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Southern Ocean Calcification Controls the Global Distribution of Alkalinity

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Key Points:

- Calcification in the Southern Ocean affects the global distribution of alkalinity
- Changes in Southern Ocean calcification affect how the ocean absorbs atmospheric carbon dioxide
- Southern Ocean calcium carbonate fluxes control the strength of the Southern Ocean alkalinity trap

Supporting Information:

- Supporting Information S1

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Abstract Biological processes in Southern Ocean surface waters have widespread impacts on global productivity and oceanic CO₂ storage. Here, we demonstrate that biological calcification in the Southern Ocean exerts a strong control on the global distribution of alkalinity. The signature of Southern Ocean calcification is evident in observations as a depletion of potential alkalinity within portions of Subantarctic Mode and Intermediate Water. Experiments with an ocean general circulation model indicate that calcification and subsequent sinking of biogenic carbonate in this region effectively transfers alkalinity between the upper and lower cells of the meridional overturning circulation. Southern Ocean calcification traps alkalinity in the deep ocean; decreasing calcification permits more alkalinity to leak out from the Southern Ocean, yielding increased alkalinity in the upper cell and low-latitude surface waters. These processes have implications for atmosphere-ocean partitioning of carbon. Reductions in Southern Ocean calcification increase the buffer capacity of surface waters globally, thereby enhancing the ocean's ability to absorb carbon from the atmosphere. This study highlights the critical role of Southern Ocean calcification in determining global alkalinity distributions, demonstrating that changes in this process have the potential for widespread consequences impacting air-sea partitioning of CO₂.

Plain Language Summary Plankton living in the Southern Ocean affect the composition of seawater through biological processes. Due to the particular oceanic circulation in the Southern Ocean, these biologically driven changes in ocean chemistry can have widespread effects on the global ocean. Species of plankton that form shells of calcium carbonate remove alkalinity from surface waters through the process of calcification. The amount of alkalinity in surface waters is important because it affects how much CO₂ the ocean can absorb from the atmosphere. We show that Southern Ocean calcifying plankton affect the global distribution of alkalinity through the presence of a Southern Ocean “alkalinity trap.” More Southern Ocean calcification yields a stronger alkalinity trap, with more alkalinity being retained in the Southern Ocean and in deep waters, away from the atmosphere. Reduced calcification in the Southern Ocean permits more alkalinity to escape the Southern Ocean and remain in the upper ocean globally. These changes affect oceanic CO₂ uptake from the atmosphere.

1. Introduction

The Southern Ocean is uniquely important to the climate system and global biogeochemistry because it is a dominant region for ventilation of the deep ocean. The biological pump deposits nutrients at depth; circulation must ultimately provide a path to return nutrients to the ocean surface; otherwise, productivity would cease. The nature of nutrient return paths is important as it determines the degree to which global ocean biogeochemistry is sensitive to climate. Broecker (1991) envisioned that nutrients were mixed across the main thermocline ubiquitously in the global ocean; this model, however, is inconsistent with observed vertical diffusivities, which are about an order of magnitude too low to account for the necessary water mass transformations (Ledwell et al., 1993). A more accurate account of nutrient return paths is that deep ocean nutrients are returned to the surface in the Southern Ocean by the global overturning circulation (Sarmiento et al., 2007). In the Southern Ocean upwelled nutrients are exposed to productivity before being returned to the subtropical thermocline in Antarctic Intermediate (AAIW) and Subantarctic Mode Water (SAMW)—or the abyssal ocean in Antarctic Bottom Water (AABW) (Figure 1). As a result, biological processes occurring in Southern Ocean surface waters have the capacity to influence global productivity and biogeochemistry (Marinov et al., 2006; Sarmiento et al., 2004).

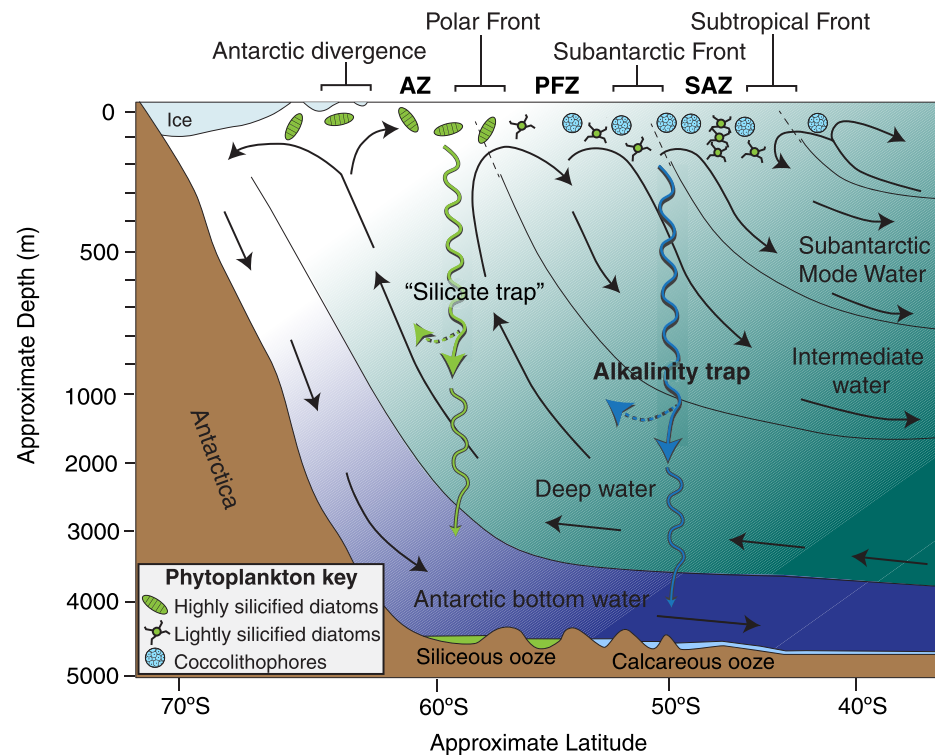


Figure 1. Schematic of idealized, zonal-mean Southern Ocean overturning circulation, showing dominant biomineralizing phytoplankton. Abbreviations: AZ = Antarctic zone; PFZ = polar front zone; SAZ = Subantarctic zone.

Latitudinal gradients in nutrients and temperature define unique environments in the Southern Ocean and impact plankton assemblages and their physiological state, which, in turn, may affect water chemistry. For example, strong iron limitation in the silicate rich waters of the Antarctic zone (AZ; Figure 1) of the Southern Ocean is conducive to the production of heavily silicified diatoms (Assmy et al., 2013; Franck et al., 2000; Leynaert et al., 2004; Smith et al., 2017). These diatoms deplete silicic acid in the surface waters to build thick, grazer-resistant, opal shells, which sink and leave less silicic acid to be distributed to the rest of the ocean as waters move north (Assmy et al., 2013; Sarmiento et al., 2004). In contrast, the Subantarctic zone (SAZ; Figure 1) is characterized by limiting silicic acid, more plentiful iron input, and warmer temperatures; these conditions create a region of competition between calcifying phytoplankton, that is, coccolithophores (Balch et al., 2016) and lightly silicified diatoms (Assmy et al., 2013; Smith et al., 2017; Tréguer et al., 2018). These distinct Southern Ocean plankton communities are reflected in the composition of material found in sediment traps (Figure 2a; Honjo et al., 2000; Rembauville et al., 2016; Wilks et al., 2017) and seafloor sediments (Figure 2b; Dutkiewicz et al., 2015). Due to differing cellular stoichiometry and physiology, these Southern Ocean plankton communities leave unique impressions on water masses and contribute to an ecological divide between the AZ and SAZ (e.g., Malinverno et al., 2016).

Several studies have explored the effect of Southern Ocean phytoplankton production on global nutrient distributions (Dutkiewicz et al., 2005; Marinov et al., 2006; Primeau et al., 2013; Sarmiento et al., 2004). In particular, a phenomenon known as Southern Ocean “nutrient trapping” is considered a mechanism that might drive reorganizations of the global nutrient inventory distribution (Holzer et al., 2014; Moore et al., 2018; Primeau et al., 2013). Nutrient trapping is possible in regions with divergent flow at the surface and convergent flow at depth; in this case, upwelled nutrients fuel export production, but sinking organic material rains back down and is remineralized at the same depths from which the upwelled water mass came. Nutrients can be effectively trapped if export production is fast relative to the time scale at which advection flushes the region; where this is true, nutrients are trapped, increasing concentrations locally and limiting lateral transport out of the region. Primeau et al. (2013) demonstrated in the context of an ocean general circulation (OGCM) that nutrients can be most effectively trapped in the Southern Ocean

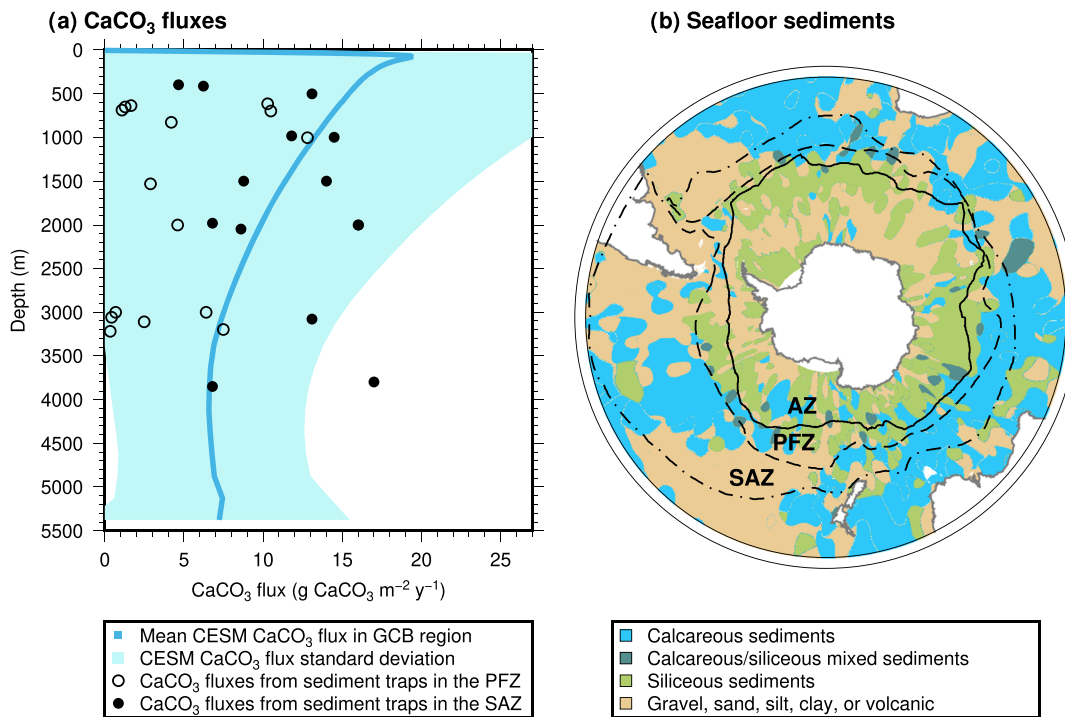


Figure 2. CaCO_3 in the water column and on the seafloor. Panel (a) shows CaCO_3 fluxes from sediment traps moored in the SAZ (filled circles) and PFZ (open circles) of the Southern Ocean and CaCO_3 fluxes from the Community Earth System Model (CESM). Data sources for CaCO_3 fluxes from sediment traps and sediment grouping specifications are described in section 2.1. The CESM CaCO_3 fluxes are an area-weighted mean underneath the $26.0 \leq \sigma_\theta \leq 27.0$ outcrop region (darker blue line) with the standard deviation of fluxes within this region indicated by the light blue shading. (b) Seafloor sediments from Dutkiewicz et al. (2015). Fronts shown on Panel (b) are, from south to north, the Polar Front (Freeman & Lovenduski, 2016), the Subantarctic Front, and the Subtropical Front (Orsi et al., 1995). Abbreviations: AZ = Antarctic zone; PFZ = Polar front zone; SAZ = Subantarctic zone.

by increasing productivity in the Antarctic Zone. This phenomenon was simulated in Earth system model (ESM) integrations conducted out to Year 2300 with continuing carbon emissions (Moore et al., 2018).

Nutrient trapping already manifests in the Southern Ocean and involves decoupling between the macronutrients silicic acid and nitrate (Sarmiento et al., 2004). Diatoms typically utilize silicic acid and nitrate in a ratio of about 1:1 under adequate light and nutrient conditions. However, as alluded to above, stress induced by light or iron scarcity causes diatoms to increase their Si:N utilization ratio (e.g., Takeda, 1998). As a result of elevated Si:N utilization in the Southern Ocean, silicic acid is preferentially removed as waters upwelled at the Antarctic Polar Front flow northward to the subduction regions north of the SAF, where AAIW and SAMW are formed (silicate trap in Figure 1), with shorter-term spatial variations in Si:N influenced by the physical supply of nutrients from below (Demuyne et al., 2020). Sarmiento et al. (2004) showed that diatom opal formation in the Southern Ocean limits the amount of silicic acid that leaves the Southern Ocean, thereby influencing diatom production in the rest of the Southern Hemisphere and North Atlantic via SAMW. Another dominant surface process in the formation region of these waters is calcification, which is especially widespread in the SAZ and PFZ of the Southern Ocean (Figures 1 and 2; Balch et al., 2011; Salter et al., 2014). The potential effect of Southern Ocean calcification on global alkalinity distributions has received limited attention.

Calcification impacts seawater alkalinity and, in turn, affects air-sea CO_2 fluxes. Producing 1 mol of CaCO_3 removes 2 mol of alkalinity and 1 mol of dissolved inorganic carbon (DIC) from ambient seawater (Sarmiento & Gruber, 2006). Sinking CaCO_3 transfers carbon to depth, creating the “carbonate pump,” but consumption of alkalinity at the ocean surface diminishes the ocean’s ability to absorb CO_2 from the atmosphere relative to a pure “soft-tissue” pump (e.g., Salter et al., 2014). Hence, the ratio of CaCO_3 to particulate organic carbon (POC) flux, the rain ratio, is an important metric of the efficacy of the biological pump (e.g., Sarmiento et al., 2002; Sigman et al., 2010). Matsumoto et al. (2002), for instance, used a simple box model to show that changes in the rain ratio can impact ocean carbon storage; by increasing diatom production in the global ocean at the expense of coccolithophores, they diminished the rain ratio, driving decreases in atmospheric

CO₂ via enhanced ocean carbon storage. This, and many other studies, have highlighted the importance of surface ocean alkalinity on CO₂ uptake and climate.

The Southern Ocean is home to the Great Calcite Belt (GCB; Balch et al., 2011), a circumpolar band of elevated particulate inorganic carbon (PIC) that is visible from space due to the high reflectivity of suspended CaCO₃ (Balch et al., 2011; Holligan et al., 2010). While there are multiple calcifying organisms in the GCB region (the SAZ and PFZ), the PIC algorithm that translates water-leaving radiances and backscattering to CaCO₃ concentrations is primarily tuned to capture coccolithophore shells (Balch et al., 2005; Gordon et al., 2001). Coccolithophore blooms in the Southern Ocean are extensive, covering $\sim 52 \times 10^6$ km² and accounting for roughly 26% of oceanic suspended PIC (Balch et al., 2005). Indeed, coccolithophores are a large driver of CaCO₃ fluxes in the SAZ, with contributions ranging from $\sim 10\%$ to $>85\%$ of total CaCO₃ (Manno et al., 2018; Rembauville et al., 2016; Rigual Hernández et al., 2020; Wilks et al., 2017). Zooplankton calcifiers, pteropods and foraminifera, also constitute significant portions of CaCO₃ fluxes in the Southern Ocean (Hunt et al., 2008; Rigual Hernández et al., 2018). For example, Manno et al. (2018) showed that pteropods comprise the majority of CaCO₃ fluxes (in the more soluble form, aragonite) during the autumn between 1,500 and 2,000 m of depth at two sites in the SAZ. A global biogeochemical model recently suggested that pteropods contribute largely to shallow CaCO₃ export globally (Buitenhuis et al., 2019), while coccolithophores and foraminifera dominate deep fluxes to sediments (Broecker & Clark, 2009). Figure 2a shows total CaCO₃ collected in sediment traps moored in the GCB region of the Southern Ocean, indicating that sinking biogenic CaCO₃ reaches deeper than 2,000 m with low dissolution. At this depth, deep waters are moving south (Talley et al., 2003), setting up the potential for Southern Ocean alkalinity trapping (Figure 1).

Observational studies have established direct links between surface alkalinity and local CaCO₃ formation and dissolution. For example, decreases in surface alkalinity resulting from biological calcification have been documented in the subtropical and subpolar North Atlantic (Bates et al., 1996; Holligan et al., 1993; Robertson et al., 1994), as well as the Southern Ocean (Balch et al., 2016). Conversely, Cross et al. (2013) observed increases in total alkalinity associated with CaCO₃ dissolution in corrosive waters of the North Pacific. In addition to CaCO₃ cycling, alkalinity is affected by freshwater fluxes and the production of organic matter through nitrate consumption. To isolate the impact of CaCO₃ cycling, we make use of “potential alkalinity (PAlk),” which is a linear combination of alkalinity and nitrate, normalized to a reference salinity (Sarmiento & Gruber, 2006). Fry et al. (2015) used PAlk as a basis for a tracer they called Alk*, from which riverine influences on alkalinity have also been removed. Alk* is remarkably consistent throughout low latitudes in all ocean basins, but increases in the North Pacific and high-latitude Southern Ocean (Fry et al., 2015; Millero et al., 1998), reminiscent of silicic acid distributions (Freeman et al., 2018; Levitus et al., 1993). Alk* declines in SAZ surface waters moving north at $\sim 40^\circ$ S, a region rich in coccolithophores and other pelagic calcifiers. Jin et al. (2006) diagnosed CaCO₃ production globally by restoring PAlk to observations within an ocean general circulation model, finding that Southern Ocean calcification accounts for more than one third of global oceanic calcification. In summary, there is widespread calcification in the northern parts of the Southern Ocean that likely imprints on ocean chemistry downstream from the Southern Ocean environment.

Given the physical dynamics of the Southern Ocean, changes in calcification in the Southern Ocean could have widespread biogeochemical consequences. In this study, we test the hypothesis that Southern Ocean calcification is modifying global alkalinity distributions. We first present observational evidence that CaCO₃ production in the Southern Ocean leaves a signature on alkalinity concentrations and could lead to alkalinity trapping in the Southern Ocean, as has been shown for silicate, other macronutrients, and carbon (e.g., Marinov et al., 2006; Primeau et al., 2013; Sarmiento et al., 2004). We then use an ocean general circulation model coupled to a biogeochemistry model to quantify the effects of Southern Ocean calcification (south of 30° S) on the global distribution of alkalinity. Our results suggest that calcification in the GCB region of the Southern Ocean modifies global alkalinity by limiting the amount of alkalinity that flows northward in the upper water column of the Subantarctic Southern Ocean. Changing Southern Ocean calcification redistributes ocean alkalinity between upper and lower cells of the overturning circulation and between the Southern Ocean and the rest of the global ocean. This has consequences on biogeochemical processes, such as global air-sea CO₂ fluxes. The results of our model experiments show that changes in calcification in the GCB region could have widespread impacts beyond the Southern Ocean and alter the overall amount of carbon that the ocean absorbs from the atmosphere globally.

2. Methods

2.1. Observational Data Sets

We used GLODAP Version 2 (Lauvset et al., 2016) to examine observational evidence of Southern Ocean calcification on alkalinity. In order to isolate the effects of CaCO_3 production and dissolution on alkalinity, we removed the influences of precipitation, evaporation, and the production and remineralization of organic matter on alkalinity distributions by calculating salinity-normalized potential alkalinity (PAlk). We calculated PAlk following Fry et al. (2015):

$$\text{PAlk} = (\text{Alk} + 1.36 \times \text{NO}_3) \frac{35}{S} \quad (1)$$

where Alk is the total alkalinity concentration, NO_3 is the nitrate concentration, and S is the salinity. The factor of 1.36 accounts for the average proportional (relative to NO_3) uptake of other ions consumed by primary production, such as phosphate and sulfate (Wolf-Gladrow et al., 2007), thus removing the influence of organic matter cycling on alkalinity. We interpolated PAlk onto σ_θ density coordinates to examine the climatological mean fields within isopycnal density ranges. We compute PAlk on output from a numerical model similarly; however, we do not apply salinity normalization to the simulated NO_3 , as freshwater fluxes are not applied to NO_3 in the model.

We used satellite-derived PIC from MODIS (Moderate Resolution Imaging Spectroradiometer; Balch et al., 2005; Gordon et al., 2001) to assess the location of the GCB, generating an annual mean PIC map for the period 2003 to 2017. We compare these to CaCO_3 concentrations simulated in the top level of the ocean model (see section 2.2), which represents the upper 10 m.

We compiled CaCO_3 flux data from sediment traps moored in the SAZ (between the subtropical front and Subantarctic front) and PFZ (between the Subantarctic front and the Polar Front) in the Southern Ocean. Data on CaCO_3 fluxes from sediment traps are from Rigual Hernández et al. (2020), Wilks et al. (2017), Trull et al. (2001), Salter et al. (2014), Northcote and Neil (2005), Wefer and Fischer (1991), Fischer et al. (2002), Manno et al. (2018), and Honjo et al. (2000). We compare this observational CaCO_3 flux data set to modeled CaCO_3 fluxes in the Southern Ocean between the 26.0 to 27.0 σ_θ isopycnal surface outcrops.

We use ocean sediment data from Dutkiewicz et al. (2015) to demonstrate the ecological divide between calcifiers and silicifiers in the Southern Ocean. Sediment fields were aggregated to distinguish between siliceous, calcareous, mixed siliceous/calcareous, and other types of sediments. Siliceous sediments included radiolarian ooze, siliceous ooze, and siliceous mud. Calcareous sediments included calcareous ooze, shells/corals, and fine-grained calcareous sediments.

2.2. Modeling Experiments

We use a pre-release version of the Community Earth System Model (CESM) version 2.2 with biogeochemistry to test the effects of Southern Ocean calcification on alkalinity and air-sea CO_2 fluxes. The ocean ecosystem is simulated using the Marine Biogeochemical Library (MARBL; marbl-ecosys.github.io). Our simulations with MARBL include an explicit coccolithophore phytoplankton functional type (PFT; Krumhardt et al., 2019). The coccolithophore PFT parameterization is based on physiological studies, where the ratio of CaCO_3 production to photosynthesis in the PFT responds to environmental conditions (temperature, nutrients, and CO_2 concentration). In this study, however, we used an updated relationship between CaCO_3 production and temperature (see supporting information Figure S1) in order to better fit physiological studies specifically with the Southern Ocean *Emiliania huxleyi* morphotype. We were also guided by comparisons with the simulated satellite observation of surface PIC concentrations in the Southern Ocean (section 2.1).

MARBL only represents phytoplankton calcification; zooplankton calcifiers, such as pteropods and foraminifera, are not simulated. Additionally, the model assumes that all CaCO_3 is produced as calcite, thus ignoring the distinction between the mineral forms calcite and aragonite, which may be important in modulating dissolution depths (Gangstø et al., 2008). Despite these details, CESM CaCO_3 fluxes in the Southern Ocean compare reasonably well to total CaCO_3 fluxes observed in sediment traps (Figure 2). Particulate CaCO_3 sinking and dissolution is parameterized according to the formulation of Armstrong et al. (2002) with a reference dissolution length scale (DLS) of 500 m that does not depend on the CaCO_3 saturation state (Ω). The CaCO_3 DLS (as well as POC and SiO_2 DLSs) increases with depth and under low oxygen conditions.

Table 1
Numerical Experiments Conducted With the Ocean Component of the Community Earth System Model (CESM)

Short name	Description	GCB CaCO ₃ flux (g CaCO ₃ m ⁻² yr ⁻¹)	Global mean rain ratio	Alk inventory in Pmol (% Δ control)	DIC inventory in Pmol (% Δ control)	Air-sea CO ₂ flux (Pg C yr ⁻¹)	DIC accumulation rate (Tmol C yr ⁻¹)	Alk accumulation rate (Tmol Alk yr ⁻¹)
control	Standard SO calcification, 500 m DLS	12.91	0.15	3,208.92	3,056.36	-0.14	23	-0.3
noGCB	No calcification south of 30°S, 500 m DLS	0	0.11	3,211.86 (+0.09%)	3,060.66 (+0.14%)	-0.24	37	9.7
2xGCB	Double calcification south of 30°S, 500 m DLS	25.82	0.19	3,205.98 (-0.09%)	3,052.03 (-0.14%)	-0.040	9.2	-10.4
100mDLS	Standard SO calcification, 100 m DLS	3.21	0.13	3,210.65 (+0.05%)	3,059.00 (+0.09%)	-0.21	32	5.6
1000mDLS	Standard SO calcification, 1,000 m DLS	16.71	0.15	3,207.77 (-0.04%)	3,055.07 (-0.04%)	-0.11	18	-4.6
-32%Global	Globally reduce calcification by 32%, 500 m DLS	8.78	0.10	3,211.62 (+0.08%)	3,060.74 (+0.14%)	-0.26	38	8.7
+32%Global	Globally increase calcification by 32%, 500 m DLS	17.04	0.20	3,206.22 (-0.08%)	3,052.0 (-0.14%)	-0.024	8.4	-9.4

Note. All metrics are computed as means over the fifth cycle of the CORE-IAF forcing (simulation Years 249–310), except for the DIC and Alk accumulation rates, which are the trends over the last two IAF cycles (simulation Years 187–310). The rain ratio is CaCO₃ flux divided by particulate organic carbon flux at 100 m of depth (mol:mol). Abbreviations: DIC = dissolved inorganic carbon; Alk = alkalinity; DLS = dissolution length scale.

Burial of CaCO₃ on the ocean floor occurs where $\Omega > \Omega_{crit}$ in the model's bottom layer; where $\Omega < \Omega_{crit}$, all CaCO₃ reaching the model's bottom layer is dissolved. In the simulations presented here, Ω_{crit} was set to a value of 1. Riverine nutrient, carbon, and alkalinity fluxes are supplied to the ocean model from a data set derived from GlobalNEWS (Mayorga et al., 2010). Riverine DIC inputs are assumed to be composed of 100% bicarbonate and are thus equal to alkalinity fluxes.

MARBL simulates two parallel carbonate systems (i.e., the prognostic DIC and Alk tracers as well as associated diagnostic quantities like pCO₂, pH, etc.). In climate projection integrations, these tracer systems are identical, except for their atmospheric CO₂ boundary conditions, thus enabling a straightforward characterization of anthropogenic CO₂ distributions inclusive of physical and biogeochemical (i.e., Revelle factor) feedbacks. We exploited this capability, using the second carbonate system (ALT_CO2) tracers to examine the impacts of Southern Ocean calcification on alkalinity, DIC, and air-sea CO₂ exchanges. Our approach was to manipulate the CaCO₃ production and dissolution terms for the ALT_CO2 tracers in the region south of 30°S. Since all other source/sink terms, atmospheric boundary conditions and physical transport fields for the primary DIC/Alk and ALT_CO2 tracers were identical, this methodology provides a very clean approach to isolating the influence of CaCO₃ production and dissolution in the Southern Ocean on alkalinity and carbon fields globally. Our hypothesis was that vertical fluxes of CaCO₃ in the Southern Ocean effect an alkalinity transfer that determines the degree to which alkalinity is “trapped” in the region. We approach this in two ways, first by directly manipulating CaCO₃ production in the surface ocean south of 30°S and second by modifying the DLSs south of 30°S, thereby affecting the vertical distribution of dissolution for a given CaCO₃ production. In the first case, where we manipulate surface CaCO₃ production, the

dissolution profile of CaCO_3 is impacted in direct proportion to changes in production; the MARBL formulation for CaCO_3 cycling requires that the column integrals of production, dissolution and burial sum to zero at each numerical time step. We ran experiments yielding simulated DIC and Alk distributions consistent with seven different conditions (Table 1). In addition to a control simulation, we ran four simulations in which we manipulate Southern Ocean calcification or the CaCO_3 DLS (noGCB, 2xGCB, 100mDLS, and 1000mDLS). Southern Ocean calcification accounts for 32% of globally integrated calcification in the control integration. Consequently, the noGCB and 2xGCB experiments result in a 32% decrease and increase, respectively, in global calcification. To examine the impact of confining these changes in calcification to the Southern Ocean, we also performed simulations in which we modified calcification globally by 32% (Table 1). Our experiments induced changes in CaCO_3 burial, leading to slight differences in total oceanic alkalinity inventory between experiments ($<0.1\%$; Table 1).

We used an ocean-sea-ice configuration of CESM similar to that described in Long et al. (2013) and Yeager et al. (2018). Ocean physics were spun up for 124 yr before simulating ocean biogeochemistry. The CESM sea-ice and ocean component models (with biogeochemistry) were then integrated at the nominal 1° resolution for five Coordinated Ocean-Ice Reference Experiment, interannual forcing (CORE-IAF; Large & Yeager, 2009) cycles (62 yr/cycle) under preindustrial conditions (atmospheric $\text{CO}_2 = 284.7 \mu\text{atm}$) for a total of 310 yr. While this is not long enough to achieve equilibrium with respect to deep ocean alkalinity distributions (which takes thousands of years), it does enable evaluating the dominant patterns of change associated with perturbing Southern Ocean calcification and its impact on alkalinity redistribution.

2.3. Analysis

We focus our analysis on the mean fields over the last 62 yr of our 310-yr, preindustrial simulation (the last interannual forcing cycle; simulation Years 249–310). Our primary method of evaluating the importance of Southern Ocean calcification is to difference fields in each experiment from the control integration (i.e., experiment minus control); we use this approach to develop a relationship between CaCO_3 fluxes in the GCB region of the Southern Ocean and mean alkalinity in the upper ocean. We examine the redistribution of the alkalinity inventory in each experiment using $\sigma_\theta = 27.4$ as the boundary between the upper and lower ocean. In order to better understand the capacity of the ocean to absorb CO_2 from the atmosphere we calculated the Revelle factor. The Revelle factor (R) was estimated by the equation from Sarmiento and Gruber (2006):

$$R = \frac{3 * Alk * DIC - 2 * DIC^2}{(2 * DIC - Alk)(Alk - DIC)} \quad (2)$$

3. Results

3.1. CESM Simulation of Southern Ocean Calcification

We compare the mean PIC inferred from MODIS (mean 2003–2017) and CESM surface CaCO_3 (Figures 3a and 3b). While CESM simulates a GCB, as in the observational estimates, it tends to be more concentrated and extends somewhat farther north than the PIC observational estimates suggest. It has been noted in several studies that the PIC algorithm likely overestimates PIC in the Southern Ocean, particularly in the AZ (e.g., see Balch et al., 2016; Trull et al., 2018). The coccolithophore PFT is the only source of biogenic CaCO_3 in CESM. Therefore, it implicitly represents all pelagic calcification (by zooplankton and phytoplankton) in a biogeochemical sense. Considering this model simplification, an overestimation of coccolithophore CaCO_3 (Figure 3b) helps to compensate for the lack of zooplankton calcifiers in the model. Indeed, simulated sinking CaCO_3 fluxes compare reasonably well with those derived from sediment traps in the SAZ and PFZ (Figure 2a).

3.2. The Signature of Calcification in Alkalinity Observations

We examined salinity-normalized potential alkalinity (PAlk) in observationally based fields for a signature of Southern Ocean calcification. In Figure 3c we present the observationally based estimates of mean PAlk averaged over the σ_θ isopycnal density range 26.0 and 27.0, which includes SAMW and some portion of AAIW. As waters flow northward from the AZ to the SAZ, PAlk within this density range drops from $> \sim 2,450 \text{ mmol m}^{-3}$ in the AZ to $\sim 2,385 \text{ mmol mm}^{-3}$ in the SAZ (see Figure S2 for a zonal view). Simulated PAlk from the CESM control simulation shows a similar decline in PAlk from south to north in this density range, losing $\sim 60 \text{ mmol m}^{-3}$ of PAlk from the AZ to the SAZ (Figure 3d). Modifying Southern Ocean

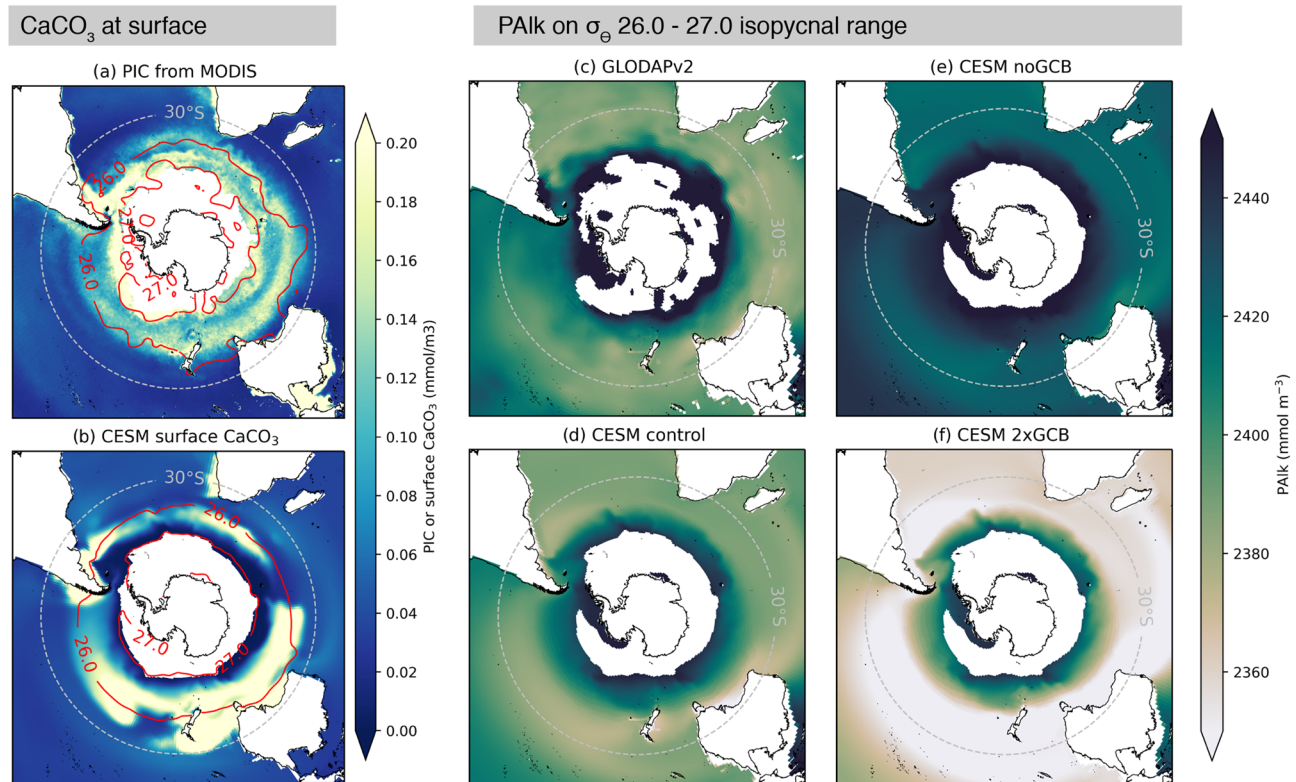


Figure 3. Suspended surface CaCO_3 and salinity-normalized potential alkalinity (PAlk) in observations and CESM. (a) mean annual particulate inorganic carbon (PIC) from MODIS, averaged over the period 2003–2017. Areas where annual mean sea surface temperature is less than 2°C are masked, due to a known temperature range limit of coccolithophores (Holligan et al., 2010) and the unreliability of PIC data near Antarctica (Balch et al., 2016; Trull et al., 2018). (b) Coccolithophore CaCO_3 from the CESM at the top level of the ocean model (0–10 m), also masked at 2°C annual mean temperature. Isopycnal outcrop surfaces for σ_θ 26.0 and 27.0 are shown by red contours. (c–f) PAlk averaged within the σ_θ 26.0 and 27.0 isopycnal range from observations: (c) GLODAP v2; (d) the CESM control; (e) the noGCB experiment; and (f) the 2xGCB experiment. Surface CaCO_3 (Panel b) and PAlk from the CESM control and experiments (Panels d–f) are averaged over the fifth IAF cycle (Years 249–310). The 30°S boundary is shown by a dashed gray line, south of which calcification was manipulated for the noGCB and 2xGCB experiments (see section 2).

calcification significantly alters the PAlk distributions relative to the control simulation. Turning calcification off (noGCB) yields a PAlk field with much smaller declines from the AZ to the SAZ (Figure 3e), which is inconsistent with the pattern in the observations. In contrast, doubling Southern Ocean calcification (2xGCB) yields a reduction in PAlk (to $\sim 2,365 \text{ mmol m}^{-3}$) that is much larger than the decline evident in the observations (Figure 3f). This comparison demonstrates that PAlk in the SAMW density range is sensitive to calcification in the GCB region and the annulus of low PAlk in observations (Figure 3c) is likely attributable to calcification in the SAZ and PFZ of the Southern Ocean. In the following, we explore the widespread impacts of Southern Ocean calcification by analyzing our experimental CESM tracers compared to the control Southern Ocean calcification shown in Figure 3b.

3.3. The Impact of Southern Ocean Calcification on Global Alkalinity Distributions

Eliminating calcification south of 30°S (noGCB) yields an accumulation of alkalinity in the upper ocean relative to the control (experiment minus control; Figures 4a–4d). Doubling Southern Ocean calcification shows the opposite effects (Figure 4e–4h). Since there is no production of CaCO_3 south of 30°S in the noGCB experiment, there is also no dissolution at depth in this region; curtailing this vertical transfer results in a deep ocean alkalinity deficit of $\sim 40 \text{ mmol m}^{-3}$ relative to the control concentrated immediately beneath the GCB region (Figure 4a). The deficit is especially strong in the Atlantic and Indian sectors of the Southern Ocean, and somewhat weaker in the Pacific (Figures 4b–4d). Again, doubling Southern Ocean calcification (2xGCB) shows precisely the opposite effect (Figure 4e–4h). Integrating alkalinity vertically shows that Southern Ocean calcification controls the horizontal transfer of alkalinity from the Southern Ocean to the rest of the ocean (Figure 5). The simulations show especially large sensitivity of the vertically integrated

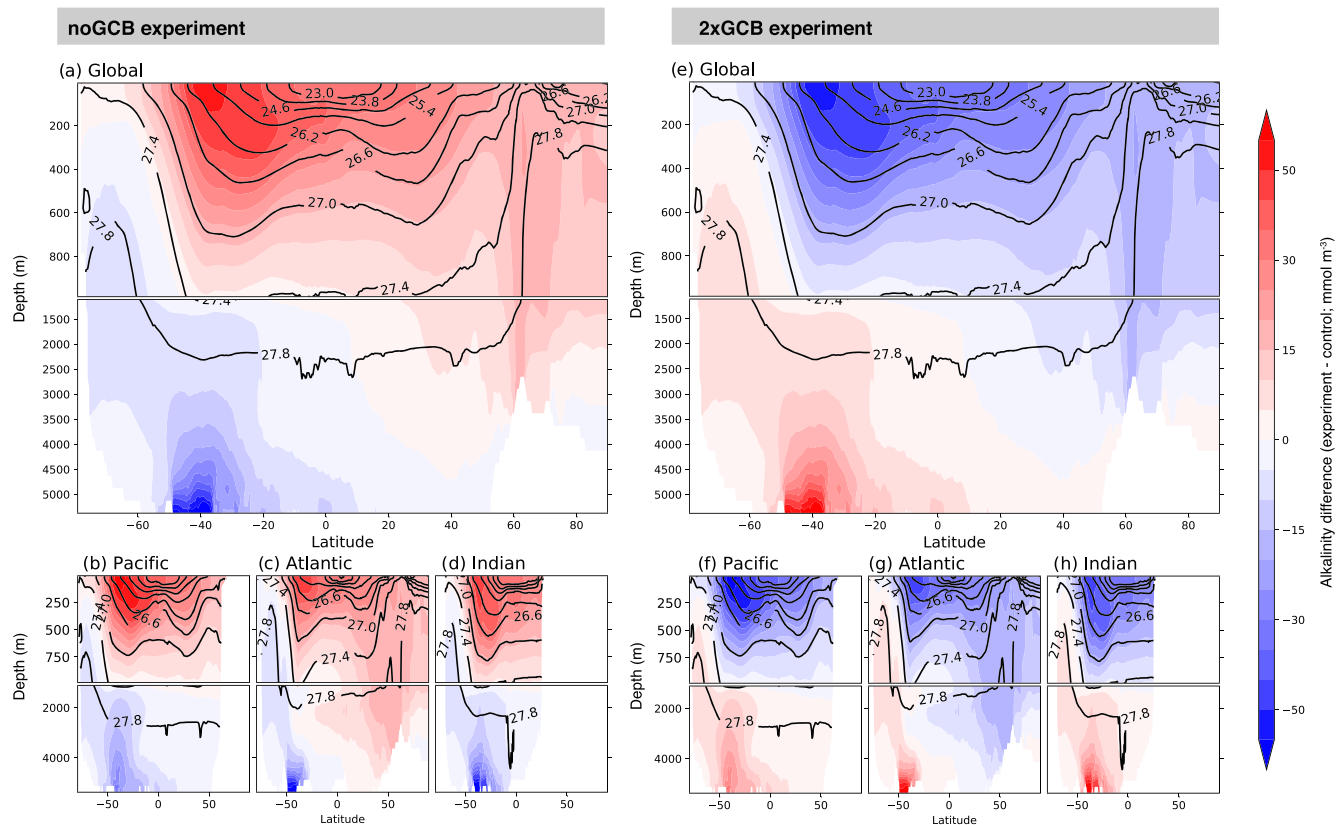


Figure 4. Zonal mean differences (experiment – control) in alkalinity between the control and the noGBC experiment (Panels a–d) and the 2xGBC experiment (Panels e–h). Global zonal mean alkalinity differences are shown on top in the larger plots, and the smaller plots show zonal mean differences within the Pacific, Atlantic, and Indian basins. Isopycnal layers in σ_0 coordinates are shown by contour lines. All data are averaged over the fifth IAF cycle (simulation Years 249–310).

alkalinity response ($\sim 80 \text{ mol m}^{-2}$) in the North Atlantic (Figure 5). Alkalinity anomalies are transported northward and propagate to depth via the formation of North Atlantic Deepwater (NADW; Figure 4c).

It is important to note that the patterns simulated here do not represent a fully equilibrated state, as there is drift in DIC and Alk inventories (Table 1; Figure S3), as well as in the partitioning of alkalinity vertically in the water column (Figures S4 and S5). The global inventory of alkalinity in each experiment changes in response to a net imbalance between riverine inputs and burial at the sea floor. The global alkalinity inventory in the control simulation happens to be relatively well-balanced, such that the global drift is modest (Table 1). Changing Southern Ocean calcification changes the distribution of Ω and the quantity of CaCO_3 incident on the seafloor; reductions in GCB calcification produce a decline in the global CaCO_3 burial and, hence, net accumulation of alkalinity in the ocean (Table 1; Figure S3). Since the model buries CaCO_3 based on an Ω threshold, the alkalinity inventory will eventually stabilize as alkalinity accumulations drive Ω increases on the sea floor and burial increases to bring the inventory back into balance. We estimate, however, that this adjustment requires $\mathcal{O}(10^4)$ yr of integration and is thus not computationally feasible via a brute-force approach. The global drift in alkalinity, however, is quite small relative to the repartitioning of the inventory between upper and low overturning cells, thus it does not ultimately impact our conclusions substantially.

In spite of the complications associated with model drift, these experiments clearly demonstrate that calcification and subsequent vertical transfer of alkalinity in the Subantarctic provides a means of alkalinity trapping. Calcification in the Southern Ocean removes alkalinity from northward flowing waters, transporting it vertically as sinking PIC and depositing it in the deeper layers of the SAZ via carbonate dissolution. These water masses feed into the upwelling at the Antarctic divergence, thus enabling the alkalinity trapping mechanism to operate effectively. In the noGBC experiment, this vertical transfer of alkalinity is eliminated, and alkalinity escapes the Southern Ocean trap; in the 2xGBC experiments, by contrast, a greater transfer

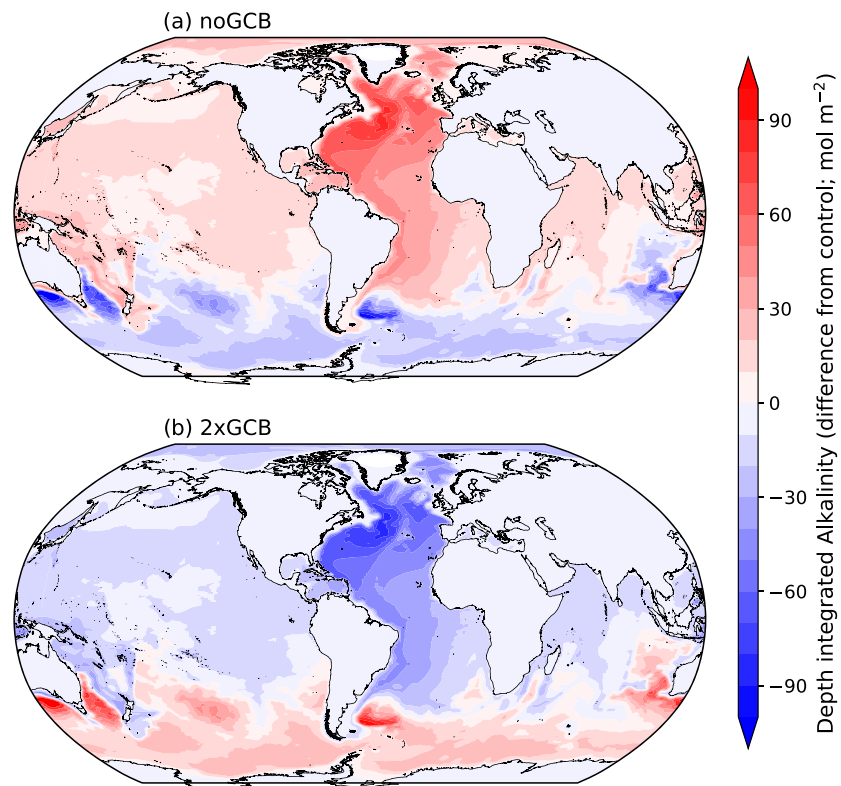


Figure 5. Horizontal shifts in depth-integrated alkalinity inventory (experiment – control). Panel (a) shows the difference between the noGCB experiment and the control, and Panel (b) shows the 2xGCB experiment difference from the control. All data are averaged over the fifth CORE-IAF cycle (simulation Years 249–310). Alkalinity is integrated over the entire water column.

of alkalinity to the deep ocean increases the efficacy of the alkalinity trap. These processes form a critical control on the distribution of alkalinity globally.

3.4. Impacts of Southern Ocean Calcification on the Ocean Carbon Inventory

Changes in Southern Ocean calcification result in widespread changes in air-sea CO_2 fluxes. The CESM simulations were forced with a constant atmospheric CO_2 of 284.7 ppm, representative of preindustrial conditions. This fixed atmospheric boundary condition effectively makes the atmosphere an infinite CO_2 reservoir. Under such a constant atmospheric boundary condition, the control simulation would be expected to equilibrate to near-zero air-sea CO_2 flux; however, the time scale to achieve such equilibrium is much longer than our 310-yr-long integrations (e.g., Lindsay et al., 2014). Moreover, a balanced DIC inventory requires riverine inputs, burial, and air-sea fluxes to sum to zero—thus the persistent drift in CaCO_3 burial, discussed above in the context of the alkalinity balance, also impacts the DIC inventory. As a result of this drift, we cannot definitively quantify the changes in equilibrium DIC inventory across our experiments. Our results are nevertheless informative in a qualitative sense, specifically highlighting the key role that Southern Ocean calcification plays in setting this inventory. The experiments show significant differences in air-sea CO_2 fluxes that are indicative of the differences we expect with fully equilibrated DIC inventories.

Over the last interannual forcing cycle (last 62 yr) of our simulation, the control had a mean oceanic CO_2 uptake of $-0.14 \text{ Pg C yr}^{-1}$ (Table 1). Shutting off Southern Ocean calcification (noGCB) resulted in a strong increase in this CO_2 uptake ($-0.24 \text{ Pg C yr}^{-1}$), while doubling calcification brought the air-sea flux to near zero ($-0.04 \text{ Pg C yr}^{-1}$; Table 1). These patterns are consistent with the large-scale transfer of alkalinity to the upper ocean in noGCB. Increasing surface alkalinity enhances the buffer capacity, effectively increasing the ocean's capacity to absorb and store CO_2 . The geographical distribution of changes in air-sea CO_2 flux shows enhanced uptake in the Subantarctic in the noGCB experiments, accompanied outgassing in the Antarctic zone of the Southern Ocean (Figure 6a). This dichotomy in air-sea CO_2 flux response in the Southern Ocean is reflected in the Revelle factor (Figure S7); indeed, it is this increase in buffer capacity that drives enhanced

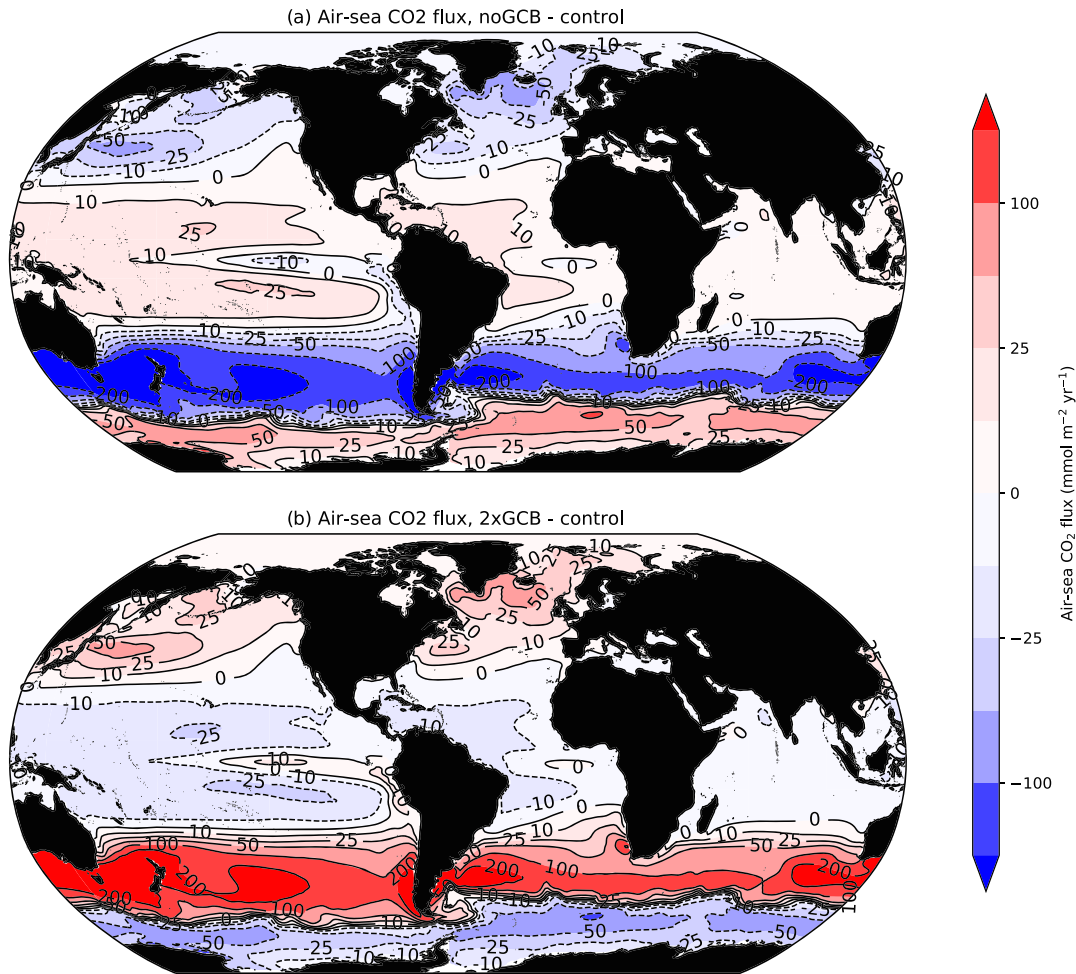


Figure 6. Differences (experiment – control) in air-sea CO₂ flux between the control and the noGCB experiment (Panel a) and the 2xGCB experiment (Panel b), where negative (blue) values represent greater CO₂ flux into the ocean, and red values represent more CO₂ fluxing out of the ocean. The control air-sea CO₂ flux is shown in Figure S6 for reference.

uptake in the Subantarctic and also in the high-latitude Northern Hemisphere ocean in the noGCB run. While buffer capacity also increases in tropical waters in noGCB, these regions display weak anomalous outgassing relative to the control.

3.5. Setting the Southern Ocean Alkalinity Trap

The Southern Ocean alkalinity trap is sustained by the vertical transfer of PIC in the Subantarctic. CaCO₃ production strips alkalinity out of northward flowing surface waters, depositing it at depth in the same water masses that feed Subantarctic surface waters from upwelling at the Antarctic divergence. The nature of this trapping mechanism is thus dependent on the magnitude of vertical fluxes of CaCO₃. To summarize this effect, we seek a relationship between the simulated alkalinity anomaly and the change in vertical CaCO₃ flux in the GCB region, which we define as the region below the 26.0 to 27.0 σ_θ surface outcrop (Figures 3a and 3b). We note that the sign of alkalinity anomalies in the noGCB and 2xGCB experiments changes around $\sigma_\theta = 27.4$ (Figure 4). Therefore, we plot the change in the upper ocean alkalinity above this surface against the change in the CaCO₃ flux across this surface in each experiment, including those where we manipulated the DLS for sinking CaCO₃ (100mDLS and 1000mDLS; Figure 7a). If the change in upper ocean alkalinity is negative that indicates the trapping of alkalinity in the deep ocean below the $\sigma_\theta = 27.4$ isopycnal (or CaCO₃ burial). The relationship is approximately linear and suggests that increasing the flux of CaCO₃ across $\sigma_\theta = 27.4$ in the GCB region by 1 g CaCO₃ m⁻² will reduce the mean alkalinity concentration above this surface by about 1.6 mmol m⁻³, effectively trapping this alkalinity at depth. Thus, we expect that variations in

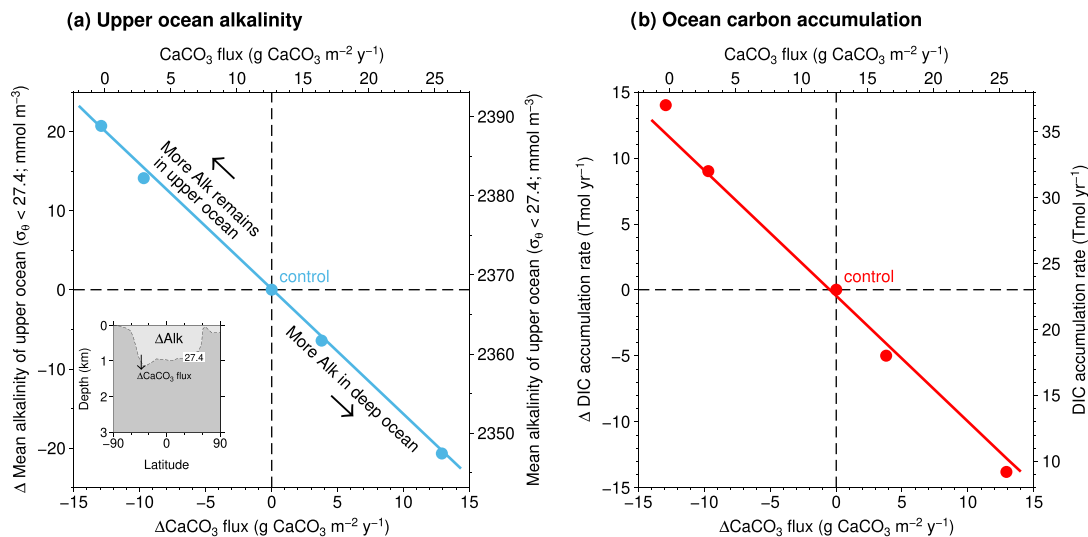


Figure 7. Mean upper ocean alkalinity (a) and DIC accumulation rates (b) as a function of GCB CaCO_3 fluxes across the σ_θ 27.4 isopycnal (with reference to control on left and bottom axes; absolute values shown on right and top axes). Dots are from five CESM model experiments; (from left to right) noGCB, 100mDLS, control, 1000mDLS, and 2xGCB (see section 2 for experimental setup). The lines on each panel are from least squares linear regressions of upper ocean alkalinity and DIC accumulation rate as a function of CaCO_3 flux (Panel a slope = $-1.58 \text{ mmol m}^{-3}/\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$; Panel b slope = $-0.95 \text{ Tmol DIC yr}^{-1}/\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$).

CaCO_3 fluxes in the Southern Ocean may contribute to variability in upper ocean alkalinity (see section 4) and thus ocean CO_2 uptake.

We further relate GCB CaCO_3 fluxes to ocean DIC accumulation rates (Figure 7b). The relationship between DIC accumulation in the ocean and GCB CaCO_3 fluxes is also approximately linear. Here, for each additional g of CaCO_3 crossing the 27.4 isopycnal in the GCB region the ocean accumulates $0.95 \text{ Tmol C yr}^{-1}$ less with an atmosphere held at preindustrial CO_2 concentrations. This relationship summarizes the effect of Southern Ocean calcification on the partitioning of carbon between the atmosphere and the ocean.

In our control simulation, Southern Ocean (south of 30°S) calcification accounts for approximately 32% of globally integrated calcification. In order to put the Southern Ocean alkalinity trap in context, we performed two additional experiments quantifying the effect of a globally distributed increase or decrease in calcification by 32% (+32Global and -32Global; Table 1). These experiments have the same globally integrated calcification as in the 2xGCB and noGCB experiments, respectively—only the spatial distribution of calcification is different. Upper ocean alkalinity changes in these global experiments are similar to those simulated in the GCB experiments (Figure S8); confining the changes in calcification to the Southern Ocean, however, is slightly more effective at driving changes in the vertical distribution of alkalinity. Surface alkalinity is controlled by the balance between circulation-mediated supply from depth and biologically mediated vertical export. Therefore, from a global mass balance perspective, it is not surprising that similar perturbations to global calcification yield similar changes in the partitioning of alkalinity between the surface and deep ocean. Since the Southern Ocean is a primary region where deep waters return to the surface, however, confining the perturbations in calcification here can be more effective at driving changes in the vertical partitioning of alkalinity. In particular, CaCO_3 export from Southern Ocean surface waters yields dissolution in the deep ocean water masses directly feeding the surface. Thus, while globally dispersed changes in calcification also induce rearrangements of alkalinity, changes isolated in the Southern Ocean are more effective at vertically redistributing alkalinity (Figures S8 and S9).

4. Discussion

It has long been recognized that biological production in the Southern Ocean influences atmospheric CO_2 and global productivity via regional nutrient utilization efficiency (Ito & Follows, 2005; Knox & McElroy, 1984; Marinov et al., 2006; Primeau et al., 2013; Sarmiento & Orr, 1991). Here we have shown that biological calcification in the Southern Ocean, primarily in the GCB region, also exerts a control on global biogeochemistry by modifying the global distribution of alkalinity. Calcification and vertical CaCO_3 fluxes

in the GCB region of the Southern Ocean lead to a net transfer of alkalinity to the deep cell of the meridional overturning circulation (Figure 4); this vertical flux sustains an alkalinity trap, retaining alkalinity in the Southern Ocean (Figure 5). The key constraint on this Southern Ocean alkalinity trap is the flux of CaCO_3 across the boundary between the upper and lower overturning cells. In CESM, this is approximately where $\sigma_\theta = 27.4$ in the GCB region of the Southern Ocean (located approximately at $\sim 1,000$ m for much of the ocean; Figure 4). Increasing the flux of CaCO_3 across this surface in the Southern Ocean strengthens the alkalinity trap, while decreasing the CaCO_3 flux permits more alkalinity to escape and remain in the upper ocean globally (Figure 7). Changes in calcification applied globally drive a similar response, but are slightly less effective at repartitioning the alkalinity inventory than fluxes in the Southern Ocean.

Calcification in the SAZ mixed layer depends on the organisms present and their physiological state. If coccolithophores out-compete other phytoplankton for nutrients, this could increase overall calcification. On the other hand, excess silicic acid could lead to an increase in diatoms at the expense of coccolithophores, reducing calcification (Matsumoto et al., 2002). Since diatom silicification rates are sensitive to iron availability, this raises the possibility that variation in iron supply might indirectly modulate calcification rates through Si drawdown patterns integrated over the Southern Ocean. More plentiful pteropods and/or foraminifera may also modulate overall calcification; their populations may be more dependent on prey availability, as well as environmental conditions (e.g., Manno et al., 2018; Meilland et al., 2016). Further, calcifying organisms may be vulnerable to ocean acidification, which may drive decreases in calcification in this naturally acidic part of the global ocean.

The Southern Ocean alkalinity trap is sensitive to the vertical distribution of CaCO_3 dissolution—and in particular partitioning of dissolution above and below the $\sigma_\theta 27.4$ (or equivalent) isopycnal. The deeper that CaCO_3 dissolves in the water column, the stronger the alkalinity trap. Likewise, Holzer et al. (2014) showed that silicic acid is efficiently trapped in the Southern Ocean, as compared to, for example, PO_4 , in part due to its deeper regeneration. In nature, the CaCO_3 dissolution profile might be sensitive to biologically mediated dissolution in microaggregates (Milliman et al., 1999). Pteropod CaCO_3 (in the form of aragonite) would be more susceptible to dissolution at shallow depths (Buitenhuis et al., 2019), especially if the aragonite saturation horizon shoals rapidly in the Southern Ocean, as has been projected (Negrete-García et al., 2019). The CaCO_3 dissolution profile is parameterized in CESM with a time-invariant DLS. The amount of deep water dissolution versus burial on the seafloor could also influence the amount of alkalinity that moves south and upwells at the Antarctic divergence.

The experiments we show here contain several important caveats and limitations. Most importantly, biases in the physical circulation of the CESM ocean component will impact the results. For example, a shallow mixed layer depth bias in the Southern Ocean affects the fidelity with which the model simulates AAIW and SAMW formation. In a previous versions of CESM, biases in mixed layer depth were linked to poor simulations of mode water and weak uptake of transient tracers, such as anthropogenic carbon and chlorofluorocarbons (Long et al., 2013; Weijer et al., 2012). While these biases may be important in controlling detailed aspects of the patterns in our results, such as the precise value of the slopes shown in Figure 7, they are not likely to impact our fundamental conclusions regarding the response of the alkalinity inventory to Southern Ocean calcification. Similarly, the ocean ecosystem model is a considerable oversimplification of reality. Our 4 phytoplankton/1 zooplankton representation of ocean ecosystems ignores the intricacies and diversity present in nature. Such a simplified system usually results in one PFT dominating over the others, rather than a more realistic, mixed plankton ecosystem. Additionally, here we only have one source of biological calcification—the coccolithophore PFT—and ignore distinctions between calcite and aragonite. Since aragonite is more easily dissolved in sinking material, this could be critical for the representation of shallow CaCO_3 dissolution and would influence how alkalinity (in the form of CaCO_3) sinks and is remineralized at depth (Buitenhuis et al., 2019; Gangstø et al., 2008; Manno et al., 2018). Since our primary intent, however, is to illustrate the sensitivity to imposed changes in calcification and dissolution profiles, these oversimplifications do not significantly impact our conclusions.

Our model configuration precludes a precise assessment of the effects of changes in GCB calcification on atmospheric CO_2 concentrations. However, the perturbations we imposed suggest that transferring the ocean alkalinity inventory from the deep cell to the upper cell yields an increase in the ocean carbon inventory due primarily to enhanced uptake from the atmosphere. Noting that the dry air mass of the atmosphere is 5.1352×10^{18} (Trenberth & Smith, 2005) and thus atmospheric CO_2 changes by a factor of

0.47 ppm (Pg C)⁻¹, we can recast the cumulative integral of air-sea flux in our experiments in terms of equivalent impacts on atmospheric CO₂. For instance, the ocean in the noGCB absorbed an additional 84 Pg C from the atmosphere relative to the control over the course of the 310-yr integration; this is equivalent to a reduction in atmospheric CO₂ of ~18 ppm. In contrast, reduced alkalinity in the upper ocean in the 2xGCB experiment led to an additional outgassing of ocean CO₂ relative to the control, equivalent to an increase in atmospheric CO₂ of ~18 ppm. These numbers provide a sense that the magnitude of these perturbations is significant, though they cannot be interpreted as explicit estimates of the alkalinity effects on atmospheric CO₂. Our integrations were conducted with a fixed atmospheric CO₂ boundary condition and none of the experiments was integrated to equilibrium.

Even though the experiments we conducted are obviously highly idealized, the Southern Ocean calcification mechanism of redistributing alkalinity between the upper and lower overturning cells may play an important role on a variety of time scales. It has long been established that reorganizations of phytoplankton communities over millennial time scales might influence the global rain ratio, with implications for atmosphere-ocean partitioning of CO₂ (Archer et al., 2000; Matsumoto et al., 2002). However, based on our study, it is possible that the low-latitude, upper-ocean alkalinity inventory also contains decadal variability, for instance, stemming from variations in Southern Ocean calcification on these time scales. To provide a crude illustration of the low-latitude response time scales associated with our Southern Ocean calcification perturbations, we tracked alkalinity anomalies over the course of our integrations in five subtropical regions (Figure S10). In the South Atlantic and South Pacific regions, alkalinity anomalies are visible ~10 yr after the calcification perturbation with some apparent interannual variability. However, alkalinity anomalies propagate more slowly to the Indian, North Atlantic, and North Pacific regions, gradually growing in magnitude as the simulation progresses, with interannual variability dampened (Figures S10a, S10c, and S10d). Time scales of influence of the Southern Ocean alkalinity trap clearly warrant further exploration. Similarly, future oceanic CO₂ uptake may include centennial-scale feedback mediated by changes in Southern Ocean calcification that alter the upper ocean's buffer capacity under transient climate change scenarios.

An additional important implication of our study is that oceanic profiles of alkalinity are not necessarily local in nature. We demonstrate this by calculating the rain ratio using the method described in Sarmiento et al. (2002), in which we compute the ratio between vertical gradients of PAlk and salinity-normalized nitrate (nNO₃) below the mixed layer (see Figure S11). Even though calcification was only altered south of 30°S for our experiments—and thus the rain ratio was not changed outside this region—the vertical gradients in PAlk and nNO₃ changed nearly everywhere in the ocean, and are particularly different in the Southern Hemisphere subtropics, the region of the thermocline most closely linked to Subantarctic surface waters. This exercise highlights the widespread impacts of Southern Ocean calcification on vertical alkalinity gradients.

This study adds to recent work demonstrating the important role of ocean alkalinity on ocean carbon storage. Wu et al. (2019) recently revisited the question of what determines the global distribution of DIC in the ocean, focusing specifically on latitudinal gradients. While temperature-driven solubility directly accounts for a large portion of elevated DIC at high latitudes, Wu et al. (2019) also showed that upwelling of high-alkalinity water contributes indirectly by allowing seawater to hold more DIC. In particular, upwelled alkalinity in the Southern Ocean contributes ~220 μmol kg⁻¹ of DIC above the average low-latitude values. Further, contrary to expectations of a melting Arctic being a sink for CO₂, Woosley and Millero (2020) showed that the Arctic Ocean is not taking up a much carbon as expected, primarily due to the dilution of alkalinity from increased freshwater supply. An understanding of the mechanisms that influence the distribution of ocean alkalinity is critical for projecting how the ocean absorbs carbon.

5. Conclusion

In this study we demonstrate the potential of Southern Ocean calcification to alter the global distribution of ocean alkalinity. After demonstrating that sinking CaCO₃ reaches depths >1,000 m setting up the potential for Southern Ocean alkalinity trapping, we identified a signature of Southern Ocean calcification in oceanic observations of alkalinity. We performed Earth system model simulations with differing Southern Ocean calcification to show that (1) when Southern Ocean CaCO₃ fluxes are lessened, more alkalinity leaves in the Southern Ocean, remaining in the upper cell of the meridional overturning circulation; (2) when Southern Ocean CaCO₃ fluxes are increased, the Southern Ocean alkalinity trap is strengthened and more alkalinity

is transferred to the deep ocean with less alkalinity leaving the Southern Ocean; and (3) changes to Southern Ocean calcification result in anomalies with respect to ocean carbon uptake and storage. The critical mechanism responsible for the Southern Ocean alkalinity trap is the flux of CaCO_3 across the σ_θ 27.4 isopycnal in the GCB region of the Southern Ocean. The Southern Ocean alkalinity trap identified here is a novel mechanism recognized in the Earth system, relevant for paleoclimate studies as well as future projections. As calcification in the Southern Ocean continues to change due to anthropogenic climate change and ocean acidification, there could be widespread effects on global alkalinity distributions and ocean CO_2 uptake.

Data Availability Statement

Data from the CESM simulations performed for this study are available at NCAR's Digital Asset Services Hub (DASH) repository (<https://doi.org/10.5065/0d1g-0t61>). Analysis scripts are published in a public repository on GitHub (https://github.com/kristenkrumhardt/GCB_ALK_analysis).

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