\circ$ box using higher-frequency surface $p\text{CO}_2$ collected from the R/V *Marion Dufresne* by N. Metzl (partial data reported elsewhere [Lourantou and Metzl, 2011]). Figure 7b shows that limited $p\text{CO}_2$ data have been collected in the region over the past 6 years since 2010.

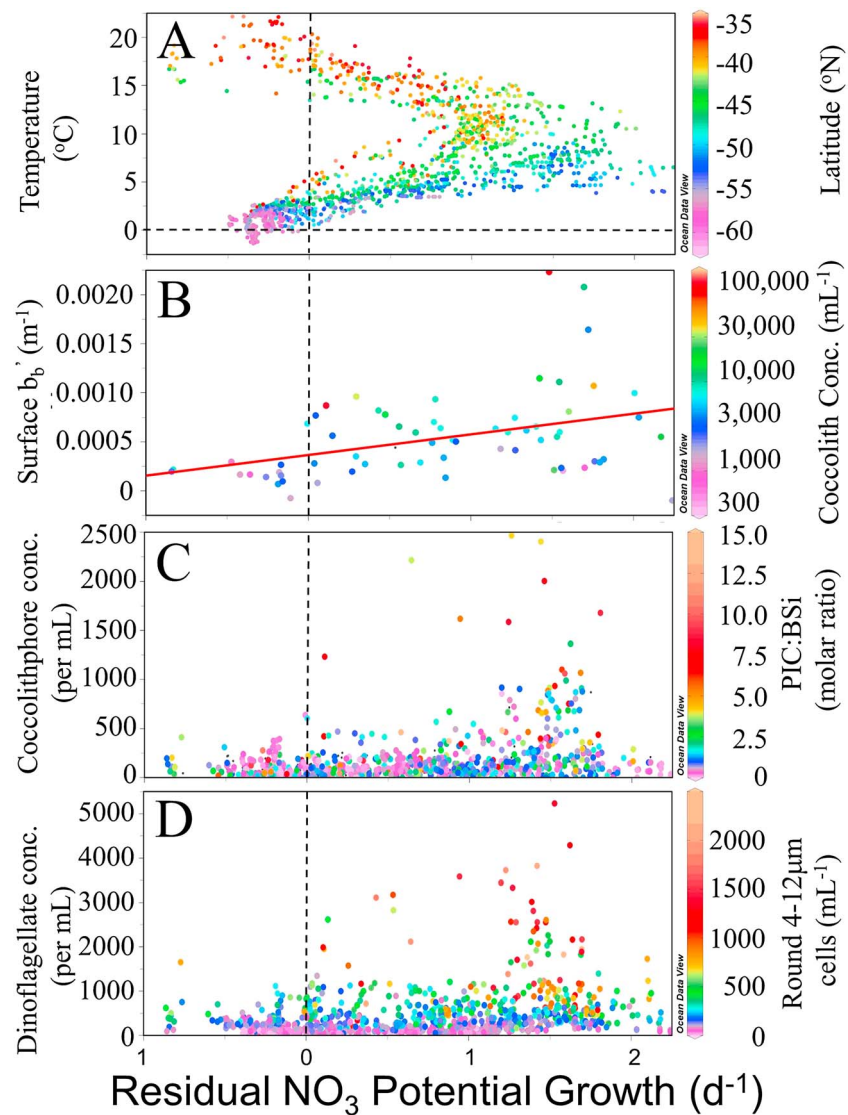


Figure 5. Residual nitrate potential growth (RNPG) plotted versus (a) temperature (y axis) and latitude (color of points); (b) surface acid-labile backscattering, b_b' (y axis; least squares linear fit to the data: $b_{b_p} = 2.108 \times 10^{-4} \times \text{RNPG} + 3.661 \times 10^{-4}$; $r = 0.386$; $n = 65$; $\text{RMSE} = 4.005 \times 10^{-4}$) and coccolith concentration (color of data points); (c) coccolithophore concentration (per mL) and PIC:BSi molar ratio (color of points); and (d) dinoflagellate abundance and concentration of 4–12 μm diameter nanophytoplankton (color of data points). Data from Figures 5a, 5c, and 5d are from multiple depths, while data from Figure 4b were collected from the surface only.

3.4. Iron Limitation of Phytoplankton Community, Including Coccolithophores and Diatoms

Incubation experiments showed significant ($p < 0.05$, one-tailed t test) responses of phytoplankton to added Fe mostly in the Indian sector of the GCB, with generally negligible responses in the Atlantic sector (Figure 8). Experiment 1 (closest to Patagonian shelf) showed a small ($6 \pm 3\%$ enhancement over the control) but significant enhancement of Chl in response to added Fe. The remaining three Atlantic experiments did not show significant Chl responses. Accumulation of BSi and PIC were not stimulated, relative to controls, in any of the Atlantic experiments. In the Indian sector, Fe stimulated significant Chl accumulation over the unamended controls in each of the experiments conducted south of subtropical waters (which had a starting nitrate concentration of just $0.1 \mu\text{M}$). The addition of Fe also stimulated growth of coccolithophores (assessed via accumulation of PIC) in the Indian sector of the GCB. PIC responded significantly to Fe in experiment 6 (in between Crozet and Kerguelen Islands) and experiment 8 (southwest of Australia). Furthermore, in both of these experiments control-normalized response of PIC was approximately 45% greater than the response

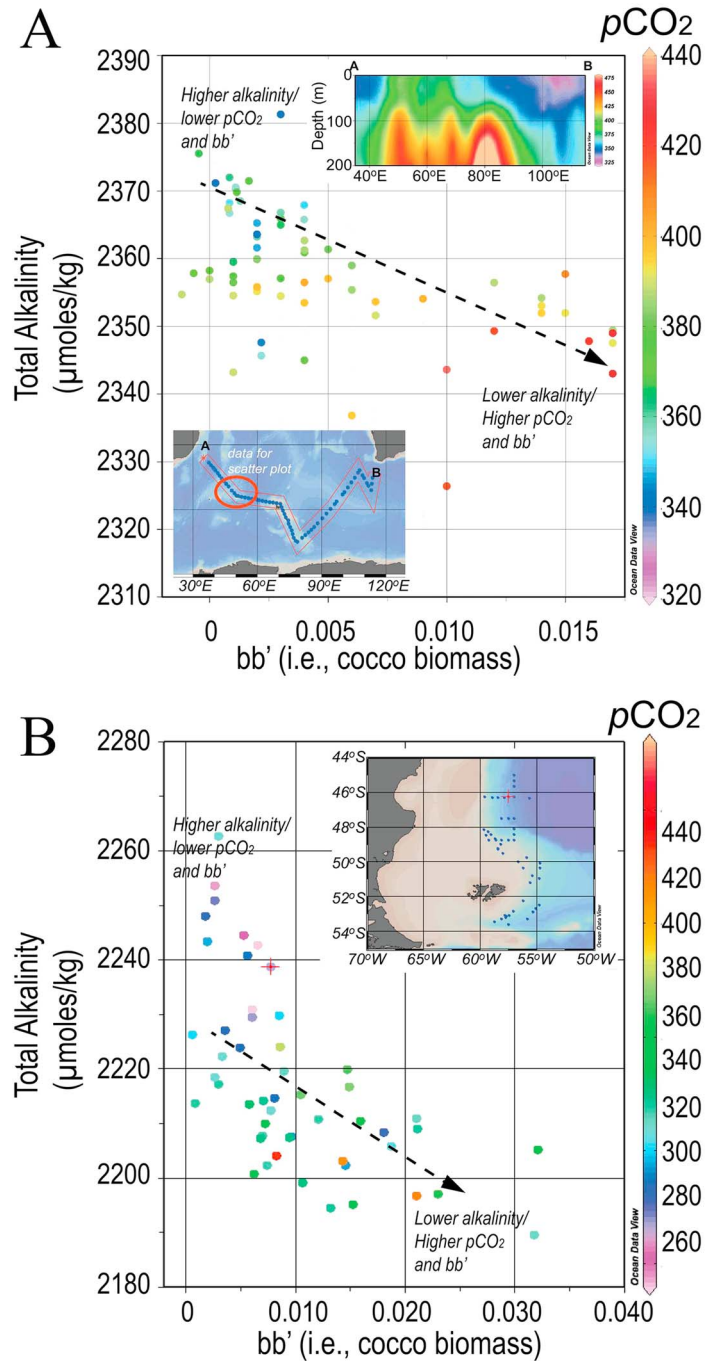


Figure 6. (a) Salinity-normalized total alkalinity versus acid-labile backscattering (bb') from region near Crozet Islands (circled in inset at bottom) and (b) in deep water offshore of the Patagonia shelf in the South Atlantic Ocean. In Figure 6 a (data from cruise RR1202), the top inset shows the seawater $p\text{CO}_2$ (color scale goes from 325 to 475 ppm), where A and B mark the start and end of the transect (also shown in bottom inset map). This inset illustrates that the surface $p\text{CO}_2$ features extend through the mixed layer. Multiple linear regression between nTA (independent variable) and bb' and $p\text{CO}_2$ (dependent variables) is shown with dashed black line: $n\text{TA} [\pm 6.678] = 2432.527 [\pm 17.369] - 6650.91 [\pm 2047.77] (bb') - 0.18785 [\pm 0.04736] \times p\text{CO}_2$. (Numbers in square brackets are the SE of each fit term.) Other statistics for multiple linear regression: $r^2 = 0.529$; degrees of freedom = 62; $p < 0.01$. In Figure 6b (including data from cruise MV1101 as well as COPAS'08 (Knox 22RR)) [Balch et al., 2014b], the top inset shows the locations of underway and CTD-hydrocast stations for similar data as in Figure 6a but around the Patagonian Shelf region. The scatterplot for total alkalinity versus bb' is also given, as in Figure 6a. Multiple linear regression between nTA (independent variable) and bb' and $p\text{CO}_2$ (dependent variables) is shown with dashed black line: $n\text{TA} [\pm 12.0810] = 2279.64 [\pm 12.8357] - 10776.85 [\pm 2568.10] (bb') - 0.1628 [\pm 0.0428] \times p\text{CO}_2$. Other statistics for multiple linear regression: $r^2 = 0.522$; degrees of freedom = 50; $p < 0.01$.

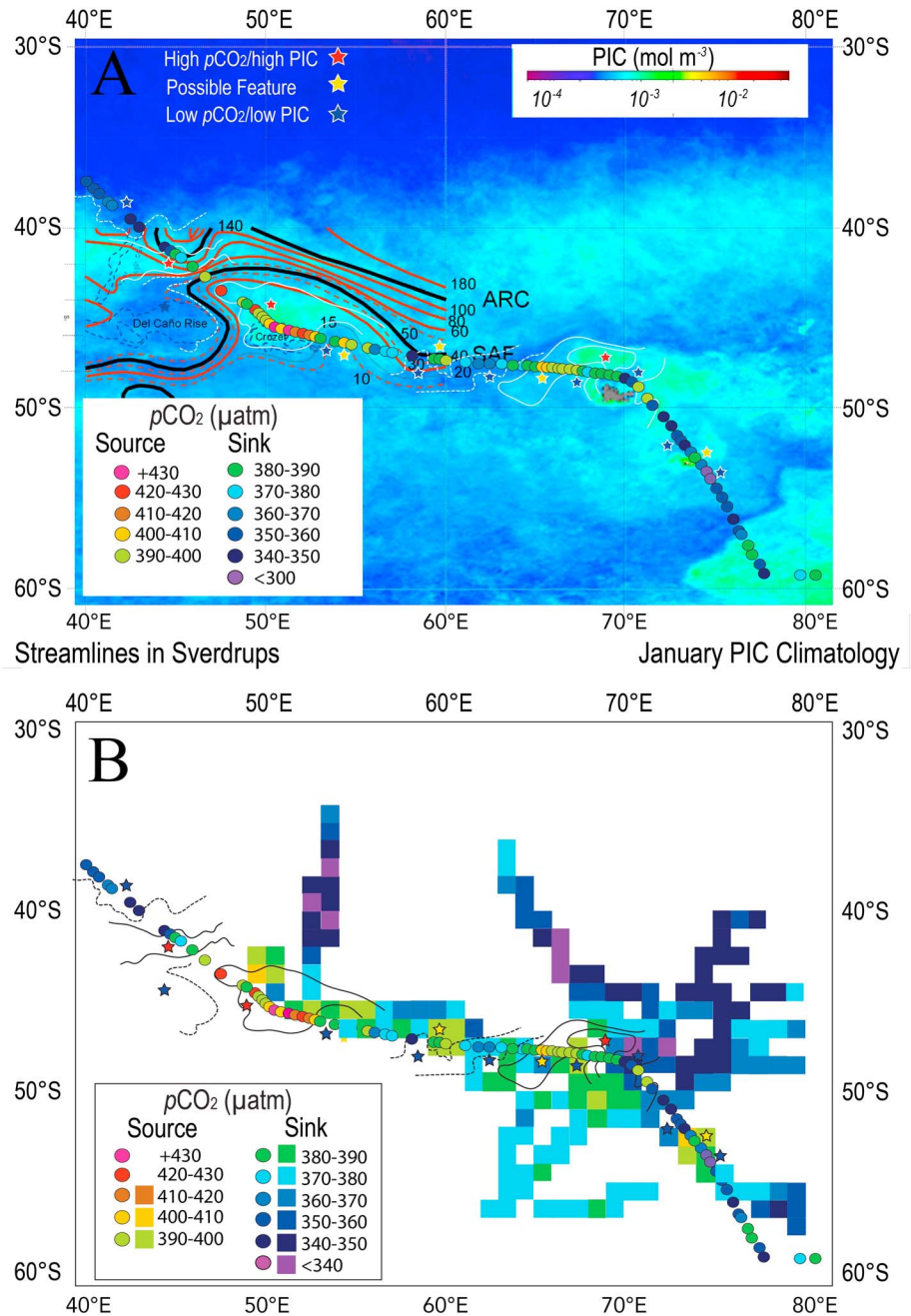


Figure 7. Results from *Revelle* no. 1202 cruise, near Crozet Islands (Indian sector of the SO) superimposed on 12 year MODIS-Aqua climatology for PIC using merged two-band, three-band PIC algorithm [Balch *et al.*, 2005; Gordon *et al.*, 2001]. (a) The color bar gives PIC concentration in mol m^{-3} , with white lines denoting approximate regions of higher PIC. Streamlines of current velocity (sverdrups = $10^6 \text{ m}^3 \text{ s}^{-1}$) also superimposed from Pollard *et al.* [2007a] (solid black lines are 0, 40, and 140 Sv isolines; from the CROZEX experiment, 2004–2005). Solid red lines give 20 Sv increments, while dashed red lines provide further intermediate levels. ARC designates the Agulhas Return Current. Seawater $p\text{CO}_2$ from our cruise (circle symbols) is shown in Figure 7a along with star symbols that denote approximate locations of high PIC or low PIC features. (b) Surface $p\text{CO}_2$ data from the Great Belt cruise are shown against underlying, gridded ($1^\circ \times 1^\circ$) surface $p\text{CO}_2$ data collected during the months of January and February from 2010 to 2015. These latter data represent the limited SOCAT data (version 3 [Bakker *et al.*, 2014; Pfeil *et al.*, 2013]) collected in the region. The approximate regions of higher PIC in the region are superimposed from Figure 7a. Location of Crozet Islands is also marked.

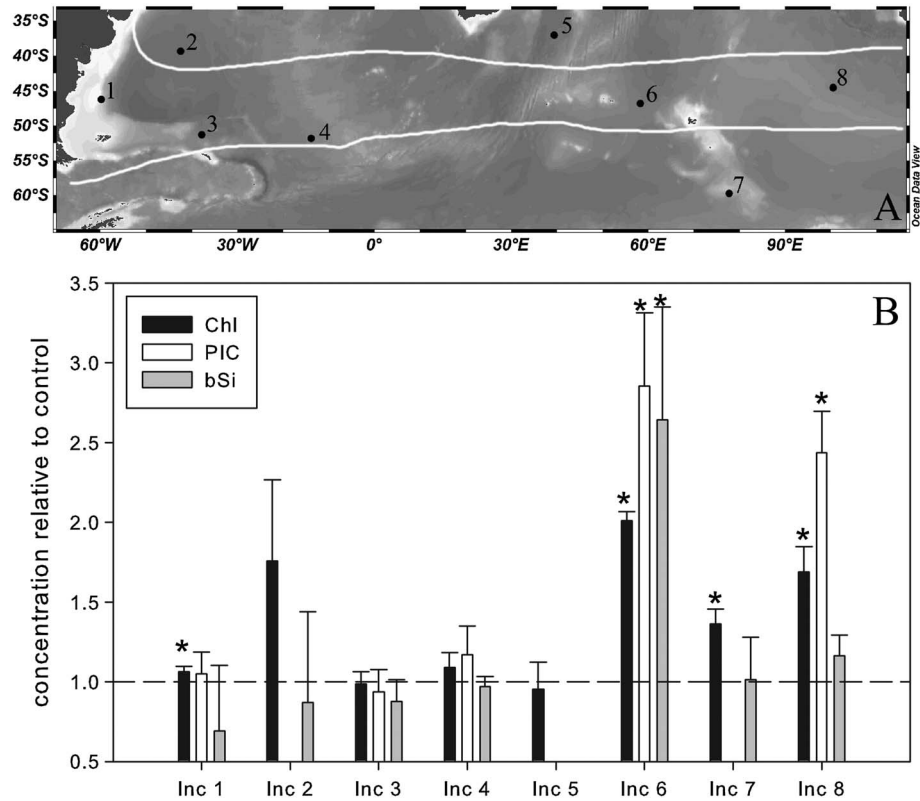


Figure 8. (a) Locations of incubation experiments. White lines represent the climatological locations of the Subtropical (northmost) and Polar (southmost) Fronts. (b) Relative response of total Chl *a*, PIC, and BSi relative to unamended control for eight different experiments, in which Fe additions were made (0.2–2 nM). Error bars represent 1 standard deviation for triplicate measurements. Asterisks indicate the values significantly greater than 1.

of total chlorophyll (Figure 8), suggesting that coccolithophores were preferentially stimulated by Fe compared to the overall phytoplankton community. In contrast, coccolithophores were not stimulated in the experiments performed in the Atlantic sector of the GCB (experiments 1, 3, and 4) nor did Fe stimulate PIC in the experiments conducted either north of the GCB (experiments 2 and 5; nitrate <1 μM) or south of the GCB (experiment 7; ambient water 1.1°C), suggesting that something other than Fe was constraining coccolithophore growth. Biogenic silica (a proxy for diatom biomass) was significantly stimulated by Fe only in experiment 6 (in the GCB between Crozet and Kerguelen).

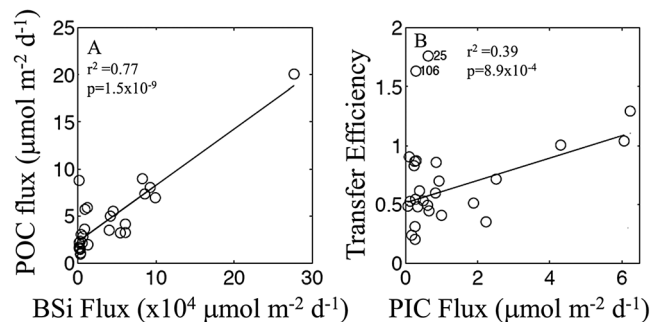


Figure 9. (a) ²³⁴Th-derived POC flux as a function of BSi flux at *z*_{PAR}. (b) POC flux transfer efficiency between the base of the euphotic zone (*z*_{PAR}) and 100 m below (defined as POC flux at *z*_{PAR} + 100 m divided by POC flux at *z*_{PAR}) as a function of PIC flux. Significant linear relationships are plotted as a solid black line. Transfer efficiency values at stations GB1-25 and GB2-106 were excluded from all correlations because of suspected sampling issues at those stations (figure adapted from Rosengard *et al.* [2015]).

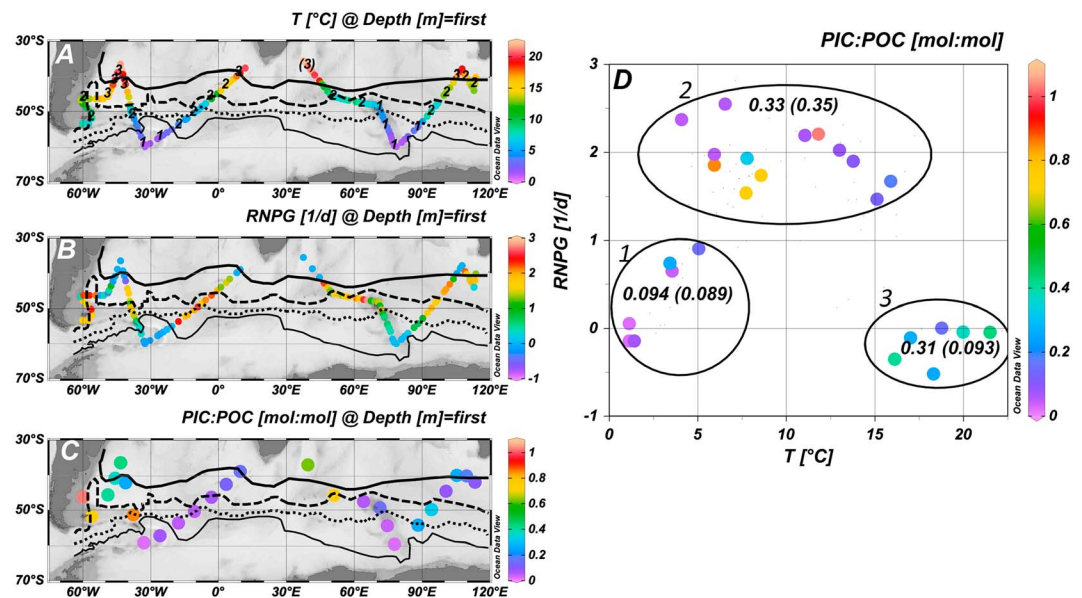


Figure 10. Relationships between temperature, RNPG, and PIC:POC. (a) Map showing sea surface temperature (numbers mark the locations of thorium flux measurements and their magnitude referring to groupings in Figure 10d), (b) map showing the surface values of residual nitrate potential growth (RNPG) along the cruise track, (c) map showing the PIC:POC export ratio at 100 m, and (d) scatterplot of RNPG versus SST (color represents the PIC:POC export ratio). PIC:POC export ratio was the ratio of PIC flux to POC flux at the base of the euphotic zone. Stations were grouped by similarities in RNPG and temperature (ovals), and the mean (1 standard deviation) PIC:POC export ratios are indicated for each group. Leftmost group is designated as the polar group (1), top middle group is the subpolar group (2), and the rightmost group is the subtropical group (3); locations and group number are indicated on the SST map in Figure 10a. Station marked in Figure 10a as “(3)” is undefined for RNPG because $\text{NO}_3 = 0$. If included in the subtropical group, PIC:POC export ratio in that group would be 0.36 ± 0.15 . Climatological frontal boundaries are indicated in Figures 10a–10c as in Figure 2.

3.5. Export Fluxes

During both cruises, the ^{238}U – ^{234}Th disequilibrium results showed that the magnitude of shallow POC export flux at the base of the euphotic zone ($z_{\text{PAR}} \sim 100$ m) was *not* correlated with PIC export flux (not shown [Rosengard *et al.*, 2015]) but rather was correlated with BSi export flux ($r^2 = 0.74$; Figure 9a). In contrast, we found a significant correlation between the transfer efficiency of POC flux in the upper mesopelagic zone—defined as the ratio of the POC fluxes 100 m below the base of the euphotic zone (at $z_{\text{PAR}} + 100$) to the POC fluxes at the base of the euphotic zone (at z_{PAR})—and the PIC export flux (Figure 9b; $r^2 = 0.39$, $p < 0.001$), but not the BSi export flux (not shown [Rosengard *et al.*, 2015]).

The minimum, median, and maximum PIC:POC export ratios (the ratio of PIC flux to POC flux at z_{PAR}) were 0.018, 0.176, and 1.03, respectively (Figure 10d). PIC:POC export ratios were grouped on the basis of observed RNPG and sea surface temperature. Polar regions (defined as $\text{RNPG} < 1$ and $\text{SST} < 10^\circ\text{C}$) and subtropical regions (defined as $\text{RNPG} < 1$ and $\text{SST} > 10^\circ\text{C}$) had low (0.094 ± 0.089) and high (0.31 ± 0.093) PIC:POC export ratios, respectively (Figure 10). The highest PIC:POC export ratios (> 0.7) were in subpolar regions ($\text{RNPG} > 1$), which also had the highest mean PIC:POC export ratio but with high variability (0.33 ± 0.35 ; Figure 10).

4. Discussion

Our results confirm that within Atlantic and Indian sectors of the SO, satellite measurements of the GCB are matched by elevated acid-labile backscattering and coccolithophore concentrations, consistent with a coccolithophore PIC source of the elevated reflectance. This finding is also in agreement with prior coccolithophore observations in the SO [Balch *et al.*, 2014b; Holligan *et al.*, 2010; Rembauville *et al.*, 2016; Smith, 2014]. Furthermore, our observations showed highest (a) coccolith light scattering, (b) PIC:BSi, and (c) abundance of coccolithophores and nonsiliceous phytoplankton when RNPG was positive (Figures 3 and 5) [Eynaud *et al.*, 1999], suggesting that potential growth of nonsiliceous phytoplankton was greater than growth of diatoms in these waters. This is the first observation over basin scales in the SO that PIC concentration covaries

with regions of greatest current velocity. We suggest that this occurs due to Ekman pumping along the frontal boundaries of the SO current system, and possible upwelling of iron [de Baar *et al.*, 1995], which combined with the elevated nitrate relative to silicate (+RNPG) made for optimal conditions for increased abundance of nonsilicious phytoplankton (including coccolithophores) as opposed to diatoms (Figures 3 and 5). The iron incubation results demonstrate that iron can control the distribution and growth of coccolithophores in the GCB, with iron limitation of coccolithophores observed in the Indian sector of the GCB, where dust sources are most remote and ambient PIC levels are lower (Figures 2a and 2b). Iron availability may thus influence the balance between calcification (e.g., NCC) and POC production (e.g., NCP) by other phytoplankton groups, as shown by the bigger response of PIC than Chl to added Fe near Crozet, with the balance also impacting seawater $p\text{CO}_2$.

The seasonal occurrence of coccolithophore calcification in the GCB has a significant impact on CO_2 dynamics near the SAF. This was also seen in data from CROZet natural iron bloom and EXport experiment (CROZEX) and the Southern Ocean CO_2 Atlas (SOCAT version 3) [Bakker *et al.*, 2014; Pfeil *et al.*, 2013]. Deepwater TA supply to the Southern Ocean increases alkalinity tracers such as TA^* [Fry *et al.*, 2015] with drawdown of TA observed in the GCB co-located with regions of high seasonal coccolithophore biomass. TA^* (in units of $\mu\text{mol kg}^{-1}$) is calculated as

$$\text{TA}^* = \text{Alk}_3 - 2300$$

where

$$\text{Alk}_3 = \frac{(\text{Alk}_m - \text{Alk}_r + (1.36 \times \text{NO}_3^-))}{5} \times 35 + \text{Alk}_r$$

and Alk_m is the observed alkalinity and Alk_r is the riverine TA end-member [Fry *et al.*, 2015].

Ignoring gas exchange and horizontal transport, the summer cooccurrence of high coccolithophore biomass with elevated $p\text{CO}_2$ (i.e., seasonal change in $p\text{CO}_2 = \text{CO}_{2\text{SEASONAL}}$) reflects the dominant influence on CO_2 due to a combination of upwelling ($\delta\text{CO}_{2\text{UPWELLING}}$), net community organic production (NCP; $\delta\text{CO}_{2\text{NCP}}$), and net community calcification (NCC; $\delta\text{CO}_{2\text{NCC}}$), such that $\text{CO}_{2\text{SEASONAL}} = \delta\text{CO}_{2\text{UPWELLING}} + \delta\text{CO}_{2\text{NCP}} + \delta\text{CO}_{2\text{NCC}}$. In areas where upwelling and Ekman pumping bring up nutrients and CO_2 , seasonal organic carbon production (i.e., NCP), $\delta\text{CO}_{2\text{NCP}}$, is likely greater than $\delta\text{CO}_{2\text{UPWELLING}}$ with the net result that seawater $p\text{CO}_2$ decreases. However, in areas of high coccolithophore growth and biomass, generation of CO_2 by calcification offsets the drawdown of CO_2 by organic production. Thus conceptually, there are three scenarios explaining the range of seawater $p\text{CO}_2$ observed across the SAF waters in the GCB: (1) where $\text{NCP} > \text{NCC}$, seawater $p\text{CO}_2$ is likely to decrease; (2) where $\text{NCP} \sim \text{NCC}$, seawater $p\text{CO}_2$ is likely to remain unchanged; and (3) where $\text{NCP} < \text{NCC}$, seawater $p\text{CO}_2$ is likely to increase. These three scenarios all likely occur in the GCB.

In the third scenario, coccolithophore calcification in the SAF can potentially shift waters from a CO_2 sink to source (Figures 2d, 6, and 7), hinted at in a few previous studies in the Sargasso Sea, Bay of Biscay, and the North Atlantic Ocean [Bates, 2007; Robertson *et al.*, 1994; Smith *et al.*, 2012]. Recently, Salter *et al.* [2014] highlighted the importance of the carbonate counter pump (long-term production of CO_2 associated with CaCO_3 precipitation [Zeebe, 2012]) in regions of the Southern Ocean, including around Crozet. We confirm this directly for the first time with measurements of seawater $p\text{CO}_2$. Such shifts in the CO_2 sink-source status of SAF surface waters have direct relevance to global air-sea CO_2 fluxes and coccolithophore- CO_2 feedback.

Another diagnostic for the importance of the carbonate counter pump is the PIC:POC export ratio (rain ratio), which is an important control for atmospheric CO_2 [Archer *et al.*, 2000]. Using an ocean biogeochemical-transport box model, Sarmiento *et al.* [2002] determined a global PIC:POC export ratio of 0.06, with highest values in subtropical gyres (~ 0.08 in the subtropical Atlantic and Indian Oceans) and lowest values in the Southern Ocean (~ 0.01 in the Southern Ocean Atlantic and Indian subpolar gyres, defined as waters south of 45°S). Our estimates of PIC:POC export ratio using the PIC:POC ratio of $> 51 \mu\text{m}$ particles were considerably higher (0.08–1.08), but the patterns we found were broadly similar, with polar and subtropical waters having consistently low and high PIC:POC export ratios, respectively (Figure 10). One notable difference was that we also found variable PIC:POC export ratios in subpolar waters. Differences in the magnitude of our estimates are likely due to the different time scales of integration represented by the two methods. The Sarmiento

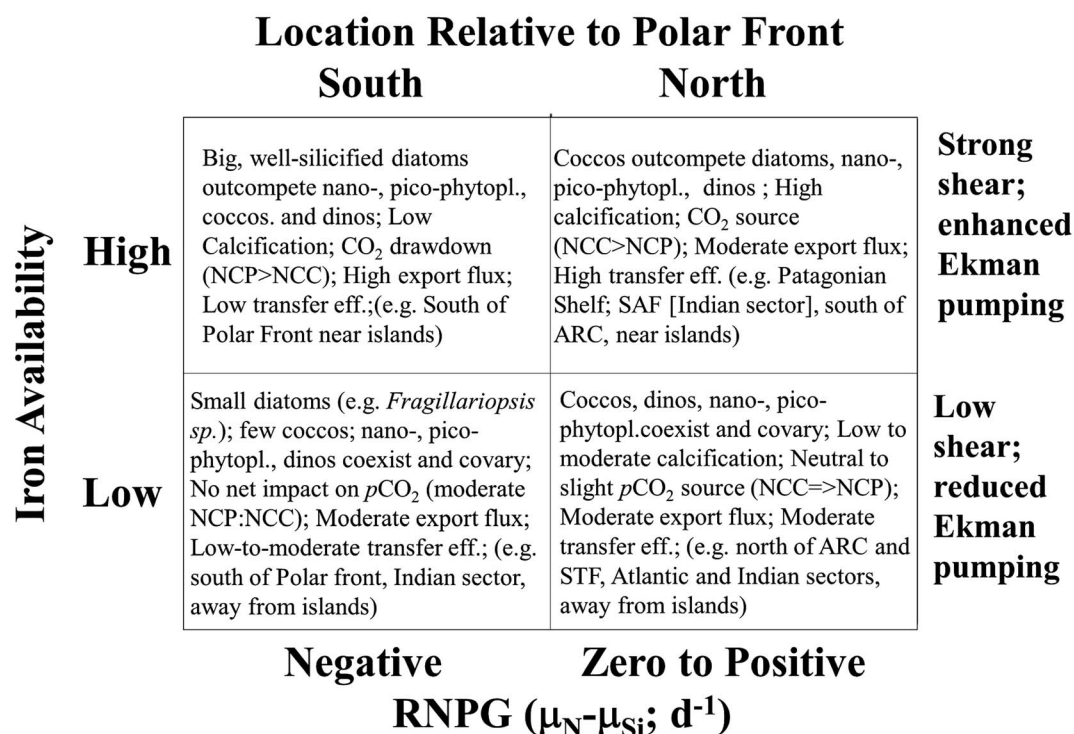


Figure 11. Conceptual model for balance of coccolithophores and noncalcifying phytoplankton growth in GCB versus diatom growth (determined as RNPG) and effects on CO₂ source/sink dynamics and sinking particle fluxes. Abbreviations used in table: coccos = coccolithophores; dinos = dinoflagellates; nanophytopl. = nanophytoplankton; picophytopl. = picophytoplankton; eff. = efficiency; ARC = Agulhas Return Current.

et al. [2002] estimate uses observed profiles of DIC, alkalinity, and NO₃, usually taken during summertime cruises, for their calculations, and represents an integration over the growing season. In contrast, our estimate is based on a snapshot of the large particle population at the time of sampling by in situ filtration. Since our cruises were timed to maximize expected coccolithophore production, our estimate may represent times of highest PIC:POC export ratio.

Time scales of integration aside, we still find that the highest PIC:POC export ratios (>0.7) were all in subpolar waters south of 45°S adjacent to the Patagonia Shelf or Crozet Island, with RNPG > 1 (Figure 10). Away from these putative trace metal sources in waters with RNPG > 1, PIC:POC export was low (Figure 10c). Export was generally not measured in fronts because of the strong current velocities and logistical difficulties in sampling in these dynamic regions. Given the high PIC detected in regions of high velocity (Figure 4), we speculate that these would also be regions of high PIC:POC export ratio. Subpolar waters with RNPG > 1 thus have very variable PIC:POC export ratios (Figure 10)—high when near a source of trace metals, and potentially in fronts, and low otherwise.

Recent global estimates of the Alk* tracer [Fry *et al.*, 2015], which isolates the effects of CaCO₃ cycling on alkalinity, show elevated Alk* in the Southern Ocean [Carter *et al.*, 2014; Fry *et al.*, 2015]. Elevated Alk* in the Southern Ocean is thought to result from the upwelling of high Alk* waters, and does not preclude calcification in surface waters, which would otherwise tend to decrease Alk*. Indeed, further evidence of sustained PIC production in the GCB comes from the sediment composition in the STF and SAF zones dominated by CaCO₃ [Longhurst, 1998]. Overall, evidence suggests that the STF and SAF zones have a relatively high PIC:POC export ratio, which would thus act to increase ocean CO₂.

Our ²³⁴Th flux results (Figure 9) add to the growing body of evidence that there is not a universal CaCO₃ ballast effect operating in the upper ocean [Le Moigne *et al.*, 2012; Riley *et al.*, 2012; Thomalla *et al.*, 2008]. Instead, the correlation between PIC flux and the transfer efficiency of POC flux through the upper mesopelagic (Figure 9b) suggests a role for PIC in extending the remineralization length scale of sinking POC.

However, regions of more efficient transfer of the exported POC flux to the mesopelagic were not high POC flux regions. We suggest that the CO₂-enhancing role of the carbonate pump is more important than any ballast-induced enhancement of the soft-tissue POC pump. A corollary to this is that any reduction in calcification due to ocean acidification should be expected to have a greater impact on the carbonate pump than the soft tissue pump and thus be an overall negative feedback on pCO₂ [Riebesell *et al.*, 2009].

Based on this work, we propose a conceptual model on the growth of phytoplankton in the SO. Our results can be divided into a four-way mandala (Figure 11), where RNPG primarily determines whether diatoms can outcompete nonsiliceous phytoplankton (including coccolithophores) when relieved of a limiting micronutrient (Figure 8), while iron further regulates the growth of all phytoplankton in ACC waters. Each quadrant has different biogeochemical ramifications to the seawater pCO₂ and export carbon fluxes.

4.1. Synthesis and Conclusions

A synthesis of our previous data and other studies demonstrates the following consistencies in our understanding of the GCB and its biogeochemical significance to the SO:

1. The GCB is *indeed* a globally substantial feature that occurs seasonally across the STF/SAF zones and has elevated concentrations of coccolithophores relative to other regions and elevated PIC:POC export ratios.
2. In the PIC-rich waters of the GCB, calculated seawater pCO₂ is elevated in comparison to adjacent waters with lower seawater pCO₂. These features are co-located with drawdown of TA and low TA:DIC ratios that, in comparison to other areas of the GCB, suggest substantial calcification.
3. Iron supply is implicated in the reduced growth of coccolithophores in the Indian sector (and likely the Pacific sector given reduced satellite-derived PIC levels there). However, the relative lack of coccolithophores to the north and south of the GCB appears to be controlled by factors other than iron availability (i.e., macronutrients or temperature).

It should be noted that the ratio of PIC to alkalinity drawdown is not uniform in the GCB, and PIC is not high enough to account for the entire alkalinity drawdown. This is likely due to the coccolithophore bloom timing and the growth of other species. The inconsistency between PIC and alkalinity is probably simply due to sinking of the PIC over the course of the season (the carbonate pump).

Our GCB observations from the Crozet region (with its strong frontal gradients in N, Si, and Fe) can be compared to the previous results of the CROZEX experiment [Moore *et al.*, 2007; Pollard *et al.*, 2007a] to address the bottom-up control of coccolithophores and other phytoplankton in the GCB, including the biogeochemical implications of differential limitation by nutrients. CROZEX was performed between November 2004 and mid-January 2005. These waters were shown to have variable iron content, such that water originating from the south or east of Crozet and flowing over shallow sediments had elevated iron while water from the north or west had low iron [Planquette *et al.*, 2007]. The October CROZEX observations primarily followed the demise of the spring diatom/*Phaeocystis* bloom [Pollard *et al.*, 2007a]. However, PIC was present in the area; between early November and early December 2004, PIC levels were 0.25–0.75 μmol L⁻¹, while from mid-December to mid-January, levels were 1–1.25 μmol L⁻¹ (as high as 1.75 μmol L⁻¹ in a large eddy), representative of levels found in a moderate coccolithophore bloom [Read *et al.*, 2007]. MODIS imagery from early January 2005 showed that the entire SAF region north of Crozet had minimal chlorophyll, but with ~50% higher 550 nm reflectance, suggesting a large region of coccolith-rich water in the SAF, precisely what we observed in the GCB. As noted earlier, the boundaries of the elevated PIC regions near Crozet corresponded to the streamlines of current velocity [Pollard *et al.*, 2007b], suggesting bottom-up forcing of PIC production associated with Ekman pumping along the current boundaries.

Strong CO₂ drawdown dominated during CROZEX early in the growing season north of Crozet [Bakker *et al.*, 2007] (our scenario NCP > NCC). During the late February 2012 cruise, coccolithophores appear to have grown sufficiently long to enhance NCC:NCP and CO₂ supply. We suspect that this temporal shift from diatom to coccolithophore production is the same as observed elsewhere when silicate is exhausted [Balch *et al.*, 2014b; Boyd *et al.*, 2010; Leblanc *et al.*, 2009], except our results suggest that iron availability can influence coccolithophore production and the seawater pCO₂ balance of the GCB. Future work should expand the regional analyses of coccolithophores and pCO₂ to other sectors of the Southern Ocean, particularly in the Australian and Pacific sectors, where few observations have been made.

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