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Impact of manmade inputs on ocean alkalinity and effect on calcifying marine organisms

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Abstract

Biological procedures in the surface waters of the Southern Ocean (SO) significantly influence global productivity and the storage of oceanic carbon dioxide (CO2). This study illustrates that biological calcification in the SO significantly influences the worldwide distribution of alkalinity (AK). The hallmark of SO calcification is manifested in observations as a reduction of potential AK in Subantarctic Phase and Intermediate Waters sections. Studies utilizing an ocean overall circulation modeling demonstrate that the calcification and consequent descent of biogenic carbonate in this area efficiently facilitates the movement of AK across the upper and lower units of the meridional overturning cycle. The calcification in the SO sequesters AK in the deep sea; a reduction in calcification allows greater AK to escape from the SO, resulting in elevated AK in the upper cell and low-latitude waterways. These processes affect carbon partitioning between the upper atmosphere and the ocean due to manmade inputs. Decreases in calcification in the SO augment the buffering capacity of surface waters worldwide, improving the ocean's capability to sequester atmospheric carbon. This investigation emphasizes the essential function of SO calcification in shaping worldwide AK patterns, indicating that alterations in this process have extensive repercussions on the air-sea exchange of CO2.

Keywords: Ocean, Alkalinity, Calcification, Marine organism

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Introduction

The Southern Ocean (SO) (Moura *et al.,* 2025) is critically significant to the climate system and worldwide biogeochemistry since it serves as a primary area for the ventilation of the deep sea. The natural pump deposits minerals at depth; circulation must finally facilitate the return of minerals to the ocean top; alternatively, production would terminate (Myers and Subban, 2022; Verma and Nair, 2025). The characteristics of nutrient return pathways are crucial as they influence the extent to which worldwide ocean biogeochemistry responds to climate change. Nutrients were uniformly distributed throughout the primary thermocline in the global oceans (Sherin *et al.,* 2023); this projection is incompatible with known vertical diffusivities, which are almost a factor of magnitude too low to facilitate the required water mass conversions. A more precise description of nitrogen return pathways is that deep ocean chemicals are brought to the surface in the SO by the worldwide overturning cycle due to manmade inputs. Biological activities in the surface waves of the SO can impact global production and biogeochemistry (Hung *et al.*, 2021).

Latitudinal variations in fertilizers and temperatures delineate distinct ecosystems in the SO (Cassavia *et al.,* 2022), influencing plankton populations and their physiological condition, which alter the chemistry of the water (Thackeray and Beisner, 2024). For instance, significant iron scarcity in the silicate-rich seas of the SO’s Antarctic Zone (AZ) promotes the proliferation of highly silicified diatoms. The diatoms use silicic acid in the surface waters to construct robust, grazer-resistant opal shells, which sink and reduce silicic acid's availability for distribution across the ocean as currents progress northward. The Subantarctic Zone (SAZ) is defined by restricted silicic acid availability, increased iron influx, and elevated temperatures (Worne *et al.,* 2022); these factors foster rivalry among calcified phytoplankton, specifically cockroaches and weakly silicified diatoms. The unique plankton ecosystems of the SO are evident in the makeup of materials collected from traps for sediment and seafloor deposits (Jaiswal and Pradhan, 2023). Variations in cellular stoichiometry and physiology among SO plankton populations create distinct influences on water weights, contributing to an ecological distinction separating AZ and SAZ.

Background

The discovery of seawater's alkalinity (AK) in the seventeenth century had a lengthy historical trajectory leading to the contemporary understanding of saltwater AK due to manmade inputs. Chemists employed AK at the beginning of the nineteenth century and adopted it across other fields, including medicine and marine science (Schneider and Matthäus, 2023). The investigation offers a comprehensive historical overview of AK in seawater, demonstrating advancements in analytical techniques and formulating a chemical framework for saltwater. Instead of reiterating the historical backdrop, the research finds it beneficial to officially differentiate between measurement AK, overall AK, and charge-balance AK, which is essential for quantifying buffering and pH variations in natural settings. Observing and experimental investigations in marine environments typically utilize galvanic AK, but theoretical, simulation, and geological investigations occasionally choose the charge balance method (Khodjaev *et al.*, 2024; Liang *et al.,* 2024). The charge-balance AK idea is frequently applied in water bodies characterized by elevated levels of dissolved biological material, commonly referred to as Excessive Negative Charge (ENC), and is associated with the explicit conservatism statement of total AK. The distinction between Titration Acidity (TA) and Charge-Balance Acidity (CBA) pertains to the formulas employed to address the chemical balance issue: The TA relies on a proton balance, whereas the CBA is founded on a charge balance closing. TA and CBA vary or are the same based on the particular issue and the system's description. The absence of differentiation between TA and CBA has engendered confusion and debate.

Several investigations have investigated the impact of Southern Sea phytoplankton output on global nitrogen patterns. The phenomenon termed SO "nutrient entrapment" is seen as a process that influences the restructuring of the world nitrogen inventory allocation due to manmade inputs. Nutrient entrapment occurs in areas with diverging surface flows and converging flow at the bottom; here, upwelled minerals enhance the manufacturing of exports, but descending organic matter returns and is remineralized at the same levels from which those upwelled waters originated. Nutrients can be efficiently sequestered if export manufacturing occurs rapidly compared to the advection period that flushes the area; in such cases, nutrients become concentrated locally, restricting lateral transit from the region. The research revealed that minerals can be optimally sequestered in the SO by enhancing production in the Antarctic Area within the framework of an ocean-wide Circulation Model.

Calcification influences seawater AK, thereby affecting air-sea CO_2 flows. The production of 1 mol of CaCO3 extracts 2 mol of acidity and 1 mol of Dissolved Inorganic Carbon (DIC) from the surrounding saltwater (Ozyilmaz, 2023). The lowering of CaCO carries carbon to depth, establishing the "carbonate work." However, the use of alkaline at the ocean top reduces the ocean's capacity to absorb CO from the environment compared to a purely "soft-tissue" pumping (Suresha and Ramesha, 2019). Therefore, the ratio of $CaCO_3$ to Powdered Organic Carbon (POC) flux, known as the rain ratio, is a crucial parameter for assessing the effectiveness of the biological pumps. The research employed a basic box model to demonstrate that variations in the rain proportion can influence oceanic carbon sequestration; by augmenting diatom manufacturing throughout the entire ocean to the detriment of coccolithophores, they reduced the rain ratio, resulting in decreased atmospheric CO2 through improved oceanic retention of carbon. Numerous studies, including this one, have underscored the significance of surface sea AK in CO2 absorption and climate dynamics due to manmade inputs.

Observational investigations have demonstrated direct correlations between surface AK and the development and breakdown of local CaCO. Reductions in surface AK due to organic calcification have been observed and recorded in the subtropical and subpolar North Atlantic, along with the SO. The study detected an increase in overall AK linked to the breakdown of $CaCO_3$ in the alkaline waters of the North Pacific. Besides CaCO, cycling and AK are influenced by freshwater influxes and the generation of organic matter via nitrate assimilation. To separate the effects of CaCO cycling, the research utilizes "potential AK (PAlk)," a linear mixture of AK and nitrates adjusted to a reference saltiness. The study used PAlk as a foundation for a tracer designated Alk*, from which the impacts of rivers on AK have been excluded. Alk* has notable consistency across lower temperatures in all the oceanic basins. However, it escalates in the North Atlantic and high-latitude SO, mirroring silicic acid patterns. AK drops in surface waters of the South Atlantic Zone at approximately 40°S, an area abundant in creatures and other migratory calcifiers due to manmade inputs. The research identified CaCO production worldwide by reinstating PAlk to measurements within a seawater overall circulation model, revealing that SO calcium constitutes over one-third of all oceanic acidification. In summary, extensive calcification occurs in the northern regions of the SO, which presumably influences the pH of the ocean descending from that setting.

Methods

Acidification of the SO

The SO, including approximately 34.8 million km^2, is expected to be one of the first and most adversely impacted regions by ocean acidification due to its inherently low levels of CaCO3, the heightened solubility of CO2 at reduced temperatures, and diminished buffering capacity. Comprehending the susceptibility of Antarctic marine calcifiers to ocean acidification is a crucial concern, recognized as one of the most rapidly warming regions on the planet. To assess the possible threat of ocean acidification to SO marine calcifiers, it is essential to evaluate various aspects that affect the susceptibility of their skeletons to ocean acidification due to manmade inputs. This encompasses interactive factors (e.g., warming), local intermittent and spatial variations in ocean water carbon dioxide science, the location of sedimentary CaCO, that provides suitable habitats for numerous benthic calcifiers, and a variety of phyla and organisms exhibiting diverse geographic categories, bones mineralogies, biological characteristics, biological processes, and methods to mitigate pH fluctuations.

Information and Parameters

Data on calcium levels, bicarbonate and hydroxide percentages (or overall dissolved inorganic carbon levels), pH, and AK were gathered from 44k sites, including lakes, reservoirs, rivers, and streams worldwide, totaling 445k water specimens from 58 nations. Of the 442k water specimens collected, 280k were sourced from streams and waterways, 165k were obtained from lakes, and 38k were collected from big lakes and dams. The worldwide Lake Ecological Observatory System participants and the worldwide river chemistry collection supplied the information. In certain instances, the evaluation of accusations became significant. The research uses the unit mEq/L^{-1} when discussing charges and the notation Ca^{2+}.

The research possessed 442k records on calcium levels, 434k data lines on pH, and 285k data points on bicarbonate AK. Carbonate AK in mEq/L was assessed as the aggregate of bicarbonates and ionized carbonate or as the amount of inorganic carbon dissolved minus the quantity of free CO2 derived from AK, pH, and water temperatures. To compare calcium levels in mg/L^{-1}, the AK values were converted to mg HCO_3/L^{-1}. Owing to significant uncertainty in computed levels of CO in very acidic, dispersed carbon-rich waterways, the research only utilized positive AK metrics, leading to an absence of AK data from the most acidic environments. Comprehensive carbonate AK, calcium, and pH data were accessible for 22k ponds and 17k rivers. Numerous lakes and flowing streams were tested over various seasons and years. For several studies, the research utilized long-term mean numbers, computed as the total median of the annual averages for every lake or flowing water site due to manmade inputs.

To assess temporal variations, the research examined comprehensive time series of calcium and pH (from 289 clean water sources), carbonate AK (from 210 clean water sources), and levels of sulfate (from 215 clean water sources; utilized here as an indicator of anthropogenic AK) spanning from 1990 to 2025. The research used site-specific annual median data for trend analysis.

Statistical analysis. All statistical analyses were conducted using JMP software, version 12.0 (SAS Institute Inc.). Due to the irregular information distributions, the research employed non-parametric statistical techniques, including the Wilcoxon procedure for subgroup between groups and Kendall's tau for correlation studies. Boxplots are standard quantile boxplots that display the 25th and 75th percentiles, with an upper limit defined as the upper quartile plus 1.5 times the interquartile range, and a lower limit specified as the lower quartile minus 1.5 times the interquartile range due to manmade inputs. The importance of temporal trends was assessed using the non-parametric Mann-Kendall pattern analysis on annual median numbers, with a threshold for significance of $P < 0.05$.

Results and Findings

Community Earth System Model (CESM) Model of Calcifying in the SO

The research analyzes the average Particulate Inorganic Carbon (PIC) derived from Moderate Resolution Imaging Spectroradiometer (MODIS) and CESM surface CaCO. Although CESM models a GCB similar to empirical projections, it is generally more concentrated and reaches slightly further north than indicated by the PIC observations. Numerous studies suggest that the PIC algorithm underestimates PIC in the SO, especially in the AZ. The coccolithophore PFT is the sole source of biogenic $CaCO_3$ in CESM. It indirectly signifies all pelagic calcium (by zooplankton and algae) in a biological context due to manmade inputs. In light of this framework's simplification, an exaggeration of coccolithophore CaCO offsets the absence of zooplankton calcifiers. Calculated sinking CaCO flows align comparably with those obtained from trapped sediments.

The Indication of Calcifying in AK Measurements

The research analyzed salinity-normalized Prospective AK (PAlk) in observing areas to identify a hallmark of calcium in the SO. The study provides observationally derived estimates of typical PAlk averaging over the isopycnal concentration ranging from 25.0 to 28.0. As fluids progress northward from the AZ to the SAZ, pH within that density range decreases from around 2.5k mmol m-3 in the AZ to around 2.4k mmol m-3 in the SAZ. The modeled PAlk in the CESM controlled simulation exhibits a comparable decrease in PAlk from east to west within this density spectrum, with a reduction of approximately 60 mmol m-3 of PAlk across the AZ to the SAZ. Altering SO calcification substantially modifies the PAlk concentrations compared to the control model due to manmade inputs. Disabling calcium results in a PAlk field with significantly reduced reductions from the AZ to the SAZ, which contradicts the observed pattern. Conversely, a doubling of SO calcification results in a significant fall in PAlk, considerably more than the decline observed in empirical data. This comparison illustrates that PAlk within the SAMW density band is responsive to deposition in the GCB region, and the observed annulus of low PAlk is likely due to calcium in the SAZ and PFZ of the SO. This study examines the extensive effects of SO calcified by comparing the field-tested CESM tracers with the controlled SO calcium.

The Influence of SO Calcifying on Global AK Versions

Removing calcification southward of 32°S increases AK in the northern ocean compared to the controls. The doubled rate of calcification in the SO exhibits contrasting impacts. Due to the absence of CaCO generation south of 32°S in the noGCB test, there is consequently no dissolving at depth in this area; this limitation on horizontal transfer leads to a deep-sea alkaline deficit of around 45 mmol m-3 compared to the control situated directly beneath the GCB region. The shortfall is most pronounced in the Caribbean and Indian areas of the SO, and considerably less severe in the Pacific. Conversely, doubling Southern Sea calcium demonstrates a contrary impact. The vertical integration of AK indicates that deposition in the SO regulates the horizontal transmission of AK to other oceanic regions. The simulations indicate a significant sensitivity of the North Ocean's vertically coupled AK reaction. AK abnormalities are conveyed northward and descend through the creation of North American Deep Water (NADW) due to manmade inputs.

Effects of SO Calcifying on the Oceanic Carbon Inventory

Alterations in SO sedimentation lead to extensive modifications in air-sea CO2 fluxes. The CESM calculations were conducted with a constant environmental CO concentration of 291.3 ppm, indicative of preindustrial circumstances. This established atmospheric boundary condition practically renders the atmosphere a limitless reservoir of CO2. Given the persistent atmospheric boundary circumstance, the control simulation is anticipated to stabilize at a near-zero air-sea CO flow; the duration required to attain this equilibrium significantly exceeds the 320-year simulations. A balanced Dissolved Inorganic Carbon (DIC) inventory necessitates that riverine inputs, funnels, and air-sea flows equate to zero; hence, the ongoing variation in calcium carbonate ($CaCO_3$) burial, previously mentioned regarding AK balancing, influences the DIC inventories. The research cannot precisely estimate the alterations in equilibrium DIC inventory during the studies due to manmade inputs. The findings are nonetheless informative qualitatively, particularly emphasizing the crucial role of SO calcifying in determining this inventory. The tests reveal substantial variations in air-sea CO2 fluxes, which reflect the anticipated discrepancies associated with completely balanced DIC stocks.

Establishing the SO AK Trap

The upward transport of particulate inorganic carbon in the Subantarctic maintains the SO alkaline trap. The generation of CaCO3 depletes AK from northern moving oceans, storing it at depth within the same bodies of water that supply Subantarctic oceans by upwelling near the Antarctic split. The characteristics of this trapping process are contingent upon the intensity of CaCO's vertical flows. The research wants to establish a correlation between the simulated AK anomalies and the alteration in vertical CaCO3 flux within the zone, defined as the area beneath the 25.0 to 28.0 °C surface outcrops. The magnitude of AK abnormalities in the tests alters at 26.5. The research graphed the variation in upper ocean AK beyond this surface about the alteration in the CaCO flux over this barrier for every test, even those in which the research adjusted the DLS for lowering CaCO due to manmade inputs. A decrease in top ocean AK signifies the sequestration of AK in the deep sea beneath the 26.2 isopycnal. The connection is nearly linear and indicates that augmenting the flux of $CaCO_3$ over 25.8 in the GCB area by 1 g $CaCO_3$ m^{-} will decrease the mean AK content above this level by roughly 1.7 mmol m^3, effectively sequestering this AK at the bottom. The research anticipates that fluctuations in CaCO3 flows in the SO influence variance in upper sea AK and ocean CO2 absorption.

Conclusion

This investigation illustrates the capacity of SO calcification to modify the worldwide pattern of ocean AK. Following the demonstration that sinking CaCO achieves depths above 1,000 m, establishing a possibility for AK entrapment in the SO, the research discerned a signature of calcification in oceanic AK data due to manmade inputs. The study conducted experiments of Earth system simulations with varying SO calcifying to demonstrate that (1) a reduction in SO $CaCO_3$ flows leads to an increased retention of AK within the top cell of the meridional reversing movement; (2) a rise in SO $CaCO_3$ fluxes enhances the SO AK trap, facilitating greater transfer of AK to the deep sea while decreasing the AK exiting the SO; and (3) alterations in SO calcification induce anomalies in oceanic carbon uptake and preservation due to manmade inputs. The essential process governing the SO alkaline trap is the flux of CaCO over the 28.7 isopycnal in the area of the SO. The SO alkali trap revealed herein is an innovative process acknowledged within the Earth system pertinent to paleoclimate research and future forecasts. As calcium in the SO evolves due to human warming and acidification of the oceans, it has extensive repercussions on global alkaline concentrations and oceanic CO2 uptake.

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